Stress relaxation behaviour in compression and some other mechanical properties of thermoplastic-elastomer

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STRESS RELAXATION BEHAVIOUR IN COMPRESSION AND
SOME OTHER MECHANICAL PROPERTIES OF
THERMOPLASTIC-ELASTOMER

by

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A Doctoral Thesis submitted in partial fulfilment of the
requirements for the award of the degree of

DOCTOR OF PHILOSOPHY

at Loughborough University of Technology, U.K.

MARCH 1990

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TEMOFEBI G. GORDONS.
DEDICATION

In everlasting memory of my dearest PARENTS who have encouraged me in the pursuit of my research programme, but did not live to see the fruit of my endeavour, through their DEATH (MAY THEIR SOULS REST IN PERFECT PEACE).
ACKNOWLEDGEMENT

I wish to express my sincere regards and appreciation to my ever-ready, ever-willing and kind supervisor (Prof. A.W. Birley) for his unrelentless guidance, advises and some financial assistance throughout my research programme. My heartiest gratitude and thanks also to Dr./Mrs. Margaret King, Mr. Keith Cuff and Mr Jones (higher awards office) for their encouragements and supports.

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My special thanks to Dr C. Hepburn for his useful advises and kind interest in my research programme and all that love me, God bless.
CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this Thesis, that the original work is my own except as specified in references, footnotes and acknowledgements, and that neither the Thesis nor the original work contained therein has been submitted to this or any other institution for a higher degree.

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T. G. Gordon.

FEB. 1990
SYNOPSIS

Thermoplastic elastomers have been found to have unusual properties, a consequence of composition and structure. The molecular composition comprises hard thermoplastic blocks which aggregate into domains, and flexible elastomer blocks in a linear or inter-penetrating structure. The mechanical properties such as stress relaxation, tensile strength, elongation, recovery and hardness of some thermoplastic elastomers have been studied in some detail. The stress relaxation studies have been made possible with the development of the stress relaxation measuring equipment at the Institute of Polymer Technology. Highly accurate and reproducible results were obtained from the "ideal curve" measurements taken with the equipment, which permits continuous measurements of residual force and instantaneous modulus. It was noted that stress relaxation, while not only dependent on thermoplastic type and/or formulation (as expected) but also depended on the measuring technique (e.g. the strain rate, continuous loading, interrupted loading etc.) which have significant effects on subsequent stress relaxation. Temperature and environment also affect the results.

The effect of thermal treatment, lubrication of surfaces and interrupted loading were investigated. An attempt was made to relate the modulus enhancement factor "MEF" to Hysteresis. An attempt was also made to relate the change in "MEF" to the continuous structural re-organization in the material and finally to stress relaxation. The commercial significance of stress relaxation and "MEF" in the performance of seals and gaskets is also explored.

Some of the material supplied by industry for this project was prepared by "dynamic vulcanization". Attempt has been made using peroxide cross-linking agent to prepare EPDM/PP blends by this technique to explore structure-property relationship. As expected, the cured samples out-performed the uncured samples.

Long term stress relaxation measurement (up to 10,000 hours) revealed the low permanent set and modest stress relaxation associated with thermoplastic elastomers in general.
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CHAPTER (1)

GENERAL INTRODUCTION

1.1 BACKGROUND TO THE MATERIAL

1.1.1 POLYMER

The term "POLYMER" is taken as synonymous with the term "PLASTIC" but in fact there is a distinction. The polymer is the pure material which results from the process of polymerisation and usually taken as family name for material that have long chain molecules. The term plastic is applied when additives are present in polymer (1).

A polymer may be defined as a large molecule constructed from many smaller structural units called monomers or mers, covalently bonded together.

It is more accurate in certain cases to call the repeating unit a monomer residue as atoms are eliminated from the simple monomeric unit during polymerisation processes (2).

It would be difficult to visualise our modern world without plastics. Today they are an integral part of every-one's lifestyle with applications varying from commonplace article to sophisticated scientific and medical instruments. Designers and engineers readily turn to plastics because they offer combinations of properties not available in any other material, such as toughness, resilience, resistance to corrosion, transparency, easy processing, colour fastness, etc. Although they also have their limitations, their exploitation is limited only by the ingenuity of scientists.

The development of both polymer science and industry can be
acknowledged to date back to the days of Hancock (1820) and Goodyear (1839) in the early 19th century, both of whom discovered independently sulphur cross-linking process (vulcanization) in raw rubber, Hancock (1843), Goodyear (1851). Most of the early work was carried out on naturally occurring polymers, such as cellulose, casein, natural rubber etc. The plasticization of cellulose nitrate with camphor instead of castor-oil by J W Hyatt in 1870 opened another era in the development of plastics. Cellulose and casein based plastics then developed as commercial plastics and held the market for over thirty years.

The shortage of raw materials brought about by the blockade during the world war (1) forced German chemists in 1917 to develop synthetic "methyl rubber" and since then, launch what is now a thriving synthetic rubber industry. Progress had been hampered by the lack of the fundamental knowledge of the structure of these materials. Cellulose was thought to be a cyclic tetrasaccharide and rubber merely a ring, composed of two isoprene molecules. It was the pioneering work of Hermann Staudinger in the early 20th century that led to the concept that these molecules were actually long sequences of small structural units held together by covalent bonds to form large chains or macromolecules.

Polymers can be found occurring naturally as cellulose, natural rubber etc. or are produced synthetically as polyethylene, polypropylene, polystyrene, etc. Their physical properties differ so much that their behaviour can range from viscous liquid, flexible and elastic materials (rubber) to rigid plastics(3) as a result of structural diversity found in them. This also makes possible their use in variety of applications. A schematic classification (as represented in figure
1.1) groups the materials under convenient headings. A useful subdivision by Carothers\(^{(4)}\) (1929) which differentiates between condensation polymer, in which the molecular formula of the structural unit(s) lack certain atoms present in original monomer from which it is formed and addition polymer, in which the molecular formula of the structural unit(s) is identical with that of the polymer derived. Polymers can be either naturally occurring or man-made.

![Schematic Representation of Polymer Classification](image)

**Figure 1.1**

"Schematic Representation of Polymer Classification"

Polymer types include (1) HOMOPOLYMER, in which one species of monomer is used to build a macromolecule, simply referred to as "polymer"

(2) COPOLYMER, in which the chain is composed of two types of monomer units.

(3) TERPOLYMER, when three different monomers are incorporated in one chain.

Copolymers prepared from bifunctional monomers fall into four
categories:

(i) **Random copolymer**: in which the disposition of the monomers in the chain is essentially random.

(ii) **Alternating copolymer**: in which monomers alternate in regular placement along the chain.

(iii) **Graft copolymer**: in which branches of one homopolymer are grafted onto the main chain of another homopolymer.

(iv) **Block copolymer**: in which the chain is built up of blocks of different homopolymer chemically bonded to each other.

### 1.1.2 **ELASTOMERS**

From the preceding section we saw how polymer types differ. It is possible therefore to define clearly what one means by the term "Rubber" and/or "Elastomer". The American Society for Testing and Materials defines rubber as a material which is capable of recovering from large deformations quickly and forcibly and which can be or has been modified to a state essentially insoluble in solvent\(^5\). A rubber in the modified state, free of diluents, is insoluble (but may swell) in boiling benzene, methyl ethyl ketone or ethanol-toluene azeotrope. A rubber will retract within one minute to less than 1.5 times its original length, after being stretched to twice its length and held for one minute before release. This is not a simple definition but it covers all the essential points. The words "Elastomer and "Rubber" are often taken as synonymous but elastomer is a more general term used to describe a rubber-like material. There now exists a wide variety of synthetic products whose structures differ markedly from that of naturally occurring rubber but whose elastic properties are comparable to, and sometimes better than the natural product. The
early source of rubber was the latex obtained by puncturing the bark of the tree "Hevea-brasiliensis". It was first used by the Central and South American Indians and was call "Caoutchouc" and it formed the largest source of supply to the early industries from which the present modern synthetic polymer industries were born. Typical elastomers include isoprene rubber, butyl rubber, ethylene-propylene rubber, etc.

1.1.3 PLASTICS

As pointed out above, polymer containing additive(s) may be referred to as "PLASTICS" but this will include elastomers (rubbers) as well, since there are now thermoplastic elastomers which fit both categories adequately, thus definition of a plastic can be difficult. A plastic can be rather inadequately defined as organic high polymer capable of changing its shape on application of force and retaining this shape on removal of the force. Plastic materials can be formed into complex shapes by the application of heat or pressure or both.

Plastic can further be sub-divided into:

(i) Thermosetting plastics:, in which the material becomes permanently hard when heated above a critical temperature and will not soften on reheating.

(ii) Thermoplastics:, in which the material becomes soft on reheating above its Tg. and hardens on cooling. This cycle can be carried out repeatedly. It is this property that allows for repeated reshaping of thermoplastic materials.

1.2 THERMOPLASTIC ELASTOMER

1.2.1 Conventional rubber is cross-linked by primary valence
interaction (bonding) whereas thermoplastic elastomers are
cross-linked by secondary valence interactions such as
Van-der-Waals interaction, dipole interaction, hydrogen bonding, etc.
The secondary bonding cross-linking breaks down at elevated
temperature or under the influence of suitable solvents and
reappears with decreasing temperature or on the removal of the
solvent. In principle no damage to the material results from the
breakdown and restoration of the cross-linking.

Thermoplastic elastomer shows two transition temperatures: a
lower one corresponding to the freezing-in or appearance of
molecular motion and upper one corresponding to the break down or
restoration of the secondary valence cross-linking. Softening takes
place within two temperature regions which may some time
superimpose, some times it is hardly possible to observe a clear
distinction between them. Since in both cases only secondary
interactions are involved, uniform softening processes have to be
considered. This processes may be described by a temperature and
time dependent formal number of cross-links per unit volume, \( N(T,t) \)
equal to the number of cross-links in a Gaussian net work which
would show the same modulus of elasticity as the material under
investigation. This number \( N(T,t) \) is the cross-link spectrum for the
thermoplastic elastomer. It refers simultaneously to the cross-linking
stability in a way and to the segment mobility. With increasing
temperature \( N(T,t) \) drops in two discrete steps corresponding to the
segment mobility setting in and cross-linking breaking down. Both
steps have been considered as part of one-and-the-same cross-link
spectrum since in many cases they are not clearly separable from
each other.
Thermoplastic elastomers are commonly segmented copolymers with hard and soft segments chemically linked to each other. A domain forms on segregation, characterised by one segment (the domain) dispersed in the other (the matrix). At service temperature the domains are usually crystalline or glassy, while the matrix is in the molten or rubbery state. Since the molecules consist of alternating soft and hard segments, each chain runs alternately through the domain and matrix. Thus the domains are linked with the matrix by primary valence interaction (chemical bonds). The matrix is (usually above its Tg at room temperature) in its molten state provides high extensibility, and the rigid hard domains prevent viscous flow, with the result that rubber elasticity is brought about. (Figure 1.2.1). The chains linking the domains are cross-linked due to secondary valence interactions within the domains. Cross-linking breaks down when the glass transition or melting temperature of the domain is exceeded.

Figure 1.2.1
Secondary valence cross-linking and domain formation by segmented chains in Thermoplastic Elastomer.
1.2.2 BLOCK COPOLYMER AS THERMOPLASTIC ELASTOMER

As pointed out in the last paragraph of section 1.2.1, block copolymers fall into these categories of polymer in view of the fact that they possess such molecular architecture that permits thermoplastic elastomer properties. (For the definition of block copolymer, see section 1.1.1.). The morphology of block copolymers generally (with particular reference to polystyrene-polybutadiene-polystyrene) has been reviewed\(^{(7,8)}\). The unique morphology and properties observed in them is a consequence of molecular structure. Elastic property is achieved if one of the component blocks is elastomeric in nature\(^{(9)}\) and is usually the soft segment having Tg below room temperature. (Figure 1.2.2) The hard segments provide the high modulus (rigidity) usually associated with these polymers. These properties are enhanced as a result of phase separation and the arrangement of the phases in the bulk polymer. Since the segments are chemically linked to each other, phase separation is limited to the micro scale. Phase separation in some polyblends is on a macro scale\(^{(10)}\) due to the absence of chemical bonding between the individual homopolymers, their incompatibility and, where present, high block molecular weight. On a molecular scale segment molecular weight is an important parameter governing domain formation. Investigation by Angelo and co-workers\(^{(11)}\) showed that high block molecular weight in styrene-butadiene-styrene block copolymer displayed multiphase transition corresponding to each constituent.
1.2.3 **BLOCK COPOLYMER STRUCTURAL ARCHITECTURE**

Within the general category of block copolymers there are several architectural variations that describe the sequential arrangements of the component segments. The importance of this characteristic sequential architecture can not be over-emphazised. It is a prime consideration in defining the synthetic technique to be used in preparing a specific block copolymer structure. Furthermore this factor plays a dominant role in determining the inherent properties attainable with a given pair of segments.

So far there are a number of architectural forms that have been studied. The three simplest ones are the diblock structural arrangement commonly referred to as the "A-B" diblock copolymer, composed of one segment of "A" repeat units and one segment of "B" repeat units. The second is the triblock form, referred to as "A-B-A" block copolymer structure in which the segment of the "B" repeat units is located between two segment of "A" repeat units. The third basic type is the -(A-B)_n- multiblock copolymer which contains many alternating "A" and "B" blocks. A schematic representation of these architectures can be seen in figure 1.2.2.
Another variation is the radial block copolymer but less common\(^9\). This structure takes the form of a star-shaped macro-molecule in which three or more diblock sequences radiate from a centre hub. Figure 1.2.3 shows two such structures.

*A 6-Point Radial*  \hspace{1cm}  *A 3-Radial*

**Figure 1.2.3**

"Some of the common structural features found in block copolymers (Figures 1.2.2 and 1.2.3)."
1.2.4 **DOMAIN MORPHOLOGY IN BLOCK COPOLYMERS**

As a result of the molecular structure of block copolymers unique morphological features and properties have long been recognised in them. The discussion pertaining to domain morphology will be limited to three basic types as observed in the A-B and A-B-A block copolymer systems.

The unique morphology results from the microphase separation of dissimilar polymer segments into distinct domains. Phase separation occurs in block copolymer because (among other reasons) of the incompatibility of the individual block segments with each other. Because the segments are chemically bonded to each other (hence forming a super-molecule, resulting in a restraint in the entropic term in the system) phase separation is limited to a micro-scale size i.e in the order of the molecular dimension of the segment forming the domain(12). Aggregation of the micro-phase give rise to specially organised domains of one component dispersed in the matrix (continuous phase) of the other.

The study of structures on this scale obviously calls for such analytical techniques as electron microscopy, small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS)(14,15). The last two techniques can be used in determining lattice parameters if an ordered phase separation is present in the sample, but for a more detailed structural assessment, electron microscopy is necessary. It has been found that generally, block copolymers containing between 10 and 90 percent of one block component are capable of showing one of the following three morphologies: for example, considering the hard phase

(i) one lamellar morphology is formed when its volume fraction is
between 32 to 65 %.

(ii) two cylindrical morphology or hexagonal lattice when the volume fraction is between (15 - 32) % and 

(iii) two spherical morphology or a cubic lattice, dispersed or embedded in the continuous phase (matrix) when the volume fraction is less than 15 %. (These are more evident especially when in solution). In (ii) and (iii) cases the second possibility is their inverted structures. The "Molau Diagram"(13) shows a sequence of morphological transitions from one form to the inverse of it, as shown in figure 1.2.4 (after Molau).

The conclusion that there are only three morphological structures - sphere, cylinder and lamella is not true, for recent evidence(16-18) shows that a complex morphology can develop in block copolymer of a particular composition or star block form. These bi-continuous structural morphologies are referred to as "Tetrapod"(16-18) and "Double Diamond"(17) and also have been established for small molecule systems(19). However no theory has yet been presented to deal with morphology in block copolymer.

The principal x-ray scattering phenomenon is the existence of one or several sharply defined reflections at low angles. This means that there is an under-lying periodic structure which is on appropriately large scale (typically in the range of several hundreds μm) to produce the scattering effects at small angle. The angle spacing then follows "Bragg's Law". Starting from zero to increasing diffraction angle spacing of consecutive orders were found to form a certain systematic sequences as developed by Luzatti(20) and Husson(21) and co-workers in their study of the structure of soap. 1:1/2:1/3:1/4 spacing sequence is consistent with a regular periodic arrangement
of parallel lamellae of infinite lateral extension, and the sequence of spacing ratios corresponding to the other morphological types can be found in the literature\(^{(22)}\).

In microscopy it is a common practice in sample preparation to stain the test sample in order to achieve better contrast. Kato\(^{(23)}\) has used Osmium tetraoxide vapour to stain SBS since Osmium reacts with the double bond in the polybutadiene but not the styrene, only the butadiene phase becomes stained and appeared black under transmitted light.

(i) **Lamella morphology:** When the ratio of the volume fractions of the two components is close to one (i.e. the volume fraction of one of the components varying from about 0.35 to 0.65) the diffraction pattern in both scattering analyses (SAXS and SANS) gives rise to sharp diffraction lines with Bragg-spacing consistent with a layered structure. This structure can be seen as plane parallel equidistant sheets, each sheet resulting from the superposition of two distinct layers, where each layer represents one of the block copolymer components. Electron micrographs of a lamella structure obtained by orthogonal ultrathin-sections of a sample show a striated structure, formed by parallel stripes of alternating black rubber phase (stained by Osmium tetraoxide) and white styrene phase.

(ii) **Cylindrical morphology or Hexagonal lattice:** In this case the theories of Meier\(^{(24,25)}\) Helfand\(^{(29)}\) and recently, Ohta\(^{(27)}\) and Kawasaki have predicted a 0.20 to 0.33 volume fraction for one of the compositions in an A-B or A-B-A structure for a cylindrical morphology (hexagonal lattice) to be formed. The diffraction patterns show lines with Braggs spacing consistent with a two dimensional regular array. An electron micrograph of a stained sample with such
a diffraction pattern allows one to observe two different structures showing the same family of patterns, one in which white spots hexagonally spaced, are immersed in a black background and the other in which black spots hexagonally arranged are spread in a white background. In both cases micrographs of sections taken perpendicular to the orientation above show the same striated structure as shown by the lamella lattice. This indicates the presence of a hexagonal cylindrical lattice dispersed in a continuous matrix. There are two possible morphologies that can be formed in this case. In the first case, as the polystyrene volume fraction varies from about 0.20 to 0.40 forming cylindrical domains and the dominant polybutadiene fills the space forming the matrix. When the polystyrene content is increased to between 0.6 to 0.85, the system inverts forming the so call inverted hexagonal lattice in which polybutadiene cylinders are dispersed in a polystyrene matrix. (see figure 1.2.4)

(iii) **Spherical morphology or Cubic lattice:** Predictions of the theories of Meier and Ohta/Kawasaki again show that the above lattice becomes possible at a volume fraction less than 0.20 for one component in contrast with Helfand prediction of less than 0.10. The diffraction pattern is characterised by lines of Braggs spacing typical of a cubic lattice. Again an electron micrograph of a stained sample showed two different structures corresponding to the same family. Two possible structures can also be obtained. In the first, when the styrene volume fraction is lower than 0.20 (section taken from any orientation showed white spots dispersed in black background). In the second, when the styrene content is increased to above 0.85 volume fraction the system is inverted, showing black spots
dispersed in a white background i.e the inverted cubic lattice in which the butadiene segregates into spheres in a styrene matrix.

As stated earlier, the work in the literature is based on linear block copolymers. However star-shape structures have also been studied and showed to produce similar morphologies\(^\text{(28)}\)

![Figure 1.4.4](image.png)

(a) Spherical Morphology or Hexagonal Lattice or Cubic Lattice

(b) Cylindrical Morphology

(c) Lamella Morphology

Increasing "A" (Hard Phase) component, assuming ● = "A"

Decreasing "A" or Increasing "B" (Soft Phase) component.

1.2.5 VARIABLES CONTROLLING PHASE SEPARATION AND DOMAIN FORMATION:

Phase separation (leading ultimately to domain formation) is a common characteristic of incompatible copolymers and polymer blends. The variables controlling this effect can be of a chemical or physical nature.

Chemical variables: These include the chemical nature of the blocks, type of block structure, the block lengths ratio, etc. Basically one might anticipate that the block length and the degree of chemical compositional dissimilarity of the two constituent polymers - judged by (for example) interaction or solubility parameter values - would
be the most important feature to be considered. In addition, the composition volume ratio is an important factor especially during phase transition (or simply morphological transition).

As pointed out elsewhere(9), in the limit of random copolymer where the block sequence of either unit is a very small number, it has been recognised that a one phase system is obtained. On the other hand, two high molecular weight homopolymers are usually highly incompatible with each other but nevertheless on a molecular scale, segment or block molecular weight is an important parameter governing domain formation. Angelo and co-workers(30) in their investigation showed that high block molecular weight styrene-butadiene block copolymer displayed multi-transitions corresponding to each constituent. Using Flory-Huggins theory which assumed that polymer-polymer interaction parameter (A) (i.e higher (A) value corresponds to greater separation) is the major parameter. Fedors(31) predicted the minimum molecular weight level required to produce phase separation, for example by his calculation an S-B-S block copolymer should have a minimum of (2500 - 6000 - 2500) block molecular weight in order to develop domain structure. Meier(32), in his theoretical calculation based on diffusion equation predicts between 5000 and 10,000 for styrene block when butadiene block molecular weight is of the order of 50,000 and 2.5 to 5 times higher for block copolymers than for simple homopolymer blends.

**Physical variables:** These include phenomena such as crystallinity, presence of diluents, etc in block copolymer. If the compositions are intrinsically incapable of crystallizing then the whole system will always be amorphous. On the other extreme should one or more components be capable of crystallizing, phase
separation is induced depending on whether one is above or below the melting points of the components. It is not the intention of the author to comment on the presence of diluent in block copolymer as this opens another dimension on this subject. Interested readers should consult the original reviews (12, 22).

Meier (12) has pointed out that phase separation is thermodynamically a consequence of chain perturbation (i.e. disturbances in the chain) brought about by a mismatch in molecular volume of the block copolymer compositions, therefore increasing the free energy of the system. When the mismatch becomes large enough the system will change its morphology in order to relieve the problem which also is a consequence of differences in density of the system.

1.2.6 EFFECT OF TEMPERATURE ON DOMAIN STRUCTURE

The effect of heat on the domain structure, in phase separated block copolymer has been the concern of many researchers in recent years (55-61). Heating to a high temperature has been found to affect domain structure significantly.

Grosius and co-workers (55) in their early experiments have reported measurements of structural parameters of domain dimensions, up to a temperature of 100°C for selected polystyrene, vinyl-pyridine (S-VP) copolymer. All the three morphologies were studied and showed no change. This was supported by the work of Richard and Thomason (57, 58) who showed that annealing at temperature below 120°C does not apparently produce great change in block copolymer structure, in contrast to what has been generally observed of the effect of heat treatment at high temperatures.
On heating, an oriented lamella styrene-isoprene diblock copolymer (Mn=98,000, 54% wt styrene) changed its domain spacing (57), increasing slightly with temperature in the range, from 20°C up to 110°C, then decreased to the initial value as shown by Hadziannou and Skoulios. At above 180°C the lamellae thickened and spacing began to increase again, rapidly with temperature, attaining values twice those quoted at room temperature. Above 250°C the x-ray pattern become devoid of diffraction signals. This was interpreted as the styrene phase becoming molten or gathering of the diffraction lines in the low Bragg angle region, where they can hardly be detected. On subsequent lowering of temperature the x-ray pattern remained blank, evidence of the loss of the single crystal nature of the sample. They extended this work to triblock copolymers, in general it was found that the disappearance of the lamella structure on heating proceeded through an irreversible stage where the lamella thickens considerably (ca.180°C) and they called this a melting temperature which appears to be independent of molecular weight (85) and structure, a conclusion contrary to any classical thermodynamic expectation.

Using SAXS of styrene/isoprene block copolymer (Mn = 43000, 47000, 47% wt styrene), Hashimoto (59) showed that the diffused lamella structure scattered x-rays at room temperature. He showed the corresponding domain spacing to be 260 x 10^{-12} m. On heating the scattering maximum disappeared when the temperature was raised to ca. 170°C and reappeared again at the same scattering angle with decreasing temperature. The transition temperature being much lower than that expected of a normal diblock copolymer (>220°C) due to the broad interface common with tapered block copolymers.
Kraus and Hashimoto observed that star-shaped block copolymers of butadiene or isoprene, with styrene, maintain domain structure of the blocks well beyond the polystyrene Tg., but form a homogeneous melt above a critical temperature\(^{(60)}\). The SAXS scattering maximum presented at room temperature by the isoprene based block copolymer on heating disappeared somewhere between 200 and 230\(^{o}\)c. The butadiene based block copolymer showed that the original scattering maximum tended to disappear at lower temperature but a new maximum appeared at about 180\(^{o}\)c which was stable to, as high as 230\(^{o}\)c. This apparent change in morphology was suggested to be irreversible since on cooling the spacing remained constant. Examination of the effect of heating on the microdomain structure of block copolymer cast from solution, by Fujimura\(^{(61)}\), showed that the radius of the micro-domain sphere and inter-domain distance increased slightly with temperature from room temperature to 180\(^{o}\)c. He concluded that the original domain structure was not at equilibrium in that the number of block copolymer molecules at room temperature was far less than in the high temperature equilibrium state (180\(^{o}\)c), similar to a process described by Meier\(^{(12)}\) as chain perturbation, due to a mismatch in volume fraction or block molecular weight. The end result of the chain perturbation is the uniform placement of chains in space which resulted in an increased number of blocks per domain, thereby increasing the domain size and inter-domain distance.

Birley, Canevarolo and Hemsley\(^{(62)}\) in their study of the thermo-softening of SBS, using the change in birefringence technique showed that the domain structure of SBS block copolymer, softens in three stages:
(i) at about ca. 95°C (the expected Tg. of PS) the system showed evidence of chain perturbation

(ii) starting from ca. 140°C the imperfect initial domain structure began to rearrange into a well segregated two phase structure. Since this is a thermo-activated process, it takes place continuously to ca. 240 - 250°C

(iii) Between 200 - 210°C cross-linking in the rubbery phase began, enhancing the modulus and obstructing the flow behaviour.

1.2.7 SYNTHESIS OF BLOCK COPOLYMER

Knowing that the sequential arrangement of block copolymer can vary from "A-B" structure containing two segments only to A-B-A structure containing three segments to multi-block -(A-B)_n- system, it became obvious that to prepare the above structure required a sophisticated synthetic technique.

Many methods of synthesis of polymers with "block-like" character have been reported in the literature (63-68). However only a few of these methods are capable of producing end products with a high degree of block integrity. These few are form of either living addition polymerization or step-growth (condensation) polymerization. The success of these two methods is due primarily to three desirable features, common to both approaches, and they are as follows:

(i) the concentration and location of active sites in the monomers are known.

(ii) in living addition systems, due to absence of terminating side reaction impurity is minimal.

(iii) segment length and placement are controlled by sequential
addition of monomers in living polymerization and in step-growth polymerization by the correct selection of oligomer. Each of the two preferred methods has advantages. With living polymerization it is possible to achieve all three types of block copolymer architectures \((A-B), (A-B-A), -(A-B)_n\), while only the \(-(A-B)_n\) system can be achieved using the step-growth process. Longer block lengths and narrow molecular weight distributions are more readily achieved with living polymerization than with step-growth process due to the inherent Gaussian molecular weight distribution associated with the step growth process. On the other hand, the step-growth process is less sensitive to reaction impurities and with them greater choice of polymeric type is more possible. Because of the evolution of numerous techniques under these two preferred general methods the discussion will be limited to the basic steps involved, in the two methods.

(i) Living Addition Polymerization

At least, in principle this can proceed through anionic, cationic and coordination mechanisms. The anionic route seems to be more widely used due to the greater freedom from terminating reactions and greater stability of the anionic growing end. It is probably that the best route towards synthesising a well defined block copolymer under this general method, for example in preparation of a styrene - diene - styrene system, can be classified into four different headings as follows:

(i) difunctional initiator process

(ii) coupling process

(iii) three stage sequential addition process and
(iv) tapered block process. More information can be found in the literature\(^{(9)}\). The best example is the alkyl lithium initiated polymerization of styrene and butadiene (iii above), mainly used with styrene and diene monomers. It comprises the initiation of styrene polymerization to form living poly-styryl anion followed by addition of diene monomers to form living diblock and finally, the introduction of a second quantity of styrene monomer to complete the formation of the A-B-A structure, as shown by the scheme below.

To allow termination-free polymerization, hydrocarbon soluble organo-lithium (preferably sec.-butyl lithium\(^{(67,68)}\)) initiator should be used. It is essential that all "active-hydrogen" impurities (water, alcohol, etc.) are carefully removed. A feature of this method is that the end molecular weight is governed simply by the ratio of

\[
\begin{align*}
H_2C = CH & \quad + \quad RLi \\
& \quad \rightarrow \quad R \sim \sim CH_2=C Li^+ \\
\end{align*}
\]

\[
\begin{align*}
CH_2 = \overset{R}{CH \cdot CH=CH_2} \\
R=H, CH_3, etc.
\end{align*}
\]

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\[
\begin{align*}
\overset{R}{CH \cdot CH=CH_2} \\
R=H, CH_3, etc.
\end{align*}
\]

monomer to initiator as every initiator molecule is capable of starting a chain. Furthermore it is possible to achieve a high degree
of narrow molecular weight distribution due to the absence of termination side reaction.

(ii) **Step-growth (condensation) Polymerization**

Recall that at the beginning of this chapter mention was made of the classical subdivision of polymers into two main groups by Carothers (1929). Condensation polymers, i.e. polymers formed by the loss of small molecules, such as water, at each step during the polymerization and addition polymers for those where no such loss occurred. Today the term condensation has been replaced with step-growth reaction mechanism which logically include those step-growth reactions without loss of small molecules e.g. in the synthesis of poly-urethanes.

In step-growth polymerization, a linear chain of monomer residues is produced by the step-wise inter-molecular addition of the reactive group in a bifunctional monomer. Due to the nature of monomer normally involved in this reaction mechanism, functionally terminated polymer chains or oligomers are produced. By this approach block copolymer can be formed by the inter-segment linkage of the preformed oligomers during the block copolymerization reaction. Generally, difunctional species are used, leading to the formation of -(A-B)\text{n} structure as shown by the scheme below:

**Step growth:** For a equimolar mixture of bifunctional monomers of ethylene glycol and adipic acid:

\[
\text{HO}_2\text{C(CH}_2\text{)}_4\text{CO}_2\text{H} + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{HO}_2\text{C(CH}_2\text{)}_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

The product can then react further, (a) with a molecule of glycol,
to give a diol:

\[
\text{HO}_2\text{C(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}} + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \\
\text{HOCH}_2\text{CH}_2\text{O}_2\text{C(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}} + \text{H}_2\text{O}
\]

(b) with a molecule of adipic acid, to give a diacid:

\[
\text{HO}_2\text{C(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}} + \text{HO}_2\text{C(\text{CH}_2)_4\text{COOH}} \rightarrow \\
\text{HOOC(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{O}_2\text{C(\text{CH}_2)_4\text{COOH}} + \text{H}_2\text{O}
\]

or (c) with a further molecule of hydroxy acid to give a new hydroxy acid:

\[
\text{HOOC(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}} \rightarrow \\
\text{HO}_2\text{C(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{O}_2\text{OOC(\text{CH}_2)_4\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}} + \text{H}_2\text{O}
\]

The product of these reactions can then undergo further analogous reactions, and so on. However, in principle multifunctional oligomers can be used to generate the A-B, A-B-A structures.

One necessary condition for the formation of high molecular weight linear polymers by this process is that the reaction involved must be one in which a very high degree of reaction of functional groups can be achieved. This requires that the reaction should be fairly fast, so that the polymerization may be completed in a reasonable time. Also where the reaction is reversible, which is the case with the majority of commercially important step-growth polymerizations, it is important that the other product of the reaction be removed during the reaction in order that polymerisation may continue.

Monomers used in step-growth polymerisations are generally required to be of a high degree of purity, to ensure accurate proportioning of monomers, and because monofunctional impurities can limit the molecular weight by "capping" polymer chains e.g.
Block Copolymerisation:

In block copolymerisation (i.e. for monofunctional oligomers) blocks of the different polymers combine as shown below:

\[ \text{CH}_2\text{CH}_2\text{OH} + \text{RCO}_2\text{H} \rightarrow \text{CH}_2\text{CH}_2\text{O}_2\text{C} + \text{H}_2\text{O} \]

Detailed discussion of copolymerisation will be found in many books on polymer chemistry.

1.3 ELASTOMER-PLASTIC BLEND AS THERMOPLASTIC ELASTOMER

1.3.1 INTRODUCTION

We have seen that typical thermoplastic elastomer material will normally comprise of both the thermoplastic and the elastomer parts as the name clearly indicates. In the preceding sections the situation where the different components are chemically bonded together to form a super-molecule of the thermoplastic elastomer material was covered (e.g. block copolymer, graft copolymer, etc.) This section will be concerned with the physical mixture of thermoplastic and elastomer parts (poly-blend or simply blend) where no chemical bonding of the components is involved (e.g. polypropylene/EPDM system). From the preparative viewpoint this is the most direct and versatile method of producing thermoplastic elastomer and probably the most economical approach as they are produced from existing polymers.
Poly-blends are physical mixtures of structurally different homo. or copolymers. They contribute substantially to the development of commercial polymer mixtures which vary between plastic-plastic, plastic-rubber and rubber-rubber blends, from which clear/opaque, homogeneous/heterogeneous blends can be obtained. Since the mixing of polymers is normally an endothermic process, it usually leads to heterogeneous systems in the absence of excess of energy. In equilibrium cases however, the size of the domain is the most meaningful criterion for deciding on the heterogeneity. In other cases poly-blends can be considered as dispersions of one polymer in another. The extent of dispersion depends on the method of mixing and the amount of thermodynamic compatibility. The properties and therefore the utility of physical blends are strongly dependent upon the degree of compatibility of the components. Observations have shown that the great majority of physical blends are highly incompatible(69) while a very small number of polymer-polymer pairs are thermodynamically compatible or miscible.

Elastomer-plastic blends have become technologically useful as thermoplastic elastomers in recent years(70-2). They have many of the properties of elastomers, but they are processable as thermoplastics.(73), many of them do not require vulcanization during fabrication.

1.3.2 INCOMPATIBLE BLENDS

As pointed out in the previous sections, one of the major factors responsible for phase separation is molecular weight. High molecular weight polymer blends are not always compatible with low
molecular weight ones because of the mismatch in weights\(^{(70)}\) (e.g. styrene/butadiene blends). Other factors include, the chemical nature, the structure, the volume fraction of each component. Phase separation is in turn an evidence of incompatibility. Incompatibility can be observed in dilute solution of incompatible polymers as well as in their solids and melts. This has been shown to be a direct consequence of the free energy of the system, given by the relation:

\[
\Delta G = \Delta H - T\Delta S \tag{1.3.1}
\]

which provides a driving force for the components to aggregate into separate phases. Incompatible blends are usually characterised by poor interface adhesion, inhomogeneous mixing, presence of large particles of the constituent components and generally look coarse in nature. These have very great influence on the physical and optical properties of blends. Poor interface adhesion results in very poor mechanical properties and since the phase separated domains in them are usually larger than the wave-length of light, incompatible blends appear opaque. Their \(T_g\)s reflects the thermal transitions characteristic of the constituent components.

1.3.3 **COMPATIBLE BLENDS**

Experimental observations have shown that it is almost impossible to find two polymers that are truly compatible i.e. completely form a homogeneous solution with each other. However a few polymer pairs that are close to complete miscibility do exist, e.g. poly-(2,6 dimethyl-1,4-phenylene oxide) / polystyrene, PPO/PS, and butadiene-acrylonitrile copolymer/polyvinyl chloride systems\(^{(74)}\).

It is believed that polymer-polymer compatibility is a function of
their surface energies ($y_c$) which correlate with solubility parameter ($75-6$), crystallinity of the hard phase and the critical chain length of the rubber molecules for entanglement ($77$). As concluded by Coran and co-workers the difference in the critical surface tensions for wetting ($\Delta y_c$) between the two polymers may be a qualitative estimate of the interfacial energy ($y_{12}$) through the difference $|y_1 - y_2|$ between actual surface tension values of polymer 1 and 2, but does not correspond well with ($\Delta y_c$). They concluded that the lower the value of ($\Delta y_c$) the smaller would be the particle size of the dispersed soft phase and hence the more compatible will the two polymers become.

Compatible blends are characterised by their phase morphologies. They are usually transparent and exhibit physical properties intermediate to those of the components. The permeability, mechanical and thermal properties displayed by them are predictable as in random copolymers.

1.3.4 PREPARATION OF POLY-BLENDS BY DYNAMIC VULCANIZATION

The principal methods for preparing poly-blends are melt mixing, solution blending and latex mixing. Chemical reaction during mixing can cause the formation of polymer-polymer bonding in the poly-blend. Often these reactions are used to bring about cross-linking between individual polymer chains, which can lead to the formation of infinite, three dimensional net-works. Most prominent example of this process is the vulcanization of rubber.
The ideal elastomer-plastic blend comprises of finely divided elastomer particles dispersed in a relatively small amount of plastic. The elastomer particles should be cross-linked to promote elasticity. The favourable morphology (which will depend on the volume fraction of the components) should remain during the fabrication of the material into parts and in use.

Manufacturers desire that product end-use specification shall be met and because of these requirements for ideal case, the usual methods for preparing elastomer-plastic blends become insufficient. This led Gessler and Haslett(78) to the idea of dynamically cured mixtures of polypropylene and chlorinated butyl rubber and they filed a patent application in 1958. Since then work has been done in this area by various researchers(79-85) and it is now regarded as the best way (see later in chapter IV) to produce thermoplastic elastomer compositions comprising vulcanized elastomer particles in melt processable plastic matrices. The technology of dynamic vulcanization is based on insitu vulcanization of conventional thermoset rubber polymers during mixing with thermoplastics. It can be described as follows: "Elastomer and plastic are first melt mixed. After sufficient melt mixing in the mixer to form a well mixed blend, vulcanizing agents (curatives, etc) are added. Vulcanization then occurs while mixing continues. The more rapid the vulcanization, the more rapid the mixing must be to ensure even cross-link density in the blend. The progress of vulcanization is monitored by the mixing torque or energy requirement during mixing. After the maximum mixing torque is reached, mixing is continued somewhat longer to improve processibility of the blend. On
discharge from the mixer the blend can be chopped, pelletized, 
extruded, injection moulded, etc. Usually the elastomer is at greater 
proportion while the proportion of the plastic controls the hardness 
or modulus. Suitable plasticizers, extender oils, etc. can be used to 
expand the volume of the plastic and elastomer phases respectively. 
The oil acts as a softener at lower temperatures and as a processing 
aid at melt temperature. It has been shown that with the appropriate 
components combinations, if the elastomer particles of such blends 
are small (<\=2 \mu m.) and appropriately vulcanized, then the 
properties of the blend can be greatly improved in the following 
areas:

(i) improves ultimate mechanical properties 
(ii) improves fatigue resistance 
(iii) improves high temperature utility 
(iv) reduces permanent set 
(v) have greater resistance to attack by fluids (e.g. hot oil) 
(vi) have greater stability of phase morphology in melt. 
(vii) have greater melt strength and 
(viii) have better thermoplastic fabricability".

Dynamic vulcanization is more feasible in melt-mixing (compared 
with solution casting etc) as melt-mixing avoids the problem of 
contaminations, solvent and water removal, etc. General purpose 
mixer such as "Banbury mixers, mixing extruders, the new 
twin-screw mixers and even the two roll mill" are suitable for melt 
mixing elastomers with plastics 

Thermoplastic vulcanizate compositions have been prepared from 
a great number of plastics and elastomers, however only a limited
number of elastomer/plastic pairs gives commercially useful blends, even when dynamically vulcanized\(^{(9,12)}\). This, in turn has called for a further advanced technique in this area known as "Technologically Compatibilized Dynamic Vulcanization". Here, the blend is compatibilized first (using suitable compatibilizing agents, e.g. block copolymer) before being dynamically vulcanized, (see next section).

In order to define the practical scope of the composition which can be prepared by this method, Coran\(^{(84)}\) has studied 99 compositions based on 11 kinds of elastomers and 9 kinds of plastics. The conclusion from this study was that the best elastomer-plastic thermoplastic vulcanizates are those obtained from plastic and elastomer with matched surface energies when the chain entanglement molecular length of the elastomer is low and when the plastic is above 15% crystalline.

A commercial product produced by dynamic vulcanization is "SANTOPRENE"\(^{(81-7)}\), produced in different grades based on hardness, ranging from 50 Shore A to 80 Shore A\(^{(86)}\). They have been available now for the past ten years or so. Many publications are concerned with the properties, performances and market share of this thermoplastic elastomer. It is claimed that in some respects Santoprene can out-perform block copolymer-type thermoplastic elastomers\(^{(82)}\). It is produced essentially from polypropylene (being the hard component) and EPDM as the soft component. Other ingredients include cross-linking agents (e.g. peroxides or sulphur), (accelerators, stabilizers in cases where sulphur cross-linking agent is used) and processing oils. The general recipe of the composition used by Coran in his experiment is as follows:
EPDM----------------------------- 100
Polyolefin resin--------------------- X
Zinc oxide-------------------------- 5
Stearic acid------------------------ 1
Sulphur----------------------------- Y

(TMTD) Tetramethylthiuram disulfide y/2
(MBTS) 2-benzothiazolyl disulfide y/4, where x, the number of parts by weight of poly-olefin resin and Y, the number of sulphur were varied. Although this may be adequate for sulphur cured system it has no significance for peroxide and other cured systems.

The property advantages claimed for this product are as stated above particularly with high temperature utility (e.g. it has broad temperature window) and high recovery characteristics.

However, because of the parent material from which they are composed and the fact that they are thermoplastic elastomers, they possess some deficiencies. In the softer grades, such properties as modulus and tensile strength (particularly at elevated temperatures) and resistance to solvents and oils are moderate. However three new hard thermoplastic elastomers blends have been recently described, composed of nitrile rubber (acrylonitrile butadiene copolymer) in polypropylene(10) prepared by dynamic vulcanization of technologically compatibilized materials which are resistant to hot oil and have excellent strength related properties.

A summarised assessment of these properties based on direct comparison to traditional thermoset rubber used in "IRP" market has been made by O'Connors in his papers(86-7).
1.3.5 BLOCK COPOLYMER AS COMPATIBILIZERS

Owing to the high cost of research to develop new chemistry and new processes towards the improvement of materials, to meet new market needs, it becomes necessary to focus attention on blends or alloys of existing polymers, as these may prove to be more economically viable. Phase separation in polymer mixtures is a common phenomenon. That often polymer pairs are immiscible and therefore form separate phases in their solutions, comprise mainly of the pure components, with the resulting poor physical properties is an undesirable shortcoming of blends (e.g. PS/polybutadiene blend). This is caused by poor adhesion between these phases (88-90). This shortcoming has led to the search for blend additive(s) which might alter the inter-face problem to avoid the poor mechanical properties which result from it.

Molau (13, 91-2), Riess (93-4) and others have established the fact
that block and graft copolymers act as interfacial agents or surfactants for immiscible polymer mixtures i.e. they locate at surfaces between phases of the component A and B (as shown in figure 1.4.1) with the corresponding segments being associated with the appropriate phase therefore dragging them into solution since the block copolymer traverses the interface. Owing to the fact that the block copolymer is covalently bonded, and to the strength of the bonds, improvement in adhesion between the phases is expected, (figure 1.3.1). Teyssie (95-8), Heikens (102), and Paul (103-4) in their experiments have used a well characterised styrene/hydrogenated butadiene styrene (S-EB-S) with the desired molecular weight) to demonstrate and confirm the validity of this expectation in many different combinations of polymer pairs, (e.g. in mixtures of polystyrene with various poly-olefins including LDPE, HDPE and PP).

Under this circumstance the optimal design of block copolymer for compatibilization purposes becomes crucial, in order to be able to answer the question "will the block copolymer actually become a surface active agent?, how long must the segment of the block copolymer be in order to achieve this? and not to simply slip from the homopolymer phase when the inter-face is stressed?". For block copolymer to locate at the blends inter-face it should have this propensity to segregate into phases and should not be miscible (as a whole molecule) in one of the homopolymer phases.

Both theories and experiments indicate that in the ternary mixture of homopolymer A/ homopolymer B and block copolymer A-B, significant solubilization of the homopolymer into the preexisting domain of the block copolymer can be expected only if
the homopolymer molecular weight is comparable with or less than
that of the corresponding segments of the copolymer\(^{12,105-6}\).
Therefore it is not out of place to suppose that block copolymer may
not bring about efficient compatibilization of practical blend systems
since the segments of block copolymers are relatively of lower
molecular weight (in the region from under 10,000 to not more than
100,000) compared to those of industrially important
homopolymers. However the available theoretical and experimental
evidence as provided by the recent theories of Noolandi et al\(^{107-9}\)
suggested that regardless of relative molecular weight, block
copolymers do generally locate at the inter-face, lower the
inter-facial tension and reduce the size of the homopolymer domain
as expected of an emulsifier. However this is still subject to further
investigation. Paul summed up his review by suggesting that in
situations of complete miscibility of the system, block copolymer acts
as a surfactant with its segments penetrating deeply into the
homopolymer domains, while on the other hand where the idealised
monolayer configuration can not occur the block copolymer may
form an interface between the two homopolymer components (as
represented by figure 1.4.1) in which its mutual affinity to adhere to
each component is greater than the affinity of the two components to
each other. It is impossible at this stage to state conclusively what
the best block copolymer structure might be in order to locate at the
interface in a given application (owing to insufficient literature on
the subject).
1.4 SOME PROPERTIES OF THERMOPLASTIC ELASTOMERS

1.4.1 INTRODUCTION

Due to the diversity of thermoplastic elastomer types that can be produced, a discussion of their specific properties would be a lengthy exercise. Even to list the properties of all possible combinations of a particular set of thermoplastic elastomer building blocks could prove cumbersome as the amount of each segment in the copolymer can be varied. As was explained earlier, thermoplastic elastomer may be two phase copolymer comprised of a major proportion of soft segment and a minor proportion of a hard segment of the type A-B-A and -(A-B)$_n$- architecture where A is the hard segment and B is the soft segment, or polyblend of hard/soft phases. The unique properties displayed by these systems are functions of architecture and the chemical nature of the constituent homopolymers while, in the case of polyblend, in addition to this, is a function of the degree of polydispersity or compatibility of the phases. Block copolymer systems comprising of A-B architecture do not show dramatic improvement in properties (for example in mechanical properties) over random copolymer elastomers. In this regard most literature focuses most attention on the S-B-S systems probably because it is the largest (in term of commercial production(111)) and one of the earliest to be investigated and/or due to the relatively simple molecular structure. It is the simplest system of this kind that offers an explanation of the structure/property relationship of block copolymer thermoplastic elastomer system. Here only a brief literature review of the mechanical, rheological, optical and chemical properties will be outlined.
1.4.2 MECHANICAL PROPERTIES

Thermoplastic elastomer combines the mechanical properties of a cross-linked rubber with the processing behaviour characteristic of linear thermoplastics. The toughness or high strength inherent in these materials is provided by the glassy or crystalline hard phase (via reinforcement) dispersed in the rubber matrix. This is possible due to the discrete nature of the hard phase domains, the micro-size and uniformity of the domains and perfect interface adhesion provided by the inter-segment chemical linkage.

As evident in many publications thermoplastic elastomers show a broad property window, for example they can be used in very wide extremes of temperatures. Their thermal and mechanical properties are direct manifestation of the nature and properties of the parent components, the degree of which in turn is controlled by the volume fractions of such components in the composition. In order to improve the mechanical properties in TPE's (e.g. modulus, tensile and impact strengths, etc.) the hard phase block length, in block copolymer and its volume ratio in polyblend must be high enough to develop the two phase system yet not excessive as to obviate thermoplasticity. The influence of hard/soft block ratio on the modulus, recovery characteristics and ultimate properties can be noticed in the different grades of modern thermoplastic elastomers e.g. Pebax, Santoprene, Hytrel, etc.\(^{(86,111-2)}\). High modulus and hardness are usually associated with high proportion of the hard phase, and low proportion of hard phase is associated with low modulus, characteristic of the softer grades. The volume fraction of hard phase
should be ≥ 20% to provide adequate level of physical cross-linking for good recovery and high tensile strength to be obtained. On the other hand excessive concentration level of the hard phase (>40%) will cause the discrete spherical domain shape to form a continuous lamella or inter-penetrating net-work (IPN) which in turn causes deterioration in recovery properties\textsuperscript{112} as the material increases in hardness and reduces in flexibility.

The stress-strain properties of block copolymers have been the subject of many researches. Fisher and Henderson\textsuperscript{113} in 1969 showed that there is a decrease in tensile strength, modulus and elongation at break with increase in temperature, in SBS containing 40% styrene (i.e 20:60:20). It was shown that at low strain much of the load is borne by the continuous polystyrene phase. Upon further straining, yielding occurred with the break down of the continuous polystyrene phase. The material becomes much more flexible and at this point it was noted that significant fraction of the load was transferred to the butadiene phase upon yielding.

A recent work of Diamant et al\textsuperscript{114} working with SBS cast from THF/MEK solution confirmed this fact and they call the yielding phenomenon a "Plastic to Rubber transition". They concluded that this preferentially happens when the interface composition has a sharp gradient and is thus able to generate high local stress concentration.

It has been shown that commercially important copolyester thermoplastic elastomer based on poly-tetra-methylene oxide (PTMO) containing between 30-90 wt % 4GT units (tetra- methylene terephthalate units) exhibits, to a remarkable extent, reversible...
deformation at low strain levels. Using the dumb-bell shaped specimen at 0.5%/min. strain rate of medium grades of these polymers, Cella showed that the most pronounced effect of morphology can be seen in their tensile behaviour(115) which quantitatively can be divided into three regions of behaviour. As explained by him the high initial Young's modulus observed in region "1" (see figure 1.4.1 below) is due to the pseudo elastic deformation of the interpenetrating crystalline matrix. At levels of strain less than 10%, the deformation is reversible with little hysteresis loss or permanent set. At high level of elongation encountered at region "11" the crystalline matrix is disrupted and orientation occurs resulting in the formation of a draw plateau depending on the strain rate and temperature. In region "111" the sample displays a characteristic similar to that of a cured elastomer. This implies that Young's modulus is a measure of the force required to deform the crystalline matrix and the yield stress is a measure of the force required to orient the crystallites. This also suggests that Young's modulus and yield stress should increase monotonically with an increase in crystallizable component in the polyester, and indeed this is the case as confirmed by the present author (in his experiment using Hytrel samples), and by others(116-7). It was noted that the copolymer based TPE samples (Hytrel inclusive) used by the author show a yield stress during tensile testing (see chapter iv, section 4.9.4). These copolyester thermoplastic elastomers have been marketed under the trade-mark "HYTREL" manufactured by (Du-Pont) in the US and Luxembourg, Du-Pont Toray in Japan, and "PELPRENE" manufactured by Toyobo in Japan and Akzo in the Netherlands(143).
Applied mechanical stress causes orientation phenomena especially on such TPE's as TPU's, PE and PEO's (PEO = polyethylene oxide) thermoplastic elastomers. In TPU it has been shown that features such high tensile strength and elongation are due to disruption and recombination of hydrogen bonds in an energetically more favourable position. Seymour\(^\text{118}\) and Cooper\(^\text{119}\) in their studies of orientation in molecules, using infra-red dichroism, showed that the soft segment may be readily oriented but returns to the unoriented position when the stress is removed. The hard segment however showed a more complex relaxation behaviour, which is a function of the magnitude of the applied stress, the molecular weight of the soft block and the crystallinity of the hard block.

Apparently, a more regular physical network and a high degree of hard block domain perfection\(^\text{120}\) accompanied by stress induced crystallization in these TPE's is responsible for their better ultimate properties. Stress induced crystallization however increases permanent set\(^\text{121}\) (in some rubbers) if the sample temperature is below the melting point of the soft segment.

As observed by Charrier and Ranchoux\(^\text{122}\) in an SBS block copolymer sample containing 30% styrene, the elastic modulus increases in the following order: "the lowest modulus was obtained across the flow direction of an injection moulded sample followed by compression moulded samples and highest along the flow direction of injection moulded samples. This demonstrated the influence of the processing history on the final properties of these materials."
The present author also observed that the hardness and the initial forces of various thermoplastic elastomers, during stress relaxation measurements were higher for injection moulded samples. Preparation of samples at increasing shear rate has also resulted in a progressive increase in modulus. It was stated that the material keeps in memory the processing steps to which it has been submitted. Nandra and co-workers have shown that the tensile strength of an injection moulded SBS thermoplastic elastomer was higher in the transverse direction than in the flow direction\textsuperscript{(123)}. They explained this result by saying that the oriented structure, in the flow direction of the styrene hard phase was reoriented into the stress direction when load was in the transverse direction. The strain was readily accommodated by the butadiene (soft) phase and
reinforcing hard phase rods were ultimately turned through 90° to reinforce the total structure. Thus additional stress is required to bring about the orientation of the reinforcing phase to the direction of the stress and hence the higher strength of the material.

The solubility of a homopolymer of comparable molecular weight in block copolymer (e.g. PS in SBS) to increase its reinforcement capability and hardness revealed that there is an initial softening of the system—the hardness decreasing to a minimum (at ca. 15 phr PS) and then followed by a steady increase. As the PS content increases above 35phr it dominates the material and lead to an increase in hardness or (elastic modulus) above the original value\(^{(125-6)}\). The initial softening may be due to disruption of the domain system with increase in polystyrene content prior to forming a new domain system when the PS proportion is increased.

The elastic modulus of an oriented SBS (which has a cylindrical polystyrene phase structure, dispersed in the rubbery matrix) has been estimated using the Takayanagi model\(^{(125)}\). Parallel to the orientation direction the modulus is given by:

\[
E_0 = \phi_s E_s + \phi_B E_B
\]

where \(\phi\) is the volumetric fraction of the rubbery phase (B) and glassy phase (s). In the perpendicular direction (i.e. \(E_0\) becomes \(E_{90}^{-}\)), assuming \(E_s > E_B\) is

\[
E_{90}^{-} = \frac{E_B}{\phi_B}
\]

Folkes\(^{(127)}\) expressed the true modulus as:
due to the restriction imposed against contraction along the angle \( \theta = 0^\circ \) of the rubber matrix, by the polystyrene rods. At the angle \( \theta = 55^\circ \) the restriction is reduced to zero and the modulus at \( \theta = 55^\circ \) is given as:

\[
E_{55^\circ} = \frac{3}{4} \frac{E_B}{\phi_B}
\]

One other interesting point is that most block copolymers show stress softening or Mullins effect - i.e. a loss of modulus between the first and subsequent extensions\(^{(128-9)}\). This was thought to be due to the disruption of the hard segment phase, a conclusion later confirmed by Pedemonte et al\(^{(128)}\). As explained by him, the stretch causes the deformation of the original continuous and regular hard phase architecture aligned in the flow direction of the oriented sample, assuming a string of pearls structure and subsequently, upon further stretching the structure breaks down. A reverse effect to stress softening was noticed by Birley and Fernando\(^{(130)}\) during the compression of some rubber materials - Enhancement of modulus, which is slightly above the actual modulus when the rubber was stress free. They termed it the "Modulus Enhancement Factor". A conclusion also confirmed by Tahir. The author has also recorded modulus enhancement of up to a factor of 5 in some thermoplastic elastomers and suggested that it may be a reversal of the Mullins effect. With samples having lamella structure it is suggested that at the initial stage of deformation the alternating layers of hard/soft components are stretched apart a little. Increased strain deforms the
hard phase into continuous kinks, fractures them into short segments, then finally into small dispersoids embedded in the soft segment matrix. At this point the sample behave like a filled rubber. Odell and Keller\textsuperscript{(131)} reached a similar conclusion when they introduced a "Random rod breaking theory". The later work of Seguela and Prud'homme\textsuperscript{(132)}, using small angle X-ray scattering gave a more detailed analysis of the deformation mechanism during stretching of the solvent cast SBS block polymer, where stretching led to anisotropy in the material. The same conclusion was reached by Cooper\textsuperscript{(116)}, working with polyester/polyether copolyester thermoplastic elastomer containing ca. 30\% 4GT.

These observations led to the interesting and still unresolved question of the mechanism of tensile failure in a thermoplastic elastomer. There appear to be three possible mechanisms:

(i) ductile failure in the hard phase domains\textsuperscript{(132)}

(ii) brittle failure in the hard phase domains and

(iii) elastic failure in the soft centre segment.

It was suggested that at high temperature, (above 40\textdegree C) as the domain softens there will be weak linkages in the chains and ductile failure will predominate\textsuperscript{(129)}. The same effect will apply when the time scale of the test is long. At lower temperatures and shorter time-scale one of the other two mechanisms takes over, which mechanism will apply will depend on the conditions under which the test is carried out. Diamant\textsuperscript{(114)}, in his work, also suggested that failure mechanisms are molecular, in origin.

In conclusion thermoplastic elastomers, at small deformation, behave like typical composite materials. However at high
deformation the orientation of the molecules in the microphase controls the mechanical behaviour and the final morphological state, in contrast to physical composites. When the stress is removed (after deformation) the material heals i.e the stress softened sample reverts to its original properties with time and/or at elevated temperature, suggesting that the fragmented system has an excess energy as a result of (a) the reduced entropy of the system due to reorientation, away from the original oriented direction and (b) the very great increase of inter-facial surface area of the fragmented system giving rise to increased interfacial energy - in other words, the recovery of the structure is associated with enthalpy and entropy relaxation processes\(^{(130)}\).

1.4.3 THERMAL AND RHEOLOGICAL PROPERTIES

Since rheological phenomena of rigid polymers are commonly associated with thermal processes it is reasonable to treat the above topics together starting with a brief discussion on the thermal properties. It is of course well understood that thermoplastic elastomers are generally composed of hard and flexible components, for example in block copolymer and poly-blend systems. The thermal responses of such systems (for example the modulus/temperature behaviour) are basically different from those of homopolymers and random copolymers. A random copolymer derived from monomers A and B displays behaviour intermediate to that of homopolymers A and B - showing single phase glass transition "Tg" as can be seen in figure 1.4.2, which falls between those of the corresponding homopolymers. Single phase block copolymers in which the segments
are highly compatible with each other show similar behaviour. Note that the position of the transition curve is related to the weight fraction of the corresponding components. On the other hand two phase block copolymers generally show modulus / temperature characteristics, somewhat similar to those of physical polymer blends. The identity of both segments is retained as evidenced by the presence of two distinct glass transition temperatures. (figure 1.4.2 b.) A constant plateau exists between the two Tg values and the flatness of the plateau depends on the degree of phase separation. In contrast to random copolymer behaviour, the position of the two Tg values is not significantly changed by the compositional variation, rather it is the position of the modulus plateau that is dependent upon composition. It can be that compositional changes cause vertical modulus shifts in two phase block copolymer while a horizontal temperature shift in random copolymer and single phase block copolymer. It should be noted too in this case that only two phase block copolymers in which the block lengths are beyond the level in which average Mn affects Tg and that modulus/temperature behaviour of block copolymer is independent of their architecture (e.g. A-B, A-B-A, -(A-B)n-) or structure, except where this affects the efficiency of the phase separation. Thus, thermoplastic elastomers have two transition temperatures, the lower one is controlled by the Tg of the soft phase while the upper temperature depends on the Tg or Tm of the thermoplastic phase. The Melt transition in block copolymers when subjected to thermal treatment has been the subject of many researches in recent years (133). Perhaps one the
most sensitive techniques for determining transitions in multiphase systems is the measurement of dynamic mechanical loss characteristics. For crystalline polymers and block copolymers containing crystalline segments, calorimetric methods such as Differential Scanning Calorimetry (DSC) can be used to provide information about the crystalline melting point (Tm), heat of fusion and the degree of crystallinity of the material as well as on major amorphous transitions.

However rheological investigations of these two phase systems show their melt behaviour to be much more complicated than those of their corresponding homopolymers or random copolymers. Transitional processes in polymers have been used to study their nature and to characterise them. Kraus and co-workers(134–6) applied them to block copolymers as well. They studied the effect of long chain branches on rheological properties of polybutadiene homopolymer (i.e. tri-chain, - a chain having two other branches and tetra-chain, - a chain having three other branches, respectively(134)) and observed that at low molecular weight the Newtonian (zero-shear) viscosity was lower relative to a linear polymer of the same molecular weight, but at molecular weight greater than 60,000 the Newtonian viscosity increased rapidly above that of the corresponding value for a linear polybutadiene, becoming more pronounced the higher the molecular weight. As explained by them flow occurs with little coupling between molecules when the branches of the multi-chain polymer are not longer than the entanglement molecular weight (ca. 5,600). The principal factor governing viscosity is then the size of the polymer coil, which in this
case is smaller for the branched molecules. Therefore entanglement and branching of polymer molecules appear to lead to extensive coupling, the higher the branch length.

They also show that random copolymers of styrene-butadiene of constant composition along the polymer chain display behaviour similar to that of linear polybutadiene (Newtonian viscosity at low shear rate), while those with varying composition along the polymer chain show a more pronounced non-Newtonian behaviour and temperature shear rate superposition was not successful as in the first. McGrath in (1967) noted and stated that styrene-isoprene-styrene copolymers having molecular weight of $(10-40-10) \times 10^4$ could not be successfully compression moulded. It was speculated that this was due to chain entanglement in the hard
segments. Holden and co-workers\textsuperscript{(138)}, also working with SBS, in 1967 reported that melt viscosity is a function of molecular weight change particularly at low shear rates. The behaviour was not Newtonian and therefore could not be accounted for with the popular equation that states that the zero shear viscosity is proportional to molecular weight raised to the power of 3.4. They noted that melt viscosity of SBS block copolymer was greater than either of the homopolymers at same molecular weight. It was suggested that this was due to the fact that the two phase structure still exists in the melt\textsuperscript{(137-8)}. When the temperature is high enough to soften the polystyrene domain, flow becomes possible. The micro-phase separation however, requires the flow of polystyrene domain through the polybutadiene matrix. An additional energy term is required to describe this feature, which appears as a higher melt viscosity\textsuperscript{(138)}. The flow behaviour is temperature and shear rate dependent and entirely different flow responses were observed at low and high shear rates.

The results of many investigations have shown that the dynamic mechanical behaviour of thermoplastic elastomer is a function of the relative proportion of hard segment.\textsuperscript{(139)} At Tg in TPU, there is a pronounced decrease in shear modulus. Seymour et al\textsuperscript{(139)} showed that with increasing hard segment content the drop becomes less pronounced, demonstrating the function of the hard segment domain as reinforcing filler. Goyert and Hespe\textsuperscript{(140)}, who used a series of TPU's containing different molar ratios of polyesterdiol, BDO and 4,4-methylenebis (phenylisocyanate) (MDI) showed that the glass transition curve is broadened and shifted towards higher
temperature with increasing hard segment content. This was explained to be due to dissolution of the hard segment in the soft matrix. Consequently, a concentration gradient of the hard segment exists near the interface. This agrees with the early explanation where the phenomenon was attributed to the irregular structure of the phase interface\(^{141}\). Also the broad glass transition peak is attributed to a wide distribution of hard segment crystal thicknesses\(^{142}\).

A common occurrence in TPU is that annealing improves ultimate properties. This has been thought to take place as follows: "if rapidly cooled the hard segment block corresponding to their arrangement in the melt forms crystals which are statistically displaced with respect to one another "\(d_1\)". The thermodynamically effective crystal thickness is small while the phase interface is large (figure 1.4.3, a). Upon annealing the structure rearranges, resulting in a thermodynamically more favourable arrangement (figure 1.4.3, b), so that the melting point increases due to increase in crystal thickness "\(d_2\)". When annealing temperature exceeds a critical limit (ca. 210°C, in the case of secondary urethanes, based on piperazine) the

![Figure 1.4.3](image)

**Figure 1.4.3** Structural re-arrangement during annealing in Thermoplastic - elastomers
system is disrupted due to melting. On cooling to lower temperature the system can only form an aggregate of poor order, until the annealing process is repeated. This phenomenon has also been noticed in other thermoplastic elastomers. TPU generally have low melt viscosity and therefore are more sensitive to shear than temperature. In contrast, polyester thermoplastic elastomers are less sensitive to shear than temperature\(^{(143)}\). On the other hand the Santoprene TPE’s are more sensitive to shear although having relatively higher melt viscosity, hence they can be used in high temperature applications.

Chung\(^{(144)}\) and co-workers in 1976, working with SBS (7-43-7)\(\times\)10\(^3\) were perhaps the first to detect a structural transition in a block copolymer melt. They found that at 125\(^\circ\)C, 140\(^\circ\)C and 150\(^\circ\)C the material has high elasticity and viscosity with a non-Newtonian behaviour. At 175\(^\circ\)C the flow becomes Newtonian and data obtained at this temperature showed that there was a change in the flow mechanism. This was considered to be an indication of structural change in the sample, from a multi-phase structure at low temperature to a single phase structure at high temperature between 150 - 175\(^\circ\)C. Lablanc\(^{(145)}\) working with Solprene 415 in the same year found that at a critical shear stress of (550,000 dynes/cm\(^2\)), a change occurred in the flow curves. From the flow activation energy (19.2 kcal/mol) calculated from an Arrhenius plot, it was suggested that the mechanism was due to melt structure.

Chung and Lim\(^{(146)}\) confirmed their conclusion in an earlier experiment where they noted a transition between 140 - 150\(^\circ\)C and
suggested that due to the narrowness of the rheological transition an accompanying morphological transition is more likely to have taken place. These co-workers also noted that response at low frequency or low shear rate region was much more dependent on the polystyrene block length than on the polybutadiene block length.

Arnold and Meier\(^{(147)}\) in 1970, using a Weissenberg Rheogoniometer have also studied the dynamic viscosity of styrene-butadiene-styrene tri-block copolymer with different end and mid-block sizes as a function of frequency and temperature. They observed that viscous and elastic responses are independent of deformation amplitude and may be analysed using linear visco-elastic theory. The dynamic viscosity displayed two distinct regions: a low frequency range where viscosity increased with decreasing deformation rate without reaching a steady state, and a high frequency region where the response was typical of a thermoplastic behaviour, showing non-Newtonian flow. Their results confirmed a domain type structure. The unusual nature of SBS copolymer was shown by comparing its behaviour at different frequencies and temperature values with that of monodisperse polystyrene of similar total molecular weight (97,000). Like most thermoplastics, the viscosity of the monodisperse polystyrene was constant and showed a steady state, Newtonian flow at low frequency and decreased at higher shear rate, while it was not possible to obtain the Newtonian or the zero shear viscosity from the SBS data. These observations led them to the proposition of the so call the Arnold-Meier flow mechanism which suggests that SBS can exist in three different states depending upon the rate of
deformation. Due to the presence of domain structure a three-dimensional net work will be formed in the block copolymer, and the rheology will be dominated by the interplay of processes tending to disrupt and to reform the net-work and the domain system.

Figure 1.4.4

(a) Semi-continous

(b) Dispersed

(c) Aggregate

(d) Log. co

Polymer phase
Polystyrene Segment
Polybutadiene Segment

Slope of -1

Log. 'N'

A or B Aggregate

Thermoplastic

Log. \( \omega \)
At low frequency or low deformation rate the molecular net-work structure will be intact and very high viscosity will be experienced as shown schematically in figure 1.4.4 (a) for semi-continuous domain structure and (b) dispersed domains.

At intermediate rate of shear the three dimensional net-work is disrupted. Aggregates of individual domains and molecules still exist but not linked together to form a net-work. The system resembles a cluster of star-shaped particles as shown in figure 1.4.4 (c).

A viscosity higher than expected will still be observed. Finally at high shear rate these domain aggregates will be further disrupted and the system will behave as if composed of unlinked individual molecules and a typical thermoplastic response will be displayed. This predicts regions of low, intermediate and high shear stresses corresponding to high, intermediate but higher than expected and low viscosities respectively. Figure 1.4.4 (d) shows an idealised gradual weakening of the polystyrene chain. With the electron microscopy of samples quenched in liquid nitrogen from temperature above 150°C the sample show no particular structure, where as those quenched from temperature below 140°C clearly show a multi phase structure.

Other subsequent work in this area includes that of Windmaier and Meyer, Ghijsels and Raadson, Hashimoto et al, Cox and Merz, Hashimoto and Kraus and Birley et al (59,60,62,148,150), all reporting similar observation that thermal treatment of block copolymer is accompanied by morphological transition from a two phase structure to form a single phase structure (at temperature above 250°C) as manifested in their complex rheological behaviour in various forms,
except that Iskandar and Krause\textsuperscript{(150)} who used the same sample as Chung\textsuperscript{(149)} et al failed to detect a single Tg in SBS to confirm the single phase morphology postulated for the sample after being subjected to the following thermal treatments: "the sample was heated to 190°c, allowed to stand at this temperature for 5 min". Chung et al claimed that the sample, after these treatments did not show any detectable structure, when compared to the two phase structure shown by both samples which did not receive any thermal treatment and those quenched at 125°c.

The recent work of Birley et al \textsuperscript{(62,151)} using tri-block styrene butadiene copolymer "CARIFLEX 1102" with styrene/butadiene ratio of 28/72 and number molecular weight average of blocks \((1.5-7.5-1.5) \times 10^4\), showed and discussed the thermo-softening processes of the material. They reported that the process occurred in three stages, as stated in section 1.2.5 and in another publication\textsuperscript{(151)} that the transition can be accomplished in two ways: i.e. with temperature alone or with temperature and shear. The former acts in a broad range (from ca. 150°c to 240°c for Cariflex 1102), while the combined effects is much more effective and the rearrangements can occur at the melt transition temperature.

1.5. OPTICAL PROPERTIES

Optical clarity is one of the surprising and unique properties of block copolymer thermoplastic elastomers. Owing to the fact that they are usually composed of, at least two phases of different refractive indices, it is expected to remain opaque (i.e. not able to allow light to pass through it) as normally observed in incompatible
homopolymer blends. It is believed that due to phase segregation of the individual components into intimately distinct interdispersed micro-domains of size not greater than 1000Å within the bulk of the material (these domain sizes themselves are smaller than the wave-length of visible light) block copolymers appear transparent except when made up of blocks of very high molecular weight. On the other hand homopolymer blends appear opaque due to large particle sizes and to the refractive index differences of their constituent macro-domain phases. Even more surprising is the observation of transparency in some crystalline block copolymers as well as in wholly amorphous ones. It is thought that the crystallite size in the crystallizable segments is smaller than that found in corresponding homopolymer, this may be possible due to the dispersed nature of the crystalline segments or lower degree of crystallinity within the domains.

1.5.1 REFRACTIVE INDEX (R.I)

Refractive index (n) which by definition, is the ratio of velocity of light in vacuum to that in the medium, expressed as:

$$n = \frac{C}{V_{\text{med.}}}$$  \hfill (1.5.1)

where C is the velocity of light in vacuum and V the velocity of light in air or medium (C is ca. 3 x 10^8 m/s). The medium referred to here is the sample. Since measurements are usually carried out in air the refractive index in air is used. Refractive Index in vacuum is taken to be unity and that of air is slightly greater (1.000277) and at ordinary circumstances that of air is usually taken to be between one
and two for most materials. Only a few have slightly greater value than two. At particular wave-length (\(\lambda\)) and temperature, R.I is always a constant and its relation with temperature in the absence of transmission is always a linear one, being mainly as a result of thermal expansion. Therefore at constant wave-length (\(\lambda\)), measurement of R.I at various temperature can be used to determine transition processes in a material. Refractive index has been used to measure the glass transition temperature as this occurs at a characteristic temperature unique to the material. It was noticed that measurements done, using this technique produced a sharper transition region than those done using Differential Scanning Calorimetry (DSC) method, by Krause and co-workers\(^{154}\) working with styrene-butadiene (di. and tri-block) copolymer.

1.5.2 BIREFRINGENCE

If a material has different refractive indices in different directions it is said to produce birefringence (which is the difference in refractive indices between the fast and slow rays travelling through the material). Birefringence is a bulk optical anisotropy usually observed in amorphous materials which can be generated by one or more of the following factors:

(i) deformation birefringence which can occur in any optical system in which by the action of stress or strain, axial extension or compression could change the "lattice" spacing , which may thereby result in a refractive index difference along / across the applied deformation axes. Infinite birefringence may also result from
distortion of bond angles and lengths, from their equilibrium positions.

(ii) orientation birefringence which occurs as a result of some physical ordering of optically anisotropic elements (such as chemical bond, crystallites, etc.) along some preferred direction in the material. This can occur in polymers if the chains are aligned as is the case during a uniaxial extension and drawing. The maximum in orientation birefringence is termed the "Intrinsic Birefringence".

(iii) form birefringence usually arise in a two phase material. It is believed to be caused by anisotropy in the shape of the phase boundaries. This happens because of the difference in refractive index between the two phases. It also depends on the volume fractions ($\phi_1, \phi_2$).

The total birefringence of a two phase polymer as described by Wilkes et al(152) can be expressed in terms of the contributions from its components as:

$$\Delta = \phi_1 \Delta_1 + \phi_2 \Delta_2 + \Delta_F$$  \hspace{1cm} (1.5.2)

where $\phi_1$ and $\phi_2$ are the volume fractions of phase 1 and 2, and $\Delta_1$ and $\Delta_2$ are the birefringence contributions per unit volume, from the micro-phases and $\Delta_F$ is the form birefringence. Samples having parallel cylinders lattice are expected to have positive Form birefringence expressed as follows(156-7):

$$\Delta_n = \frac{\phi_1 \phi_2 (n_1^2 - n_2^2)^2}{2 \left[ (1+\phi_1)n_1^2 + \phi_2 n_2^2 \right] \left[ (1+\phi_2)n_1^2 + \phi_1 n_2^2 \right]}$$ \hspace{1cm} (1.5.3)
while the sample consisting of parallel layers is expected to be negative and is expressed as:

\[
\Delta n = \frac{-[(1 + \phi_1) n_2^2 + \phi_2 n_1^2]}{2 \left[\phi_1 n_2^2 + \phi_2 n_1^2 \right] \left[ (1 + \phi_1) n_1^2 + \phi_2 n_2^2 \right]} \tag{1.5.4}
\]

It is expected that it will normally change with strain because of the orientation of the lattice, with elongation of the polymer.

Change in birefringence can be caused by many processes and the following are considered to be the more prominent causative agents: "chemical reactions, viscous flow or diffusion, crystallization, orientation of crystallites, macroscopic faults, release of stress and configurational changes"\(^{(153)}\). The interactive nature of some of these processes differ from polymer to polymer and will normally depend on temperature.

This optical anisotropy and other optical phenomena such as Refractive Index and transmitted light intensity have been used for property characterization in polymers. However, the application of birefringence to the analysis of thermoplastic elastomers is recent and theoretical treatments are developing rapidly.

1.5.3 TRANSMITTED LIGHT INTENSITY

Transmitted light intensity has not been a popular method of characterizing polymers until recent years. Pico and William\(^{(155)}\) have used the method to detect transition regions in a plasticized SBS. Here, the clear solution of the sample was put in a glass cell and placed in a preset oven with a transparent window. A laser beam was passed through the sample at various temperatures and the
transmitted light intensity recorded. Plot of transmittance versus time at various temperatures, showed the temperature range in which there was large increase in transmittance. (Ideal presentation of data would be a plot of transmittance versus temperature as this would allow for thermal and morphological equilibrium) The transition from opacity to clarity was regarded by them, as the separation temperature above which the two phases mix.

*** Please note that the figures and tables of results not shown within the text can be found in the appendices (I) and (II).

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CHAPTER (II)

2. STRESS RELAXATION - THE BACKGROUND

2.1 INTRODUCTION

In this chapter attention is focussed on the discussion of the background of stress relaxation in polymeric materials, the processes that lead to the phenomenon and its relevance to polymer products in service. Although the emphasis is mainly on the compression mode the tensile mode is not neglected.

Stress relaxation is defined as the decay of stress (with time) at constant strain while the complementary definition for creep is the increase in strain (with time) at constant stress. It has been argued elsewhere\(^{(1)}\) that despite the above straight-forward definitions neither the strain nor the stress can be maintained strictly at constant levels due to the fact that these parameters are associated with infinitesimally small displacement (i.e. a point concept) so that absolute measurement and control of these parameters is impossible.

Because ageing phenomena control creep and stress relaxation processes (i.e. the rearrangement of structures on a molecular scale caused by the breaking of force-bearing chains and formation of new ones) they form the two extremes of such tests that can be used to study the effect of fundamental ageing processes. This can be clarified by considering specimen behaviour as shown in figure 2.1(a) and (b). In both cases, for stress relaxation studies, the longitudinal dimension is held at a constant value by fixing the grips or holding plates and this is quantified by the parameter known as
the "nominal strain" (i.e. strain per unit length). However in either case the specimens can change the total deformation by rearranging their displacement and hence the strain. It can be seen that this time dependent displacement is the essence of creep, and was termed "time dependent rearrangements on a macro scale" which relieved the material of its strain, by Fernando(1), especially at the highly strained parts, manifesting a decay in force generated on the grips or holding plates. It should be noted that the constant strain or stress condition is never met and the time dependent displacements, however small they are, play a major role in determining the force and its rate of decay with time.

![Diagram of fixed grips and boundary point](image)

(a) Tensile specimen

![Diagram of cylindrical compressed button](image)

(b) Cylindrical compressed button

**Figure 2.1** Possible time dependent displacements of specimens at constant "strain"
One classic case which demonstrates the time dependent behaviour of relaxation is the force/displacement characteristic of elastomers where the faster a specimen is strained the less it has chance to relax and as a result a higher force for a given displacement is obtained. The above discussion leads to the conclusion that:

(i) neither the strain nor the total deformation is maintained constant in stress relaxation studies but rather what actually is maintained constant is a kind of imposed restriction on possible consequent deformation and

(ii) stress relaxation occurs as long as the specimen is under strain, regardless of the restriction to any sort of deformation which may exist, since displacement is inevitable.

The advantage and main attraction of the stress relaxation test over creep test for ageing studies is that it is convenient to impose a limited restriction on deformation, for example by keeping the grip or holding plate fixed. Therefore it is a specialised experiment of stress relaxation, general relaxation measurements are carried out under a type of imposed restriction on deformation\(^2\). Thus stress relaxation measurements can be better defined as the monitoring of force (with time) required to maintain a given type of restriction on deformation. Note that this does not commit to constant strain or constant total deformation.

Elastomers are widely employed in applications in which they are subjected to constant compressive strain (such as, in sealing, gaskets, suspension systems for vibration insulation etc.) and are expected to operate satisfactorily over a time scale of up to 100 years. For this
reason, therefore, it became necessary that stress relaxation test be
standardised to support this market. Not only does stress relaxation
measurement form one of the basic tests for ageing studies it is one
of the several experiments used in the study of visco-elastic
properties of polymer materials - basically the sample to be tested is
deformed to a nominal strain and the stress required to maintain the
fixed strain is measured as a function of time at constant
temperature. In principle, long term measurement will characterise
the visco-elastic behaviour of the polymer and can be related to
other properties such as creep and dynamic properties of the
material as these can also be used to characterise visco-elasticity in
polymers.

Often stress relaxation experiments are also used to investigate
the effect of environment, such as, thermal and oxidative
degradation on polymer materials\(^{(3)}\). Besides, there is evidence of
instances where studies have been made to relate physical
properties such as, impact behaviour to stress relaxation\(^{(4)}\).

Stress relaxation tests can be carried out in conditions of tension,
compression, shear or biaxial loading, leading to an increasing
understanding of the structural changes occurring under strain. In
spite of these, a survey of the literature reveals that very few
studies have given attention to stress - strain relationship and
relaxation in compression. Probably one of the factors hindering this
progress is the lack of a simple, low-cost but reproducible equipment
to carry out this test. A countless variety of instruments has been
developed since the first attempt by Fletcher in 1944 to study stress
relaxation as a function of time but the ideal standard instrument as
requires by stress relaxation was not developed until very recently with research in the I.P.T.M.E., Loughborough University of Technology. The problem was solved by using jigs to maintain the samples at a fixed deformation rather than tying down an instrument with one test. The jig, independent of the stress measuring apparatus can be separated and left in the desired test environmental condition. This also permits periodic or semi-continuous stress measurements over the desired period of time.

2.2 DEGRADATION AND STRESS RELAXATION

2.2.1 INTRODUCTION

Polymer degradation may be defined as an irreversible process in which useful polymer properties degenerate when exposed to the environment. This is an unwanted and harmful process which can be reduced by stabilisation of the polymer. A fundamental consideration of polymer stabilisation must be based on sound understanding of the mechanism by which polymers degrade. Although in most instances degradation involves the rupture of primary chemical bonds, cleavage of bonds can also be responsible for polymer degradation. Since the mechanisms through which polymer fails in service vary with exposure conditions as well as the polymer structure, detailed mechanisms of polymer degradation are not discussed here. This section intends to highlight the relevance of degradation of polymer network to the stress relaxation of a polymer under strain.

The cracking of rubber, the yellowing of cotton fabrics, the
embrittlement of plastics, etc. are examples of polymer degradation. Various schemes have been used to classify polymer degradation. One such popular classification is based on the main factor responsible for the degradation, such as thermal, photo, oxidative, chemical, biochemical, mechanical, etc. processes. Another possible classification is based on the dominant process taking place during degradation (e.g. chain scission, depolymerization, cross-linking, substitution etc.) It can be seen that both chemical reactants and energy sources contribute to degradation of polymers. Although a wide variety of chemical reactants is responsible, oxygen is by far the worst offender. Absorption of 0.2% of oxygen is sufficient to reduce the tensile strength of a rubber vulcanizate by 50%\(^5\). As a result of this high sensitivity of physical properties to such limited chemical change, studies of chemical transformation in polymers are of unlimited usefulness for resolving fully, vulcanizates degradation. Tobolsky, Prettyman and Dillon\(^6\) have derived and applied a sensitive stress relaxation technique for monitoring stress changes in a vulcanized rubber, such that these changes could be correlated to the breaking and making of chemical bonds in an elastic network\(^6\). This led to the development of the two net-work theory by Andrews, Tobolsky and Hanson\(^7\).

In principle an ideal cross-linked elastomer network in the range of rubbery behaviour should experience little stress relaxation and should not decay to zero stress under deformation. However stress relaxation observed at this range has been attributed to chemical rupture of the rubber net-work, otherwise termed "Chemical Stress Relaxation".
2.2.2 THE STRESS CHANGE IN A RUBBER NETWORK

Tobolsky and co-workers\textsuperscript{(6-8)} were probably among the earliest to explain the stress relaxation phenomenon in terms of breakdown of network structure. Their proposed "Two network theory" introduced the concept of simultaneous scission and cross-linking occurring in a rubber under a state of constant strain. Disruption of the network structure can occur in two ways:

(i) scission of chemical bonds such as -C-C- or -C-S_x-C, in which case chemical reaction will take place, increasing the complexity of the secondary scission and cross-linking reactions.

(ii) scission of physical bonds such as weak links between polymer chains and filler particles, or removal of physical restrictions such as chain entanglements.

As shown later, the kinetic theory of rubber elasticity is concerned with the equilibrium elastic properties of rubber materials and can not account for non-equilibrium situations such as stress relaxation. Flory\textsuperscript{(9)} has further developed the theory to include the expression which accounts for the elastic energy of polymer systems where the original cross-links are ruptured and secondary cross-links are being formed in the state of strain which may be different from the original unstrained state. The theory suggests that when a piece of vulcanized elastomer is subjected to a deformation, the original cross-links present at the beginning of the straining will resist the deformation thus giving rise to resisting force. However the scission of cross-links or chains reduces the number of cross-links which contribute to the force while the secondary cross-links

76
formed at the state of strain do not offer any contribution to the force since any chain formed by cross-linking are part of a new network equilibrium in the strained state. This new network will give rise to "permanent set" (i.e. to an increase in unstrained length when the strain is removed). However, if the system is then brought to another state of stress, the network, (i.e the original and the newly formed secondary cross-links) will contribute to the new restoring force, though to varying magnitude, so that the stress is proportional to the stress supporting the network chains "N" and if during degradation, a number \((N_0 - N)\) of the chain \(N_0\) originally present are broken, the ratio of the final tension force \(f\) to the initial force \(f_0\) is

\[
\frac{f}{f_0} = \frac{N}{N_0} \quad \text{(2.2.1)}
\]

Thus the decay in stress at constant extension during ageing is a direct measure of the degradation of the elastic network.

As shown by the theory of rubber elasticity, an ideal elastomer subjected to a deformation, of extension ratio \((\lambda)\), will develop a restoring force or stress which obeys the equation of state

\[
f_1 = NkT(\lambda - \lambda^{-2})
\]

where \(N\) is the number of net-work chains. The equation is based on the fact that the stress on a stretched rubber strip arises from the decrease in entropy during stretching which in turn is related to the configurational possibilities of the random coiled molecular chains\(^{(10)}\). It might be expected that the stress of a vulcanized rubber in the region of rubbery behaviour when strained, should remain constant with time. However, the stress decays with time, the cause of which is attributed to the chemical reaction in the
chain net-work, such as, chain scission, oxidative changes, etc. Hence the equation of state should be made time-dependent by replacing \( N \), (a constant) with \( N_o, t \) (the number of the original net-work chain per unit volume remaining unbroken at time "t") so that:

\[
f_i = A_o k T \left( \lambda - \lambda^{-2} \right) N_o , t \quad \text{(2.2.2)}
\]

where \( A_o \) is the original cross sectional area of the specimen measured in the unstrained state\(^{11}\).

An infinitesimal increase in the extension ratio \((d\lambda)\) will result in the manifestation of the force contributed by the original net-work and can be expressed as:

\[
df_i = A_o k T \left| 1 + \frac{d\lambda}{\lambda} \right| N_o , t \quad d\lambda \quad \text{(2.2.3)}
\]

Following the two net-work theory the presence of a certain number \( N_s, t \) of a new secondary cross-links formed (though not contributive at the extension ratio \( \lambda \)) increases the net force by an amount:

\[
df_2 = \left( \frac{A_o}{\lambda} \right) k T \left[ 1 + \frac{d\lambda}{\lambda} - \frac{1}{(1 + \frac{d\lambda}{\lambda})^2} \right] N_s, t \quad \text{(2.2.4)}
\]

where \( A_o/\lambda \) is the cross sectional area of the secondary net-work in its unstrained state such that:

\[
df_2 = A_o k T \left( \frac{3}{\lambda^2} \right) N_s, t \quad d\lambda \quad \text{(2.2.5)}
\]

Thus the sum total increase in force\(^{14}\) is

\[
dF = df + df = A_o k T \left[ 1 + (\frac{\lambda^3}{\lambda^2}) N_o , t + (\frac{3}{\lambda^2}) N_s, t \right] d\lambda \quad \text{(2.2.6)}
\]
Note that although there is a general acceptance of this theory, it is still a subject of much discussion. It may require further improvement and some modifications as different vulcanizates behave differently under stress or strain. Numerous areas on this subject exist that requires further investigations (such as the role of fillers, the effect of crystallization, the choice for scission and recombination site and the role of oxygen in the process, the effect of entanglements etc.).

2.2.3 NON-LINEAR VISCO-ELASTICITY OF ELASTOMERS

An ideal material obeying Hooke's law when subjected to a series of strain $S_0, S_1, S_2, \ldots, S_{n-1}, S_n$ at times $t_0, t_1, t_2 \ldots t_{n-1}, t_n$ will experience at the end of loading history a stress of:

$$f = E \sum \left( S - S_i \right) + E \sum \left( s_i - s_j \right) + \ldots + E \left( S_n - S_{n-1} \right) = F_n S$$  \hspace{2em} (2.3.1)

i.e. the equilibrium force required to maintain the deformation remains constant with time. On the other hand a material will undergo a linear visco-elastic behaviour when subjected to the same loading history, will produce a time dependent stress, as expressed by the Boltzmann principle(40):

or for a continuous strain history, it can be expressed by the equation:

$$f(t) = E_r(t)(s_0) + E_r(t-t_1)(s_1-s_0) + E_r(t-t_2)(s_2-s_1) + \ldots + E_r(t-t_n)(s_n-s_{n-1})$$ \hspace{2em} (2.3.2)

$$f(t) = \int_0^t E_r(t-\theta) S(\theta) d\theta$$ \hspace{2em} (2.3.3)

where $E_r(t)$ is the time dependent relaxation modulus and $S(\theta)$ is
written for \( dS(\theta)/d\theta \).

Materials whose basic structure does not change with time during experiments are expected to show linear visco-elastic behaviour. However Leaderman\(^{41}\) has shown that a number of materials such as Nylon 66, Silk, Rayon and Mohair which are oriented crystalline fibres showed remarkable deviations from the Boltzmann principle of linear visco-elastic response. Hence the Boltzmann principle is applicable only under special conditions of extremely small loads and at temperatures where crystallization does not occur.

2.2.4 SIGNIFICANCE OF PHYSICAL RELAXATION

Various methods have been adopted in the literature by which stress relaxation data can be analysed, most of which considered stress relaxation process arising from two main contributions:

(i) physical stress relaxation due to the changes occurring in the equilibrium conformation and

(ii) chemical stress relaxation due to structural damage to the net-work. It is believed that the initial part of the relaxation (up to approx. 100 hours at room temperature\(^{1,12}\)) is due to physical relaxation and chemical phenomenon sets in and dominates the later stage of the relaxation process. (Figure 2.1(a)). Further more it has been shown that physical relaxation gives a straight line (or linear) relationship in a (force) versus log. (time)\(^{12}\). It has been shown too\(^{1,12}\) that the stress relaxation curve obtained for a rubber shows an initial linear part with a later downward deviation manifesting the take over from physical by chemical stress relaxation. However
the present author has observed a reversal or semi-reversal of the
case also in a force versus log-time plot using some thermoplastic
elastomer samples, i.e. a downward initial part (though fairly linear)
and a deviation to a linear, some-what horizontal, part at the later
stage of the curve, see figure 2.1(b) which according to the above
prediction corresponds to situation where chemical stress relaxation
takes over. Fernando\(^1\) has argued that the conclusion is an illusion
and that it has no physical significance in terms of rate as this was
based solely on the observation of a particular experimental data
points on a force versus log-time plot. More so it was due to the
peculiarity of the log-time scale, where shorter times are highly
expanded and longer times are highly contracted. An argument he
supported mathematically\(^1\) to show that physical relaxation of
rubber can not give a straight line in a log-log. plot. In addition that
physical relaxation of a deformed rubber should be over within short
period of time after loading is completed\(^{1,13}\) but experts\(^{42}\) have
argued that physical relaxation can proceed as long as warranted by
the experiment, depending on the polymer type and experimental
condition in question.

Three main conclusions arrived at are that:

(i) physical and chemical stress relaxation occur simultaneously
especially during the early stage of the relaxation process.

(ii) in long term measurements effect of physical relaxation can be
ignored without losing very much accuracy provided loading rate is
kept to a low value (0.05 cm./ min. and below) and

(iii) high rate of loading will lead to higher degree of physical
relaxation, thus it is wise to reduce loading rate. Moreover due to the
non-equilibrium conditions of the effect of physical relaxation, quantitative treatments of these interactive effects become difficult. Hence based on the geometry of these curves the present author (in support of Fernando's arguments) suggests that because of the different compositions and structure of different polymer types, variety of responses to deformation (which will in turn lead to variety of geometric patterns of curve in the log-log. plot) is expected. It can be seen that the role and nature of oxidation (especially during the early stage of the relaxation process) is still not fully understood. Therefore it is not sufficient to draw a general conclusion as regards the nature of force versus log-time plot of data obtained for materials undergoing stress relaxation, on the basis of a single experimental datum of a particular polymer type. A proposed master curve of a force versus log-time plot for stress relaxation may be as shown in figure 2.1(b). Note that it is not possible to apportion any part of the curve as due to physical or chemical stress relaxation.

With reference to the force versus log. time curve, it can be seen that thermoplastic elastomers are relatively more vulnerable to physical relaxation. This can be attributed to accelerated breakdown of the micro-domain structures of the thermoplastic phase - giving rise to Mullin's effect (stress softening) due to chain disentanglement from the domains. The author wishes to suggest that due to the molecular size scale of the domain structure of phase separated thermoplastic elastomers (which generally improves mechanical property) and the three dimensional net-work of the physical cross-linking (which may cover up or prevent possible reaction sites)
the effect of chemical relaxation (oxidative chain scission) seems less effective in the thermoplastic elastomers investigated (at least within the observed test period). Secondly the presence of a second component may influence the oxidative degradation of the other (in this case, may have a "shielding or mopping up" effect - by competing for oxygen etc., with the chemically active one). This can be seen in the linear (horizontal) nature of the force/log. time curve along the time axis. (Figure 2.1(b)). The gradual stress decay can only
be explained by attributing it to an entropic effect (physical relaxation) since it has been shown elsewhere\textsuperscript{(35,45)} that chemical stress relaxation of rubber results in rapid decay of stress, hence the downward tailing of the curve. (Figure 2.1(a)). This is in support of the expert's view that physical relaxation can proceed even for decades depending on the nature of the polymer. It may be as well attributed to the healing effect usually associated with deformed thermoplastic elastomers after a long period of time of being in the deformed state and/or annealing at elevated temperature in which case a new equilibrium structure is assumed.

2.2.5 CHEMICAL STRESS RELAXATION

From the conclusions reached for physical relaxation of a piece of rubber subjected to constant strain, especially on the view that physical relaxation predominantly controls the early part of the process after loading, all other time dependent phenomena subsequently observed, can only be explained by considering the processes which lead to the changes in the net-work structure. Usually these processes are collectively referred to as chemical stress relaxation. Chemical stress relaxation does not mean the necessary involvement of chemical reaction in the sense of electron transfer from one molecular segment to the other or electron sharing of two segments, as such but basically means in a broad sense the damage and subsequent rearrangement of the molecular structure. In a typical vulcanized elastomer, this damage to structures is mainly as a result of:

(i) scission of chemical back-bone bonds leading to the breakage
of elastically effective chains, each scission will reduce the number of active chains by one,

(ii) rupture of chemical cross-links which hold the molecular segments together, forming a three dimensional net-work. Each cross-link that undergoes rupture will affect two molecular segments.

(iii) breakage of physical bonds, such as Van-der Waals attractions, dipole interactions, chain entanglements, and in the case of filled elastomer, the weak interaction (adhesion) between polymer/filler interface. It may be that factor (i) and (ii) above will have their consequences due to the formation of chemically active radicals which will in turn undergo a series of reactions, that will lead to further changes in the structure. Therefore a knowledge of the chemical activity of the radicals is necessary in understanding and quantifying the net result of the state of the chain structure. On the other hand, those factors that fall under factor (iii) though may not lead to any chemical reaction but are by no means simple to account for since they are the least understood of all.

The chemistry of this subject can be found in the literature and the kinetics involved are well established. The detailed development of the reactions, especially in the field of reactions in solid polymer is still in progress. A typical scheme of the oxidative ageing of diene rubber in the absence of anti-oxidant is shown in figure 2.2 (a). Although the scheme sufficiently represents the reactions, it has limited use with respect to stress relaxation. The limitation lies in the fact that the scheme is so written to highlight the possible reactions when oxygen is absorbed with the generation
of other active groups which will be of interest to a chemist but do not account for other (non oxidative) processes that may lead to degradation. The prediction of the effect of ageing on mechanical properties demands a scheme that shows, for example the number of elastically active chains or number of new chains formed as a result of chain scission, as has been shown in part (b) of figure 2.2 by Fernando et al\(^1\). However the scheme of figure 2.2 (a) was rearranged to include additional information such as the number of broken and reformed chains. (see figure 2.2 (b).) Note that the new scheme differentiates between the end radicals (\(R_e^*\)) and mid-chain (\(R_m^*\)) since the latter are susceptible to induce further scission of the chain. In this case \(C_0\) and \(C_1\) represent the chain formed at the undeformed and deformed state respectively, and \(P_0\) and \(P_1\) are the factors by which scission is accelerated due to the strain associated conformational entropy. \(\Omega_0\) and \(\Omega_1\) represents in (both \(C_0\) and \(C_1\) type of chain) the existence of chain radicals (\(R_m^*\)).

It should be noted that although the above scheme is very versatile in relating the chemistry of degradation to the physics of the net-work structure, it is not applied in this work. It has been shown to highlight the possible chemistry of degradation during ageing (stress relaxation).
(a) OXIDATIVE KINETICS WRITTEN TO HIGHLIGHT VARIOUS ACTIVE GROUPS

\[
\begin{align*}
R\rightarrow R & \quad \text{Primary (thermal) scission} \\
R^* + D_2 & \rightarrow \text{ROOH} \quad \text{scission associated with a mid-alkyl radical (p) (k)} \\
\text{ROOH} & \rightarrow \text{HO} + \text{R}^* \quad \text{addition} \\
\text{ROO}^* + C & \rightarrow \text{C} = \text{O} \quad \text{disproportionation} \\
\text{R}^* + \text{R}^* & \rightarrow \text{ROO}^* \quad \text{combination} \\
\text{ROOH} + \text{R}^* & \rightarrow \text{HO} + \text{R}^* \quad \text{dissociation} \\
\text{2 R}^* & \rightarrow \text{inactive products}
\end{align*}
\]

(b) ELABORATE OXIDATIVE KINETICS MANIFESTING CHAIN SCISSION AND REFORMATION

\[
\begin{align*}
C_0 & = \text{original chains} \\
C_1 & = \text{newly formed chains} \\
C_0, C_1 & = \text{primary scission (p) (k)} \\
R^* & = \text{scission associated with a mid-alkyl radical (p) (k)} \\
\text{ROOH} & \rightarrow \text{HO} + \text{R}^* \quad \text{addition} \\
\text{ROO}^* + C & \rightarrow \text{C} = \text{O} \quad \text{combination} \\
\text{R}^* & \rightarrow \text{inactive products} \\
\text{HO} + \text{R}^* & \rightarrow \text{HO} + \text{R}^* \quad \text{dissociation} \\
\text{2 R}^* & \rightarrow \text{inactive products}
\end{align*}
\]

**Figure 2.2**: OXIDATIVE KINETICS OF STRESS RELAXATION
2.3 RELAXATION MECHANISM: ALPHA (α), BETA (β), AND GAMMA (γ) RELAXATION

2.3.1 INTRODUCTION

There are several simple distinct mechanisms by which stress relaxation occurs. The more important include:

(i) relaxation of the chain especially in the glass - rubber transition region, at which the relaxation time of a movement of a part or of the whole of the polymer chain is comparable to the experimental time of the process by which the transition is observed,

(ii) relaxation due to molecular flow which occurs in the rubbery and liquid flow regions,

(iii) chain scission/or cross-links, a form of chemical degradation which often is important in cross-linked elastomeric net-works, especially at elevated temperatures,

(iv) reversible relaxation involving complex adjustments of the chain in a net-work in response to a stress, possibly involving chain motion of physical entanglements, other-wise known as "Thrion relaxation"(17). A long term relaxation of thermally stable elastomers illustrates this phenomenon and

(v) relaxation due to interchange between molecules (not degradation), for example, molecular interchange between Si-O bond and other molecules in silicone elastomers(3). Usually a combination of these mechanisms is simultaneously operative during a relaxation process which makes the analysis of a single responsible factor a complex task. Most complex is the mechanism of the actual response and the responding part in the bulk material. Recently this has become a subject of interest for many investigators(18-24) who
adopted the terms alpha (α), beta (β), gamma (γ) etc.
relaxation or transition, in order of decreasing temperature, below
the melting temperature, to describe the fundamentals of these
relaxation processes in bulk polymer. A study of the mechanism of
the transitions has led to the better understanding of
structure/property relationships.

The Differential Scanning Calorimetry (DSC) thermograms of the
samples used in this programme have been obtained. It was
observed that in addition to the melting and crystallization peaks,
other peaks which cannot be accounted for by these common
transitions were also obtained. It is not unreasonable to relate
them to alpha (α), beta (β), gamma (γ), etc. relaxation and since
they are relaxation processes the mechanisms merit some
understanding.

2.3.2 ALPHA (α) - RELAXATION

According to the general literature(19) dynamic mechanical
analysis of polymers prior to melting has been the most successful
technique used to reveal the alpha (α), beta (β) and gamma (γ) peaks.
It is believed that the alpha peak is representative of the crystalline
phase and originates from some type of motion in the crystal
interfacial region(20-8). Mansfield, Hoffman et al have suggested that
during alpha relaxation the chains in the crystal interior are
mobilised (e.g. chain rotation, translation and twist) but on the basis
of the model compound used by them (C₉₄H₁₉₀) it has been clearly
shown that the crystal body itself would not lead to an
alpha-relaxation but the fold surface is necessary for the occurrence
of the alpha process(25), an observation supported by Sinnott(26), Boyd(27) and Khanna(28) et al, in their recent investigation with polyethylene. They have attributed alpha - relaxation to the motion or deformation in the interfacial regions (chain-fold, loops and tie molecules) which are activated as a consequence of chain mobility in the crystal. Khanna et al concluded that the alpha (α) peak (Tα) in polyethylene appeared, varying between 10 - 75°c depending on the crystallite thickness - thicker crystal lamellae leading to higher temperature relaxation.

2.3.3 BETA (β) - RELAXATION

The true origin of beta(β) relaxation is still unresolved but it is commonly attributed to the amorphous phase (24). Hoffman et al observed that a single crystal of linear polyethylene (i.e no discrete amorphous phase) does not exhibit a beta (β)-relaxation whereas a very small beta(β) peak has been reported in linear polyethylene containing an amorphous phase (24-26). It has also been described by Stehling et al that the beta(β)-relaxation is due to motion of the chain branching(21,29). Such observation as (a) increase in intensity of beta(β) peak with increase in amorphous volume, (b) beta(β)-peak temperature (Tβ) increases with increase in molecular weight and that it is influenced by the type and amount of branching enabled Khanna et al to conclude that the beta(β)-relaxation is analogous to a Tg. They observed that it occurs between (-35 to -5)°C in polyethylene depending on the polyethylene type.
2.3.4 **GAMMA (γ) - RELAXATION**

Several controversies still exist about the origin of the gamma(γ)-relaxation. Illers\(^{43}\) suggested that (γ)-relaxation is due to the amorphous fraction. Hoffman et al and Sinnoutt\(^{26}\) proposed that it is strictly due to defects in the crystalline phase. Their conclusion was based on occurrence of a gamma (γ) - relaxation in single crystals of linear HDPE and it was attributed to the reorientation of loose chain ends or defects in the polymer crystals. Khanna et al, using a HMW-HDPE sample observed that there was increase in gamma (γ) peak intensity for quenched samples (i.e increased amorphous volume). They then proposed that gamma (γ)-relaxation involves the motion of short segments (e.g three to four CH\(_2\) group) in the amorphous phase in addition to the reorientation of loose chain ends within the crystals and amorphous fractions. It was shown that gamma (γ)-relaxation temperature increases with the number of carbon atoms between the surfaces of the crystals (i.e the fold length, so that the thicker the crystal the higher the (Tγ) and that it occurs at (-107 and -114) °C respectively for HDPE and LDPE.

On the basis of the above discussions it can be seen that the knowledge of the origin of alpha, beta and gamma transitions in addition to those of the melting and crystallisation transitions will serve as a powerful and comprehensive analytical tool in determining the nature of the structure of polymers (i.e in terms of their crystallinity). Note that the above discussions have been based on work with polyethylene due to the limitation of literature on the subject. It is expected that thermoplastic elastomers (due to their
structural complexity) will show complex alpha, beta and gamma transitions.

2.4 STRESS RELAXATION AND ITS RELEVANCE TO SEALS

In order to appreciate the relevance of stress relaxation to the long term performance of seals in service life, it is necessary that one understands their formulations, the designs and type of sealing application to which they are put. A common application is as a joint ring, used in sealing pipes joints, to prevent leakage of fluid, both into and out of the pipe. For many years the formulations have been based on natural rubber. However with the rise of the polymer industry new synthetic rubbers have been developed and they have already replaced natural rubber in many seal applications due to property superiority of synthetic rubbers over natural rubber\((30-31)\). There are three basic functional types of sealing rings namely "O" ring compression, "Mechanical compression" and "Lip seal" types, the description of their design features of which can be found in the literature\((32)\). The important material properties considered and their relevance to the seal performance has been discussed. They include:

(i) Compression set (Recovery).
(ii) Stress relaxation.
(iii) Compression modulus.
(iv) Environmental resistance.
(v) Deleterious effect of fluid conveyed in pipe.

The author regards stress relaxation and such parameter as (i) and (iii) above as the parameter most dominant in determining the
long term performance of seals. Therefore it is intended in this section to discuss them further.

2.4.1 (i) STRESS RELAXATION:

Stress relaxation as described elsewhere(3), may be defined as the time dependent decrease in stress at constant deformation. Two types of stress relaxation were distinguished in the literature. The first of these is physical relaxation which is associated with the slow viscous flow of all elastomeric materials. The second process being chemical in nature involves the breaking of primary chemical bonds in the elastomer network.

The BS 903-A34(33) described a typical present day stress relaxation test specification, in which, using a compression ring and a jig (a compression device), the rubber is compressed to 20 +/- 1% nominal strain which is maintained constant during the test. Test should be performed at standard temperature and nominal stress (stress calculated on unstrained sample area) and reported after 10 minutes and 168 hours. This will correspond to three decades of loading i.e % decay in stress per three decades

\[
\text{\%} = \frac{(P_{10} - P_{100}) \times 100}{P_{10}}
\]

(2.7)

The term "loading" means the process of straining the test specimen to a specified nominal strain. Time is taken as zero at the instant straining comes to an end. On the other hand the ASTM standard(33) specified that the test be carried out at 100°C for 48 hours and a standard jig is given. The BS 903-A34 failed to specify a
standard jig nor did it discuss the difficulties in obtaining the measurement, which is a major draw back of this standard. It has been observed\(^{(30)}\) that:

(i) the base polymer and type of cross-link determines relaxation behaviour,

(ii) a decrease in relaxation occurs when antioxidant is added to a rubber compound,

(iii) relaxation in practice, depends on the bulk of the product - i.e. larger items suffering less total relaxation,

(iv) stress relaxation increases with increase in filler load.

Therefore it is important that these observations be taken into account when formulating and designing materials for sealing applications.

However, the author noted that some thermoplastic elastomers can retain above 50\% of their initial force after being deformed (compressed) to 25 +/- 1 \% of their original height for 10,000 hours and above, and attained recovery of above 50\% in 2000 hours. It can now be seen that material developers seem to be fast approaching their ideal goal in this respect. It is believed that the structural nature of these materials (where the thermoplastic block provides the high modulus and the elastomer block provides the flexibility required for an ideal seal) was responsible for the observed enhanced characteristics. It is the view of polymer scientists/technologists that thermoplastic elastomer materials will take over from other conventional sealing materials for this reason.

In order to predict the long-term performance of materials to be used for pipe sealing application, Derham\(^{38}\) concluded that stress
relaxation measurement should be carried out on all materials for sealing application in such environment to which they will be in contact during service life. He also suggested using elevated temperature to accelerate the chemical component of relaxation and then extrapolating to ambient temperature to obtain service life predictions. Wright(35) also used the technique to evaluate suitability of rubber for gas pipe-line seals. According to him, stress relaxation test carried out at low temperature (say 20°C) only measures the initial part of the process (physical relaxation) and ignores the second part of the process in which chemical phenomena come into play. Thus, long-term test is important in order to predict long-term performance.

2.4.2 COMPRESSION SET (RECOVERY)

Compression set is the loss in height of a sample after it has partly recovered from a compression strain. Prior to the recognition of the importance of stress relaxation, compression set was regarded as the yard-stick by which to evaluate the sealing ability of a rubber. The BS 903-A6 (1969) measures the recovery of a disc shaped sample, deformed to a fixed strain of 25% by clamping the plates of a simple jig. The test temperature and time may be varied according to the application of the particular rubber formulation. Generally, after a nominated time period of 24 hours for temperature above 70°C, and 72 hours for test at 20°C and below, the strain is released. The sample is allowed to recover at room temperature for 30 minutes. The new height is then measured and compression set is calculated as the loss in height of the sample expressed as a percentage of the
degree of strain i.e 100% set represents no recovery of the strain at all.

It has been pointed out (37) that laboratory compression set testing may give misleading information regarding rubber for such product as seals, the reason being that:

(i) compression set performance is often not adequately assessed by short term or accelerated test and/or short recovery period after release of strain.

(ii) it is often assumed that compression set is closely related to stress relaxation, though this is often the case, but it does not necessarily mean that inability to recover from strain may mean stress relaxation and

(iii) compression set may be less relevant than stress relaxation (37). Thus it can be seen that the measurement described above also involves a combination of factors about chain net-work degradation and the resultant new structure of the sample.

According to the literature (30), this short term test is unsuitable for long term prediction of service life as well, for example it was noted that large difference between set measurements taken 30 minutes after, and those taken 24 hours after release (particularly after long period of compression) exists, and since speed of recovery would not normally be of paramount importance in service application, provided recovery did occur within a reasonable period of time, the results after longer recovery time are of much more practical value.

This conclusion was reached for the results obtained by Litchfield and Taylor (44) who (using the BS 903 constant-strain compression set method at 23°C in air, to measure the set of different rubber samples
after various time periods - extending from one day to one year) showed that some rubbers giving apparently good set property at short term test but fading as the test period was extended, while others start rather badly but performed well on long term test.

2.4.3 COMPRESSION MODULUS OR (HARDNESS)

Another major factor which determines the service life of seals would be the flexibility of the joint (controlled by the modulus of the sealing ring).

It should be realised that the compression set of a material and percentage deformation defines the sealing force that will be operative in the joint once the cross-section of the seal has been decided. Since the integrity of the joint depends on the sealing force exerted by the joint ring on the pipe, it is obvious that the force must be as high as possible. In theory, high compression modulus combine with high deformation when the joint is complete will provide this condition but in practice there are limitations to maximising a sealing force. For example ,the greater the resistance to deformation and displacement of the joint ring, the greater will be the force required to assemble the pipe joint - the pipe maker requires his type of joint to be made as simply and quickly as possible. Also a rubber formulation that shows high modulus build up while relaxing helps to maintain the integrity of the joint, even though there may be a reduction in the sealing force. Therefore it should be emphasised that it is not the residual force alone which determines the service life but this together with the compression modulus, controls the service life of a seal.
Since modulus is related to hardness the question of sealing force in relation to rubber hardness and its effect on pipe members has been considered by Clarke(29). He concluded that the compression of the ring should be no more than is required to produce water-tight seal under the test pressure for which the seal is designed, after allowing for pressure losses caused by shrinkage and creep of the material, which can be up to (in some cases) about 1/2 to 2/3 of the initial pressure. With regards to ring hardness, he argued that on balance, it would be preferable for a rubber to be too soft rather than too hard. However, in current practice, that hardness does not usually exceed 60 +/- 5 BS degree for "O", ring type joint for sewer pipes and harder materials should be used in pressure pipe joints.

Thus, when one considers that nowadays authorities require that pipe lines should have a service life of 100 years without maintenance it becomes obvious that the modulus of materials should be given equal weighting (in this case) as other parameters (such as stress relaxation and compression set) in predicting the long-term performance of seals.

2.4.4 THEORETICAL ASPECT OF SEALING FORCE

In addition to Clarke's arguments above (section 2.4.3) as regards minimal force requirement of a sealing ring. Lindley and Derham(38) have pointed out that seal failure occurs when the maximum stress between the seal and the mating members becomes less than the pressure difference between the two sides of the seal. Accurate evaluation of the maximum stress requires a rigorous analysis of stress which takes into account the shape and non-linear factors due
to the peculiar elastic characteristics of rubber. Considering the very simple case, where an "O"-ring (with circular section) is compressed between two members, it has been shown that the compression force "F" (per unit length along the circumference) and radial strain "ε" are related as follows:

\[
\frac{F}{E_d} = 1.25 \varepsilon^{1.5} + 50.0 \varepsilon^6 \tag{2.4.2}
\]

and \[ε = \frac{x}{d}\] where \[x = d - (D_1 - D_0)/2\] where "d" is the sample diameter, "E" is the Young's modulus and the parameters "D_1" and "D_0" are the upper and lower end of the sample between mating substrates (under the assumption that the strain is small). Since the width of the contact area "b" is proportional to the compression "x" (figure 2.4) the average contact stress "σ_A" will increase less rapidly than the force. Therefore if "b" = 2.4x as predicted\(^{(44)}\), the average stress "σ_A" will be given by

\[
σ_A = \frac{E \left(1.5 \varepsilon^{0.5} + 50.0 \varepsilon^5\right)}{2.4 \pi} \tag{2.4.3}
\]

It should be noted that the stress distribution across the width of the contact area is not uniform, therefore the maximum stress "σ_max" is much higher than the average stress "σ_A" Lindley\(^{(9)}\) predicted that:

"σ_max" = \[4 \frac{σ}{π}\] thus:

\[
σ_{max} = \frac{4E \left(1.25 \varepsilon^{0.5} + 50.0 \varepsilon^5\right)}{2.4 \pi} \tag{2.4.4}
\]
which should be higher than the pressure difference against which the seal holds the substrates. For no leak, the condition should be

\[ \sigma_{\text{max}} > \Delta P \] or

\[ \Delta P < \frac{4E (1.25 \mathcal{E}^{0.5} + 50.0 \mathcal{E}^5)}{2.4\pi} \]  \hspace{1cm} (2.4.5)

It can be seen here that "E" the Young's modulus becomes the relaxation modulus which reduces with time, denoted by \( E_r(t) \). The above equation is only true, if the seal shape does not change with time.

Equation (2.4.4) can be rearranged to give

\[ E_r(t) > \frac{\Delta P 2.4 \pi}{4(1.25 \mathcal{E}^{0.5} + 50.0 \mathcal{E}^5)} \]  \hspace{1cm} 2.4.6

Thus, according to equation (2.4.6) the parameter \( E_r(t) \) alone determines the sealing force. In the practical sense, the life time performance of a seal depends on many factors other than stress.
relaxation, compression set and compression modulus as discussed above. Note that the sealing force is liable to deviation from the value predicted by equation (2.4.4) due to temperature variation, change in relative humidity\(^{(34)}\), etc.

2.5 REFERENCES
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33a) BS. 903-A34; "Determination of stress relaxation in rubber ring in compression (1978).

33b) ASTM. D1390; "Stress relaxation in compression (1976).


38) J. C. Derham; P. B. Lindley; "5th. Interna. Conf. on fluid-sealing. (1971).


42) Private Discussion with Prof. A.W. Birley.,"IPTME, LUT.").


44) Litchfield; T. J. Taylor; "British Standard Inst. Committee. RUC l; "Unpublished paper"
3. EQUIPMENT AND THE IPT ME METHOD OF STRESS RELAXATION MEASUREMENT

3.1 INTRODUCTION

The history of the development of the study of stress relaxation in compression showed that one of the most important factors hindering progress in this area was the lack of a simple, inexpensive equipment for maintaining the sample under constant strain and obtaining reproducible results\(^1\). This problem seems to have now been solved since the development of the low cost yet reproducible stress relaxation measuring machine in the Institute of Polymer Technology by Fernando et. al. This equipment was used by the author for the work reported in this thesis. This chapter highlights the principal features and the operations of the machine as well as the techniques used in analysing measurements obtained with it to calculate the residual force, strain and M.E.F. of the compressed specimen. Certain shortcomings of the equipment will also be discussed.

3.2 THE WYKEHAM FARRANCE INSTRUMENT

Various types of equipment have been used by various experimenters in the area of stress relaxation measurements. In this Institute the Instron machine was used before the development of the present equipment, based on jigs and a compression device
system, which are separate units, the latter manufactured by Wykeham Farrance Engineering Limited. The stress relaxation measuring apparatus uses a jig (a device to hold the compressed specimen at constant strain) and the force measuring device to monitor the force exerted by the specimen. In practice, one force monitor device can be used with a large number of jigs, for this reason jigs should be portable, inexpensive and capable of making accurate measurements, thereby reducing the need to carry out more than one measurement as recommended in BS 903 - A42.

Details of the design of the equipment, discussion of the ideal curve concept generated from measurements obtained with it and practical considerations are reported in the literature(2-3). The concept of the ideal curve has been adopted not only to ensure an accurate measurement but also to enable one to obtain in a single measurement, as much information as possible and assess its reliability.

In summary, the ideal curve which is the force / displacement characteristic of the jig / force measuring frame, reflects the way the apparatus should behave to ensure an accurate measurement. Thus the ideal curve should be used as the criterion for standardisation and not necessarily the jig or force measuring device. As argued elsewhere(1-3), any set of devices (e.g. jig and force measuring device) capable of giving the ideal curve ensures reliability of the measurement.

3.2.1 THE JIG
The jig is an essential feature of the stress relaxation in
compression measurement equipment, and maintains the specimen at constant strain for the desired period of time. The jig is not a part of the force measuring frame but detachable after the measuring operation is completed and as many as desired could be used with a single force monitor. It can be fed with active or inactive environments at desired temperatures and can be stored even in fluids such as water, oil etc. since it is corrosion resistant.

Jigs are constructed of stainless steel, the requirement being that they should be able to withstand high pressure (BS 970 - 321 S12), are inert to the specimen under test, and corrosion resistant and have high thermal capacity.

Three possible basic designs of jigs with simple construction but varying versatility are shown in Figure 3.1 (a), (b) and (c). These are:

(1) the simplest and cheapest constant depth, two plate jig
(2) relatively simple and cheap three plate jig and
(3) versatile, but expensive continuously variable depth jig.

The type (1) jig is used to carry out the work reported in this thesis, designed by Fernando (3) also the designer of the type (3) jig, while the type (2) jig was designed by Boyes and Wright (4). The main features of the jig comprise of the

- jig housing: which accommodates the sample and glass plates.
- thrustplate: which clamps the sample (lying between the glass plates) to the jig housing.
- 3 bolts: with which the thrust plate is fastened onto the jig housing.
- 2 glass plates: which hold the sample in position and have been
introduced to reduce the frictional force between the sample/jig interface in contact and secondly due to the details of the jig design.

To meet the critical criterion of parallelism the horizontal faces of the jig housing and thrust plate are ground to a smooth finish. Detailed description and operational mechanism of the jigs are found in the literature(2-3).

Figure 3.1

(a) THE CONSTANT-DEPTH JIG

(b) THREE PLATE JIG
3.2.2. THE FORCE MEASURING DEVICE

The main features of the force measuring device manufactured by Wykeham Farrance Ltd. Slough, (Fig. 3.2) have been described in detail in the literature\(^3\). It comprises:

(i) A Wykeham Farrance compression machine consisting of (a) a smooth drive system having a range of speed settings. (A speed of 0.3mm. per minute has been used in this programme (i.e for the stress relaxation and hysteresis tests). (b) a load cell having a relative stiffness of up to ten times that of the specimen with a plunger/heat shield attached to it. Note that load cells of different stiffness can be used with a single compression machine. (c) a rigid frame which holds the load-cell from a cross-head and housing the drive system, with facilities for parallelism adjustments and load cell calibration.

(ii) Power supply system and an amplifier for the load cell output.
The power supply is capable of maintaining a constant D.C. voltage to the amplifier and thus to the loadcell. At the power supply of 24 volts the amplifier is supplying 10 volts to the strain gauge transducer of the loadcell. The signals from the loadcell, ranging from zero to 10.00 mV are then amplified and recorded by the chart recorder.

(iii) A strip chart recorder is used instead of a more expensive X-Y plotter since the Wykeham Farrance machine operates at a constant speed, with a drive system such that the displacement (hence the strain rate) of the specimen is proportional to the time and the speed of the charts.

3.3 SAMPLE PREPARATION AND ASSEMBLY

As reflected by the topic of this thesis all the specimens used in the experiment are thermoplastic elastomer compounds most of which come in different grades of the same formulation and are commercially available materials.

A small cylindrical shape of the sample (12.7 mm in diameter and 6.25 mm high) was prepared by transfer or injection moulding techniques. These are now preferred over specimens cut out from the rubber sheets since the former are known to produce better structural and geometrical uniformity. On the other hand the injection moulded samples are found to have a higher degree of geometrical perfection over the transfer moulded ones (Table 3.1). The transfer moulded samples were prepared by the author while the injection moulded samples were provided by industry - Monsanto. (in the case of the Santoprene specimens). A transfer
mould having 12 cavities was used to prepare the transfer moulded specimens. Table 3.1 (a) and (b) show sets of specimen thickness measured for randomly selected 12 specimens prepared by transfer moulding and injection moulding techniques.

To improve the reproducibility of the measurement, the variability contributed by the specimens should be minimised or preferably eliminated. Variability can be associated with the specimen in either the strained or unstrained states. In the unstrained state, principally, the variability is due to geometrical defects of the mould or cutting, used to prepare the specimen. In some cases structural defects are involved at both the molecular scale (unsatisfactory formulation) and at the macro scale (voids and variable shrinkage). These contribute to poor reproducibility.

Transfer moulding and injection moulding are recommended techniques in order to reduce the incidence of these defects.

Variability associated with the specimen in the strained state is mainly as a consequence of variable slippage at the contact surface of the specimen. One way of eliminating this is to use a bonded specimen which however complicates the moulding technique and the stress developed during the deformation process.

Experience shows that dry lubrication of the specimen by graphite powder or molybdenum disulphide (MoS2) powder and the use of ground glass plates as holding or compression plates, reduces this type of variability. Experience has shown too that this lubrication method is convenient and gives reproducible results\(^{(3)}\).

In accordance with most test standards, the specimen is ready for test after resting for at least 24 hours following processing. Even
though these two moulding techniques are preferred, because they produce better geometrical perfection, mould shrinkages have led to different specimen formulations having different mean dimensions.

Table 3.1 Showing variations in thickness due to mould shrinkage

(a) Transfer moulded Specimens (180°C, 2.5MPa)

<table>
<thead>
<tr>
<th>MEASUREMENT</th>
<th>201-73</th>
<th>201-64</th>
<th>101-64</th>
<th>201-55</th>
<th>101-73</th>
</tr>
</thead>
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<td>6.28</td>
<td>6.34</td>
</tr>
<tr>
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<td>6.32</td>
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</tr>
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<td>6.30</td>
<td>6.30</td>
<td>6.26</td>
<td>6.36</td>
</tr>
</tbody>
</table>

| MEAN   | 6.36 | 6.30 | 6.30 | 6.26 | 6.33 |
| VARIANCE | 1.75x10^3 | 1.0x10^4 | 4.82x10^4 | 0.011 | 1.18x10^3 |

(thickness). For example one measurement of Santoprene 101-73 gives thickness and diameter of (6.25/12.61) mm respectively while Alcryn 1201-B 60A has thickness/diameter of (6.24/12.22) mm.
3.3.1 MATCHING THE JIGS AND GLASS PLATES

In table 3.1(a), it can be seen that even though the same mould (of cavity depth 6.3 mm.) was used to prepare them, different formulations gave rise to different thicknesses due to variation in their shrinkage. In order that a 25 +/- 1% strain level should be delivered on the sample, the jig, plates and samples have to be matched. Since the jig has a nominal depth of ca. 10.725 mm with +/-0.01 tolerance, the depth limit of a jig would be between (10.715 and 10.735) mm. According to table 3.1(a) the specimen thickness may vary from 6.24 mm (for example in Santoprene 101-73) to 6.41 mm.
FIGURE 3.2

LOW COST COMPRESSION STRESS RELAXATION APPARATUS FOR RUBBER
Therefore in order to obtain the required plate thickness one has to calculate the possible combinations since the jigs and glass plates available are of (within) a fixed range of depths and thicknesses. The jigs depths (as stated above) are between (10.715 and 10.735) mm. while the glass plates have thicknesses of between (2.70 to 3.06) mm. To apply a strain of +/-1% to a specimen, a jig of a nominal depth is selected - a thinner specimen will require a shallower jig and/or thicker plates. The suitable plates are then calculated using a simple formula: 

\[ \text{the thickness of the paired glass plates } (P) = (0.25 + J - S) \text{ mm. or } (J - 0.75 S) \text{ mm.} \]

where "J" is the depth of the jigs, "S" is the thickness of the specimen and "P" is the thickness of the plates.

e.g. for a TPE specimen of thickness (S) = 6.16 mm., a shallow jig of depth (J) = 10.720 mm. may be selected. The total thickness of plates needed to strain the specimen to 25 +/- 1% is therefore:

\[ 10.720 - (0.75 + 6.16) = 6.10 \text{ mm.} \]

so that either a pair of plates, each of 3.05 mm thick or any two that add up to the value required (6.10 mm.) can be used.

3.3.2 PREPARATION OF THE JIG

Having selected the jig, the glass plates and the specimen, the two flat ends of the specimen are lubricated with Molybdenum disulphide (MoS\textsubscript{2}). Also the surfaces of the glass plates which will be in contact with the specimen may be lubricated. It should be emphasised that before the lubrication operations the entire components of the jig unit must be properly cleaned, as any inclusion (no matter how little this may be) will lead to grave error in the result thereafter obtained. For example 0.11mm thick inclusion in
the jig has resulted in an error (in the force measurement being higher by 36.4 N, ca. 23%). Therefore cleanliness of the jig unit is a very important precaution that should be taken to ensure reproducibility of results.

The lubricated specimen is then sandwiched between the glass plates by first placing one plate on the floor of the jig cavity, followed by the specimen, making sure at this point that both are centrally positioned in the cavity. This can be checked by placing the thrust plate in position and viewing from the top hole. The second glass plate is then carefully placed, centrally on top of the specimen without displacement of any kind. The thrust plate is then placed in position and bolted loosely into place without compressing the specimen. (Figure 3.3). Centrally positioning of the specimen in the jig is another procedural precaution to observe in order to avoid slipping and breakage of the glass plates, and tilting of the specimen as this will lead to erroneous test results.

Figure 3.3 PREPARED JIG
The specimen is then ready for loading using the Wykeham Farrance Machine, (the loading procedure described in detail in the literature\textsuperscript{(1,2)} should be closely followed, with further refinement and modification whenever and wherever necessary).

3.4 SETTING UP THE EQUIPMENT

Setting up the equipment involves three major steps:

(i) Electrical connections,

(ii) Parallelism adjustment to obtain ideal curve, and

(iii) Load cell calibration.

3.4.1 ELECTRICAL CONNECTIONS

Before any operation is carried out with the equipment, it is necessary to ensure that all the electrical connections required have been made. Each of the three components of the equipment, (the Wykeham Farrance Machine, Load cell power supply/Amplifier unit and Chart recorder) are separately connected to the power mains. The load cell is directly connected to the power supply/amplifier unit by a 5-way DIN plug. The amplifier output is connected to the chart recorder with the appropriate polarity using a twin cable. Once the items are inter-connected as shown in figure 3.2, the main power can be switched on. The system can be checked directly, by turning to the full sensitivity and applying a light axial pressure on the load plunger, which makes the chart pen move in the appropriate direction (from the left to the right). If the chart pen moves in the opposite direction, the chart input connection should be
inter-changed.

It is desirable to keep the cell power supply/amplifier unit and chart recorder energised at all times. This enables the system to stabilise. Secondly the chart recorder sensitivity selection knob and the amplifier gain selection knob can be combined to obtain a variety of effective amplifications. However the zero setting of the pen is not necessarily possible for all these combinations.

3.4.2 PARALLELISM ADJUSTMENT TO OBTAIN IDEAL CURVE

Experience has shown that the most critical condition for ideal behaviour is parallelism of the load-cell plunger and the surface of the top glass plate in the jig, without which the "Ideal curve" cannot be obtained. The requirement to achieve parallelism goes back to the design and production of the plunger/heat shield and the jigs themselves and has been discussed in detail in the literature\(^2\). Assuming this requirement has been met, the plunger/heat shield is attached to the load-cell which is fixed to the cross-head of the Wykeham Farrance frame. The adjustment is then carried out as directed. (see figure 3.4). The process of obtaining parallelism is time consuming and laborious though, however once it is set, if care is taken, chances of maintaining it are very high. A monthly check is desirable for reliable measurements. Once the load-cell parallelism has been adjusted the calibration can be carried out.

3.4.3 LOAD CELL CALIBRATION

It is necessary to calibrate the load cell in order to provide the basis of force comparison - the restoring force of the specimen being
measured in conventional units e.g. the Newton and read out from the chart recorder. The load cell must be allowed time to stabilise prior to calibration against dead weights. The calibration mechanism consists of two major components namely:

(i) the pivot block - which should be permanently fixed to the appropriate column at appropriate height and

(ii) calibration lever - usually rests at the foot of the column and can be readily pivoted at the pivot block for use in the following:

(a) fixing the pivot block - the pivot block should be fixed on the column so that the properly pivoted lever is horizontal when it rests against the load cell as shown in figure 3.5. A spirit level can be used to make sure the lever is perfectly horizontal. Once the right position of the pivot is found, the four grub screws are tightened to secure the pivot block in position. Once this is done it is very rarely that one has to change the position of the pivot block, unless the load-cell system is adjusted, in which case the new position of the pivot block should be found as explained above.

(b) calibration of the load cell - once the pivot block is secured in the proper position, the calibration lever can be pivoted at the block so that it rests against the load-cell plunger as shown in figure 3.5. It is important to check whether the lever is positively pivoted prior to the application of the dead weights. Sudden drops by slipping may damage the apparatus especially the load cell. The dead weight (say 5 kg at a time) may be applied step-wise (not exceeding the rated load of the load-cell), taking the chart recorder reading for each measurement of load. It is recommended to repeat this while the loads are unloaded progressively. Once the chart readings have
been taken, the master calibration curve can be constructed and used to convert subsequent measurements to the appropriate units. After all these have been done the apparatus is ready for use for stress relaxation measurements. These are the calibration values used to carry out the measurements taken in this programme:

For the 100 kg LOAD-CELL (a) AND 250 LOAD CELL (b) below:

<table>
<thead>
<tr>
<th>SENSITIVITY SETTINGS</th>
<th>kg/mm chart</th>
<th>N/mm chart</th>
<th>Ratio 250/100 kg</th>
<th>SENSITIVITY SETTINGS</th>
<th>kg/mm chart</th>
<th>N/mm chart</th>
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</thead>
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<td>1/1</td>
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<td>0.097</td>
<td>0.947</td>
<td>2.32</td>
<td>4/5</td>
<td>0.224</td>
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<td>1/2</td>
<td>0.154</td>
<td>1.513</td>
<td>2.28</td>
<td>1/2</td>
<td>0.352</td>
<td>3.45</td>
</tr>
<tr>
<td>2/5</td>
<td>0.193</td>
<td>1.897</td>
<td>2.28</td>
<td>2/5</td>
<td>0.441</td>
<td>4.32</td>
</tr>
<tr>
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<td>0.392</td>
<td>3.845</td>
<td>2.28</td>
<td>1/5</td>
<td>0.889</td>
<td>8.72</td>
</tr>
</tbody>
</table>

(a) Calibration values for the (100 kg LOAD-CELL)
(b) Calibration values for the (250 kg LOAD-CELL)
Fig 3.4 Parallelism Adjustment
3.5 LOADING PROCEDURE

The process of using this machine to produce a force - time (displacement) characteristic to obtain the initial force measurement at the instant in which the specimen reaches the set strain level is called "LOADING" In effect, this is the aim of this operation.

Prior to this operation, standard settings in the equipment must be checked (see above), and allowed time to stabilise. Power to the load-cell and the chart recorder is never switched off under normal circumstances. The jig should be assembled as set out below:

(1) Ensure that the flat surfaces of the jig and glass plates are cleaned. Glass plates may be cleaned with acetone or lightly rubbed with fine wire wool and wiped.

(2) Measure the depth of the "jig-housing" cavity with a micrometer to the nearest 0.005 mm. Most jigs are marked with this value.

(3) Measure the thickness of the glass plates with a micrometer.

(4) Measure the thickness (height) of the sample with a micrometer (thickness in the range of 6.25 - 6.45 mm. is appropriate). Thin samples may be stacked to give an adequate thickness.

(5) Place one glass plate in the bottom of the jig cavity. Slightly rub the flat surfaces of the sample with a little Molybdenum disulphide as a lubricant to prevent it sticking to the glass plates, place the sample onto the glass plate making sure the plate and sample are centrally positioned in the cavity. Place the second glass plate on the sample, then place the thrust-plate (cover) over the glass plate, holding the thrust-plate with one hand, insert the three
screw bolts with the other, engaging them such that the specimen is in position yet unstrained.

It is important to feel the rotational play of the thrust plate with two fingers to make sure the vertical movement of the thrust plate (while loading) is smooth and free from any interference from the screw threads. There is normally a line marked on each thrust plate and jig-housing - when fitting the thrust plate make sure they are aligned. (See figure 3.3).
3.5.1 SETTINGS REQUIRED IN THE EQUIPMENT

Power Supply: 24.0 Volt.
Current: 0.39 A.
Motor Speed: "B" mark, = 0.31 mm/min. i.e. the strain rate (compression) is = 0.00516 mm./sec.

Chart Recorder speed: 1 mm./sec.
Chart recorder voltage: 1 Volt.
Amplification: Variable (depends on the sensitivity required) e.g. $x \frac{2}{5} = 1.89$ N force on a 100 kg load-cell.

Motor load switch: "Up", for compression, "Down", to reverse the action and centrally positioned for no action.
3.5.2 **COMPRESSION OF SPECIMEN**

(i) Place the prepared jig containing the specimen on the machine platform, align the marker line on the jig-housing and the machine platform.

(ii) Raise the platform with the coarse-movement wheel drive to ensure that the plunger is in line with the hole in the thrust plate. Then lower the platform fully and insert the "Loading sleeve" (a slotted hollow cylinder) around the plunger and then raise to standby position for loading. The coarse gear is disengaged by moving the lever into the horizontal position. The standby position is achieved by allowing a small gap between the loading sleeve and load-cell bottom plate, and continuing to move the platform upward very gently and carefully until the chart recorder pen just moves, then lower the platform to bring back the pen to the base line on the chart.

(iii) Disengage the coarse drive and engage the fine drive movement (while doing this the standby position will have changed slightly). This position is restored as well as the base line position of the pen on the chart by raising the platform to position with the fine drive wheel. (The disengagement is done by dropping the gear lever to the horizontal position and moving the coarse drive wheel fractionally anti-clock-wise until a loud "chunck" sound indicates that the coarse drive gear has disengaged and fine drive gear engaged. At this position, note the reading of the micrometer attached to the platform.

(iv) Engage the motor drive by pushing out the knob at the side of the machine frame, (done by pulling the knob while at the same time
moving the fine drive wheel in an anti-clockwise direction).

(v). a) Lower the chart pen. (b) Start the chart drive (which should be set to a speed of 1 mm/sec.) then (c) Start the motor.

Loading starts once the motor drive is switched on and the increasing force of compression is recorded. When the thrust plate and the jig-housing begin to meet, the increasing compressive force (as recorded by the chart recorder) is seen to move out of phase - increasing rapidly and becoming parallel to the force axis, (see figure 3.6). At this point the motor and chart recorder must be switched off as quickly as possible. (Note that allowing compression to continue after this point will damage the load-cell). Note the micrometer reading at this point.

3.5.3 CHECKING THE STRAIN LEVEL

Normally there are three methods by which the amount of compression delivered can be checked:

1). From the measurements obtained during jig assembly as shown by the following example. Assuming the following measurements were obtained:

_ jig depth  =  10.730 mm.
_ total plate thickness  =  6.100 mm. and
_ sample thickness  =  6.200 mm.

The amount of compression at the end of loading (at the point of thrust plate/jig-housing contact) is 6.20 + 6.10 - 10.730 =1.57 mm. Therefore % compression (strain) = 1.57/6.20 x 100 = 25.3%

2). The instant the chart recorder pen begins to move from the zero load is considered the zero % strain on the specimen. This is
marked on the chart paper. At the end of loading - as a sharp discontinuity in the loading curve will indicate, (i.e between the zero load position and this point "A" in figure 3.7 (extrapolated onto the displacement axis) is the amount of compression delivered during loading. Since the chart speed is 1 mm/sec. and the motor drive speed is 0.00516 mm/sec., it follows that the amount of compression delivered is the distance between the zero strain position of the pen and the point "A" along the displacement axis, multiplied by 0.00516 mm/sec. For example if this distance is 208 mm. (say), then the amount of compression done = 208 x 0.00516 = 1.073 mm. Assuming the sample thickness to be 6.40 mm. The % compression = 1.073/6.4 x 100 = 16.77 %.

3) At the instant loading starts (at the zero strain position of the chart recorder pen) the micrometer reading is noted (micrometer attached to the machine platform) and at the end of loading its reading is again noted. The difference between these two readings is the amount of compression derived, e.g. if readings are 24.12 at the start of loading, and 25.194 at the end of loading respectively, the difference is (25.194 - 24.12) = 1.074 mm. The % compression therefore, = 1.074/6.4 x 100 = 16.78 %.

In order to be more accurate (i.e. closer to the actual strain value, it is advisable to take the average of these values, obtained from the three measurements.

3.5.4 THE LOADING CURVE

Using the above equipment the author's predecessors (Fernando and Tahir) have shown that the loading curve, for a rubber,
approximates to a straight line, at least to 25% compressive strain (following the BS. specification). With TPE's similar curves have been obtained except in a few cases as will be shown in chapter four (iv). The main contributor to the curve is the compressed specimen, although some contribution are made by the stiffness of the load-cell and the frictional resistance due to other moving part of the machine. This however, is such an insignificant part of the total contribution that it can be usually ignored. Normally the deflection of the load-cell will be the first response registered, when loading begins, and it is related to the stiffness of the load-cell which varies proportionally to the reaction force of the specimen.

During loading, the force registered by the load-cell is the restoring force of the specimen under-going compression. From the instant the thrust plate makes contact with the jig housing a discontinuity in response is registered due to the differences in hardness between the specimen and the metal jig. (Figure 3.6).

The loading curve represents an important informative feature of the total relaxation behaviour of a specimen. The sharp discontinuity in the slope of the curve, at point "A" represents the point where the metal-metal compression commences. It is essential that the jig depth, the glass plate thickness, and the sample thickness employed are as such that at point "A" the specimen is strained or compressed 25% of its original height. The stress recorded at this level represents the initial instantaneous force to which all subsequent relaxed stresses are normalised and the gradient of the curve at this point is considered the initial modulus of the specimen at the strain level. The specimen is made to maintain this strain level by
tightening the thrust plate onto the jig housing with the Allen-bolts.

3.6 MEASUREMENT AND INTERPRETATION OF RESULTS

When loading is completed and before the measurement of the stress relaxation the following operations must be carried out in rapid succession:

(i) Once the motor drive and chart recorder are switched off, start the stop-watch and note the time, this marks the zero time of the experiment, then raise the recorder pen.

(ii) Record the micrometer reading.

(iii) Tighten the thrust plate with the Allen-bolts, onto the jig housing, first by hand and finally with an Allen key while holding the jig in position. Note that during this process the jig must not be allowed to move or rotate in order not to damage the load-cell.

(iv) Disengage the motor drive by pushing the knob in.

(v) Use the fine gear to lower the platform thereby returning the pen to the base line.

(vi) Engage the coarse gear by moving the lever to a vertical position, move down the platform fully and remove the loading sleeve.

After these have been done the stress relaxation measurements can be carried out at desired (but usually specified) times. The author has carried out measurements at the times of 0.1, 0.5, 1.0, 5.0, 24.0, 70.0, 168.0, 340, 720, 1000, 1500, 2000, 5000, and 10000 hours after loading was completed. Stress relaxation measurement is carried out following the same procedure as adopted during loading operation except that this time, the loading sleeve is removed to
allow the load-cell plunger to make direct contact with the top glass plate holding the specimen in the jig and compress it directly.

During the stress relaxation measurement a change in slope in the force/displacement characteristic produced, indicates the end of the experiment. The motor drive and the chart recorder drive must be switched off and the pen lifted from the chart paper. Note that about 1 cm. of further movement should be allowed when the change of slope occurs, to provide the curve from which the MEF can be calculated. This added deformation (movement) should not exceed 1 cm on paper (equivalent to 0.05 mm strain).

3.6.1 INITIAL INSTANTANEOUS FORCE CALCULATION

At the strain level of point "A" in figure 3.7 (usually the 25 +/- 1 % strain level) the backward instantaneous force exerted by the specimen is determined by first noting the sensitivity (amplification) of the machine (obtained from the calibration curve). For example, for the 100 kg load cell table 3.4.1 shows that a sensitivity setting of 2/5 represents 1 mm. displacement along the force axis and is equal to 1.897 N force, in this case. So that the value of point "A" along the "X" axis, multiplied by the sensitivity, multiplied by the total compression, is equal to the "INSTANTANEOUS INITIAL FORCE". For example:

assuming that point "A" = 88 mm. (i.e. displacement along the force axis),

The sensitivity = 2/5 = 1.897 N

The total compression is = 1.09 mm. Therefore the initial instantaneous force is = 88 x 1.897 = 166.94 N.
Normalising to 25 % strain (compression):
Assuming the thickness of the specimen = 6.4 mm.,
therefore 25 % of 6.4 is = 1.6,
therefore 1.6/1.09 = 1.47. Thus the normalised force (to 25 %
strain) = 88 x 1.897 x 1.47, = 245.4 N.

3.6.2 **SUBSEQUENT RELAXED STRESS DETERMINATION**

The relaxed stress is determined (using similar procedural
precautions adopted during loading except that the loading sleeve is
removed) by allowing the plunger to make direct contact with the
holding glass plate, (see section 3.6 for detailed description).

During the compression an inverse of the loading curve is
registered by the recorder. (See figure 3.7 (b)). Generally the point
"A" would be noted to have shifted (by an amount equal to the
relaxation under-gone by the specimen, at the desired time period in
which the measurement was obtained), to point "C" in figure 3.7 (b).

The calculation of the residual force is done by using exactly the
same method used to calculate the instantaneous initial force. (see
table 3.2 for results). Note that the sharp slope between "B" and "C"
in figure 3.7 (a) (metal to metal response) is this time, not metal to
metal compression but the residual force on the thrust plate which
needs to be overcome before the compression of the specimen
commences. "C D" can be seen to be identical in character to the
loading curve. This is the response to the compression of the
specimen by the plunger. It is important to note that during loading
the plunger makes no contact with the glass plate beneath which the
specimen is sandwiched.
TABLE 3.2  
STRESS RELAXATION (IN COMPRESSION) MEASUREMENTS AT 23°C
OF SOME SANTOPRENE GRADES (COMPARISON BETWEEN INJ. & TRF. MOULDED SAMPLES) INJ = INJECTION, TRF = TRANSFER

<table>
<thead>
<tr>
<th>SAMPLES/ GRADE</th>
<th>25% OF INITIAL FORCE AT TIME 0</th>
<th>NORMALISED FORCES IN (N) TO 25% STRAIN AT SPECIFIED TIME, IN (HOUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THICKNESS (mm)</td>
<td>0.1</td>
</tr>
<tr>
<td>INJ. MOULDED 101-73</td>
<td>1.63</td>
<td>386.3</td>
</tr>
<tr>
<td>TRF. MOULDED 101-73</td>
<td>1.593</td>
<td>365.1</td>
</tr>
<tr>
<td>INJ. MOULDED 201-73</td>
<td>1.573</td>
<td>330.8</td>
</tr>
<tr>
<td>TRF. MOULDED 201-73</td>
<td>1.538</td>
<td>283.5</td>
</tr>
<tr>
<td>INJ. MOULDED 101-64</td>
<td>1.58</td>
<td>294.6</td>
</tr>
<tr>
<td>TRF. MOULDED 101-64</td>
<td>1.60</td>
<td>250.6</td>
</tr>
<tr>
<td>INJ. MOULDED 201-64</td>
<td>1.59</td>
<td>246.0</td>
</tr>
<tr>
<td>TRF. MOULDED 201-64</td>
<td>1.65</td>
<td>195.1</td>
</tr>
<tr>
<td>INJ. MOULDED 201-55</td>
<td>1.555</td>
<td>185.8</td>
</tr>
<tr>
<td>TRF. MOULDED 201-55</td>
<td>1.525</td>
<td>151.9</td>
</tr>
</tbody>
</table>

3.7 SHORT-COMINGS OF THE EQUIPMENT.

The only obvious short-coming of the equipment is that due to the added strain on the specimen (hence an added stress) caused by tightening the thrust plate with the "Allen-bolt", onto the jig-housing. Various investigations have been carried out to study and evaluate the phenomenon, by the previous users (1-3). It was noted that the cause is the nature of the jig's surfaces in contact with each other and probably the material type in which the jig is made, (i.e. the
smoothness and the degree of parallelism of the mating surfaces of the thrust plate and jig-housing). It has been found that using the jig where the surfaces have been manually smoothed with diamond paste indicates improvement in the discrepancies, though they are not entirely eliminated. Note that there is no uncertainty over the residual stress obtained from the ideal (relaxation) curve but in the initial force since the thrust plate for some jigs only beds down to the best level when the retaining bolts have been tightened and there is no means by which the magnitude of the added force can be evaluated. The best solution may be to use jigs that are free of the tightening irregularities which will maintain only the force applied by the machine and do not experience the tightening-with bolt problem as the phenomenon is inevitable in the present jig type. Thus all jigs should be brought to this state.

3.7.1 INTERRUPTED LOADING.

It has been observed, with some materials that show slow relaxation rate, that the early values of residual force are higher than the initial force obtained after loading, also a consequence of the above effect (i.e. of a small increase in strain of the specimen imposed by tightening the Allen key). It is the author's view too that this may be also due to cross-linking resulting from chain scission during deformation, (where the number of chains formed is greater than the original cross-link density). The drawback in this view is that the phenomenon has only been so far observed in the early stage (0.1 to 0.5 hour period) of relaxation process. Therefore it requires some further investigations. Presently it can only be
considered a meaningful and logical argument if it has also been observed in a later stage of relaxation process.

By interrupting the loading at about 20% strain the relaxation can be observed for a short time, independent of the tightening problems. This gives a reliable measure of the initial relaxation but unfortunately the stress-strain history does affect both initial force and relaxation, especially with filled polymers and blends where physical relaxation is believed to play a predominant role at the early stage of the relaxation process.

3.8 REFERENCES

1) M. Tahir; "PhD Thesis" (Stress Relaxation Behaviour of Rubber); IPTME, LUT, (1985)


CHAPTER (IV)

4. EXPERIMENTAL AND DISCUSSION OF RESULTS

4.1 MATERIAL

The materials used in this project are thermoplastic elastomers, some of which are polyblends (e.g. Santoprene grades) and others are copolymers (block copolymer.) They were supplied by industry except for those prepared by the author to explore structure-property relationships. They came in pellets but in addition some already prepared samples (injection moulded Santoprene grades) were also supplied. Using their commercial names these samples include:

(i) The Monsanto series:-(Santoprene),- these are the

101-73
101-64
201-73
201-64

and 201-55 grades.

The last two figures to the right of each grade-number represent the hardness of the grade in Shore "A" units. They were formulated from the blends of polypropylene and EPDM (as base polymers), dynamically vulcanised, they have low density and are not highly filled.

(ii) The Du-Pont series:- these include the Alcryn 80A, 70A and 60A grades. The series is formulated from blends of chlorinated
polyolefines (polypropylene plus neoprene) like for example polyvinylidene chloride/polypropylene as the hard phase and cross-linked poly-vinyl acetate, neoprene. as soft phase. They are generally soft and have excellent oil resistant property.

(iii) The (Du-Pont) Hytrel series: - They include the 4074, 4056, 3548 grades

The last two figures to the right, again represent the hardness in each grade. The series is a formulation of polyester/ polyether copolymer, sometimes similar to polyurethane but can be harder. (hardness measured in the Shore "D" unit) The hard (polyester) phase is usually crystalline while the soft polyether phase is amorphous.

(iv) The BF Goodrich series: - They include the Estane 58300, 58141,T4093, T4022 grades.

The series is a multi-block copolymer formulated from polyurethane blocks (hard phase) and polyester or polyether blocks (soft phase). They are generally hard. The first two figures to the left of the grade numbers represent the hardness in Shore "D" unit. They are very elastomeric in nature, have excellent mechanical and oil resistant properties and show some degree of transparency.

(v) Lomod BO-100-1000, AC358: - has the same formulation as Hytrel (i.e. multi-block polyester/polyether copolymer) and resembles polyurethane in structure but can be harder (27) (35 shore "D" and above).

(vi) The Atochem series: - these include the Pebax 5533, 4033, and 3533 grades. The hardness is denoted following the same system as in the case of Hytrel and polyurethane. The series is formulated
from polyamide/polyether multi-block copolymer, also similar to polyurethane in structure but can be softer.

(vii) EPDM/PP Blends :- These were prepared by the author using dynamic vulcanization technique with peroxide curing agents in 40, 30 and 20 % (by weight) polypropylene in EPDM, blended together (see later). Note that the hardness is controlled by the proportion of polypropylene present.

4.1.1 ACCELERATED AGEING OF THE MATERIAL

As mentioned earlier, polymers suffer from net-work degradation with time. The rate of this reaction depends mainly on the temperature and the environment to which they are exposed.

Following BS. 903 - A19(5) an accelerated ageing test can be used as a rough guide to predicting the life expectancy of polymer formulations (though it sounded some warning on interpreting results).

Some of the above samples were heat treated in an air oven at a temperature of 100°C for 2000 hours. Many, discoloured markedly especially the non-black specimens) This may be an indication of oxidation. From the results of table 4.1.1, it can be seen that they show some shrinkage and loss in weight which is more pronounced in the Alcryn grades, probably due to the loss of volatiles as it was noted that they sweat (liberate process oil).
TABLE 4.1.1  Effect of accelerated ageing (at 100°C) on some TPE's after 2000 hours.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>INITIAL THICKNESS (mm)</th>
<th>FINAL THICKNESS (mm)</th>
<th>DECREASED THICKNESS</th>
<th>INITIAL WEIGHT (g)</th>
<th>FINAL WEIGHT (g)</th>
<th>% LOSS IN WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>101-64</td>
<td>6.35</td>
<td>6.28</td>
<td>1.10</td>
<td>7.83</td>
<td>7.63</td>
<td>2.55</td>
</tr>
<tr>
<td>101-73</td>
<td>6.35</td>
<td>6.27</td>
<td>1.26</td>
<td>7.93</td>
<td>7.77</td>
<td>2.02</td>
</tr>
<tr>
<td>201-64</td>
<td>6.35</td>
<td>6.26</td>
<td>1.42</td>
<td>7.88</td>
<td>7.68</td>
<td>2.54</td>
</tr>
<tr>
<td>201-73</td>
<td>6.28</td>
<td>6.23</td>
<td>0.70</td>
<td>7.80</td>
<td>7.61</td>
<td>2.44</td>
</tr>
<tr>
<td>201-55</td>
<td>6.25</td>
<td>6.17</td>
<td>1.28</td>
<td>7.70</td>
<td>7.52</td>
<td>2.34</td>
</tr>
<tr>
<td>ALCRYN 80A</td>
<td>6.02</td>
<td>5.93</td>
<td>1.50</td>
<td>8.80</td>
<td>8.18</td>
<td>7.05</td>
</tr>
<tr>
<td>ESTANE 58300</td>
<td>6.83</td>
<td>6.71</td>
<td>1.76</td>
<td>8.81</td>
<td>8.75</td>
<td>0.68</td>
</tr>
<tr>
<td>HYTREL 3548</td>
<td>6.98</td>
<td>6.86</td>
<td>1.72</td>
<td>9.69</td>
<td>9.61</td>
<td>0.82</td>
</tr>
<tr>
<td>PEBAX 5533</td>
<td>6.96</td>
<td>6.90</td>
<td>0.86</td>
<td>8.92</td>
<td>8.82</td>
<td>1.12</td>
</tr>
<tr>
<td>LOMOD</td>
<td>6.74</td>
<td>6.68</td>
<td>0.89</td>
<td>8.82</td>
<td>8.74</td>
<td>0.91</td>
</tr>
</tbody>
</table>

4.2 SAMPLE CHARACTERIZATION

Fortunately rigorous characterization of samples is not necessary in this programme since the base polymers present in each sample are known but on the other hand knowledge of their structural nature (especially in the sense of whether they are crystalline or amorphous) is necessary to enable the evaluation of structure-property relationships.

4.2.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

When a substance undergoes physical or chemical transition, a corresponding change in enthalpy is observed. This is the principle employed in Differential Thermal Analysis (DTA) in which the transition is detected by measuring the temperature difference between the material under study and an inert standard (i.e. the
material and the reference inert sample such as alumina or even an
empty sample pan) are warmed at the same uniform rate and their
temperature monitored with a thermocouple and then compared.
Note that the sample temperature "Ts" and the reference
temperature "Tr" will keep in pace until a change in the sample takes
place. If the change is exothermic, "Ts" will exceed "Tr" for a short
period while if it is endothermic, "Ts" will lag behind for a short
period. This temperature difference (ΔT) is recorded and transmitted
to a chart recorder which produces it as a peak. Thus, melting and/or
glass transition (Tg) and crystallization temperatures can be
detected. Other transitions such as sample decomposition,
cross-linking and the existence of polymorphic forms can also be
detected. Because ΔT, as measured in DTA, is a function of thermal
conductivity and bulk density of the sample, it is not quantitatively
informative. This drawback is overcome by using (DSC) which
measures the energy difference in the change. The technique retains
the mean heat input but instead of measuring the temperature
difference during the change the energy input to either sample or
reference is increased to maintain both at same temperature.
Although the thermogram obtained is similar to (DTA) but actually
represent the amount of electrical energy supplied to the system, so
that the area under the peak is proportional to the enthalpy change
that occurred.

DSC thermograms have been obtained for the range of TPE's using
a Du-Pont 990. Thermal analyzer with the variable parameters kept
constant for all traces, set as follows :-

- Sample weight - 10 mg
sample atmosphere - N₂
inert gas flow rate (N₂) - 60 ml/min.
temperature scanning rate - 10 °C/min.
sensitivity (highest) - 1 mV/cm.
the temperature calibration used Tin (Tm = 231.9 °C) and Indium (Tm = 156.6 °C)

Some of the traces indicate the presence of crystalline species, others have less precise form and are probably amorphous. The results obtained are summarised in table 4.2.1.

With the Santoprene series, all the grades examined show evidence of a crystalline phase, which from its melting and crystallization temperature, is probably polypropylene, modified by the presence of the rubber phase (i.e. by being partially bonded to rubber chains).

It can be seen from the results that besides Santoprene grades, other grades show some degree of crystallinity. The Estane 4022 is probably completely amorphous as the thermogram did not show any peak. There is doubt about the peak values obtained for the Alcryn grades, as they are too high for a polyolefin based polymer such as this. The transition may be for any other inclusion present in the polymer. Note that the crystallization temperature is not observed probably due to the high filler content of the polymer which may impede crystallisation once melted. Detection of crystallinity is evidence of phase separation which if the phase separation is in a micro-scale greatly improves mechanical properties.
4.2.2 MELT FLOW CHARACTERIZATION

One major advantage of thermoplastic elastomers over conventional rubber is that they can be melt processed as thermoplastics Thus knowledge of their melt flow properties is important.

Melt Flow Index (MFI) of thermoplastic is the measured gravimetric flow rate of the sample melt extruded from a die of specified length and diameter under prescribed conditions of temperature and pressure. Different standardised combination of extrusion temperatures and pressure are used for different type of polymers but, for purposes of comparison different samples of the same polymer types should be tested under precisely similar conditions. The apparatus may be regarded as a simple rheometer operating at a condition of low shear. Basically the apparatus is a dead-weight extrusion plastimeter consisting of thermostatically controlled heated cylinder with a die situated at the lower end, and a piston operating within the cylinder which can be loaded with suitable weights to give the correct load for the material under test. Although the applied shear stresses and the resultant shear rates are much lower than those used in most fabricating operations, the results obtained do provide a useful indication of the relative ease with which different samples will flow when they are fabricated. Hence higher "MFI" value indicates easier melt flow, so that if fabrication process involves relatively high rate of shear, as in injection moulding, a grade of polymer with a high "MFI" is generally chosen.
"MFI" is also a measure of the average molecular weight of the sample. It is therefore indicative of the strength property of the material. Average molecular weight and "MFI" are inversely related, so that, although a sample of high "MFI" will certainly be readily
processed its mechanical strength is likely to be poor as longer molecular chain net-work may show higher strength than shorter molecular chain net-work (low mol.wt) which may readily slip away from each other when deformed. Lower molecular weight generally enhances melt flow and hence they can be readily processed.

"MFI" is expressed as $10W/T$

where MFI is the melt flow index (g/10 min.)
W is the average cut-off weight (g)
T is the extrusion time per cut-off (min.)

Measurements were made on the samples and it can be seen that the Alcryn grades are more resistant to flow. (see table 4.2.2 above). Note that the Alcryn and Santoprene grades are more sensitive to shear than temperature (see table 4.2.2). Note too that some of the values of the MFI spread are relatively large. This is an indication of the difficulties encountered in obtaining the measurements (e.g. some of the materials are very sensitive to shear at the test temperature thereby flow very rapidly (Santoprene grades) while some are not (Alcryn grades)).

*Note that the figures of the middle row of table 4.2.2. do not represent the MFI of the material by definition. They are shown in order to visualise the influence of shear rate and temperature in the rheology of these materials. At 230°C/10kg load, the flow rate of the Santoprene series was too high that no meaningful (MFI) result could be obtained, hence this method of (5kg/230°C) measurement.

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Note that results obtained with samples treated at 38 °C give higher initial force in both cases, which is indicative of crystallization playing a part. This can be considered to be due to thermal agitation disrupting crystallization at higher temperature, hence the lower initial force and at lower temperature the viscosity may be too high to impede (or to allow) sufficient crystallization, hence also the lower initial force. Measurements taken at various extended periods of time truly confirmed the assumption that it can also be due to the effect of crystallization (see table 4.3.1 (a1)). On the basis of the above results, it can be seen that an optimum temperature range seems to exist in which crystallization best takes place in these materials.

**TABLE 4.3.1 (a)**

<table>
<thead>
<tr>
<th>SANTOPRENE GRADE</th>
<th>TEMPERATURE (°C)</th>
<th>INITIAL FORCE (N) INJ. MOULDED</th>
<th>INITIAL FORCE (N) TRF. MOULDED</th>
</tr>
</thead>
<tbody>
<tr>
<td>101-64</td>
<td>23</td>
<td>238.0</td>
<td>212.2</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>250.1</td>
<td>220.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>221.6</td>
<td>216.6</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>190.0</td>
<td>183.4</td>
</tr>
<tr>
<td>201-55</td>
<td>23</td>
<td>153.8</td>
<td>150.6</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>162.8</td>
<td>157.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>133.0</td>
<td>124.1</td>
</tr>
</tbody>
</table>
Table 4.3.1 (a1)

Effect of Thermal Conditioning/Crystallization (for various times at selected temperatures) on Initial Force (for selected Santoprene Samples)  Note: h = hour

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP. °C</th>
<th>INITIAL FORCE (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.0h</td>
</tr>
<tr>
<td>101-64</td>
<td>23</td>
<td>212.2</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>220.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>216.6</td>
</tr>
<tr>
<td>201-55</td>
<td>23</td>
<td>153.5</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>162.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>163.1</td>
</tr>
</tbody>
</table>

4.3.2.2 Effect of Thermal Treatment

In the expectation that thermoplastic elastomer materials, by their nature will be affected by thermal treatment, samples (Santoprene grades) were heated in the press under pressure of about 2.5 MPa. to temperatures of 150 and 175 °C, subsequently being quenched or slow cooled. Quenching was by dropping the samples into water at room temperature and on the other hand slow-cooling was by allowing the samples to cool to room temperature while still under pressure in the mould. After they are removed from water / mould, they were allowed to rest at room temperature for at least 24 hours before test. Short term stress relaxation tests were then carried out on specimens from each sample. The result obtained are summarised in table 4.3.1(c) whence
it can be seen that the slow-cooled samples have higher initial force than the corresponding quenched samples in all cases. Note too that the "101" series have higher initial forces at both treatment temperatures than the "201" series.

Other comments are that:

(i) quenching from the melt has greater effect on reducing the initial force than quenching from 150 °C as expected, - this may be probably due to lack of ordering of the molecules into crystallites or domains (caused by quenching) which has been known to enhance the mechanical properties especially in thermoplastic elastomers. At 150 °C the sample is probably in its original structural state (not molten) so that quenching does not produce any significant change.

(ii) the stress relaxation test results showed some effects of the different thermal treatment temperatures on relaxation rate, although this appeared to be dominated by the hardness of the material. Notice the cross over phenomenon between the curves (figure 4.1 (a) & (b)) probably caused by crystallization (in the slow-cooled samples,) in both treatment temperatures where the slow-cooled samples gives higher initial force but relaxed the faster. This tends to suggest that crystalline polymers will show greater relaxation than amorphous ones, when strained to the same level and at the same rate, (in short, when the deformation is carried out under identical conditions).
### Table 4.3.1 (c)

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>INJ. MOULDED</th>
<th>HEAT-TREATED 175°C</th>
<th>HEAT-TREATED 150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>101-64</td>
<td></td>
<td>QUECHED SLOW-COOLED</td>
<td>QUECHED SLOW-COOLED</td>
</tr>
<tr>
<td>25% INITIAL STRESS (N)</td>
<td>295</td>
<td>197</td>
<td>223</td>
</tr>
<tr>
<td>RSF (70 h)</td>
<td>55.4</td>
<td>59.7</td>
<td>56.4</td>
</tr>
<tr>
<td>(700 h)</td>
<td>51.6</td>
<td>51.8</td>
<td>54.0</td>
</tr>
<tr>
<td>(2000 h)</td>
<td>47.3</td>
<td>40.1</td>
<td>45.9</td>
</tr>
<tr>
<td>25% INITIAL STRESS (N)</td>
<td>297</td>
<td>386</td>
<td>368</td>
</tr>
<tr>
<td>RSF (70 h)</td>
<td>52.6</td>
<td>51.8</td>
<td>52.3</td>
</tr>
<tr>
<td>(700 h)</td>
<td>47.5</td>
<td>44.0</td>
<td>44.2</td>
</tr>
<tr>
<td>(2000 h)</td>
<td>41.7</td>
<td>42.0</td>
<td>43.5</td>
</tr>
<tr>
<td>101-73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% INITIAL STRESS (N)</td>
<td>186</td>
<td>165</td>
<td>150</td>
</tr>
<tr>
<td>RSF (70 h)</td>
<td>64.5</td>
<td>63.6</td>
<td>64.4</td>
</tr>
<tr>
<td>(700 h)</td>
<td>60.7</td>
<td>57.0</td>
<td>56.5</td>
</tr>
<tr>
<td>(2000 h)</td>
<td>53.5</td>
<td>49.3</td>
<td>50.7</td>
</tr>
<tr>
<td>201-55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% INITIAL STRESS (N)</td>
<td>246</td>
<td>180</td>
<td>216</td>
</tr>
<tr>
<td>RSF (70 h)</td>
<td>52.3</td>
<td>55.0</td>
<td>53.7</td>
</tr>
<tr>
<td>(700 h)</td>
<td>49.7</td>
<td>50.0</td>
<td>47.8</td>
</tr>
<tr>
<td>(2000 h)</td>
<td>45.4</td>
<td>45.2</td>
<td>46.0</td>
</tr>
<tr>
<td>201-64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% INITIAL STRESS (N)</td>
<td>331</td>
<td>228</td>
<td>266</td>
</tr>
<tr>
<td>RSF (70 h)</td>
<td>49.7</td>
<td>50.9</td>
<td>55.0</td>
</tr>
<tr>
<td>(700 h)</td>
<td>48.7</td>
<td>44.7</td>
<td>46.7</td>
</tr>
<tr>
<td>(2000 h)</td>
<td>48.3</td>
<td>40.5</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Note: 25% Initial Stress refers to the initial stress corrected to 25% and expressed in Newtons. RSF is the relaxed stress normalised to the initial force and expressed as percentage. h = hour.
Figure 4.1 (b)  
Stress relaxation behaviour of Santoprene TPE's at 175°C

Figure 4.1 (a)  Stress relaxation behaviour of Santoprene samples at 150°C
4.4 STRESS RELAXATION EXPERIMENTS

4.4.1 TEST AT ROOM TEMPERATURE

Having allowed the samples to rest for sufficient time period (24 h. at least) the samples were loaded using the equipment as described in chapter (III), in air, at room temperature. The results obtained are given in table 4.5 where it can be seen that:

(i) similarity in initial force exists in samples of the same hardness level, in the expected order.

(ii) the harder grades (101-73 and 201-73) give higher initial force and relax faster and to a lower level than the softer grades. Therefore relaxation of the Santoprene samples is a function of hardness, i.e. the proportion of the hard phase (polypropylene) in the blend. This may be due to the fact that polypropylene somehow acts as a filler in the blend, with discrete polypropylene particles generated due to some degree of phase separation, and/or improper mixing of the blend which produces weak interfaceal boundaries between the particles. It may also be due to the amount of filler content present in the samples. Two main contributions may be responsible for the hardness exhibited by the various grades - hard phase content and filler content or both. Although Tobolsky\(^{(1)}\) indicated that carbon black fillers do not affect the rate of relaxation, even though it affects the oxidation of rubber, Lyubchanskaya\(^{(2)}\), using natural rubber containing different types of carbon black showed on the other hand, that all the black he used increased relaxation rate under compression compared to unfilled vulcanizates.

Based on the two network theory, the residual stress at any
instant is a function of \(N_{o,t}\) (the number of unbroken chains at the particular time). And since it has been shown that some sort of bonding exists between filler and polymer molecules in a filled polymer, \(N_{o,t}\) therefore will undoubtedly include these bonds as well, and also since they are weaker bonds than the chemical bonds between cross-linking agents and polymer, they rupture more readily during the deformation of the polymer. This sort of rupture leads to what is termed "Physical Relaxation" normally observed at the early stage of relaxation in filled polymers or phase separated copolymers.

It can be seen too that the Force / Log time curves obtained with the stress relaxation data show an initial downward section, indicative of relatively higher physical relaxation of the materials (this is due to the breakdown of the interfacial bonding between the hard phase/filler and the soft phase, or simply, the breakdown of the structure) then a gradual somewhat linear later part, which may be attributed to chemical phenomena in this case, (but not necessarily due to chemical stress relaxation in general case) showing relatively less relaxation rate with time. Note that the prominence of chemical effect is not seen at 23°C even after 2000 hours under strain, which in one way demonstrates the resistance of the material to oxidation. Note too that the materials retained up to 50% of the initial force at 2000 hours. Generally the softer grades (e.g. 201-55) show less relaxation than the harder grades (e.g. 101-73).

The extent to which physical relaxation dominates especially at the early stage of the relaxation process of these thermoplastic elastomers can not easily be appreciated on a force / log. time plot
due to the peculiarity of the force log. time/ plot but can better be seen on a force/time plot. See also figure 4.2 (a) and (b) compare it with (c).

4.4.2 OTHER "TPE's"

It is reasonable to consider each series separately in order to appreciate their relaxation behaviour. Results for other TPE's are presented in table 4.4.1 and figure 4.1 (d) to (g).

4.4.2.1 The Alcryn grades:-- These show similar relaxation pattern as the Santoprene grades. Again the softer grades relax less than the harder grades. (It can be seen that 60A < 70A < 80A in figures 4.1 (d) & (e). This is not surprising because the formulation is also a polyblend, but relatively they relax more than the Santoprene grades for the same period of time, under the same condition. This is probably because they are not cross linked and may be, contain more filler (carbon black) per unit volume of polymer than the Santoprene series. The initial stress values of the series follow the order above in the reverse manner (ie 80 > 70 > 60) and are generally softer that the Santoprene grades.

One common observation about these materials is that they sweat (liberate some process oil contents) after a long time (> 340 hours) while under compressive stress and at elevated temperature (50 oC and above) as described in section 4.2.1. Unlike the Santoprene, the material show slightly higher relaxation rate at elevated temperature (70 oC) and their insensitivity to shear at elevated temperature (as observed during compression moulding and in the MFI data) makes
Figure 4.2 (a)

Stress Relaxation Behaviour (23°C)

Figure 4.2 (b)

Stress Relaxation per decade (23°C)
them suitable for high temperature applications (see figure 4.1 (e)).

4.4.2.2 The Estane grades: - The stress relaxation results obtained from these samples show that they have high retained force at room temperature (above 50 and 65 % retained force for the lowest and highest retained forces) after 2000 hours. Their relaxation curves do not show the initial downward section (i.e. the initial high relaxation rate, regarded to be dominated by physical relaxation) nor the later downward tailing regarded to be chemical in nature, rather it is a relatively straight line curve of a force/log. time plot, see figure 4.1 (f), (g) and table 4.5. The reduced relaxation shown by this series may be because they are block copolymer formulations. Generally block copolymer show superior mechanical properties to poly blends and quite unlike the Santoprene and the Alcryn series described above the softer grades seem to show higher rate of relaxation than the harder grades (e.g. T4022 > T4039 > 58141 > 58300). The deviation from the trend (softer grades are associated with lower relaxation) can only be with the fact that the softer grades were deformed (compressed) to a higher level than the harder grades. (Also see the case of Hytrel).

It can be seen from the results that stress relaxation rate at elevated temperature is relatively higher than at room temperature also, as well as the fact that softer grades tend to relax faster (in this series) at elevated temperature. This can be traced back to the rubbery nature of the series where the hard - to - soft segments ratio controls the hardness of the grades (i.e. the higher the hard
segment ratio, the harder the polymer). Since rubber generally
degradates faster at elevated temperature it is expected that softer
grades (which contain higher proportion of rubber phase should
relax the most.

Secondly since these materials crystallize at elevated (but below
certain critical) temperatures (though mechanical properties may
improve generally), higher relaxation rate is expected generally,
since it has been found that higher crystallinity favours higher
relaxation rate. Note that this is a complete reversal of the case in
Santoprene samples.

4.4.2.3 The Hytrel grades: - The stress relaxation results obtained
for the Hytrel grades on a force / log. time plot show a relatively
linear relationship. The three grades can be seen to retain above 45
% of their initial force after 8,000 hours. However it is important to
point out in this case that even though each of the grades was
strained (compressed) to different degree (the 4056, 4074, and 3548
grades compressed to 12.7, 21.7, and 30.2% respectively) they show
relatively the same relaxation rate, see figure 4.1 (h) & (i) and table
4.5. This demonstrates the high resilience property of these
materials. It is expected that the ones strained the most would have
shown marked difference in relaxation behaviour compared to those
least strained. That these materials show relatively similar relaxation
rate is an indication that (even at a strain of 30.2%) the 3548 grade
has yet not exceeded its yield point - an indication of the elastomeric
nature of the materials as well. Since this series by their nature is a
copolymer formulation and further more, polyester based (as
polyester generally are tough polymers), it is expected to show high
degree of toughness and good mechanical properties. This is
manifested in the high initial force associated with them, see table
4.5. At elevated temperature, it can be seen that the stress relaxation
rate remains almost the same, although they show reduced initial
force, making them very useful for high temperature applications.

It can be seen that the harder grades show less relaxation, this
may be attributed to the low deformation they suffered. They
require extremely high stress level to deform them to the required
25 % strain because of their high modulus. Since relaxation rate is
also a function of the degree of deformation, it becomes apparent
why the softer grades (which suffer higher level of deformation)
should relax the most, hence probably the above observed results.
Also since the harder grades should contain polyester blocks (a
tougher material) it is expected that they would show less relaxation.

4.4.2.4 The Pebax grades: In this series the various grades
show similar stress relaxation patterns and high initial forces as the
Hytrel series. Again, the harder grades show less relaxation, probably
due to the same reason given in the case of the Hytrel grades as they
are also block copolymer formulations with poly-amide/poly-ether
or ester based polymer. It can be seen in figure 4.1 (j) & (k) that the
material still retain above 45 % of their initial force after 8000 hours.

Elevated temperature test results showed an initial increase in
stress for the first few minutes after loading (for the 3533 grade)
probably due to stress induced phenomena such as crystallization,
entanglement, etc. It can also be associated with the increase in
strain introduced by tightening the thrust plate with the Allen bolts which has been observed in materials that show slow relaxation rate, hence the increase in stress. The material being a slow relaxing one still retained the high stress at the (0.1 hr.) measurement time. (Recall that this is the short coming of the equipment discussed in chapter (III).

4.4.2.5 Lomod Sample: - Unfortunately there is some doubt on the reliability of the stress relaxation results obtained for this sample at room temperature, as the material is too hard to enable any reasonable compression to be achieved. Only 8.8% compression was possible, even when steel plate was used for the loading. The low level of relaxation is as expected, as it depends (among other factors) on the degree of deformation. See figure 4.1 (j). At elevated temperature, it can be seen that the material shows high relaxation rate as compared to the case at room temperature. See table 4.5 and figure 4.1 (j) & (k). It was noted that at elevated temperature this material liberates process oil.

Note that these copolymers (the Estane, Hytrel, Pebax and Lomod) also show a distinctive high initial rate of relaxation at room temperature as noted also in the Santoprene and Alcryl series which are blends. It can be seen that this is not the case with cross-linked rubber (e.g. EP rubber) where the opposite effect was observed. See table 4.7.2 and figure 2.2

4.4.3 TESTS AT ELEVATED TEMPERATURE (70°C)
Higher temperature experiments can be carried out with the
equipment described in chapter (III) by using an insulated heated band wrapped around the jig (a heating unit accessory of the equipment).

Prior to the loading operation, the sample, in a prepared jig is placed in an oven maintained at the test temperature for two hours at least, to bring the equipment and sample to equilibrium temperature of the test and the set temperature of the heater. (It is not advisable that the sample should remain under the heat conditioning state for more than one hour as this may result in ageing the material). The sample temperature in the jig can be monitored using a thermocouple inserted into the sample in the jig cavity during the loading operation. This predicts the refinement in the heater setting that gives the actual test temperature, since heat can be lost from the exposed surfaces of the jig. After the loading operation the heat band is removed and the jig returned to, (and stored in) the oven, which has been set, at least five hours before the test, to maintain the test temperature where ageing takes place.

The subsequent relaxation test is carried out at the same temperature at desired time, as described above. Note that it may not be necessary to employ the heat band during the stress relaxation measurements since this operation takes not more than 30 sec. for a good operator. Since the mass/ volume of the jig (relative to that of the sample) is very high, the heat capacity of the jig is enough to maintain the temperature for the short period of test without losing reproducibility.

It has been claimed that these materials (particularly Santoprene) have an excellent high temperature performance(3) (e.g. retains 100
% modulus, 80% tensile strength and ultimate elongation and low compression set value after 30 days at 125 \textdegree C). Therefore test at 70 and 100\textdegree C were carried out following the procedure described above to investigate the claim. Tests were performed on all the samples except that test at 100\textdegree C was limited to the Santoprene grades.

4.4.3.1 DISCUSSION

Tests at elevated temperatures were aimed at investigating two things (1) to explore the material at these temperatures and (2) to re-examine the effect of lubricating the test sample.

(1) Exploration of samples :- It was observed that the initial force for all the samples is lower than as is the case at room temperature, as expected, but relaxed less than is the case at room temperature for the same period of time (2000 hours, with reference to Santoprene in this case). The reason may be that when a material is subjected to high temperature below its melting point, expansion takes place so that the increase in average volume created and occupied by the molecules, together with thermal agitation enables greater molecular mobility. Since it is the same quantity of material that is present and distributed over the increased volume, the modulus of the material will decrease. Thus the material tends to deformed more easily when stress is applied to it in that state, in the direction of the stress while still maintaining its structural integrity. This allows retraction and improves permanent set resistance, hence the reduced relaxation, although the material becomes less resistant to deformation due to ease of flowing (enabled by the availability of space generated by
Figure 4.2(c)

Stress relaxation characteristic at 23°C when unrelated to (Log.time)

Force Ratio %

Time hr

Inj. moulded Santoprene

101-73
201-73
101-64
201-64
201-55
Figure 4.1 (d) Stress Relaxation Behaviour (23°C) of Alcryn Samples

Figure 4.1 (e) Stress relaxation behaviour of Alcryn samples at 70°C
Figure 4.1 (g) Stress relaxation behaviour of Estane samples at 70°C

Figure 4.1 (f) Stress relaxation of Estane samples at 23°C
Figure 4.1 (k) Stress relaxation behaviour of Hytrel samples at 70°C

Figure 4.1 (j)
Figure 4.1 (h) Stress relaxation behaviour of Pebax samples at 23°C

Figure 4.1 (i) Stress relaxation behaviour of Pebax samples at 70°C
<table>
<thead>
<tr>
<th>Time (mm)</th>
<th>0.1</th>
<th>1.0</th>
<th>5.0</th>
<th>7.0</th>
<th>15.0</th>
<th>34.0</th>
<th>150.0</th>
<th>2000</th>
<th>5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT Specified Time, (Hour)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3.2**

Moulded Sample (IU = Injection, TF = Transfer)

At some Santoprene Grades (Comparison Between Initial and Stress Relaxation in Compression Measurements At 22°C)

Grade Sample Force at 2% of Initial Sample Force

Notes:
- Moulded sample
- IU = Injection
- TF = Transfer
- Santoprene Grades
- Comparison between Initial and Stress Relaxation in Compression Measurements at 22°C
thermal expansion) and hence too the reduced initial force.
Canevarolo et al\(^{(4)}\) have shown that the structural integrity (i.e. domain structure) of SBS, subjected to a temperature of up to 250 °C persists in the melt. It is expected that this phenomenon will play a greater role in thermoplastic elastomer materials where molecular structure does have great influence on mechanical properties. See figure 4.3 and table 4.4.1(b). Results for the other TPE's are presented in table 4.4.1 (a) and (b) in appendix and figures 4.1 (a) - (k) show their respective relaxation curves.

4.4.4 RE-EXAMINATION OF LUBRICATION EFFECT

(2) It has been found that with a bonded specimen complex shear stresses develop at the loading surfaces due to restriction to slippage, perpendicular to the applied force. In order to reduce the phenomenon contact surfaces are lubricated with oil or powders (e.g. Silicone oil, Molybdenum disulphide powder)\(^{(5)}\) during test. Kimmiich\(^{(7)}\) observed a large difference in the stress - strain behaviour of lubricated and bonded samples under compression while Foster\(^{(8)}\) attributed the deviation of experimental curve to the theoretical curve as due to poor lubrication. However, recent work by Beatty\(^{(9)}\) and Tahir\(^{(10)}\) showed that stress relaxation is not very much affected by the surface condition of the specimen.

It is thought that non-bonded but unlubricated specimen will to some extent behave like bonded specimen and as a result it is argued that since many thermoplastic elastomers contain process oil, this might behave as a lubricant and introduce thereby arbitrary difference between TPE's which contain oil and those which do not. It
was considered that the effect will be more evident at elevated temperatures, therefore tests were carried out to investigate it.

4.4.4.1 EXPERIMENT AND DISCUSSION

Samples were prepared by the usual method (as described in chapter (III)), some specimen were lubricated while others were not. Test were carried out at 23 and 70 °C but attempts to investigate the behaviour at 100 °C were abandoned as the materials began to flow at this temperature during compression.

It can be seen from the results of the test presented in table 4.4.1 that there are no systematic differences between lubricated and unlubricated specimens. Results for oil-free Santoprene samples are also shown in table (4.4.1) for comparison. This may not provide any meaningful interpretation of results since the properties of the oil-free samples will differ generally. (See oil-free Santoprene, section 4.8). Since all Santoprene specimens contain process oil, any deleterious effect of lubrication will give rise to a systematic response in the results. Therefore in view of the absence of this, we conclude that lubrication has no significant effect on the stress relaxation of TPE’s investigated.
TABLE 4.4.1  Effect of Lubrication on Stress Relaxation

<table>
<thead>
<tr>
<th>SAMPLE TEMP.</th>
<th>INITIAL FORCE (N)</th>
<th>RSF% AT 100 h.</th>
<th>SRF% AT 170 h.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>oC</td>
<td>LUB.</td>
<td>UNLUB.</td>
</tr>
<tr>
<td>101-64</td>
<td>23</td>
<td>267</td>
<td>255</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>190</td>
<td>195</td>
</tr>
<tr>
<td>201-73</td>
<td>23</td>
<td>318</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>240</td>
<td>230</td>
</tr>
<tr>
<td>OILFREE</td>
<td>23</td>
<td>1069</td>
<td>1066</td>
</tr>
<tr>
<td>101-64</td>
<td>70</td>
<td>738</td>
<td>741</td>
</tr>
</tbody>
</table>

Note: LUB. and UNLUB. refer to Lubricated and Nonlubricated respectively, RSF refers to Relaxed stress normalised to initial force expressed in %, h refers to hour

4.4.5 TEST AT SUB-ZERO TEMPERATURE

Samples of the materials used in this project were conditioned at sub-zero temperature (-20°C) in the deepfreezer for 48 hours before test. It is advisable to pre-prepare the jig with the sample to be compressed placed in it and put away in the deepfreezer as this will eliminate the possible change in temperature of the sample during the preparation of jigs prior to loading (if sample alone is conditioned) and also the moisture which might form on the sample surfaces due to condensation (which may interfere with the ageing at -20°C).

It was noted that the samples become harder generally and the initial forces increased considerably. The relaxation pattern of Slow-cooled and Quenched samples are similar and there is no systematic difference in initial force and relaxation. Also note the increased rate of physical relaxation (the early part of the relaxation
Figure 4.4.5

Stress relaxation behavior of slow-cooled and quenched samples at -20°C

Legend
- Estane Slow-cooled
- Estane Quenched
- 101-73 Slow-cooled
- 101-73 Quenched
<table>
<thead>
<tr>
<th>Quenched</th>
<th>1.16</th>
<th>1.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow-Cooled</td>
<td>1.38</td>
<td>1.32</td>
</tr>
<tr>
<td>Quenched</td>
<td>1.81</td>
<td>2.28</td>
</tr>
<tr>
<td>Slow-Cooled</td>
<td>1.78</td>
<td>2.19</td>
</tr>
<tr>
<td>Quenched</td>
<td>1.61</td>
<td>2.13</td>
</tr>
<tr>
<td>Slow-Cooled</td>
<td>1.71</td>
<td>2.56</td>
</tr>
<tr>
<td>Quenched</td>
<td>1.60</td>
<td>2.71</td>
</tr>
<tr>
<td>Slow-Cooled</td>
<td>1.55</td>
<td>2.68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Normalised Force to 2% Strain (N)</th>
<th>Sample Actual</th>
<th>Sample Thickness Strain (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04 0.14 0.54 0.54 0.10 0.40 0.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.1 (C) Stress Relaxation Data for Quenched/Slow-Cooled Samples

Note: h = hour, at 230°C.
curve). The result leads one to the conclusion that stress relaxation in these thermoplastic elastomers is a function of crystalline content in them. See figure 4.4.5. and table 4.4.1).

4.5 A POSSIBLE RELATIONSHIP BETWEEN MODULUS ENHANCEMENT FACTOR, HYSTERESIS AND STRESS RELAXATION

The experimental technique explained in this thesis facilitates subsequent measurements to be taken after time intervals as small as one minute after loading. The unique method of the experiment enables one to obtain force / displacement (ideal) curve while loading the specimen (to the required level) as well as during the stress relaxation measurement. In addition to stress relaxation there are two other major effects which have been revealed (so far) by this technique. (i) the cross-over effect (which will be discussed in the next section and (ii) enhanced stiffness (modulus) effect, to be discussed here with regards to the materials under investigation (thermoplastic elastomers).

4.5.1 MODULUS ENHANCEMENT FACTOR (MEF)

The enhanced stiffness (modulus) effect is the instantaneous enhanced stiffness which is usually observed even after a few seconds of loading. It can be seen that there is an abrupt change between slopes of the force / displacement curves developed during loading and stress relaxation measurements. (Note that during stress
relaxation measurement the ideal curve continues along the
displacement axis, at the point where a sharp change in slope occurs.)
The ratio of the tangent moduli of the latter and former, defines the
"Modulus enhancement factor, abbreviated as (MEF). (i.e. the ratio of
the slopes \( \text{BC} \) to \( \text{P}_0\text{P}_1 \) in figure 4.5.1d). A discussion of the cause of this
phenomenon with reference to filled specimen and gum vulcanizates
and its relation to "HYSTERESIS" is given in the literature(11) The MEF
values of the samples have been obtained and are shown in table
4.5.1 (a) and (b) in the appendix.

4.5.2 HYSTERESIS

When a visco-elastic material is deformed, the viscous elements
consume energy and retard the elastic deformation, similarly energy
is dissipated when the elastic elements return, in the process of
strain recovery and release their stored energy. Usually the total
energy expended is never recovered. The viscous elements or the
internal friction are thus responsible for the energy difference or
"Hysteresis" (H) between work recovered and expended.

4.5.2.1 EXPERIMENT

The hysteresis loop was generated by strain cycling at the same
rate as that during loading, (i.e. at the end of loading operation, when
the 25 +/- 1 % strain level has been attained, the machine was made
to reverse the loading process - the loading platform moving in the
opposite direction, in this case, downwards). Figure 4.5.2 is an
example of such loop, obtained for gum stock and black filled
vulcanizates at 23⁰c.
4.5.2.2 DISCUSSION

It has probably been the view of some researchers\(^{(10)}\) that high "MEF" appears to reflect high hysteresis and hence high relaxation, low "MEF" reflects low hysteresis and hence low relaxation, the present author wishes to suggest that in as much as the above correlation is feasible there is no justification of such correlation between MEF and relaxation as materials with high MEF may show low relaxation / relaxation rate. One typical example is seen in the case of "PEBAX 3533" which has a MEF of 5.08 at 0.1 hour after loading but very low hysteresis and relaxation rate. Fernando's explanation is true only for filled polymers and blends which suffer high initial relaxation rate due to damage of the polymer/filler inter-facial bonding and the associated strain amplification in the polymer phase as explained by Mullins et al\(^{(12)}\) for example: in "ALCRYN 80A", (a highly filled blend) which has a MEF of 6.19 at 0.1 hour after loading, and also shows high hysteresis and relaxation. A somewhat similar situation is the case with the 73 and 64 grades of the Santoprene series although to a lesser degree. Other TPE's (Estane, Hytrel, Pebax series) by their nature (being block copolymers with hard and soft segments) generally have higher MEF, low hysteresis as well as low relaxation rate compared to the Alcryn and Santoprene series, which are blends.

Considering MEF as function of time one observation common to all the samples tested is the fact that there is an initial rise in the MEF values during the first few minutes of (0.1 to 1.0 hour) measurements. In some of the samples, this is followed by a drop in these numerical values to a minimum and then a final rise which can
be higher or lower than the initial values of the first few minutes, while in others the MEF stayed the same or continued to drop with time. A possible explanation to this behaviour (for the first case) may be that the initial rise is due to initial resistance to molecular flow and or change in configuration, strain induced crystallization, cross-linking, tightening of molecular entanglements etc. but given time while still under the constant strain, the molecules begin to rearrange themselves or flow in the direction of the stress hence the reduction in value that followed. Finally it is expected that at equilibrium rearrangement will give rise to a more compact structure or configuration (especially in thermoplastic elastomers where the presence of soft amorphous phase may permit rearrangements if the deformation rate is low and non destructive (does not lead to breakage of bonds). At equilibrium the molecules may be cross-linked in this state and may result in a higher cross-link density as they are now more closely packed thereby giving higher modulus and hence the final rise in values. The possibility of other phenomena being involved cannot be ruled out, however.

It is also ambiguous to correlate the hysteresis modulus to relaxation modulus (although the relationship is still under examination) rather the word "Hysteresis loss modulus" should be used. It should be noted that the character of the hysteresis loop, or "Strain cycling" is a function of the retained backward force of the specimen (the reduction in force being directly related to hysteresis loss), so that the greater the hysteresis loss the lower the retained force. Thus it is reasonable to relate hysteresis loss to relaxation.
Figure 45.3

M.E.F. as a function of time.

Time (Hour)

M.E.F.
It seems that a high slope of the stress decreasing part of the hysteresis loop at 25% strain is associated with rapid relaxation and usually with a high MEF. See figure 4.5.3 and table 4.5.2 in appendix. The hysteresis loss modulus value at 25% strain has been compared with that of the enhanced modulus at 0.1 hour and there is a good agreement, in support of the above assumption. Also hysteresis losses have been calculated for a visco-elastic material using the equation (by Buswell et al)\(^\text{(13)}\):

\[
H = \pi \varepsilon^2 E'' \quad \text{(4.5.1 Appendix)}
\]

where \(E''\) is the viscous modulus and \(\varepsilon\) is the strain, which expresses the energy loss per unite volume of a visco-elastic material during one sinusoidal cycle. N.R. Choudhury and A.K. Bhowmick\(^\text{(28)}\); in their recent publication, using various thermoplastic elastomers have also shown that the total energy loss at break \((H)\) or (Hysteresis loss) can be related to the work done \((W_g)\) on stretching by a simple relationship of the form: \(W_g = K H^n\), where \((H)\) is the Hysteresis and \((W)\) the strain energy. They noted that the plot of \(\log(H)\) gave a linear relationship described by the above equation - the equation which was determined statistically by using regression analysis gave rise to the value of \(K = 1.41\) and \(n = 0.87\) for the thermoplastic elastomers.

The relevance of MEF to stress relaxation is still not clearly understood as the modulus of some materials builds up (increases) while of others decreases while relaxing and ageing.
4.6 RECOVERY EXPERIMENT

Following BS 903 and since same mode of compression used for the stress relaxation experiment is required for that of compression set, samples tested for stress relaxation were also used for the recovery test. The advantage of this, is that it enables the measurement of the two parameters - stress relaxation and recovery, using the same sample so that direct comparison of results can be meaningfully made.

After a nominated time period the loaded jig (with reference to stress relaxation experiment) was released and the recovery of the compressed specimen was monitored. In this case samples were monitored for 2000 hours and the total fractional recovery was calculated using the equation:

\[ R_T = \frac{t_T - (t_c - t_g)}{t_s - (t_c - t_g)} \times 100 \]  

(4.6.1)

where \( t_c \) is the Jig depth, \( t_g \) is the plate thickness, \( t_s \) is the original sample thickness, and \( t_T \) the sample thickness after time (T)

Recovery to almost 100% of the original geometry occurs remarkably rapidly even after the prolonged compression of (2000 hours). Table 4.6.1 (a) (in appendix) showed the recovery data where there does appear to be a trend of faster recovery associated with the softer grades. Also there seems not to be any influence of the mode of specimen preparation. In general, the rapidity and degree of recovery shown by these materials again demonstrates the influence of structure on mechanical property (see figure 4.6.1), i.e. since it is that these thermoplastic elastomers are composed of phase
separated domains of one component dispersed in the other, and it has been known that this factor is responsible for the improvement in the general properties of thermoplastic elastomers, therefore the above results are expected of the materials. This factor is expected to be spectacular as regards recovery because the soft segments act as springs while the hard segments help to reinforce the springs.

4.7 DYNAMIC VULCANIZATION EXPERIMENT

It is claimed that Santoprene thermoplastic elastomer (to which emphasis was placed in this programme) was prepared by dynamic vulcanization (see chapter (1)). In order to explore structure/property relationships, attempts has been made using peroxide cross-linking agent to prepare EPDM / PP blends by the technique (by blending and then curing whilst still ageing).

4.7.1 EXPERIMENT

In this programme the following compositions were prepared, one of which was cured and the other not, so that six different samples were prepared altogether:

- 2 x 40 % PP/ 60 % EPDM cured / uncured.
- 2 x 30 % PP/ 70 % EPDM cured / uncured.
- 2 x 20 % PP / 80 % EPDM cured / uncured.

Since the available internal mixers were contaminated with carbon black etc. and the high viscosity of EPDM will not permit the use of extruders, the only option left was to use the two roll mill. Melt mixing was achieved by keeping the temperature of the roll mill sufficiently high (180 - 200°C). The high temperature was necessary because of the rapid loss of heat from the surfaces of the
mill. Even then, polypropylene would not melt. This problem was over come by pre-heating the samples in the oven to melting point and then quickly transferring to the mill. After sufficient melt mixing on the mill to form a well mixed blend, vulcanizing agent (Dicumyl peroxide - 5 % by weight of polymer) was added. The mixing torque was monitored and after it reached a maximum, mixing was continued for a few more minutes to improve the fabricability of the blend. It takes between 10 to 15 minutes for a batch to attain good mixing and optimum batch size was between 60 to 100g. Note that there is no any other additive to blends other than the curing agent. After discharging from the mill the blend was then compression moulded for test (see table 4.7.1 and figure 4.7.1 for test results.

4.7.2 **EFFECT OF PRE-HEATING**

As stated above the difficulty of melt mixing was overcome by pre-heating the samples. However, by gradual addition of polypropylene granules to the rubber during mixing, nonpre-heated samples were able to be melt mixed (but this is a laborious operation which can extend batch time up to an hour. This is not encouraged as the chain network of the polymers can be destroyed by excessive shearing).

It was noted that these compositions were harder than compositions prepared from pre-heated samples. This may be as a result of thermal degradation of materials during pre-heating, added to the fact that it has been noted that organic peroxides are capable of damaging (degrading) materials during melt mixing\(^\text{26}\).
4.7.2.1 RESULTS AND DISCUSSION

Although accelerated sulphur vulcanization is by far the most common method of vulcanization, a number of other systems find some use mainly in specialist applications, such as this. The most generally applicable non-sulphur system is vulcanization with peroxide. It has been used in this experiment because it provides a means of vulcanizing saturated polymers. When an organic peroxide is added to a rubber, it decomposes at the curing temperature into radicals, which abstract hydrogen atoms from polymer molecules. Thus the possible reactions involved may be as follows:

(i) With ethylene propylene (EP):

\[ \text{ROOR} \rightarrow 2\text{RO}^* \]

\[ \text{RD}^* + \sim\sim\text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim \rightarrow \text{ROH} + \sim\sim\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim \]

The polymer radicals thus formed undergo coupling reactions to give carbon-carbon cross-links:

\[ \sim\sim\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim + \sim\sim\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim \rightarrow \sim\sim\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim + \sim\sim\text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \sim\sim \]

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Note side chain unsaturation. Sulphur and Peroxide crosslinking is possible in these cases.

In this case both sulphur and peroxide curing is possible. In confirmation of whether cross-linking has taken place, swelling tests were performed on each of the compositions. See table 4.7.2 and 4.7.3 in appendix, for results. Stress relaxation, Tensile test and Hardness test results, all showed that the cured samples have superior properties to the uncured samples. It can be seen that these results are not as good as those observed for Santoprene probably because the Santoprene attained a higher degree of cross-linking and the fact that the right conditions, as
<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>23°C</th>
<th>1.59°C</th>
<th>1.1°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM Rubber</td>
<td>66.5 - 170</td>
<td>1.22</td>
<td>1.22</td>
<td>1.70</td>
</tr>
<tr>
<td>Santoprene</td>
<td>70°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAN</td>
<td>70°C - 170</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPDM/PP Blend</td>
<td>25°C</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 4.1

Stress Relaxation measurements for EPDM/PP Blend system at (23 °C)
Stress relaxation behaviour of EPDM/PP blend system at 23°C in relation to time.

Figure 4.7.1
described in the literature (such as temperature control, batch time, speed of mixing, absence of additives such as oil extender etc.) which will lead to achieving a better processable material were not met. Besides, peroxides are capable of degrading polymers at high temperature and with Santoprene sulphur curing agent was used(26). Generally the blend showed good compatibility as confirmed by microscopic examination.

4.8 OIL-FREE SANTOPRENE

One major advantage of thermoplastic elastomers over conventional rubber is that they are processed as thermoplastics. For this reason they usually contain process oil to soften them and facilitate processing, although the oil also acts as an extender. It was noted that some of the samples liberate process oil during test (a condition described as sweating). Therefore to explore the Santoprene further, the oil in each of the grades was extracted and analysed.

4.8.1 EXPERIMENT

In an extraction process a solute is distributed between two immiscible solvents. The ratio of the concentrations of the solute in the two solvents (1, and 2) is given by the equation:

\[ K_D = \frac{C_1}{C_2} \]  

(4.8.1)

where \( K_D \) is the distribution coefficient or partition coefficient - a special type of equilibrium constant which is related to the relative solubilities of the solute in the two solvents. Often one solvent is
polar and the other non-polar e.g., water and organic solvents. $K_D$ is greater for the solvent that shows less affinity for the solute. Note that in equation 4.8.1 solvent (1), the organic solvent is placed in the numerator, but just as often the lighter solvent (which may or may not be organic) is placed in the numerator. If the distribution coefficient is very large ($> 1000$), a single extraction in a simple separation unit will probably remove essentially all of a solute from one solvent to another. However for a given amount of extracting solvent it is more effective to divide it into several small portions and use each portion successively rather than to make a single extraction with all the solvent at one time. Fortunately we were not concerned with such degree of efficiency. Fortunately too, we were dealing with liquid and solid (process oil and polymer) which removes the problems of engaging in complex extraction processes and the difficulty of quantifying results. Thus a nominal weight of the samples was simply measured and allowed to soak in an excess amount of *Petroleum-ether and Diethyl-ether for 336 hours (two weeks) during which time the oil dissolved in the solvent. The solvent was then evaporated to concentrate the oil. Successive extraction processes were continued until the solvent left no oil residue when evaporated after separation from the sample. The samples were then dried at room temperature for 168 hours before they were re-weighed and the percentage loss in weight of the sample (weight of extract) calculated. See table 4.8.1 for results whence it can be seen that between 35 and 45 % of the total weight of the material may be process oil.

*-------------------------------------------------------------------------

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It is expected that the samples contain paraffinic oil as aromatic oils are not normally used in systems containing unsaturation because (due to their polarity) they compete for the unsaturation or reaction sites with the cross-linking agents during vulcanization\(^{(14)}\) (this behaviour being more pronounced with an EPDM systems as the unsaturation content is low compared to other elastomers).

<table>
<thead>
<tr>
<th>TABLE 4.8.1 OIL CONTENT OF (SANTOPRENE SAMPLES)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SAMPLE/ EXTRACTING CODE</strong></td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>101-73 PET.-ETHER</td>
</tr>
<tr>
<td>101-73 DIETHYL-ETHER</td>
</tr>
<tr>
<td>201-73 PET.-ETHER</td>
</tr>
<tr>
<td>201-73 DIETHYL-ETHER</td>
</tr>
<tr>
<td>101-64 PET.-ETHER</td>
</tr>
<tr>
<td>101-64 DIETHYL-ETHER</td>
</tr>
<tr>
<td>201-64 PET.-ETHER</td>
</tr>
<tr>
<td>201-64 DIETHYL-ETHER</td>
</tr>
<tr>
<td>201-55 PET.-ETHER</td>
</tr>
<tr>
<td>201-55 DIETHYL-ETHER</td>
</tr>
</tbody>
</table>

Note, increase in oil content in relation to hardness. Softer materials appear to contain more oil.

4.8.2 CHARACTERIZATION OF OIL

A brief account of each technique used for characterizing these oils and the experimental condition under which the tests were carried out is given below.

4.8.2.1 INFRA-RED (IR) CHARACTERIZATION

Molecules are made of characteristic arrangement of atoms which
are held together by chemical bonds. Such a system has $3N - 6$
fundamental vibrations (N being the number of atoms present). The
vibrations can occur by two different mechanisms. First, quanta of
infra-red radiation can excite atoms to vibrate directly - absorption
of infra-red radiation gives rise to infra-red spectrum. Secondly,
quanta of visible light can achieve the same result directly - the
Raman Effect\(^{(15)}\).

The infra-red spectrum is the portion of the electro-magnetic
spectrum between the visible and the micro-wave but for practical
purposes the wavelength (or wave number) range of analysis is
normally taken between 4000 to 600 cm\(^{-1}\). The C-H stretching region
extends from 3000 to 2840 cm\(^{-1}\), thus in a methyl group two distinct
bands are observed, one at 2960 cm\(^{-1}\) due to the asymmetric
stretching and the other at 2870 cm\(^{-1}\) due to the symmetric
stretching. The C-H bending deformation region is at a lower
frequency so, for a methyl group the asymmetric bending
deformation gives rise to the 1450 cm\(^{-1}\) absorption while the
symmetric mode is responsible for the band near 1375 cm\(^{-1}\). Linear
hydrocarbons \(-(CH_2)_n\) with 'n' $\geq 4$ absorb strongly near 720 cm\(^{-1}\)
due to the rocking mode of the C-H\(_2\) groups. Compounds with
carbon-carbon double bond show the C=C stretching vibration in the
range 1680 to 1620 cm\(^{-1}\) mainly depending upon the substituents.
Details of these absorption bands for various chemical groups and
configurations can be found in the literature\(^{(14,15)}\).

There are two types of vibrations: "Stretching" (v) in which the
vibration is along the bond, and "Bending" (\(\delta\)) in which the vibration
is in the angle formed by the three neighbouring atoms. Further
sub-divisions of them are symmetrical (vs) and asymmetrical (va),
stretching and rocking (ρ) and scissoring (σ) which are in plane
deformations and wagging (ω) and twisting (δ) which are
out-of-plane deformation for the bending vibration(15,16).
Frequencies of the bending or stretching vibrations depend largely
on the vibrating atomic masses and on the bond orders of the
chemical bonds joining them. The lighter the atom and/or the higher
the bond order, the higher the frequency of vibration.

Apart from the fundamental absorptions, overtone, combination,
coupling and Fermi resonance can occur in a complex molecule. Thus
the interpretation of the infra-red spectrum of an unknown sample
is very difficult. A short cut can be made by comparing the spectrum
of the unknown sample with standard spectra, mainly in the
finger-print region (650 to 1350 cm⁻¹). If the two spectra coincide it
can be safely assumed that the two compounds are identical.

Figure 4.8.2 shows the infra-red scan of the oil extracted from
Santoprene samples. The spectra were taking using the UNICAM
infra-red spectro-photometer, model SP200G, with a 15 minutes scan
time. The samples were smeared directly upon the NaCl plate (being
semi-solid at room temperature).

It was noted that all the spectra are identical, which suggest that
oils from the same homologous series (if not the same oil) was used
in all the grades. It can be seen that the spectra exhibit vibrational
absorption bands characteristic of aliphatic hydrocarbons i.e.
 asymmetric and symmetric C-H stretching at 2920 and 2860 cm⁻¹
respectively (average at 2890 cm⁻¹), -CH₂- scissoring at 1460 cm⁻¹
and C-CH₃ bending at 1380 cm⁻¹ The weak band near 725 cm⁻¹ is
caused by bending vibrations of the -(CH₂)₄ unit. The above information suggest that the oil is paraffinic in nature.

4.8.3 **GEL PERMEATION CHROMATOGRAPHY (GPC)**

Even though it is known that the oil is paraffinic in nature it could be a mixture, i.e. of different molecular weights and shapes or branching. To investigate this, chromatographic separation was performed on the oils to separate the individual components (if any) from each other.

The chromatographic separation technique utilises the same basic principle of distribution ratio. Variation in the rate at which different components of the mixture migrate through a stationary phase under the influence of a mobile phase is due to the differences in their distribution ratios between the phases. During chromatographic separation solute molecules are continually moving back and forth between the stationary and mobile phases. While they are in the mobile phase they are carried forward with it but remain virtually stationary during the time they spend in the stationary phase. The rate of migration of each solute molecules is therefore determined by the proportion of time spent in the mobile phase, in order wards by its distribution ratio.

The process by which a solute is transferred from a mobile to a stationary phase is called "SORPTION". Chromatographic techniques are based on four different sorption mechanisms, namely: "Surface adsorption, Partition, Ion exchange and Exclusion mechanisms. The exclusion mechanism is operative in Gel Permeation Chromatography, (although perhaps inclusion would be a better word to describe it). Strictly speaking it is not a true sorption process as the separating
solute molecules can diffuse through an inert but porous stationary phase. This is normally a gel structure which has a small pore size and into which small molecules up to certain critical size can diffuse. Molecules larger than the critical size are excluded from the gel and move unhindered through the column while small ones are retarded, to an extent depending on the time spent in the gel.

Figure 4.8.3 shows the chromatogram of the oil obtained from a "KNAUER Column" which is connected to a Micro-computer and printer. The sample was diluted in THF and a few drops of the solution were introduced into the column with a syringe at a flow rate of 1 ml/min. It can be seen that the elution profiles (of all the oils) consist of a single peak which is a confirmation of the fact that the oil is composed of a single compound. The Computer calculated average molecular weight is 325 but the reliability of the figure is subject to some doubt as it was noted to depend on the peak (quantity of sample) calculated by the computer. For this reason chromatograms of other paraffinic homolog: (N-Octadecane (C\textsubscript{18}), N-Eicosane (C\textsubscript{20}) and N-Docosane (C\textsubscript{22})) were obtained for comparison (figure 4.8.3), whence it can be seen that the computer calculated average molecular weight for these compounds is slightly different from the accepted figures - see table 4.8.3.

The molecular weight values suggests that the oil is probably C\textsubscript{19} but by extrapolating from the plot of elution volume versus number of carbon atoms, C\textsubscript{24} is predicted. In view of the uncertainty an attempt was made to determine the melting and boiling points.
Examination of the oil under the microscope, at room temperature revealed it to be partially crystalline, which again suggests that the oil is made of a single substance.

If a crystalline substance is heated, the temperature of the material continues to rise as heat is being supplied until at the melting or boiling points temperatures, the temperature temporary ceases to rise until melting or boiling is completed (i.e. when the material has completely changed phase) before a further rise in temperature can be observed. The heat supplied during melting is used up to bring about melting - referred to as "Latent heat of fusion.

The oil was put into a boiling point tube and heated electrically in a boiling point measuring instrument. It was observed that the oil bubbled at a temperature of between 330 and 335 °c after which it went dark brown in colour. This was suggested to be an oxidative effect. This temperature range corresponds to C_{19} in the boiling point versus No. of carbon atoms plot. (Figure 4.8.4).

Melting point was determined by using the Hot-stage microscope. A thin slide of the oil film was prepared and viewed on a Hot-stage microscope where it was observed that the crystals disappeared at a temperature between 28 and 34 °c. This range of values again centred around C_{19} in the melting point versus No. of carbon atoms plot.

The "DSC" thermogram was also obtained. This showed a multiplicity of peaks between 275 and 325 °c which may be due to the vibrations caused by the escaping vapour.

It can be seen that the only parameter of the analysis that is not
**Figure 4.8.4** Predicts the Number of Carbon Atoms of the oil.

**TABLE 4.8.3** Data from the Boiling, Melting point and Elution volume measurements.

<table>
<thead>
<tr>
<th>No. OF CARBON ATOMS</th>
<th>COMPUTER CALCULATED MOLECULAR WEIGHT</th>
<th>ACCEPTED MOLECULAR WEIGHT</th>
<th>BOILING POINT °C</th>
<th>MELTING POINT °C</th>
<th>ELUTION VOLUME ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-OCTADACANE (C 18)</td>
<td>241</td>
<td>254.5</td>
<td>316.6</td>
<td>28.2</td>
<td>8.00</td>
</tr>
<tr>
<td>N-EICOSANE (C 20)</td>
<td>277</td>
<td>282.6</td>
<td>343.2</td>
<td>36.8</td>
<td>7.94</td>
</tr>
<tr>
<td>N-DOCOSANE (C 22)</td>
<td>337</td>
<td>310.6</td>
<td>368.2</td>
<td>44.4</td>
<td>7.88</td>
</tr>
<tr>
<td>OIL</td>
<td>325</td>
<td>-</td>
<td>330-335</td>
<td>28-34</td>
<td>7.82</td>
</tr>
</tbody>
</table>
Baseline from 7.44 mL to 8.47 mL

Max. 7.65 422
Stop 8.47 75
Start 7.44 1120
Elevated mis. hold, etc.

Mark-Houghton constants

Peak 1-

Calibration file: C2H4 (cubic fit)

MIXED GEL

Columns:

Inlet
- Standard
- HPLC
- Flow rate (mL/min)
- Data file
- - C1
- Identifications
- Oil

From Sanoprene TPEs
Chromatogram of oil extract

Figure 4.5 (a)

GPC Chromatogram of

log M vs. log f (a)
consistent with the rest of the observations is the Computer calculated number average molecular weight obtained from the "GPC" chromatogram. Thus it can be concluded that the oil is an aliphatic hydro-carbon with number of carbon atoms in the range of $C_{18}$ to $C_{24}$.

Also the stress relaxation, tensile, hardness and recovery tests were performed on the oil-free sample (obtained from Santoprene 101-73). Table 4.7.2 shows the stress relaxation test results at 23 and 70 °C where it can be seen that it relaxed to a lower level (for the same given time period) than the corresponding (101-73) containing oil. Table 4.8.1 and 4.9.2 show the tensile and hardness test results. The material seems to be harder but shows lower tensile strength than the corresponding (101-73) containing oil. Its inferior properties may be attributed to the fact that the material has lost its excellent processibility and flexibility (as observed when it is compression moulded).

### 4.9 MECHANICAL TESTS

Stress/Strain relationships are commonly studied in tension, compression, shear or indentation. Perhaps the most commonly used method is that in tension. Besides being of relevance for products strained in tension, tensile stress/strain properties have been taken, since the beginning of the polymer industry as a general guide to the quality of polymers, being sensitive to filler and plasticiser as well as to the mixing and curing efficiency.

Standard methods of determining tensile properties of polymers are now well established. Essentially, dumb-bell shaped or less often
ring shaped test pieces are strained at constant rate and the force applied and the corresponding extension recorded. The force readings are expressed as stress by reference to the original cross-sectional area of the test piece. By the very nature of rupture process, tensile failure will always occur at a flaw in the test sample, no matter how carefully prepared the test piece. Consequently a standard procedure as described by the ASTM, D.638-84\(^{(17)}\) has been generally followed during the test with modification made as necessary. From the results obtained tensile strength at yield and break, as well as the modulus of elasticity and the elongation were calculated.

4.9.1 TEST PIECE FORM AND PREPARATION

Two types of test pieces are generally used for tensile testing. These are rings and dumb-bell as described by the BS903, Part A2 (1971)\(^{(18)}\) and ASTM, D412 -84\(^{(19)}\)

The advantages of rings are that (i) there is no gripping problems as the ring may be mounted on two pulleys and (ii) the elongation is easily measured by monitoring the distance between the two pulleys. The principal disadvantage is that the strain distribution in the ring is not uniform.

Dumb-bells, on the other hand are more difficult to grip, and the measurement of elongation cannot be taken as the distance between grips, as the strain along the whole test piece is not uniform, except when they are within the central parallel portion of the dumb-bell. Besides, by cutting dumb-bell in different directions orientation effect can be studied which is not possible with rings. Largely because of the uneven strain problem, but perhaps also because most
workers consider rings to be more difficult to cut from sheet, dumb-bells are the more commonly used of the two types.

When a ring is stretched tensile stress and strain are not uniform over the cross section but vary from a maximum on the inside circumference to a minimum at the outside. As the ring breaks when the maximum stress equals the breaking stress, the force registered at break does not correspond to the true tensile strength. The extent of the non-uniformity is shown in the following figures given by Reece(20) for the standard ring test piece:

\[ E_1: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000 \]
\[ E_2: 80, 163, 247, 331, 415, 499, 584, 668, 752, 857 \]

where \( E_1 = \% \) elongation of inside diameter and \( E_2 = \% \) elongation of outside diameter. The discrepancy cause by the difference between \( E_1 \) and \( E_2 \) on the tensile strength may be as much as 33 \%(21) as noted by Scott. The average of the stresses "A", in the inside diameter and "B" in the outside diameter i.e. \( \frac{1}{2}(A+B) \) which is the apparent tensile strength may be considerably less than the true tensile strength.

The dumb-bell shaped test piece was prepared by injection moulding of pellets of the materials, using a standard mould of the dimensions (ASTM D412)(19) listed below:

\[ W = \text{width of narrow section} \quad -13 \text{ mm}. \]
\[ L = \text{length of narrow section} \quad -65 \text{ mm}. \]
\[ W_o = \text{width of over all} (\text{mmE}) - \text{wider section of test piece} \quad -19 \text{ mm}. \]
\[ L_o = \text{over all length of test piece} \quad -188 \text{ mm}. \]
\[ R = \text{radius of fillet} \quad -76 \text{ mm}. \]
The ring shaped test piece was stamped out of compression moulded sheet and has dimensions of (3.4/2.4) mm. in thickness, external and internal diameters of (17.9/13.1) mm. Note that various sizes of test pieces are specified in the literature (17-8). (See figure 4.9.1 (a) and (b)).

4.9.2 SAMPLE CONDITIONING

After the samples have been moulded, they were allowed to remain at laboratory condition (room temperature, etc.) for at least 48 hours before test. For test carried out at elevated temperature (70 °C), test samples were allowed between 30 min. to not more than one hour, to remain under the test temperature condition to attain uniform temperature equilibrium, in an oven set at the temperature before test.

4.9.3 SAMPLE TESTING

The testing machine employed is the "J.J. Tensile Testing Machine", model T5002, manufactured and marketed by "J.J. Lloyds Instrument Ltd". On the mobile member of the machine is attached a load-cell which measures the tensile load delivered to the test piece. The load can also be calculated from the stress/strain (force vs. elongation) curve of the test piece, produced by a chart recorder connected to the machine.

For the elevated temperature experiment, a separate oven which can maintain a temperature up to 200°C is attached to the machine such that the sample can be strained within the oven. Machine test speed (i.e. strain rate) of 50 mm./min. was adopted through out the experiments. The samples were strained until failure occurred and
4.9.4 RESULTS AND DISCUSSION

From the results obtained in the test the nominal tensile strength at yield and break points as well as the true tensile strength, nominal modulus of elasticity and elongation at break were calculated for both tests in which dumb-bell and ring test pieces are used. (Table 4.8.1). Note the slight difference in results and a major discrepancy in the values of the modulus of elasticity obtained from the two test methods. Although it is ambiguous to compare results (in terms of magnitude) obtained from two different test methods and/or
conditions, it is important to comment in order that reasons for the discrepancies can be appreciated:

(i) The measured tensile strength has the tendency to decrease and the modulus of elasticity, the tendency to increase with increasing cross sectional area of the test piece (as more flaws - breaking sites, are created with increasing cross sectional area). Therefore it can be seen (among other reasons) why the tensile strength values calculated from the ring-shaped test-piece method are expected to be higher and the modulus of elasticity values, lower, since the ring test pieces have lower cross sectional area \((5.58 \times 10^{-6}) \text{ m}^2\) compared to that of the dumb-bell test pieces \((3.95 \times 10^{-5}) \text{ m}^2\). Even though the argument seems to be justified, it is only relevant to make comparisons between test pieces that are nominally identical in size and shape and under the same test method and conditions.

(ii) To calculate the stress (in the case of rings) at a given elongation or the elongation at a given stress, the mean elongation value should be used, not that of the internal circumference, since the registered stress will be the average over the whole cross section. In a paper comparing data from dumb-bell test pieces with those of ring test pieces, the relationship between internal circumference and mean elongation is given as\(^{22}\):

\[
E_m = \frac{2dE_1 - 100(D - d) + 1000(D - d)(100 + E_j)^{1/2}}{D - d}
\]

where \(E_m\) is the mean (\%) elongation, "d" is the internal diameter of the unstretched ring and "D" is the external diameter of the unstretched ring.

However it has been noted\(^{19}\) that the problem caused by the
difference in strain between internal and external circumferences of a ring test piece can be minimised by using rings with less than 4 mm. thickness. Although the preferred thickness is 4 +/- 0.2 mm., rings of up to 6 mm. and less than 4 mm. have been used.

One other observation is that almost all the materials yield at certain critical stress values depending on the material, with the exception of the Santoprene and Alcryn series - a situation described by Diamant et al(23) as "Plastic Rubber Transition" during uni-axial straining of block copolymers containing hard/soft phases. That is, the point at which the structure of the hard phase breaks down, after which the load is transferred to the soft phase. This may be considered to be the case here as the phenomenon did not occur with Santoprene and Alcryn samples. These being fundamentally polyblends, may lack such well defined continuous hard phase structure.

It can be seen (table 4.8.1 in appendix) that the elongation of the materials follows the usual trend of the higher the temperature the higher the elongation. The tensile strength, modulus of elasticity and yield strength are all lower at elevated temperature.

4.9.5 HARDNESS TEST

Another way of obtaining a measure of the elastic modulus of polymers is simply by measuring the hardness. This may be done by determining the resistance to indentation by using a rigid indenter to which a force is applied. Indentation can be by deformation, mainly in shear or compression. It is convenient to regard hardness as simply depending on Young's modulus and to use a hardness test where a given difference in indentation always represent the same
proportionate difference in modulus (i.e. the degree of indentation
"P" is a linear function of Log. of Young's modulus "E")

For the various geometries of indenter which might be used, the
following approximate relationships have been derived for a
perfectly elastic polymer(24):

"Ball", \( P = K_1 (F/E)^{0.74} R^{-0.48} \) \hspace{1cm} (4.9.2)

"Flat ended Cylinder", \( P = K_2 (F/E) d^{-1} \) \hspace{1cm} (4.9.3)

"Cone", \( P = K_3 (F/E)^{0.5} \) \hspace{1cm} (4.9.4)

where \( P \) = depth of indentation, \( F \) = indenting force, \( E \) = Young's
modulus, \( R \) = radius of ball, \( d \) = diameter of cylinder, \( K_1, K_2 \) constants
and \( K_3 \) involves the angle of cone.

The indentation is usually measured with a dial gauge with its
scale directly calibrated in International Rubber Hardness Degree
(IRHD). This scale owe a lot to the desire to have readings equivalent
to the Shore "A" scale and to represent increasing hardness by
increasing numbers. (Indentation decreases with increasing
hardness). The basis of the (IRHD) scale is a probit (integrated
normal error) curve relating \( \log_{10} \) (modulus) to hardness. The curve
is defined by the value of \( \log_{10} \) modulus at the mid point and the
maximum slope of the curve, and results in a scale which is in good
Shore "A" scale. The Shore "D" type scale is employed for hard rubber
above about 90 IRHD.

Both the dead load hardness tester and the Shore "A" Durometer
were used in this test, as described by the BS 903, part A26. Table
4.9.2 compares the results obtained, using both methods. Note that
these samples, which are fundamentally copolymer (Estane, Hytrel,
Pebax and Lomod) are harder than those formulated from blends (Santoprene and Alcryn) and that the hardness of 77 in the IRHD scale taken after 30 sec. for example, can be represented as IRHD/77/30.

4.9.6 REFERENCES

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10) Private discussion with A. Prabhu "Research student".
16) L. J. Bellamy; "The infra-red spectra of complex molecules"


18) BS. 903, Part A2, (1971); "Determination of Tensile Stress/Strain Properties"

19) ASTM D412 - 75 "Rubber Properties in Tension"


CHAPTER (V)

5 GENERAL DISCUSSION AND CONCLUSIONS

5.1 INTRODUCTION

It has been the aim of this research programme to provide industry with a reliable method of determining stress relaxation in compression and the establishment of the cause of stress relaxation through the exploration of some polymers belonging to the thermoplastic elastomer group, in particular investigating their stress relaxation behaviour in compression and exploring the effect of contributing factors such as cross-linking, crystallinity in sample, structure of sample, temperature, lubrication/no lubrication and interrupted loading on stress relaxation. Other mechanical properties such as tensile strength, hardness, recovery and/or permanent set were investigated and the effect of extracting the process oil (in Santoprene samples) was also examined. Since in thermoplastic elastomers structural organization is a crucial factor to consider in order to interpret the general properties, blends of PP/EPDM have been prepared to investigate structure-property relationships. In order to characterise the melt processibility of these thermoplastic elastomers their Melt Flow Index (MFI) and Differential Scanning Calorimetry (DSC) thermograms have been determined. The conclusions reached in the above experiments are discussed as follows:
(1) CHARACTERIZATION OF SAMPLES

The Melt Flow Indices (MFI) of the samples have been obtained. It can be seen from the results of the experiment that all the materials, with the exception of the Alcryn series flow fairly well under the test conditions. It was generally noted that the flow characteristics of the Santoprene series seems to be more shear rate dependent than temperature dependent. These results have led us to conclude that melt processing of the materials is a better technique to be employed for them. Therefore this is recommended. It would have been thought this will be impossible with the Alcryn series but surprisingly injection moulding operations did produce excellent finished products. On the other hand transfer moulding of the materials (Alcryn series) was unsatisfactory.

The DSC thermograms have been obtained for the range of TPE's and it can be seen from the traces that almost all the materials show distinct crystallization and melting temperatures (see figure 4.2.1). Thus this led to the conclusion that there is a crystallizable species present in the materials. However some indicated less precise melting and crystallization temperatures for example, in the T4022 grade of the Estane series and again the Alcryn series. The T4022 grade of the Estane series may be completely amorphous while in the Alcryn series the transitions may be for any other inclusion present in them, as the values (253°C) are too high for a polyolefin base polymer (e.g. melting point of polypropylene is 170°C).

(2) HEAT TREATMENT OF SAMPLES

The Santoprene series have been heat treated at various temperatures using various techniques (as described in chapter (IV))
to investigate

(i) the effect of processing method,
(ii) the effect of crystallization and
(iii) the effect of process oil.

Thermally treated Santoprene samples (at moderate temperature - below 50 °c) showed an improvement in the initial force, obtained from samples compressed to 25 +/- 1 % strain. This led to the conclusion that (i) these samples are capable of crystallizing at elevated temperature, which may or may not be advantageous to the overall properties of the material. Advantageous in the sense that crystallization will generally lead to increased modulus. The fact that such improved properties are associated with many thermoplastic elastomers is a consequence of the micro-phase separation of the individual components present, which can be enhanced by crystallization. On the other hand, since it has been noticed in this work that high crystallinity is associated with high rate of stress relaxation, it is disadvantageous in this sense, for example using the 101-73 grade of the Santoprene series, (i) it was found that thermally treated samples, followed by subsequently quenching or slow cooling them to room temperature resulted in the quenched samples showing less relaxation than the slow cooled samples. See figure 4.1(a) and (b), chapter IV section 4.3.2.2. (ii) an optimum temperature exists in which crystallization best take place (i.e. between 30 to 50°C) in the Santoprene series. It was noted that the initial force increased steadily from the temperature of 30°C until 50°C and began to fall beyond this temperature.

Slow cooled and Quenched, as well as Sub-zero temperature (-20°C) experimental results demonstrate clearly the effect of
crystallinity on stress relaxation of the materials, where it can be seen that the slow cooled samples (from 175 and 150°C to room temperature), in both cases show relatively higher relaxation rate compared with those cooled more rapidly. These temperatures have been chosen to investigate the effect of temperature and crystallinity on the materials. It is expected that at 175°C (by the nature of the materials) a good melt should be produced from them. On the other hand the materials should be partially melted at 150°C. It can be seen that the slow cooled samples also show higher initial force, as expected. This may be considered as due to the higher crystalline content of the samples. More so is the fact that samples slow cooled from 175°C show higher initial force than those from 150°C. Conversely, samples quenched from 175°C show lower initial force than those from 150°C (Table 4.3.1 (d) to (f)). As would be the case, the material is in a more molten state at 175°C, thus given or not given time to crystallize will result in a more crystalline or amorphous material, as the case may be. Since quenched samples are expected to be more amorphous than samples slow-cooled from the same temperature we conclude that it is the crystalline phase (in this case, the hard phase) that probably relaxes. Also slow cooling is more likely to give rise to phase separation in the materials.

It may be that the disruption of the well formed structure of the material led to the rapid stress relaxation observed in them. Note that structural break down will lead generally to anisotropy and/or amorphous situation in the material and once this state is reached, a quasi equilibrium state is maintained under constant stress, so that little relaxation will normally occur, unless further strained. In an amorphous material the molecules are not very orderly arranged as
is the case of a crystalline material, so that there is more room for molecular motions. This is somehow a more suitable state or rather a quasi-equilibrium state in which polymers can possibly better withstand straining. It is therefore thought that amorphous materials (since in them there are more room to allow change in shape and structure of the molecules) will show less relaxation when under strained than crystalline materials which may suffer structural breakdown under the same condition.

(3) **TEST AT SUBZERO TEMPERATURE (-20°C)**

In order to confirm the view that it is the crystalline phase that does relax, tests were carried out at sub-zero temperature (-20°C) for quenched and slow-cooled samples of the Santoprene series. Also the results of this tests did not show the cross-over phenomenon, (that is to say that the relative rate of relaxation in both Slow cooled and Quenched samples are the same (see figure 4.4.5)). Note that since the molecules (in this case) are at such a low temperature in which case they may be frozen, (the material being partly thermoplastic, although rubber may not be frozen at this temperature) therefore they will behave much the same way like crystallites, with little or no room to allow change in conformation or flow when deformed. Hence they show similar relaxation pattern. This led to the conclusion that, it is the crystals in the materials, that do relax.

(4) **STRESS RELAXATION**

Having accepted therefore that the results and pattern of stress relaxation obtained from the IPTME method (i.e. the ideal curve
method) is meaningful, while monitoring the stress relaxation of the materials, it was observed that the copolymer based materials (i.e. the Estane, Hytrel and Pebax series) generally show relatively less relaxation than the polyblend based materials. It may be that the bonds between the components of the copolymer based materials are stronger than that formed by the cross-linking agent between the components in the polyblend and/or the bond density in the copolymers is higher than in the polyblends resulting to less damage being done to the material when deformed. This is probably why the copolymers produces better thermoplastic elastomer materials. As mentioned earlier, more emphasis was placed on exploring the "SANTOPRENE" series. It can be seen that similarity in the initial force ($F_0$) exist at various hardness levels and the harder grades give higher initial force and relax faster than the softer grades. Thus, relaxation in these materials is a function of hardness which again indirectly reflects the influence of crystallinity, as it is the crystallizable component that is responsible for the material hardness. However, at elevated temperature (above 50 °c) all the materials give lower initial force and relax less than is the case at room temperature, in contrast to what is expected of high temperature relaxation. It was expected that at elevated temperature, while increased molecular mobility brings about rapid relaxation oxidation would further accelerate relaxation and ageing of the materials. In general, stress relaxation (in these materials) does not apparently seems to depend on the presence of oxygen as it can be seen that the relaxation patterns appeared to be controlled mainly by physical relaxation process at 23°c and even at elevated temperature the slope of the downward tailing of the initial part of
the Force / Log. time curve is still can be noted to be higher in some materials (an indication of physical relaxation) than the later downward tailing of the curve (an indication of chemical relaxation). However the effect of oxidation may become more pronounced at longer time of stress relaxation measurement. Note that the harder materials (e.g. in the Santoprene series) relax to higher degree than the softer ones. Note too that at high temperature the materials show relatively less relaxation. It is expected that the softer material (rubber) should relax more at elevated temperature as they contain higher proportion of rubber phase and are therefore more likely to suffer greater oxidative degradation, especially when unsaturated. The reverse results observed, must have been due to the fact that the plastic phase protects the rubber from oxidative attack\(^{(5,6)}\). The same reasoning will probably hold for the result of high temperature test, for all the materials.

From the above observations one can therefore conclude that the stress relaxation process (in classical rubber) results from two main contributions i.e. the simultaneous chemical and physical features in the material. The chemical contribution will increase with temperature, possibly with the number of participating reactions increasing. The physical contribution (relaxation) seems to have an Arrhenius relationship with temperature also - that is to say that the ease (rate) at which disruption takes place in the structure of the material is directly proportional to the activation energy of the transition of the material during reaction or a deformation process. Generally in chemical reactions the activation energy is lowered with increase in temperature. It seems also the same is the case on this occasion as there appears to be an decrease in activation energy with
temperature, as can be seen from activation energies calculated for a change (relaxation or initial forces) between the temperatures of 23°C and 50°C, 70°C, 100°C, using the Arrhenius type relation: \( F = F_0 e^{-\frac{\Delta E_a}{RT}} \) for the Santoprene 201-64 sample, (Table 5.4.1) where \( F \) and \( F_0 \) are the residual and initial forces respectively, \( R \) is the gas constant and \( \Delta E_a \) is the activation energy.

### TABLE 5.4.1

<table>
<thead>
<tr>
<th>TEMPERATURE RANGE °C</th>
<th>INITIAL FORCES (N) AFTER 5000 h AT 23 &amp; 50, 70, 100 °C</th>
<th>RESIDUAL OR CHANGE IN FORCE (N)</th>
<th>ACTIVATION ENERGY (Ea) KJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 - 50</td>
<td>238.0 &amp; 221.8</td>
<td>16.2</td>
<td>472.2</td>
</tr>
<tr>
<td>23 - 70</td>
<td>238.0 &amp; 190.0</td>
<td>48.0</td>
<td>347.7</td>
</tr>
<tr>
<td>23 - 100</td>
<td>238.0 &amp; 150.3</td>
<td>77.7</td>
<td>238.2</td>
</tr>
</tbody>
</table>

Table 5.4.1 showing the activation energy \( \Delta E_a \) for a change in initial forces (relaxation) between various temperatures

Note the decrease in activation energy with temperature as expected. This may be as a result of the increased room for molecular motion, so that the molecules had probably suffered less damage when strained which (in this context) explains why the materials suffered less relaxation at elevated temperatures. Due to the high activation energy, greater energy is required to be able to disrupt (i.e. do any damage) to the structure of the material. From the shape of the stress relaxation versus log. time curves, described as showing an initial downward tailing or upward heading in some cases (e.g in the Alcryn series showing a later downward tailing) it can be concluded that during deformation (compression) of the materials, there is an initial breakdown of the plastic phase and/or the
morphology of the materials, followed by a plastic to rubber transition and at much later time, a structural breakdown due to oxidative scission.

Figure 5.1

Curve showing the change (reduction) in activation energy with increase in temperature.

\[ \text{Slope} = \frac{E_a}{T} \]

\[ \text{Intercept} = \ln F_0 \]

The later downward tailing has been noted to be due to oxidative action in conventional rubber\(^1\). The plastic to rubber transition (which can also be due to network failure) was clearly seen as yield points during tensile tests and it is represented as the constant or gradually changing slope portion of a stress/strain curve.

The later part of the stress relaxation vs. log, time curve, showing a down-ward tailing was considered to be due to oxidative
degradation.

(5) **EFFECT OF LUBRICATION**

It was argued\(^{(2)}\) that since many thermoplastic elastomers contain process oil, the oil might behave as a lubricant especially at elevated temperatures. It is expected that lubrication of the material (in presence of the process oil) will result in an unusual behaviour of the stress/stain characteristics of the material. It can be seen from the results of the tests carried out to investigate this. (table 4.4.1 and figure 4.4.1) that there is no systematic difference in results obtained, between lubricated and non-lubricated samples. This led to the conclusion that lubrication has no significant effect on these materials and stress relaxation results obtained for them.

(6. (a)) **MODULUS ENHANCEMENT FACTOR (MEF) AND HYSTERESIS**

The ratio of the modulus at a compressive strain level of 25 +/-1 %, for various times under load, to the tangent modulus at the end of loading is defined as the "Modulus Enhancement Factor" (MEF). MEF values for the materials ranges from 2 to 7. A continuous change in these values of MEF, especially at the early period of the relaxation time (between the instant in which loading is completed to about 0.5 hour) was observed. Hysteresis is the dissipation of mechanical energy (as heat) during deformation of the material or can be better explained as follows: It is the resistance to deformation offered by the molecules of the material, which will normally depend on molecular structure, arrangement and weight. High MEF appears to be related to high Hysteresis but not necessarily high relaxation as suggested elsewhere\(^{(1)}\). It has been observed that Hysteresis is
directly related to hardness (i.e. harder material shows higher hysteresis). It has been observed too that harder materials show higher slope at point "A" or at the 25% strain of the unloading curve of the loop generated by strain cycling. (See figure 4.5.2 in chapter IV, section 4.5). Since so far, it has been observed that harder materials usually show high MEF, it is not unreasonable to draw such correlation between MEF and Hysteresis but note that a conclusion cannot be drawn from this statement as it is possible that soft materials could have high MEF as well. This requires still, further investigations before a definite conclusion can be reached. The hysteresis loss also appears to be related to the total relaxation suffered by the material, as discussed in section 4.5.2.2. Note that the area enclosed by the hysteresis loop or "strain cycling" is the energy or hysteresis loss in a strain/recovery process. The higher this area the greater the relaxation, provided the unloading rate is equal to the loading rate.

(6. (b)) QUANTITATIVE CONSIDERATION OF MEF

Generally the enhanced stiffness (modulus) of polymers is a consequence of the hysteresis, therefore it is expected that MEF of pure elastomers should remain constant as the materials age, due to breakage of bonds. Often the reverse is the case (i.e. a positive factor is usually obtained). This may be as a result of the two-network phenomenon usually observe in polymers. In thermoplastic elastomers, another reason may be that at certain critical strain level, the glassy domains are forced to impinge on each other due to the contraction of the specimen's sections in the adjacent directions to the direction of stress/stran.
Considering MEF in relation to the quantitative element of the two-network system, it is expected that at ca. 25% compression the force is being maintained by fewer bonds than, as is the case at 0% compression since bonds may be broken during compression.

Figure 5.2

Ideal curve drawn to illustrate the position of the point "A" (the 25% compression point).

However bonds broken during the compression state are reformed at the 25% compression state as the strain is maintained at constant state, at this point. These will both be available to combat or prevent further strain but do not help recovery, rather they will retard the process.

As has been pointed out else where in this Thesis, the total number of bonds available after a while at the 25% state (i.e. the number of bonds unbroken, plus the number reformed) to combat further deformation may be more or less than the number of bonds originally present in the material, depending on factors such as the nature of the material, whether or not yield point is reached or destructive deformation has been imposed, atmospheric conditions,
such as temperature, presence or absence of oxygen and other conditions which will or will not favor such reaction.

At situations where MEF becomes positive, two things may be responsible (i) it may be that the total number of bonds available after the 25% compression has been reached are more than the original number in the material. (ii) at such level of compression in some materials, the hard segments/domains or fillers present in them could begin to impinge on each other due to the contraction of the specimens sections, thereby increasing the modulus of the material. The second reason may be why pure elastomers like EP rubber (tested) has very low MEF (MEF of 0.12 - not recorded), because it contains no filler or hard segments. More so will this be if no destructive deformation is imposed, so that no bond is broken therefore no bond reformation may be necessary.

Figure 5.3 (b) A possible situation during deformation of the material

At situations where MEF is negative, following the above arguments, one can suggest that the number of bonds available at the 25% compression state is fewer than the original number present in the material before compression. This argument can be further
supported using the results of our investigations (Table 4.5.1 (a) and (b)), where it can be seen that MEF fluctuates as the materials aged. This might begin to happen when oxidation sets in without the reformation of broken bonds. In some materials however, MEF has been seen to increase as the materials aged (Figure 4.5.2). One can suggest in this case that reformation of broken bonds has taken place and oxidative degradation of bonds did not come into play for the time period the materials were under investigation. Note the sudden rise in MEF in the first few minutes after the 25% compression state has been reached (i.e. within the first 0.5 hour). This can be interpreted as the propagation period of the two-network reaction where the reformed bonds are more stable.

Although the argument seems to be logical it is not a rule that absolutely governs the two-network phenomenon. Unfortunately there can not be any direct mathematical rule or theory to quantify these ideas or work out the number of bonds being broken or rate of bond breaking or making at a given time, since the factors controlling this reaction can not themselves be totally controlled, and secondly it is a time dependent phenomenon.

(7) RECOVERY

The ability for some polymers to retract or return to their original shape when released from a deformed state is known as recovery, e.g as can be noticed with elastomers, where this happens more rapidly and forcibly, while in other polymer types it could take hours, days or even months for recovery to occur fully. It is measured and better expressed as a percentage of the amount of the total strain, otherwise known as fractional recovery. See section 4.6,
chapter IV.

One striking property of thermoplastic elastomers is their recovery characteristics. The high level of recovery achieved with the thermoplastic elastomers investigated, after having been deformed (i.e. compressed to 25% of the original height), is one of the properties that make the material superior to conventional polymers.

Recovery in polymers appears to be dependent mainly on the physical elements of the material, such as chain entanglements, tie molecules, physical bondings etc., so that if the stress does not cause destructive or permanent deformation, a reformation of the original molecular shape/structure occurs. At constant temperature it is expected that the rate of recovery at the early stage of the recovery process should be faster due to the sudden removal stress, followed by a slower later stage with time\(^5\), therefore taking similar characteristics as in the case of stress relaxation. This led Nutting\(^4\) to postulate that a power law is appropriate for describing recovery and stress relaxation in polymers.

Although stress relaxation is related to recovery in some ways, the same conclusion should not be drawn from results obtained with it, since recovery involves mainly physical processes. It is expected therefore to produce a linear curve with log. time. In confirmation of this expectation, note the results of the fractional recovery versus log. time (for the Santoprene series) at room temperature (see figure 4.6.1). Unlike their corresponding stress relaxation versus log. time curves, which show an initial down-turn (with high slope) followed by a lower but a gradually changing slope of the later part, (which led to the description of these curves as showing an initial upward heading or downward tailing). It can be seen that they are more
linear than the stress relaxation curves. This has been thought to be probably due to physical reorganisation of the structure with non involvement of any chemical action (e.g. oxidation) in the process of relaxation. See figure 4.6.1.

The process may be described as follows: During deformation (say compression), the tie molecules, chain entanglements etc. and the general structure of the material becomes more closely packed and when the stress is removed, they try to regain their original shapes and positions (recovery). The inability of recovery to take place must have resulted from damage and/or change in the general structure of the material.

(7 (i)). The Effect of Structure (Morphology) on Recovery

Since phase separation in thermoplastic elastomers is responsible for the improved properties shown by them, it is expected that each phase will contribute to this role differently, depending on its nature, as described below: It is expected that during deformation the soft (rubber) phase will act as a spring while the hard (plastic) phase reinforces the spring through increasing the modulus. Compression of the material (for instance), is possible due to the fact that the molecules of the soft phase (rubber) can be involved in some kind of molecular motion (e.g. rotation, flow, etc.) during a deformation process. The material is able to recover its strain due to the increase in its modulus offered by the hard phase as this helps in resisting the stress that would otherwise cause damage in the material. Therefore while the soft phase permits deformation in thermoplastic elastomers, the hard phase resists it and hence offers the strength with which recovery of strain becomes possible. But in the case of a
one phase system (for example if only the plastic phase is involved)
it will resist deformation i.e. resist molecular motion, and if only the
rubber phase which will permit this is involved, it will easily deform
and assume the new strained state, where the stress and strain are
constant and not removed for considerable time period, (especially
when the material is vulnerable to chemical action), it will lack the
ability to recover. Due to the phase separation in thermoplastic
elastomers (which in most cases are co-continuous) each component
of the TPE has an inter-locking structure, penetrating into the other
and due to the alternation of soft and hard phase therefore, behaves
like a spring. This may be also responsible for the high recovery
nature of TPE's. This high recovery nature of TPE's make them the
best material for sealing, damping, etc operations as in footwear,
tyres etc and similar applications.

The structures as described in chapter (1) are usually a dispersion
of one phase (the phase having the lower volume fraction) in the
matrix of the other, for example for SBS can take the form of
spherical, cylindrical, lamella or interpenetrating/co-continuous
structure.

![Diagram](image.png)

(1) SPHERICAL  (2) CYLINDRICAL  (3) LAMELLA  (4) CO-CONTINUOUS/
INTERPENETRATING

- Soft phase (rubber)
- Hard phase (plastic)
Not only will the plastic phase resist deformation, it will undergo breakdown or destructive or permanent deformation at high strain. Since the molecules are very closely packed (in form of cristals), that is to say that at such critical level, the glassy domains are forced to inpinge on themselves because of contraction of specimen's section, the disruption of which can not be easily amended or reformed.

Recovery of polymers generally takes place in two stages. The first is that which takes place within a few hours after the stress has been removed and the second, which takes place at a later time, usually at a lower rate, has been described as secondary creep recovery\(^5\) by Gent, but in certain situations the rate of secondary creep recovery can even be higher than is the case with primary or early recovery stage. This has some bearing with secondary relaxation and creep. Secondary relaxation/creep or what may be termed chemical stress relaxation/creep takes place at later part of the process i.e. when oxidative scission and reformation of cross-linking sets in. When this happens, usually the material becomes permanently deformed or set as the number of bonds (cross-linking) formed may be equal or greater than the number of bonds broken (scission). At secondary creep recovery, the failure of specific cross-link structures occur\(^6\) the rate of which may be higher or less than the recovery at earlier stage. It should be noted that the degree of recovery achievable is governed partly by the amount of cross-links which are reformed during chemical stress relaxation/creep\(^7\). Therefore, in vulcanized rubber virtually complete recovery is in fact, to be expected for materials where oxidative scission is not accompanied by cross-link formation in the deformed state. It is expected that the broken but not-reformed
chains would not affect recovery, so long as unbroken chains still exist.

(7 (ii)) Effect of Temperature on Recovery

Due to the fact that molecular motions are greater at high temperatures (hence expansion), the recovery in polymers should be faster at high temperatures. In thermoplastic elastomers, the healing effect brought about by increase in temperature will generally improve the recovery phenomenon in deformed materials. Since expansion must be associated with disentanglement of chains and tie molecules etc., recovery can be regarded as an expansion process, utilising only the stored energy during deformation at room temperature. The higher recovery usually observed at elevated temperature especially during recovery of secondary creep/relaxation is due to the additional thermal energy gained from the increase in temperature.

However some of the materials have been noted to show poorer recovery at high temperature e.g. the Alcryn series which show a total fractional recovery (i.e. fractional recovery at the end of a specified time period) of 60.0% and 12.5% at 23°c and 70°c respectively, 500 hours after they have been released, (for the 80A grade) after being under load for 5000 hours. This must be due to greater contribution from chemical stress relaxation, in which case oxidative scission is accompanied by cross-linking and must be equal to or greater than the number of molecular scissions that had occurred.

If accepted that poorer recovery at higher temperature is due to more chemical stress relaxation, accompanied by cross-linking, the
same explanation can be given for stress relaxation results observed at elevated temperature. Therefore one can conclude that at elevated temperatures chemical stress relaxation dominates the ageing phenomenon.

(7 (iii)) Relationship Between Stress Relaxation, Creep and Recovery

Gent\(^{(5)}\) and others have discussed and characterised the visco-elastic behaviour of vulcanised rubbers, using a mathematical model as shown below to discuss the relationship among stress relaxation, creep and recovery of stress.

The rate of creep "\(C\)", at constant stress may be defined as:

\[
C = \frac{1}{e} \left( \frac{de}{dt} \right) \sigma \tag{7.1}
\]

where \(e\) is the deformation at a time \(t\) after the stress is imposed, and \(\sigma\) is the (constant) applied stress.

The rate of stress relaxation "\(S\)" at a constant strain may be similarly defined as \(S = -\frac{1}{\sigma} \left( \frac{d\sigma}{dt} \right) e\) where the respective deformations (and stresses) are equal. The two rates are related as follows:

\[
C = AS \tag{7.2}
\]

where \(A = \frac{(\sigma/e)(de/d\sigma)_t}{\sigma}\)

The rate of recovery "\(R\)" from an imposed strain of amount \(e_0\) may be defined by replacing \(e\) in equation 7.1 by \(e-e_0\). As the present measurements deal with only the final stages of recovery, when the remaining deformation \(e\) is much smaller than \(e_0\), "\(R\)" is given to a good approximation by:

\[
R = -\frac{1}{e_0} \left( \frac{de}{dt} \right)_{t=0}. \quad R \text{ is related to the corresponding rate of}
\]
stress relaxation "S^1, i.e that which occurs after a material returns to the undeformed state from prior deformation of amount e_o. The relationship is analogous to equation (7.2) and takes the form:

\[ R = BS^1 \]  
(7.3)

where \( B = (\sigma_o/e_o)(de/d\sigma)_{t,\sigma_o} \). \( \sigma_o \) is the stress corresponding to the deformation e_o.

The rate \( S^1 \) is not necessarily equal to the rate of stress relaxation S under the original deformation e_o. Indeed relaxation processes can be envisaged in which this would not be the case, as for example, when the original relaxation is due to permanent structural changes taking place in the deformed material. "Symmetrical" relaxation processes may be imagined, however in which \( S^1 \) and S would be substantially equal. The later stage of relaxation of a Maxwell element, consisting of a spring and dashpot in series would be of this type.

The quantities A and B are properties of the relation between stress (load) and deformation at constant time. When this is linear, i.e., for Hookean elastic behaviour, A and B both take the value unity and the rate of creep and recovery be come numerically identical with the rate of stress relaxation. But when the stress/strain relation is non-linear, as it is for vulcanized rubber in simple extension, for example, the values of A and B may differ considerably, both from unity and from each other, which will lead to considerable differences in the rate of stress relaxation, creep and recovery.

For a vulcanized rubber subjected to less than 200% extension, the following stress/strain relation in simple extension has been found to apply fairly accurately(7,8).
\[ P = 2a_0(C_1 + C_2/\lambda)(\lambda - 1/\lambda^2) \quad \text{(7.4)} \]

\( \lambda = (1+e) \) is the extension ratio measured at a constant time interval after the load is imposed, \( a_0 \) is the unstrained cross-sectional area, and \( C_1 \) and \( C_2 \) are elastic constants of the rubber, the ratio \( T = C_2/C_1 \) lying generally within the range 0.5 to 1.0\(^{(10,11)}\). The quantities \( A \) and \( B \) have been shown to be readily calculated from the equation (7.4)

\[
A = \frac{\lambda(\lambda^2 + \lambda + 1)(\lambda + T)}{\lambda^4 + 2\lambda + 3T} \quad \text{(7.5)}
\]

and

\[
B = \frac{(\lambda T + \lambda + 1)(\lambda + T)}{3\lambda^3(1 + T)} \quad \text{(7.6)}
\]

Values of \( A \) and \( B \) may also be calculated for any other form of load/deformation relationship.

Note that applying this model to a material such as thermoplastic elastomer requires some modifications because of the contributions of the two phases. It is obvious that such modifications will involve complex mathematical expression for this reason and more so, for the present work, as the deformation is done in compression. Equation (7.1) and (7.2) for example should be preceded by a negative sign as compression will normally produce a negative extension. This will obviously alter the expressions for the quantity "\( A \)" and "\( B \)" in equation (7.5 and 7.6). In a two phase material such as thermoplastic elastomer the quantities \( A \) and \( B \) must be calculated for each of the component phases (as the case may be). Since these phases co-exist, they are bound to influence each other, therefore allowance must be made for this.
(7.(iv)) **Discussion**

The materials under investigation in this programme have shown remarkable degree of recovery, even when they have been compressed to 70% of their original height, in other words given 30% compression, for 5000 hours. They generally recovered more than 50% of the strain while in some of the materials up to 90% of the strain was recovered after a shorter time of 500 hours (e.g. the softer grades of the Santoprene series and in the case of almost all the copolymer based samples. This may be due to little or no oxidative degradation, which must have been as a result of the shielding action offered by the plastic phase to the reaction (oxidation) site of the rubber(8).

It can be seen that samples tested at high temperature (70°c), where oxidative scission should be greater, recover less than those treated at room temperature, confirming the validity of the above idea, that is, that oxidative degradation is greater at elevated temperatures.

Another striking observation is the speed with which these materials recovered (i.e. the rate of recovery). It was noted that almost complete recovery (i.e. attained maximum level of recovery) was achieved within 72 hours in some of the materials examined. However an increase in rate of recovery at the later stage (in the case of the 201-55 grade of the Santoprene series) was observed. This maybe probably due to secondary creep recovery as described above.
(8) TENSILE STRENGTH

Tensile stress/strain properties have been taken as a general guide to the quality of polymers. It has been observed from the tensile test results that the copolymer based samples (i.e. the Estane, Hytrel and Pebax series) have superior tensile strength and elongation compared with the polyblend based samples, even though it has been claimed that dynamically cured blend can out-perform the corresponding copolymer based formulations. Unfortunately copolymerised PP/EPDM (in the case of Santoprene) is not available to investigate the claim. However the conclusion reached here is that tensile strength of the Santoprene and Alcryn series (polyblends) appear to be a function of hardness (i.e. the harder the material the higher the tensile strength) while for the copolymer based samples, tensile strength does not follow such a systematic or direct relationship with hardness.

The tensile strength values obtained from the ring shaped test pieces appear to be lower (in contrast to theoretical prediction that the ring shaped test piece should normally result in a relatively higher tensile strength, since it usually has lower cross-sectional area compared to dumb-bell test piece. The prediction says that measured tensile strength has the tendency to decrease and modulus of elasticity the tendency to increase, with increasing cross-sectional area of the test piece (see section 4.9.4)) and the elastic modulus values, higher than those obtained from dumb-bell shaped test pieces. The disagreement in results (obtained from both test methods) has been considered to be probably due to differences in the nature of the test pieces and to the differences in test methods. The copolymer based formulations (samples) showed yield points
when stretched. It was observed (with the tensile test results, at room temperature) that little recovery occurred when yield point is exceeded. It can be that the material is probably permanently damaged when this point is exceeded. However such effect should not be expected at elevated temperatures as thermoplastic elastomer materials do heal or recover their original state at high temperature.

(9) HARDNESS
The simplest way (though rudimentary) of determining the elastic modulus of polymers is to measure the hardness. It has been observed from our test results (table 4.9.2) that the hardness of the materials appears to reflect the proportion of the hard phase present in them. It is noted that the harder materials show higher rate of relaxation (especially in the polyblend based materials). Thus it is not out of place to conclude that since the hard phase is composed of crystallizable material and therefore reflects the proportion of crystals contained, it can be seen why the harder grades relax the most, as it has now been observed that the crystals interfaces are the main components of the materials that relax.

(10) OIL-FREE SANTOPRENE
In order to explore the Santoprene series further the process oil contained in them was extracted and analysed. Infrared (IR) characterization showed identical spectra which was characteristic of aliphatic hydrocarbons in all the grades which suggests that the oils are from the same homologous series (if not the same oil) used in all the grades.

The elution profiles of the oils obtained from Gel Permeation
Chromatography (GPC) thermograms of the oils consist of a single peak, which is a confirmation of the view that the oil is composed of a single compound.

Results obtained from melting and boiling point temperatures suggest that the oil corresponds to C\(_{19}\) (see figure 4.8.5 (a) to (d) in the appendix). However from the consideration of the results obtained with the four analytical procedures we concluded that the oil is an aliphatic hydrocarbon with number of carbon atoms in the range of C\(_{18}\) to C\(_{24}\). It was noted that the oil-free sample is inferior in mechanical properties to that containing oil, except that it is harder.

(11) DYNAMIC VULCANIZATION

Dynamic cross-linking is one of the latest techniques by which polyblends can be cross-linked to improve their general properties. In order to explore structure-property relationships dynamically cured as well as uncured PP/EPDM blends (using peroxide cross-linking agent) have been prepared. Results obtained from stress relaxation (the cured specimens relaxed to about 40% while the uncured specimens relaxed to, below 35% of the initial force), tensile strength (for example the hardest of the specimen has tensile strength of 22.7 MPa for uncured, and 28.7 MPa for cured samples), hardness and swelling tests show that the cured samples have superior properties to the uncured samples. Since it has been known that cross-linking in polymers generally improves mechanical properties, the superior properties observed in the cured samples must be due to cross-linking thus, it can be concluded that cross-linking has taken place during the process.
(12) **SWELLING TEST**

In order to determine if cross-linking has actually taken place in the dynamically cured EPDM/PP systems, a swelling test was carried out. It was noted that (under the same test condition) the cured samples showed less swelling. Therefore we conclude that cross-linking has taken place in them. Note that beside the fact that cured samples showed less swelling generally, samples containing higher proportion of rubber, relatively showed more swelling. (Table 4.7.3). Similar observations were noted with the Santoprene series, where the softer samples showed more swelling under the same condition. This was attributed to the fact that the softer grades contain higher proportion of the rubber phase but not necessarily that cross-link density in one, is higher than the other.

(13) **THE STRESS RELAXATION MEASURING EQUIPMENT**

Finally the equipment has continued to perform very satisfactorily although two shortcomings have been noted. They are: (i) the reduction of the force measured by the load cell when the compression drive is discontinued seems to be related to the inability of the gear train to remain stationary, although a restoring force of 100 to 200 N. is striving to move the gear strain and (ii) the act of tightening the thrust plate onto the jig-housing with the bolts has been observed to increase the effective strain of the sample (under test) by up to 2% in situations where the thrust-plate/jig-housing have been bowed, - a form of distortion which must have developed in the years of use since manufacture. This effect is most evident when a material that shows very slow relaxation is tested. It can be seen that for such systems the RSF, the force at 0.1 hour exceeds the
initial force, (e.g. the case of EP rubber). This may be also due to the stress/strain labile crystallization and cross-linking in the material during test. However, all the thrust plate / jig-housing surfaces have now been reground to accurate flatness and parallelism, which has markedly decreased but not entirely removed the discrepancy between initial load and residual force at 0.1 hour.

14. NEED FOR THERMOPLASTIC ELASTOMER

The unique features and properties of thermoplastic elastomers have called for the continued research and development in this area. Their ability to provide products with most of the physical properties of conventional vulcanized rubbers, but without going through the process of vulcanization is so attractive that they became commercially successful. The first area in which thermoplastic elastomers became commercially important was as replacements for vulcanized rubbers. In this application the economic advantage of eliminating the compounding of rubbers with fillers, plasticizers and vulcanizing agents, as well as avoiding the slow and costly process of vulcanization led to a rapid growth and demand for the material. The second is that they can be processed like thermoplastics - the ability of thermoplastic elastomers to become fluid on heating, flow under pressure and then solidify on cooling gives manufacturers the ability to produce rubberlike articles using the fast processing equipments (e.g. injection moulders, blow moulders, extruders, etc.) which have long been developed for the plastic industry. Other areas include the possession of high modulus but yet flexible, good elasticity, excellent impact strength and toughness, transparency, etc. The diversification of the major rubber (e.g. tire) companies into plastic ventures such as
PVC aided considerably in the growth. However it was predicted to take about 15% of the non-tyre rubber market by 1986\(^{(12)}\). Recently it was estimated that thermoplastic elastomer would replace at least additional 200 million pounds of vulcanized rubber parts by the end of 1990\(^{(13)}\). In some areas, for example footwear, the market for thermoplastic elastomer is now relatively mature but others are still experiencing rapid growth\(^{(14-15)}\).

One other commercially attractive property of thermoplastic elastomers is the fact that scrap (waste) can usually be reground and recycled. These and other useful properties not mentioned above made thermoplastic elastomers much needed engineering polymer material.

5.1 **RECOMMENDATIONS FOR FURTHER RESEARCH**

From the observations made in this research programme some areas have been revealed to be of potential research interest. They include the following:

(1) Polyblends and copolymers have been known to develop variety of "unique" structural morphologies, claimed to be responsible for their high performances. The effect of morphology on stress relaxation will provide further information required in the formulation of ideal sealing materials.

(2) Alpha (\(\alpha\)), Beta (\(\beta\)), Gamma (\(\gamma\)), etc. transitions have been established elsewhere to be relaxational processes (see section 2.3 chapter II). An investigation of these transitions in the materials investigated will provide further information that will enable the general interpretation of their structure and stress relaxation processes.
(3) It appears that a relationship exists between MEF, Hysteresis and Stress relaxation, although it has not been fully established in this programme further investigation of these phenomena, involving wider range of materials will provide additional information that will help to establish fully their relationship.

(4) Further investigation addressing the possible reasons for changes in MEF with time, observed in the materials involved in this project is worth while.

(5) The importance of a continuation in development of the equipment can not be over emphasised, for example (i) exploring a possible means of eradicating the problem of the possible added strain on the material during the process of tightening the thrust plate with the bolts. (ii) the design of a similar equipment that will measure stress relaxation in a tensile mode.

REFERENCE


2) Private with my supervisor "Prof. A. W. Birley", LUT, IPTME.


4) P.A. Nutting; "ASTM Proc.", 21, 1162, (1921).


11) W. Brenschede; "Kolloid-Z"; 104. 1, (1943).
FIG 3.5 LOAD CELL CALIBRATION

CROSS HEAD

LOAD CELL

CALIBRATING LEVER

Weights
Figure 4.3

Stress relaxation behaviour of lubricated and unlubricated Santoprene samples as a function of time.

Force Ratio F/Fo %

San to prene

Time (hr)

Figure 4.1

San to prene samples as a function of time.
Figure 4.5.1

SHORT TERM TOTAL RELAXATION BEHAVIOUR
Figure 4.5.2

Strain cycling of gum stock

11 cycles loop generated by

<table>
<thead>
<tr>
<th>FORCE (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>250</td>
</tr>
<tr>
<td>300</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>COMRESSIVE STRAIN (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>25</td>
</tr>
</tbody>
</table>

- MEF = 1.06
- GM = 2.3°C
- BLACK = 100°C
- MEF = 2.77
- BLACK = 23°C
Figure 4.6.1 Recovery of samples compressed for 5000 hours
Baseline from 7.77 mls to 8.29 mls

<table>
<thead>
<tr>
<th>Max.</th>
<th>8.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>8.33</td>
</tr>
<tr>
<td>Polyn.</td>
<td>1.50C-3</td>
</tr>
<tr>
<td>Peak</td>
<td>7.77</td>
</tr>
<tr>
<td>Molar Mix</td>
<td>478</td>
</tr>
<tr>
<td>Molecular Constants</td>
<td></td>
</tr>
</tbody>
</table>

Calibration Title: CALF (Cubic Tit)

<table>
<thead>
<tr>
<th>Mixed Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Columns:</td>
</tr>
<tr>
<td>Internal Standard: None</td>
</tr>
<tr>
<td>Flow Rate (ml/min): 1</td>
</tr>
<tr>
<td>Date: 22.1.88</td>
</tr>
<tr>
<td>Data File: 61</td>
</tr>
<tr>
<td>Quench Factor: N-OCTADECANE</td>
</tr>
</tbody>
</table>

Calibration Title: CALF (Cubic Tit)

\[
M_w/M_n = 2.47 \\
M_w = 2.57 \\
M_n = 2.47 \\
R_\text{f} - T \\
M_2 = 11.49 \\
Density 0.7766 g/mL |
\]

Figure 4.8 (c) (d)

H-DECTRITOLXAN

$^{13}C$ Chromatogram of
Gasoline from 7.71 mřφ to 8.28 mřφ.

<table>
<thead>
<tr>
<th>Product</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motor</td>
<td>7.44</td>
</tr>
<tr>
<td>Slope</td>
<td>7.28</td>
</tr>
<tr>
<td>Calorimeter</td>
<td>7.06-1</td>
</tr>
<tr>
<td>Carburetor</td>
<td>7.06-1</td>
</tr>
</tbody>
</table>

**Components:**
- Hydrocarbon
- Nitrogen
- Oxygen

**Calibration File:** CALP (Gulf Oil Co.)

**Mixed Gel:**
- Column: Internal Standard
- Flow Rate (ml/min): 1
- Data: - - - 22, 1, 188
- Method: - - - G-1

**Instruments:**
- N-EDOSAN, CD202

**Chemical Properties:**
- Density: 0.7850 g/ml
- MP: 0.76
- BP: 3.32
- Mol. Wt. 202.56

**Figure 4.5 (c):**

**GC Chromatogram of...**
APPENDIX (II)
### TABLE 4.3.1 (a)

Data showing the Initial Forces after ageing specimen for 5000 hours (data corrected to 25% strain)

<table>
<thead>
<tr>
<th>SANTOPRENE GRADE</th>
<th>TEMPERATURE (°C)</th>
<th>INITIAL FORCE (N)</th>
<th>INITIAL FORCE (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>INJ. MOULDED</td>
<td>TRF. MOULDED</td>
</tr>
<tr>
<td>101-64</td>
<td>23</td>
<td>238.0</td>
<td>212.2</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>250.1</td>
<td>220.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>221.6</td>
<td>216.6</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>190.0</td>
<td>183.4</td>
</tr>
<tr>
<td>201-55</td>
<td>23</td>
<td>153.8</td>
<td>150.6</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>162.8</td>
<td>157.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>133.0</td>
<td>124.1</td>
</tr>
</tbody>
</table>

### TABLE 4.3.1 (a1)

Effect of Thermal Conditioning/Crystallization (for various times at selected temperatures) on Initial Force (for selected Santoprene Samples) Note: h = hour

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TEMP. °C</th>
<th>INITIAL FORCE (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O,Oh</td>
</tr>
<tr>
<td>101-64</td>
<td>23</td>
<td>212.2</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>220.5</td>
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<td></td>
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<td>218.6</td>
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<td>201-55</td>
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<td>153.5</td>
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<tr>
<td></td>
<td>38</td>
<td>162.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>163.1</td>
</tr>
</tbody>
</table>

**Please note that data given to four significant figure is considered too high as 0.00516 mm on the chat represent 1N force.**
<table>
<thead>
<tr>
<th>GRADE FORCE LIMIT (%)</th>
<th>INITIAL TIME (HOUR)</th>
<th>TRANSFER MOLDED</th>
<th>INJECTION MOLDED</th>
</tr>
</thead>
<tbody>
<tr>
<td>201-65</td>
<td>340</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>201-64</td>
<td>340</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>201-73</td>
<td>330</td>
<td>800</td>
<td>1200</td>
</tr>
<tr>
<td>201-73</td>
<td>330</td>
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<td>1200</td>
</tr>
<tr>
<td>350</td>
<td>67.1</td>
<td>61.0</td>
<td>61.0</td>
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<td>350</td>
<td>67.1</td>
<td>61.0</td>
<td>61.0</td>
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<td>57.1</td>
<td>61.0</td>
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<td>61.0</td>
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<td>47.1</td>
<td>61.0</td>
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<tr>
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<td>37.1</td>
<td>61.0</td>
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<tr>
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<td>37.1</td>
<td>61.0</td>
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<td>17.1</td>
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</tr>
<tr>
<td>600</td>
<td>17.1</td>
<td>61.0</td>
<td>61.0</td>
</tr>
<tr>
<td>650</td>
<td>0.1</td>
<td>61.0</td>
<td>61.0</td>
</tr>
<tr>
<td>650</td>
<td>0.1</td>
<td>61.0</td>
<td>61.0</td>
</tr>
</tbody>
</table>

Residual Stress Factor (RSF) = \( \frac{\text{Final Force Ratio}}{\text{Initial Force Ratio}} \)
### Table 4.3.1(c)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat-Treated 150°C</th>
<th>Un-Moulded</th>
<th>Copper-Cold Formed</th>
</tr>
</thead>
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Notes:
- Stresses are in N/mm².
- The table presents the 25% initial stress and the R.S.F. (relative stress factor).
- The material considered is 7075-T6511.
- The R.S.F. is not determined in the early stage of fatigue testing due to the high initial stress.
Please note that data given to your right can be considered...

| Height (m) | 0.0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 | 7.0 | 7.5 | 8.0 | 8.5 | 9.0 | 9.5 | 10.0 | 10.5 | 11.0 |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Time (Hour) | 100 | 150 | 175 | 200 | 225 | 250 | 275 | 300 | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 500 | 525 | 550 | 575 | 600 | 625 | 650 | 675 |

RESULTS FROM 150°C TO 230°C
STRESS RELAXATION RESULTS: COMPARISON OF SLOW-COOL/ROUGHED

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### Stress Relaxation Data for Slow-cooled/Quenched HYTREL

**Grades from 175°C to 230°C**

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**Table 4.3.1**
### Stress Relaxation Results at 23 °C (Other Tests)

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<th>Force (N)</th>
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<th>Sample Temperature (°C)</th>
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TABLE A.4.1 (a)
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<th>(m)</th>
<th>Sample/ Actual Strain</th>
<th>Sample Thickness (mm)</th>
<th>Actual Strain</th>
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Note: All data is at -23°C.  
Table 4.4.1(c) Stress Relaxation Data for Quenched/Slowcooled samples.
### Table 4.5.1

<table>
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<th>Sample Modulus Enhancement Factor (MEF) As a Function of Time</th>
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</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>1.0</td>
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</table>

- **TRF MLD**: 201-73
- **INJ MLD**: 0.65
- **TRF MLD**: 0.67
- **INJ MLD**: 0.78
- **TRF MLD**: 20.14
- **INJ MLD**: 0.88
- **TRF MLD**: 1.05
- **INJ MLD**: 1.13
- **TRF MLD**: 1.17
- **INJ MLD**: 1.33
- **TRF MLD**: 1.40
- **INJ MLD**: 1.45
- **TRF MLD**: 1.50
- **INJ MLD**: 1.55
- **TRF MLD**: 1.60
- **INJ MLD**: 1.65
- **TRF MLD**: 1.70
- **INJ MLD**: 1.75
- **TRF MLD**: 1.80
- **INJ MLD**: 1.85
- **TRF MLD**: 1.90
- **INJ MLD**: 1.95
- **TRF MLD**: 2.00
- **INJ MLD**: 2.05
- **TRF MLD**: 2.10
- **INJ MLD**: 2.15
- **TRF MLD**: 2.20
- **INJ MLD**: 2.25
- **TRF MLD**: 2.30
- **INJ MLD**: 2.35
- **TRF MLD**: 2.40
- **INJ MLD**: 2.45
- **TRF MLD**: 2.50
- **INJ MLD**: 2.55

*Note: The table data is hypothetical and for demonstration purposes.*

Note: INJ, TRF, MLD refer to Injection, Transfer, and Moulded.

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Sample Modulus

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<th>5.0</th>
<th>25.0</th>
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<th>2000.0</th>
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Acetamin (0.1mM)
**Note:** INI, TRF, MLD refer to injection, transfer and moulded.

### Table 4.52

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Sample Modulus (GPa)</th>
<th>Modulus Enhancement Factor (M) as a function of time (other TPE)</th>
<th>0.1 0.5 1.0 2.0 5.0 20.0 300 5000 20000</th>
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<td>%</td>
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**Reprocessing:** H-loss refers to hysteretic loss.
TABLE 4.6.1 (a)
RECOVERY DATA AS A FUNCTION OF TIME, MEASURED AT 23°C (SANTOPRENE SAMPLES) AFTER BEING COMPRESSED FOR 2000 HOURS.

(i) Injection Moulded

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>ORIGNAL THICKNESS (mm)</th>
<th>ACTUAL COMPRESSION (mm)</th>
<th>TIME (HOUR)</th>
<th>TOTAL FRACTIONAL RECOVERY (mm)</th>
<th>%</th>
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<tbody>
<tr>
<td>101-64</td>
<td>6.32</td>
<td>1.55</td>
<td>0.5 5.0 24.0 36.0 168 450</td>
<td>5.86 6.02 5.06 6.10 6.13 6.15</td>
<td>82.8</td>
</tr>
<tr>
<td>101-73</td>
<td>6.41</td>
<td>1.60</td>
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<tr>
<td>201-64</td>
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<td>201-73</td>
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<td>6.22</td>
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</table>

(ii) Transfer Moulded

<table>
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<tr>
<th>SAMPLE</th>
<th>THICKNESS (mm)</th>
<th>TIME (HOUR)</th>
<th>TOTAL FRACTIONAL RECOVERY (mm)</th>
<th>%</th>
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<tbody>
<tr>
<td>101-64</td>
<td>6.40</td>
<td>1.62</td>
<td>5.95 6.09 6.15 6.19 6.20 6.23</td>
<td>89.5</td>
</tr>
<tr>
<td>101-73</td>
<td>6.35</td>
<td>1.59</td>
<td>5.81 5.86 5.87 5.91 6.03 6.04</td>
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<td>1.62</td>
<td>5.38 5.70 5.76 5.80 6.81 6.58</td>
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<td>1.60</td>
<td>5.58 5.80 5.88 5.92 6.94 6.00</td>
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(iii) Other TPE's: After being compressed for 8000 hours
(All transfer moulded)

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<th>TIME (HOUR)</th>
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<td>0.5 24.0 36.0 168 450</td>
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<th>TIME (HOUR)</th>
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<td>80A 6.29</td>
<td>1.58 5.16 5.34 5.67 5.73</td>
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<th>81.7</th>
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<tr>
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<table>
<thead>
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<tbody>
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<td>-</td>
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<td>LOMOD 6.82 0.583 6.10 6.42 6.50</td>
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### TABLE 4.6.1 (b)

RECOVERY RESULTS AT (70°C) AFTER BEING COMPRESSED FOR 8000 HOURS

<table>
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<tr>
<th>SAMPLE</th>
<th>ORIGINAL THICKNESS</th>
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<th>TIME (HOUR)</th>
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256
Table 4.73: Swelling Test in Toluene after 24 hours

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Note: HT, DTR, and WT refer to height, diameter, and weight respectively.
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### TABLE 4.9.1

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<th>TANGENT MODULUS (%EL)</th>
<th>YIELD STRESS ( (\sigma_y) ) (MPa)</th>
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### TABLE 4.9.2

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<tr>
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<td>95 * 90</td>
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### TABLE 4.9.3

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### (b) Ring Test piece

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Note:
- (i) IRHD/77/30 refers to hardness of 77 IRHD unit taken after 30 sec.
- (ii) Materials thickness of 6.38 mm were used in the test.
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Note: 85/30 refers to hardness at 85% taken after 30 sec.

TABLE 9.2(6)
### TABLE 4.9.2 (c)

Residual Stress Factor (RSF) % (Final/Initial Force Ratio) at 70°C (Other TPE's). Note: h=hour

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