Effects of humidity and ageing on epoxy-based stereolithography materials

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Metadata Record: https://dspace.lboro.ac.uk/2134/16585

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Effects of Humidity and Ageing on Epoxy-Based Stereolithography Materials

By

Naguib Saleh

Doctoral thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

June 2005

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Abstract

In recent years, the use of Stereolithography (SL) to produce end-use parts has increased rapidly. However, only limited applications have been considered as there are several problems that impede the conversion of Stereolithography to be used as a mainstream manufacturing process. One of the major problems is the instability of the SL parts post-build when subjected to environmental factors.

This research included long-term material testing to investigate the effects of ageing, humidity and temperature on the mechanical properties of the SL parts. This work was carried out at a temperature range of -40°C to +100°C over differing ageing and humidity conditions (dry (10%RH), controlled (50%RH) and wet (100%RH)). The results indicated that the main degradation factor was humidity. It was therefore selected for further investigation in this research. This is the most comprehensive analysis and characterisation of materials data yet compiled for additively manufactured materials.

Stereolithography materials tested have been shown to significantly degrade over time when subjected to a high level of relative humidity. Therefore, it was the primary aim of this research to identify the mechanism of hygroscopic degradation of Epoxy-based SL materials. This was achieved using various techniques including mechanical tests, Differential Scanning Calorimetry (DSC) and Attenuated Total Reflectance (ATR).

Modelling of water penetration into SL Epoxy-based parts was undertaken and the type of diffusion was found to be anomalous (non-Fickian). Therefore a dual-Fickian model was developed to identify the diffusion coefficients of the investigated materials. Additional equations were developed to model the profiles of moisture concentration and Young’s Modulus within a specimen and to predict the stiffness of an SL material at a certain age. The methodology that has been developed in this work can now be further used to predict the mechanical properties of any future Epoxy-based SL material providing the diffusion coefficient(s) of the material are known.
Acknowledgements

The author of this work is indebted to a number of people who have helped during this work. As ever, it is impossible to name everyone to whom thanks are due but a special mention must go to the following people:

Dr Richard Hague, Prof Phill Dickens and Dr Russell Harris for their invaluable supervision throughout this work. Their guidance, enthusiasm, and willingness to make time have been a positive influence during this work.

Innovative Manufacturing Research Centres (IMRC) / Engineering and Physical Sciences Research Council (EPSRC), 3D Systems and Huntsman for providing the funding for this research. Also, a particular mention should be given to Richard Broad at Huntsman and Manfred Hofmann at 3D Systems for their help and advice.

The influence of the people of the Rapid Manufacturing Research Group at Loughborough University should be recognised in providing a creative and friendly environment over the years. Special thanks should be extended to Mark East for his help with the mechanical tests and to Dr Chris Tuck for reading most of this thesis.

All the staff in the Mechanical and Manufacturing Engineering Department at Loughborough University for their help, with particular mention to Dr Ian Ashcroft for his help with the modelling work. Also, thanks to Prof Marianne Gilbert at Institute of Polymer Technology and Materials Engineering (IPTME) and Dr Ian Sutherland at Department of Chemistry at Loughborough University.

Special appreciation and thanks are dedicated to my parents for their support, encouragement and help during this work.
Publications Arising from the Current Research

Journals


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<tr>
<td>3D CAD</td>
<td>Three-Dimensional Computer Aided Design</td>
</tr>
<tr>
<td>3DP</td>
<td>Three-Dimensional printing</td>
</tr>
<tr>
<td>3D Systems</td>
<td>Manufacturer of different RP machines and materials</td>
</tr>
<tr>
<td>%Elong</td>
<td>Percentage Elongation at Break</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile Butadiene Styrene</td>
</tr>
<tr>
<td>ACES</td>
<td>Accurate Clear Epoxy Solid: Build style used for creation of solid Epoxy models on SLA</td>
</tr>
<tr>
<td>AF</td>
<td>Auto Fabrication</td>
</tr>
<tr>
<td>ALM</td>
<td>Additive Layer Manufacturing</td>
</tr>
<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
</tr>
<tr>
<td>Absorption</td>
<td>The process in which incident radiated energy is retained without reflection or transmission on passing through a medium; &quot;the absorption of photons by atoms or molecules&quot;</td>
</tr>
<tr>
<td>Anisotropic</td>
<td>Having properties that vary with direction within a material</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>Build Orientation</td>
<td>The direction of a part in which it can be built</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>Cationic Polymerisation</td>
<td>Reaction ends up with an atom or group of atoms carrying a positive charge</td>
</tr>
<tr>
<td>Degradation</td>
<td>change in the chemical structure of a plastic involving a deleterious change in properties</td>
</tr>
<tr>
<td>DFM</td>
<td>Design for manufacture</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Bisphenol-A Diglycidyl Ether</td>
</tr>
</tbody>
</table>

- IX -
DSC  Differential Scanning Calorimetry
DPM  Di-Propylene Glycol Monomethyl Ether
Elongation at Break  Increase in length of a specimen under tension (at failure), usually expressed as a percentage of the original length
Extensometer  A measuring device used for measuring the change in the gauge length of a material
FDM  Fused Deposition Modelling
Flexural Strength  The maximum stress the specimen resists under bending before failure, expressed in MPa
Flexural Modulus  The ratio of stress to strain within the elastic limit; it is used to indicate the bending stiffness of a material, expressed in MPa
F.M  Flexural Modulus
F.S  Flexural Strength
FTIR  Fourier Transform Infrared
ISO  International Standard Organisation
Isotropic  Having properties that do not vary with direction within a material
Layer Thickness  The thickness of the cross sectional profiles used to build rapid prototype models
LS  Laser Sintering
M  Monomer
Modularisation  Production of modules that can be bolted together in varying configurations that give the economics of mass production but allows some customisation in the product
Monomer  Compound consisting of molecules each of which can provide one or more constitutional units
NMR  Nuclear Magnetic Resonance
<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPM</td>
<td>Normal Post-Curing</td>
</tr>
<tr>
<td>P</td>
<td>Photo-initiator</td>
</tr>
<tr>
<td>$P'$</td>
<td>Excited Photo-initiator</td>
</tr>
<tr>
<td>$P'$</td>
<td>Reactive initiator molecule</td>
</tr>
<tr>
<td>Photo-Curable</td>
<td>A resin cured when exposed to photo-radiation</td>
</tr>
<tr>
<td>Photo-initiator</td>
<td>Molecule which becomes excited when subjected to UV radiation</td>
</tr>
<tr>
<td>Photo-Polymer</td>
<td>A polymer in which polymerisation is initiated by exposure to light</td>
</tr>
<tr>
<td>Polymerisation</td>
<td>The process of linking small molecules called monomers into larger chains that form polymer</td>
</tr>
<tr>
<td>Post-Curing</td>
<td>Further curing of a part which takes place after completion of the Stereolithography build process</td>
</tr>
<tr>
<td>Post-Processing</td>
<td>Work required after the rapid prototype model has been built</td>
</tr>
<tr>
<td>Recoating</td>
<td>The process of adding a new layer of resin</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity (expressed in percentage)</td>
</tr>
<tr>
<td>RM</td>
<td>Rapid Manufacturing</td>
</tr>
<tr>
<td>RP</td>
<td>Rapid Prototyping</td>
</tr>
<tr>
<td>SFF</td>
<td>Solid Free Form Fabrication</td>
</tr>
<tr>
<td>SLA</td>
<td>Stereolithography Apparatus</td>
</tr>
<tr>
<td>SLA 7000</td>
<td>Stereolithography Apparatus model 7000</td>
</tr>
<tr>
<td>Sorption</td>
<td>A process where water penetrates into a material under specified test conditions</td>
</tr>
<tr>
<td>Stereolithography (SL)</td>
<td>The method of producing a three-dimensional object directly from a CAD model by the use of laser and photo-polymer technologies</td>
</tr>
<tr>
<td>STL</td>
<td>Surface Tessellation Language</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Strain</td>
<td>Nominally the ratio of the increase in length and the original length of a material</td>
</tr>
<tr>
<td>Strain at Break</td>
<td>The percentage elongation when the specimen breaks which is the ratio of change in length as a result of the applied force to the original length.</td>
</tr>
<tr>
<td>Stress</td>
<td>Nominally the relationship between an applied force and the cross-sectional area.</td>
</tr>
<tr>
<td>Support Structure</td>
<td>An additional part of a rapid prototype model which is to connect the model to the platform and give support to over-hanging or separated areas during part building.</td>
</tr>
<tr>
<td>Thermoplastic</td>
<td>A plastic material that is softened by heating and hardened by cooling in a reversible process.</td>
</tr>
<tr>
<td>Thermoset</td>
<td>A plastic material that is hardened by an irreversible chemical change.</td>
</tr>
<tr>
<td>TMA</td>
<td>Thermomechanical Analysis</td>
</tr>
<tr>
<td>TPC</td>
<td>Thermal Post-Curing</td>
</tr>
<tr>
<td>TPM</td>
<td>Tri-Propylene Glycol Monomethyl Ether</td>
</tr>
<tr>
<td>Oligomer</td>
<td>A substance composed of molecules containing group of atoms linked to each other</td>
</tr>
<tr>
<td>Ultimate Tensile Strength</td>
<td>The maximum stress the specimen can reach before it fails. It is expressed in MPa</td>
</tr>
<tr>
<td>Uncured Resin</td>
<td>Photo-polymer resin not cured by the laser during part building that remains within the Stereolithography model prior to curing</td>
</tr>
<tr>
<td>Up-facing Surface</td>
<td>A surface on a Stereolithography part that is orientated in the X-Y build direction and facing the top of the vat of photo-polymer during part building.</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-Violet</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>Ratio of stress to the corresponding strain below the proportional limit (within the elastic stage)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>α</td>
<td>Diffusion system’s parameter</td>
</tr>
<tr>
<td>A</td>
<td>Cross-sectional area</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion Coefficient</td>
</tr>
<tr>
<td>δ</td>
<td>Deflection</td>
</tr>
<tr>
<td>e</td>
<td>Exponential</td>
</tr>
<tr>
<td>E</td>
<td>Young’s Modulus</td>
</tr>
<tr>
<td>F</td>
<td>The rate of transfer per unit area</td>
</tr>
<tr>
<td>K</td>
<td>Diffusion system’s parameter</td>
</tr>
<tr>
<td>l</td>
<td>Thickness</td>
</tr>
<tr>
<td>L</td>
<td>Gauge length</td>
</tr>
<tr>
<td>M</td>
<td>Mass of penetrant absorbed</td>
</tr>
<tr>
<td>P</td>
<td>Applied force</td>
</tr>
<tr>
<td>S</td>
<td>Stiffness</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T_g</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>w</td>
<td>Width</td>
</tr>
<tr>
<td>x</td>
<td>Distance</td>
</tr>
<tr>
<td>X</td>
<td>Equation variable (in the model)</td>
</tr>
<tr>
<td>Y</td>
<td>Equation variable (in the model)</td>
</tr>
</tbody>
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Chapter 1  Introduction and Literature Review

1.1 Introduction

There are a group of technologies currently available that are used to generate physical parts directly from 3-Dimensional Computer Aided Design (3D CAD) models by building them in additive layers. Collectively they are known as Rapid Prototyping (RP). Other associated names include Solid Freeform Fabrication (SFF), Additive Layer Manufacturing (ALM), Auto Fabrication (AF) and Additive Manufacturing (AM). There are different RP processes that are widely used worldwide such as Stereolithography (SL), Laser Sintering (LS), Fused Deposition Modelling (FDM), 3-Dimensional Printing (3DP) and others. As stated by Jacobs [1], RP technologies have gained diversity, complexity, sophistication and popularity since their introduction in the late 1980’s. Sambu et. al. [2] discussed that the ease, speed and low cost of fabricating models using RP has had a very significant impact on the product development cycle due to eliminating the need for complex process planning.

There is a specific approach which is used in all of the RP processes; this is to produce parts by sequentially building them additively with the general principle that material is added together in the form of joined layers to build the desired component. The additive manufacturing approach is now being adapted for end-use-parts, which is known as Rapid Manufacturing (RM). The term RM does not
solely suggest that parts are produced rapidly, but that they are manufactured using the additive approach.

There are different examples [3,4,5] of RM that are being undertaken with existing RP systems to produce functional end-use parts. However, no current RP method can really be considered as a true manufacturing process as there are significant problems with the speed, resolution and repeatability that need to be overcome to achieve standards of conventional manufacturing processes. Also the parts presently have certain inherent drawbacks and limitations. Poor surface finish, lack of dimensional accuracy and the limited information about the materials have long been considered the Achilles heel with regards to RP processes [6,7]. Additionally, the range of materials available to these processes is, at present, limited and expensive in comparison to common manufacturing processes. In the case of injection moulding, for example, there are thousands of materials available that can be processed in the same machine compared to those used in RP [8]. Another constraint concerns the build-time for components which is very long in comparison to conventional manufacturing, especially for large parts. This was highlighted in previous work by Hopkinson [9]. However, the number of RM applications are increasing due to the ease of the RP processes additive approach and the limitations that can be found in the common manufacturing techniques. Considering injection moulding for example, there are some disadvantages, such as [10]:

- High tooling costs, which means a large volume of parts, must be produced to amortise the cost of tools [11]
- The length of setting-up time for pre-production
- The difficulty for tool designers to determine the location of the split line (parting line) for asymmetrical products [12]
- Injection moulding is unsuitable for the economic production of custom parts due to the high upfront cost of tools
Despite the restrictions related to RP, limitations connected to conventional manufacturing techniques along with the rapid improvement in the different aspects of RP are allowing RM to take place now. This trend will increase in the near future [5]. In this Chapter, RM is discussed along with its benefits to companies and customers. In addition, the problems related to the current RP materials that restrict their use in RM are also discussed. Emphasis will be given to Stereolithography (SL), as it is one of the most developed RP processes and has potential to be used for manufacturing in the near future, and is therefore the main RP process which is used throughout this research. The chemical components of SL materials are introduced in order to study the effects of different degradation factors, especially humidity, on the mechanical properties and cross-linking of the SL materials. The hypothesis of the PhD will then be detailed.

1.2 Rapid Manufacturing (RM)

More work is required to convert “Additive Manufacturing” into viable manufacturing techniques that can be more universally exploited. However, during the last few years, the RP industry has undergone significant improvements in developing machines and materials [2]. It is anticipated that true RM manufacturing systems will become available within a ten year period and according to Griffiths [13] and Hague et. al. [14], their introduction will truly amount to a new industrial revolution. In order to achieve this, different research areas are being investigated to eliminate the disadvantages that are currently associated with RM [15,16].

Hague et. al. [17] further discuss the impact that RM will have on the manufacturing environment. The principle advantage of the additive manufacturing processes (including most, but not all of the currently available RP techniques) is the ability to manufacture parts of virtually any geometry without
the need for tooling [18]. If this principal were extended to true manufacturing processes then the opportunities for product design and manufacturing are immense. The need for tooling in conventional manufacturing represents one of the most restrictive factors for today’s product development. The absence of tooling with additive manufacturing processes means that many of the restrictions of traditional “Design for Manufacture” (DFM) that are necessary for economic manufacturing are no longer valid. The ability to produce virtually any geometry that is created in a 3D CAD system means that one is entering a new dimension of “Manufacture for Design” rather than the more conventional DFM philosophy. This was discussed previously by Campbell et. al. [19]. In addition, as no tooling is required, there will no longer be a need to produce many thousands of parts in order to amortise the cost of expensive tooling. Thus the potential for cost-effective custom manufacturing becomes apparent.

True customisation is not feasible at present for the mass-market and thus mass-customisation is currently achieved by “modularisation” [20], i.e. the production of modules that can be bolted together in varying configurations that gives the economics of mass production but allows some customisation in the product. Standard manufacturing techniques are still employed for the modules and therefore there is still a need for costly tooling. With RM, not only is complexity independent of cost, but also the RM techniques are able to produce virtually any geometry [21]. Additionally, high volumes do not need to be manufactured to offset the cost of tooling. Thus the possibilities for affordable, highly complex custom parts become apparent. In theory, each part that is produced could be a custom part (with a different design) [22].

Another benefit of RM will be that it offers the potential to change the paradigm of manufacturing, service and distribution with opportunities for producing highly complex, custom products at low cost, at locations outside the conventional factory, possibly by the distributor, retailer or customer. Also RM will affect both manufacturers as well as customers. For manufacturers, costs will be dramatically
reduced, as less tooling is required. For customers, affordable, complex, individualised products will be cost effectively made that can be configured to personal use thus giving the potential for much greater product satisfaction. However, for true customisation to occur, the involvement of the customer in the design process is not only desirable but essential, as in order to truly individualise a product, there will be a need to digitise all or part of a customer’s body profile and generate designs that were partly or completely developed by the customer. But the location of where this design-customisation is performed and how is it to be realised and how it can be executed in a timely and cost-effective manner are all questions that need addressing. How the customer interacts with the 3D data is also far from clear as current 3D CAD systems are expert systems that require significant training [14,19].

In addition to the previously mentioned benefits of RM, another advantage is the ability to produce physical objects of any complexity in a relatively short period of time along with the capability of changing or modifying the design at any time. This cuts the completion time taken to produce end-use parts which will help in the product development cycle. Designers will have various benefits when using RM [21]. These include:

- Increase part complexity with little effect on lead-time and cost
- Create more organic, sculptured shapes for functional reasons
- Optimise part design to meet customer requirements
- Minimise time-consuming discussions and evaluations of manufacturing possibilities

Despite all of the previously mentioned benefits, RM is still at an early stage and in order to study the possibilities for manufacture, it is required to resolve the current RP limitations and convert the current RP machines to fully functional RM systems. The promise of true engineering products produced by actual RM systems will be realized through machine and material improvements. However,
the lack of RP engineering materials is one of the most significant barriers to the growth of this technology. Choosing the part material is not generally a problem in many conventional manufacturing processes, as there are a wide selection of materials to choose from (depending on the required properties and the usage of the part). In RP, there are limited numbers of materials [23] and with a few exceptions [24], the materials used differ from one process to another; each process has its own materials, which cannot generally be used in other RP techniques. Therefore, materials tend to be process specific and thus designers are limited to the available materials of each process.

There has been much work centred on investigating the properties of RP materials in order to increase the number of the materials that can be used in RP and therefore increase the possibilities of evolving RP to RM [25,26,27,28]. Materials available now include metals (such as Steel), and plastics (such as Acrylate, Epoxy, Nylon, PolyCarbonate, Polystyrene and ABS) [24]. These materials are used in different forms such as powder, paste or resin depending on the process and how the machine operates. This has been explained elsewhere [29]. However, the concern of this research is mainly dedicated to Epoxy-based Stereolithography parts. SL is one of the processes that are currently used for limited manufacturing purposes and also shows the potential for being used for various manufacturing applications in the near future due to its high accuracy [1]. Therefore, it is of importance to discuss the potential of using SL as a manufacturing process. The other processes are covered in detail by other sources [30,31,32,33,34,35,36].

1.2.1 Stereolithography for RM

The SL process has always been one of the most significant RP technologies and it is considered to be suitable as a future end-use part manufacturing system due to its accuracy and consistency [14]. Some well-documented current applications of RM using Stereolithography include:
- **Formula 1 Motor Racing**: Companies are currently producing Stereolithography (SL) parts for use as functional components in the race cars. Also, they use the same technique to produce the wind tunnel models that are used in the constant battle to refine aerodynamic performance [37].

- **Hearing Aids**: Siemens and Phonak use Stereolithography (SL) machines for the fabrication of custom hearing aid bodies [38].

Other examples of where the SL process has been used for actual end-use applications were discussed in previous work [30,39]. However, the number of end-use parts is limited due to different factors, such as the low number of materials compared to those used in conventional manufacturing techniques. There is also limited and incomplete information about the materials currently used as there are large gaps in the data set. More importantly, there is evidence of long-term instability of the parts post-build [40]. However, if designers become aware of the properties of the SL resins, they will have more confidence in employing the suitable material for the required application.

There is a significant effort being expended by the manufacturers of the SL resins and researchers to improve the material properties and make them equivalent to those currently used in the conventional techniques. Thus the characterisation and analysis of the properties of these materials under various ageing, temperature and humidity conditions is of importance. The methodology of operation for RP processes in general and SL specifically is explained in Section 1.3.

### 1.3 Stereolithography (SL)

The word Stereolithography is derived from the word 'Stereo' which means having or dealing with three dimensions of space, and the word 'Lithography', which means the process of printing on a surface [41]. Stereolithography was the
first RP process to be commercially developed; it was introduced during the late 1980s by 3D Systems in the USA [42]. The use of SL technologies has widely increased worldwide in different sectors. Traditional applications of SL [5,24] include:

- **Model Making & Verification**: Models are made to assure correct dimensions and to verify that the design contains the features desired and, conversely, does not contain any features that are not required. This is done prior to spending money producing tools for mass production [43]

- **Medical Procedures**: SL offers the possibility of modelling bones or body organs to be used for pre-operative planning, simulation, shaping implant devices and teaching [44]

- **Architecture**: Architects have always used models as a way of conveying their design concepts to the public and these models can be produced using SL [45]

- **Visualisation and Evaluation**: The best way to be certain that a part contains exactly the features intended is to hold it in the hand and look at it from all sides [46]

- **Iteration & Optimisation**: With SL, it is possible to go through multiple design iterations within days as the geometry can be modified in CAD and the part can be easily rebuilt [47]

One of RP's benefits (including SL) is to reduce the time taken to produce a part by eliminating the additional sequences required in other conventional techniques, such as design and production of the required tools, as RP techniques produce solid objects directly from 3D CAD models [24,48]. There are several RP systems that are commercially available and each process has its own method of operation. However, the process flow of producing a part using the majority of the RP techniques (including SL) currently available is explained in Figure 1-1.
The SL technique, depicted in Figure 1-2, is based on the process of photo-polymerisation, in which a photo-sensitive liquid resin is converted to a solid polymer by computer controlled exposure to ultraviolet radiation by a laser [44].
The photopolymer is selectively cured on an additive layer-by-layer basis where the cured area corresponds to a particular cross-section of the required shaped article to be produced, which has been derived from the 3D CAD model of the part.

Figure 1-2: Schematic diagram of the Stereolithography process [49]

1.3.1 CAD Model Preparation

Referring to Figure 1-1, firstly the required part is modelled in three dimensions using any available 3D CAD software and then the file must be translated to a “tessellated file”, which is in a format called ‘STL’. This type of conversion transforms the surfaces of a solid CAD model to a model defined by a set of triangles with the appropriate normal orientation.

The triangles in the STL file are classified into three types: Flat, Near Flat & Steep triangles, according to the planar orientation and the unit normal direction, as shown in Figure 1-3. This type of format is compatible with the
Stereolithography Apparatus (SLA) and all other RP systems, and increasingly other applications such as High Speed Milling (HSM) [50].

![Image of STL file and classification of triangles](image)

Figure 1-3: STL file and classification of triangles

1.3.2 Orientating, Supporting and Slicing of the Part

After transferring the file to ‘STL’ format, the build orientation of the part is then defined. There are different factors to be considered when orientating a part, such as:

- **Part Size**: This should be considered, especially for large parts, according to the build envelope (vat size: 508 x 508 x 584 mm for SLA 7000) which determines the build orientation and whether the part can be built as one piece or not.

- **Part Aesthetics**: The up-facing surfaces produced by SLA usually have a better surface finish compared to the down facing and side surfaces. This is because down facing surfaces are affected by the support structures and the side surfaces are affected by the steps formed from building the layers.

- **Build Time Reduction**: Reducing the number of layers saves time, as the build time is highly dependent on the part height [51]. For example, if the part required to be built is rectangular, as shown in Figure 1-4, the more suitable way to build and save time is to choose the side orientation (Figure 1-4 (B)) as this orientation requires less layers in the vertical direction.
- **Reduce the Amount of Supports**: In the SL technique, the supports are generated from the same material as the required part and therefore need to be removed after building. The choice of build orientation will affect the amount of supports required [51], as also shown in Figure 1-4.

![Figure 1-4: Selection of the build orientation and how it affects the amount of supports](image)

As described, there are different factors affecting the selection of the build orientation and it is difficult to satisfy all the criteria (e.g. minimum amount of supports, minimum build time and best surface finish) and thus there should be a "preferred" factor when deciding the build orientation which is normally the surface finish of the resultant part.

Supports can be generated automatically using computer software (e.g. Materialise MAGICS [52] or 3D Lightyear [53]). These software packages also allow a change in the support structure to increase the amount of supports if required. The supports are an important issue in SL as they are used to anchor the part to the build platform during the build process and provide a gap between the platform and the part to ensure ease of removal. Also they facilitate supporting of overhanging features [54].

The basic structures of supports that are now commonly used consist of strand and projection supports, as shown in Figure 1-5. The strand type is vertically oriented...
to provide support to the part while it is being built and the projection supports are angular members that give the structure some rigidity.

![Support Structure Diagram](image)

Figure 1-5: The support structure commonly used in SLA [41]

The following step for the software is to slice the part and supports into discrete 2D horizontal slices to guide the building process, as shown in Figure 1-6. The software connected to the machine automatically carries out this operation but the operator can control the thickness of the slices (within limits). As the slices become thinner, the better the surface finish of the product that will be obtained on side walls but also the time taken to build the part will increase [44]. Slice data contains information related to the type of scan used by the machine. This includes whether it is border, hatch (normal layers) or skin fill (used for up-facing, down-facing and rounded surfaces) as shown in Figure 1-6.

![Slicing Diagram](image)

Figure 1-6: Slicing the part [41]
1.3.3 Building the Required Part

After completing the procedures discussed in the previous Section, the part is now ready to be built. Using the SL technique, the required article is built-up from a photo-curable resin with the aid of recurring alternating sequences that have been explained in various literature [41,55,56,57]. These sequences are:

1. The platform starts just below the surface of the resin and the support structures are built first using radiation from a computer-controlled laser source. The cured area corresponds to the desired cross-section of the required shape. The default height of the supports is (normally) 12mm.

2. After building the supports, the platform moves down to a specified clearance from the surface equivalent to the layer thickness, as shown in Figure 1-8. SL offers the smallest layer thickness compared to the other RP processes within the range of 0.025 to 0.1524 mm (this is found in the SLA 7000 by 3D Systems) [54].
3. When the required supports have been produced (usually 12mm) and after the resin settles, the laser scans the first layer of the actual part, as shown in Figure 1-9.

![Figure 1-9: Laser scans the first layer of the actual part](image)

4. The solidified layer is lowered, it is then covered with a new layer of resin by the sweeper (recoating blade) shown in Figure 1-10, which moves over the surface at specified speed (sweep speed). The number of movements of the recoating blade can be adjusted to insure that the whole surface is covered with resin.

![Figure 1-10: Blade moves across the vat](image)

5. If required, more supports are built to support overhanging features at the same time when building the actual part, as shown in Figure 1-11.

![Figure 1-11: Building more supports](image)
6. The process is repeated until a green model of the required shape is finished, as shown in Figure 1-12.

![Figure 1-12: Finished part](image)

The build parameters (e.g. laser power, border speed, hatch speed and fill speed) are usually specified by the resin manufacturer. The build style which is mainly used in SLA’s is ‘Accurate Clear Epoxy System - ACES’, where the photo-curable liquid resin is being cured in “parabolic shapes” that overlap horizontally to form layers. Theses layers overlap vertically to form solid parts as shown in Figure 1-13 [58].

![Figure 1-13: Schematic diagram shows the ACES build style used in SLA](image)

### 1.3.4 Post-Processing of the Part

At the end of the building process, the platform is raised to lift the object clear. It is then drained, washed and supports removed from the parts. The parts then need to be washed, usually in a chemical solvent such as Di-Propylene Glycol
Monomethyl Ether (DPM) or Tri-Propylene Glycol Monomethyl Ether (TPM), to remove this residual resin film that is on the surface of the part as it is a hazardous material when uncured. The parts are then cleaned in water [48]. For most SL resins, TPM is generally used as it has been found to cause the least swelling distortion. Additionally, it is much less volatile, has little odour and it is very effective with most of the approved SL resins compared to DPM. However, in the past, Alcohols (Methyl, Isopropyl, or denatured Alcohol) were also commonly used to clean SL parts, but it was found that these solvents cause swelling and distortion and therefore reduce part accuracy [44].

After the cleaning stage, the green model is not fully cured and requires further curing. Therefore the part is post-cured in a UV Post-Cure Apparatus (PCA) for a period of time depending on the size and the geometry of the model (between 1 and 2 hours) to ensure that all the resin has been cured and to get rid of the tacky surfaces [59,60]. Thermal post-curing (TPC) can also be applied to stabilise the mechanical properties of the part (normally the parts are kept for two hours at 80°C). The decision of whether to thermally post-cure is dependent on the particular SL material being used. The use of a thermal post-cure accelerates the ageing mechanism and can also have deleterious effects if not controlled correctly. This is discussed in detail in Chapter 2. After post-processing, the parts are finished and ready for the purpose that they were produced for.

1.4 Stereolithography Resins

SL resins are photo-polymers and they are primarily cured using a UV light source [61]. Polymers consist of macromolecules that are composed of monomeric units. Smith [62] explained that these units are joined together by chemical bonds that are in the macromolecular chain and connect various atoms (side groups) within the chain. There are different types of chemical bonds that
exist in the polymeric structure. The large molecules are held together by covalent bonds. Rodriguez [63] showed that there are also intermolecular forces known as “Van Der Waals” that attract the separate molecules to each other. These bonds can be generally found in most polymeric structures, including SL photo-polymers.

The majority of SL resins mainly consist of thermoset resinous elements such as Epoxy and Acrylate, or a combination of them both, with the addition of a light curing agent (photo-initiator). This is also known as a hardener as it causes phase conversion and subsequent material polymerisation (solidification) when they are exposed to UV radiation [64]. Thermosets cannot be melted and reshaped due to the strong bonds (chemical cross-linking) between molecules. This leads to different mechanical properties and temperature resistance compared to thermoplastics that can be re-melted and reshaped [65,66].

1.4.1 History of SL Resins

Acrylate-based resins

The first photopolymer systems used for SL were based on Acrylate monomers, which polymerise through a free-radical mechanism [67]. Acrylate-based SL photopolymers are generally characterized by high reactivity, although fully cured surfaces may not be achieved due to Oxygen inhibition. For these materials, polymerisation was accompanied by significant shrinkage. Cationic photopolymerisation (where the reaction ends up with an atom or group of atoms carrying a positive charge) is not influenced by the presence of Oxygen and cure shrinkage is quite limited. For this reason, cationic photopolymer monomers are currently used in SL. However, as explained by Decker and Moussa [68], cationic photopolymers show a prolonged continued curing, usually called “dark reaction”, even after the light source has been removed. An increase of green strength due to the dark reaction (up to a certain limit), even at room temperature, may be
substantial for a cationic system and particularly beneficial for SL. In Acrylate-based resins the dark reaction is negligible compared to other systems and the green strength does not substantially change once the part has been laser cured.

**Epoxy-based resins**

Over time, modifications were carried out to improve the functionality of SL resins. The structure mainly consisted of Epoxy and other chemical elements (without Acrylate). It was found that the parts produced solely from Epoxy resins show high relative geometrical accuracy, but suffer from very low elongation to break along with low impact strength due to their relative brittleness [55]. Attempts were made to solve this problem. As SL resins were Acrylate-based materials in the past, most of the efforts concentrated on the Acrylate-based compositions that use Acrylate Urethane oligomers, (note: an oligomer is a substance composed of molecules containing a group of atoms linked to each other [69]). This is due to the high flexibility and toughness of the Acrylate polymers, which improves the impact resistance of SL materials. However, there are some disadvantages that should be considered when adding Acrylate, such as:

- Atmospheric Oxygen retards the polymerisation process [70]
- Large cure shrinkage [70]
- Acrylate Urethane compounds are hazardous materials [71]
- Reduction in the cure-speed, due to the acid generated from the disassociation of the cationic photo-initiator (which is responsible for the polymerisation of the Epoxy ring or any other cationically cured compound), reacting with the Nitrogen of the Urethane group, thus prohibiting cationic photo-polymerisation reaction from taking place [72]

Due to these disadvantages, the percentage of Acrylate has been decreased in the SL compositions and low to medium range molecular weight Polyols (e.g. Polyether Polyols) were used instead. They rely on the reduction of the cross-link density of the three dimensional network as a means of reducing the brittleness of
the cured object [70,73]. This negatively affects the thermal properties as the Glass Transition Temperature ($T_g$) is reduced. Mechanical properties, such as rigidity, are also reduced along with the material’s ability to resist different environmental conditions (e.g. humidity), which can lead to material degradation.

1.4.2 Chemistry of SL Resins

The majority of Epoxy-based SL resins consist of [44,70]:

- Liquid multifunctional Epoxy monomers (difunctional or trifunctional – this is according to the number of reactive molecules)
- Cationic photo-initiators
- Free-radical photo-initiators
- At least one liquid Poly(Meth)Acrylate
- At least one liquid DiAcrylate
- A Polyol component selected from the group consisting of OH-terminated Polyethers, Polyesters and PolyUrethanes
- Other additives and fillers

The percentage of each element varies from one type of resin to another and is dependant on the required properties of a particular SL resin. Other chemical elements can be optionally included such as Vinyl-Ether-based resins or other cationically cured components (e.g. Oxetanes and Spiro-Ortho Esters) to further control mechanical properties [70].

**Polymerisation mechanism**

Polymerisation is the process of linking small molecules (called monomers) into larger molecular chains that form the polymer (which is comprised of many monomer units) [74]. The process of photo-polymerisation which occurs in most of the SL resins can be explained as follow [44,75,76]:
- A mix of photo-initiator molecules (P) and monomers (M) is exposed to a UV source. UV consists of actinic photons that are in the form of radiation and provide energy which allows a photochemical reaction to occur in the SL resin. This is represented by “UV” in Figure 1-14.

- The photo-initiators absorb some of the photons and convert them to an excited photo-initiator species (P') which are then converted to reactive initiator molecules (P*). These reactive molecules are free radicals and have enough energy to be involved in a chemical reaction.

- The reactive initiator molecules (free radicals) react with the monomer molecules to form a polymerisation initiating species (PM*), which is defined as the chain initiation step. This reaction is exothermic, which produces energy in the form of heat. This heat helps the reaction to occur more rapidly.

- Additional monomers continue to react during the chain propagation step forming longer chains (PMMMMM*) until a chain inhibition process ends the polymerisation reaction.

Figure 1-14: Simplified free radical photo-polymerisation sequences [67]
Continuing the reaction for the required time, the resin will be converted to a high molecular weight and shear strength increases, therefore, the system changes from liquid to solid. The average distance between groups decreases resulting in an increase in density (shrinkage). With the difunctional monomers (two reactive sites per molecule), the polymerised material becomes highly viscous and eventually becomes a super viscous solid. However, Schultz [77] stated that, in the case of the monomer molecules that have three or more reactive chemical groups, the resulting polymer will be cross-linked.

The photo-polymerised species must hold sufficient green strength to remain structurally intact; this is facilitated by the inclusion of the more rapidly curing Acrylate element. As the laser cured SL photopolymer is post-cured with additional UV radiation, the reaction proceeds further; this increases the degree of polymerisation and the cross-link density. Cross-linking is formed by strong covalent bonds that connect the polymer chains to each other.

**Dark reaction**

After the post-curing stage is completed and the part is ready, further polymerisation takes place even in dark conditions (dark reaction), which is due to the existence of un-reacted monomers and dangling bonds within the cross-linked polymer network. This further polymerisation converts at a certain stage of the life of the SL part to consecutive stages of stability followed by degradation due to the extent to which the reaction can continue. This is one of the degradation factors that occur in SL parts. However, there are other factors such as humidity, radiation, ageing and temperature. The different degradation factors that can affect the main constituents (Epoxy and Acrylate) of the current Epoxy-based SL resins are discussed in Section 1.5.
1.5 Epoxy/Acrylate Degradation

This Section discusses the different factors that cause degradation and how these factors can affect the main chemical constituents of current SL materials. The mechanisms of degradation of these main components are discussed with respect to their chemistry. This is to achieve an understanding of what can happen within the chemical structure of the Epoxy-based SL material due to the different factors of degradation.

Degradation can be defined as "the exposure to different factors such as temperature, humidity, radiation and chemicals that deteriorate the properties of the material and ruin its outward appearance" [69,78]. Deteriorative reactions occur during the useful life of materials, when they are subjected to degradation factors. The factors of degradation and the mechanisms of degradation must be understood if the technology and application of polymers are to continue to advance [79].

The lifetime of any material is not only dependent on its chemical structure, but also on its surrounding environment. Different factors may cause material degradation, such as moisture, light, Oxygen, Ozone, high-energy radiation, mechanical stresses, atmospheric pollutants, high temperature, temperature variation, chemical attack and various combinations of these factors [80]. These factors affect the material in different ways but they all result in degradation of the material. However, the main factors of degradation of polymers found in common environments are discussed below:

1.5.1 Elevated Temperature

Increasing the temperature of any thermoset causes the amplitude of segmental vibrations inside the polymer to be increased. In a transitional state, the chain segments have sufficient energy to overcome intermolecular bonding forces,
causing the chain segments to perform rotational and transitional motions. Before exceeding the glass transition temperature \( (T_g) \), the elasticity of the material increases as the segmental motions become very rapid. However, the molecular motion is restricted by chain entanglements. With increasing temperature, the degree of entanglements decrease and the slippage of molecules increases; at the same time, there is some elasticity shown, which was discussed by Grassie and Guy [81]. After exceeding the glass transition temperature, the slip increases and the elasticity disappears as the conformational freedom of the thermoset can be compared to that in a solution (liquid state). Since the mobility of the chains and radicals increases above \( T_g \), Oxygen diffusion occurs more rapidly and therefore increases the amount of Carbonyl compounds (volatile elements) causing weight loss of the material [82] and increases the rate of degradation [83].

Increasing the temperature leads to an increase in the rate of degradation of a polymer, as shown in Figure 1-15. When the temperature reaches a certain level, after exceeding the stage of breaking the cross-linking in the polymer network and weight loss takes place due to the existence of volatiles, the material can reach a stage where it is converted to black Carbon powder (burned material). This occurs at a much higher temperature than the melting point and \( T_g \) in thermoplastics and thermosets, respectively. However, if the temperature is reduced at a specific stage (dependent on the type of the polymer), the polymer can return to its original state. This happens mostly in thermoplastics and different rearrangements of the polymer network can be achieved. A thermoplastic polymer can withstand high temperatures above its melting point as it stays at the liquid stage without significant change, unless the temperature reaches the level where the liquid material produces volatiles [84].
The case is different for thermoset polymers as they do not melt. If the temperature effect has stopped at a stage before exceeding the glass transition temperature of the polymer ($T_g$), the material might go back to its original status. $T_g$ is material dependent and governed by the chemical structure and the hygrothermal history of the material. If the temperature effect stopped at a stage where $T_g$ was exceeded and volatiles were produced, it is difficult for the material to retain its original status due to the weight loss that took place during the degradation process. This causes shrinkage of the material and subsequent crack propagation [85].

There have been various investigations carried out to identify the effects of elevated temperatures on different types of Epoxies. A study was conducted by Bishop and Smith [86] to investigate the thermal degradation of an Epoxy resin and it was found that at 400°C, the Amine cross-linked resins yielded Hydrogen, Methane, Carbon Dioxide and water as they contain [-CH$_2$-CHOH-CH$_2$-] groups. The degradation and the number of degradation products were found to increase relatively with temperature [87]. Another study by Chen et. al. [88] shows that, at a temperature around $T_g$, Epoxy resins exhibited a rubbery behaviour. This was also proved in other work by Lemay et. al. [89].
Ciutacu et. al. [90] found that applying an Oxygen pressure along with a high temperature (thermo-oxidation) is a further degradation factor. Also, it was found that the mechanical properties of glass-reinforced Epoxy are affected more at lower temperatures when an Oxygen pressure was applied, as it accelerated the degradation process. In both cases, thermal degradation and thermo-oxidation, the mechanism of degradation was found to be the same.

1.5.2 UV Radiation

UV radiation results in a photo-oxidation reaction. A study was carried out by Frazza and Schmitt [91] to investigate the effects of UV radiation and how it led to a mechanism of photo-oxidation. The study showed that photo-oxidation in some types of thermostets increased the amount of Carbonyl compounds (groups in which an Oxygen atom is double-bonded to a Carbon atom (O=C). The Carbon atom then has two additional bonds to attach to the rest of the molecule [92]). Some Carbonyl groups act as sensitizers by UV light absorption, which forms free radicals. The free radicals are groups of monomers that disconnect from the main polymer network and start to behave differently and react to rearrange the Hydrocarbon chains. This leads to a rapid reduction in the molecular weight of the polymer and hence degradation, which is shown in the form of brittleness in the polymer [93]. Photo-oxidation reaction occurs and affects only the skin of the part, while the bulk material is protected by the degraded surface layers that are usually different in colour to the bulk material [94].

It was shown by Monney et. al. [95] that the photochemical degradation of an Epoxy material occurs due to the gradual ablation of the organic matrix by loss of volatile photo-degradation products. Identification of the volatile photo-products of a photo-oxidised Epoxy matrix was highlighted in other work, also by Monney et. al. [96]. Five Benzene compound products were identified by mass spectroscopy. They include: Benzene, Styrene, Benzaldehyde, Benzophenone and Benzoic Acid.
Nano-indentation was used in another investigation by Delobelle et al. [97], which showed that the mechanical properties of a Bisphenol-A Diglycidyl Ether (DGEBA) Epoxy increased with irradiation time and continuously decreased with the indentation depth. These decreases are characteristic of the presence of a hard film on a softer substrate (estimated at about 2μm). This is due to the fact that the photo-degradation of Epoxy leads to the formation of a thin photo-oxidation layer at the matrix surface, which then spatially advances into the matrix of the polymer. This was shown in previous work using physico-chemical analysis by Monney et al. [98].

1.5.3 Humidity

In polymer matrices, moisture absorption can lead to a wide range of effects, both reversible and irreversible. These effects include plasticization by weakening of the intermolecular interactions among the functional groups of the chains [99,100] and de-bonding at filler-matrix interfaces [101,102,103]. They also include leaching of un-reacted functional groups [104], structural damage such as micro-cavities or crazes [105,106] and chemical degradation of the polymer matrix due to hydrolysis and oxidation during long-term exposure to water, which was proved by Antoon and Koenig [104]. In addition to the previous effects of water on polymers, thermal properties, such as $T_g$ were investigated by Moy et al. [107] and Ivanova et al. [99], along with the mechanical properties that were investigated by Kasturiarachchi and Pritchard [102], Lawrence et al. [108] and Butkus et al. [109]. It was shown that both $T_g$ and mechanical properties can be significantly affected by humidity.

The significant role of water lies in the combination of its physical properties with its chemical reactivity. Hamid [110] and Al Andrady [111] have identified that moisture can have different influences on polymers. One is a chemical influence due to the hydrolysis of unstable bonds. Another is physical, which is due to the destruction of bonds in the polymer network which leads to swelling and
softening. A further influence is that water helps the degradation to occur more rapidly, which involves a generation of free radicals or other reactive species that can react with other chemical factors. Different studies have been dedicated to identify the different mechanisms of degradation that can occur in thermosets due to humidity. Ritter et. al. [112] and Salmon et. al. [113] have shown that water acts as a plasticizer as well as a reactant and that long-term exposure causes a decrease in the molecular weight of polymers due to chain scission (breaking of the cross-links that form the chains in the polymer network) [114,115].

Adamson [116] showed that the transport of water is a three-phase process in which the absorbed water first fills the free volume, then bounds to the network site and finally enters the densely cross-linked region. However, different researchers [117,118,119] showed that water absorbed by the polymer can be divided into free and bound water. Water molecules that are contained in the free volume of the polymer are relatively free to travel through micro-voids and holes and are identified as free water. Water molecules that are dispersed in the polymer matrix and attached to the polar groups of the polymer are designated as bound water, as shown in Figure 1-16.

Figure 1-16: Schematic diagram shows the water in the polymer network
Further research by Yasufuku and Todoki [120], has suggested that bound water within the polymer network can be recognised as loosely bound water, which can be released upon heating, and strongly bound water that is a part of the network which is difficult to remove from the polymer. However, in other research by Antoon et. al. [121], it was found that water absorbed in an Epoxy resin usually interacts with the polar groups by Hydrogen bonding and the Epoxy-water interactions are completely reversible. Another investigation by Delasi and Whiteside [114] has suggested that water in certain Epoxy systems is not bonded to any polar groups or Hydrogen-bonding sites. Clearly, the interactions between absorbed water and Epoxy resins are different for different Epoxy systems and further investigation is needed for specific Epoxy-Acrylate systems.

For both Epoxy and Acrylate, the mechanism of degradation caused by the effect of humidity is the same. The material absorbs water and this water permeates into the polymer matrix, which causes swelling of the part. It behaves as a plasticizer causing a diminution in the tensile strength and often increases elongation. During water absorption, compressive stresses dominate externally due to the pressure of water while tensile stresses dominate internally as a reaction of the compressive stresses, as shown in Figure 1-17. These stresses disappear once moisture equilibrium is achieved [83]. However, these stresses affect the chemical bonds in the polymer network and help in accelerating the degradation process.

Water diffusion in polymers has been described by many researchers using different models. In many cases, the kinetics of water diffusion is assumed to
follow the one-dimensional Fick’s second law, which considers that the driving force of diffusion is the water concentration gradient. Some other models have also been applied to describe more complex diffusion processes. In previous research by Jacobs [122] and Jones [123], Fick’s law was extended to consider the existence of a two-phase Epoxy material with different densities. In other research by Lefebvre et. al. [124,125], a diffusion model was proposed to incorporate temperature and strain as well as penetrant concentration terms in the equation of the diffusion coefficient. This model was based on free volume theories and assumed that the transport kinetics is governed by the constant redistribution of the free volume which is temperature, strain and penetrant concentration dependent. It has been shown that there are four factors that play key roles in the coefficient of moisture diffusion into the Epoxy resin: the polymer network structure, the polymer polarity, the physical morphology of the polymer and the creation of micro-damage in the material [106].

The water absorption effects on the different types of Epoxies were investigated by Zhou and Lucas [126,127], using various analysis techniques. Investigations included determining the effects of humidity on Epoxy resin using Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA) and Nuclear Magnetic Resonance (NMR) techniques, where it has been reported that water molecules bond with Epoxy resins via Hydrogen bonding. Three different modes for water sorption in an Epoxy resin were proposed in a different study by Apicella et. al. [128], these include:

- Bulk dissociation of water in the polymer network
- Moisture sorption onto the surface of holes that define the excess free volume of the glassy structure
- Hydrogen bonding between hydrophilic groups of the polymer and water

In the same study, it was reported that the processing conditions as well as the chemical structure of the polymer matrix constituents influence the resulting
polymer networks and hence the properties of the cross-linked polymer in a wet environment. Also, it was shown by Xiao and Shanhan [129] that the rate of swelling of a polymer is less than that attributed to the mass of water absorbed initially and the swelling process is not reversible. Absorption of 1% water was found to decrease the glass transition temperature ($T_g$) of a filled Epoxy resin (which was used as a structural adhesive) by 8°C [130]. Another study by Monney et. al. [131], proposed that the thickness of an Epoxy glass fibre composite decreases when exposed to humidity along with UV radiation. The study compares the performance of samples that underwent normal environmental exposure (Besançon – France) and those that underwent a method of accelerating degradation (Suntest Instrument). In both cases, a linear correlation was obtained between erosion depth and time of exposure, as shown in Figure 1-18.

![Figure 1-18 Exposure time and decrease in thickness [131]](image)

The same study by Monney et. al. shows that there is a large difference in erosion rate between samples exposed in different locations (Besançon and Bandol – in France). The erosion rate in Besançon was found to be about 40% higher than the rate in Bandol. However, the samples in Bandol obtain about 60% more radiant energy than those in Besançon. This erosion is due to the fact that the amount of rain in Besançon (eastern France) is 3.5 times higher than in Bandol (south east – France).
1.5.4 Ageing

Ageing is the term which is given to the process where irreversible chemical and physical processes occur in the polymer network over time [69], which subsequently leads to deterioration of the polymer network. Previous studies were carried out to investigate the effects of ageing on the mechanical properties of thermosets [73,117]. It has been found that the ageing time on its own, in the absence of any other factor of degradation, does not have a significant influence on the properties of the material. However, if any other factor of degradation is included in the surrounding environment (such as Oxygen, radiation, or humidity), this leads to the development of the ageing stage where the major changes in the polymeric properties occur due to the formation of free radicals and therefore the formation of volatile products [132].

The existence of any degradation factor for a sufficient time may affect the properties of the polymer. One of the degradation factors that causes degradation to take place after enough age is the presence of Ozone. Ozone is a colourless gas (O₃) which is a strong oxidizing agent that exists in the air. It can be obtained from discharge of electricity in Oxygen or by the action of UV radiation on Oxygen [92]. It was found in a previous work by Rashkovan et. al. [133] that Ozone caused the same effects to the polymer network as found by oxidation. However, UV light also causes photo-oxidation, which speeds up the process of degradation as mentioned previously.

In Amine cured Epoxy resin, it was found that photo-oxidation along with ageing led to the formation of Carbonyl or Amide free radicals. The concentration of Amide depends on the Amine component. However, the concentration of the Carbonyl groups does not depend only on the Amine as they are formed from the Amine and the Epoxy resin itself, as shown by Bellenger and Verdu [134] and Zhang et. al. [135]. Further ageing along with absorption of energy (in the form of radiation – range 300 to 330nm) can cause the formation of free radicals [136], as shown in Figure 1-19.
Pairs of radicals are formed from the reactions that are due to the absorption of energy along with ageing. The first reaction leads to chain splitting and therefore a reduction in the molecular weight. The chain scission and the subsequent conversions of these molecular weight products produce volatiles such as Benzene, Styrene, Benzoic Acid, Benzaldehyde and Benzophenone [136].

Ageing along with UV radiation below 300nm can also affect Acrylics, causing chain scission of the polymer backbone (breaking of the chains included in the polymer network). This is due to the free radicals that are formed from radiolysis (molecular disintegration resulting from radiation [92]) on the bonds that are in the side groups as shown in Figure 1-20. This causes a reduction of the molecular weight [137]. The low molecular weight radicals may recombine or undergo further changes forming volatiles (e.g. CH₃OH, H₂CO and HCOOCH₃) and gaseous products (e.g. CO₂ and CO) [138,139].
1.5.5 Chemical Solvents

Chemical solvents are not commonly found in most environments, but when they exist, they deteriorate the material and result in a rapid rate of degradation.

Chemical solvents usually attack the outside layer of the material and cause this to dissolve the part due to the chemical reaction. Once the outside layer is degraded, this allows the chemical solvents to attack the layers underneath. This process is continuous until the part is taken out of this environment. The rate of this process is mainly dependent on the type of the material, the chemical solvent and its concentration.

1.6 Degradation of SL Materials

One of the critical problems related to parts produced by the SL process for manufacturing applications is that they are greatly affected by the various degradation factors such as temperature, UV radiation, ageing and moisture. SL materials have been found to degrade quicker than materials used in conventional manufacturing [140]. However, the effects of degradation factors upon the properties of SL parts have rarely been investigated. UV radiation has been found to affect the parts produced by SL as they are made of photo-curable resins and these resins are highly affected by radiation [141]. The colour of most Epoxy-based parts tends to change and become darker as shown in Figure 1-21, which shows the difference in colour between SL parts that were subjected to sunlight along with normal room-light for one year (yellow samples) and other SL parts made of the same material (SL7560) and at the same time, but they were kept in a dark enclosure (white samples). The change in colour is usually accompanied by an increase in brittleness.
The process of ageing in cationically cured photopolymers (including SL materials) is different to other polymers as there is further curing (dark reaction) which is shown even in the absence of any source of radiation and temperature [68,141]. This further curing leads to degradation after the material reaches the stage where it is fully cured. The time taken to reach the stage of degradation due to ageing is different from one SL material to another depending on the chemical structure, as discussed in Section 1.4.2.

Humidity is considered to be one of the most effective degradation factors that negatively affect the properties of polymers in general and SL materials specifically. However, there is a gap in the research related to this area and also the prior investigations into the effects of humidity on the properties of SL resins have not conclusively identified the exact mechanism of degradation due to humidity. A previous study by Colton and Ottemer [26] showed that humidity caused a drop in the mechanical properties and also $T_g$ of different photo-curable resins that are used in SL. It is therefore important to investigate the mechanism of degradation of the current SL materials in order to improve the resistance of the future resins to humidity and make them more stable, and thus more applicable for RM applications. Also, it is beneficial for designers to be aware of the properties
of the current Epoxy-based SL materials at various working conditions, so they can employ the most appropriate material for the required application.

As humidity was found to be one of the most harmful degradation factors, it was therefore required to investigate the different types of water diffusion into polymers. This is discussed in Section 1.7.

1.7 Types of Diffusion

The diffusion process in polymers has been classified into different cases according to the relative rates of diffusion and polymer relaxation (which is the time taken for the molecular rearrangements to conform with the presence of the penetrant and is dependent on concentration, temperature, pressure, thickness and the hygro-thermal history of the polymer [126,142]). It can be identified using Equation 1-1, which is valid for expressing the initial shape of the absorption curves, as proved by Nogueira et. al. [143].

\[
\frac{M_i}{M_s} = K t^\alpha \quad \text{(Equation 1-1)}
\]

Where \( M_i \) indicates the mass of the total amount of penetrant absorbed at time \( t \), \( M_s \) is the corresponding mass at saturation, \( K \) and \( \alpha \) are system parameters. The diffusion process can be classified into the following three cases [144]:

- **Case I (or Fickian diffusion) \( (\alpha = \frac{1}{2}) \)**, where the rate of diffusion is much less than that of relaxation and can be described by one parameter, i.e. the diffusion coefficient \( D \) [128,145,146,147]. Relaxation is the time taken for the molecular rearrangements to take place after moisture penetration [142]
- **Case II diffusion \( (\alpha \geq 1) \)**, where the diffusion is very rapid compared to the relaxation process. This case can be described by the constant velocity of an advancing front, which marks the innermost limit of penetration of the
diffusant and is the boundary between swollen gel and glassy core. The penetrant (and hence swelling front) moves into the polymer at constant speed, regardless of the distance into the material, confirming that the kinetic mechanism is not diffusive). A molecular diffusion mechanism would require a slowing of the front as the distance into the material increased. The rate which controls this mechanism must therefore be occurring at the front and is generally accepted to be related to the relaxation of polymer molecular chains under the pressure of the penetrant [148,149,150,151]

- **Case III**, non-Fickian or anomalous diffusion lies between case I and case II ($\frac{1}{2} < \alpha >1$), where the rates of diffusion and relaxation are comparable, and this type can be described by various different parameters in addition to the diffusion coefficient ($D$) of case I

### 1.7.1 Fickian Diffusion

Diffusion of water can be presented in a quantitative manner by adopting the mathematical equation of heat conduction derived by Fourier in 1822, as shown by Fick in 1855 [149]. The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of a diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section [152]. This is shown in Figure 1-22.

![Figure 1-22: Diffusion of water in polymers](image-url)
This hypothesis can be presented in a form of mathematical Equation, which is denoted by Fick’s first law in Equation 1-2.

\[ F = -D \frac{\partial c}{\partial x} \]  
(Equation 1-2)

Where \( F \) is the rate of transfer per unit area of section \( A \) (in g s\(^{-1}\) cm\(^2\)), \( C \) is the concentration of diffusing substance (in g cm\(^{-3}\)), \( x \) is the space coordinate measured normal to the section (in cm), and \( D \) is the diffusion coefficient (that is measured in cm\(^2\) s\(^{-1}\)). The negative sign in Equation 1-2 is due to the fact that diffusion occurs in the direction opposite to that of increasing concentration [149].

Considering the total transport of moisture into and out of a two dimensional differential element, as shown in Figure 1-23, the rate of change of moisture with time can be obtained, as presented in Equation 1-3.

\[ \frac{\partial F_y}{\partial y} \delta y + \frac{\partial F_x}{\partial x} \delta x = \frac{\partial c}{\partial t} \]  
(Equation 1-3)

Figure 1-23: Two dimensional moisture transport [145]
Where $t$ is time (in s). Substituting Equation 1-2 into Equation 1-3, the general governing equation for moisture concentration in two dimensions can be derived as shown in Equation 1-4.

$$
\frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial c}{\partial y} \right) = \frac{\partial c}{\partial t}
$$  

Equation 1-4

If $D$ is independent of direction and the concentration of the penetrant, Equation 1-4 can be simplified to Equation 1-5.

$$
D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) = \frac{\partial c}{\partial t}
$$  

Equation 1-5

For one-dimensional diffusion through semi-infinite plate of thickness $(l)$, Fick’s second law reduces to Equation 1-6 [145,149].

$$
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{(Equation 1-6)}
$$

Equation 1-6 can only be used in the case of Fickian diffusion. Measuring the diffusion coefficient from an absorption experiment requires knowledge of both the initial slope of the weight gain and the equilibrium uptake profiles. This calculation is made under the assumption that the diffusion coefficient is constant during the absorption process. Fick’s second law, shown in Equation 1-6, can be used to determine the value of $D$ when considering the diffusion of a penetrant into a specimen at time $t$, if the region $x$ ($-l < x < l$) is initially at uniform concentration $C_o$ and the surfaces are kept at a constant concentration $C$, (Equation 1-7) [145,149].

$$
\frac{C - C_o}{C_t - C_o} = 1 - 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \int_0^t e^{\frac{-D(2n+1)^2 x^2 t}{4l}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) dx
$$  

(Equation 1-7)
Equation 1-7 can be integrated with respect to $x$ to determine the total mass of water absorbed at time $t$. If $M_t$ indicates the mass of the total amount of penetrant absorbed at time $t$ and $M_i$ is the mass at saturation, then:

$$\frac{M_t}{M_i} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{D(2n+1)^2 \pi^2 t}{4l^2}}$$  \hspace{1cm} \text{(Equation 1-8)}$$

It is well known that Fick's law is often inapplicable for describing moisture diffusion into various polymers and polymer composites [145]. Non-Fickian, or anomalous, diffusion typically occurs when the rates of diffusion and relaxation in a polymer are comparable, and the ambient temperature is below the $T_g$ of the polymer [149,154]. As a result, it is necessary to take into account the time-dependent response of a polymer, analogous to relaxation of mechanical properties, in constructing such a model.

### 1.7.2 Time Dependent Diffusion

In previous work by Frisch [155], it was suggested that a polymer below its $T_g$ must possess history-dependent diffusion coefficients and experience time-dependent changes in surface concentrations in order to maintain sorption-equilibrium at its boundaries. These time-dependencies are intrinsically related to the relaxation times for molecular rearrangement within the polymer.

As mentioned in Section 1.7.1, mathematical solutions can be presented for various problems using Fick's law if the diffusion coefficient is constant. However, these solutions can also be adapted for the case where the diffusion coefficient depends on the time but is independent of other variables. In this case the equation of diffusion in one dimension can be presented as shown in Equation 1-9.
Where $D(t)$ is the time varying diffusion coefficient, which is assumed to be uniform through the thickness of the polymer. Equation 1-9 can be rewritten as below (Equation 1-10).

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2} \quad \text{(Equation 1-9)}$$

Where $T$ is a new time-scale which is a function of $t$. The solutions for constant $D$ can therefore be used to give concentration $C$ as a function of $x$ and $T$, and $T$ is then converted into $t$ using Equation 1-11 [149].

$$dT = D(t)dt \quad \text{(Equation 1-10)}$$

$$T = \int_0^t D(t')dt' \quad \text{(Equation 1-11)}$$

If the integral in Equation 1-11 cannot be evaluated directly, the relationship between $T$ and $t$ has to be obtained either by graphical or numerical integration. If the surface concentration is a given function of $t$, this function must be rewritten in terms of $T$ in order to obtain the solution of Equation 1-12 in $x$ and $T$ [149,156].

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial x^2} \quad \text{(Equation 1-12)}$$

The application of this type of model is relatively limited as it does not cover the wide range of water diffusion cases in all types of polymers, especially when diffusion is dependent on other variables than time. As a result, it is necessary to consider other types of non-Fickian diffusion that are discussed in Section 1.7.3.
1.7.3 Non-Fickian Diffusion

In various types of polymers, the diffusion behaviour cannot be described by the time-dependent form of Fick's law with constant boundary conditions, especially in glassy polymers that exhibit anomalous or non-Fickian behaviour when the penetrant causes an extensive swelling to the polymer. There are two main reasons for the anomalous effects [149]:

1. They may be directly related to the influence of the changing polymer structure due to diffusion
2. They may result from the internal stresses exerted by one part of the medium on another as diffusion proceeds

Different types of behaviour can be considered under the term anomalous (non-Fickian) diffusion. Previous research summarized these behaviours in comparison to the Fickian behaviour as shown in Figure 1-24 [149].

Figure 1-24: Non-Fickian sorption & desorption curves compared to Fickian type curve [149]
Figure 1-24 shows that the sorption process is slower than the desorption process as in the sorption process, the polymer has to change its molecular structure to conform with the presence of the penetrant, which is a time dependent process (relaxation time) [142]. The types of the diffusion shown in Figure 1-24 are explained below:

(a) In the case of pseudo-Fickian diffusion, the initial portion of the curve persists for a shorter time when compared to Fickian [149]. The difference between the sorption and desorption curves is due to the difference between the kinetics of the sorption and desorption processes. In the sorption process, at the initial stages of absorption, the polar sites become saturated and at later stages of sorption, free water molecules are presented and steady state transport is enhanced until equilibrium. However, in the case of desorption, the initial slope highlights the equilibrium state where the steady-state transport is dominated by free water [146].

(b) Sigmoid diffusion has been observed experimentally in various systems [149]. The sorption curves are considered to be sigmoid type when the shape of the curve includes a single point of inflexion which is often around 50% equilibrium sorption. The initial rate of desorption exceeds that of sorption, but desorption then becomes slower and the curves cross [149].

(c) The two-stage sorption type shown in Figure 1-24 has been attributed to changes in the polymer structure induced by water and has often been related to stresses exerted by one part of the medium on another as diffusion proceeds [157]. The process occurs as follows; an initial rapid uptake (linear) where the increase of weight is proportional to time is observed, followed by an apparent equilibrium, which is in turn followed by a slow approach to a final true equilibrium. The second stage of sorption is coupled with an increase in surface concentration, which happens slowly compared to the diffusion process, and is the rate-determining factor for sorption [149,157].
Various researches [156,158,159,160,161] have investigated the different forms of non-Fickian (anomalous) diffusion and various models were introduced for various types of polymers. The development of anomalous models is discussed, along with methods of fitting theoretical models to experimental data, in detail in previous work by Bond [148].

1.8 Hypotheses

The main problem that restricts the use of the SL process for manufacturing concerns the unknown instability of the materials post-build compared to the materials used in conventional techniques such as injection moulding. Therefore, this research was undertaken to investigate and model the hygroscopic degradation of the Epoxy-based SL materials. The hypotheses of the research include:

- SL Epoxy-based materials are anecdotally known to be hygroscopic and their mechanical properties degrade over time when subjected to a humid or wet environment. However, there is no published data that quantifies the extent of degradation over extended time periods. It is therefore required to prove and quantify the extent of hygroscopic degradation for a range of SL Epoxy-based materials over time.
- The mechanism of hygroscopic degradation is not known. However, in order to utilise the SL technique as a RM process, it is important to reach the stage where the stability of the SL materials can emulate the stability of conventional materials. To fulfil this target, it is important to understand the exact mechanism of hygroscopic degradation of the current SL resins.
- As it is difficult to predict the change in mechanical properties of the currently available SL materials over time under certain conditions, a mathematical model should be developed to achieve this target. Both
manufacturers and designers will be able to use this model to predict the mechanical properties of any SL Epoxy-based material at certain conditions.

The aim of this work was to obtain an understanding of the mechanism of degradation of the current Epoxy-based SL materials due to humidity and ageing. This aim was achieved by breaking the task down into separate objectives. Each objective was addressed in a sequential manner to form the structure of the thesis. The objectives include:

**Test:**
- Preliminary investigations to establish the effects of the different build and post-processing methods on the mechanical properties of the SL materials and identify the suitable parameters for this research. This is discussed in Chapter 2.
- Long-term tests to investigate the effects of humidity and ageing on the mechanical properties of the SL materials at different temperatures. This will assist in bridging the gap in the knowledge by providing a broad range of experimental data for different Epoxy-based materials under different conditions. This is discussed in Chapter 3.

**Analyse:**
- Experiments including mechanical, thermal and chemical analysis techniques to broadly investigate the mechanism of degradation due to the effects of humidity along with ageing. This is discussed in Chapter 4.

**Modelling:**
- Investigate the diffusion of water into different SL Epoxy-based resins to identify the mechanism of water penetration into the SL materials. This will allow the generation of a model which can be used to predict the mechanical properties of the SL Epoxy-based materials under different humidity conditions. This is discussed in Chapter 5.
Chapter 2  Establishing the Effects of Different Build and Post-Processing Methods

2.1 Introduction

There have been various investigations into the mechanical properties of different SL resins but few studies have been carried out to identify the effects of the different build and post-processing parameters on the mechanical properties of SL parts [162,163,164]. Therefore, before embarking on the wider tests to determine the effects of humidity, it was important to identify the methods of building and post-processing the SL samples that were to be used in this investigation.

In this Chapter, the preliminary experimental work that was carried out to investigate the mechanical properties of Accura SI40, SL7560 and SL7580 materials using different build and post-processing methods is discussed. The materials to be tested were among the latest range of SL materials that were particularly marketed for final product use. The initial experimental work included in this Chapter has been carried out to set the boundaries for the ageing tests that are included throughout this research. The work included:

- Isotropy tests
- Tensile behaviour for the temperature range -40°C to 140°C
Effects of different methods of post-curing on the mechanical properties

The reasoning for selection of the tests and the benefits gained from each test are explained under the individual Section for each type of test. Two different types of mechanical tests (tensile and flexure that are discussed in Section 2.2) were carried out.

2.2 Mechanical Tests

There are different types of mechanical tests that can be applied to investigate the change in the mechanical properties of the Epoxy-based SL parts. However, tensile and flexural properties were found to be the most important mechanical properties in plastic parts as they are required by industry and researchers for different purposes including mechanical applications and modelling [165].

Tensile properties can be used as an indicator of the behaviour of the material under loading in tension. Figure 2-1 shows a schematic of a stress strain curve for plastics (this is different from one material to another).

![Figure 2-1: A schematic stress-strain curve for a polymer](image)
There are different properties [166] that can be obtained from the tensile test including:

- **Ultimate Tensile Strength (UTS):** This is the maximum stress the specimen can reach before it fails. It is expressed in MPa

- **Strain at Break (%Elong):** The percentage elongation when the specimen breaks which is the ratio of change in length as a result of the applied force to the original length

- **Young’s Modulus (E):** This is the stress value divided by the strain value at an early stage of the test (elastic region), expressed in MPa

Flexural properties describe the mechanical properties of the material under a bending force. The flexural properties include [167]:

- **Flexural Strength (F.S):** It is the maximum stress the specimen resists under bending before failure, expressed in MPa

- **Flexural Modulus (F.M):** It is the ratio of stress to strain within the elastic limit; it is used to indicate the bending stiffness of a material, expressed in MPa

### 2.3 Equipment and Manufacture of the Test Samples

The equipment used to build the test samples was a 3D Systems SLA 7000. The build volume for this machine is approximately 508mm x 508mm x 584mm (XYZ). Various parameters can be adjusted to optimise and customise the process for a specific task and obtain the best properties, with the most significant of these being over-cure, hatch-cure, layer thickness and the recoating parameters [44]. The definition and impact of each of these parameters are given elsewhere [168,169,170]. However, it should be noted that for each resin the build
parameters (shown in Appendices A, B and C) that were used were provided and recommended by the resin supplier and were used consistently when manufacturing the required test specimens. The build style used was based on the ACES (Accurate Clear Epoxy Solid) format, which was designed specifically for use with the Epoxy-based resins [171].

All the samples for each set of tests were produced during the same build for each type of material and then cleaned and post-cured at the same time. They were kept in a dark controlled environment (50% relative humidity & 20°C) to prevent further UV post-process curing prior to testing.

A Zwick Z030 tensile testing machine with 10KN load cell was used to investigate the tensile and flexural properties in accordance with the ISO standards for determining the tensile and flexure properties [166,167]. The mechanical properties that have been investigated include:

- Ultimate Tensile Strength (UTS)
- Young’s Modulus (E)
- % Elongation at Break (%Elong)
- Flexural Strength (F.S)
- Flexural Modulus (F.M)

### 2.4 Isotropy Tests

Due to the additive layer-wise manufacturing techniques that were utilised, it was necessary to evaluate whether the samples would behave in an isotropic manner. If they were isotropic, this would allow freedom in choosing the build orientation and would help reduce the build time and also the amount of support structures needed without affecting the mechanical properties of the parts. This was also of
great relevance to the number of tests to be performed when testing any material because if the parts produced are anisotropic, the number of tests performed would potentially have to be increased three-fold to consider the three main build orientations.

When SL first started to be used to build prototypes, it resulted in anisotropic parts due to the in-build curing technique that was used in the SL machines [172]. However, since the beginning of the 1990s, there were various modifications and investigations dedicated to improving the performance of SL machines to produce isotropic parts. The most significant of these improvements was the ACES build style.

In previous work by Hague and Dickens [173] SL5170 Epoxy-based resin was used to investigate the isotropic behaviour of SL parts. The results had a variation of less than 10%, and therefore the material was considered isotropic. However, in other research by Dulieu and Fulton [170], SL5510 resin was investigated. It was shown that the variation between the different build orientations was 2% for most of the investigated mechanical properties except the values of percentage elongation at break which had a difference of 85% between the results. Therefore, the material was considered as anisotropic. Therefore, the isotropy tests explained throughout this Section were carried out to confirm whether the new resins could be considered as isotropic materials or not.

2.4.1 Methodology

Tests were carried out at a temperature of 20°C ±1°C for samples that were built using three different orientations (Flat, Upright, and Edge) as shown in Figure 2-2. The same orientations were used to build the flexural samples.
The tensile and flexural samples were prepared in exactly the same manner as each other. Ten samples of each orientation were tested for each of the two types of mechanical tests. Unless otherwise stated, all the parts were normally post-cured.

2.4.2 Isotropy Results

The average results of the isotropy mechanical tests are given in Table 2-1 and Figure 2-3 to Figure 2-7 for the three different SL materials.

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>Accura SL40</th>
<th>SL7560</th>
<th>SL7580</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat</td>
<td>Edge</td>
<td>Upright</td>
<td>Flat</td>
</tr>
<tr>
<td>UTSM (MPa)</td>
<td>70.0</td>
<td>73.3</td>
<td>73.2</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>3.30</td>
<td>3.30</td>
<td>3.21</td>
</tr>
<tr>
<td>%Elong</td>
<td>5.2</td>
<td>5.3</td>
<td>5.8</td>
</tr>
<tr>
<td>F.S (MPa)</td>
<td>106.7</td>
<td>102.4</td>
<td>106.9</td>
</tr>
<tr>
<td>F.M (GPa)</td>
<td>2.35</td>
<td>2.46</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 2-1: Mechanical properties of the three different build orientations
It can be clearly seen from Table 2-1 and Figure 2-3 to Figure 2-7 that, for the three investigated materials, the maximum percentage variation of the average of each set of samples tested at the three different build orientations for all of the mechanical properties was less than 5%, except for values of %Elong that had
percentage variations of 10%. However, this specific mechanical property shows the largest range bars.

From the results, shown in Table 2-1 and Figure 2-3 to Figure 2-7, and as most of the mechanical properties varied for the three different build orientations within a range of 10%, these materials can therefore be considered as isotropic as the build orientation did not have a significant anisotropic effect on the parts produced. This is consistent with most previous published data [48,174] and therefore, it was decided to adopt the upright build orientation throughout this research as it produced a maximum number of samples in a single build platform.

2.5 Tensile Behaviour in the Range of -40°C to 140°C

Current Epoxy-based SL photopolymers are limited in their working temperatures, as discussed in previous work by Ullett et. al. [175]. As a result, the applications of SL parts are potentially limited when used for manufacturing when the materials are required to be used in a wide working temperature range. In this Section, the tensile properties were investigated under the temperature range of -40°C to 140°C, which is a typical range, required by industry (for example in automotive applications) [140]. These initial temperature tests were carried out to determine the temperature range for the future long-term tests.

2.5.1 Methodology

The upright orientation was used to build all of the required samples of each individual material on a single platform. All the samples of each material underwent exactly the same post-processing procedures as stated in Appendices A, B and C. Tests were carried out at a temperature of -40°C to 140°C with an interval of 10°C.
2.5.2 Temperature Test Results

The average of five samples at each temperature (10°C interval) is shown in Figure 2-8 to Figure 2-10, for the values of UTS, %Elong and E of the three SL materials. For Accura SI40 and SL7560 and at low temperatures, between -40°C to -10°C, the values of UTS, shown in Figure 2-8, were found to be lower than the values around the ambient temperature. However, the same was not shown for SL7580 material, which indicates that the UTS of this material was not significantly affected at low temperatures compared to the other two materials. Increasing the temperature above 0°C decreased UTS for the three materials, which could be due to weakening of the cross-links within the polymer-network as discussed in Section 1.5.1.

![Figure 2-8: Change in UTS with temperature](image)

The values of %Elong of the three investigated materials shown in Figure 2-9 were found to be lowest at temperatures from -40°C to 20°C. Increasing the temperature further (from 30°C to 70°C) increased %Elong, which could be due to the increase in the amplitude of the segmental vibrations within the polymer network as discussed by Grassie and Guy [82]. At temperatures close to the glass
transition temperatures of the investigated materials, the highest values of %Elong were shown, which could be due to the segmental motions that were very rapid within the polymer network. Increasing the temperature above $T_g$ caused a slippage of the molecules within the network. After exceeding the glass transition temperature (from 80°C to 140°C), %Elong was reduced which could be due to further increase in the slippage of the molecules [82].

![Figure 2-9: Change in % Elong with temperature](image)

The values of Young’s Modulus shown in Figure 2-10 were found to be highest at low temperatures which could be due to the existence of stiff cross-links within the polymer network. Increasing the temperature reduced the Young’s Modulus of the three materials, as increasing the temperature can weaken the cross-links within the polymer network as discussed in Section 1.5.1. Above $T_g$ (between 60°C to 80°C for the investigated SL materials according to the materials datasheets), little stiffness remains.
From the results shown in Figure 2-8 and Figure 2-10, it can be clearly seen that from 100°C and above, the change in tensile strength and modulus were negligible. Therefore, based on these initial temperature tests, it was concluded that for all the future experimental work of these specific materials, the tests would not be performed at temperatures above 100°C.

### 2.6 Effects of Different Methods of Post-Curing on the Mechanical Properties

All the samples produced for the previous investigations underwent a process of post-processing, which including cleaning and further UV curing. Additional thermal curing was found to improve some of the mechanical properties in some materials due to further cross-linking in the polymer network [176]. However, increasing the thermal curing might lead to a stage of degradation as mentioned previously in Chapter 1. The aim of this test was to investigate the effects of
thermal post-curing after UV curing took place on the parts made of Accura SI40, SL7560 and SL7580 Epoxy-based materials.

2.6.1 Methodology

As in all the previous investigations, all the samples of each material were built at the same time and underwent exactly the same post-curing procedures, but extra thermal curing was given to a different group of samples to investigate the effect of thermal post-curing on the mechanical properties of SL materials. The two types of curing used were:

- *Normal Post-Curing (NPC)*: Cleaning and 90 minutes in PCA
- *Thermal Post-Curing (TPC)*: Cleaning, 90 minutes in PCA and 2 hours at 80°C

2.6.2 Different Methods of Post-Curing Results

The results of the two types of curing are detailed in Table 2-2 and Figure 2-11 to Figure 2-15.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Properties</th>
<th>Flexural Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UTS (MPa)</td>
<td>E (GPa)</td>
</tr>
<tr>
<td>NPC TPC</td>
<td>NPC TPC</td>
<td>NPC TPC</td>
</tr>
<tr>
<td>Accura SI40</td>
<td>54.3 76.6</td>
<td>2.39 3.05</td>
</tr>
<tr>
<td>SL7560</td>
<td>55 63.8</td>
<td>2.71 2.94</td>
</tr>
<tr>
<td>SL7580</td>
<td>61.7 60.4</td>
<td>2.64 2.43</td>
</tr>
</tbody>
</table>

Table 2-2: The effect of different methods of post-curing
From Table 2-2 and Figure 2-11 to Figure 2-15, it can be seen that most of the mechanical properties of Accura SI40 and SL7560 increased with thermal post-curing. This could be due to the further cross-linking in the polymer network which improved the mechanical performance of the materials. However, for
SL7580, there was a slight decrease in most of the mechanical properties. This indicates that the thermal post-curing has cured the material and advanced the curing stage to a level of degradation.

It can also be seen that thermal post-curing is material dependent and can lead to two different effects:

- Improving most of the mechanical properties. This could be due to more cross-linking within the polymer network. This has an implication that mechanical properties of some Epoxy-based SL materials can improve when applying thermal post-curing up to a certain limit (before reaching the stage of degradation)

- Material degradation. This could be due to breaking the cross-links within the polymer network. This can take place after the material exceeds the curing stage caused by heat, which in turn decreases most of the mechanical properties. This indicates that thermal post-curing can negatively affect the mechanical properties of most of the Epoxy-based SL materials after a significant time, which is dependent on the chemical structure of the material

The SL parts directly produced from the SLA are not fully cured and require further curing using a post-curing apparatus (PCA), which in some cases is enough for the material to be sufficiently cured. This is entirely dependent on the chemical structure of the material. In other cases thermal curing is required to complete the curing stage of the material. However, excessive thermal-curing can lead to degradation in some cases. This was shown in previous work by Ottemer [73], where two different types of SL materials were thermally post-cured at different temperatures (from 100°C to 200°C) and for a range of time (100 hours). The study proved that thermal post-curing had two possible effects, improvement or degradation of the tensile properties of the materials.
From the results of the two types of curing shown throughout this Section, it was decided to apply only the normal post curing method for all the future experimental work of these specific materials. This was to avoid any thermal effects on the properties of the materials.

2.7 Review

Different initial investigations were explained throughout this Chapter to identify the effects of the different build and post-processing methods on the mechanical properties of three SL materials (Accura SI40, SL7560 & SL7580). The SL machine parameters differ from one resin to another and are defined by the resin manufacturer. The preliminary investigations carried out throughout this Chapter were undertaken to find optimum parameters for the future ageing tests that are discussed in Chapter 3.

From the isotropy tests, the results of UTS shown in Figure 2-3 indicated that the best build orientation to be used is the edge orientation as it resulted in the highest values of UTS for the three materials. The flat orientation came second as it had lower values than the edge orientation and higher values than the upright orientation. Figure 2-4 which shows the values of Young’s Modulus for the three materials confirmed that the edge build orientation gave the highest values of Young’s Modulus for the three materials. However, for the rest of the mechanical properties, shown in Figure 2-5 to Figure 2-7, it was found that the highest values differ from one material to the other. For Accura SI40, upright build orientation had the highest values and for SL7560 and SL7580, edge orientation was found to offer the highest values in most of the other mechanical properties. However, the difference between the values of the isotropy results of each material was less than 10%. It can be therefore concluded that changing the build orientation does not have a significant anisotropic influence on the mechanical properties of SL parts.
Therefore, the upright build orientation could be used to build all the tensile and flexure samples required for this research. This was important as it maximised the amount of parts that could be produced at any one time and ensured that all the test parts were consistent.

Accura SI40 had the highest values for most mechanical properties compared to the other two resins. However, this material was found to have the largest range bars in most of the mechanical properties which is typical for more brittle materials [65]. This is shown in the values of %Elong of Accura SI40, as these were lower compared to the other materials.

The investigation of the tensile behaviour of SL materials in the temperature range of -40°C to +140°C has shown that new SL materials are required for higher temperature applications as the mechanical properties were found to decrease with increasing temperature. This reduction was due to degradation of the materials, as when a polymer sample is heated, the distance between the molecules increases as the vibration amplitude increases. This increase allows the molecules to move more freely, enabling the material to flow in the macroscopic level [177]. Accura SI40 was found to degrade at lower temperatures than the other two materials (SL7560 and SL7580) as there was a sudden drop which occurred at a temperature just above ambient. This can be observed from Figure 2-8 and Figure 2-10 that show the change in the values of UTS and Young's Modulus, respectively. Accura SI40 had lower temperature resistance compared to the other two materials that did not show the same sudden drop. However, increasing the temperature of Accura SI40 (from 40°C to 90°C) increased the elasticity of the material more than the other two materials and therefore increased the %Elong as shown in Figure 2-9. It can be seen that above 100°C, the behaviour of the mechanical properties is the same. Therefore, it was decided to mechanically test the SL materials only up to this temperature for the further investigations included in this research.
Thermal post-curing was found to have a positive influence by improving the mechanical properties of some SL materials which was probably due to more cross-linking in the polymer network as in the case of Accura S140 and SL7560. However, for SL7580, it induced degradation, but this could potentially have been avoided if thermal post-curing was used for less time. As shown from Table 2-2, the mechanical properties of the first two materials improved as the value of UTS increased by 30% and 14% for Accura S140 and SL7560 respectively and decreased by 2% for SL7580. The other mechanical properties of Accura S140 and SL7560 improved, such as Young’s Modulus which increased by 21% and 8% respectively. However, Young’s Modulus reduced by 8% for SL7580 and Flexural Modulus decreased by 6%. Flexural Modulus increased by 5% and 2% for Accura S140 and SL7560 respectively. Therefore, it can be concluded from these results that the effects of thermal post-curing on the mechanical properties are material, temperature and time dependent. Thus it was decided to apply the normal post-curing method to the samples required for the further research to avoid any degradation effects due to thermal post-curing.
Chapter 3  Ageing Characteristics of SL Resins

3.1 Introduction

As discussed previously in Section 1.8, Epoxy–based SL resins are hygroscopic materials and their mechanical properties degrade over time when subjected to a humid environment. However, there is no published data that quantifies the degradation over extended time periods with the evidence being more anecdotal; this is especially true when also considering the combined effects of ageing, humidity and temperature. The aim of this Chapter is to fill the gap in the knowledge by investigating the characteristics of different SL resins under different temperature, humidity and ageing conditions.

The results are presented by a series of summary graphs that are included throughout this Chapter. As it was necessary to build a high number of samples, it was essential to maintain the build procedures and parameters for each individual type of material. These are shown in Appendices A, B and C for the investigated materials. Tables that include the detailed results and graphs with range bars are shown in Appendices D, E and F for Accura SI40, SL7560 and SL7580 resins, respectively.
3.2 Equipment and Manufacture of the Test Samples

An SLA 7000 produced by 3D Systems was used to build the samples. The build parameters were provided and recommended by the supplier of each resin individually and were used consistently to build the test specimens. From the results of Chapter 2, it was decided to adopt an upright build orientation for the tensile and flexure samples as it produced a maximum number of samples in a single build platform. All the samples for each individual type of mechanical test and each type of material were produced using the same build parameters and then cleaned and post-cured using exactly the same procedures for consistency. The samples were stored in a dark place to prevent further post-process UV curing and at different humidity levels. These included:

- **Dry**: 10% Relative Humidity (RH)
- **Controlled**: 50%RH
- **Wet**: 100%RH (samples were soaked in water)

All the samples were stored at a constant temperature (20°C) prior to testing. A time interval of 1, 4, 13, 26 and 52 weeks was selected to conduct this work. These intervals were selected to investigate the change in the mechanical behaviour over a broad range of time (one year).

3.3 Experimental Method

All the tests were conducted in a controlled environment (40%RH) using a temperature range of −40°C to +100°C at 10°C intervals. This temperature range was determined from the initial work discussed in Chapter 2. One limitation upon the usefulness of the results is that the specimens were tested immediately that they reached the specified temperature and it is recognised that this may not
replicate "real world" conditions. However, due to the significant volume of tests being conducted within this research, the effects of temperature cycling was considered to be beyond the scope of this particular study and has been recommended for further consideration in the "future work" section at the conclusion of this thesis.

The tensile and flexural tests were performed on a Zwick 1030 tensile testing machine, with 10KN load cell and a temperature chamber with a possible temperature range of -80°C to +250°C [178]. The same mechanical properties as mentioned in Chapter 2 were investigated throughout this Chapter. For tensile and flexural tests, the crosshead speed of 5 mm/min was adopted to measure UTS, %Elong, F.M & F.S according to ISO standards. However 1mm/min was adopted to measure the value of Young’s Modulus (E) in a separate test using a bi-axial extensometer with a gauge length of 25mm. The reason for having separate tests for E and UTS along with %Elong was to prevent a temperature drop when opening the temperature chamber to detach the extensometer. For each mechanical property, the final result is an average of five samples that were tested at each temperature. The number of samples produced for each material and each test is shown in Table 3-1:

<table>
<thead>
<tr>
<th>Type of test</th>
<th>Tensile 1</th>
<th>Tensile 2</th>
<th>Flexure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical property</td>
<td>UTS</td>
<td>%Elong</td>
<td>E</td>
</tr>
<tr>
<td>No. of samples of each test</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>For the 3 humidities</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>For the range (-40 to 100°C)</td>
<td>225</td>
<td>225</td>
<td>225</td>
</tr>
<tr>
<td>For the 5 age intervals</td>
<td>1125</td>
<td>1125</td>
<td>1125</td>
</tr>
<tr>
<td>Total number of samples</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-1: The number of samples produced for each material

For each specimen, the maximum time between taking the specimen out of the storage and placing it into the temperature chamber was five minutes. To ensure that the test specimens were at the correct temperature at the time of testing each individual specimen, a thermocouple was attached to the centre of a sample made of the same material and was placed inside the temperature chamber to monitor
the temperature of the material. This was done using a calibrated thermocouple device, as shown in Figure 3-1. The maximum time that was required to heat or cool a specimen to a specific temperature (in the range -40°C to +100°C) was five minutes.

![Figure 3-1: Schematic diagram showing the thermocouple attached to a specimen made of the same material as the tested sample](image)

### 3.4 Results

In this Section, the impact of ageing, humidity and temperature on the tensile and flexural properties of Accura SI40, SL7560 and SL7580 are shown. The experiments were undertaken to show that there is a degradation problem related to the Epoxy-based SL materials post-build when subjected to humidity. They were also to investigate the tensile and flexural behaviours under temperature range from -40°C to 100°C at different ages. More advanced investigations are discussed in Chapter 4 to identify the mechanism of degradation due to humidity.
The results of Young’s Modulus (E), Flexural Modulus (F.M) and % Elongation at Break (%Elong) are shown in Figure 3-2 to Figure 3-20, with each mechanical property being represented by the average of 5 tests according to ISO standards [166,167]. The rest of the results are not included as the results discussed throughout this Chapter were representative of how the general change in mechanical properties due to ageing, temperature and humidity occurred. The full results are shown in Appendices D, E and F.

3.4.1 Effects of Ageing, Humidity and Temperature on the Mechanical Properties of Accura SI40

Figure 3-2 and Figure 3-3 show the results for Young’s Modulus of Accura SI40 for dry (10%RH) and controlled (50%RH) parts, respectively. Between 0°C and 60°C, as the ageing process proceeds, the Young’s Modulus improved with ageing. This is consistent with previous work [68,141] which confirmed that this is due to the increased curing of the material (more cross-linking within the polymer network) over time (dark reaction). This topic is addressed later in Chapter 4. Also, the values of UTS, F.M and F.S improved over time as shown in Appendix D.

Figure 3-2: Accura SI40 Young’s Modulus vs. temperature (Dry (10%RH))
Figure 3-3: Accura SI40 Young’s Modulus vs. temperature (Cont (50%RH))

However, from the results of the wet (100%RH) samples shown in Figure 3-4 and Figure 3-5 for Young’s Modulus and Flexural Modulus, respectively, it was found that the mechanical properties decreased with the advance of age. This is most-likely due to the penetration of water into the SL parts and the interaction between water and the polymer network (degradation).

Figure 3-4: Accura SI40 Young’s Modulus vs. temperature (Wet (100%RH))

- 68 -
Figure 3-5: Accura SI40 Flexural Modulus vs. temperature (Wet (100%RH))

At low temperatures (below 20°C), the values of %Elong of the dry (10%RH), controlled (50%RH) and wet (100%RH) samples, shown in Figure 3-6, Figure 3-7 and Figure 3-8 respectively, were found to be lower than the values of %Elong above 20°C. However, the values of Young’s Modulus and Flexural Modulus were found to be the highest (stiff cross-links within the polymer network). This is consistent with the results obtained previously in Section 2.5.

Figure 3-6: Accura SI40 Elongation vs. temperature (Dry (10%RH))
Increasing the temperature to ambient levels and further (from 30°C to 70°C) has increased %Elong, which could be due to increasing the amplitude of the segmental vibrations within the polymer network as discussed in previous research [82]. Further increase of temperature (from 80°C to 100°C) above the glass transition temperature, which is around 60°C for this specific material [179], reduced %Elong which could be due to further increase in the slippage of the
molecules [82]. This indicates that the material reached a degradation level due to the effects of elevated temperatures.

Referring back to Figure 3-6 and Figure 3-7, it can be seen that at 40°C and above, the values of %Elong at the age of 1 week were less compared to the rest of the results at the other ageing intervals. This is consistent with the concept of the dark reaction of the parts during the first few weeks which can increase the cross-linking within the polymer network as discussed in previous work [68].

Humidity has affected the values of %Elong and caused an increase of %Elong in the temperature range from 0°C to 30°C, and a decrease above 30°C as shown in Figure 3-8. This is due to the penetration of water into the polymer network and the interaction between water and polymer which might have increased the elasticity of the material as discussed in Section 1.5.3. However, further increase of temperature (40°C and above) reduced %Elong of the wet (100%RH) samples compared to %Elong of the dry (10%RH) and controlled (50%RH) samples that are shown in Figure 3-6 and Figure 3-7, respectively, which indicates that elevated temperature along with humidity can increase the degradation rate (possibly chain scission) of the material.

3.4.2 Effects of Ageing, Humidity and Temperature on the Mechanical Properties of SL7560

The mechanical behaviour of SL7560 material was found to be similar to Accura SI40 in terms of humidity effects and the effects of temperature. At temperatures below ambient, the values of Young’s Modulus and Flexural Modulus were found to be the highest, as shown in Figure 3-9 to Figure 3-12. However, further increases of temperature reduced the mechanical properties of the material, as in the case of Accura SI40.
At low temperatures (0°C and below), the values of Young’s Modulus and Flexural Modulus of samples that were stored under wet (100%RH) conditions increased with reducing temperature, as shown in Figure 3-11 and Figure 3-12. This could be due to increasing the stiffness of the material and also due to the bound-water within the polymer network that tended to freeze. This indicates that the degradation in the material could be due to a change in the polymer network.
For %Elong results of the dry (10%RH) samples shown in Figure 3-13, at temperatures from -40°C to 40°C, the values of %Elong was low compared to %Elong at 50°C and above, which indicates that the material tended to be more brittle at low temperatures and this brittleness disappeared at higher temperatures (50°C to 70°C). A further increase in temperature (above T_g, which is around 70°C for this material [180]) caused a reduction in the %Elong, which indicates degradation.
Figure 3-13: SL7560 Elongation vs. temperature (Dry (10%RH))

Figure 3-14 shows the values of %Elong of samples stored under wet (100%RH) conditions prior to testing. The %Elong values at temperatures between -40°C to 40°C were higher compared to %Elong of the dry (10%RH) samples shown in Figure 3-13, which is due to the penetration of water into the polymer network. A general reduction in the overall values of %Elong at 40°C and above was shown for the wet (100%RH) samples shown in Figure 3-14, compared to the dry (10%RH) samples shown in Figure 3-13, which is consistent with other findings in previous work [181,182] that investigated the effects of temperature along with water on the mechanical properties of non-RP/RM thermoset resins.

Figure 3-14: SL7560 Elongation vs. temperature (Wet (100%RH))
3.4.3 Effects of Ageing, Humidity and Temperature on the Mechanical Properties of SL7580

From the tensile and flexural results of Accura SI40 and SL7560 materials, it was found that the results for Young’s Modulus and Flexural Modulus against temperature tended to follow the same trend. Therefore, it was decided to reduce the number of tests and investigate only the tensile properties of SL7580 material using the same time intervals used for Accura SI40 and SL7560.

The Young’s Modulus results of SL7580 material indicate that for the dry (10%RH) and controlled (50%RH) parts, shown in Figure 3-15 and Figure 3-16 respectively, at a temperature range from -40°C up to 50°C, as the ageing process proceeds, Young’s Modulus generally improved with ageing, which is consistent with the results of the other two materials (Accura SI40 and SL7560). This is due to the increased curing of the material over time (dark reaction). However, to prove this, further investigations were required. These investigations are discussed in Chapter 4.

Figure 3-15: SL7580 Young’s Modulus vs. temperature (Dry (10%RH))
From the results of the dry (10%RH) samples shown in Figure 3-15, the values of Young’s Modulus at the age of 52 weeks started to decrease at 50°C and above, which indicates that the material became more affected by elevated temperatures at the age of one year compared to the other ages (due to degradation). The same occurred with the controlled (50%RH) samples, shown in Figure 3-16, but at a lower temperature (40°C) and earlier age (26 weeks), which is due to the higher amount of humidity that was absorbed by the samples that were stored at 50%RH compared to the dry (10%RH) samples. However, the results of Young’s Modulus of the wet (100%RH) samples shown in Figure 3-17 indicate that the mechanical properties decrease with advancing age.
The results of %Elong of the dry (10%RH) and controlled (50%RH) samples, shown in Figure 3-18 and Figure 3-19 respectively, show that at low temperatures (-40°C to 20°C), the values of %Elong were found to be low compared to %Elong at higher temperatures (30°C to 70°C). Increasing the temperature of the material further (above Tg, which is around 70°C [183]), a degradation level was reached due to the effects of elevated temperatures which weaken the bonds and cross-linking of the polymer, as was shown in previous work [82]. Figure 3-20 shows the change in %Elong of the samples that were kept soaked in water (100%RH) prior to testing.

![Figure 3-18: SL7580 Elongation vs. temperature (Dry (10%RH))](image1)

![Figure 3-19: SL7580 Elongation vs. temperature (Cont (50%RH))](image2)
It can be seen that humidity increased the values of %Elong in the temperature range from 20°C to 60°C compared to the dry (10%RH) and controlled (50%RH) results shown in Figure 3-18 and Figure 3-19 respectively. Water also reduced %Elong of the wet (100%RH) samples at temperature above 60°C compared to the results of the dry (10%RH) and controlled (50%RH) samples, which is due to the higher amount of water absorbed by the wet (100%RH) samples.

3.5 Review

As discussed in Section 1.5.1 and from the results shown in Section 3.4, increasing the temperature of the Epoxy-based SL materials can increase the amount of the segmental vibrations within the polymer network [82]. This is shown in the gradual reduction of Young’s Modulus and Flexural Modulus. Just before exceeding $T_g$, %Elong reached the highest values, which is most likely due to the rapid motions of molecules within the polymer network [82]. With a further increase of temperature (above $T_g$), slippage of molecules can occur, which massively reduces the mechanical properties of the investigated SL Epoxy-based materials.
Elevated temperatures affected the materials causing softening due to the weakening and breaking of polymer cross-linking, especially after exceeding the \( T_g \) of the material. This is shown from the results of the investigated SL resins, where the main drop happened above 60°C for the samples that were kept at the dry (10%RH) and controlled (50%RH) conditions prior to testing. However, for the wet (100%RH) samples, the main drop took place at lower temperatures depending on the age of the material, as it was found that the mechanical properties began to decrease at lower temperatures during the ageing process. This proves that there was a drop in the \( T_g \) of the investigated materials when stored at high levels of humidity (100%RH), this is consistent with previous work by Moey et. al. [107] and Ivanova et. al. [99]. However, for the dry (10%RH) and controlled (50%RH) samples, it was shown that when testing around ambient temperature, Accura SI40’s, SL7560’s and SL7580’s Young’s Moduli (also Flexural Moduli of Accura SI40 and SL7560) were improved with advancing age.

As the three materials were stored in dark enclosures at 20°C, the experimental work discussed throughout this Chapter ensured that the mechanical properties of the materials were affected only by humidity and ageing and were not affected by any other degradation factor (e.g. UV light or temperature). In long-term exposure, water causes a decrease in both the molecular weight and the mechanical properties due to breaking the chains of the polymer network [114,115]. A previous study by Colton and Ottemer showed that humidity caused a drop in the mechanical properties and the glass transition temperature (\( T_g \)) of different photo-curable SL resins [26]. This was also confirmed for the SL materials discussed throughout this Chapter.

Stress-strain curves of Accura SI40 at different ages for dry (10%RH) and controlled (50%RH) conditions tended to behave in a similar way in terms of the shape of the curve, as shown in Figure 3-21 and Figure 3-22. These graphs show the typical stress-strain curves for samples of Accura SI40 that were tested at
20°C at dry (10%RH) and controlled (50%RH) conditions, respectively, at different ageing intervals.

From Figure 3-21, it can be seen that for the dry (10%RH) results, there is not a significant difference in the shape of the stress-strain curves for all the different ages. However, for the controlled (50%RH) results (shown in Figure 3-22), it can be noted that there is a relatively small change in the behaviour of the material when testing at different ages, which indicates that the 50%RH condition has affected the mechanical behaviour of the material. This is shown also in the values of %Elong that were slightly higher for the controlled (50%RH) samples than the dry (10%RH) samples at most of the ages. Further confirmation that humidity increased the %Elong around ambient temperature at early ages can be seen in Figure 3-23, which presents typical stress-strain curves for samples of Accura SI40 that were stored at wet (100%RH) condition and tested at 20°C.
It is also shown in Figure 3-23 that %Elong increased massively between the age of 1 week and 26 weeks, which indicates that the material has achieved a high level of flexibility which could be due to softening of the material [111]. %Elong then began to reduce before the age of 52 weeks, which could be due to breaking of cross-links. Also, it is shown that the absorption of water has greatly affected the mechanical behaviour of the material and decreased the values of UTS as mentioned previously.

Absorbed water can exist in a polymer network as bound water and loose free water [118]. The latter can escape with increasing temperature. However, there is still tightly bound water, which is the penetrant water that might have partly interacted with functional groups of the SL materials and strongly attached through Hydrogen bonding to the functional groups. This is strongly confined in the polymer network and requires additional energy to be removed. For the SL7560 material, humidity increased %Elong as shown in Figure 3-24 and Figure 3-25 that show the typical stress-strain curves at different ageing intervals of SL7560 samples that were kept at dry (10%RH) and controlled (50%RH) conditions and tested at 20°C.
The samples that were stored at controlled (50%RH) condition produced different stress-strain curves at the defined ageing intervals. However, the curves of the samples that were stored in a dry (10%RH) condition produced fairly consistent curves, as was also the case of Accura S140. Also, the same occurred to the SL7580 material, as shown in Figure 3-26 and Figure 3-27, that show the typical stress-strain curves at different ageing intervals of samples that were kept at dry (10%RH) and controlled (50%RH) conditions and tested at 20°C.
The more moisture the material absorbs, the more %Elong is shown when testing around ambient temperature levels. This is shown in Figure 3-28 and Figure 3-29 that present the typical stress-strain curves of SL7560 and SL7580 parts that were stored at wet (100%RH) condition and tested at 20°C.

Figure 3-28: Typical SL7560 stress-strain curves for wet (100%RH) samples at different ages (20°C)

Figure 3-29: Typical SL7580 stress-strain curves for wet (100%RH) samples at different ages (20°C)

Figure 3-28 show the effects of 100% humidity on samples that were made of SL7560, and tested at different ages. It can be seen that the reduction in UTS of SL7560 material is less than with Accura SI40 as shown in Figure 3-23. This
indicates that the SL7560 material has higher resistance to the absorption of water compared to Accura SI40.

Ageing of the SL materials was found to have a positive influence on most of the mechanical properties when stored under a dry (10%RH) condition. Figure 3-30 and Figure 3-31 show the various temperature stress-strain curves of Accura SI40, at ages of 1 week and 26 weeks for dry (10%RH) samples. This improvement proves that dark reaction has occurred to the materials that have been cationically cured, which is consistent with previous work [184].

The value of % Elong increased when the temperature increased. This occurred up to a certain level, and then it started to decrease again when elevated temperature was above T_g. The same behaviour occurred to the samples that were stored at controlled (50%RH) condition, as shown in Figure 3-32 and Figure 3-33, that show the various temperatures stress-strain curves of Accura SI40 at age of 1 week and 26 weeks for controlled (50%RH) samples.
Figure 3-32 and Figure 3-33 show that the values of %Elong are roughly the same for the controlled (50%RH) samples as for the dry (10%RH) samples (shown in Figure 3-30 and Figure 3-31, respectively) at the different time intervals used.

Ageing has improved the mechanical properties for both dry (10%RH) and controlled (50%RH) humidity conditions. However, ageing in wet (100%RH) conditions has increased %Elong of Accura SI40 parts as shown in Figure 3-34 and Figure 3-35 that show the stress-strain curves for wet (100%RH) samples (at temperatures from -40°C and up to 100°C) of Accura SI40 at age of 1 week and 26 weeks respectively.
For the wet (100%RH) samples, the effect of water diffusion into Accura SI40 material was found to be higher than in SL7560 material as the values of Young’s Modulus at 20°C decreased by 99.3% for Accura SI40 after one year. However, it was reduced by 93% and 87.4% for SL7580 and SL7560, respectively, during the same period. This means that the SL7560 material has better resistance to water diffusion compared to SL7580. However, for the dry (10%RH) samples, the values of Young’s Modulus was found to increase by 10.8%, 9.8% and 9.5% for Accura SI40, SL7560 and SL7580, respectively, which means that more cross-linking has taken place inside the polymer network of Accura SI40.

The parts were brittle at low temperatures. %Elong of Accura SI40 parts increased when temperature was increased. However, increasing the temperature to a certain level above T_g reduced the elasticity of the material. The values of most of the mechanical properties are high at low temperatures as the material is stiff and they tend to be weaker with increasing temperature, as shown in Figure 3-30 to Figure 3-35.

The same is shown for the parts that were made of SL7560 and SL7580. They had less %Elong at low temperatures. %Elong increased when temperature was increased, as shown in Figure 3-36 and Figure 3-37, that show the results of different SL7560 and SL7580 parts that were tested at different temperatures (at the age of 4 weeks and stored at 50%RH).
From these results, it can be clearly seen that when samples are stored in dry (10%RH) and controlled (50%RH) conditions, ageing improved most of the mechanical properties of SL materials. This is most likely due to the dark reaction. However, elevated temperatures negatively affected the mechanical properties. Moisture uptake was found to greatly affect the mechanical properties of SL materials. The analysis included here is built upon the literature research that was carried out and the results of the mechanical tests.

The results described throughout this Chapter clearly show that the level of humidity has an obvious effect on the mechanical properties of the SL materials, which means that further cross-linking and degradation may have chemically changed the materials and resulted in a permanent change in the materials properties. More comprehensive investigations were therefore required to identify the mechanism of degradation of SL materials due to humidity. This is discussed in detail throughout Chapter 4.
Chapter 4 Detailed Material Analysis for SL7580 Resin

4.1 Introduction

The mechanical test results discussed in Chapter 3 confirmed that a consistent pattern of degradation in the mechanical properties of the Epoxy-based SL materials occurred when they were subjected to humidity. This confirms previous anecdotal evidence and has quantified, in a mechanical properties sense, the extent of the degradation for the materials tested. However, though hygroscopic degradation has been shown to occur, the exact mechanism of degradation was still not clear. It is therefore the aim of this Chapter to detail further in-depth investigations that were undertaken to give a comprehensive explanation of the mechanisms of hygroscopic degradation.

Analyses were done by undertaking simultaneous investigations of the degree of cure, chemical structure and mechanical properties over a period of one year. These results were then cross-correlated to determine the mechanism of degradation. As the pattern of hygroscopic degradation was similar and consistent for all the SL materials tested, it was decided to base these further long term studies on just one material, SL7580.
4.2 Analysis Techniques

Before the year-long tests are detailed, a review of the appropriate analysis techniques is given.

4.2.1 Methods for Determining the Degree of Cure

In this Section, a description of the most common technique that can be used to measure the degree of cure of any thermoset material is given, namely, Differential Scanning Calorimetry (DSC). This technique is discussed as it is widely used for routine determination of the degree of cure because it provides reliable and consistent results [185].

DSC is a thermal analysis technique which generates a linear heating rate and subsequently measures the energy required to maintain the heat flow into the sample during heating over a period of time (usually 10°C/min) [186]. A DSC apparatus consists of an enclosed cell which contains two aluminium pans that are connected to thermocouples to monitor the temperature in each, as shown in Figure 4-1.

![Figure 4-1: Schematic Diagram of the DSC apparatus](image-url)
One of the pans includes the sample to be examined (weighing between 5 and 20 milligrams) [186]. The other pan is used as a reference as it can include a sample where all thermal properties are known and does not have any transition in the measuring range used (such as glass). It can also be empty. The machine is usually connected to a control unit which performs the required calculations. Both the amount of heat input and the temperature rise of the tested sample are compared to the reference pan (whether it includes a material or not) while both are subjected to a constant linear temperature change [187].

Heat is supplied to ensure that the temperature increase between the two aluminium pans are exactly the same. The pan that includes the test sample typically absorbs more heat than the reference pan. The results produced from the DSC identifies the amount of energy absorbed by the sample until it is completely cured ($H_{\text{spec}}$). This is represented by the area under a curve as shown in Figure 4-2 that shows a typical DSC curve for a partially cured SL7580 specimen.

![Figure 4-2: Typical DSC curve of a partially cured specimen (SL7580)](image-url)
The area under the DSC curve, which denotes the amount of thermal energy required to fully cure a material, reduces for increased levels of cure (e.g. heat, UV radiation and ageing). The area is reduced until no further curing can be instigated as shown in Figure 4-3.

![DSC Curves](image)

**Figure 4-3: Schematic DSC curves at different levels of cure**

Therefore, DSC is appropriate for comparing and determining the change in the degree of cure of the materials investigated.

### 4.2.2 Methods for Determining the Change in Chemical Structure

Spectroscopy can be used to monitor the change in the chemical characterisation of polymers. It can also be used to confirm the presence of a particular functional group and to detect free radicals or additives [188]. There are different types of spectroscopic techniques that have been discussed in previous work [189,190,191,192]. However, in this Section, only Fourier Transform Infra-Red (FTIR) spectroscopy is discussed as it has been found to be a suitable technique for assessing the cure of an Epoxy-Amine system [193]. Also, and of particular
interest to this research, it can be considered as an analysis technique which is sensitive to the interaction between water and polymeric systems (including Epoxy-based materials) [194,195,196,197,198].

In FTIR, the net absorption of monochromatic (single frequency) light is monitored as the electromagnetic radiation is swept over a range of frequencies that are used to study molecular vibrations. This technique can be used to investigate the change in the chemical structure of a material by measuring and observing the change in the molecular vibrations within the polymer network [191]. Different investigations have been carried out using FTIR to monitor the kinetics of cure and analyse different Epoxy systems [199,200,201]. The Infra-Red (IR) absorption frequencies are dependent upon the mass of the atoms involved in the vibrations (these are light when they possess high energy and heavy when they possess low energy) and the bond strength (which is dependent on the other functional groups attached to the bond) [191,193].

However, it should be noted that there is a disadvantage related to standard FTIR which makes it unsuitable to be used in this research. It concerns the thickness of the sample that is required to be examined, which should typically be less than 20µm [193,202]. This sample thickness is difficult to produce using SLA and it is also problematic to cut a larger sample to the thickness required. This is because any thermal or mechanical process (e.g. microtome) may affect the material and cause further cure to the material due to the heat produced from the continuous friction between the specimen and the rotating cutting tool, thus distorting the result.

This problem has been solved by adapting the normal FTIR to work as a surface analysis technique, which is known as “Attenuated Total Reflectance (ATR)” spectroscopy. The spectrum obtained from this technique is independent of the sample thickness, as the reflected radiation penetrates the sample to a depth of
only a few microns [203]. ATR spectroscopy can also be used to examine liquid, gel and opaque samples [203].

There are three types of ATR that have different wavenumber regions (wavenumber is the reciprocal of wavelength in cm⁻¹). The mid region (4000 to 400cm⁻¹) is the most commonly used region for polymers. Other regions include far-infrared (400 – 10cm⁻¹), which is generally used to identify vibrations of heavy atom groups (e.g. metals) and near-infrared (15000 – 4000cm⁻¹) which is used to identify overtones [189]. Thus in this work, a mid region ATR apparatus was used as it is most appropriate for use with polymeric materials.

The ATR unit, schematically shown in Figure 4-4, consists of two 45° fixed incident angles and a horizontal plate with a Zinc Selenide (ZnSe) or Germanium (Ge) crystal. These crystals provide transmission of the beam with a minimum loss of energy. The ZnSe works as an internal reflection element [204].

![Figure 4-4: Schematic Diagram of the ATR Unit](image)

The exit beam is analysed and a plot (Absorption vs. Wavenumbers in cm⁻¹) is produced which represents the amount of absorption of each type of chemical bond inside the material. An example of a typical ATR plot for SL7580 is shown in Figure 4-5 that shows the typical spectrum representing the chemical structure of SL7580 Epoxy-based material.
It can be seen in Figure 4-5 that the spectrum is divided into 13 different peaks and these are identified in Table 4-1. These peaks were determined according to previous work [98,205,206,207] and published tables [189,190,208].

![Figure 4-5: Typical spectrum showing the different peaks for SL7580](image)

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak Type</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-OH (Hydroxyl)</td>
<td>3150 - 3700</td>
</tr>
<tr>
<td>2</td>
<td>CH- (Methine): CH₂ (Methylene) &amp; CH₃ (Methyl)</td>
<td>2800 - 3050</td>
</tr>
<tr>
<td>3</td>
<td>C=O (Carbonyl)</td>
<td>1300 - 1800</td>
</tr>
<tr>
<td>4</td>
<td>C=C (Aromatic Ring)</td>
<td>1600</td>
</tr>
<tr>
<td>5</td>
<td>CH- (Methine)</td>
<td>1500</td>
</tr>
<tr>
<td>6</td>
<td>CH₂-O</td>
<td>1450</td>
</tr>
<tr>
<td>7</td>
<td>-C-CH₃</td>
<td>1370</td>
</tr>
<tr>
<td>8</td>
<td>C-O-C (Epoxide)</td>
<td>1260</td>
</tr>
<tr>
<td>9</td>
<td>O=C-O (Ester)</td>
<td>1180</td>
</tr>
<tr>
<td>10</td>
<td>C-O-C (Aliphatic Ethers)</td>
<td>1100</td>
</tr>
<tr>
<td>11</td>
<td>O-H (Hydroxyl)</td>
<td>920</td>
</tr>
<tr>
<td>12</td>
<td>C-O-C (Epoxide)</td>
<td>780-900</td>
</tr>
<tr>
<td>13</td>
<td>C₆H₆ (Benzene Ring)</td>
<td>580 - 780</td>
</tr>
</tbody>
</table>

Table 4-1: Definition of the different peaks of SL7580 Epoxy-based material

It can be noted that from Table 4-1 there are some peaks that are repeated (e.g. Hydroxyl and Epoxide). This could be due to the fact that these peaks have different types of molecular movement within the chemical structure of the
Typically, there are two types of molecular movement that can be found in any polymeric structure, and include "stretching" and "bending" [209]. Figure 4-6 shows the two specified types of molecular motion.

![Diagram of molecular movement](image)

**Figure 4-6**: Schematic diagram shows the two types of molecular movement.

In the "stretching" movement type, the atoms in the functional group move closer to or further away from each other. In the bending movement type, the atoms in the functional group do not move toward each other but rather around each other. This can be considered as lower energy motion compared to the stretching movement type [209].

The ATR method described throughout this Section is used as a surface analysis technique, and does not allow investigations of the bulk of the specimen. However, identifying the change in chemical structure at the surface can provide an indication of the change throughout the whole specimen. As the increase in water concentration will initially cause these changes to occur at the surface of the material, the results obtained at the surface may vary slightly from the changes occurring throughout the bulk of the specimen. However, by minimising the thickness of the specimen, these differences can be reduced to negligible levels. The reaction described here is controlled by the water concentration, which increases over time causing the change in the polymer network. This chemical change continues for a period of time, dependent on the structure of the polymer network, even after reaching saturation. This is known as "polymer relaxation", which was discussed in Section 1.7.
Of relevance to this work, it is expected that some of the peaks, as shown in Figure 4-5, would change with the application of a method of curing or a degradation factor. For example, the area under the Hydroxyl peak is expected to increase over time when the sample absorbs water, as schematically shown in Figure 4-7.

Similarly, when curing takes place, the area under the Epoxide peak is expected to increase as schematically shown in Figure 4-8.

Figure 4-7: Schematic of expected change of the Hydroxyl peak at different stages of water absorbance

Figure 4-8: Schematic of the Epoxide peak at different stages of cure
Other peaks are only slightly affected when degradation or curing occurs to the material. An example is the Aliphatic Ethers peak and as such this peak can be disregarded. Identifying the change in the area under the peaks that do vary due to curing or degradation can indicate a change in the chemical structure of the material investigated and therefore the mechanism of the cure reaction or degradation can be identified.

4.3 Methodology Used for the Detailed Material Analysis

The work of Chapter 3 showed that hygroscopic degradation occurred in SL parts that were soaked in water (100%RH). However, the exact mechanism of hygroscopic degradation was not determined. Therefore, the aim of the work discussed in this Chapter was to identify the mechanism of degradation of SL materials due to humidity. This has been achieved by dividing the aim into different objectives that include:

- Manufacture the different samples required for the specified tests
- Identify the change in the tensile properties due to humidity over time
- Investigate the change in the degree of cure of the SL material tested
- Study the change in the chemical structure of the material due to the effects of humidity
- Compile the results obtained from the previous objectives to identify the mechanism of degradation

These more in-depth studies were undertaken for a period of one complete year using two week time intervals. This was in order to monitor the changes that occurred to the material in narrower time intervals than those used in Chapter 3 so that a deeper understanding could be obtained. This was undertaken for samples that were made of SL7580 resin and stored at the three different levels of humidity (dry (10%RH), controlled (50%RH) and wet (100%RH)) as for previous tests.
All the samples were stored and tested at 20°C. Five samples were tested for each type of individual analysis technique at each level of humidity. A total number of 400 samples of each specimen type were built.

4.3.1 Manufacture of the Required Test Samples

An SLA 7000 was used to build the test samples. Three different types of samples were produced and included:

1. Tensile samples were built according to ISO 3167 standard [210]. Upright build orientation was used to build the samples required.
2. DSC samples were built on top of the tensile samples (attached to them), as shown in Figure 4-9, with the same thickness (4mm) and width (10mm) as the narrow parallel-sided portion of the tensile test specimen and a length of 20mm. The reason for building the DSC samples at the same time was so that it could be guaranteed that the same build and post-processing parameters were used for both DSC and tensile samples.

Figure 4-9: Schematic diagram showing DSC sample attached to tensile sample
3. ATR samples (10x10x1mm) were built in a flat orientation in a different build platform than the one that was used to build the tensile and DSC samples. The reason for building the ATR samples separately was due to time constraints, as the ATR samples were tested at alternative two week intervals to the DSC and tensile samples. However, the ATR samples underwent exactly the same build and post-processing procedures that were performed on the tensile and DSC samples.

4.3.2 Mechanical Tests
As before, the tensile tests were performed on a Zwick 1030, with 10KN load cell which is located in a temperature controlled room (20°C ±1°C). The crosshead speed of 5 mm/min was adopted to measure UTS, %Elong, according to ISO 527-1 and 2 standards [166]. However, 1mm/min was adopted to measure the value of Young’s Modulus in the same test using a bi-axial extensometer with a gauge length of 25mm. For each mechanical property, the final result taken was an average of five samples that were stored at the individual humidity conditions and tested at different time intervals.

4.3.3 DSC Analysis
The DSC apparatus used was a calibrated Shimadzu DSC 60WS. Aluminium crimping pans (with lids) were used to contain the tested samples. The upper temperature limit of these aluminium pans was 400°C. The DSC samples were snapped off the tensile test specimens. Pliers were used to cut the small DSC sample to be tested out of the core of the original DSC specimen, with a weight of 5 to 15mg. A digital scale by Mettler Toledo with an accuracy of 0.1mg was used to weigh the samples before sealing them in the pans.
Two aluminium pans (of the same weight) were used to carry out each test, one of them included the sample and the other was empty. A manual crimper apparatus (SSC-30) by Shimadzu was used to seal the pans. For each DSC analysis, the final result taken was an average of five samples that were stored at the three humidity conditions and tested at different time intervals.

4.3.4 ATR Analysis

The apparatus used in this research was a mid-infrared ATR Shimadzu FTIR 8300 Spectrometer. Different settings were tested and the settings that were found to provide consistent results in terms of the clarity of the peaks were:

- **Number of scans**: The spectrometer considers the average of $2^n$ scans. An average of 64 scans for each sample was found to be sufficient to obtain the required results (the more measurement performed, the more the quality of the spectrum improves due to the accumulation of measurement results)

- **Resolution**: 2cm$^{-1}$. This setting controls the resolution of each spectrum which visually separates the overlapped peaks. The resolution selected can be considered as “high resolution” (the resolution available for this apparatus is from 16cm$^{-1}$ to 0.5cm$^{-1}$)

- **Measuring mode**: Absorption, it is a mode in which the apparatus provides the amount of radiation absorbed by the material tested

- **Scan speed**: 2.8mm/sec. This speed is considered as a low speed to obtain reliable results as it controls the speed of a moving mirror

- **Range**: High: 4000cm$^{-1}$ and Low: 400cm$^{-1}$ (which is the range offered by the apparatus and includes all the peaks for the materials investigated)

Each sample was mounted individually on a Germanium (Ge) crystal included in the ATR apparatus with the smooth surface of the sample (the one that did not include the supports) facing the crystal. For each ATR analysis, the final result is
an average of five samples that were stored at the three humidity conditions and tested at different time intervals.

Each peak shown in Figure 4-5 represents a specific type of chemical bond. Spectra were taken to investigate the change in the chemistry of the samples that were stored at different humidity levels and tested at different ages (over one year). All the spectra are shown in Appendix K, L and M. The area under each peak was calculated using “IR Solution 1.2” software package by Shimadzu.

As the ATR spectra varied over time due to the effects of humidity and ageing on the chemical structure, it was therefore required to standardise the results obtained. To enable this, a peak with the least change in area was selected (constant peak, i.e. Aliphatic Ethers). The ratio of the changing peaks to the constant peak of the same spectrum was calculated for all spectra. This method was used in previous work by Fouchal [193] to investigate the cure of an Epoxy Amine system, Vione et. al. [211] to monitor the degradation of Phenol and Benzoic acid and Ho and Ma [212] to identify the change of Silicon resin coating on metal when polymeric binders have been added.

### 4.4 Detailed Material Analysis Results

In this Section, the results of the tensile, DSC and ATR two weekly tests are given. It should be noted that all the tests were undertaken at 20°C.

#### 4.4.1 Mechanical Test Results

The results of UTS of the samples that were stored at the specified humidity conditions are shown in Figure 4-10.
Figure 4-10: Effects of humidity and ageing on UTS of SL7580

Confirming the work of Chapter 3, but in much greater detail, it can be seen that the tensile strength of the samples that were stored under dry (10%RH) conditions were improved by 11.3% over one year. The results of the samples stored at controlled (50%RH) condition were roughly stable over time. However, the results of the parts that were stored soaked in water (100%RH) showed a great decrease (82%) in the strength of the material.

The results of Young’s Modulus, shown in Figure 4-11, represent the effects of humidity and ageing on the SL7580 parts that were stored at dry (10%RH), controlled (50%RH) and wet (100%RH) conditions prior to testing.
The results indicate that the value of Young’s Modulus of the samples that were stored at dry (10%RH) condition was improved with a percentage of 22.6%. The results of the samples stored at a controlled (50%RH) condition show less improvement (10%) compared to the dry (10%RH) samples. However, the results of the parts that were stored soaked in water (100%RH) show a great reduction in Young’s Modulus of 90%.

The results of %Elong are shown in Figure 4-12, which details the effects of humidity and ageing on the values of Elongation at Break of the SL7580 parts that were stored under dry (10%RH), controlled (50%RH) and wet (100%RH) conditions, respectively, prior to testing.
It can be noted that the elongation at break of the samples that were stored under dry (10%RH) conditions was reduced by 35% over time. The results of the samples stored under controlled (50%RH) conditions show roughly the same reduction in %Elong of the material. However, the results of the parts that were stored soaked in water (100%RH) demonstrate an increase of 45% in the %Elong of the material after one year.

4.4.2 DSC Results

The detailed DSC results of SL7580 at different ages and humidity conditions with the individual graphs are shown in Appendices H, I and J. They show the results of the dry (10%RH), controlled (50%RH) and wet (100%RH) samples respectively. The general trend of each humidity condition is shown in Figure 4-13.
It can be seen in Figure 4-13 that a reduction in the heat of fusion, which is the energy required to fully cure the material, has occurred over time. This was identified by calculating the area under the curves obtained from the DSC analyses. An obvious reduction of 87.4% occurred to the dry (10%RH) samples after one year as shown in Figure 4-14 and Figure 4-15.
However, for the controlled (50%RH) and wet (100%RH) samples, a reduction of 96% and 98.8% respectively occurred over one year. This is shown in Figure 4-16 and Figure 4-17 that show the DSC curves of two different samples that were kept at controlled (50%RH) and wet (100%RH) conditions for one year prior to testing.
Figure 4-17: Typical DSC curve of SL7580 at 52WKs (wet (100%RH) sample)

Figure 4-17 shows that for the wet (100%RH) sample, at the age of 52 weeks, a great reduction in the heat of fusion has occurred. Also, degradation began to take place at lower temperatures compared to the dry (10%RH) and controlled (50%RH) samples of the same age. Absorption of water into the wet (100%RH) samples greatly reduced the heat of fusion, which is the amount of energy required to fully cure the material. This occurred at an earlier stage compared to the dry (10%RH) and controlled (50%RH) samples.

The DSC results indicate that the heat of fusion was reduced over time for the three humidity conditions. This could be due to either curing or degradation of the material (or both). However, the tensile test results shown in Section 4.4.1 indicate that the heat of fusion was reduced due to further curing (Young’s Modulus increased over time) or degradation (Young’s Modulus decreased over time). However, in order to obtain better understanding of what has changed within the polymer network, the ATR analysis was carried out and the results are shown in Section 4.4.3.
4.4.3 ATR Results

Figure 4-18 shows the spectrum which represents the chemical structure of SL7580 material. The spectrum is divided into 13 different peaks.

From the spectra obtained, different peaks were found to be changing over time due to the effects of humidity and ageing. These peaks include:

- Peak 1: Hydroxyl (-OH)
- Peak 3: Carbonyl (C=O)
- Peak 4: Aromatic Ring (C=C)
- Peak 5: Methine (CH-)
- Peak 8: Epoxide (C-O-C)

In previous work that is proprietary to the resin vendor, spectra were taken of the different constituents that form most of the currently available Epoxy-based resins (Difunctional and Trifunctional Epoxies, Difunctional Aromatic and Aliphatic Acrylates, Polyol and Initiator). The peaks mentioned above were mainly found in Difunctional and Trifunctional Epoxies, which indicates that most of the reaction occurs within the Epoxy monomer and thus the role of the Acrylate and other elements found in these materials are not considered in this study. For the other peaks, little change occurred and therefore only the ratios of the area under the
peaks that were found to be changing over time to a peak with a constant area (peak 10) were investigated. Peak 10 (Aliphatic Ethers C-O-C) was selected to be the reference peak, as this peak showed the least change in the area over time. The results for the changing peaks are shown in Figure 4-19 to Figure 4-28. It should be noted that for each Figure, different scales were used in order to elucidate the results for each particular peak.

The Hydroxyl peak (Peak 1) has increased with advancing age for the samples that were stored at the three different humidity levels. This is shown in detail in Figure 4-19 (a), (b) and (c) that represent the specific changes in the Hydroxyl peaks for the dry (10%RH), controlled (50%RH) and wet (100%RH) samples respectively.

![Typical spectra show the increase in intensity of the Hydroxyl peak over time for SL7580 samples stored at the three humidity conditions](image-url)
Figure 4-20 shows the change in the area under the Hydroxyl peak over one year for the dry (10%RH), controlled (50%RH) and wet (100%RH) samples in graphical form.

For the Carbonyl peaks (Peak 3), an increase took place with advancing age for the dry (10%RH) and controlled (50%RH) samples as shown in Figure 4-21 (a) and (b) respectively. However, a slight decrease occurred to the Carbonyl (C=O) peak of the wet (100%RH) samples over time, as shown in Figure 4-21 (c).
Figure 4-21: Typical spectra show the change in intensity of the Carbonyl peak over time for SL7580 samples stored at the three humidity conditions.

Figure 4-22 shows the change in the area under the Carbonyl peak over one year.

Figure 4-22: Change in the area under the Carbonyl peak referenced to the area under Aliphatic Ethers peak
For the Aromatic Ring (C=C) peaks (Peak 4), the area has increased for the three different humidity conditions as shown in Figure 4-23.

![Figure 4-23: Typical spectra show the increase in intensity of the Aromatic Ring peak over time for SL7580 samples stored at the three humidity conditions.](image)

However, more increase occurred in the wet (100%RH) samples compared to the dry (10%RH) and controlled (50%RH) samples as shown in Figure 4-24, which shows the change in the area under the Aromatic Ring (C=C) peaks over one year for the three investigated levels of humidity.
Figure 4-24 also shows that the increase in the area under the Aromatic Ring (C=C) peak for the samples that were stored at wet (100%RH) condition prior to testing started from age of 2 weeks and continued up to 16 weeks. The peak area then started to become more stable up to the age of 36 weeks, after that, it started to increase further.

For the Methine peak (Peak 5), a slight increase occurred in the dry (10%RH) samples as shown in Figure 4-25 (a). However, The controlled (50%RH) samples shown in Figure 4-25 (b) indicate that there was not a significant change occurring compared to the wet (100%RH) samples, shown in Figure 4-25 (c), which showed an obvious decrease in the Methine peak over time.
Figure 4-25: Typical spectra show the change in intensity of the Methine peak over time for SL7580 samples stored at the three humidity conditions.

Figure 4-26 shows the change in the area of the Methine peak to the area of the Aliphatic Ethers peak over time.

Figure 4-26: Change in the area under the Methine peak referenced to the area under Aliphatic Ethers peak.
For the Epoxide peak (Peak 8), the changes in the peak area for the three investigated levels of humidity are shown in Figure 4-27 (a), (b) and (c).

![Typical spectra](image)

(a) Dry (10%RH)  
(b) Controlled (50%RH)  
(c) Wet (100%RH)

Figure 4-27: Typical spectra show the change in intensity of the Epoxide peak over time for SL7580 samples stored at the three humidity conditions.

There was an increase which occurred in the dry (10%RH) samples. The controlled (50%RH) samples showed roughly no change in the overall trend over time. However, a reduction occurred in the wet (100%RH) samples, as shown in Figure 4-28.
Figure 4-28: Change in the area under the Epoxide peak referenced to the area under Aliphatic Ethers peak

4.5 Review

Figure 4-29 details a summary of the results for the change in Young’s Modulus and the corresponding change in degree of cure over one year for the SL7580 samples stored at dry (10%RH), controlled (50%RH) and wet (100%RH) conditions. All the samples were stored and tested at 20°C.
It can be clearly seen that for the samples subjected to relatively low levels of humidity (dry (10%RH) and controlled (50%RH)) there has been an increase in the Young’s Modulus that corresponds to an increase in the degree of cure of the material (represented by a drop in the heat of fusion). This clearly indicates that the increased Young’s Modulus is a result of the increased polymerisation (cross linking) within the polymer network. In the absence of any other ageing influence, as the samples were stored in a dark, sealed environment, this result can only be due to the dark reaction phenomenon [68,141] where the cationic photopolymerisation – initiated by the UV cure of the SL laser – has continued.

However, it should be noted that even for relatively low levels of humidity experienced by the controlled (50%RH) samples that there has been a reduction in the Young’s modulus with respect to the dry (10%RH) samples. Most interestingly, there has also been a correspondingly large effect on the heat of fusion.
fusion that has fallen significantly. This drop in the heat of fusion could be due to two possible effects:

1. Increased polymerisation due to dark reaction.
2. Hygroscopic degradation.

As the Young’s modulus has also increased over the period of one year, it is likely that, though there has clearly been some hygroscopic degradation (evidenced by the reduction in the heat of fusion), the overriding influence for samples stored at these relatively low values of humidity is that of dark reaction that is a result of the cationic curing mechanism. However, the results of the controlled (50%RH) showed hygroscopic degradation compared to the dry (10%RH) samples.

The results for the samples stored at the wet (100%RH) condition, prior to testing, showed a great decrease, not only in the sharp reduction of Young’s Modulus, but there was also a significant reduction in the heat of fusion. In this case, it is most likely that the drop in the heat of fusion was not related to the mechanism of the dark reaction, but was predominantly a consequence of hygroscopic degradation. This indicates that chain-scission of the polymer network has occurred. This was shown by the increase of Elongation at Break of the material as shown in Figure 4-12. To confirm this, it is necessary to refer to the results of the ATR tests.

The results obtained from the ATR analyses of the wet (100%RH) samples, shown in Section 4.4.3, indicate that there was an obvious effect of water on the construction of the polymer-network of the investigated Epoxy-based parts. Water penetration into the wet (100%RH) parts has massively increased the intensity of the Hydroxyl peak (shown in Figure 4-20) compared to the dry (10%RH) and controlled (50%RH) samples. This major increase in the Hydroxyl peak of the wet (100%RH) samples was noticed with different changes within the polymer network. These changes included:
1. Increase of Aromatic Ring (C=C) (shown in Figure 4-24).
2. Reduction in Methine (CH-) (shown in Figure 4-26).
3. Reduction in Epoxide (C-O-C) (shown in Figure 4-28).

The change in the intensity of the peaks mentioned above occurred as a result of the penetration of moisture into the polymer network; this caused softening to the material which was observed to increase over time. This softening of the material is due to chain scission (breaking of the cross-links that form the chains within the polymer network) which is consistent with previous work by Ritter et. al. [112] and Salmon et. al. [113]. This is due to the fact that water acts as a plasticizer as well as a reactant, which causes chemical degradation of the polymer matrix due to hydrolysis and oxidation during long-term exposure to water as was proved by Antoon and Koenig [104]. In other research by Antoon et. al. [121], it was found that water absorbed in an Epoxy resin usually interacts with the polar Hydrogen atoms causing chain scission to the Epoxy monomer. Therefore, it can be concluded that the reduction in Epoxide within the wet (100%RH) samples indicates that breaking of the Epoxide ring took place due to the process of water absorption. Also, the reduction in Methine indicates that breaking of the cross-links that connect the Hydrogen atoms to the Carbon atoms within the Methine monomer (CH-) took place. This separation of the cross-linked molecules can increase the Aromatic ring (C=C) along with the Hydroxyl groups (-OH) as discussed in previous work [194,196]. This is shown in Figure 4-30.
The chain scission occurred within the polymer network – especially the breaking of the cross-links that connect the Epoxide ring has resulted in free Oxygen and Carbon atoms. However, the breaking occurred to the cross-links that connect the Methine monomers has produced free Carbon and Hydrogen atoms. These free atoms were increased gradually while the interaction between water and polymer was proceeding, at the same time these atoms (Oxygen, Hydrogen and Carbon) were connected together forming Hydroxyl groups and Aromatic rings as shown in Figure 4-30. The aromatic rings formed can be considered as free radicals that have the availability to connect with other elements such as Hydrogen and Oxygen atoms forming volatiles and free species. However, The Hydroxyl groups formed from the previous reaction along with the Hydrogen atoms included within the structure of the Epoxy monomer have a high ability to connect with the absorbed water molecules. This is consistent with previous work by Apicella et.
Figure 4-31 shows the connection of water molecules to the polymer network when water penetrates into the material.

As shown in Figure 4-31, the penetrant water can connect to the Hydroxyl groups formed from the reaction shown in Figure 4-30 and also it can connect to the polar Hydrogen groups that found within the polymer network as was explained by Apicella et. al. [128]. The reaction shown in Figure 4-30 was the main reason that caused the formation of the Hydroxyl groups. The increase of the Hydroxyl groups (OH) occurred gradually within the polymer network as more moisture penetrated into the polymer network as shown in Figure 4-31, which resulted in forming more Hydroxyl groups. This is consistent with previous work by Antoon et. al. [121]. This inter-molecular reaction that has occurred within the polymer network can be considered as the main reason that caused the degradation of the
wet (100%RH) parts. This was represented by the sharp reduction of Young’s Modulus along with the significant reduction in the heat of fusion, shown in Figure 4-29.

The change in the area under the peaks that represented the different chemical bonds of the controlled (50%RH) samples was between those shown in the dry (10%RH) and wet (100%RH) samples. This indicates less water penetration into the controlled (50%RH) samples than into the wet (100%RH) samples. An interaction was observed between water and the polymer network as indicated by the ATR results. This can also be seen in the DSC results shown in Figure 4-29. This interaction was not sufficient to cause degradation of the samples at this level of humidity as indicated by the slight improvement of Young’s Modulus after one year, as shown in Figure 4-29. However, this improvement was slightly less than that of the dry (10%RH) samples. Therefore, it can be seen that the effect of the amount of water absorbed by the controlled (50%RH) samples over the year was between that of the dry (10%RH) and the wet (100%RH) samples. This effect did not cause such significant degradation to the material as was seen in the wet (100%RH) samples. At the same time, it eliminated the noticeable improvement of Young’s Modulus observed in the case of the dry (10%RH) samples.

However, the ATR results obtained showed the lowest increase in the Hydroxyl peak within the dry (10%RH) samples compared to the increase that was shown for the other humidity conditions as shown in Figure 4-20. This indicates that the dry (10%RH) samples absorbed less water than the controlled (50%RH) and wet (100%RH) samples. However, an increase was recognised in the Carbonyl, Methine and Epoxide peaks that are shown in Figure 4-22, Figure 4-26 and Figure 4-28, respectively. This confirms that the dark reaction (cross-linking), discussed previously, may have taken place within the polymer network, indicating that the dry (10%RH) samples have experienced further curing over time.
This work has finally established the extent of degradation that occurs in Epoxy-based SL materials due to the action of humidity and has also identified the exact degradation mechanism. Following this, it is useful to model the diffusion of water into SL materials and understand the kinetics of water absorption. Understanding the type of diffusion and the relationship between moisture content and mechanical properties will help to predict the change in mechanical properties of an SL material over time. This is discussed in Chapter 5.
Chapter 5  Modelling of Water Diffusion into SL Parts

5.1 Introduction

Polymers exposed to water are subject to different effects, such as changes in dimensions and in the properties of the material. It has been shown that water can have a harmful influence on the mechanical properties of a polymer and therefore its useful lifetime [148]. Moisture diffusion into polymer networks is related to the availability of molecular sized holes in the polymer structure (free volume) and the affinity of the polymer to moisture as discussed in previous work by Wong and Brotman [142].

The availability of holes depends on the polymer microstructure, cross-link density, degree of cure and molecular chain stiffness of the polymer [106]. In previous work by Wong and Brotman [142] and Han and Drzal [213], it was shown that the degree of cure of an Epoxy controls the extent and distribution of the absorbed water molecules. The affinity of a polymer to water is highly dependent on the presence of Hydrogen bonding sites along the polymer chains, which create attractive forces between the polymer and water molecules as discussed in Chapter 4. Water molecules that are free to move through the holes, or free volume, are often referred to as “unbound molecules”. As this unbound moisture is filling a free volume, it does not cause dimensional changes of the
polymer. However, the water molecules that attach to the polymer chain via 
Hydrogen bonding (i.e. bound molecules) disrupt the inter-chain Hydrogen 
bonding, which causes swelling and plasticization of the polymer [107,214].

To date, there has not been a study to investigate the diffusion of moisture into SL 
materials. Most of the current SL materials are Epoxy-based resins as discussed in 
Chapter 1. In Epoxies, there are significant amounts of free volume [215]. Also, 
the Epoxy-water affinity is relatively strong because of the polar Hydroxyl groups 
(-OH) that are created by the Epoxide ring-opening reaction with primary and 
secondary Amines, as discussed previously by Barton [216]. Owing to the 
existence of these Hydroxyl groups, a certain amount of freedom is retained; thus 
they can Hydrogen bond with similar groups located nearby [116]. However, 
polar water molecules can also Hydrogen bond with these Hydroxyl groups, thus 
disrupting the inter-chain Hydrogen bonding [217]. The molecular structure is 
then altered to adapt to the presence of the moisture (known as polymer 
relaxation).

In this Chapter, an investigation to characterise the diffusion of water into 
currently available Epoxy-based SL materials is described. This is undertaken 
firstly to model the diffusion of water into the investigated SL materials and 
secondly to predict the change in mechanical properties of an SL material over 
time. This will lead to a better knowledge of the effects of moisture on the 
mechanical properties of the SL materials. The following Section will describe the 
methodology used for this work.
5.2 Methodology

The methodology which was used to achieve the required targets has been divided into four different stages:

- **Stage I**: Identifying the type of diffusion of water into the three different SL materials (Accura SI40 by 3D Systems, SL7560 and SL7580 by Huntsman)
- **Stage II**: Determining the diffusion coefficients of these materials
- **Stage III**: Modelling the change of concentration and Young’s Modulus within a specimen at specific time (SL7580)
- **Stage IV**: Predicting the stiffness and modelling of water uptake over time for SL7580 material

5.2.1 Stage I: Type of Diffusion

- The samples were produced using an SLA 7000 by 3D Systems in a flat orientation to ensure ease of specimen removal. All the samples were made the same size (60x60x1mm) as stated in ISO 62 [218]
- Three samples of each SL material were produced
- A digital scale by Mettler Toledo with an accuracy of 0.1mg was used to weigh the samples before the drying stage
- The samples were put in an oven at 50°C for 24 hours and then kept in a desiccator to cool to room temperature before weighing them; this process was repeated until the mass of the specimens was constant. 956 hours were taken to completely dry the samples
- The samples were kept fully immersed in water containers (100% RH) and kept at a constant temperature of 20°C. The specimens were extracted at 4, 8, 12, 20, 32, 44, 68 and 92hrs, and then at time intervals of 24hrs. On extraction, surface water was removed with a clean, dry cloth, and the sample was weighed to the nearest 0.1mg, within 1 min of removing it from
the water. This process was repeated until saturation was reached, as indicated by a constant weight

- A graphical plot of water uptake \((M_t/M_i)\) against \((\sqrt{t/l})\) was made for each material, where \(M_t\) indicates the mass of the total amount of penetrant absorbed at time \(t\); \(M_i\) is the corresponding mass at saturation and \(l\) is the specimen thickness

- According to previous work by Abdel-Wahab et al. [145], Equation 5-1, which was derived from Fick’s law, can be used to identify whether the diffusion is Fickian or not by calculating the diffusion coefficient \(D\) at different areas of the curve at the low concentration stage

\[
D = \pi \left(\frac{l}{4M_i}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{l_2} - \sqrt{l_1}}\right)^2
\]  
(Equation 5-1)

- If all the values of the diffusion coefficient \(D\) are constant for a particular material, the diffusion can be considered to be Fickian

- Equation 1-8 shown in Section 1.7.1 was used to produce the best fit Fickian curve and compare it to the experimental results

### 5.2.2 Stage II: Determination of Diffusion Coefficients

After identifying the type of diffusion, various models were studied from the literature. Wong and Broutman introduced a model which was used to identify a dual sorption diffusion mechanism of water into glassy Epoxy resins [161]. A different model by Loh et al. was designed to identify anomalous moisture uptake of rubber toughened Epoxy adhesive [219]. Another model by Roy et al. was used to identify anomalous moisture diffusion in viscoelastic polymers [156]. An additional model by Cai and Weitsman was used to investigate the non-Fickian moisture diffusion into polymeric composites [220]. These models were applied but it was difficult to obtain a suitable model that could accurately represent
diffusion of water into the chosen Epoxy-based SL materials. Therefore, it was decided to use two different equations to model the diffusion. The first equation (Equation 5-2) was derived by Crank [149] from Equation 1-1, shown in Section 1.7, and this equation was used to model the diffusion at a stage of low concentration as a part of the dual-Fickian model.

\[
\frac{M_t}{M_i} = 4 \left[ \frac{D_l t}{\pi} \right]^{1/2}
\]

(Equation 5-2)

Where \( \frac{M_t}{M_i} \) is the rate of water uptake as a function of time \( (t) \), \( D_l \) is the coefficient of diffusion at low concentration, \( t \) is time in hours and \( l \) is thickness of the specimen in mm.

Equation 5-2 has been used to identify the coefficient of diffusion at the low concentration stage. However, a dual-Fickian model which is shown in Equation 5-3 was developed as a part of this research to identify the value of \( D_2 \).

\[
\frac{M_t}{M_i} = \left[ 1 - \sum_{n=0}^\infty \frac{8}{(2n+1)^2 \pi^2} \left( \frac{D_2(2n+1)^2 \pi^2 t}{4t^2} \right)^{1/2} \right] X + \left[ 1 - \sum_{n=0}^\infty \frac{8}{(2n+1)^2 \pi^2} \left( \frac{D_2(2n+1)^2 \pi^2 t}{4t^2} \right)^{1/2} \right] Y
\]

(Equation 5-3)

Where \( D_2 \) is the coefficient of diffusion at high concentration, \( X \) and \( Y \) are equation variables that can be changed to provide the best fit of the model to the experimental results \((X+Y=1)\).

The dual stage uptake model consists of two Fickian diffusion models in parallel, as shown in Equation 5-3. Both of the Fickian diffusion models use a single Fickian model (Equation 1-8 in Section 1.7.1), which was introduced previously by Crank [149], with separate diffusion coefficients \((D_l \) and \( D_2 \)) and saturation levels \((M_i/M_{iI} \) and \( M_i/M_{i2} \)), respectively. The sum of both saturation levels gives
the total saturation. This dual Fickian model has provided the value of \( D_2 \) which is the second coefficient of diffusion at a stage of high concentration. Both \( D_1 \) and \( D_2 \) are coefficients of diffusion that identify the diffusion of water into the SL materials. The models shown in Equations 5-2 and 5-3 were used in commercial mathematical programming package “MATHCAD” to obtain the best fit diffusion parameters \((D_1, D_2, X \text{ and } Y)\) for the experimental results.

5.2.3 Stage III: Modelling of Moisture Concentration and Young’s Modulus

Considering one-dimensional diffusion of moisture into a specimen as shown in Figure 5-1, the concentration of water across the sample will vary according to Equation 5-4 which is driven from Equation 1-7, shown in Section 1.7.1, for Fickian diffusion.

\[
\frac{C_i}{C_o} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{D(2n+1)^2\pi^2}{4l^2}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) \quad \text{(Equation 5-4)}
\]

Where region \(-l < x < l\) is initially dry (i.e. \( C_o=0 \)) and the surface is kept at constant concentration \((C_o)\), diffusion only in \(x\)-direction and the diffusion coefficient \((D)\) is constant. However, for the dual-Fickian, Equation 5-4 can be
duplicated to include the two different Fickian stages with the two identified diffusion coefficients ($D_1$ & $D_2$) as shown in Equation 5-5.

$$\frac{C_i - C_j}{C_i} = \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{-D(2n+1)^2\pi^2 t}{4l^2}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) \right] X + \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{-D_2(2n+1)^2\pi^2 t}{4l^2}} \cos \left( \frac{(2n+1)\pi y}{2l} \right) \right] Y$$

(Equation 5-5)

The concentration at a specific point increases with time inside the specimen due to water penetration. Figure 5-2 shows five different concentration profiles at different times ($t_1$ to $t_5$). Each profile shows the concentration at specific points within the specimen. As moisture is absorbed, this increases the concentration at a specific point within the specimen over time, as shown in Figure 5-2. This can reduce the value of Young’s Modulus ($E$), which gradually varies from the dry modulus ($E_d$) to the saturated modulus ($E_s$), as shown in Figure 5-3, which shows different Young’s Modulus profiles at specific points within the specimen at different times ($t_1$ to $t_5$).

---

Figure 5-2: Moisture concentration profiles at specific points inside the sample at different times

Figure 5-3: Young’s Modulus at specific points inside the sample at different times
As the dotted line at the centre divides the specimen into two halves, this indicates that the shape of the concentration and stiffness profiles is symmetrical (the line works as a mirror), as shown in Figure 5-2 and Figure 5-3. Therefore, it was decided to model the concentration and Young’s Modulus for only half of the specimen as shown in Figure 5-4, and the other half should be the same as the first but in the opposite direction.

![Concentration and Young's Modulus Profiles](image)

**Figure 5-4**: Moisture concentration and Young’s Modulus profiles at specific points inside the sample at time $t$

Young’s Modulus ($E$) varies with the concentration ($C$) according to Equation 5-6, which was developed as a part of this research to identify the value of Young’s Modulus within the specimen at specific time and compare it to the concentration at that time for Fickian diffusion.

$$E_t = E_d - \left[ \frac{C_t}{C_i} (E_d - E_s) \right]$$

(Equation 5-6)

Where $E_t$ is the Young’s Modulus at time $t$. Therefore, for Fickian diffusion, Equation 5-4 can be used in Equation 5-6, which can be presented as shown in Equation 5-7.
\[ E_t = E_d - \left[ \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n e^{-\frac{-(D_t(2n+1) \pi l)}{4l^2}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) \right) (E_d - E_s) \right] \]  
(Equation 5-7)

For dual Fickian diffusion, Equation 5-7 can be duplicated to include the two different Fickian stages with the two identified diffusion coefficients \((D_1 \& D_2)\) as shown in Equation 5-8.

\[ E_t = E_d - \left[ \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n e^{-\frac{-(D_1(2n+1) \pi l)}{4l^2}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) \right)X + \right. \]
\[ \left. \left( 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n e^{-\frac{-(D_2(2n+1) \pi l)}{4l^2}} \cos \left( \frac{(2n+1)\pi x}{2l} \right) \right)Y \right] \]

(Equation 5-8)

5.2.4 Stage IV: Prediction of Stiffness and Modelling of Moisture Uptake

The purpose of this Section is to produce a model which can be used to predict the long term stiffness behaviour of any Epoxy-based SL material at a specific age. The results produced from the model are compared to the one year ageing results of SL7580 that are shown in Chapter 4.

When the Young’s Modulus \((E)\) value is uniform over a cross-Section of a specimen which is shown in Figure 5-5, the stiffness of the material can be calculated according to Equation 5-9.
Figure 5-5: Specimen under load

\[ S = \frac{P}{\delta} = \frac{EA}{L} \]  
(Equation 5-9)

Where \( P \) is the force applied to the specimen, \( \delta \) is the deflection, \( E \) is Young’s Modulus, \( A \) is the cross Section area of the specimen and \( L \) is the gauge length of the specimen. If the Young’s modulus varies in \( x \) and \( z \) directions, Equation 5-9 can be presented as shown in Equation 5-10.

\[ S = \frac{1}{L} \int_{0}^{L} \int_{0}^{w} E(x, z) dx \, dz \]  
(Equation 5-10)

If the Young’s modulus varies in \( x \) direction only, Equation 5-10 can be presented as shown in Equation 5-11.

\[ S = \frac{w}{L} \int_{0}^{L} E(x) \, dx \]  
(Equation 5-11)

Substituting Equation 1-8, which is shown in Section 1.7.1 and can be used to identify the amount of water uptake at time \( t \) into Equation 5-11 gives Equation 5-12. Equation 5-12 can be used to identify the change of stiffness over time in case of Fickian diffusion.
\[ S_t = \frac{wL}{E_d} \left[ E_d - \left( \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{(2n+1)^2 \pi^2 t}{4L^2}} \right) \left( E_d - E_s \right) \right] \] (Equation 5-12)

Where \( S_t \) is the stiffness at time \( t \), \( A \) is the cross-section area of the specimen and \( L \) is the gauge length of the specimen. For dual Fickian diffusion, Equation 5-12 can be duplicated to include the two different Fickian stages with the two identified diffusion coefficients \( (D_1, D_2) \) as shown in Equation 5-13.

\[ S_t = \frac{wL}{E_d} \left[ E_d - \left( \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{(2n+1)^2 \pi^2 t}{4L^2}} \right) X \right] + \left( \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-\frac{(2n+1)^2 \pi^2 t}{4L^2}} \right) Y \] (Equation 5-13)

As discussed in Chapter 1, the more water absorbed, the mechanical properties will be lower. Therefore, the profile of the water uptake \( (M/M_i) \) should be in the opposite direction of the stiffness profile as shown in Figure 5-6. This is modelled in Section 5.3.4.

Figure 5-6: Schematic change in stiffness and water uptake profiles over time
5.3 Results

In this Section, the results of the four different stages that were explained in Section 5.2 are discussed individually.

5.3.1 Stage I: Type of Diffusion

To identify the type of water diffusion for the three chosen Epoxy-based materials, three samples of each material were produced and soaked in water (100%RH) until the saturation was reached. The average result of the three samples obtained for each material is shown in Figure 5-7 to Figure 5-9. The figures show a relation between water uptake \( \frac{M_t}{M_s} \) and \( \sqrt{t/l} \), where \( M_t \) is the mass of the specimen at time \( t \), \( M_s \) is the mass at saturation and \( l \) is the specimen thickness. Equation 1-8 was used to produce the best fit Fickian curve and compare it to the experimental results as shown below.

![Figure 5-7: Diffusion of water into Accura SI40 (experimental results against the best-fit Fickian curve)](image)
From Figure 5-7 to Figure 5-9, it can be seen that, for each material, the Fickian curve is different than the curve which presents the experimental data, especially at the high concentration stage. Also, Equation 5-1, shown in Section 1.7.1, was used to identify the Fickian diffusion coefficient $D$ for the experimental data. The
The value of the diffusion coefficient \( D \) for each individual material was found to be changing throughout the initial portion of each curve, which means that it is non-Fickian diffusion as mentioned in Chapter 1. Since the initial portion of the curve persists for a shorter time, therefore the diffusion here can be considered as pseudo type or “Fake-Fickian”, as the shape of the curve looks like the Fickian diffusion curve [149].

### 5.3.2 Stage II: Determination of Diffusion Coefficients

The models shown in Equations 5-2 and 5-3 in Section 5.2.2 were used in MATHCAD programming to obtain the best fit diffusion parameters \((D_1, D_2, X \text{ and } Y)\) for the experimental results. This was to model the diffusion of water into the chosen SL materials and identify the diffusion coefficients of these materials. The results are shown in Table 5-1 and Figure 5-10 to Figure 5-12.

<table>
<thead>
<tr>
<th>Material</th>
<th>( D_1 ) (cm(^2)/s)</th>
<th>( D_2 ) (cm(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accura SI40</td>
<td>5.2( \times )10(^{-9})</td>
<td>4.8( \times )10(^{-9})</td>
</tr>
<tr>
<td>SL7560</td>
<td>4.2( \times )10(^{-9})</td>
<td>4.0( \times )10(^{-9})</td>
</tr>
<tr>
<td>SL7580</td>
<td>12.9( \times )10(^{-9})</td>
<td>12.7( \times )10(^{-9})</td>
</tr>
</tbody>
</table>

Table 5-1: Values of coefficients of diffusion for the three materials

![Figure 5-10: Modelling of water diffusion into Accura SI40 material](image-url)
In Figure 5-10 to Figure 5-12, the summation of $D_1$ and $D_2$ curves represents the curve of $(D_1 + D_2)$, which is the dual-Fickian curve.

![Graph showing the summation of $D_1$ and $D_2$ curves](image1)

Figure 5-11: Modelling of water diffusion into SL7560 material

![Graph showing the summation of $D_1$ and $D_2$ curves](image2)

Figure 5-12: Modelling of water diffusion into SL7580 material
5.3.3 Stage III: Modelling of Moisture Concentration and Young’s Modulus

As mentioned in Section 5.2.3, Equations 5-5 and 5-8 were used to model the concentration and Young’s Modulus profiles at specific points within the specimen at different times. Figure 5-13 and Figure 5-14 show different concentration and Young’s Modulus profiles, respectively, at different times.

Figure 5-13: Concentration inside the specimen at different times (SL7580)

Figure 5-14: Young’s Modulus inside the specimen at different times (SL7580)

Figure 5-13 and Figure 5-14 show that when the concentration of moisture was increased over time due to more moisture absorbed, the Young’s Modulus was reduced.
5.3.4 Stage IV: Prediction of Stiffness and Modelling of Moisture Uptake

As mentioned in Section 5.2.4, Equation 5-3 and Equation 5-13 were used to develop a model using a commercial mathematical programming package "MATLAB" to predict the stiffness of the material at different times. The results obtained from the model compared to the experimental results are shown in Figure 5-15.

![Figure 5-15: Comparison between the actual values of stiffness and the values obtained from the model (SL7580)](image)

Figure 5-15 shows that the data obtained from the model provides a good prediction of the experimental data. There is a tendency for the model to under-predict the initial reduction in stiffness (at age before 100 days). After that the results from the model start to get closer to the experimental data.

The amount of water uptake at different times was identified using Equation 5-3 shown in Section 5.2.2. The results are shown in Figure 5-16, which shows that as the amount of water absorbed increased over time, the value of stiffness reduced over time.
5.4 Review

It is important to identify the type of diffusion of water into different types of Epoxy-based SL materials. Identifying the type of diffusion and finding the right model can help with accurate determination of the mass concentration profile within a specimen as a function of time. Also, it can help with identifying the diffusion coefficient(s) of any SL material using the same procedures that were explained throughout this Chapter. The type of diffusion was found to be pseudo or fake-Fickian diffusion for the chosen SL materials as Equation 5-1 in Section 5.2.1 was applied to check if the diffusion was Fickian or not. The behaviour of all the curves shown in Figure 5-17 of the three materials is very close to the Fickian behaviour, but the value of diffusion coefficient was found to be changing from one area to another at the stage of low concentration. It was found that the diffusion of water into these materials can be modelled using the dual-Fickian model.
From Figure 5-17 and Table 5-1, it can be seen that SL7560 has the lowest diffusion coefficients and therefore the highest resistance to water absorption over time compared to Accura SI40 and much lower than SL7580. The amount of water absorbed by each material was found to be different at the saturation stage as shown in Figure 5-19. SL7580 was found to be absorbing the lowest amount of water compared to SL7560 and Accura SI40.
To accurately model the diffusion of water into the chosen Epoxy-based materials, a dual-Fickian model was implemented. The curve of each material was divided into two different levels of concentration, low and high concentration levels. Equation 5-2 in Section 5.2.2 was used to identify the value of $D_1$ for each material, which is the diffusion coefficient at low concentration. Using the value of $D_1$ in Equation 5-3 (dual Fickian model – Section 5.2.2), the value of $D_2$ can be obtained which is the diffusion coefficient at more advanced level of concentration. The values of $D_1$ and $D_2$ shown in Table 5-1 confirm that the highest level of water resistance over time is shown in the SL7560 Epoxy-based material which had the lowest diffusion coefficients compared to the other two materials as shown in Figure 5-19 which shows the coefficients of diffusion of the three materials.

![Figure 5-19: Values of the diffusion coefficients of the three materials](image)

A mathematical model was designed using Equations 5-5 and 5-8 in Section 5.2.3 to identify the water concentration at specific points inside the specimens. This was then used to compare the concentration at these points to the values of Young’s Modulus at the same points within the specimen at different ageing intervals, as shown in Figure 5-13 and Figure 5-14. These Figures show the modelled concentration of moisture and Young’s Modulus inside the specimen,
respectively. It can be noted that the concentration increased over time within the specimen. However, Young’s Modulus decreased over time due to the penetration of moisture into the material with weakening of the cross-linking within the polymer network as proved in Chapter 4.

Another model was designed using Equations 5-3 and 5-13 in Sections 5.2.2 and 5.2.4, respectively, to predict the change in stiffness (S) over time. The model was used to predict the change in the stiffness of SL7580 Epoxy-based material over one year. It was found that the value of stiffness obtained from the model, shown in Figure 5-15, up to the age of 100 days, the values of stiffness obtained were lower than the actual values obtained experimentally. After the age of 100 days and up to 364 days, the values of the stiffness that were obtained from the mathematical model were slightly higher than the experimental values. This was especially so from the age of 100 days and up to the age of 200 days, after that the mathematical results were very close to the experimental data.

For SL7580, as shown in Figure 5-16, it was found that with an increase in moisture absorbed, there was a corresponding reduction in stiffness. The maximum stiffness was for the samples that were tested straight after build (just before soaking them in water), at the same time, the water uptake was the lowest. Once the samples were stored at 100% RH, the penetration of water into the samples started to increase and therefore the concentration was increased which reduced the stiffness of the material.
Chapter 6  Discussion

6.1 Introduction

Although the use of Stereolithography (SL) has started to increase during the past few years for producing end-use parts, there are problems that currently exist that impede the conversion of SL to a manufacturing process. These problems have been explained in Chapter 1. One of the major problems related to SL is the instability of the material post-build, particularly when it is subjected to a high level of humidity over time. Therefore, this work has concentrated on the effects of humidity and ageing on the properties of different Epoxy-based SL materials.

The results of the experimental work obtained throughout this research have confirmed that humidity can harm the mechanical properties of an SL material. The literature review included in Chapter 1 showed that this area has rarely been investigated. Therefore, this work was carried out firstly to identify the mechanism of degradation of the chosen Epoxy-based SL materials due to humidity, and secondly to produce a model which can be used to predict the change in mechanical properties of these materials over time. In order to achieve this, several concurrent objectives were identified. These objectives are shown in Figure 6-1 and explained in detail below.
1. Set the boundaries for the ageing tests by determining the suitable build and post-processing methods that can be used to serve the purpose of this research. This was required to maintain the consistency of the work.

2. Investigate the effects of humidity, temperature and ageing on the mechanical properties of different SL materials. This was undertaken firstly to identify the main degradation factor(s) that can harm the mechanical properties, and secondly to fill the gap in the knowledge as the information related to this type of materials were not sufficient.

3. After confirming that humidity is the main degradation factor, it was required to identify the specific mechanism of degradation due to humidity.

4. Modelling the diffusion of water into the investigated SL materials was required as this can help with predicting the change in mechanical properties over time.

The results obtained from this research can ultimately be used by a variety of interested parties. For example, the comprehensive data produced can therefore provide more knowledge and confidence to designers when specifying a material for particular application. Also the manufacturers of the SL resins can use the information provided to study the mechanical behaviour of the materials under certain conditions and therefore improve future resins. The research also provided an explanation to the hygroscopic mechanism of degradation which was not clear.
previously. This degradation mechanism can also be studied to improve future resins. As a part of this research, a mathematical model was developed, which can be used to predict the change in mechanical properties of an Epoxy-based SL material over time. Although, due to time constraints and the volume of work undertaken, this model was applied to just one material (SL7580), it is expected that it can be transferred to other SL materials to predict their mechanical behaviour over time. This is an aspect of “future work” covered in Chapter 8.

At the end of each of the experimental Chapters (2, 3, 4 and 5), a review was given to clarify the major points and to reveal the reasoning for consequent actions that would present a logical flow of the research. This Chapter summarises the findings obtained from each Chapter individually and discusses the procedures that were used to achieve the purpose of this work.

6.2 Set the Boundaries for the Ageing Tests

Investigating the effects of humidity on the mechanical properties of SL materials over one year demanded the production of a large amount of samples for each individual material. Therefore, before taking this step, suitable methods of building, post-processing and testing the SL parts had to be established. This was discussed in detail in Chapter 2.

Isotropy tests were required in order to identify the build orientation that could be used for producing the samples that were used in the ageing tests (discussed in Chapter 3 and Chapter 4). The tensile and flexural test results obtained from the isotropy tests for the three materials showed that Epoxy-based SL materials can be considered isotropic within a 10% variation in mechanical properties. This allowed freedom in choosing the build orientation and helped in reducing the build time without affecting the mechanical properties of the parts. This also
reduced the number of tests that had to be performed. If the parts produced were found to be anisotropic, the number of tests performed would have to be increased three-fold to consider the three main build orientations, shown in Figure 2-2.

Another set of experimental work was required in order to investigate the effects on the tensile properties when varying the temperature from -40°C to +140°C (with an interval of 10°C). This is a typical range required by industry, for example, automotive applications [140]. This was undertaken to determine the range of temperatures that would be used when applying the ageing tests. The results obtained showed that the values of the mechanical properties were nearly the same at 100°C and above. Therefore, it was decided to perform the ageing tests at a temperature range from -40°C up to 100°C.

The SL parts produced from the SLA are not fully cured and require further curing using a post-curing apparatus (PCA). This is often enough for the material to be sufficiently cured, but is entirely dependent on the chemical structure of the material. However, in some cases, thermal curing is required to complete the curing stage of the material. An additional investigation was required to obtain the post-curing method that could be used for the SL samples in the ageing tests explained in Chapter 3 and Chapter 4. The aim of this test was to investigate the effects of thermal post-curing after UV post-curing took place on parts made of Accura SI40, SL7560 and SL7580 Epoxy-based materials. This was to confirm whether thermal post-curing can improve the mechanical properties or not. Two different methods were used:

- **Normal Post-Curing (NPC):** Cleaning and 90 minutes in PCA
- **Thermal Post-Curing (TPC):** Cleaning, 90 minutes in PCA and 2 hours at 80°C

These two methods were suggested by the manufacturers of the materials and can usually be found in the datasheets for the currently available SL resins. Most of the mechanical properties of Accura SI40 and SL7560 increased with TPC, which
was possibly due to further curing. The case was different for SL7580; there was a slight decrease in most of the mechanical properties. This indicated that TPC over-cured the material to a stage of degradation, as mentioned in previous work [73]. Therefore, from the results obtained, it was decided to apply only the normal post-curing method. This was to avoid any detrimental thermal effects on the properties of the materials.

6.3 Investigate the Effects of Different Degradation Factors on the Mechanical Properties of SL Materials

Ageing characteristics of different SL materials (Accura SI40, SL7560 and SL7580) were investigated under different humidity conditions and at a temperature range of (-40°C to 100°C). This was carried out to fill the gap in the knowledge as there was no published data that quantified the degradation of the SL materials over extended time periods. Therefore, these materials were investigated under different factors of degradation.

An upright build orientation was adopted when building the tensile and flexure samples required. This build orientation produced a maximum number of samples in a single build platform. All the samples made of the same material were produced using the same build parameters and then cleaned and normally post-cured using the same procedures for consistency. The samples were stored in dark enclosures to prevent any further post-process UV curing prior to testing. To investigate the effects of humidity on mechanical properties, different humidity levels were used. These included:

- **Dry**: 10% Relative Humidity (RH)
- **Controlled**: 50% RH
- **Wet**: 100% RH (samples were soaked in water)
It should be noted that one of the limitations of this research is that only the three levels of humidity mentioned above were used. However, it should also be noted that the shear number of experiments needed for just these three conditions was excessive (over 5000 individual tests per material) and thus testing more levels of humidity would be beyond the scope of this research. However, it would be beneficial to explore the effects of differing levels of humidity, and this is suggested in the future work (Chapter 8).

All the samples were stored at a constant temperature (20°C) prior to testing. A time interval of 1, 4, 13, 26 and 52 weeks was selected to conduct this work. These intervals were selected to investigate the change in the tensile and flexural behaviour over a broad range of time (one year) and therefore identify the effects of ageing along with humidity on the mechanical properties of the investigated materials. Also to investigate the effects of temperature, all the tests were conducted using a temperature range of −40°C to +100°C at 10°C intervals.

Elevated temperatures were found to be negatively affecting all the mechanical properties of the three different SL materials. However, for the samples that were stored at wet (100%RH) conditions prior to testing, the drop in mechanical properties took place at lower temperatures compared to the other humidity conditions.

Ageing up to one year of the SL materials was found to have a positive influence on most of the mechanical properties when stored under dry (10%RH) and controlled (50%RH) conditions. This could be due to the dark reaction that has happened to the materials [68,141]. However, for the samples that were stored at wet (100%RH) condition prior to testing, ageing along with the high level of humidity have negatively affected the mechanical properties of the materials. This confirmed that the materials were hygroscopic and they degraded over time when they were subjected to a high level of humidity. Therefore, it was required to identify the exact mechanism of degradation of these materials due to humidity.
This was to obtain an understanding of how these materials degrade and therefore enable better materials with higher resistance to water to be developed by the manufacturers of the SL materials.

6.4 Identify the Mechanism of Degradation Due to Humidity

The mechanical test results shown in Chapter 3 confirmed that a consistent pattern of degradation in the mechanical properties of the Epoxy-based SL materials investigated occurred when they were subjected to a high level of humidity. Therefore, more in-depth experimental work was required to identify the mechanism of degradation of Epoxy-based SL materials due to humidity, which was carried out and explained in Chapter 4. Advanced investigations included DSC and FTIR/ATR analyses along with mechanical tests were carried out to monitor the change in the degree of cure, the chemical structure and the mechanical properties of SL7580 material.

It was decided to carry out the detailed material analyses for one complete year using a time interval of two weeks. This was to monitor the changes that occurred to the material in closer time intervals compared to those used for the ageing tests discussed in Chapter 3 and therefore, a better and deeper understanding could be achieved. This was undertaken for samples that were made of SL7580 resin and stored at the three identified different humidity conditions. All the samples were stored and tested at 20°C.

From the results obtained at this stage, Young’s Modulus was found to be increasing for the samples that were stored at dry (10%RH) and controlled (50%RH) conditions over time. This could be due to the dark reaction that took place and increased the cross-linking within the polymer network over time [68,141]. This was proven by the DSC results that showed a reduction in the
heat of fusion with advancing age. However, for samples kept at controlled (50%RH) condition prior to testing, some penetration of humidity into the material took place as the mechanical properties did not improve as much as the dry (10%RH) samples. This penetration also reduced the heat of fusion required to fully cure the material quicker compared to the dry (10%RH) samples.

The ATR results obtained showed that less penetration of water took place into the dry (10%RH) samples compared to the controlled (50%RH) samples and an increase in some of the chemical components (e.g. Carbonyl, Methine and Epoxide) occurred. This could have been due to the dark reaction occurring [68,141]. However, the ATR results of the controlled (50%RH) samples showed less increase in these chemical components compared to the dry (10%RH) samples, which indicates that more cross-linking took place within the polymer network of the dry (10%RH) samples, compared to the controlled (50%RH) samples. This indicates that moisture absorption can reduce the dark reaction of the SL materials.

The samples that were kept soaked in water (100%RH) showed a massive decrease in both Young's Modulus and heat of fusion. This reduction could be due to breaking of the main cross-links within the polymer network, which was due to the reaction between the polymer and water that took place over time as shown by the ATR results.

The ATR results showed an obvious increase in the intensity of the Hydroxyl peak of the wet (100%RH) samples over time. This can be linked to the reduction in the intensity of the Epoxide and Methine peaks as water penetration could have helped in breaking the cross-links within these elements. This caused a formation of Hydroxyl monomers as shown in Figure 4-30. Hydroxyl monomer has an affinity to connect with water molecules absorbed as shown in Figure 4-31. This shows the connection of water molecules to the polymer network when water penetrates into the material.
The increase in the intensity of the Hydroxyl peak within the chemical structure of the wet (100%RH) samples indicated that more water has been gradually absorbed by the material. This water absorption was found to cause a drop in both the mechanical properties along with the heat of fusion of the material. The increase in the Hydroxyl peak along with the decrease in the heat of fusion of the material is shown in Figure 6-2.

![Graph showing increase in intensity of Hydroxyl peak and decrease in heat of fusion](image)

**Figure 6-2:** Increase in the intensity of the Hydroxyl peak correlated to the decrease in the heat of fusion of the material

From the analyses throughout Chapter 4, it was concluded that humidity is one of the most significant degradation factors that can affect most of the Epoxy-based SL materials. Therefore, it was required to model the diffusion of water into SL materials and develop an equation which could be used to predict the change in mechanical properties over time, which was discussed in Chapter 5.
6.5 Model of Diffusion of Water into SL Materials

The investigations described in Chapters 3 and 4 assessed the change in the mechanical properties of each individual material at regular intervals throughout a period of one year. These results were then used to develop a mathematical model to predict the change in stiffness of SL7580 over time under certain conditions, as discussed in detail in Chapter 5. This model was developed to predict the change in mechanical properties over time of future Epoxy-based SL materials, without the need for extensive experimental work. The modelling of diffusion of water into SL materials was divided into four different stages that included:

- Identification of the type of diffusion of water into the three different SL materials
- Determination of the diffusion coefficients of each material
- Modelling the change of concentration and Young’s Modulus within a specimen at specific time
- Prediction of the stiffness and modelling the water uptake over time for SL7580 material

A summary of the results obtained from each stage is shown below.

6.5.1 Type of Diffusion

Three different samples of each material were dried and then immersed in water until saturation was reached. This was carried out to produce an absorption curve for each material which was used to identify the type of water diffusion into SL materials. Equation 5-1 was used to identify the diffusion coefficient of each individual material. This was found to be changing at the early stages of the diffusion curve and indicated that non-Fickian or anomalous diffusion occurred as the shape of the curve looked like the Fickian diffusion curve [149].
6.5.2 Determination of the Diffusion Coefficients

A dual-Fickian model was implemented to obtain the best fit diffusion curve for the experimental results. The curve of each material was divided into two different levels of concentration, low and high concentration levels. Equation 5-2 was used to identify the value of $D_1$ for each material, which was the diffusion coefficient at low concentration. Using the value of $D_1$ in Equation 5-3, the value of $D_2$ was obtained which was the diffusion coefficient at a more advanced level of concentration.

The values of $D_1$ and $D_2$ were identified for each material. The results are shown in Table 5-1. The results confirmed that the highest level of water resistance over time was in SL7560 material which had the lowest diffusion coefficients compared to the other two materials. It was important to determine the diffusion coefficients as they were used in another model to predict the change in the mechanical properties over time.

6.5.3 Model the Change in Concentration and Young's Modulus

It was expected that different profiles of water concentration and Young's Modulus could be found within a specimen at different times. Therefore, it was decided to model this change, which delivered a better understanding of what happened within the specimen tested. Equations 5-5 and 5-8 were used to model the profiles of water concentration and Young's Modulus over time. The results showed that water concentration was increased over time within a specimen. However, Young's Modulus was decreased over time due to breaking of the cross-links within the polymer network when concentration increased, as shown in Chapter 4.
6.5.4 Predict the Change in Stiffness over Time

Prediction of the change in mechanical properties due to absorption of water over time was determined. This can help in selecting the right material for a specific application when knowing the mechanical properties of this material. Equation 5-13 was used to develop a model to predict the stiffness of SL materials at different times. The results obtained from the model were compared to the mechanical results of SL7580 material obtained experimentally. It was found that the values of stiffness obtained from the model up to 100 days were lower than the actual values obtained experimentally. After the age of 100 days and up to day 364, the values of the stiffness that were obtained from the mathematical model were slightly higher than the values of stiffness experimentally obtained, especially from the age of 100 days and up to the age of 200 days. It can be concluded that the mathematical results were very close to the experimental data.

The reduction in the stiffness of the wet (100%RH) samples can be correlated to the increase in the Hydroxyl peak deduced from the ATR results shown in Chapter 4. This relation is shown in Figure 6-3, which shows the increase in the Hydroxyl groups within the chemical structure of the material correlated to the decrease in the stiffness of the material.

![Figure 6-3: Increase in the Hydroxyl peak correlated to the reduction in stiffness over time](image-url)
It can be seen from Figure 6-3 that as the Hydroxyl groups were increased within the chemical structure of the material over time, the stiffness was gradually reduced which indicates that the material started to get weaker due to the dissociation (breaking the cross-links within the polymer network) occurred within the chemical structure of the material investigated. This is due to that water acting as a plasticizer as well as a reactant, as was shown in previous work [112,113]. This dissociation was also confirmed by the DSC results explained in Chapter 4 as a sharp reduction in the degree of cure was shown for the wet (100%RH) samples compared to the dry (10%RH) and controlled (50%RH) samples. These results along with the description of the hygroscopic degradation mechanism clarify the reason for the reduction in the mechanical properties of the wet (100%RH) samples (of the three investigated SL materials) and answer the question of why these materials were degrading over time.
Chapter 7  Conclusions

1. The contributions to original knowledge obtained from this work include comprehensive analysis and characterisation of different Epoxy-based SL materials at different humidity levels, a temperature range (from -40°C to 100°C) and different ageing intervals. Also, the mechanism of hygroscopic degradation was clearly identified and a model was developed as a part of this work to predict the change in mechanical properties of an Epoxy-based SL material over time under certain environmental conditions.

2. The work carried out to establish the effects of different build and post-processing methods, confirmed that the chosen Epoxy-based SL materials can be considered isotropic (within a 10% variation) in the mechanical properties investigated.

3. Thermal post-curing was found to have two different effects on the mechanical properties of the chosen SL materials. One can further cure the material and therefore improve the mechanical properties as in the case of Accura SI40 and SL7560. The other possibility is material degradation which can negatively affect the mechanical properties, as in the case of SL7580.

4. The mechanical properties of the chosen materials were found to be greatly affected at elevated temperatures. The preliminary tests carried out showed
that the mechanical properties were roughly the same at 100°C and above for the three materials (Chapter 2). Therefore, the ageing tests were carried out up to only 100°C (Chapter 3). This indicates that further modifications and improvements are required by the manufacturers of the resins to produce materials that can be used for high temperature applications.

5. Tensile and flexural tests were carried out for one year to provide knowledge about the mechanical behaviour of different SL materials under different conditions. The samples stored at dry (10%RH) and controlled (50%RH) conditions showed a slight improvement in most of the tensile and flexural properties when tested at temperatures around ambient, which indicates that further curing (dark reaction) took place within the polymer network.

6. The results obtained from testing different Epoxy-based SL materials at a high level of humidity (100%RH), shown in Chapter 3, proved that these materials are hygroscopic and also proved that a great reduction occurred to Young's Modulus and Flexural Modulus over time. This was due to penetration of moisture into the polymer network and the interaction between water and polymer as shown in Chapter 4.

7. Advanced investigations into the mechanical properties, degree of cure and chemical structure were carried out over one year (using 2 weeks time intervals). These investigations identified the mechanism of degradation of the Epoxy-based SL materials due to humidity and ageing. This is explained in detail in Chapter 4. Three different levels of humidity were investigated (dry (100%RH), controlled (50%RH) and wet (100%RH)). An improvement was shown in the tensile properties of the samples stored at dry (10%RH) condition. This confirmed that further cross-linking (dark-reaction) took place within the polymer network of the dry (10%RH) samples as reflected by the DSC and ATR results. The controlled (50%RH) samples showed less improvement compared to the dry (10%RH) samples. This indicates that less
dark-reaction occurred to the controlled (50%RH) samples as the amount of humidity absorbed was higher than this absorbed by the dry (10%RH) samples. This was highlighted by the ATR results.

8. The samples that were soaked in water (100%RH) prior to testing showed a sharp reduction in the values of Young's Modulus and heat of fusion over time. The ATR results proved that water has penetrated into the polymer network and caused breaking of the cross-links of the Epoxide and Methine monomers as shown in Figure 4-30. This has helped in forming more Hydroxyl monomers. The ATR results showed that the Hydroxyl (O-H) peak has increased over time for the wet (100%RH) samples compared to the other samples that were kept at lower levels of humidity. These Hydroxyl monomers have a strong affinity with water. This has increased the amount of water within the polymer network, as shown in Figure 4-31, and therefore further breaking of the cross-links took place which reduced the Young's Modulus of the material over time.

9. The type of water diffusion into three different SL Epoxy-based materials was investigated. The diffusion was found to be pseudo type or fake-Fickian. The rate of water uptake was found to be different from one material to another, which indicates that the chemical structure of the material plays an important role in terms of the rate of water penetration into the polymer network.

10. A dual-Fickian model was developed and used to identify the diffusion coefficients of the materials. Different diffusion coefficients were obtained for the materials investigated, which confirmed that the rate of water penetration into a polymer is different from one material to another, depending on the chemical structure.
11. A relation between moisture content and stiffness was identified. It was found that when moisture concentration increased within the polymer network, this reduced the stiffness of the Epoxy-based SL material.

12. Equations were developed to model the concentration profiles of water within a specimen with advancing age. These equations were used to model the change in Young's Modulus profiles within a specimen over time. The results showed that increasing the concentration level reduced the values of Young’s Modulus of an Epoxy-based specimen.

13. The amount of water content within a specimen was found to be increasing over time and also dependent on the humidity level at which a sample was kept. This proves that the level of humidity can affect the properties and therefore the performance of any Epoxy-based SL material.

14. A model was designed to predict the change in stiffness of a material over time when this material is subjected to humidity. The mathematical results produced from the model were compared to the experimental results of SL7580 Epoxy-based material. The same model was used to predict the relation between stiffness and the amount of water uptake over time. It was found that when the water uptake increased over time, the stiffness of the material was proportionally reduced.

15. The experimental work included detailed methods for examination of the change in mechanical properties, degree of cure and chemical structure of the current Epoxy-based SL materials. The same techniques could be used to investigate any current or future SL material. Also, the modelling work detailed methods and procedures for investigating the effects of water on any SL material. It also could be used to predict the change in mechanical properties of an SL material over time.
Chapter 8   Recommendations for Future Work

1. All the SL Epoxy-based specimens for this work were built on an SLA 7000 by 3D Systems using the apparatus settings provided by the resin manufacturers. Each type of resin had different settings. The ACES build style was used to build all the required samples. This build style includes extra curing at the borders (border-cure) of the parts produced. It is important to investigate the difference between the properties of the material at the border and at the core of a specimen (bulk material). Also investigating the diffusion of water into border-less samples is an area of interest.

2. Further work is required to investigate the effects of thermal post-curing on the mechanical properties of different SL Epoxy-based materials at different curing temperatures and for different time intervals. This is required in order to identify the stage of where the material can degrade after certain time and at specific temperatures.

3. This work provided various data showing the change in mechanical properties of different SL Epoxy-based materials over time. The parts were stored at different humidity conditions and constant temperature (20°C) prior to testing. Subjecting the parts to different temperature cycles over time could improve or negatively affect the mechanical properties of the materials. Therefore, it is an area of interest to investigate methods of
improving the mechanical properties of the SL Epoxy-based materials by subjecting the SL parts to different temperature cycles.

4. Investigating different methods to protect the SL parts against harsh environments would be beneficial, especially when using Stereolithography to produce parts for manufacturing purposes. One of these methods could be coating, as it can provide a protection of the SL parts against UV radiation, temperature and humidity, which could increase their lifetime. However, there are some limitations related to this application, such as the thickness of the coating material that can increase the overall thickness of the SL part; the difficulty of coating the interior of complex parts and the possibility of damaging weak parts and covering features if the coating process is not fully controlled. Previous work by the author [221] proved that electroplating can improve the mechanical properties of SL parts using metallic coating. However, further work is required to investigate other types of coatings and processes.

5. This work stated a method of modelling and predicting the stiffness of any Epoxy-based SL material under wet (100%RH) conditions over time. The same procedures can be used as a guide to produce further models that can be used to predict other mechanical properties under different humidity conditions. These models could be beneficial when there is a need to predict the mechanical performance of an SL Epoxy-based material at a specific relative humidity over time. This can be achieved when diffusion coefficients are identified at this specific relative humidity.

6. The work included in this thesis concentrated on the effects of humidity and ageing on the performance of different SL Epoxy-based materials. However, the effects of other degradation factors such as UV radiation have not been investigated. Considering the fact that SL Epoxy-based resins are photo-
curable materials, it is therefore required to investigate the effects of UV radiation on the mechanical properties of the SL parts over time.

7. Accelerated ageing is a method which can be used to increase the rate of degradation of materials. Various equipment is available in the market, which can be used to reach an artificial stage of degradation in less time compared to the degradation in natural environments. Investigating a comparable method between the artificial and natural environments could save a lot of time for long-term material testing.
References


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[166] ISO 527-1 and 2; Plastics – Determination of Tensile Properties, 1996.


[176] Bryant, E. and Chartoff, R., “Crosslink density and glass transition in thermosetting polymers”, Website: http://www.udri.udayton.edu/rpdl/paper_crosdens/paper.htm, July-02,


[178] Zwick Roll, Website: www.zwick.com


[204] Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) Spectroscopy, Website:


Appendices

Appendix A  Accura SI40 Build Procedures and Parameters
Appendix B  SL7560 Build Procedures and Parameters
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Appendix N  Journal Papers
Appendix A

Accura SI40 Build Procedures and Parameters

Build Procedures

Workstation Stage:
1. Start the application (3Dlightyear)
2. Load empty platform
3. Check the type of the resin and make sure it is Accura SI40
4. Open (stl file)
5. Select (stl file)
6. Orientate the parts
7. Create supports for all parts (or selected parts)
8. Print out the orientated parts
9. Prepare the file (slice the parts and ensure the standard parameters)
10. Give it a name (.BFF) and save it
11. Drag the BFF file and drop it into the SLA folder

SLA Stage:
12. Load file (add file)
13. Choose the BFF file
14. Preview with Accura SI40 resin
15. The machine gives estimated build time (to be written in the production sheet)
16. Install the platform
17. Lower the platform slowly (not to create bubbles)
18. Press start button (top up the resin if desired & close the door)
19. Record the start build time when the machine starts the build
20. Print out the log parameters
21. After the build is finished, record the finished time
22. Leave the platform to be drained for 30 minutes

Post-Cure Stage:
23. Make sure that the windows are shut in the cleaning room
24. Take the platform out of the machine
25. Put the platform in the TPM for 30 minutes
26. Put the platform in the water for 30 minutes
27. Leave the platform to be drained for 10 minutes
28. Change the TPM in the ultrasonic
29. Take the samples off the platform
30. Clean the supports
31. Put the samples in the ultrasonic for 15 minutes
32. Shake the samples in the water for 30 seconds
33. Dry the samples using tissues
34. UV-Curing for 90 minutes
**Storage Stage:**
35. Separate the samples into groups of 5 samples each
36. Attach the barcode labels
37. Put the samples in the net bags
38. Store the samples under defined condition (dry, controlled & wet) in the correct container
39. Attach the production datasheet to the container and put a label on the container
40. Store the samples in the metallurgy lab

**Build Parameters (using SLA7000)**

![Build Parameters Screen](image-url)
Large Spot Parameters

Hatch | Fill | Border Overcut

Layer Border Overcut: 0.0000
Layer Border Prime Overcut: 0.0000
Down Border Overcut: 0.0000
Up Border Overcut: 0.0000
Support Border Overcut: 0.0000
Support Interface Up Border Overcut: 0.0000
Support Interface Down Border Overcut: 0.0000

Recoat Style Parameters

Style: Part_AccuSi^40_EXACT_1000m
Start Z: 12 mm
End Z: 198 mm

Description: SLA 7000 Accura SI 40 0.1mm EXACT Coating Style

Recoater Properties

Preferred Blade Gap: 0.0080 mm
Number of Sweeps: 3

Blade gap (%)

#1: 300.0000
#2: 300.0000
#3: 300.0000
#4:
#5:
#6:
#7:

Velocity (units/sec)

#1: 50.0000
#2: 50.0000
#3: 50.0000
#4:
#5:
#6:
#7:

Dip Parameters

Z Wait: 10 sec
Pre-dip delay: 0 sec
Z Dip Velocity: Normal
Z Dip Distance: 0.00000 mm

OK
Cancel
Appendix B

SL7560 Build Procedures and Parameters

Build Procedures

**Workstation Stage:**
1. Start the application (3Dlightyear)
2. Load empty platform
3. Check the type of the resin and make sure it is SL7560
4. Open (stl file)
5. Select (stl file)
6. Orientate the parts
7. Create supports for all parts (or selected parts)
8. Print out the orientated parts
9. Prepare the file (slice the parts and ensure the standard parameters)
10. Give it a name (.BFF) and save it
11. Drag the BFF file and drop it into the SLA folder

**SLA Stage:**
12. Load file (add file)
13. Choose the BFF file
14. Preview with SL7560 resin
15. The machine gives estimated build time (to be written in the production sheet)
16. Install the platform
17. Lower the platform slowly (not to create bubbles)
18. Press start button (top up the resin if desired & close the door)
19. Record the start build time when the machine starts the build
20. Print out the log parameters
21. After the build is finished, record the finished time
22. Leave the platform to be drained for 30 minutes

**Post-Cure Stage:**
23. Make sure that the windows are shut in the cleaning room
24. Take the platform out of the machine
25. Put the platform in the TPM for 30 minutes
26. Put the platform in the water for 30 minutes
27. Leave the platform to be drained for 10 minutes
28. Change the TPM in the ultrasonic
29. Take the samples off the platform
30. Clean the supports
31. Put the samples in the ultrasonic for 15 minutes
32. Shake the samples in the water for 30 seconds
33. Dry the samples using tissues
34. UV-Curing for 90 minutes
**Storage Stage:**
35. Separate the samples into groups of 5 samples each
36. Attach the barcode labels
37. Put the samples in the net bags
38. Store the samples under defined condition (dry, controlled & wet) in the correct container
39. Attach the production datasheet to the container and put a label on the container
40. Store the samples in the metallurgy lab

**Build Parameters (using SLA7000)**

![Build Parameters](image)
### Small Spot Parameters

**Hatch**
- Number of Up Fills: 4
- Number of Down Fills: 4

**Fill**
- Up Fill Angle: 
  - #1: 0.0000°
  - #2: 0.0000°
  - #3: 0.0000°
  - #4: 0.0000°
- Down Fill Angle: 
  - #1: 0.0000°
  - #2: 0.0000°
  - #3: 0.0000°
  - #4: 0.0000°

**Border Overcure**
- Up Fill Cure Depth: 
  - #1: 0.2032 mm
  - #2: 0.2032 mm
  - #3: 0.2540 mm
  - #4: 0.2540 mm
- Down Fill Cure Depth: 
  - #1: 0.2032 mm
  - #2: 0.2032 mm
  - #3: 0.3810 mm
  - #4: 0.3810 mm
- Up Fill Spacing: 
  - #1: 0.1524 mm
  - #2: 0.1524 mm
  - #3: 0.1000 mm
  - #4: 0.1000 mm
- Down Fill Spacing: 
  - #1: 0.1524 mm
  - #2: 0.1524 mm
  - #3: 0.1000 mm
  - #4: 0.1000 mm

### Small Spot Parameters

**Hatch**
- Layer Border Overcure: 0.3566 mm
- Layer Border Prime Overcure: 0.35560 mm
- Down Border Overcure: 0.35660 mm
- Up Border Overcure: 0.35560 mm
- Support Border Overcure: 
- Support Interface Up Border Overcure: 
- Support Interface Down Border: 

[OK] [Cancel]
### Large Spot Parameters

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#### Retractions

- Stagger Weave
- Alternate Sequencing

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### Large Spot Parameters

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Appendix C

SL7580 Build Procedures and Parameters

Build Procedures

Workstation Stage:
1. Start the application (3Dlightyear)
2. Load empty platform
3. Check the type of the resin and make sure it is SL7580
4. Open (stl file)
5. Select (stl file)
6. Orientate the parts
7. Create supports for all parts (or selected parts)
8. Print out the orientated parts
9. Prepare the file (slice the parts and ensure the standard parameters)
10. Give it a name (.BFF) and save it
11. Drag the BFF file and drop it into the SLA folder

SLA Stage:
12. Load file (add file)
13. Choose the BFF file
14. Preview with SL7580 resin
15. The machine gives estimated build time (to be written in the production sheet)
16. Install the platform
17. Lower the platform slowly (not to create bubbles)
18. Press start button (top up the resin if desired & close the door)
19. Record the start build time when the machine starts the build
20. Print out the log parameters
21. After the build is finished, record the finished time
22. Leave the platform to be drained for 30 minutes

Post-Cure Stage:
23. Make sure that the windows are shut in the cleaning room
24. Take the platform out of the machine
25. Put the platform in the TPM for 30 minutes
26. Put the platform in the water for 30 minutes
27. Leave the platform to be drained for 10 minutes
28. Change the TPM in the ultrasonic
29. Take the samples off the platform
30. Clean the supports
31. Put the samples in the ultrasonic for 15 minutes
32. Shake the samples in the water for 30 seconds
33. Dry the samples using tissues
34. UV-Curing for 90 minutes
Storage Stage:
35. Separate the samples into groups of 5 samples each
36. Attach the barcode labels
37. Put the samples in the net bags
38. Store the samples under defined condition (dry, controlled & wet) in the correct container
39. Attach the production datasheet to the container and put a label on the container
40. Store the samples in the metallurgy lab

Build Parameters (using SLA7000)
### Appendix D

#### Mechanical Test Results of Accura SI40 over a Year

**Mechanical Property:**  
**Ultimate Tensile Strength (MPa)**

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<th>13 Weeks</th>
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**Tensile Strength (MPa)**

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**Ultimate Tensile Strength (MPa)**

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**Tensile Strength (MPa)**

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<th>Age (Weeks)</th>
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<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
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<tbody>
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<td></td>
<td>0-10</td>
<td>20</td>
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<tr>
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<td>Max</td>
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<td>65.3</td>
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<td>64.6</td>
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</table>
Mechanical Property: Ultimate Tensile Strength (MPa)

Accura Si40 Tensile Strength Vs. Temperature (1 Week)

Accura Si40 Tensile Strength Vs. Temperature (4 Weeks)

Accura Si40 Tensile Strength Vs. Temperature (13 Weeks)
Mechanical Property: Ultimate Tensile Strength (MPa)

Accura Si40 Tensile Strength Vs. Temperature (26Weeks)

Accura Si40 Tensile Strength Vs. Temperature (52Weeks)
## Mechanical Test Results of Accura SI40 over a Year

### Mechanical Property: Young's Modulus (MPa)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Avg.</td>
<td>4469.76</td>
<td>4322.62</td>
<td>4163.24</td>
<td>4095.12</td>
<td>4138.82</td>
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<tr>
<td>Min</td>
<td>4266.1</td>
<td>4100.9</td>
<td>4022.3</td>
<td>3974.2</td>
<td>3932.2</td>
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</tbody>
</table>

| **Cont.**        |        |         |          |          |          |
| Avg.             | 4317.36| 4258.12| 4177.14| 4157.26| 4175.86|
| Min              | 4206.6| 3959.9| 4022.0| 3874.8| 3832.6|

| **Wet**         |        |         |          |          |          |
| Avg.             | 4312.16| 4199.68| 4037.14| 4036.80| 4066.52|
| Min              | 4244.8| 3887.7| 3868.9| 3828.7| 3802.1|

### Young's Modulus (MPa)

<table>
<thead>
<tr>
<th>Age</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Dry</strong></td>
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<td></td>
</tr>
<tr>
<td>Avg.</td>
<td>4264.43</td>
<td>4095.35</td>
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<tr>
<td>Min</td>
<td>4236.8</td>
<td>4056.7</td>
</tr>
</tbody>
</table>

| **Cont.** |        |          |
| Avg.     | 4454.35| 4253.25|
| Min      | 4244.2| 4043.2|

| **Wet** |        |          |
| Avg.     | 4341.42| 4144.92|
| Min      | 4236.4| 4036.4|

| **Dry** |        |          |
| Avg.     | 4382.50| 4207.46|
| Min      | 4238.4| 4038.4|

| **Cont.** |        |          |
| Avg.     | 4475.43| 4245.97|
| Min      | 4265.6| 4065.6|

| **Wet** |        |          |
| Avg.     | 4514.23| 4277.37|
| Min      | 4382.4| 4182.4|

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Mechanical Property: Young's Modulus (MPa)

Accura SI40 Young's Modulus Vs. Temperature (1 Week)

Accura SI40 Young's Modulus Vs. Temperature (4 Weeks)

Accura SI40 Young's Modulus Vs. Temperature (13 Weeks)
Mechanical Property: Young's Modulus (MPa)

Accura Si40 Young's Modulus Vs. Temperature (26 Weeks)

Accura Si40 Young's Modulus Vs. Temperature (52 Weeks)
# Mechanical Test Results of Accura SI40 over a Year

## Mechanical Property: % Elongation at Break

| Age | Temp (°C) | -40 | -30 | -20 | -10 | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|-----|-----------|-----|-----|-----|-----|---|---|---|---|---|---|---|---|---|---|---|-----|
Mechanical Property: \( \% \text{ Elongation at Break} \)

Accura SI40 Elongation Vs. Temperature (1 Week)

Accura SI40 Elongation Vs. Temperature (4 Weeks)

Accura SI40 Elongation Vs. Temperature (13 Weeks)
Mechanical Property:  % Elongation at Break

Accura SI40 Elongation Vs. Temperature (26 Weeks)

Accura SI40 Elongation Vs. Temperature (52 Weeks)
Mechanical Test Results of Accura SI40 over a Year

Mechanical Property:  Flexural Strength (MPa)

<table>
<thead>
<tr>
<th>Age (Weeks)</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0 00</td>
<td>10 00</td>
<td>10 00</td>
<td>10 00</td>
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<tr>
<td>Dry</td>
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<td></td>
<td></td>
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<tr>
<td>Cont</td>
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<tr>
<td>Wet</td>
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<td></td>
</tr>
<tr>
<td>Mean</td>
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<td>Range</td>
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</table>

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Mechanical Property: \textit{Flexural Strength (MPa)}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Accura_Si40_Flexural_Strength_Vs_Temperature_1_Week.png}
\caption{Accura Si40 Flexural Strength Vs. Temperature (1 Week)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Accura_Si40_Flexural_Strength_Vs_Temperature_4_Weeks.png}
\caption{Accura Si40 Flexural Strength Vs. Temperature (4 Weeks)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Accura_Si40_Flexural_Strength_Vs_Temperature_13_Weeks.png}
\caption{Accura Si40 Flexural Strength Vs. Temperature (13 Weeks)}
\end{figure}
Mechanical Property:  

**Flexural Strength (MPa)**

Accura S140 Flexural Strength Vs. Temperature (26 Weeks)

Accura S140 Flexural Strength Vs. Temperature (52 Weeks)
### Mechanical Test Results of Accura SI40 over a Year

#### Mechanical Property: Flexural Modulus (MPa)

<table>
<thead>
<tr>
<th>Age</th>
<th>Temp (°C)</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-40 -30 -20</td>
<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
<td>-40 -30 -20</td>
<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
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</tr>
<tr>
<td></td>
<td>Dry</td>
<td>Cont</td>
<td>Wet</td>
<td>Dry</td>
<td>Cont</td>
<td>Wet</td>
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Mechanical Property:  \textit{Flexural Modulus (MPa)}
Mechanical Property:  

**Flexural Modulus (MPa)**

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**Accura SI40 Flexural Modulus Vs. Temperature (26 Weeks)**

---

**Accura SI40 Flexural Modulus Vs. Temperature (52 Weeks)**
## Appendix E

### Mechanical Test Results of SL7560 over a Year

#### Mechanical Property: Ultimate Tensile Strength (MPa)

<table>
<thead>
<tr>
<th>Age (Week)</th>
<th>4 Weeks</th>
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<tr>
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<td>50 60 70</td>
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<td><strong>Cont</strong></td>
<td>Avg.</td>
<td>Max.</td>
<td>Min.</td>
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<td>Max.</td>
<td>Min.</td>
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</table>

**Notes:**
- The values in the table represent the tensile strength of SL7560 over different aging periods at various temperatures.
- The results are categorized into dry, constant (cont), and wet conditions.
- The table provides average (Avg.), maximum (Max.), and minimum (Min.) values for each condition and age period.

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Mechanical Property:  

**Ultimate Tensile Strength (MPa)**

**SL7560 Tensile Strength Vs. Temperature (1 Week)**

**SL7560 Tensile Strength Vs. Temperature (4 Weeks)**

**SL7560 Tensile Strength Vs. Temperature (13 Weeks)**
Mechanical Property: $\textit{Ultimate Tensile Strength (MPa)}$

**SL7560 Tensile Strength Vs. Temperature (26 Weeks)**

**SL7560 Tensile Strength Vs. Temperature (52 Weeks)**
# Mechanical Property:

## Young's Modulus (MPa)

<table>
<thead>
<tr>
<th>Age</th>
<th>Temp (°C)</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-40 -30 -20</td>
<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
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<td>Age</td>
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<td>4 Weeks</td>
<td>13 Weeks</td>
<td>26 Weeks</td>
<td>52 Weeks</td>
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<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
<td>-10 0 10 20 30 40 50 60 70 80 90 100</td>
</tr>
</tbody>
</table>
Mechanical Property:  
Young's Modulus (MPa)

SL7560 Young's Modulus Vs. Temperature (1 Week)

SL7560 Young's Modulus Vs. Temperature (4 Weeks)

SL7560 Young's Modulus Vs. Temperature (13 Weeks)
Mechanical Property: \textit{Young's Modulus (MPa)}

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{SL7560_YM_Vs_Temp_26_Weeks}
\caption{SL7560 Young's Modulus Vs. Temperature (26 Weeks)}
\end{figure}
\end{center}

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{SL7560_YM_Vs_Temp_52_Weeks}
\caption{SL7560 Young's Modulus Vs. Temperature (52 Weeks)}
\end{figure}
\end{center}
### Mechanical Test Results of SL7560 over a Year

#### Mechanical Property: % Elongation at Break

<table>
<thead>
<tr>
<th>Age</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
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<tr>
<td></td>
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</tr>
<tr>
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<td>Temp (°C)</td>
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</tr>
<tr>
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<td>Wet</td>
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<td></td>
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<tr>
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<td>1.3</td>
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</tr>
<tr>
<td><strong>Min.</strong></td>
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<td><strong>Max.</strong></td>
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</tr>
</tbody>
</table>

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Mechanical Property: % Elongation at Break

SL7560 Elongation Vs. Temperature (1 Week)

SL7560 Elongation Vs. Temperature (4 Weeks)

SL7560 Elongation Vs. Temperature (13 Weeks)
Mechanical Property: \% Elongation at Break

**SL7560 Elongation Vs. Temperature (26 Weeks)**

**SL7560 Elongation Vs. Temperature (52 Weeks)**
Mechanical Test Results of SL7560 over a Year

### Mechanical Property: Flexural Strength (MPa)

<table>
<thead>
<tr>
<th>Age</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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<td>Dry</td>
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<tr>
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<td>Min</td>
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<tr>
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<td>Avg/Min</td>
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<tr>
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<td>Min</td>
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<tr>
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<td>Avg/Min</td>
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</table>

**Notes:**
- Data provided for different aging durations: 1 Week, 4 Weeks, 13 Weeks, 26 Weeks, and 52 Weeks.
- Results are given in MPa for bending strength under various conditions.
- The data includes maximum (Max), minimum (Min), and average/minimum (Avg/Min) values for each condition.
Mechanical Property: \textit{Flexural Strength (MPa)}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{SL7560_1_week}
\caption{SL7560 Flexural Strength Vs. Temperature (1 Week)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{SL7560_4_weeks}
\caption{SL7560 Flexural Strength Vs. Temperature (4 Weeks)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{SL7560_13_weeks}
\caption{SL7560 Flexural Strength Vs. Temperature (13 Weeks)}
\end{figure}
Mechanical Property:  

*Flexural Strength (MPa)*

**SL7560 Flexural Strength Vs. Temperature (26 Weeks)**

![Graph showing flexural strength over temperature for 26 weeks.](image1)

**SL7560 Flexural Strength Vs. Temperature (52 Weeks)**

![Graph showing flexural strength over temperature for 52 weeks.](image2)
### Mechanical Test Results of SL7560 over a Year

#### Mechanical Property: Flexural Modulus (MPa)

<table>
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<tr>
<th>Age</th>
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<th>4 Weeks</th>
<th>13 Weeks</th>
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<th><strong>Avg.</strong></th>
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- 235 -
Mechanical Property: Flexural Modulus (MPa)

SL7560 Flexural Modulus Vs. Temperature (1 Week)

SL7560 Flexural Modulus Vs. Temperature (4 Weeks)

SL7560 Flexural Modulus Vs. Temperature (13 Weeks)
Mechanical Property: \textit{Flexural Modulus (MPa)}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{SL7560 Flexural Modulus Vs. Temperature (26 Weeks)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{SL7560 Flexural Modulus Vs. Temperature (52 Weeks)}
\end{figure}
## Appendix F

### Mechanical Test Results of SL7580 over a Year

#### Mechanical Property: Ultimate Tensile Strength (MPa)

**Table: Ultimate Tensile Strength (MPa)**

<table>
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<tr>
<th>Age</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
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</table>

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Mechanical Property:  Ultimate Tensile Strength (MPa)

SL7580 Tensile Strength Vs. Temperature (1 Week)

SL7580 Tensile Strength Vs. Temperature (4 Weeks)

SL7580 Tensile Strength Vs. Temperature (13 Weeks)
Mechanical Property: **Ultimate Tensile Strength (MPa)**

**SL7580 Tensile Strength Vs. Temperature (26 Weeks)**

**SL7580 Tensile Strength Vs. Temperature (52 Weeks)**
### Mechanical Test Results of SL7580 over a Year

#### Mechanical Property:

**Young's Modulus (MPa)**

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Age</th>
<th>1 Week</th>
<th>4 Weeks</th>
<th>13 Weeks</th>
<th>26 Weeks</th>
<th>52 Weeks</th>
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<tbody>
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<td>Min.</td>
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<td>Avg.</td>
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<td>Min.</td>
<td>Max.</td>
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</tbody>
</table>

### Table

- **Temp (°C):** -40, -30, -20, -10, 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100
- **Age:** 1 Week, 4 Weeks, 13 Weeks, 26 Weeks, 52 Weeks
- **Dry, Cont., Wet:** Mechanical Test Results
- **Young's Modulus (MPa):** Mechanical Property

**Notes:**

- The table above summarizes the mechanical test results of SL7580 over a year, with data provided for various temperatures and ages, including Young's Modulus values in MPa. The results are categorized into Dry, Cont., and Wet conditions, with specific temperature ranges and age durations presented for each category.
Mechanical Property:  

Young's Modulus (MPa)

**SL7560 Young's Modulus Vs. Temperature (1 Week)**

**SL7560 Young's Modulus Vs. Temperature (4 Weeks)**

**SL7560 Young's Modulus Vs. Temperature (13 Weeks)**
Mechanical Property: Young's Modulus (MPa)

SL7560 Young's Modulus Vs. Temperature (26 Weeks)

SL7560 Young's Modulus Vs. Temperature (52 Weeks)
# Mechanical Test Results of SL7580 over a Year

## Mechanical Property: % Elongation at Break

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<th>26 Weeks</th>
<th>52 Weeks</th>
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<td>21.2 23.5 23.5</td>
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<th>13 Weeks</th>
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Mechanical Property: % Elongation at Break

SL7560 Elongation Vs. Temperature (1 Week)

SL7560 Elongation Vs. Temperature (4 Weeks)

SL7560 Elongation Vs. Temperature (13 Weeks)
Mechanical Property: \(\%\) Elongation at Break

**SL7560 Elongation Vs. Temperature (26 Weeks)**

**SL7560 Elongation Vs. Temperature (52 Weeks)**
Appendix G

SL7580 Tensile Results (2 Weeks Tests)

Mechanical Property: Ultimate Tensile Strength (MPa)

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![Graph showing ultimate tensile strength over age (wk) for different conditions](image-url)
### SL7580 Tensile Results (2 Weeks Tests)

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**Diagram:**

- **Dry (10%RH)**
- **Controlled (50%RH)**
- **Wet (100%RH)**

- **Age (wk):** 0 to 52
- **Young's Modulus (MPa):** 0 to 4000

- **Legend:**
  - Dry (10%RH)
  - Controlled (50%RH)
  - Wet (100%RH)
### SL7580 Tensile Results (2 Weeks Tests)

#### Mechanical Property: % Elongation at Break

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0 2 4 6 8 10 12 14 16 18 20

% Elongation at Break

- Dry (10%RH) - Controlled (50%RH) - Wet (100%RH)
Appendix H

SL7580 DSC Results (Dry (10%RH) Samples – 2 Weeks Tests)

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Dry (10% RH)
Age: 00WK

Figure H- 1: Sample 1
Figure H- 2: Sample 2
Figure H- 3: Sample 3
Figure H- 4: Sample 4
Figure H- 5: Sample 5
Dry (10% RH)
Age: 02WKS

Figure H- 6: Sample 1

Figure H- 7: Sample 2

Figure H- 8: Sample 3

Figure H- 9: Sample 4

Figure H- 10: Sample 5
Dry (10% RH)

Age: 04WKS

Figure H-11: Sample 1

Figure H-12: Sample 2

Figure H-13: Sample 3

Figure H-14: Sample 4

Figure H-15: Sample 5
Dry (10% RH)
Age: 06WKs

Figure H-16: Sample 1

Figure H-17: Sample 2

Figure H-18: Sample 3

Figure H-19: Sample 4

Figure H-20: Sample 5
Dry (10% RH)
Age: 08Wks

Figure H-21: Sample 1

Figure H-22: Sample 2

Figure H-23: Sample 3

Figure H-24: Sample 4

Figure H-25: Sample 5
Dry (10% RH)
Age: 10Wks

Figure H- 26: Sample 1

Figure H- 27: Sample 2

Figure H- 28: Sample 3

Figure H- 29: Sample 4

Figure H- 30: Sample 5
Dry (10% RH)
Age: 12WKs

Figure H- 31: Sample 1

Figure H- 32: Sample 2

Figure H- 33: Sample 3

Figure H- 34: Sample 4

Figure H- 35: Sample 5

- 257 -
Dry (10% RH)
Age: 14 WKS

Figure H- 36: Sample 1
Figure H- 37: Sample 2
Figure H- 38: Sample 3
Figure H- 39: Sample 4
Figure H- 40: Sample 5
Dry (10% RH)

Age: 16WKS
Dry (10% RH)
Age: 18Wks

Figure H-46: Sample 1

Figure H-47: Sample 2

Figure H-48: Sample 3

Figure H-49: Sample 4

Figure H-50: Sample 5
Dry (10% RH)
Age: 20Wks

Figure H- 51: Sample 1

Figure H- 52: Sample 2

Figure H- 53: Sample 3

Figure H- 54: Sample 4

Figure H- 55: Sample 5

- 261 -
Dry (10% RH)
Age: 22Wks

Figure H-56: Sample 1

Figure H-57: Sample 2

Figure H-58: Sample 3

Figure H-59: Sample 4

Figure H-60: Sample 5
Dry (10% RH)

Age: 24WKs

Figure H-61: Sample 1

Figure H-62: Sample 2

Figure H-63: Sample 3

Figure H-64: Sample 4

Figure H-65: Sample 5
Dry (10% RH)
Age: 26Wks

Figure H- 66: Sample 1
Figure H- 67: Sample 2
Figure H- 68: Sample 3
Figure H- 69: Sample 4
Figure H- 70: Sample 5
Dry (10% RH)
Age: 28WKs

Figure H- 71: Sample 1

Figure H- 72: Sample 2

Figure H- 73: Sample 3

Figure H- 74: Sample 4

Figure H- 75: Sample 5
Dry (10% RH)
Age: 30Wks

Figure H- 76: Sample 1

Figure H- 77: Sample 2

Figure H- 78: Sample 3

Figure H- 79: Sample 4

Figure H- 80: Sample 5
Dry (10% RH)

Age: 32Wks

Figure H-81: Sample 1

Figure H-82: Sample 2

Figure H-83: Sample 3

Figure H-84: Sample 4

Figure H-85: Sample 5
Dry (10% RH)
Age: 34Wks
Dry (10% RH)
Age: 36Wks

Figure H- 91: Sample 1

Figure H- 92: Sample 2

Figure H- 93: Sample 3

Figure H- 94: Sample 4

Figure H- 95: Sample 5
Dry (10% RH)

Age: 38WKs

Figure H-96: Sample 1

Figure H-97: Sample 2

Figure H-98: Sample 3

Figure H-99: Sample 4

Figure H-100: Sample 5
Dry (10% RH)
Age: 40WKs

Figure H- 101: Sample 1

Figure H- 102: Sample 2

Figure H- 103: Sample 3

Figure H- 104: Sample 4

Figure H- 105: Sample 5
Dry (10% RH)
Age: 42Wks

Figure H-106: Sample 1

Figure H-107: Sample 2

Figure H-108: Sample 3

Figure H-109: Sample 4

Figure H-110: Sample 5
Dry (10% RH)

Age: 44Wks

Figure H-111: Sample 1

Figure H-112: Sample 2

Figure H-113: Sample 3

Figure H-114: Sample 4

Figure H-115: Sample 5
Dry (10% RH)

Age: 46WKs

Figure H-116: Sample 1

Figure H-117: Sample 2

Figure H-118: Sample 3

Figure H-119: Sample 4

Figure H-120: Sample 5
Dry (10% RH)
Age: 48Wks

Figure H-121: Sample 1
Figure H-122: Sample 2
Figure H-123: Sample 3
Figure H-124: Sample 4
Figure H-125: Sample 5
Dry (10% RH)

Age: 50Wks

Figure H- 126: Sample 1

Figure H- 127: Sample 2

Figure H- 128: Sample 3

Figure H- 129: Sample 4

Figure H- 130: Sample 5
Dry (10% RH)
Age: 52Wks

Figure H-131: Sample 1

Figure H-132: Sample 2

Figure H-133: Sample 3

Figure H-134: Sample 4

Figure H-135: Sample 5
# Appendix I

## SL7580 DSC Results (Controlled (50%RH) Samples – 2 Weeks Tests)

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Controlled (50% RH)
Age: 00WK

Figure I-1: Sample 1

Figure I-2: Sample 2

Figure I-3: Sample 3

Figure I-4: Sample 4

Figure I-5: Sample 5
Controlled (50% RH)
Age: 02Wks

Figure 1-6: Sample 1
Figure 1-7: Sample 2
Figure 1-8: Sample 3
Figure 1-9: Sample 4
Figure 1-10: Sample 5
Controlled (50% RH)
Age: 04WKs

Figure I-11: Sample 1

Figure I-12: Sample 2

Figure I-13: Sample 3

Figure I-14: Sample 4

Figure I-15: Sample 5
Controlled (50% RH)
Age: 06WKs

Figure I-16: Sample 1

Figure I-17: Sample 2

Figure I-18: Sample 3

Figure I-19: Sample 4

Figure I-20: Sample 5
Controlled (50% RH)
Age: 08WKS

Figure 1-21: Sample 1

Figure 1-22: Sample 2

Figure 1-23: Sample 3

Figure 1-24: Sample 4

Figure 1-25: Sample 5
Controlled (50% RH)
Age: 10WKs

Figure I-26: Sample 1

Figure I-27: Sample 2

Figure I-28: Sample 3

Figure I-29: Sample 4

Figure I-30: Sample 5

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Controlled (50% RH)
Age: 12WKS
Controlled (50% RH)
Age: 14Wks

Figure I- 36: Sample 1
Figure I- 37: Sample 2
Figure I- 38: Sample 3
Figure I- 39: Sample 4
Figure I- 40: Sample 5
Controlled (50% RH)
Age: 16Wks

Figure I- 41: Sample 1
Figure I- 42: Sample 2
Figure I- 43: Sample 3
Figure I- 44: Sample 4
Figure I- 45: Sample 5

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Controlled (50% RH)
Age: 18WKs

Figure I-46: Sample 1

Figure I-47: Sample 2

Figure I-48: Sample 3

Figure I-49: Sample 4

Figure I-50: Sample 5
Controlled (50% RH)
Age: 20Wks

Figure I-51: Sample 1

Figure I-52: Sample 2

Figure I-53: Sample 3

Figure I-54: Sample 4

Figure I-55: Sample 5
Controlled (50% RH)
Age: 22WKs

Figure 1-56: Sample 1

Figure 1-57: Sample 2

Figure 1-58: Sample 3

Figure 1-59: Sample 4

Figure 1-60: Sample 5
Controlled (50% RH)
Age: 24WKs

Figure I-61: Sample 1

Figure I-62: Sample 2

Figure I-63: Sample 3

Figure I-64: Sample 4

Figure I-65: Sample 5
Controlled (50% RH)
Age: 26WKs

Figure 1-66: Sample 1

Figure 1-67: Sample 2

Figure 1-68: Sample 3

Figure 1-69: Sample 4

Figure 1-70: Sample 5
Controlled (50% RH)
Age: 28Wks

Figure 1-71: Sample 1

Figure 1-72: Sample 2

Figure 1-73: Sample 3

Figure 1-74: Sample 4

Figure 1-75: Sample 5
Controlled (50% RH)
Age: 30WKs

Figure I-76: Sample 1

Figure I-77: Sample 2

Figure I-78: Sample 3

Figure I-79: Sample 4

Figure I-80: Sample 5
Controlled (50% RH)
Age: 32WKS

Figure I-81: Sample 1

Figure I-82: Sample 2

Figure I-83: Sample 3

Figure I-84: Sample 4

Figure I-85: Sample 5
Controlled (50% RH)
Age: 34WKs

Figure I- 86: Sample 1
Figure I- 87: Sample 2
Figure I- 88: Sample 3
Figure I- 89: Sample 4
Figure I- 90: Sample 5
Controlled (50% RH)
Age: 36WKS

Figure I-91: Sample 1

Figure I-92: Sample 2

Figure I-93: Sample 3

Figure I-94: Sample 4

Figure I-95: Sample 5
Controlled (50% RH)

Age: 38Wks

Figure I-96: Sample 1

Figure I-97: Sample 2

Figure I-98: Sample 3

Figure I-99: Sample 4

Figure I-100: Sample 5
Controlled (50% RH)
Age: 40Wks

Figure I-101: Sample 1

Figure I-102: Sample 2

Figure I-103: Sample 3

Figure I-104: Sample 4

Figure I-105: Sample 5
Controlled (50% RH)
Age: 42WKs

Figure I- 106: Sample 1

Figure I- 107: Sample 2

Figure I- 108: Sample 3

Figure I- 109: Sample 4

Figure I- 110: Sample 5
Controlled (50% RH)
Age: 44Wks

Figure I-111: Sample 1

Figure I-112: Sample 2

Figure I-113: Sample 3

Figure I-114: Sample 4

Figure I-115: Sample 5
Controlled (50% RH)
Age: 46WKs

Figure I-116: Sample 1

Figure I-117: Sample 2

Figure I-118: Sample 3

Figure I-119: Sample 4

Figure I-120: Sample 5

- 302 -
Controlled (50% RH)
Age: 48WKs

Figure I-121: Sample 1

Figure I-122: Sample 2

Figure I-123: Sample 3

Figure I-124: Sample 4

Figure I-125: Sample 5
Controlled (50% RH)
Age: 50Wks

Figure I-126: Sample 1
Figure I-127: Sample 2
Figure I-128: Sample 3
Figure I-129: Sample 4
Figure I-130: Sample 5
Controlled (50% RH)
Age: 52Wks

Figure I-131: Sample 1
Figure I-132: Sample 2
Figure I-133: Sample 3
Figure I-134: Sample 4
Figure I-135: Sample 5

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### Appendix J

**SL7580 DSC Results (Wet (100% RH) Samples – 2 Weeks Tests)**

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- 306 -
Wet (100% RH)
Age: 00WK

Figure J-1: Sample 1
Figure J-2: Sample 2
Figure J-3: Sample 3
Figure J-4: Sample 4
Figure J-5: Sample 5
Wet (100% RH)
Age: 02WKs

Figure J-6: Sample 1

Figure J-7: Sample 2

Figure J-8: Sample 3

Figure J-9: Sample 4

Figure J-10: Sample 5

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Wet (100% RH)
Age: 04WKs

Figure J-11: Sample 1

Figure J-12: Sample 2

Figure J-13: Sample 3

Figure J-14: Sample 4

Figure J-15: Sample 5
Wet (100% RH)
Age: 06WKs

Figure J-16: Sample 1
Figure J-17: Sample 2
Figure J-18: Sample 3
Figure J-19: Sample 4
Figure J-20: Sample 5
Wet (100% RH)
Age: 08Wks

Figure J-21: Sample 1

Figure J-22: Sample 2

Figure J-23: Sample 3

Figure J-24: Sample 4

Figure J-25: Sample 5
Wet (100% RH)
Age: 10Wks

Figure J-26: Sample 1

Figure J-27: Sample 2

Figure J-28: Sample 3

Figure J-29: Sample 4

Figure J-30: Sample 5
Wet (100% RH)
Age: 12Wks

Figure J-31: Sample 1

Figure J-32: Sample 2

Figure J-33: Sample 3

Figure J-34: Sample 4

Figure J-35: Sample 5

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Wet (100% RH)
Age: 14Wks
Wet (100% RH)
Age: 16Wks

Figure J- 41: Sample 1

Figure J- 42: Sample 2

Figure J- 43: Sample 3

Figure J- 44: Sample 4

Figure J- 45: Sample 5
Wet (100% RH)
Age: 18Wks

Figure J-46: Sample 1

Figure J-47: Sample 2

Figure J-48: Sample 3

Figure J-49: Sample 4

Figure J-50: Sample 5
Wet (100% RH)
Age: 20WKs

Figure J-51: Sample 1

Figure J-52: Sample 2

Figure J-53: Sample 3

Figure J-54: Sample 4

Figure J-55: Sample 5
Wet (100% RH)
Age: 22Wks

Figure J-56: Sample 1

Figure J-57: Sample 2

Figure J-58: Sample 3

Figure J-59: Sample 4

Figure J-60: Sample 5
Wet (100% RH)  
Age: 24WKs
Wet (100% RH)
Age: 26WKS

Figure J-66: Sample 1

Figure J-67: Sample 2

Figure J-68: Sample 3

Figure J-69: Sample 4

Figure J-70: Sample 5

- 320 -
Wet (100% RH)
Age: 28WKs

Figure J-71: Sample 1
Figure J-72: Sample 2
Figure J-73: Sample 3
Figure J-74: Sample 4
Figure J-75: Sample 5
Wet (100% RH)
Age: 30Wks

Figure J-76: Sample 1
Figure J-77: Sample 2
Figure J-78: Sample 3
Figure J-79: Sample 4
Figure J-80: Sample 5
Wet (100% RH)
Age: 32WKs

Figure J-81: Sample 1
Figure J-82: Sample 2
Figure J-83: Sample 3
Figure J-84: Sample 4
Figure J-85: Sample 5
Wet (100% RH)
Age: 34WKs
Wet (100% RH)
Age: 36WKs

Figure J-91: Sample 1
Figure J-92: Sample 2
Figure J-93: Sample 3
Figure J-94: Sample 4
Figure J-95: Sample 5
Wet (100% RH)
Age: 38Wks

Figure J-96: Sample 1
Figure J-97: Sample 2
Figure J-98: Sample 3
Figure J-99: Sample 4
Figure J-100: Sample 5
Wet (100% RH)
Age: 40 WKs

Figure J-101: Sample 1

Figure J-102: Sample 2

Figure J-103: Sample 3

Figure J-104: Sample 4

Figure J-105: Sample 5
Wet (100% RH)
Age: 42WKs

Figure J-106: Sample 1
Figure J-107: Sample 2
Figure J-108: Sample 3
Figure J-109: Sample 4
Figure J-110: Sample 5
Wet (100% RH)
Age: 44WKs

Figure J-111: Sample 1

Figure J-112: Sample 2

Figure J-113: Sample 3

Figure J-114: Sample 4

Figure J-115: Sample 5
Wet (100% RH)
Age: 46WKs

Figure J-116: Sample 1

Figure J-117: Sample 2

Figure J-118: Sample 3

Figure J-119: Sample 4

Figure J-120: Sample 5

- 330 -
Wet (100% RH)
Age: 48WKs

Figure J-121: Sample 1
Figure J-122: Sample 2
Figure J-123: Sample 3
Figure J-124: Sample 4
Figure J-125: Sample 5
Wet (100% RH)
Age: 50WKs

Figure J-126: Sample 1
Figure J-127: Sample 2
Figure J-128: Sample 3
Figure J-129: Sample 4
Figure J-130: Sample 5
Wet (100% RH)
Age: 52WKs

Figure J- 131: Sample 1

Figure J- 132: Sample 2

Figure J- 133: Sample 3

Figure J- 134: Sample 4

Figure J- 135: Sample 5
Appendix K

SL7580 ATR Results (Dry (10% RH) Samples – 2Weeks Tests)

Figure K-1: ATR Results at 00WK (Dry)

Figure K-2: ATR Results at 02WKs (Dry)
Figure K-3: ATR Results at 04WKs (Dry)

Figure K-4: ATR Results at 06WKs (Dry)

Figure K-5: ATR Results at 08WKs (Dry)
Figure K-6: ATR Results at 10WKs (Dry)

Figure K-7: ATR Results at 12WKs (Dry)

Figure K-8: ATR Results at 14WKs (Dry)
Figure K-9: ATR Results at 16WKs (Dry)

Figure K-10: ATR Results at 18WKs (Dry)

Figure K-11: ATR Results at 20WKs (Dry)
Figure K-12: ATR Results at 22WKs (Dry)

Figure K-13: ATR Results at 24WKs (Dry)

Figure K-14: ATR Results at 26WKs (Dry)
Figure K-15: ATR Results at 28WKs (Dry)

Figure K-16: ATR Results at 30WKs (Dry)

Figure K-17: ATR Results at 32WKs (Dry)
Figure K-18: ATR Results at 34WKs (Dry)

Figure K-19: ATR Results at 36WKs (Dry)

Figure K-20: ATR Results at 38WKs (Dry)
Figure K-21: ATR Results at 40WKs (Dry)

Figure K-22: ATR Results at 42WKs (Dry)

Figure K-23: ATR Results at 44WKs (Dry)
Figure K-24: ATR Results at 46WKs (Dry)

Figure K-25: ATR Results at 48WKs (Dry)

Figure K-26: ATR Results at 50WKs (Dry)
Figure K-27: ATR Results at 52WKs (Dry)
Appendix L

SL7580 ATR Results (Controlled (50% RH) Samples – 2 Weeks Tests)

Figure L- 1: ATR Results at 00WK (Controlled)

Figure L- 2: ATR Results at 02WKs (Controlled)
Figure L-3: ATR Results at 04WKs (Controlled)

Figure L-4: ATR Results at 06WKs (Controlled)

Figure L-5: ATR Results at 08WKs (Controlled)
Figure L- 6: ATR Results at 10WKs (Controlled)

Figure L- 7: ATR Results at 12WKs (Controlled)

Figure L- 8: ATR Results at 14WKs (Controlled)
Figure L-9: ATR Results at 16WKs (Controlled)

Figure L-10: ATR Results at 18WKs (Controlled)

Figure L-11: ATR Results at 20WKs (Controlled)
Figure L-12: ATR Results at 22WKs (Controlled)

Figure L-13: ATR Results at 24WKs (Controlled)

Figure L-14: ATR Results at 26WKs (Controlled)
Figure L-15: ATR Results at 28WKs (Controlled)

Figure L-16: ATR Results at 30WKs (Controlled)

Figure L-17: ATR Results at 32WKs (Controlled)
Figure L-18: ATR Results at 34WKs (Controlled)

Figure L-19: ATR Results at 36WKs (Controlled)

Figure L-20: ATR Results at 38WKs (Controlled)
Figure L-21: ATR Results at 40WKs (Controlled)

Figure L-22: ATR Results at 42WKs (Controlled)

Figure L-23: ATR Results at 44WKs (Controlled)
Figure L- 24: ATR Results at 46WKs (Controlled)

Figure L- 25: ATR Results at 48WKs (Controlled)

Figure L- 26: ATR Results at 50WKs (Controlled)
Figure L-27: ATR Results at 52WKs (Controlled)
Appendix M

SL7580 ATR Results (Wet (100%RH) Samples – 2 Weeks Tests)

Figure M-1: ATR Results at 00WK (Wet)

Figure M-2: ATR Results at 02WKs (Wet)
Figure M-3: ATR Results at 04Wks (Wet)

Figure M-4: ATR Results at 06Wks (Wet)

Figure M-5: ATR Results at 08Wks (Wet)
Figure M- 6: ATR Results at 10WKs (Wet)

Figure M- 7: ATR Results at 12WKs (Wet)

Figure M- 8: ATR Results at 14WKs (Wet)
Figure M-9: ATR Results at 16WKs (Wet)

Figure M-10: ATR Results at 18WKs (Wet)

Figure M-11: ATR Results at 20WKs (Wet)
Figure M-12: ATR Results at 22WKs (Wet)

Figure M-13: ATR Results at 24WKs (Wet)

Figure M-14: ATR Results at 26WKs (Wet)
Figure M-15: ATR Results at 28WKs (Wet)

Figure M-16: ATR Results at 30WKs (Wet)

Figure M-17: ATR Results at 32WKs (Wet)
Figure M-18: ATR Results at 34WKs (Wet)

Figure M-19: ATR Results at 36WKs (Wet)

Figure M-20: ATR Results at 38WKs (Wet)
Figure M-21: ATR Results at 40WKs (Wet)

Figure M-22: ATR Results at 42WKs (Wet)

Figure M-23: ATR Results at 44WKs (Wet)
Figure M-24: ATR Results at 46WKs (Wet)

Figure M-25: ATR Results at 48WKs (Wet)

Figure M-26: ATR Results at 50WKs (Wet)
Figure M-27: ATR Results at 52WKS (Wet)
Appendix N

Journal Papers


- 364 -
Feature
Design opportunities with rapid manufacturing

Richard Hague
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Keywords
Rapid prototypes, Design, Manufacturing systems

Abstract
The advent of rapid manufacturing (RM) will have profound implications on all aspects of product development and manufacture. Within the design discipline, three areas are of importance, namely, design freedom, material properties and changes to the design process. These issues are currently under investigation as part of an EPSRC funded research project and this paper will outline the effects of RM on the design process with the introduction of RM and give the progress of the project to date.

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1. Introduction
Rapid manufacturing (RM) is evolving from the now mature rapid prototyping (RP) technologies – such as stereolithography (SL) and laser sintering (LS) (amongst others) (Anon, 2001). With RP techniques, objects are created from a 3D CAD model without the use of either moulding or tooling. This is achieved by taking discrete 2D slices of the 3D CAD file and, either through the deposition of material, the sintering or binding of powder or by selectively changing the state of a UV sensitive liquid resin into a solid using a light source, objects are built-up layer-by-layer until the part is complete. Having been developed and commercialised over the last 15 years, layered manufacturing plays an integral role in the modern product development cycle. RP processes are routinely used for the production of functional and technical prototypes, visualisation and marketing models and even for the production of “rapid tooling” cavities – although the value of some of these so-called rapid tooling techniques is questionable.

An on-going EPSRC funded research project is currently being undertaken that is investigating the implications on product design by the introduction of RM (EPSRC, GR/R13517/01). An assumption is made that the problems of accuracy, surface finish, speed, etc. have been resolved and that RP machines have been converted to proper manufacturing systems. The example processes that are being investigated within the project include the SL process and LS – it is recognised that these currently have limitations, but it is the principle of manufacturing with an additive process that is important more than the process used on this project.

The main areas of the project include the following.

Design freedom. Without the restriction of removing a product from a tool, designers will be free to design any complex geometry they desire and RM machines will be able to make them. This will have profound implications on the way designers are accustomed to working as they are normally restricted to designing for a particular manufacturing process (e.g. design for injection moulding). Staff on the
project are working with the designers at the partner companies to get them to free their imagination and arrive at designs that would be unimaginable if conventional manufacturing techniques were used.

Materials properties. One of the larger issues concerning the uptake of RM is that designers have very little material data available to them. For automotive applications, designers typically need material properties ranging from $-40$ to $+140^\circ$C. Therefore, the project is undertaking extensive material testing for a range of materials over this temperature range with different humidities and also over extended time-periods to consider the ageing of the materials. An extensive range of mechanical properties, such as tensile and flexural stress and modulus, Young’s modulus, Poisson’s ratio and impact strength are being investigated. Without this materials data, the designers will be reluctant to “design for rapid manufacture”. This will be the most significant data collation for materials being used in RP and RM to date.

Changes to the design process. The design process is likely to change with the advent of RM. Designs are normally “signed off” at the prototype and tooling stages – with RM, no tooling exists and thus this sign-off will not occur. The project will investigate what changes to the design process occur and how this will affect the product development cycle. The impact of RM on design for manufacture (DFM), assembly (DFA) and service (DFS) will be investigated.

   The project is due to last until September 2003 and is scoping rather than solving the issues raised. The project partners include (in alphabetical order): 3D Systems, Batbox, Delphi Automotive, Jaguar Cars, MG Rover, RimCast and Vantico.

   The following will give an overview of the three areas above and give an indication of the results to date. As this is a new subject for discussion, the authors intend that this paper be viewed as a precursor to further work that is needed.

2. Design

For years, designers have been restricted in what they can produce as they generally have to DFM – that is, adjust their design intent to enable the component (or assembly) to be manufactured using a particular process or processes. In addition, if a mould is used to produce an item, there are therefore automatically inherent restrictions to the design imposed at the very beginning.

   Taking injection moulding as an example, in order to process a component successfully, at a minimum, the following design elements need to be taken into account:

1. geometry;
   - draft angles,
   - non re-entrants shapes,
   - near constant wall thickness,
   - complexity,
   - split line location, and
   - surface finish.

2. material choice;

3. rationalisation of components (reducing assemblies);

4. cost.

   With the advent of the RM techniques, there is the potential for many of the current obstacles to be removed. The following sections discuss the above points and also deal with some potential problems that are likely to occur with the onset of RM in general.

2.1 Design complexity

   One of the major benefits of the additive manufacturing processes is that it is possible to make any complexity of geometry at no extra cost – this is virtually unheard, as in every conventional manufacturing technique there is a direct link to the cost of a component to the complexity of its design. Therefore, for a given volume of component, it is effectively possible to get the geometry (or complexity) for “free”, as the costs incurred for any given additive manufacturing technique are usually determined by the time to build a certain volume of part that in turn is determined by the orientation that the component is built in.

   However, during the project investigations, it has been established that all the existing part complexity measures are based on the cost of manufacturing, assembly, serviceability, etc. Typical examples of this would include the Boothroyd et al. (1994) and Miyakawa and Ohashi (1986) methods. With RM, these cost-based measures of complexity are, in many respects, no longer valid as RM processes are able to manufacture any design with the cost of component being mainly determined by build volume. Thus, for RM, a new measure of design complexity is required. The subject area and definition of “complexity” is non-trivial. Initial investigations highlighted that shape
complexity should be investigated, where shape = geometry + topology. Detailed analytical investigations have been started and will be reported in due course.

2.2 Design freedom
Additionally, the advent of RM will have profound implications for the way in which designers work. Generally, designers have been taught to design objects that can be made easily using current technologies - this being mainly due to the geometry limitations that exist with available manufacturing processes. For parts that are moulded, this means that draft angles, constant wall thickness, location of split lines, etc., have to be considered in the design. However, with the additive manufacturing technologies, these limitations are removed as it is not necessary to withdraw the part from the mould and therefore it would be possible to have re-entrant shapes without complicating manufacturing, no draft angles, variable wall thickness and no split lines. This new design freedom will place much more responsibility on the designer to think about the exact requirements of a part - with the unlimited geometry capability designers will therefore need to be much more imaginative to make full use of the new manufacturing processes. In the past, the processes have severely restricted designers and so they have become accustomed to designing relatively simple geometries.

2.3 New design paradigm
RM will change the divide between mechanical and aesthetic design. As demonstrated in the case study featured in Section 5, the ability for industrial designers to create the parts that they design without the need to consider issues such as draft angle and constant wall thickness (needed for injection moulding) means that, in effect, they are able to produce end-use items rather than just creative design briefs that are made manufacturable by mechanical designers. Because of this, there will be a requirement for industrial designers to consider much more issues such as the integration of other components (such as batteries, key-pads, etc.). Conversely, mechanical designers will be able to manufacture any complexity of product they require. It is therefore suggested that there will be a need to create a new breed of hybrid designer where mechanical and aesthetic designers are educated in each other's fields in order to produce better products.

2.4 Effect of graded materials on product design
When objects are formed in moulds, they are generally formed in one homogeneous material. Even in the case of an over-moulded component, where there can be two or more homogeneous materials in one finished part, there is a definitive boundary between one material and the other. In the future, with some of the additive manufacturing processes there is the potential to mix and grade materials in any combination that is desired, thus enabling materials with certain properties to be deposited where they are needed (Anan, 2001; Jacobs, 2002).

The over-moulding technique is a classic example of how design can be influenced by the availability of a manufacturing technique. Over-moulding allows designers, within limits, the ability to produce parts that have added functionality and enhanced design. Indeed, the design of over-moulded components very often incorporates the different material combinations to accentuate the design to the extent that designers are able to exploit the delineation of the different materials used to produce design features as well as extra functionality. This is perfectly illustrated by the simple case of a toothbrush - an everyday item that will often include over-moulding to give a handle that is stiff, with an over-moulded grip and a different material at the neck to give a flexible head. This is shown in Figure 1.

Figure 1 Example of how over-moulding improves design and functionality
Undeniably, the use of two materials in the toothbrush example has enabled a better product to be produced with enhanced functionality and improved design. Therefore, the question should be posed that, if a combination of just two materials is able to bring such a significant benefit in design and ergonomics, what effect will the potential of multiple materials have? This is something that is currently being investigated within the project.

3. Materials properties

RP machines are rarely used to produce fully functioning end-use parts and therefore, there has not been an overriding demand to know the full material properties. However, if designers are to have confidence in specifying the materials that are produced on the RM machines for end-use parts then it is vital that they are fully conversant with the various material properties. Some of this information is already available but there are large gaps in the data set. Therefore, a large part of the project involves the testing of existing materials to complete the data set.

3.1 Testing of existing materials to complete data set

An extensive materials testing programme is currently being performed to determine the properties of the state-of-the-art materials that are currently available for use on RP machines. The materials that are or will be investigated include:

- Vantico SL7560 – a ABS simulant (SL);
- RPC Accuflex – a polypropylene simulant (SL); and
- Duraform – (LS).

The data are being completed to ISO standards. The tests that are being performed include:

- tensile (Young’s modulus, UTS, Poisson’s ratio);
- flexural; and
- impact.

These tests will be performed within a temperature range of −40 to +140°C, at three humidities (dry, wet and control (20°C, 50 per cent relative humidity)) and at time intervals of 0, 1, 3, 6 and 12 months. It is estimated that each material will require around 5,700 individual tests which equates to 6 months testing per material. These tests are on-going.

3.1.1 Isotropy tests

Due to the additive layer-wise manufacturing techniques that are utilised, it was necessary to evaluate whether the samples produced behave in an isotropic or anisotropic manner. This has a great relevance to the number of tests that are to be performed as if the parts produced are anisotropic, then the number of tests performed would have to be increased threefold to consider the three main build directions. In order to test this for the SL materials, ISO standard tensile tests bars were produced in three different orientations as shown in Figure 2.

The test samples were produced using SL7560 and the results of the tests performed can be seen in Figure 3.

It can be seen that, for SLs, the build orientation has no anisotropic effect on the parts produced. This is consistent with the earlier work (Hague and Dickens, 1995). Tests for anisotropy for the LS materials are
currently being investigated. It is expected that these tests will show that there is in fact a degree of anisotropy in LS parts.

3.2 Impact test
In addition to the isotropy tests, for the SL parts, an investigation into the build parameters on the performance of the parts was conducted. This was achieved by undertaking impact tests. In conventional impact testing, a sample is produced and then a notch is mechanically added to the sample by means of a notching machine. However, with RP/RM methods, it is entirely possible to include the notch into the STL file and manufacture this design detail as the part is being built. Figure 4 shows machine-notched and SL-notched samples (respectively) of parts that were built on the SL machine in SL7540 (a fore-runner of SL7560). For the SL-notched sample, the border-scan that has produced the notch profile can clearly be seen. The averaged results for these samples can be seen in Table 1.

It is clear that the impact resistance of the SL-notched sample is almost a multiple of three higher than that for the machine-notched samples. This result has definite implications for the design of features such as self-tapping screw threads; in that it clearly demonstrates that if the thread is modelled into the CAD model and is therefore produced on the RM machine, then a much greater resistance to failure will be afforded to the product. The effects of manual or machine notchting on laser sintered parts will also be investigated.

![Figure 4 Machine-notched and SL-notched impact test samples](image)

Table 1 Results for machine- and SL-notched samples

<table>
<thead>
<tr>
<th>Impact test results for SL7540</th>
<th>SL-notched samples (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine-notched samples</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>SL-notched samples</td>
</tr>
</tbody>
</table>

4. Changes to the design process

4.1 DFM guidelines for injection moulding
It is likely that RM products will, in the first instances, compete with plastic processes such as injection moulding. Therefore, the main design rules associated with that process are given below. An introduction to injection moulding and a range of products produced by this process is given in Degarmo et al. (1997) and Kalpakjian and Schmid (2001).

1. **Wall thickness consideration**: components with thin walls solidifies faster, hence reducing warpage and twisting.
2. **Uniform wall thickness**: to aid the flow of material so that premature freezing of the molten plastic does not occur.
3. **Avoiding sharp corners**: they will provide tensile, compressive and shear stress on the moulded parts, which in turn will become stress concentrated points, leading to part failure.
4. **Minimising weld lines**: when different flow fronts (due to obstruction within the mould or various gates) meet each other, they create weld or fusion lines. They are a source of weakness within the part and should be minimised during design.
5. **Minimising sink marks**: they are formed when a thin section becomes solid sooner than a developed thicker section. Sink marks could be less apparent by adequate consideration during design.
6. **Draft angles**: these are important for ease of removal of parts from moulds. The inclusion of draft angles at design stage is very important, but often omitted.
7. **Minimising re-entrant features**: an easy to manufacture part must be easily ejected from the die. Designing undercuts requires side cores. This in turn will require moving parts in the dies that add tooling costs considerably. Simply some parts containing features such as blind holes and gullies are impossible to manufacture without using very complex and expensive tooling arrangements.
8. **Parting line**: the direction of mould closure and parting line are also crucial in tooling and injected parts. Much consideration and deliberation is needed for their selection.
9. **Ejection pin marks and gate marks**: these could have adverse aesthetic effect on the injection-moulded part. However, with
adequate consideration their impact could be minimised.

4.1.1 Impact of RM on DFM guidelines for injection moulding

As mentioned earlier, in a manufacturing environment, RM processes will, in the first instance, be considered as an alternative to injection moulding. RM unlike injection moulding, is a tool-less process which does not involve any melting and subsequent solidification of materials within the confines of tool. Therefore, considerations for constant wall thickness (to aid the flow of material), avoidance of sharp corners and minimising weld lines, sink marks, ejection pins, gate marks and draft angles will no longer need to be considered.

However, the main impact of RM is on the guidelines associated with minimising complex geometries and features such as under-cuts, blind holes, screws, etc. Incorporating such features in conventional injection moulding are not impossible, but often require expensive tooling, extensive tool set ups, testing runs, prototyping, etc. This inevitably leads to undesirable lead-times and costs. However, the complexity of a part is not important and any complex shapes or features produced by CAD can be directly translated into the final product. This is unheard for any conventional manufacturing process.

Additionally, in conventional manufacturing processes such as injection moulding, the selection of the right location for the split line, in particular for asymmetrical and complex shaped components, is quite difficult and is largely dependent on the experience of the tool designer. By adopting RM processes and not using any tooling, designers will be entirely freed from this task.

5. Bafbox case study

Bafbox is an Oxford-based company that manufactures custom designed plastic enclosures without using expensive mould tooling. The techniques that are adopted to produce the box are based on the use of relatively simple, but effective plastic-sheet fabrication methods. However, due to the manufacturing process employed, the design opportunities available are limited.

As an organisation, Bafbox are interested in extending the design opportunities that they can offer to their clients and this can only be achieved if a different manufacturing strategy is employed. Due to the low build volumes that are usual for their business, RM has the potential to be the enabling technology for their needs.

5.1 Objective of the enclosure re-design project

The main aim of the project was to investigate a new industrial design and manufacture methodology for an existing enclosure product. The product chosen for the study, which is typical of the type of component that is produced by the plastic-sheet fabrication method used by Bafbox, can be seen in Figure 5.

5.2 Current limitations of conventional process

For Bafbox, the key to success is a commitment to giving service to their customers efficiently. However, their current fabrication technology limits the designer’s concept creativity and design possibilities. For example:

- Complex and aesthetically attractive surfaces are impossible by this flat plastics-sheet fabricating method and thus products are limited in their design intent. The appearance of boxes is mostly angular and the ergonomics of them is also restricted.
- Normally working with just two standard wall thicknesses (3 and 4 mm) the constant thickness reduces the scope in product design.

Additionally, most of these enclosures require an assembly step as the products have to be
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made in two or three components in order to make a finished product. This is demonstrated in Figure 6.

5.3 Design criteria
The criteria for the design of the new enclosure was based on the following points.
- The new design had to accommodate the existing engineering components. This immediately puts restrictions on the design possibilities.
- To produce a more aesthetic and ergonomic design utilising RM techniques.
- Consider a reduction in components - the existing enclosure had a number of components that required assembly.

5.4 The concept creative process
After beginning the task of designing a new product, the key role for the industrial designer is to create a design that closely adheres to the initial design brief and specifications. Following these initial specifications, the process of concept generation began with sketches. A wide range of hand drawn sketches was produced in order to explore and document ideas and concepts.

The ability to sketch is a fundamental skill for the industrial designer - it is the process whereby three-dimensional relationships can be quickly and effectively manipulated using a simple two-dimensional medium. Using little more than pencil and paper it is possible - via sketching - to externalise, evaluate, and develop a concept until it reaches a reasonable level of acceptability. Figure 7 shows a number of iterations with the chosen design being shown in Figure 8.

Having chosen the final design, the sketch was then converted to a 3D CAD model using Unigraphics. Rendered images detailing the internal and external aspects of the finished design can be seen in Figure 9.

NB. It can be seen that, although similar to the chosen design, there are some differences in representation - this highlights the difficulties in converting a freehand sketch into a 3D CAD model. This is discussed in more detail in Section 5.7.1

5.5 Manufacture of parts
The parts were manufactured on an SL7000 SL machine using SL7540 resin. The total build time for five products was about 18 h. On top of this was the breakout and finishing which took further 5 h. The five parts, orientated for best all-round surface finish, can be seen in Figure 10.

Surface processing and coating were necessary as many of the issues of surface finish, etc. that differentiate RM from RP are yet to be resolved. The newly designed part was finished in a textured surface coating. The finished part can be seen in Figure 11.

5.6 Comparison of designs
Figure 12 shows a comparison of the features and design of the new enclosure in comparison to the original design.
5.7 Discussion

There are several benefits that have been derived from the current case study. The RM technologies open up a variety of benefits within the product design and manufacturing phase. The ability to create, manufacture and sell new products in a short time would enhance the sales opportunity and potentially create new markets for Bafbox.

The final design could not be manufactured with Bafbox's current technologies as the design has departed from the flat/angular designs produced with the current manufacturing process. One of the obvious examples from the Bafbox project is the rear of the new design, which has a re-entrant surface for covering the inner component. Such a feature would require more expensive tooling costs even if manufactured conventionally in injection moulding (Figure 13).

RM may significantly enhance the degree of concurrency that can be employed by industrial designers. The use of RM afforded by a CAD model extends the boundary of the communication between the industrial and mechanical designers. The introduction of RM has wider implications since the digital CAD model created can be used as the basis for the interaction of other downstream engineering functions. In the future, it is likely that a new breed of "super-designer" who is able to function with both aesthetic and mechanical design will be required—these two functions are generally separated in the conventional product design phase. In the Bafbox project, the final SLA part fitted the inner component perfectly even after applying the surfacing and coating (Figure 14).

5.7.1 CAD issues

One of the most important issues to be overcome for RM in the future will be the limitations and difficulties of using current CAD systems. The CAD design produced was, in essence, what was originally sketched, but lacked some of the spontaneity of the creative design sketch. This difficulty of interpreting the design intent is compounded by the fact that CAD systems are "expert
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Volume 23 • Number 4 • 2003 • 346-356

Figure 12 Comparison between original enclosure and new design proposal

<table>
<thead>
<tr>
<th>Original Box</th>
<th>New Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square Flat surface</td>
<td>More attractive and stylish shape</td>
</tr>
<tr>
<td>Constant wall thickness</td>
<td>Design with re-entrant structure features</td>
</tr>
<tr>
<td>Too many parts for a simple inner component</td>
<td>Reduced part count from 3 to 1</td>
</tr>
<tr>
<td>Limited choice of radius giving limited ergonomics</td>
<td>More rounded for aesthetics and ergonomics</td>
</tr>
</tbody>
</table>

systems” that require extensive training. One of the advantages of RM will be the possibility of producing more custom designs – however, there is a dichotomy between an increase in custom design that will necessitate more CAD input and the difficulty in producing those designs using current CAD.

Considering the current design, some design ideas were "killed" by the constraints of the current CAD design system. Some of the initial designs were adventurous and organic; these would have been ideal for the RM research, but would have been complicated to produce in CAD systems and also would have been time-consuming. The result is that the initial creative idea could not be produced faithfully as some complicated details had to be changed or ignored through the current CAD package.

It should also be noted that the time to produce the CAD model far outweighed the time to actually manufacture the product. In conventional manufacturing, the manufacture of the tooling to produce the

Figure 13

Figure 14
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injection-moulded components (for example) is usually the longest part of the product development process. When utilising RM, the CAD takes the longer time and therefore becomes the bottleneck.

The complexity of the CAD systems also has the effect of limiting those who can and want to use the RM technologies (Sawford, 2001). The “ease of use” requirement has traditionally been the stumbling block for the most existing CAD systems.

5.7.2 Assembly constraints

Unfortunately, a freeform design that completely capitalizes on the freedoms given by RM is not necessarily suitable to receive the components and mechanisms required to make it work. In this case, the organic freeform shapes are not suited to house the square internal components. The outcome of this is that a design that is produced for RM is basically not limited by the constraints of conventional manufacturing, but by the fact that products require components to be assembled inside them.

5.7.3 Cost issues

Table II shows the relative costs of the conventionally manufactured box in comparison to a new design that has been produced on SL and LS systems. The costs are commercial that were obtained from RP bureaux, and are based on a batch of 50 being produced.

It can be seen that the SL and LS costs are far higher than for the conventional route. This is likely to be one of the limiting factors for the uptake of RM as a viable manufacturing route as, despite the fact that the box would be suitable for end-use, the cost would currently preclude its use. However, costs will decrease as the processes improve and speed up.

6. Conclusions

RM will have a profound affect on the way the designers work. Key points to emerge from the on-going design for RM project includes the following.

Table II Relative costs

<table>
<thead>
<tr>
<th>Production method</th>
<th>Average cost per part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current design</td>
<td>£20</td>
</tr>
<tr>
<td>New design – SL</td>
<td>£210</td>
</tr>
<tr>
<td>New design – LS</td>
<td>£120</td>
</tr>
</tbody>
</table>

(1) Design for RM will actually be “Design for SL” or “Design for LS”:
- Common rules will apply, but material properties will be important and thus characterisation of these properties by companies will be the key.

(2) Still need to consider:
- design for assembly (inclusion of non-RM components); and
- design for maintenance.

(3) With the advent of the RM technologies, designers will be able to manufacture any freeform shape that they design and will no longer be constrained by the limitations imposed by either the conventional moulding process or the tool making process.

(4) The conversion of the industrial design sketches to a useable CAD model is non-trivial as there is difficulty in re-producing the exact design intent.

(5) As all tooling is eliminated, the CAD modelling phase becomes the most time-consuming aspect of the project and therefore CAD becomes the bottleneck that requires a skilled operator to produce.

(6) In conventional product design, the industrial designer would pass the initial design ideas to a mechanical designer who would incorporate the “internals” and consider the manufacturing route. As the industrial designer is able to “print” a part directly, much more consideration of mechanical design is needed by the industrial designer, or a general designer in the future. Thus, it is likely that the advent of RM will lead to a new breed of unique multi-skilled designer.

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Materials analysis of stereolithography resins for use in Rapid Manufacturing

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The use of Rapid Prototyping (RP) techniques for the production of end-use parts is increasing to a stage where Rapid Manufacturing is being undertaken. This paper documents significant initial investigations into the properties of Accura SL40 and SL7560 resins which represent two state of the art stereolithography resins that are aimed at end-use part manufacture. This information has previously been unavailable and is vital for their consideration in end-use part manufacture. The impact of various levels of post curing (ultraviolet and thermal) on the tensile, flexural and impact properties are investigated and correlated with differential scanning calorimetry (DSC) analysis. The isotropy/anisotropy nature of the two materials and also the effect of the notch creation method on the impact resistance were also studied. © 2004 Kluwer Academic Publishers

1. Introduction
There are three generic methodologies for the production of prototypes or manufactured parts that include [1]:

1. Subtractive: Processes that remove material from a bulk material such as milling, turning, electro-discharge machining (EDM), etc.
2. Formative: The use of a tool to produce a part in processes such as injection moulding, die casting, forging, etc. (NB: it should be noted that usually the tool is produced by subtractive methods.)
3. Additive: This is a relatively new approach to the manufacture of prototypes or end-use parts and is generally referred to as either Rapid Prototyping (RP) or increasingly Rapid Manufacturing (RM). This additive manufacturing principle and one process in particular (stereolithography) is the subject of this paper.

Rapid Prototyping (RP) is the collective name for a set of different technologies and processes used to manufacture models directly from a three-dimensional (3D) Computer Aided Design (CAD) model by constructively building them in layers. The RP processes include, amongst others, Stereolithography (SL), Laser Sintering (LS), Fused Deposition Modelling (FDM) and 3-Dimensional Printing (3DP). Other associated names include Solid Freeform Fabrication (SFF) and Layered Manufacturing (LM). RP technologies have gained diversity, complexity, sophistication and popularity since their introduction in the late 1980's. The use of RP in product design and development has had a significantly positive effect and has been shown to reduce development costs by 40 to 70% and the time to market by as much as 90% [2]. RP parts have been used in a range of areas such as design visualisation, pattern building, assembly verification and functional testing. However, it is not the aim of this paper to describe the various RP processes, as they are well documented elsewhere [3-5].

The concept of Rapid Manufacturing (RM)—the production of end-use parts from additive manufacturing systems—is evolving from RP. The principal advantage of the additive manufacturing processes (including most, but not all, of the currently available RP techniques) is the ability to manufacture parts of virtually any complexity of geometry entirely without the need for tooling. If this principle were extended to true manufacturing processes then the opportunities for product design and manufacturing are immense. Though some well-documented 'Rapid Manufacturing' is being undertaken today, these examples are being undertaken with existing RP systems [6, 7]. However, no current RP technology can be truly considered as a manufacturing process as there are several limitations that impede their use as manufacturing systems. The most important areas of concern include:

1. The machines are designed for prototyping and not for manufacturing which means that they are working at slow speed, relatively low accuracy and produce parts with poor surface finish [8].
2. Current high cost of machines (up to £750 K) and materials (£160/kg for SL resins) [8].
3. The limited number of materials (around 46 SL & 15 LS materials in USA & Europe) [6]. This is small
compared to other manufacturing techniques such as injection moulding that has thousands of available materials.

4. The very limited information about the mechanical properties of the materials at different temperatures, humidity and ages, which is one of the main reasons that designers do not have any confidence in specifying RP materials for producing end-use parts.

Therefore, there is much work to be undertaken to convert the principles of additive manufacturing into viable manufacturing techniques that can be exploited more universally. However, it is anticipated that true RM manufacturing systems will become available within a 5 to 10 year period and their introduction will truly amount to a new industrial revolution [9]. One such research project that is looking into the possibilities for RM is the "Design for Rapid Manufacture" project at Loughborough University [10]. The project is funded by Engineering Physical Sciences Research Council (EPSRC) as part of Loughborough's Innovative Manufacturing Research Centre (IMRC). The project industrial partners include: 3D Systems, Custom Design Technologies Ltd., Delphi Diesel Systems, Jaguar and Land Rover Research, MG Rover Group and Huntsman (formerly Vantico).

In addition to the design aspects [11], one of the main areas of the Design for Rapid Manufacture project concerns the characterisation and analysis of the mechanical properties of two materials manufactured using a stereolithography RP machine. The materials tested were SL 7560 by Huntsman [12] and SI40 by 3D Systems [13]—both materials represent the state of the art in SL materials and are aimed more for manufacturing purposes as it is considered that their mechanical properties are approaching those of traditional engineering plastics which will allow them to be used in more demanding end-use applications.

1.1. Scope of the investigations
As RP machines have historically rarely been used to produce fully functioning end-use parts, there has not been an overriding need or demand to know their full material properties. However, as mentioned previously, increasingly RP parts are being used in end-use part manufacture (RM) and therefore it is vital that designers are made aware of the various mechanical properties of the materials produced on the RP systems to give them more confidence in specifying the materials in their designs. Limited information is available but there are large gaps in the data set.

For automotive applications, designers typically need material properties ranging from -40°C to +140°C. Therefore, the research project is undertaking an extensive material's testing program for the two SL materials over this temperature range, at three different humidities (dry, 50% relative humidity (RH) and totally immersed in water) and also over extended time periods (1, 4, 13, 26 and 52 weeks) to consider ageing of materials. This represents the most significant data generation for materials being used in RP and RM to date, with each material requiring around 5500 individual tests. In order to conduct the proposed investigations, initial tests were conducted which yielded some interesting aspects of these two resins. It is these initial investigations that are detailed in the paper. The on-going ageing results will be published in due course.

1.2. Objectives
The objectives of this paper are to:

1. Investigate the isotropy/anisotropy of SL7560 & Accura SI40.

2. Investigate the effects of different methods of post-curing on the mechanical properties of Accura SI40 and relate these properties with the level of polymerisation within the test samples using differential scanning calorimetry (DSC).

3. Compare the impact strength of mechanically notched test specimens with those that have the notch built on the SL machine for SL7560 and Accura SI40 resins.

2. Methodology
In order to conduct the investigations and achieve the objectives of the project the following equipment and experimental approaches were adopted:

2.1. Stereolithography apparatus
Despite the fact that true "RM" does not exist, there has been a significant increase in the use of RP technologies for end-use part manufacture which has mainly been afforded by the marked development of the processes and materials during the past 15 years. Of the available RP processes, the stereolithography (SL) process has always been one of the most significant RP technologies and it is one of the technologies that is considered to be suitable as a future manufacturing process [11]. It is this process and the mechanical properties of the materials that are produced by it (specifically SL7560 and Accura SI40) that are the subject of this paper.

The SL technique is based on the process of photopolymerisation, in which a liquid resin is converted to a solid polymer on exposure to computer controlled ultraviolet laser radiation [14]. The photopolymer is selectively cured on a layer by layer (additive) basis where the cured area corresponds to the desired cross-section of the required shaped article to be formed, which is in turn taken from the 3D CAD model of the part being produced. The solidified layer is then lowered by the amount of the required layer thickness and a recoating blade moves over the surface to apply a new layer of resin. The process is repeated until a green model of the required shape is finished. It should be noted that support structures are used to anchor the part to the build platform during the build process and to enable the production of over-hanging features. On completion of the build, the model is usually post-cured under high intensity ultraviolet radiation to complete the curing process [2]. Thermal post curing is often,
but not always employed to stabilise and increase the mechanical properties of the produced part, though the decision of whether to thermally post cure is dependent on the particular SL material being used. For example, the Accura SI40 resin tested benefits greatly by the use of a thermal post curing stage whilst the effect on the SL7560 is far less pronounced and its use is therefore debatable. The use of a thermal post curing stage is in effect an accelerated ageing mechanism and can also have deleterious effects if not controlled correctly.

2.2. Test specimens manufacture and preparation

The equipment used to build the test samples was a SLA7000 by 3D Systems. The build volume for this machine is approximately 500 mm x 500 mm x 600 mm (XYZ). Various parameters can be adjusted to optimise and customise the process for a specific task, with the most significant of these being "over-cure," "hatch-cure," layer thickness and the recoating parameters [14]. The definition and impact of each of these parameters are given elsewhere [2]. However, it should be noted that for each resin the build parameters were provided and recommended by the resin suppliers and were used consistently for the test specimen’s manufacture. The build styles used were based on the ACES (Accurate Clear Epoxy Solid) format which was designed specifically for use with epoxy resins.

All the samples for each set of tests were produced during the same build and then cleaned and post cured at the same time. They were kept in a dark place to prevent further post process ultraviolet curing and in a controlled environment (50% RH & 20°C) prior to testing. For tests investigating the impact of post curing on the materials properties, 13 samples were produced for each series of tests and three of them were randomly selected for DSC analysis with the remainder being used for mechanical testing.

The build orientation and its affect on the isotropy of the material is one of the aspects considered in this paper and is covered in Section 3.1. However, it should also be noted that the build orientation also has a profound affect on the surface finish of the completed part due to the layer-wise manufacturing process employed [15], though this aspect is not considered in this paper as it has no bearing on the tests undertaken.

2.3. Test procedure and standards

The mechanical properties investigated in this work included: Tensile (Young’s modulus, ultimate tensile strength and % elongation at break), Flexural (flexural modulus and strength) and impact strength (using Izod tests). The tests were strictly conducted according to ISO standards [16–18] and all the test specimens were produced from 3D CAD models to the dimensions specified in the relevant standard.

All the tests were conducted in a temperature and humidity controlled room. The tensile and flexural tests were performed on a Zwick 1030 [19] tensile test machine with a nitrogen facility for low temperature tests combined with a Zwick heated cabinet for the higher temperature tests. A Zwick 5102 pendulum impact tester, configured for Izod tests was used for impact analysis.

2.4. Differential scanning calorimetry (DSC)

For this work it was required to establish and quantify the degree of polymerisation of the SL materials. To achieve this differential scanning calorimetry (DSC) analysis was conducted. DSC is a thermal analysis technique used to directly measure the temperature and heat flow to a sample during heating in a controlled atmosphere over a period of time. This technique provides quantitative information about physical changes by monitoring endothermic and exothermic processes that represent material transitions. Specific information that can be obtained include: glass transition, melting point, crystallisation, phase change; etc., but most importantly with respect to this work is the amount of heat expelled as a relation to the further curing experienced during the DSC analysis.

The DSC apparatus consists of an enclosed cell containing two aluminium vessels which are connected to thermocouples. Contained in one vessel (pan) is the sample to be examined and the comparison pan is kept empty.

Inside the DSC cell, the sample pan and the reference pan sit on a raised platform on the cell’s heater. As heat is transferred, the differential heat flow to the sample and comparison sample is monitored by area thermocouples. The heat input and temperature rise for the material under test is compared to those for the comparison pan while both are subjected to constant linear temperature increase. The results from these measurements allow the heat flow to be plotted as a function of temperature that can indicate the periods of thermal transition of the sample material [20].

The apparatus used was a modulated DSC machine by TA Instruments, model 2920 [21]. The cell atmosphere was provided by refrigerated nitrogen cooling system produced by TA instruments. The temperature range of the DSC analysis used was 10 to 170°C with a heating rate of 10°C/min. The recommended weight for each DSC analysis sample was 5–20 mg [20].

3. Experimental method, results & discussion

For ease of reporting, the experimental method and results for the various experiments conducted are given with a corresponding discussion of the results contained in the same section. This is followed by conclusions of the results that are given in Section 4.

3.1. Isotropy/anisotropy validation

Due to the additive layer-wise nature of the SL build process, there is some debate as to whether the produced materials are isotropic or anisotropic. Therefore, before proceeding to the full range of ageing tests where a significant amount of test coupons are to be built, it was important to ascertain and confirm previous work
into the isotropy (or otherwise) of the material with the aim of consolidating the number of subsequent tests. Isotropy, or rather anisotropy, can also have a particular influence on how a part is designed and thus its determination is of importance.

The investigations included tensile, flexural and impact tests that were conducted at a temperature of 20°C. The samples were produced in three different orientations (Flat, Upright and Edge) as depicted in Fig. 1 (for the tensile samples). Similar build orientations were used for the impact and flexural test samples. The tests were conducted according to ISO standards and Table I shows the average values (for 10 samples) of the conducted tests for SL7560.

It can be seen from the results in Table I that the maximum variation in mechanical properties of SL7560 resin is less than 5%. Similar results were found for the Accura SI40 resin. Therefore, it can be concluded that the stereolithography process produces broadly isotropic parts and that the build orientation has little effect on the mechanical properties of parts. These results are fully consistent with previous published works [2, 22].

Therefore, from this work it can be concluded that for the SL process, the build orientation can be optimised for either the reduction of build time, limitation of support structures or improvement of surface finish (to reduce the stair-step effect) without any consideration for influencing the mechanical properties.

### 3.2. The impact of post-curing methods on materials properties

As mentioned previously, the "green" part that has been produced on the SL machine needs to undergo subsequent post curing operations to polymerise the materials to an extent that they can be safely handled. This is usually achieved by exposure of the green part in a UV chamber for a period of approximately 1 h. In addition, much work has been undertaken that shows that a thermal post cure cycle can improve the mechanical properties for some SL materials [23-27]. During a thermal post cure cycle the resin is further cured by thermal means and therefore it also becomes more brittle; this consequently reduces the impact strength and the % elongation at break. For a given geometry of part, as the material cures, a flexible part will therefore be converted to a stiffer part which will result in an increased Young's modulus. Also, the extra cross-linking which takes place will improve the ultimate tensile strength of the material whilst at the same time, the flexural strength and flexural modulus will also increase [28, 29].

For the purposes of this study, the effects of thermal post curing on some of the mechanical properties of Accura SI40 have been investigated. To achieve this, the following three methods of post curing were applied:

1. **Normal post curing (NPC):** 90 Min in UV post curing apparatus
2. **Thermal post curing 1 (TPC1):** NPC + 2 h at 80°C (Some prototypes or parts will undergo this cycle for improved properties, depending on the particular resin used)
3. **Thermal post curing 2 (TPC2):** NPC + 24 h at 80°C (NB. This curing cycle is excessive and no prototypes or parts would normally undergo this level of post curing as it will result in highly embrittled parts. However, exposing the material to this level of cure is similar to an extreme accelerated ageing of the samples and thus the results are indicative of how further curing will influence the materials properties and are important if the parts are for end-use).

#### 3.2.1. Mechanical tests

The upright build orientation was selected for the tensile and flexural test samples, whilst the impact test samples were produced in a flat orientation. The results for tensile, flexural and impact properties are given in Table II. These results confirm that as the above thermal post curing cycles are executed, the samples become more brittle and the impact strength and % elongation at break reduce whilst Young's modulus, maximum tensile strength, flexural modulus and strength have increased. These results are in accordance with those obtained by other researchers [30].

#### 3.2.2. Confirmation by DSC analysis

To validate the mechanical test results, DSC analysis was conducted where the degree of cure due to the post-curing history were quantified. Fig. 2 shows a typical
TABLE 11 Changes in mechanical properties of Accura SI40 due to three levels of post curing

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (MPa)</th>
<th>Max. tensile strength (MPa)</th>
<th>% Elongation at break</th>
<th>Flexural modulus (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Impact strength (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC</td>
<td>2337.55</td>
<td>52.65</td>
<td>7.62</td>
<td>1842.73</td>
<td>88.04</td>
<td>4.68</td>
</tr>
<tr>
<td>TPC1</td>
<td>3038.95</td>
<td>80.49</td>
<td>7.06</td>
<td>1993.9</td>
<td>112.9</td>
<td>3.05</td>
</tr>
<tr>
<td>TPC2</td>
<td>3072.39</td>
<td>84.12</td>
<td>6.75</td>
<td>2002.79</td>
<td>114.89</td>
<td>2.53</td>
</tr>
</tbody>
</table>

DSC plot that was obtained for the SI40 in its Normal Post Cure (NPC) state. The peak in the plot represents an exothermic reaction due to the curing of the resin during its slow heating in DSC process. The area under the curve can be related to the amount of cure by comparison that has taken place to fully cure the sample. This result shows that there is still a significant amount of curing that can be achieved in samples that have only undergone UV post curing.

Figs 3 and 4 detail the DSC plots for the thermally post cured samples (TPC 1 & TPC 2) which show that there is a progressive reduction in the amount of cure after a thermal post cure stage. The amount of dissipated heat from the samples in their different states of
post cure (that is inversely proportional to the level of cure of the samples) is detailed in Table III. These results are calculated from the area under the DSC curves and are averaged for three samples per post curing state.

Figs 2-4 and Table III validate the results of the mechanical tests (Table II). As the level of cure of the samples tested increases (from NPC through to TPC2), the heat dissipated by the samples is shown to decrease—confirming and increase in initial curl—which further correlates to a matching change in the mechanical properties of the materials.

3.3. Effect of notch manufacture method on impact strength

In conventional impact testing, the required notches are usually mechanically introduced into the test samples—indeed, this is specified in the relevant ISO Standard [18]. However, with RP/RM processes it is entirely possible to include the notch into the CAD file and manufacture this design detail as the part is being built.

Notches were introduced into a group of ten Accura SI40 impact samples using a mechanical method (Izod notchig was used). These samples were tested and compared with another group that were produced with notch being introduced using the SL machine. Similar investigations were carried out for SL7560. In order to minimise the staircase effect of the build process on the notch profile, all the samples under investigation were built in the flat orientation, as shown in Fig. 1 (for tensile test samples). The averaged impact strength for all groups of samples being produced is shown in Table IV. Fig. 5a and b show scanning electron microscope (SEM) pictures of mechanically and SL-notched samples for Accura SI40 resin, respectively.

From Table I, it can be observed that the impact resistance of the SL-notched samples has improved considerably in comparison with the mechanically notched samples for both the SL7560 and SI40 materials. Fig. 5b, shows the border curing, which has resulted from the notch profile being manufactured on a Stereolithography machine and it is this border curing that has had the profound affect on the impact strength. This effect clearly does not exist on the mechanically manufactured notch as shown in Fig. 5a which has also shown to be damaged during the notching phase.

This increase in the impact strength has potentially a great impact on the design of features such as self-tapping screw threads, gear teeth, etc. If the screw thread were actually designed into the CAD model and then produced via the RM process, then this would afford a much greater resistance to failure than if the self-tapping screw was directly screwed into the produced part.

<table>
<thead>
<tr>
<th>TABLE III</th>
<th>Average heat dissipated during curing for three post curing cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV only</td>
</tr>
<tr>
<td>Sample 1</td>
<td>86.770</td>
</tr>
<tr>
<td>Sample 2</td>
<td>77.300</td>
</tr>
<tr>
<td>Sample 3</td>
<td>82.210</td>
</tr>
<tr>
<td>Average</td>
<td>82.093</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE IV</th>
<th>RP vs. machine manufactured notch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Impact strength (kJ/m²)</td>
</tr>
<tr>
<td>Material</td>
<td>Mechanically manufactured</td>
</tr>
<tr>
<td>SL7560</td>
<td>2.4</td>
</tr>
<tr>
<td>Accura SI40</td>
<td>2.5</td>
</tr>
</tbody>
</table>
4. Conclusions
This paper has detailed significant initial results from an ongoing research project that is investigating the material properties of two state of the art stereolithography materials that are aimed for end-use part manufacture. The isotropy, effects of thermal post curing and impact test notch introduction methods have been presented.

Investigations into the isotropy/anisotropy behaviour of SL7560 and Accura SI40 concluded that the parts produced are broadly isotropic and that the build orientation does not affect their mechanical properties. This work confirms previous work and has important implications for the design of parts produced via stereolithography.

Three different post-curing cycles were selected and the tensile, flexural and impact properties of Accura SI40 were investigated. It was shown that by exposing the Accura SI40 material to a thermal post curing cycle further polymerises the resin. Consequently, Accura SI40’s Young’s modulus, ultimate tensile stress, flexural modulus and strength improved while its impact strength and % elongation at break reduced. DSC analysis correlated the results obtained from the mechanical tests. This indicates that the mechanical properties can be adjusted according to the post-curing methodology used which may be desirable in the design of the end-use part.

The method of creating the notch in impact samples was found to greatly influence the results of the tests. Creating the notch within the 3D CAD file and producing this directly on the SL machine significantly improves the impact resistance with respect to mechanically notched samples. This result reveals that if design features such as screw threads or gear teeth are included at the 3D CAD design stage and subsequently manufactured by SL, then this will increase their resistance to damage due to the increased impact strength afforded to the parts.

Acknowledgements
UK Engineering & Physical Science Research Council (EPSRC) and the project partners that include: 3D Systems, Custom Design Technologies Ltd., Delphi Automotive Systems, Jaguar & Land Rover Research, MG Rover Group and Huntsman (Vantico).

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Received 26 December 2002 and accepted 8 December 2003
1. Introduction

1.1 Rapid prototyping and rapid manufacturing

Rapid prototyping (RP) is the collective name for a set of different technologies and processes used to manufacture models directly from a three-dimensional (3D) computer aided design (CAD) model by constructively building them in layers. The RP processes include, amongst others, stereolithography (SL), laser sintering (LS), fused deposition modelling (FDM) and 3 dimensional printing (3DP). Other associated names include solid freeform fabrication (SFF) and layered manufacturing (LM). RP technologies have gained diversity, complexity, sophistication and popularity since their introduction in the late 1980s. The use of RP in product design and development has had a significantly positive effect and has been shown to reduce development costs by 40-70 per cent and the time to market by as much as 90 per cent (Dulieu-Barton and Fulton, 2000). RP parts have been used in a range of areas such as design visualisation, pattern building, assembly verification and functional testing. However, it is not the aim of this paper to describe the various RP processes, as they are well documented elsewhere (Cooper, 2001; Groover, 2002).

The concept of rapid manufacturing (RM) (i.e. the production of end-use parts from additive manufacturing systems) is evolving from RP. The principal advantage of the additive manufacturing processes (including most, but not all, of the currently available RP techniques) is the ability to manufacture parts of virtually any complexity of geometry entirely without the need for tooling. If this principle were extended to true manufacturing processes then the opportunities for product design and manufacturing are immense.

Though some well-documented “Rapid Manufacturing” is being undertaken today, these examples are using existing RP systems (Masers and Mathy, 2002; Wholers, 2001). However, no current RP technology can be truly considered as a manufacturing process as there are several limitations that impede their use as manufacturing systems. The most important areas of concern include the following.

(1) The machines are designed for prototyping and not for manufacturing which means that they are working at a slow speed, relatively low accuracy and produce parts with poor surface finish (Hague, 2002).

(2) Current high cost of machines (up to £750K) and materials (£160/kg for SL resins).

The use of stereolithography (SL) and laser sintering (LS) was shown to be true in physical tests predicted values were lower than the predicted values especially for thicker coatings. Physical tests also confirmed that thicker coatings increased UTS and impact energy but had a minimal effect on the ductility of parts.

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Rapid Prototyping Journal
Volume 10 · Number 5 · 2004 · pp. 305-315
© Emerald Group Publishing Limited · ISSN 1355-2546
DOI 10.1108/13552540410562340

Received: 14 January 2004
Revised: 16 July 2004
Accepted: 16 July 2004
Therefore, there is much work to be undertaken to convert the principles of additive manufacturing into viable manufacturing techniques that can be exploited more universally. However, despite the fact that true \textit{"RM"} does not exist, there has been a significant increase in the use of RP technologies for end-use part manufacture which has mainly been afforded by the marked development of the processes and materials during the past 15 years. It is anticipated that true RM manufacturing systems will become available within a 5-10 year period and their introduction will truly amount to a new industrial revolution (Griffiths, 2002).

1.2 Objective

One of the main limitations facing RP manufacture of parts for end-use is the material properties of the parts produced. Improvements in material properties, most notably with SL, have allowed an increasing range of uses of SL and LS, however, further improvements, particularly with respect to stiffness, strength and toughness are required to expand the envelope of applications.

Post-processing allows for improvements in material properties and performance of RP parts; however it does add time and cost to the manufacturing process. Various forms of post processing have been used to improve the performance of SL and LS parts including infiltration and cryogenic treatment (Fritz, 2001; Zarringhalam, 2003).

This paper investigates the use of electroplating to improve the properties of parts made by SL and LS to enable them to be used as end-use components.

2. Background

2.1 Stereolithography

Of the available RP processes, the SL process has always been one of the most significant RP technologies and it is one of the technologies that is considered to be suitable as a future end-use part manufacturing process (Hague et al., 2003).

The SL technique is based on the process of photo-polymerisation, in which a liquid resin is converted to a solid polymer on exposure to computer controlled ultraviolet laser radiation (Jacobs, 1992). The photopolymer is selectively cured on a layer by layer (additive) basis where the cured area corresponds to the desired cross-section of the required shaped article to be formed, which is in turn taken from the 3D CAD model of the part being produced. The solidified layer is then lowered by the amount of the required layer thickness and a recoating blade moves over the surface to apply a new layer of resin. The process is repeated until a green model of the required shape is finished. It should be noted that support structures are used to anchor the part to the build platform during the build process and to enable the production of over-hanging features. On completion of the build, the model is usually post-cured under high intensity ultraviolet radiation to complete the curing process. Thermal post curing is often, but not always employed to stabilise and improve the mechanical properties of the produced part, although the decision of whether to thermally post cure is dependent on the particular SL material being used. The use of a thermal post curing stage is in effect an accelerated ageing mechanism and can also have deleterious effects if not controlled correctly.

The main strength for SL lies in its ability to produce parts with tight tolerances and fine resolution when compared with other RP processes. However material properties tend to degrade over time. The application of a protective electroplated coating should add rigidity to parts and also reduce any effects of aging caused by absorption of water or ultra-violet light, however it may adversely affect feature resolution and tolerance.

2.2 Laser sintering

LS was first commercialised in the early 1990s and allows the production of parts using a wide variety of materials including polymers, metals and ceramics. The process works in a similar layer by layer approach to the SL process but instead of a liquid photopolymer, powdered materials are used. LS of polymers generally results in improved mechanical properties over those achieved in SL, though unlike SL, the parts produced tend to be anisotropic in their material properties and thus more emphasis on the build direction is required. Resolution and accuracy of LS parts are not as good as their SL counterparts.

2.3 Electroplating

Electroplating has been practiced for many years in industries such as electronics and jewellery.
manufacture. The process involves placing an anode and a cathode in a solution and applying a potential difference between them. Ions are discharged from the anode and bond to the cathode so that the cathode becomes plated by the metal from the anode (Kalpakjian, 1995).

2.3.1 Electroplating non-conductive parts
In order to plate the cathode it must be conductive. Consequently, polymer parts first need to be coated in a conductive material. Initial plating of polymer parts may be by the application of silver paint (Arthur and Dickens, 1996); copper and nickel filled conductive paints can also be used. Another method of coating polymer parts is by electroless deposition of metals such as nickel or copper. Other common methods used to make plastic parts conductive include rubbing with graphite or spraying with chemically reduced silver.

2.3.2 Electroplating materials
A typical sequence used for decorative electroplating would include copper as a base layer, followed by nickel and then a flash of chromium (ASTM B604-91, 1997). Combinations of metals may be used to create alloys (Lowenheim, 1974). The thickness of an electroplated coating may vary from a few atomic layers to 0.05 mm or more (Kalpakjian, 1995). However, plating thickness can vary especially where the cathode has a complicated geometry including sharp corners. Electroplated finishes depend on a good bond to the substrate to hold them in place and their function is usually to enhance appearance or hardness or to improve the corrosion resistance of the substrate surface. With a good bond to the substrate, high gloss finishes and/or very hard surfaces can be made but these plated layers are often very highly stressed, can be brittle and will flake off if there is a poor bond.

The materials used in this work are low stress acid copper and sulfamate nickel coatings that have been optimised for fabrication of freestanding structural parts via electroforming. These coatings are more tolerant of a weak bond to the substrate. These low stress coatings, running at close to room temperature, were chosen since it is not practical to optimise etching and bonding procedures for the large variety of materials used in RP particularly at the low volumes of parts produced.

2.3.3 Geometrical issues associated with electroplating
Field strength in an electroplating bath affects plating thickness; there are always gradients in the field strength around a cathode in an electroplating bath but these can be minimized through the use of shields, auxiliary anodes and/or "thieves". Objects that are flat with no exposed corners will generally have the most uniform current distribution and hence produce a more even coating. If there are critical features on a part which are prone to excess metal build up, a field control element might be employed in that region. Finally, the areas that are most prone to metal build up are usually very exposed and accessible. Excess material can be removed from critical areas using small files so that parts fit together properly.

2.3.4 Electroplating rapid prototyped parts
From the mid 1990s there has been some interest in electroplating SL parts for use as electrode discharge machining (EDM) electrodes (Arthur et al., 1996; Bocking et al., 2000; Ryall, 1996; Soar and Dickens, 1996; Yarlagadda et al., 1999). The general view from this body of research suggests that great care is required and slow deposition rates need to be employed in order to achieve an even electroplated coating especially where complicated geometries and deep slots are involved. Further, electroplated SL parts should be used cautiously with low amperages and wear rates in order to avoid overheating of the electrodes during the EDM process. None of this work however commented on the suitability of using electroplated parts for testing or end use manufacture.

Figure 1 shows some RP parts made by the object process using an acrylate based photopolymer that have been electroplated. The threads on the parts in Figure 1 indicate the high degree of surface detail that may be maintained when RP parts are electroplated. The typical metal coating applied to RP parts is around 50 μm, which is usually less than the error on the model.

In order to take into consideration the thickness of the applied coating, it is possible to displace the CAD file surfaces inwards by the coating thickness. Also, most parts that have tight tolerance requirements or have specific locations that have to hold tighter tolerances (such as a hole...
Effects of electroplating on the mechanical properties of stereolithography

N. Saleh, N. Hopkins, R.J.M. Hague and S. Wise

diameter and location) and others that will not be as critical. In such cases, the holes can be opened up with an oversized drill to allow for plating or the hole might be masked so it is not plated and its dimensions are never changed.

Several multinational OEM's are using metal-coated RP models in engineering development of new products. The most extensive use is at Pinney Bowes Corp (n.d.). Many parts in their products are designed to be manufactured from fibre-reinforced plastics, die cast metal or sheet metal. While SL models are suitable for form and fit testing, they will often break prematurely or not function at all due to poor stiffness, strength and creep characteristics when used as part of a mechanism in dynamic testing. SL models plated with only 50 μm of metal will function as well as the fibre reinforced plastic parts that are to be used in production. This allows several design iterations to be tested on loaded parts without having to resort to prototype tool manufacture and part moulding. SL models with 120 μm of metal have been used for parts designed for die cast metal and have held up well in dynamic testing (Pinney). However, when SL parts are used in very wet conditions, usually fail within days due to swelling. The absorption of water leads to a softening of the parts and therefore weaker mechanical properties (Saleh, 2003a, b). This problem can be eliminated with metal coating.

Aerospace companies use coated RP models but in a somewhat different way. Large RP models are often made to create mock-ups of modules or vehicles in development. Since aerospace structures are usually made from stiff materials like aluminium or continuous fibre composites it is difficult to recreate the geometry in RP resins and obtain a stable part without resorting to significant modification of the geometry such as increasing wall thickness. The metal coating applied to RP models improves their durability while nearly eliminating creep and distortion often observed with very large RP models. Metal-coated RP models are also used to increase radar reflectivity and to improve durability in simulator components.

3. Methodology

3.1 Manufacture of test samples

3.1.1 Test standards

The mechanical properties investigated in this work included: Tensile (Young's modulus, ultimate tensile strength and per cent elongation at break), and impact strength (using Izod tests). The tests were strictly conducted according to ISO standards (ISO 180, 2001; ISO 527, 1996) and all the test specimens were produced from 3D CAD models to the dimensions specified in the relevant standard.

3.1.2 Production of stereolithography parts

The equipment used to build the SL test samples was a SLA7000 from 3D Systems. The build volume for this machine is approximately 500 × 500 × 600 mm (X,Y,Z). Various parameters can be adjusted to optimise and customise the process for a specific task, with the most significant of these being “over-cure”, “hatch-cure”, layer thickness and the recoating parameters (Jacobs, 1992). The definition and impact of each of these parameters are given elsewhere (Dulieu-Barton and Fulton, 2000). However, it should be noted that the build parameters were provided and recommended by the resin suppliers and were used consistently for the test specimens' manufacture. The build styles used were based on the ACES (Accurate Clear Epoxy Solid) format which was designed specifically for use with epoxy resins.

Thirty tensile test parts were built for this research in the vertical build orientation from SL7560 Epoxy-based resin. They were built along with a further 720 parts (used for other purposes) in a single build. The total build time for 750 parts was 90 h followed by 5 h of manual finishing and 1.5 h of post curing using a UV light box.

Thirty impact test parts were built from SL7560 resin for this research. They were built along with a further 210 parts (used for other purposes) in a single build. The total build time for 240 parts was 7.2 h followed by 2 h of manual finishing and 1.5 h of post curing using a UV light box.

After removal from the SL machine, both types of samples were cleaned by submerging them first in TPM for 30 min, then in water for 30 min and finally placing them in an ultrasonic tank containing TPM for 15 min.

3.1.3 Production of laser sintered parts

The equipment used to build the LS parts was a Vanguard SL LS system from 3D Systems. The build volume for this machine is approximately 355 × 305 × 430 mm (X,Y,Z). The parts were built using virgin Duraform PA powder.

For this work, 30 tensile test parts were built in the vertical build orientation. It is recognised that for the LS process, build orientation affects the isotropy/anisotropy of the resultant parts and thus the weakest orientation was chosen.

Thirty impact test parts were built from Duraform powder for this research and were subsequently mechanically notched.

3.2 Electroplating

Once the parts were finished they were shipped to be electroplated with different thicknesses of copper/nickel. Prior to the electroplating process,
the parts were made conductive by electroless plating of nickel – this was chosen as it provides a better bond than painting with a silver coating. Electroless plating of nickel involved a sequence of preparatory steps before coating the parts in a room temperature electroless nickel (RTEN) batch for 20 min, this results in a nickel coating of nominally 1 μm.

The subsequent electroplating process involved coating the parts with copper followed by nickel. This was to make a laminate coating with the two metals in equal proportions. Table I summarises the parts made and parameters used to apply coatings. After electroplating the parts were lightly filed in positions where small lumps of copper had amalgamated.

3.3 Measurement of electroplated material thickness
While Table I shows the intended thickness of electroplated material, the true thickness was measured using an eddy current sensor. The sensor used was an ISOSCOPE MP3-CU (Plate 1) and it was used to measure the thickness of metal on top of the non-conductive RP part, this includes the layer of electroless plated nickel which was minimal when compared with the thickness of electroplated copper/nickel. The sensor was quoted to have an accurate working range from 0 to 150 μm with a resolution of 1 μm and a maximum reading of 176 μm.

For each specimen, five readings for thickness were taken at positions that were not close to any edges. Care was taken to ensure that readings were not taken in positions where small lumps of copper had been filed away after electroplating.

3.4 Surface roughness
One drawback often associated with RP parts is surface roughness. LS parts have uniform but rough surfaces when compared with their SL counterparts. Plated samples were subjected to surface roughness tests using a Talysurf profilometer. For each of the sample sets shown in Table I, three parts were selected at random and on each of these three separate readings of surface roughness (Ra) were recorded at positions away from any edges. An optical microscope was also used to qualitatively assess the deposition of metal and its effect on surface roughness.

3.5 Prediction of mechanical response of plated parts
Electroplating a polymer part creates a composite product and standard composite theory was used to predict the mechanical response of the tensile specimens produced. Assuming there is strain compatibility between the constituent parts, the rule of mixtures allows the prediction of Young’s modulus of a composite given the cross sectional area of the component materials and their respective Young’s modulus values using the equation shown below (Hyer, 1998):

$$E = E' \cdot V_f + E^m(1 - V_f)$$  (1)

where $E$ is the Young’s modulus for the composite; $E'$ the Young’s modulus for the filler; $V_f$ the volume fraction of the filler (cross sectional area); and $E^m$ the Young’s modulus for the matrix.

However in this case the RP part is plated by copper and then by nickel (the electroless deposited nickel may be discounted as it’s thickness is negligible) and so equation (1) must have an extra term added to account for the third component material. Figure 2 shows a schematic that was used to calculate the volume fractions of the different component materials.

The area fractions of each of the component materials shown in Figure 2 were calculated as shown below:

Total
Area = $A_t = (10 + 2T_c + 2T_n)\times (4 + c + 2T_n)$

Area fraction of polymer $A_p = (10 \times 4)/A_t$

Area fraction of copper $A_c = [(10 + 2T_c)\times (4 + 2T_c)]/A_t$

Area fraction of nickel $A_n = [(A_t - (10 + 2T_c))\times (4 + 2T_c)]/A_t$

The Young’s modulus for each part was calculated using the following equation using the area fractions described above and in Figure 2:

$$E = E_p \cdot A_p + E_c \cdot A_c + E_n \cdot A_n$$  (2)

Table I Electroplating parameters for tensile and impact specimens

<table>
<thead>
<tr>
<th>Specimen description</th>
<th>Target thickness (μm)</th>
<th>No. of specimens of each process</th>
<th>Plating time (minutes)</th>
<th>Current Density (Amps/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SL and LS) Tensile</td>
<td>20</td>
<td>5</td>
<td>120</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5</td>
<td>390</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>5</td>
<td>660</td>
<td>0.8</td>
</tr>
<tr>
<td>(SL and LS) Impact</td>
<td>20</td>
<td>5</td>
<td>130</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>5</td>
<td>390</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>5</td>
<td>660</td>
<td>0.8</td>
</tr>
</tbody>
</table>

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Plate 1 Eddy current sensor in place over a coated sample

Figure 2 Schematic of cross-section of coated tensile test part

where $E_p$ is the Young’s modulus for the RP polymer part; $E_c$ the Young’s modulus of copper; and $E_n$ the Young’s modulus of nickel.

3.6 Test procedure
All the tests were conducted in a temperature and humidity controlled room. The tensile and flexural tests were performed on a Zwick 1030 (Zwick-Roell, 2003) tensile test machine with a nitrogen facility for low temperature tests combined with a Zwick heated cabinet for the higher temperature tests. A Zwick 5102 pendulum impact tester, configured for Izod tests was used for impact analysis.

4. Results

4.1 Electroplated material thickness
Table II shows the percentage of the total metal volume, the average, standard deviation (STDEV) and range of measured thickness of electroplated material for each of the target thicknesses on SL and LS tensile test parts.

Table II shows that, for all sets of parts tested, the average thickness was within 10 μm of the target thickness. The results for standard deviation and range in Table II show that as coating thickness is increased the control of tolerances of thickness is reduced. The ranges of coating applied reached a maximum of 42 μm for the SL parts with a target thickness of 120 μm, this tolerance range is tighter than may be expected to be achieved for the RP process itself indicating that electroplating should not have an adverse affect on tolerances that may be achieved.

Figure 3 shows the measured thickness plotted against the target thickness for all SL samples. This indicates that there was a tendency to over plate at the lower target thickness of 20 μm and a tendency to under plate at the higher target thickness of 120 μm.

Figure 4 shows the measured thickness plotted against the target thickness for all laser-sintered samples. As with the SL samples, this shows that there was a tendency to over plate at the lower target thickness of 20 μm and a tendency to under plate at the higher target thickness of 120 μm.

Figures 3 and 4 show that the range of plating thickness increases with total material deposited, this may create a tolerance issue for parts with thicker plating.

4.2 Surface roughness
Figure 5 shows optical microscope pictures of sections of coated SL samples. These images show that an equal coating of copper and nickel were deposited on each sample.

Figure 6 shows optical microscope pictures of sections of coated laser sintered samples. These images are in marked contrast to those for the SL parts and show how the surface roughness of the RP part leads to a complicated pattern of deposition. The effect of the increased layers is to smooth out the surface roughness of the surface of these parts but once again there appears to be an equal overall deposition of copper and nickel.

Figure 7 shows the surface roughness measured from both SL and laser sintered samples. The SL samples are much smoother than their laser sintered counterparts as might be expected given the roughness of parts produced by the processes and the images shown in Figures 5 and 6. With SL parts, the roughness shows a small increase as layer thickness increases, however the converse is true for laser-sintered parts as supported in Figures 10 and 11. The electroplating process clearly has the effect of smoothing the rough parts produced by LS and so, as more metal is deposited, then less of the original roughness remains.

4.3 Prediction of response of plated parts
Equation (2) was used to calculate the effective/ composite Young’s modulus for the parts...
Table II Summary of measured thickness of electroplating

<table>
<thead>
<tr>
<th>Total metal volume (per cent)</th>
<th>Target thickness (µm)</th>
<th>Average (µm)</th>
<th>STDEV (µm)</th>
<th>Range (µm)</th>
<th>Average (µm)</th>
<th>STDEV (µm)</th>
<th>Range (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>20</td>
<td>22</td>
<td>2.21</td>
<td>8</td>
<td>21</td>
<td>3.45</td>
<td>12</td>
</tr>
<tr>
<td>4.06</td>
<td>60</td>
<td>58</td>
<td>5.33</td>
<td>17</td>
<td>58</td>
<td>4.53</td>
<td>17</td>
</tr>
<tr>
<td>7.83</td>
<td>120</td>
<td>111</td>
<td>11.47</td>
<td>38</td>
<td>119</td>
<td>11.68</td>
<td>42</td>
</tr>
</tbody>
</table>

Figure 3 Measured thickness plotted against the target thickness for all SL samples

Figure 4 Measured thickness plotted against the target thickness for all laser sintered samples

Figure 5 Optical microscope pictures of sections of coated SL samples
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Figure 6 Optical microscope pictures of sections of coated laser sintered samples

Figure 7 Surface roughness from SL and laser sintered samples

produced. Calculations assumed that the target dimension for manufacture of SL/LS parts and plating thicknesses were achieved. The values of Young's modulus used are shown in Table III.

Table IV shows the predicted values for Young's modulus found from equation (2) for electroplated SL and laser sintered samples. As expected, the results predict a significant increase in stiffness with thicker electroplated coatings. Also as parts made from SL7560 are stiffer than those made by Duraform the SL parts were predicted to have a higher Young's modulus than their laser sintered counterparts.

4.4 Tensile tests
Figure 8 shows the predicted and measured values for Young's modulus for the coated SL and laser sintered samples. As expected, the samples with thicker coatings had higher values of Young's modulus. The predicted values rise more sharply with increased plating thickness than the actual values, this may be due to the fact that under higher loads there is some slippage between different material layers and so the assumption of strain compatibility becomes invalid.

Figure 9 shows the UTS recorded for the SL and laser sintered samples. Again, thicker coatings lead to higher mechanical properties as would be expected although there does not appear to be any convergence of the trend-lines as the volume fraction of the metal increases.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL7560</td>
<td>2.5</td>
</tr>
<tr>
<td>Duraform PA</td>
<td>1.6</td>
</tr>
<tr>
<td>Copper</td>
<td>125</td>
</tr>
<tr>
<td>Nickel</td>
<td>200</td>
</tr>
</tbody>
</table>

Table IV Predicted values of young's modulus for electroplated SL and laser sintered samples

<table>
<thead>
<tr>
<th>Total metal volume (per cent)</th>
<th>Target coating thickness (µm)</th>
<th>Values of young's modulus (GPa) obtained from equation (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL</td>
<td>SL</td>
<td>SL/LS</td>
</tr>
<tr>
<td>1.4</td>
<td>20</td>
<td>4.714 3.827</td>
</tr>
<tr>
<td>4.06</td>
<td>60</td>
<td>9.002 8.139</td>
</tr>
<tr>
<td>7.83</td>
<td>120</td>
<td>14.997 14.16</td>
</tr>
</tbody>
</table>
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Figure 8 Predicted and measured values for Young's modulus for the coated SL and laser sintered tensile test parts

![Graph showing Young's modulus vs. coating thickness for SL and LS parts]

Figure 9 UTS recorded for the SL and laser sintered samples

![Graph showing UTS vs. coating thickness for SL and LS parts]

Figure 10 shows the elongation at break results from the plated SL and laser-sintered samples.

The elongation results show that increasing plating thickness results in a lower elongation for laser sintered parts and an increase value for SL parts. For low plating thickness the elongation values are similar to those for uncoated samples (~5 per cent for SL and ~8 per cent for LS) as might be expected. The trend-lines suggest a convergence of elongation at break in the region of 5-6 per cent for parts coated with thicker layers of copper and nickel.

4.5 Impact tests
Figure 11 shows the results from the impact tests with laser sintered parts having higher impact strength than SL parts. As with the results for measured thickness of electroplated material, there is an increase in variability as the target thickness is increased from 20 to 120 μm. The trend-lines in Figure 11 also show how the average impact results appear to converge — this may be due to the coating materials which are the same for both types of RP part becoming more dominant in affecting the properties of the composite parts.

5. Conclusions
Coatings of copper and nickel on SL and laser sintered parts result in increases in Young's modulus, UTS and impact strength; they also tend to smooth the surface of laser-sintered parts. The increase in Young's modulus of the composite after applying the coating is only 2/3 the amount expected for the LS materials and just over half the expected stiffening in the SL material, based on a rule of mixtures prediction. Ultimate tensile
The effects of plating on elongation at break are less pronounced and tend to a value ~5 per cent for thicker coatings. The effect of electroplating on part tolerance was not significant for the parts made in this work; however for more complicated geometries and thicker coating then tolerance of coatings may be an issue.

The improvements of mechanical properties given by electroplating SL and laser sintered parts should lead to increased use for functional prototypes and end use products made by these processes.

References


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Pitney Bowes Corp. (n.d.), 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.


Zwick-Roell (2003), available at: www.zwick.com

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Material and design considerations for Rapid Manufacturing

R. HAGUE†*, S. MANSOUR† and N. SALEH†

An investigation into how the advent of Rapid Manufacturing will influence an individual designer's approach to product design and materials selection is detailed. The assumption is made that Rapid Prototyping machines have evolved into viable manufacturing systems and all associated problems with accuracy, surface finish and repeatability have been resolved. Without the restriction of removing a product from a tool, designers will be free to design any complexity of geometry that they either desire or require. This tool-less approach to manufacturing will have profound implications on the way designers are accustomed to working and will eliminate most Design for Manufacture considerations. Design investigations are presented to highlight the potential importance and scope of Rapid Manufacturing. With advances in a new range of materials, some Rapid Manufacturing is happening today—albeit with existing Rapid Prototyping equipment. However, to enable designers to use existing Rapid Prototyping equipment for manufacturing purposes, there is a need for comprehensive information relating to the mechanical properties of the available materials. This is required to enable ‘Design for Rapid Manufacture’. The most comprehensive analysis to date of three new materials aimed for end-use part manufacture at differing ages, humidities and temperatures is presented.

1. Introduction

Rapid Prototyping (RP) is the collective name for a set of different technologies and processes used to manufacture models directly from a three-dimensional (3D) computer-aided design (CAD) model by constructively building them in layers. The RP processes include, amongst others, stereolithography (SL), laser sintering (LS), fused deposition modelling (FDM) and 3D printing (3DP). Other associated names are solid freeform fabrication (SFF) and layered manufacturing (LM). RP technologies have gained diversity, complexity, sophistication and popularity since their introduction in the late 1980s. It is not the aim of this paper to describe the various RP processes as they are well documented elsewhere (Cooper 2001, Groover 2002).

The concept of Rapid Manufacturing (RM)—the production of end-use parts from additive manufacturing systems—is evolving from RP. Though some well-documented ‘RM’ is being undertaken today, these examples are being undertaken with existing RP systems. However, no current RP method can be considered as a true manufacturing process as there are many problems with surface finish, resolution, accuracy and repeatability that need to be overcome. There is much work...
to be undertaken to convert the principles of additive manufacturing into viable manufacturing techniques that can be exploited more universally. However, it is anticipated that true RM manufacturing systems will become available within 5–10 years and their introduction will truly amount to a new industrial revolution (Griffiths 2002, Hague et al. 2003).

The principal advantage of the additive manufacturing processes (including most, but not all, of the currently available RP techniques) is the ability to manufacture parts of virtually any complexity of geometry entirely without the need for tooling. If this principle was extended to true manufacturing processes, then the opportunities for product design and manufacturing are immense.

The need for tooling in conventional manufacturing represents one of the most restrictive factors for today’s product development. The absence of tooling within the additive manufacturing processes means that many of the restrictions of ‘design for manufacture’ (DFM) that are essential in a modern manufacturing environment are no longer valid. The ability to produce whatever geometry that is created in a 3D CAD system actually means that one is entering a new dimension of ‘manufacture for design’ rather than the more conventional DFM philosophy (Campbell et al. 2003). In addition, as no tooling is required, there will no longer be a need to produce many thousands of parts in order to amortize the cost of the (usually expensive) tool. Thus, the opportunity for cost-effective custom manufacturing becomes apparent.

This freedom of design is one of the most important features of RM and extremely significant for producing parts of complex geometry, which could result in reducing the lead time and ultimately the overall manufacturing costs for such items. RM will affect manufacturers and customers alike. For manufacturers, costs will be dramatically reduced as no tooling is required and for customers, complex, individualized products will be made cost effectively that can be configured to personal use, thus giving the potential for much greater customer satisfaction (Hague et al. 2001).

Due to significant developments in different aspects of RP technologies during the past 15 years, some of the RP processes have started to be used as RM systems to produce end-use parts. Production of custom design hearing aids by Siemens Hearing Solutions and Phonak Hearing Systems are examples of this approach (Masters and Mathy 2002).

However, there is much research work being undertaken to improve the RP processes to enable them to be used as manufacturing alternatives. A current research project that is looking into one of the important aspects is the ‘Design for Rapid Manufacturing’ project at Loughborough University, UK (EPSRC 2001). The aim of the project is to investigate how the advent of RM will affect the design and manufacturing phases of complex plastic components and to characterize fully and analyse the material properties of state of the art RP materials that are aimed at end-use manufacture, to enable designers to have confidence in specifying the materials for their designs. The research project is funded by the Engineering Physical Sciences Research Council (EPSRC), as part of the Innovative Manufacturing Research Centre (IMRC) at Loughborough. The project’s industrial partners include: 3D Systems, Custom Design Technologies Ltd, Delphi Automotive Systems, Jaguar and Land Rover Research, MG Rover Group and Huntsman (formerly Vantico). They represent a mixture of SME’s, leading world RP machine and materials suppliers and a cross-section of the UK’s car manufacturers and suppliers.
Material and design considerations for RP

In addition to the design aspects (Hague et al. 2003), one of the main areas of the Design for Rapid Manufacture project concerns the characterization and analysis of the mechanical properties of two materials manufactured using a stereolithography RP machine. The materials tested were SL7560 by Huntsman and SI40 by 3D Systems—both materials represent the state of the art in SL materials and are aimed more for manufacturing purposes as it is considered that their mechanical properties are approaching those of traditional engineering plastics which will allow them to be used in more demanding end-use applications.

The overall objectives of the research project are as follows:

- **Materials data:** One of the main reasons that RP processes are rarely used to produce end-use parts is the lack of data on materials available to designers. If designers want to use RP and future RM machines for manufacturing purposes, a comprehensive set of materials data is required to give them the necessary confidence to select the right material for the intended service environment.

- **Design approach:** RM processes can produce parts of any shape complexity without need for any tooling. This ability enables designers to be free from the constraints of DFM and therefore they are able to design products without any constraints. The objective of this aspect is to investigate the freedom of design afforded by RM. To achieve this, a number of design investigations have been conducted throughout the Design for Rapid Manufacture project.

The work being undertaken on the research project is the first to be conducted in the area worldwide. Therefore, the Design for Rapid Manufacture project is scoping rather than solving many of the issues raised with many new research areas evolving from the investigations.

### 1.1. Limitations

Current RP machines cannot be considered as full RM machines as the produced parts have certain inherent drawbacks and limitations. Poor surface finish, lack of dimensional accuracy and generous tolerances have long been considered the Achilles’ heel with regards to the RP processes (Shen et al. 2000, Volpato et al. 2000). In addition, the range of materials available to these processes is at present limited and expensive in comparison with existing manufacturing processes. In the case of injection moulding, for example, there are multiple materials available that can be processed in the same machine (Dickens 2001). Another constraint concerns the build-time for components, especially for large parts, which is very slow in comparison with conventional manufacturing (Hopkinson 2000).

To study the possibilities for design, it is assumed that the above-mentioned problems have been resolved and that RP machines have been successfully converted to fully functional RM machines. RP machines are used on the project and though it is recognized that there are limitations with these processes, it is the concept of using the additive manufacturing methodology that is important, rather than the specific processes used. The two RP machines selected for use on this project are: SLA 7000 (stereolithography) and LS Vanguard Si2 (laser sintering). However, these high-end systems were selected due to their potential for conversion to future manufacturing systems and though the materials tested were produced on prototyping rather ‘manufacturing’ machines, it is considered that their material properties are such that they are suitable for end-use part manufacture — indeed, there are now several
examples of where these processes and materials have been used for actual end-use applications (Hague 2003, Tuck et al. 2003). Thus the characterization and analysis of the properties of these materials under various ageing, temperature and humidity conditions is of importance.

Investigations are confined to plastic materials as the RM processes are considered, in the short term, to be a suitable alternative to conventional plastic manufacturing processes such as injection moulding. Also, currently, the usage of non-plastic materials in RP/RM processes is limited.

1.2. Scope of the investigations

As RP machines have historically rarely been used to produce fully functioning end-use parts, there has not been an overriding need or demand to know their full material properties. However, as mentioned previously, increasingly RP parts are being used in end-use part manufacture (RM) and therefore it is vital that designers are made aware of the various mechanical properties of the materials produced on the RP systems to give them more confidence in specifying the materials in their designs. Limited information is available but there are large gaps in the data set.

For automotive applications, designers typically need material properties ranging from $-40$ to $+140^\circ C$. Therefore, the research project is undertaking an extensive material's testing program for the two SL materials over this temperature range, at three different humidities (dry, 50% relative humidity (RH) and totally immersed in water) and also over extended time periods (1, 4, 13, 26 and 52 weeks) to consider ageing of materials. This represents the most significant data generation for materials being used in RP and RM to date, with each material requiring around 5500 individual tests. To conduct the proposed investigations, initial tests were conducted which yielded some interesting aspects of these two resins. Along with the design aspects, it is these initial investigations that are detailed in the paper. The on-going ageing results will be published in due course.

2. Materials' data

To generate the required data, three RP plastic materials have been selected for this investigation. Two of them are stereolithography based (SL7560 resin from Huntsman (formerly Vantico) and Accura S140, from 3D Systems) and one for the Laser Sintering process (Duraform PA, also from 3D Systems).

2.1. Proposed investigations

An extensive range of mechanical properties, including tensile, flexural and Izod impact tests, are being investigated according to various International Standards Organisation standards (1996, 1997a, b, 2001). These tests were selected in close consultation with the project’s industrial partners that are predominantly comprised of materials suppliers and car manufacturers. Although other material properties such as hardness, fatigue and creep are also important to them, it was necessary to rationalize the number and variety of tests conducted due to the time restrictions involved and thus the tests that were selected represent the most critical ones for the project partners. For many industries and in particular the automotive sector, which is the main beneficiary of this project, designers need material properties ranging from $-40$ to $+140^\circ C$. Therefore, the above mentioned properties for the three plastics were investigated over this temperature range with different humidities (dry, controlled (50% RH) and wet) and also over extended times (1, 4, 13, 26,
52 weeks) to consider how these properties change over time. All samples were stored at 20°C.

Before undertaking the research project’s main programme of comprehensive materials testing, as detailed above, the results of which will be disseminated due course, a range of essential preliminary investigations were undertaken which yielded some interesting results. In this paper, three of these initial investigations are presented. The merits and reasons for conducting each preliminary investigation are given in its respective section. The default fabrication parameters, recommended by the machine and materials suppliers were used for building the parts.

All the tests were undertaken in a temperature and humidity controlled room. The tensile and flexural tests were performed on a ZWICK Z030 (Zwick) tensile test machine with a nitrogen facility for low temperature tests combined with a ZWICK heated cabinet for the higher temperature tests. A ZWICK 5102 pendulum impact tester, configured for Izod tests, was used for the impact analysis.

2.1.1. Isotropy tests

Due to the additive layer-wise manufacturing techniques used, it was important to evaluate and confirm previous work concerning the isotropic/anisotropic behaviour of the processes. If isotropic, this would allow the freedom of choosing the build orientation without affecting the mechanical properties of produced samples or parts. In addition, if parts produced are anisotropic, it means the number of samples to be tested would potentially be increased threefold to consider the three main build orientations.

The investigations included tensile, flexural and impact tests that were conducted at 20°C. The samples were produced in three different orientations (flat, upright and edge) as depicted in figure 1 (for the tensile samples). Similar build orientations were used for the impact and flexural test samples. The tests were conducted according to ISO standards and table 1 shows the averages (for 10 samples) of the conducted tests for SL7560.

Figure 1. Three build orientations (for tensile specimens).
It can be seen from the results in table 1 that the maximum variation in mechanical properties of SL7560 resin is less than 5%. Similar results were found for the Accura SI40 resin. Therefore, it can be concluded that the stereolithography process produces broadly isotropic parts and that the build orientation has little effect on the mechanical properties of parts. These results are fully consistent with previous published works (Hague 1997, Dulieu-Barton 2000).

Therefore, from this work it can be concluded that for the SL process, the build orientation can be optimized for either the reduction of build time, limitation of support structures or improvement of surface finish (to reduce the stair-step effect) without any consideration for influencing the mechanical properties.

Table 2 shows the results of a similar investigation of the laser sintered Duraform material. It can be seen that the percentage variations in mechanical properties exceed 5% and therefore this material can be considered to be anisotropic. This is also consistent with other published works that indicates the mechanical properties of parts produced on LS machines are dependent on the build orientation (Gibson and Shi 1997, Hur et al. 2001).
This anisotropy that is found in laser sintered parts is further exacerbated by the scanning methodology employed in the particular laser sintering machine used (Vanguard SI by 3D Systems) which only hatch-scans in the ‘x’ direction for each successive layer. This scanning methodology can lead to further anisotropic effects being displayed. Other researchers (Srithonbchai et al. 2003) have highlighted problems associated with the anisotropy of the materials in employing the laser sintering processes for manufacturing structural parts from Duraform PA.

2.1.2. Effect of notch manufacturing method on impact strength

In conventional impact testing, the required notches are usually mechanically introduced into the test samples—indeed, this is specified in the relevant ISO Standard. However, with RP/RM processes it is entirely possible to include the notch into the CAD file and manufacture this design detail as the part is being built.

Notches were introduced into a group of ten Accura SI40 impact samples using a mechanical method (Izod notching was used). These samples were tested and compared with another group that were produced with notch being introduced using the SL machine. Similar investigations were carried out for the SL7560 and Duraform materials. To minimize the staircase effect of the build process on the notch profile, all the samples under investigation were built in the flat orientation, as shown in figure 1 (for tensile test samples). The averaged impact strength for all groups of samples being produced is shown in table 3. Figures 2(a, b) show scanning electron microscope pictures of mechanically and SL-notched samples for Accura SI40 resin, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mechanically manufactured</th>
<th>Build process manufactured</th>
<th>Percent improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SL7560</td>
<td>2.4</td>
<td>5.7</td>
<td>137.5</td>
</tr>
<tr>
<td>Accura SI40</td>
<td>2.5</td>
<td>4.2</td>
<td>68.0</td>
</tr>
<tr>
<td>Duraform PA</td>
<td>3.8</td>
<td>4.5</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 3. RP versus machine manufactured notch.

Figure 2. Scanning electron microscope presentation of Accura SI40 resin after sputter coating (tilt angle = 45°): (a) mechanically manufactured notch; (b) stereolithography manufactured notch.
Table 3 shows that the impact resistance of the SL-notched samples has improved considerably and, in the case of the stereolithography process, the improvement has been considerable in comparison with the mechanically notched samples. Figure 2(b) shows the border curing, which has resulted from the notch profile being manufactured on a stereolithography machine and it is this border curing that has had the profound affect on the impact strength. This effect clearly does not exist on the mechanically manufactured notch as shown in figure 2(a), which has also shown to be damaged during the notching phase.

This increase in the impact strength has potentially a great impact on the design of features such as self-tapping screw threads, gear teeth, etc. If the screw thread were actually designed into the CAD model and then produced via the RM process, then this would afford a much greater resistance to failure than if the self-tapping screw was directly screwed into the produced part.

2.1.3. Effect of temperature on materials properties

One of the main objectives of the project is to investigate the materials properties of the selected RP plastics at a temperature range of -40 to 140°C and under three humidities (dry, controlled and wet) and over intervals of 1, 4, 13, 26 and 52 weeks. These investigations are currently being conducted for all three materials and results will be published in due course. However, some interesting initial results of the temperature range work are given here.

Figure 3 shows the ultimate tensile strength of SL7560, Accura SI40 and Duraform PA, respectively, over the temperature range -40 to 140°C. It can be seen that at ambient and lower temperatures, the ultimate tensile strength (UTS) of two SLA resins are higher than the LS thermoplastic material. However, the Duraform PA exhibits more stable UTS characteristics at a wider temperature range (-40 to +50°C). In addition, at the temperature of above 80°C, the UTS of the two SL resins deteriorate considerably in comparison with the LS material.

Investigations into the Young's Modulus of these materials showed similar patterns. However, above 70°C, this mechanical property reduces to virtually zero for both the SL resins tested due to the materials passing their glass transition temperatures (T_g) (Hague 1997).

![Figure 3. Ultimate tensile strength versus temperature for the three investigated materials.](image-url)
3. Design and Rapid Manufacturing

The main feature of RM processes is the ability to produce parts of any shape complexity without the need for any tooling. The impact of this factor on the validity of guidelines which designers comply with when they are designing for manufacture (DFM) and assembly (DFA) are investigated.

3.1. Design for Manufacturing

DFM is a philosophy or mindset in which manufacturing input is used at the earliest stages of design in order to design parts and products that can be produced more easily and more economically. Design for manufacturing is any aspect of the design process in which the issues involved in manufacturing the designed object are considered explicitly with a view to influencing the design. Some principles are used for efficient manufacturing, such as: developing a modular design, using standard components, designing for multi-use and to be multifunctional. By far the most important principle is to design for ease of manufacture and fabrication, which could be different depending on the manufacturing processes adopted. These guidelines are well documented elsewhere (Boothroyd et al. 1994, Poli 2001).

3.1.1. DFM guidelines for injection moulding

As the range of plastic products being produced by RP and RM processes are quite comparable with those of injection moulding of plastics, some of the rules necessary for injection moulding are given to provide a basis for the consideration of design rules for RM:

- **Draft angles**: Important for ease of removal of parts from moulds. The inclusion of draft angles at the design stage is very important, but often omitted.
- **Minimizing re-entrant features**: ‘An easy to manufacture part’ must be easily ejected from the mould. Designing undercuts requires the use of side cores. This in turn will require moving parts in the dies that add to the tooling costs considerably. Some parts containing features such as blind holes and galleries are impossible to manufacture without using very complex and expensive tooling arrangements.
- **Wall thickness consideration**: Components with thin walls solidify faster, hence reducing warpage and production costs.
- **Uniform wall thickness**: Non-uniform wall thickness will result in compression and expansion of molecules, resulting in compressive and tensile stresses. The stress in turn will result in cracks, crazing or fractures of moulded parts.
- **Minimizing weld lines**: When different flow fronts (due to obstruction within the mould or various gates) meet each other, this creates weld or fusion lines. These are a source of weakness within the part and should be minimized during design.
- **Avoiding sharp corners**: Will provide tensile, compressive and shear stress on the moulded parts, which in turn will become stress concentration points, leading to part failure.
- **Ejection pin marks and gate marks**: Could have an adverse aesthetic effect on the injection-moulded part. However, with adequate consideration their impact could be minimized.
• **Parting line**: The direction of mould closure and parting line is also crucial in tooling and injected parts. Much consideration and deliberation is needed for their selection.

• **Minimizing sink marks**: Are formed when a thin section becomes solid sooner than a developed thicker section. Sink marks could be less apparent by adequate consideration during design.

### 3.1.2. Design for Assembly (DFA)

By adopting DFA guidelines at the design stage, significant reductions in manufacturing cost and improvements in the ease of assembly can be achieved (Fox *et al.* 2001). A few of these guidelines are briefly given here (Boothroyd *et al.* 1994, Poli 2001).

- **Reducing parts count**: Eliminating unnecessary parts, combining parts or eliminating or reducing the number of fasteners could achieve this.

- **Reducing handling time**: A few simple, logical and effective rules such as avoiding tangling and nesting parts or using easy to handle symmetrical parts, would result in a more efficient assembly.

- **Ease of insertion**: Designing parts that are easy to align, easy to insert and self locating with no need to be held in place before insertion of the next part.

### 3.2. Impact of RM on DFM and DFA

As the first RM processes will most probably be plastic processing systems, the most immediate competition will be with injection moulding. RM, unlike injection moulding, is a tool-less process, which does not involve any melting and subsequent solidification of materials within the confines of a tool. Therefore, considerations for constant wall thickness (to aid the flow of material), avoidance of sharp corners and minimizing weld lines, sink marks, ejection pins, gates marks and draft angles will no longer need to be considered.

However, the significant impact of RM will be on the guidelines associated with minimizing complex geometries and features such as under-cuts, blind holes, screws, etc. Incorporating such features in conventional injection moulding is not impossible but often requires expensive tooling, extensive tool set ups, testing runs and prototyping. This inevitably leads to undesirable lead times and costs. In addition, any simple modification in design requires a new set of tooling. However, as RM is a tool-less process, the part complexity is not important and any complex shapes or features produced by CAD can be directly translated into the final product. This is in marked contrast to conventional manufacturing processes.

Also, in injection moulding, the selection of the correct location for the split line—in particular for asymmetrical and complex shaped components—is quite difficult and is largely dependent on the experience of the tool designer. However, by adopting RM processes and not using any tooling, designers will be entirely freed from this task.

By using RM technologies, it will be possible to reduce the number of parts within an assembly. Therefore, the most important DFA guideline, which concerns the reduction in part count, is easily achievable. In theory it is possible to reduce the number of parts to just one, though in practice this may not feasible as parts are
generally not being used in isolation and their interaction with other components would impose limitations on parts count.

4. Design Investigations
To investigate the above-mentioned impact, a number of parts being produced by industrial partners on this project were considered and two of them are discussed. Through these design investigations, a number of guidelines for design for rapid manufacture (DFRM) and assembly were established. Designers should adopt these general rules when they are designing for rapid manufacturing.

4.1. Front plate of a diesel fuel injection system
Delphi Diesel Systems (DDS, Gillingham, UK, part of Delphi Automotive Systems) nominated the part for this case study. With the continued increase of diesel fuel penetration around the world and especially in Europe, DDS has a strong position in diesel fuel injection systems.

Figure 4 represents an isometric view of the fuel injection system assembly that has been designed for diesel engines in cars, vans and heavy-duty vehicles. The front component, i.e. the subject of this design investigation, is not yet in mass production. However, for vehicle evaluations, 1000 pumps will be produced in 2003. Though the exact production volumes are still unclear, Delphi has a high level of variety with these parts as they interface to the customer’s engine and a typical forecast for one variety is around 350,000 parts per annum.

The pump is fitted either to the end of the cylinder head or to the timing case of an engine. The operating temperature could be as high 200°C due to a heat-sink effect. It has to cope with exposure to water, oil, diesel fuel (including biofuels—fuel with a vegetable oil content) and salt spray. The environmental testing and usage ranges from −40 to +140°C. Investment casting followed by a number of machining operations will produce the first evaluation batch. The production parts are likely to be gravity castings, which are currently being developed.
The produced castings will subsequently undergo secondary operations that consist of machining (drilling holes with long gun-drills), deburring, resin impregnation to avoid any porosity and, finally, the assembly of blanking balls to block off the ends of the long drilled holes. Cleanliness is critical with these plates, so washing and sealed packaging are the final activities at the suppliers before the parts are shipped to Delphi for final assembly.

4.1.1. Redesigning for Rapid Manufacturing

The proposed manufacturing requires dedicated machine tools and gun-drills for secondary operations to create long holes that are subsequently required to be blanked off. Figure 5 shows the sectional view of the CAD model of such a plate with holes numbered 1–4 that need to be blanked off. This is expensive and time consuming. It also allows the possibility of fuel leakage during the service life of the part. This is not just messy, but a potential safety hazard. In addition, the inability to create non-straight galleries has imposed some constraints regarding facilitating low-pressure circuit fuel flow and a small footprint for installation on different engine sizes.

Delphi Automotive Systems is currently investigating the possibility of using injection moulding for producing this front plate. Concurrently, with the advent of properties of RP and RM materials, a feasibility study of its manufacturing by a plastic RM technique has also been considered.

Therefore, the front plate was redesigned for RM and figure 6 shows the sectional view of a laser-sintered part. The blind galleries and non-straight hole have been incorporated within the part (for better presentation these are sprayed with a black colour). The part was also produced in SL7560 resin. However, removing support structures within the inside of the galleries and especially the blind holes proved difficult, time consuming and at times impossible with parts produced via the SL process.

Through this case study, a number of limitations associated with conventional manufacturing processes have been removed. The potential benefits gained by

![Figure 5. Sectional view of a front plate computer-aided design model.](image-url)
Figure 6. Sectional view of a laser sintered part.

<table>
<thead>
<tr>
<th>Feature</th>
<th>RM approach</th>
<th>Proposed approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elimination of secondary machining</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Introduction of non-straight holes</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Eliminating blanking off holes</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Creating blank holes</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Removal of draft angles</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Non-straight flow path</td>
<td>✓</td>
<td>✕</td>
</tr>
<tr>
<td>Selecting materials with correct properties</td>
<td>✕</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 4. Features offered by RM and Delphi's proposed manufacturing approach.

Delphi Diesel Systems for future manufacturing were considerable. By adopting RM techniques it would be possible to eliminate extensive secondary operations needed in conventional manufacturing, creating encapsulated blank holes, introducing a labyrinth of non-straight holes that not only improves the fuel flow path, but that could reduce the part footprint and thus minimize the material usage. In addition, blanking holes have been eliminated, thus removing the potential for fuel leakage during the service. Table 4 shows a comparison between various features offered by the two manufacturing approaches. However, the major limitation associated with RP and RM processes is the selection of a suitable material to withstand the operating environment for this part. Currently the usage of metals in RP and RM is very limited (Mansour et al. 2003), therefore the only alternative is plastic (thermoplastics and thermosets) which currently do not satisfy the operating temperature range of $-40$ to $140^\circ$C, as specified by Delphi.

4.1.2. Cost analysis

To evaluate the financial feasibility of using the current RP process for the production of the front plate, a cost analysis exercise was conducted in conjunction with Delphi Diesel Systems. The front plate is currently in the evaluation phase
Table 5. Cost analysis for manufacturing evaluation of parts.

<table>
<thead>
<tr>
<th>Number of parts</th>
<th>SLA tooling</th>
<th>Conventional tooling</th>
<th>Laser sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>up to 10</td>
<td>£1080/part</td>
<td></td>
<td>£59.65/part</td>
</tr>
<tr>
<td>up to 50</td>
<td>£760/part</td>
<td></td>
<td>£59.65/part</td>
</tr>
<tr>
<td>200–1000</td>
<td>£243.30/part</td>
<td></td>
<td>£59.65/part</td>
</tr>
</tbody>
</table>

before full production with the cost of production at this phase largely being dependent on the number of evaluation parts being produced. For producing up to 80 parts, investment casting with stereolithography tooling for producing waxes is used. For larger volumes of up to 10 000 units, investment casting using aluminium tooling for producing waxes has been adopted. Therefore, depending on the number of evaluation parts being produced, a considerable variation in production costs has been obtained. The cost analysis is given in table 5, which also includes the cost of producing the front plate with laser sintering system (obtained from a number of RP bureaux).

There is number of issues contained in table 5 that should be taken into consideration:

- All the costs shown for investment cast parts (SL or aluminium tools) do not include the secondary machining operations (gun-drilling, blanking off blind holes, etc.). These operations would have a significant effect on the cost of the part, though it should be noted that for the investment castings from SL tooling that the costs reduced with an increase in production volume (due to the amortization of the jigging and fixturing set-up costs).
- For low volume production, such as for evaluation parts, Laser Sintering is quite comparable with the investment casting process. This supports other research in this area (Hopkinson 2000) which has concluded, depending on the dimensions and complexity of the part geometry considered, that for low to medium volume production, RP processes, are already competitive with conventional manufacturing processes. No costs were available at the time of writing for the production parts.

4.2. Electronic enclosure

Custom Design Technologies Ltd is an SME and manufacturer of custom designed plastic enclosures. These are made without the need for expensive and traditional mould tooling. This is a fast moving market requiring well engineered, high quality products in small to medium quantities ranging from one to a maximum of 1000 parts, with 200–300 being a more representative production volume. This company combines a flat sheet-plastic fabrication processes with computer numerical control (CNC) machining to provide a fast, cheap and flexible alternative to injection moulding for the manufacturing of electronic enclosures. Two types of sheet plastic are mainly used and these include high impact polystyrene (HIPS) and ABS.
There are a number of limitations and disadvantages associated with this manufacturing approach:

- Simple appearance: due to the manufacturing processes employed, it is only possible to produce flat surfaces with angular corners that give a somewhat dated appearance. Additionally, few aesthetical and ergonomic features can be added and thus the scope for enhanced design is extremely limited.
- High parts count: again, due to the manufacturing process, it is usually necessary to produce the enclosures in several pieces, therefore necessitating an assembly stage.

Figure 7 shows a typical part that is currently being produced.

The low manufacturing volumes and current design restrictions lends the type of component built by Custom Design Technologies as ideally suited to be considered for RM. Therefore an investigation was initiated to redesign the enclosure featured in figure 7 for RM.

Like any product development exercise, after establishing the initial customer specifications, the process of concept generation began with an industrial designer sketching a number of alternative proposals. After a number of iterations, the industrial partner selected a design. The final design represented a balance between functional and aesthetic requirements and included a number of features that were ideal for RM. The chosen design can be seen in figure 8.

In the detailed design stage, a Unigraphics CAD system was used to create the model of the selected design. Finally, using the stereolithography process, the CAD model was converted to a physical part. Five pieces were produced simultaneously, lasting 18 hours and a further 15 hours was taken up by post-processing and finishing. The newly redesigned part for RM was surface processed and coated to provide a textured finish. Figure 9 shows the final coated product.
This case study, due to imposed constraints by the components interacting with it, was relatively simple to be redesigned for RM. However, it illustrates well some of the advantages of RM. Though subjective, the redesigned part is more stylish, attractive and contains more flexible feature lines for both aesthetic and ergonomic considerations. It also contains re-entrant features that would be difficult or expensive to manufacture by other means. Additionally, the number of parts is reduced from three to one, which improves the assembly issues.

5. Conclusions

This paper explored the design aspects of RM processes. Additionally, DFM guidelines for injection moulding process and DFA rules were investigated. It was concluded that due to the tool-less nature of these processes, any part geometry complexity could be obtained without consideration for constraints imposed by the need to remove the produced part from a mould or die. A number of design investigations to support this have been conducted and two were introduced.

Engineering and aesthetic design are carried out as part of the early stages of the product design and development process, and the shortest lead times are often achieved when the various activities incorporate as much concurrency as possible. The introduction of RM has wider implications since the digital CAD model created can be used as the basis for the interaction of other downstream engineering functions. In the future, it is likely that a new breed of ‘super designer’ able to function with both aesthetic and mechanical design will be required—these two functions are generally separated in the products design phase.

As part of this research, a comprehensive materials data generation exercise was also carried out and three RP/RM materials, namely SL7560 and Accura SI40 stereolithography resins and Duraform PA laser sintering, were investigated.

The results of the impact tests show that, potentially, if features such as screw threads or gear teeth are introduced at the design stage, then this will increase their resistance to damage due to the increased impact strength afforded to the parts. However, the percentage of improvement varied among the three materials.

The effect of temperature on UTS and Young's modulus of the three materials was investigated. It can be concluded that the UTS and stiffness of SLA resins are higher than LS material, but Duraform PA maintains these properties at a wider temperature range.
In addition, it can be concluded that the SL parts are broadly isotropic and that the build orientation does not affect their mechanical properties. However, laser-sintered parts are anisotropic and build orientation will affect the surface quality and production time as well as their materials properties, and this will affect the design of the parts produced via laser sintering.

Appendix: Notation

- $\sigma_{\text{UTS}}$: ultimate tensile strength,
- $\varepsilon$: elongation at fracture,
- $\sigma_f$: flexural strength,
- $E_f$: flexural modulus,
- $a_i$: Izod impact strength.

Acknowledgements

The authors thank the UK Engineering and Physical Research Council (EPSRC) and the project partners, which included 3D Systems, Custom Design Technologies Ltd, Delphi Automotive Systems, Jaguar and Land Rover Research, MG Rover Group and Huntsman.

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Zwick Co. (available at: http://www.zwick.com/).