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CERAMERS FROM AQUEOUS POLYMER SOLUTIONS OF POLY (ETHYLENE OXIDE)

By

Ishak bin Manaf

A Doctoral Thesis Submitted in Partial Fulfilment of the Requirements for the Award of the Degree of Doctor of Philosophy of Loughborough University

June 2001

Supervisor: Dr. L. Mascia

Institute of Polymer Technology and Materials Engineering (IPTME)

## CONTENTS

**ABSTRACT** ........................................................................................................... v  
**ACKNOWLEDGEMENTS** ...................................................................................... vii  
**CHAPTER 1** .......................................................................................................... 1  
**INTRODUCTION** .................................................................................................. 1  
1.1 GENERAL CONSIDERATION. ........................................................................... 1  
1.2 ORGANIC-INORGANIC HYBRIDS. ................................................................... 2  
1.3 SOL-GEL TECHNOLOGY. ................................................................................ 3  
1.3.1 INTRODUCTION. ........................................................................................... 3  
1.3.2 HISTORICAL DEVELOPMENT. .................................................................... 4  
1.3.3 THE SOL-GEL PROCESS. ............................................................................ 5  
   a) Aqueous colloidal route .................................................................................. 5  
   b) Metal alkoxide route ..................................................................................... 5  
1.4 ADVANTAGES AND DISADVANTAGES OF SOL-GEL PROCESSING. .......... 7  
1.5 AIMS OF THE STUDY. .................................................................................... 9  
**CHAPTER 2** .......................................................................................................... 11  
**LITERATURE SURVEY** ...................................................................................... 11  
2.1 SOL-GEL PROCESS .......................................................................................... 11  
2.1.1 MECHANISM OF HYDROLYSIS AND POLYCONDENSATION REACTION OF ALKOXYSilANES. .............................................................. 11  
   a) Hydrolysis. ...................................................................................................... 11  
   b) Condensation. ................................................................................................ 13  
      i. Below the Isoelectric Point (pH≈2) ........................................................... 13  
      ii. Above the Isoelectric Point (pH≥2) ......................................................... 14  
2.1.2 THE EFFECT OF REACTION PARAMETERS ON THE STRUCTURE VARIANS IN SOL-GEL SILICATES. ......................................................... 15  
   a) The role of catalyst and pH or the solution ................................................... 15  
   b) Water content ............................................................................................... 18  
   c) Effect of type of solvent................................................................................ 20  
   d) Effect of type of alkoxides and steric factor ................................................ 20  
   e) Drying Techniques ........................................................................................ 21  
2.1.3 COUPLING AGENTS. .................................................................................... 23  
   a) Introduction .................................................................................................. 23  
   b) Chemistry of Silane Coupling Agents ......................................................... 24  
2.1.4 APPLICATIONS OF SOL-GEL PROCESS. .................................................. 27  
2.1.5 ORGANIC-INORGANIC HYBRID MATERIALS. ......................................... 28  
   a) General Introduction .................................................................................... 28  
   b) Ceramers Development ............................................................................... 29  
   c) Biodegradable and Biocompatible Ceramers .............................................. 32  
   d) Poly(ethylene oxide)/Silica Hybrids ............................................................. 33
2.2 POLYETHYLENE OXIDE (PEO) .................................................. 33
   2.2.1 INTRODUCTION. .............................................................. 33
   2.2.2 PROPERTIES. ................................................................. 34
       a) General Properties ......................................................... 34
       b) Solution Technique ..................................................... 36
       c) Solution Properties ..................................................... 37
   2.2.3 PEO BLENDS. ................................................................. 44
   2.2.4 COMMERCIAL APPLICATIONS. ....................................... 45
2.3 CERAMER BLENDS .............................................................. 47
   2.3.1 INTRODUCTION ............................................................. 47
   2.3.2 POLYVINYL CHLORIDE (PVC) ....................................... 48
       a) Introduction ............................................................... 48
       b) Properties of PVC ..................................................... 48
   2.3.3 EPOXY RESIN .............................................................. 49
       a) Introduction ............................................................... 49
       b) Curing Agents for Epoxy Resins .................................... 50
       c) Properties of Epoxy Resins ......................................... 51

CHAPTER 3 ................................................................................. 54
EXPERIMENTAL ........................................................................... 54
3.1 PEO-SiO₂ CERAMERS ........................................................... 54
   3.1.1 MATERIALS. ................................................................... 54
       a) Poly (ethylene oxide)-PEO ............................................. 54
       b) Alkoxysilane-Silicate Precursor Solution ....................... 54
       c) Coupling Agents ......................................................... 55
       d) Solvent and Water ....................................................... 56
       e) Catalyst ....................................................................... 56
   3.1.2 PREPARATION AND EVALUATION OF THE SOL-GEL
       PRECURSORS. ................................................................... 56
       (a) Polymer solution ....................................................... 56
       (b) Alkoxysilane solution ................................................ 56
       (c) The effect of pH on polymer solution viscosity .............. 58
   3.1.3 PREPARATION OF THE PEO-SiO₂ CERAMERS MATRIX .... 59
       (a) Introduction ............................................................... 59
       (b) Effect of pH on Gelation Time of ceramer solutions ...... 59
       (c) Effect of maturation time on viscosity of the ceramer solutions 60
   3.1.4 MORPHOLOGICAL STUDIES OF PEO-SiO₂ CERAMERS .... 62
       (a) Effect of silica content ................................................. 62
       (b) Effect of mixing time ............................................... 62
       (c) Effect of mixing temperatures .................................... 62
       (d) Effect of the amount of GOTMS coupling agent ......... 63
       (e) Effect of other coupling agents ................................... 63
       (f) The solvents effect ..................................................... 64
       (g) Preparation and Characterisation of GOTMS-CA adducts . 64
   3.1.5 CHARACTERISATION OF THE PEO-SiO₂ CERAMERS ....... 67
       (a) Appearance of the PEO-SiO₂ ceramer films ................. 67
       (b) Microscopically Study .............................................. 68
       (c) Differential Scanning Calorimetry (DSC) ..................... 70
3.2. PEO-SiO₂ CERAMER BLENDS.

3.2.1. PEO-SiO₂ CERAMER BLENDS WITH PVC.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1.1. Materials</td>
<td>76</td>
</tr>
<tr>
<td>3.2.1.2. Blend Preparation</td>
<td>76</td>
</tr>
<tr>
<td>3.2.1.3. Characterisation of the PEO-SiO₂ Ceramers Blends with PVC</td>
<td>78</td>
</tr>
<tr>
<td>3.2.1.4. Morphology stability of the PEO-SiO₂/PVC blends</td>
<td>82</td>
</tr>
</tbody>
</table>

3.2.2. PEO-SiO₂ CERAMERS BLENDS WITH EPOXY RESIN.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.2.1. Materials</td>
<td>82</td>
</tr>
<tr>
<td>3.2.2.2. Blend Preparations and Characterisations</td>
<td>83</td>
</tr>
</tbody>
</table>

CHAPTER 4

RESULTS

4.1. PEO-SiO₂ CERAMER SYSTEM

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.1. PREPARATION AND EVALUATION OF THE SOL-GEL PRECURSORS.</td>
<td>85</td>
</tr>
<tr>
<td>a) Solubility study of the PEO polymer in water</td>
<td>85</td>
</tr>
<tr>
<td>b) The effect of pH on PEO polymer solution viscosity</td>
<td>86</td>
</tr>
<tr>
<td>4.1.2. PREPARATION OF CERAMER SOLUTIONS.</td>
<td>87</td>
</tr>
<tr>
<td>a) The effect of pH on gelation time of ceramer solutions</td>
<td>87</td>
</tr>
<tr>
<td>b) The effect of maturation time on viscosity of ceramer solutions</td>
<td>87</td>
</tr>
<tr>
<td>4.1.3. MORPHOLOGY OF CERAMERS.</td>
<td>88</td>
</tr>
<tr>
<td>a) The effect of silica content</td>
<td>88</td>
</tr>
<tr>
<td>b) The effect of mixing time at 60°C</td>
<td>89</td>
</tr>
<tr>
<td>c) The effect of mixing temperature</td>
<td>90</td>
</tr>
<tr>
<td>d) The effect of the amount of epoxy coupling agent, GOTMS.</td>
<td>90</td>
</tr>
<tr>
<td>e) The effect of other coupling agents</td>
<td>91</td>
</tr>
<tr>
<td>f) The solvent effect on PEO-SiO₂ ceramics</td>
<td>93</td>
</tr>
<tr>
<td>4.1.4. INTERACTION OF THE GOTMS COUPLING AGENT WITH CHLORENDIC ANHYDRIDE (CA)</td>
<td>93</td>
</tr>
<tr>
<td>a) Infrared spectroscopy study on GOTMS/CA interaction</td>
<td>93</td>
</tr>
<tr>
<td>4.1.5. DIFFERENTIAL SCANNING CALORIMETRY (DSC).</td>
<td>95</td>
</tr>
<tr>
<td>4.1.6. THERMOGRAVIMETRIC ANALYSIS (TGA).</td>
<td>100</td>
</tr>
<tr>
<td>a) PEO samples</td>
<td>100</td>
</tr>
<tr>
<td>b) PEO-SiO₂ ceramer films</td>
<td>100</td>
</tr>
</tbody>
</table>

4.2. SURFACE AREA MEASUREMENT.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1. BLENDS OF PEO-SiO₂ CERAMERS WITH PVC</td>
<td>103</td>
</tr>
<tr>
<td>a) Differential Scanning Analysis (DSC)</td>
<td>103</td>
</tr>
<tr>
<td>b) Dynamic Mechanical Thermal Analysis (DMTA)</td>
<td>103</td>
</tr>
<tr>
<td>c) Scanning Electron Microscopy (SEM)</td>
<td>105</td>
</tr>
<tr>
<td>d) Transmission Electron Microscopy Analysis (TEM)</td>
<td>106</td>
</tr>
<tr>
<td>e) Tensile Tests</td>
<td>107</td>
</tr>
<tr>
<td>f) Morphology stability of the PEO-SiO₂/PVC blends</td>
<td>107</td>
</tr>
<tr>
<td>4.1.2. BLENDS OF PEO-SiO₂ CERAMERS WITH EPOXY RESIN.</td>
<td>107</td>
</tr>
<tr>
<td>a) Dynamic Mechanical Thermal Analysis (DMTA)</td>
<td>107</td>
</tr>
<tr>
<td>b) Scanning Electron Microscopy Analysis (SEM)</td>
<td>108</td>
</tr>
</tbody>
</table>
CHAPTER 5 DISCUSSION

5.1. PEO-SiO₂ CERAMERS.

5.1.1. Gelation of the PEO-SiO₂ precursor solutions

5.1.2. Viscosity of the ceramer solutions.

5.1.3. PEO-SiO₂ ceramer morphology

a) The effect of silica content.

b) The effect of mixing time and temperatures.

c) The effect of amount of GOTMS coupling agent and other coupling agent.

d) The solvent effect on PEO-SiO₂ ceramer.

5.1.4. Surface Area Measurement of the PEO-SiO₂ ceramers.

5.2. BLENDS OF PEO-SiO₂ CERAMERS WITH OTHER POLYMERS.

5.2.1. Blends of PEO-SiO₂ Ceramer with PVC.

5.2.2. Blend of PEO-SiO₂ Ceramer with Epoxy Resin.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

6.1. CONCLUSIONS

6.2. RECOMMENDATIONS FOR FURTHER STUDIES.

REFERENCES
ABSTRACT

The combination of inorganic and organic components in single materials makes accessible an immense new area of materials science that has profound implications in the development of novel materials, exhibiting a wide range of multifunctional properties. The so-called “sol-gel” process is normally used for the production of an inorganic phase within an organic polymer or cross-linkable oligomers. When the domain size of such materials is reduced to nanometer levels and the phases are interconnected, the hybrid materials are usually called “ceramers”.

The systems considered in this work are based on a water-soluble polymer, Poly (ethylene oxide) (PEO) and silica (SiO₂) networks produced by the sol-gel method. The PEO precursor solution was prepared by dissolving the resin in water at room temperature. Tetraethoxysilane (TEOS) was used as the alkoxysilane precursor. Different types of alkoxysilane precursors were prepared, based on TEOS and silane coupling agent. The silica present in the hybrid system was formulated to be at 25%, 35% and 50% w/w.

Ceramer films were obtained by casting and drying the PEO-SiO₂ ceramer precursors. The morphology of the ceramer film produced was particulate (opaque) and very coarse unless the compatibilising agent was used in the alkoxysilane solution. The influence of several parameters such as pH, type of solvents, mixing temperature and mixing time, as well as the nature of compatibiliser was found to be extremely important in controlling the morphology and properties of the fine ceramer films.

It was found that compatibilisation of PEO-SiO₂ systems is achieved exclusively with the use of γ-Glycidyloxypropyltrimethoxysilane (GOTMS) coupling agent.

The use of PEO-SiO₂ hybrids as “in-situ generated fillers” was also investigated with the view of achieving reinforcement with toughening effect. Plasticized poly (vinyl chloride) and epoxy resins were used in this study as the matrix polymer systems. It
was found that an efficient reinforcement of the hybrid systems based on plasticised PVC was not achieved. The PEO-SiO$_2$ ceramer blend with PVC produced opaque films due to the precipitation of the PEO-SiO$_2$ phase as large discrete particles with size approximately ranging from 6 to 10 $\mu$m. However, the tensile modulus $E'$ of the system was higher compared to that for the blend of PVC and PEO. Contrary to these the blend of PEO-SiO$_2$ ceramer with epoxy resin produced transparent film with only one $T_g$ being observed.
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Special thanks also go to all the technical staff and postgraduate students of the Institute of Polymer Technology and Materials Engineering (IPTME). I am grateful for their direction, encouragement and provision of facilities for completing this work.

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Dedication

In Memory to My Father
CHAPTER 1

INTRODUCTION

1.1 GENERAL CONSIDERATION.

Inorganic materials usually have high thermal stability, good optical properties and high modulus, but are very brittle. Inorganic materials are normally incorporated into polymers in the form of fine particles to act as fillers or as reinforcing agents. Mineral fillers are normally used to dilute, and hence to reduce the amount of final polymers used in the shaped structures, thereby lowering the cost. Reinforced polymers, on the other hand, display an increase in modulus, hardness, tensile strength, tear resistance, abrasion, and resistance to fatigue. Characteristics of the reinforcing agents, such as particle size, chemical composition and structure of the particle surface, level of hydration, surface acidity and adhesion between particles and polymer, play an important role in increasing the service life of articles produce from reinforced polymers.

Although large improvements in strength for many polymeric materials have been achieved, particularly by the incorporation of high performance fibres, such as carbon fibres, there is still significant need for producing polymeric materials with extremely high levels of stiffness and hardness.

Blending polymers with conventional inorganic fillers or short fibres do not produce high performance material because they have a low aspect ratio and are, therefore, not efficient in transferring stresses from the matrix onto the inorganic phases.
1.2 ORGANIC-INORGANIC HYBRIDS.

The combination of inorganic and organic or bioactive components in single materials makes accessible an immense new area of materials science that has extraordinary implications in the development of novel materials, exhibiting a wide range of multi-functional properties.

Hybrid materials with isolated organic and inorganic phases, mutually interpenetrating networks, or complex hierarchical structures can be designed by methods often referred to as "soft chemistry" or "sol-gel" processing. Sol gel chemistry allows the adjustment of the degree of interpenetrating of organic and inorganic components from the sub-micronics range down to the nano scale level. Consequently, it provides an easy method to synthesize new nano-composites, known also as ceramers or simply, organic-inorganic hybrid materials.

In recent years, much attention has focused on the novel combination of organic species with inorganic minerals and network because of the exiting range of properties demonstrated by these hybrid materials and the potential they offer to mimic the vast array of structures on display in nature (1-6). In organic-inorganic hybrids, the organic phase can impart unusual optical, mechanical, rheological, or bioactive properties to the inorganic material for applications such as sensors, non-linear optic (NLO) materials, laser, selective membranes, catalysts, and protective coatings. The organic phase can also be removed in some terminal step of the process to produce control porosity materials with innovative implications in the field of membranes and catalysts.

The most common approach for the preparation of hybrid organic-inorganic materials has involved the sol-gel process, including the combination of
inorganic oxides, particularly silica with polymers \(^{(5-8)}\). This method uses the well established hydrolytic route to the oxide, involving the hydrolysis and condensation reactions of alkoxide or other precursors, usually in a solvent system carefully chosen to avoid the common problem of premature phase separation.

Another method for the synthesis of inorganic oxides involves the reaction of a metal halide with an oxygen donor, such as an alkoxide, an ether or, an alcohol under non-aqueous conditions and is known as a non-hydrolytic sol-gel route. This approach has a number of associated advantages, including the potential to avoid the use of solvents, with their various drawbacks.

1.3 SOL-GEL TECHNOLOGY.

1.3.1 INTRODUCTION.

The term sol-gel processing usually refers to the fabrication of inorganic oxides using either a metal alkoxide precursor or the sol of hydrous oxides \(^{(9-13)}\). Sol-gel processes can produce inorganic materials with high purity and homogeneity than high temperature conventional processes. One of the most attractive features of this process is the capability to produce compositions not possible with conventional method.

However, a major disadvantage of the system, is that the cracking may occur upon drying of the gel after its production. Drying process of the gel is one of the most important stages in the preparation of these materials. Such cracks may occur during the initial stages of the drying process due to the occurrence of large capillary stresses when the solvent is evaporated from the micropores in the gel. This will make it difficult to produce monolithic glasses (where the smallest dimension of the material is more than a few millimetres).
Although these difficulties can be partially alleviated by very slow drying rates (several months) which will reduce the forces caused by rapid solvent evaporation, this approach is rather impractical.

The term "sol-gel" refers to two physico-chemical states of the system, which arise during the process. The word "sol" refers to solutions formed by polymerisation of inorganic monomers such as metal alkoxides in alcoholic solution. When a polymeric chain grows and crosslinks its forms a gel. By definition, "Sol" is a colloid suspension of solid particles in a liquid and "Gel" is the structure produced as a result of the percolation of gel and consists of a continuous solid skeleton which encloses a continuous liquid phase.

1.3.2 HISTORICAL DEVELOPMENT.

Geffcken and Berger (14) reported preparation of single oxide coatings through sol-gel process more than half century ago. The development of a thin film physics for this process using many single oxide and mixed oxide layers was pioneered by Schroeder (15) and the first products appeared in the market in 1953. Bulk production of automotive rear-view mirrors (TiO_2-SiO_2-TiO_2) started in 1959 and followed by anti-reflection coating (TiO_2-SiO_2) in 1964 and the sunshielding windows in 1969 (16).

In 1969, Dislich and Hinz elaborated the chemical basis for the preparation of multi-component oxides and patent applications in 1969 (17). The patent was granted in industrial countries. The patent includes the basic principle of the chemical reactions and process technology. The details of the processes were published in 1971 (18).
1.3.3 THE SOL-GEL PROCESS.

Sol-gel process can be divided into two different ways, namely the aqueous colloidal route and the alkoxide solution route.

a) Aqueous colloidal route

Amorphous ceramics can possibly be produced using a colloidal system in an aqueous medium (19). The technique relies on generating a stable dispersion of colloidal particles in water, which is removed later by drying and then sintering to give amorphous ceramics (19-20). The particles are discrete, dense spheres classified according to size typically 10 nanometres containing stabilizing ions, usually either sodium or ammonia.

b) Metal alkoxide route

Probably the best starting materials for sol-gel preparation are the class of materials known as metal alkoxides. Metal alkoxides are members of the family of metal organic compounds, which have an organic ligand, attached to a metal or metalloid atoms.

The following equations describe the fundamental reactions, which allow the conversion of the metallic alkoxide monomers into gel and subsequently to ceramics or glasses.

**Hydrolysis**

\[
\begin{align*}
M(OR)_x + H_2O & \rightarrow M(OR)_{x-1}OH + ROH \\
M(OR)_{x-1}OH + H_2O & \rightarrow M(OR)_{x-2}(OH)_2 + ROH
\end{align*}
\]

(1)  (2)

The series of reactions continue until $M(OH)_4$ is theoretically produced.
Condensation

\[ \text{M-OH} + \text{OH-M} = \text{M-O-M} + \text{H}_2\text{O} \]  
\[ \text{M-OH} + \text{OR-M} = \text{M-O-M} + \text{R-OH} \]  
\[ \text{M-OR} + \text{OR-M} = \text{M-O-M} + \text{R-O-R} \]

The reaction from an alkoxysilane to a solid material is not a simple one, but many possible intermediates are possible. The hydrolysis reaction proceeds in the presence of a catalyst, and acid or a base. The rate of hydrolysis depends on the nature of the metal ion and the alkoxy group. Aelion \(^{(21)}\) studied the reactivity of different alkoxysilanes in an acid catalyst system and found that the hydrolysis rate decreases drastically as the chain length increases in the radical R of the alkoxysilane Si(OR)\(_4\). Another researchers \(^{(22)}\) have found that the alkyl group had little effect on either hydrolysis or condensation processes.

It is very difficult to separate hydrolysis from condensation because the reactions occur simultaneously. As soon as an M-OH group is formed, there is the theoretically possibility of the reactions (4) and (5), therefore perpetuating the reaction by regeneration of reactants. The polymerisation from monomer to large particles and gel or powder has been represented systematically by Iler \(^{(23)}\) as illustrated in Figure 1.1.
pH < 7 OR pH 7-10 WITH SALTS PRESENT

A

pH 7-10 WITH SALTS ABSENT

B

THREE-DIMENSIONAL GEL NETWORKS

Figure 1.1: Polymerization Behaviour of Aqueous Silica

a) In basic solution (B) particles grow in size with decrease in number
b) In acid solution or in the presence of flocculating salts (A) particles aggregate into three-dimensional networks and form gel

1.4 ADVANTAGES AND DISADVANTAGES OF SOL-GEL PROCESSING.

Mackenzie outlines some of the major advantages and disadvantages of the sol-gel process over conventional melt processing to produce organic-inorganic hybrid materials.
Major advantages include:

a) The production of high purity inorganic glasses with structural integrity normally requires high temperature fusion processes (~900°C), but the sol-gel process can lead to the production of glasses with almost similar structure by sintering the dried gel at relatively low temperatures, leading to greater efficiency of preparation. Due to the low temperature preparation of the sol-gel processes, therefore its saves energy and minimizes evaporative losses.

b) Provided that the sintering of the dried gel is not carried out, oligomeric organic components can be incorporated into the matrix of the gel to produce organic-inorganic hybrid materials or ceramers. New special products such as films and fibres can be produced.

A major disadvantage of the sol-gel process, however, is that cracking may occur upon drying of the gel. Therefore, the drying process is one of the most important stages in the preparation of these materials. Such cracks may take place during the initial stages of the drying process due to the occurrence of large capillary stresses, when the solvent is evaporated from the micropores in the gel. This makes it difficult to produce monolithic glasses where the smallest dimension of the materials is more than a few millimetres. This difficulties can be eliminated by very slow drying rates, (which may takes several months), but usually impractical. Strawbridge (25) reported that the size of the capillary forces developed depends very much on the pore size of the gel and the rate of evaporation. A larger pore size and stronger networks lead to the development of fewer cracks.
The problems with the drying of gels has been discussed by Iler (19) and he proposed that the shrinkage of gel can be avoided by the following:

a) Strengthening the gel with reinforcement,

b) Replacing the water solvent in the hydrolysis-condensation reaction with a polar liquid of lower surface tension,

c) Increasing the pore diameter with an aging or hydrothermal process (reducing the surface tension forces),

d) Making the silica surface hydrophobic

Besides the cracking and shrinkage problems, the residual hydroxyl, residual carbon, longer processing times and health hazards of organic solvent are also including in the disadvantages of the sol-gel process.

1.5 AIMS OF THE STUDY.

Synthetic organic chemicals, particularly solvents, present a growing threat of pollution in many areas of the world. Many such organic compounds are reported to be toxic, even at a very low concentration. For example, the common chlorinated organic solvents present serious and most insidious pollution risks to the environment, especially to the water system. Even a small spill is capable of contaminating a large volume of water system to a troublesome level.

Polyethylene oxide (PEO) is chosen as the base material for the production of organic-inorganic hybrids due to its solubility in water, which is the most environmentally safe solvent known to mankind. PEO contains ether oxygen along the polymer chain that is capable of forming hydrogen bonds (26-27), hence its form strong interaction with silica. Its refractive index is as low as
1.4537, which matches that of porous, loosely cross-linked silica xerogel \(^{(28)}\). Finally, PEO is stable with respect to hydrolysis even in highly acidic environments. PEO is also inherently flexible, tough and resistant to most oils and greases. It is also soluble in several organic liquids and compatible with many polymers, which makes it very versatile for different possible applications.

The broad aim of this work is to investigate the influence of several parameters such as pH, catalyst, mixing temperature, mixing time, type of silane compatibilizer molecular weight as well as drying and curing processes for the production of PEO-silica ceramers. In addition, this work also seeks to find applications for such materials, particularly in areas where they can be used as additives or auxiliary components to improve the performance of other polymeric materials.

The specific aims of this work were to study:

a) The way to achieve co-continuous silica phases at nanometres scale within the poly (ethylene oxide) polymer.

b) The effect and influence of several processing parameters on the morphology and properties of PEO-SiO\(_2\) ceramers.

c) The association and effect of various silane coupling agents on the properties of ceramers

d) The possibility of producing PEO-SiO\(_2\) ceramers mixed with suitable polymers in order to achieve reinforcement with toughening effects. A preliminary evaluation of the structure properties such as blend miscibility, particle sizes, thermal and physical properties of the blends were to be carried out to determine the practical feasibility of the approach.
CHAPTER 2

LITERATURE SURVEY

2.1 SOL-GEL PROCESS

2.1.1 MECHANISM OF HYDROLYSIS AND POLYCONDENSATION REACTION OF ALKOXYSILANES.

a) Hydrolysis.

The hydrolysis of alkoxysilanes and subsequent polymerization is catalyzed by both acids and bases. In acidic conditions the alkoxysilane molecules are rapidly used up due to the fast hydrolysis reactions, which are believed to occur by the attack of protonated water molecules $\text{H}_3\text{O}^+$ on the alkoxy group in an electrophilic manner. Electron density is withdrawn from silicon, making it more electrophilic and thus more susceptible to attack by water. The hydronium ion should readily attack the basic alkoxysilane oxygen to form an activated complex that decomposes to an alcohol and silanol group. The first attack would be expected to be easier than the subsequent substitutions. As a consequence of this, the formation of $\text{Si(OH)}_4$ is unlikely and thus the condensation reactions are likely to begin before hydrolysis is complete producing lightly crosslinked species. The mechanism of the hydrolysis of alkoxysilane in acidic condition is shown in Figure 2.1.

Figure 2. 1: Mechanism of the Hydrolysis of Alkoxy silane in Acidic Conditions
Base catalysed hydrolysis of silicon alkoxide proceeds much more slowly than acid catalysed hydrolysis at an equivalent catalyst concentration, the tetraalkoxides being particularly resistant to the attack. The alkoxy groups around the silicon atom hinder the attack by OH\(^-\) group, because of their size and negative charge. Hydrolysis proceeds stepwise and when one of the alkoxy groups has been substituted the attack becomes easier. Therefore the hydrolysis tends to completion.

Therefore, more highly hydrolysed silicones are more prone to attack. Due to this, mechanism would have a penta-coordinated silicon atom in the activated complex; hence the hydrolysis of polymer would be more sterically hindered than hydrolysis of monomer. Figure 2.2 shows the basic mechanism of alkoxy silane.

![Figure 2.2: Basic catalyzed mechanism for the hydrolysis of alkoxy silane.](attachment:image)

Above pH = 2 or the isoelectric point (i.e. the point where the electrical mobility of the silica particles is zero) a different mechanism has been proposed by Okkerse \(^{61}\). Ionization equilibrium is established to produce deprotonated silicon anions, which is subsequently condensed by reacting with the silanol group. Figure 2.3 shows the mechanism of silicon above the isoelectric point.
Although hydrolysis in alkaline solution is slow, it is still tends to be completed and irreversible, if extensive polymerisation does not occur first. Imann (32) and Timms (33) have proposed the other mechanism on oxysilane hydrolysis.

**Condensation.**

Nucleophilic substitution mechanism is though to take place in the condensation of alkoxysilanes (19,34). Okkerse (31) has proposed two different catalytic reactions which govern the condensation process of silicates above and below the isoelectric point (near pH =2)

**Below the Isoelectric Point (pH=2)**

Below the isoelectric point the condensation reaction is catalyzed by $H^+$ ions. Equilibrium condition is established between the $H^+$ ion and the silanol -OH groups, leading to temporarily positively charged species of the form $-OH^+$, which attract the remaining silanol groups according to the following equations:

$$\begin{align*}
H^+ & \\
-\text{OH}_2^+ & + \quad \equiv \text{Si} (\text{OH})_4 \quad \rightarrow \equiv \text{Si-O-Si} (\text{OH})_3 & + \text{H}_2\text{O}
\end{align*}$$

$H^+$ is removed later by the water from another $\equiv \text{Si} (\text{OH})_4$ molecules. The most acidic silanols is preferentially attack by the $\equiv \text{Si-OH}_2^+$ moieties. A silanol is generally increases in acidity according to the number of substituents ched to the silicon atoms, hence the silanol is most likely to participate in condensation reactions (6). As a result, condensation in this pH range
promotes the formation of linear chains or weakly crosslinked branched structures.

Figure 2.3: The Mechanism of Alkoxysilane above the Isoelectric Point (pH > 2)

ii. Above the Isoelectric Point (pH ≥2)

The reaction is catalysed by hydroxy ions and takes place by a different mechanism. Depending on the pH of the medium, ionization equilibrium is established according to equation (7) to produce deprotonated silicon anion, $\equiv$Si-O$^-$, which later condense with silanol group according to equation (8).

\[
\begin{align*}
\text{RO-Si-OH} + \text{OH}^- & \rightarrow \text{RO-Si-O}^- + \text{H}_2\text{O} \\
\text{OR} & \quad \text{OR} \\
\text{OR} & \quad \text{OR}
\end{align*}
\]

Where $R=H$ or alkyl group
The nucleophilic nature of condensation mechanism requires the negatively charged deprotonated silanols to preferentially attack the most acidic silanols that are linked to the silicate moiety of the highest degree of condensation (i.e. middle of the chain rather than end group silicon atoms). As a result, and in contrast to the H⁺ catalyzed condensation, the OH⁻ catalysed system favours the formation of discrete and lightly condensed clusters.

### 2.1.2 THE EFFECT OF REACTION PARAMETERS ON THE STRUCTURE VARIANTS IN SOL·GEL SILICATES.

The hydrolysis of tetraalkoxysilanes leads to the formation of an organosiloxane polymer by polycondensation reactions. This process is strongly affected by certain parameters which include the catalyst and pH value of the solution, water/alkoxysilane ratio, alkoxyisilane content (silicate content), type of solvent used and type of alkoxyisilane. The drying process of the gel is also affected the final structure of the silicate network.

#### a) The role of catalyst and pH or the solution.

It is known that a catalyst can dramatically influence the gelation process. The gelation process of metal alkoxides involves both hydrolysis and polymerization reactions. The effect of catalysts in both of these reactions is complex, depending not only upon pH, but also upon the reaction mechanism of each catalytic agent. Aelion et al. (21) had observed that the hydrolysis rate of TEOS is linearly proportional to the concentration of HCl and base. Sakka et al. (35) have shown that a high concentration of HCl leads to precipitation of particles and solution become less spinnable as shown in Table 2.1.
Yamane et al. \(^{(36)}\) observed the effect of catalysts on gelling time and the properties of obtained gel from hydrolysis of TMOS. Pope et al. \(^{(37)}\) and Brinker et al. \(^{(38)}\) also supported this observation. In acid catalyzed hydrolysis alkoxysilane molecules rapidly disappear as a result of fast hydrolysis. On the other hand, under basic hydrolysis, alkoxysilane molecules remain until gelation because of the low rate of hydrolysis. In trying to explain this phenomenon, it has assume that in the presence of acid, the hydrolysis of alkoxysilane is caused by the nucleophilic attack of hydronium \(H_3O^+\), and so the reactivity decrease as the number of OR radical on the Si decreases with the progression of hydrolysis. As a result \(Si(OH)_4\) is easily formed and some alkoxysilane molecules tend to remain unhydrolyzed. The formation of \(Si(OH)_4\) is small and the condensation reactions start before the complete hydrolysis of \(Si(OR)_4\) to \(Si(OH)_4\) has taken place.

It is desirable to relate the catalytic mechanisms of the gelation process with resulting microstructure and properties of the dried and fired silica gels. The combination results between Ilter \(^{(19)}\) on the effect of pH on the polymerization reaction and Aelion’s \(^{(21)}\) on the relationship of the catalyst concentration on the hydrolysis, explained on the microstructure differences between acid and base catalyzed gel. In acid catalysed solutions, alkoxysilane molecules with unhydrolysed alkoxy group (OR) condense with each other producing silicates with a low degree of crosslinking. However, in basic solutions \(Si(OH)_4\) molecules participate in the condensation reaction leading to highly crosslinked silicates, as shown in Figure 2.4.

Pope et al. \(^{(37)}\) have also observed the effect of the acid strength on the gel time and gel appearance of the silicates.
Figure 2. 4: Schematic representation of gel desiccation \(^{(12)}\)

(a) Acid-catalyzed gels
(b) Base-catalyzed gels
(c) Colloidal gel aged under conditions of high silica solubility
(d) Colloidal gel composed of weakly bonded particles
Table 2.1: Effect of HCl Content on Gelation Properties of TMOS/H$_2$O/Methanol/HCl Solutions Matured at 40 °C in Open System\(^{(35)}\)

<table>
<thead>
<tr>
<th>Composition (mole)</th>
<th>Gel Appearance</th>
<th>Gel Time (hrs)</th>
<th>Spinnability</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O/ TMOS</td>
<td>HCl/ TMOS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>0.01</td>
<td>Transparent</td>
<td>12.6</td>
</tr>
<tr>
<td>2.00</td>
<td>0.40</td>
<td>Transparent</td>
<td>0.6</td>
</tr>
<tr>
<td>1.70</td>
<td>0.01</td>
<td>Transparent</td>
<td>13.4</td>
</tr>
<tr>
<td>1.70</td>
<td>0.40</td>
<td>Opalescent</td>
<td>1.0</td>
</tr>
<tr>
<td>1.44</td>
<td>0.10</td>
<td>Transparent</td>
<td>17.2</td>
</tr>
<tr>
<td>1.44</td>
<td>0.40</td>
<td>Opalescent (sedimentation)</td>
<td>1.4</td>
</tr>
<tr>
<td>1.53</td>
<td>0.01</td>
<td>Transparent</td>
<td>14.5</td>
</tr>
<tr>
<td>1.53</td>
<td>0.15</td>
<td>Opalescent</td>
<td>3.6</td>
</tr>
<tr>
<td>1.53</td>
<td>0.20</td>
<td>Opalescent</td>
<td>2.9</td>
</tr>
<tr>
<td>1.53</td>
<td>0.25</td>
<td>Opaque</td>
<td>2.5</td>
</tr>
<tr>
<td>1.53</td>
<td>0.30</td>
<td>Opaque</td>
<td>1.9</td>
</tr>
<tr>
<td>1.53</td>
<td>0.35</td>
<td>Opaque/sedimentation</td>
<td>1.6</td>
</tr>
<tr>
<td>1.53</td>
<td>0.40</td>
<td>Opaque/sedimentation</td>
<td>1.3</td>
</tr>
</tbody>
</table>

b) Water content.

The effect of water concentration is one of the most important parameters in determining the chemical make-up, morphology and size distribution of polyalkoxysilane polymers. Unlike other parameters, the water is directly involved in the hydrolysis and condensation reactions that form the molecular structure. An increase in water content will increase the number of hydrolysed alkoxysilane group (OH) and retard the condensation reaction\(^{(38,39)}\). This would be favoured for the formation of highly crosslinked products. However,
reduction in water content increases the probability of condensation reaction of partially hydrolyzed alkoxy silanes molecules, leading to lightly crosslinked silicates.

The role of water in alkoxy silane solution was systematically investigated by Konrad et al. in 1929 (40). They carried out the hydrolysis of TMOS [Si(OCH₃)₄] with an addition of under-stoichiometric water in varying amounts. They found out that the degree of polymerization follows the equation (9).

\[ P = \frac{n}{n-m} \] (9)

Where

- \( p \) = number of Si-atoms in the polymer
- \( n \) = moles of Si(OCH₃)₄
- \( m \) = moles of water.

Sakka and Kamiya (41) investigated the effect of \( \text{H}_2\text{O} / \text{TMOS} \) ratio on the properties of the final solutions catalyzed with HCl and matured at 30°C. They observed that in the solutions where the \( \text{H}_2\text{O} / \text{TMOS} \) mole ratios were less than 4, a fibre could be spun from the solution which was not possible with \( \text{H}_2\text{O} / \text{TMOS} \) ratios greater than 4. This may be attributed to the fact that for \( \text{H}_2\text{O} / \text{TMOS} \) ratios less than 4, uncrosslinked silicates with necklace joint fine particles are formed. Whereas with \( \text{H}_2\text{O} / \text{TMOS} \) ratios more than 4, only large round and highly crosslinked silicate particles are produced, i.e. highly condensed polymers are formed.

Glaser et al. (42) studied the effect of the \( \text{H}_2\text{O} / \text{TMOS} \) ratio for the preparation of nitridation of silica sol / gel films. They observed that the density of the initial microporous dried gel film increases with the \( \text{H}_2\text{O} / \text{TMOS} \) ratio. Consequently, the amount of film shrinkage observed during thermal treatments in \( \text{N}_2 \) or \( \text{NH}_3 \) decreased with increasing \( \text{H}_2\text{O} / \text{TMOS} \) ratio. Brinker
et al. \(^{(43)}\) found out that by increasing the \(\text{H}_2\text{O} / \text{TMOS}\) ratio will increase the initial density or condensation of the gel film. In bulk gels, the opposite situation is observed where by increasing the ratio resulted in dried gel of lower density.

c) **Effect of type of solvent.**

Mackenzie \(^{(44)}\) showed that the specific surface area of gel from TMOS solution containing different solvent is small when the vapour pressure of the solvent is high. This indicates that the selection of the solvent is important in order to obtain a gel that has desirable pore and surface properties.

d) **Effect of type of alkoxides and steric factor.**

The reactivity of the metal alkoxide differs depending on its type. Aelion et al. \(^{(21)}\) showed that the rate of hydrolysis decreases with increasing size of alkoxyl groups belonging to the alkoxide. Chen et al. \(^{(45)}\) showed that the gelling time of the alkoxide solution increases with increasing size of the alkoxyl group and explained this effect on the basis of the rate of hydrolysis and the concentration of the solution. S. Sakka et al. \(^{(35)}\) observed that the gelling time of various silicon alkoxides, \(\text{Si(OR)}_4\) having \(\text{CH}_3\), \(\text{C}_2\text{H}_5\), \(\text{C}_3\text{H}_7\), or \(\text{C}_4\text{H}_9\) were more than 100 days except for TMOS solution which was gelled in 5 days as shown in Table 2.2
Table 2.2. Gelling Time of Silicon Alkoxide Solutions having the Composition Si (OR)₄: ROH: H₂O: HCl = 1:7:2:0.01 in mol Kept at 40°C in the Closed System

<table>
<thead>
<tr>
<th>System</th>
<th>Gelling Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OCH₃)₄-CH₃OH-H₂O-HCl</td>
<td>5</td>
</tr>
<tr>
<td>Si(OCH₂H₅)₄-C₂H₅OH-H₂O-HCl</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Si(i-OC₃H₇)₄-i-C₃H₇OH-H₂O-HCl</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Si(n-OC₄H₉)₄-n-C₄H₉OH-H₂O-HCl</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

e) Drying Techniques.

When a liquid is evaporated from microporous or "spongy" solids such as metal oxide gels, jellies, or biological tissues, a capillary force due to the interfacial tension of the liquid develops a high stress on the solids during drying. These capillary forces depend on the rate of evaporation, which in turn depends on solvent vapour pressure, and pore size. Larger pore size tends to reduce cracking; however, a distribution of pore sizes affects the monolithicity of the gel. This drying stress can distort and deform the submicron objects and can cause collapsing of the micropores, leading to high shrinkage and cracking during drying. Thus the drying technique of the gel is very important in determining the pore volume, pore size, and pore morphology.

Kistler (46) found a solution to the problem of shrinkage during drying of metal oxide gels by removing the liquid around and above its critical point (in an autoclave), where the liquid changes imperatively to a gas without passing a phase boundary. At the critical point, the microscopic density (dᵣ) of both the liquid and vapour phases becomes identical, and the liquid transforms to one fluid phase whose surface tension is zero. Each liquid has a characteristic critical temperature (Tᵣ) and a critical pressure (Pᵣ). The values of Tᵣ and Pᵣ of
some common solvents that have been used for supercritical drying are given in Table 2.3. This drying technique is called supercritical drying or hypercritical drying (HCD) of gel. However, the effects of supercritical operational parameters such as pressure, temperature, and solvent can change the pore structures and pore morphology, so an understanding of the effects of these parameters is necessary to predict and control the structure and microstructure aerosol.

The CPD method consists of placing the gel in an autoclave (under pressure) in the presence of liquid CO₂ which will replace the solvent in the pores at temperature below 40°C. Tewari et al. (47) in drying TEOS gel in the presence of liquid CO₂ at temperature and pressure below 40°C and 8.4 MPa (1200 psi) respectively, have found that drying time was reduced from 2 to 3 days to 8 to 10 hours. The gel produced by this technique was similar to those obtained by the high temperature process. Low density silicate gel can be produced by the HCD technique since no shrinkage takes place during drying.

Other technique to reduce the cracking of gel is the addition of organic liquids called “Drying Control Chemical Additives” (DCCA) which control the vapour pressure of the solvent in the process. Hench et al. (48) have observed that dimethylformamide (DMF) in TMOS gel makes the average pore size larger, leading to a drastic reduction in gel cracking.
Table 2.3: Critical Constant of Fluids Used in Critical Point Drying\(^{(47)}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Critical Temperature, (T_c) (°C)</th>
<th>Critical Pressure, (P_c) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>31.1</td>
<td>7.511</td>
</tr>
<tr>
<td>Nitrous oxide (N(_2)O)</td>
<td>36.5</td>
<td>7.378</td>
</tr>
<tr>
<td>Freon-13 (CCIF(_3))</td>
<td>28.9</td>
<td>3.927</td>
</tr>
<tr>
<td>Methanol</td>
<td>240</td>
<td>8.085</td>
</tr>
<tr>
<td>Ethanol</td>
<td>243</td>
<td>6.489</td>
</tr>
<tr>
<td>Water</td>
<td>374</td>
<td>16.128</td>
</tr>
</tbody>
</table>

### 2.1.3 COUPLING AGENTS.

#### a) Introduction

When two materials do not adhere to each other, the bond at the interphase can be increased with the used of a coupling agent. A coupling agent is used at a very low level in composite i.e. about 0.2% on fibreglass; about 1% on mineral fillers. Yet it makes a tremendous difference to the physical properties of composites. Coupling agents do not only improve the initial properties, but also allows these properties to be maintained over the life span of the composite.

Silane coupling agents are known to improve the wettability of resin to fibre, to increase the compatibility of the two materials, to enhance the physical, mechanical, and chemical bonding between filler/fibre and polymer, and also to give greater durability and resistance to water attack at the interface. Silane coupling agents also improve the bond of vulcanized elastomer and that room temperature curing polymer to glass and metal.
The commercial use of organic silane derivatives has steadily developed since 1950’s by researchers at Dow Corning led by Dr. John Speier et al. \(^{(49)}\). Starting from early observations on the strength of polyester/glass fibre composites \(^{(50)}\), where the chemical resistance (specially water resistance) of the bond across the interface was improved, the concept of the organosilicon alkoxide as "coupling agents" has evolved into other areas, including that of hybrid organic-inorganic materials or ceramers \(^{(51)}\).

b) Chemistry of Silane Coupling Agents

A general formula of classical silane coupling agents can be represented as \((ROhSiR'X,\) where \(X\) represents a functional group such as amine, methacrylate, epoxy and others. There is a stable hydrocarbon linkage \(R'\) between the functional group and the silicon. \(R'\) usually is a \(-CH_2)_x\) group. The three \(RO\) groups are usually methoxy, ethoxy, or acetoxy group. When attached to silicon these groups are hydrolysable and react with water to form a reactive silanetriol \(-Si(OH)_3\) functionality. The silanetriol will condense readily with the surface hydroxy groups of glass, mineral fillers, and metals to form a covalent bond. The organic group is then readily available to react with the resin.

Pleuddemann et al. \(^{(52)}\) has evaluated over a hundred of organofunctional silanes as coupling agents in glass reinforced polyester and epoxy composites. He developed the hypothesis that the effectiveness of the silane coupling agent is related to the reactivity of its organofunctional group with the resin. This interaction may result in covalent bonding of organofunctional group to the polymer or it may consist of a copolymerization reaction at the interphase. This organofunctional on the silane-coupling agent must diffuse into the resin phase and copolymerize or form interpenetrating network (IPN)
with the matrix resin. For bonding a polymer to a mineral reinforcement, it is important to choose the silane with optimum organoreactivity, which is capable of reaction or interaction with the polymer.

Silane coupling agents are generally applied to inorganic substrate from dilute aqueous or organic solution and then dried, or are sometimes added to the polymer directly during the processing. Silanol (SiOH) groups may first form hydrogen bonds with substrate surface, and during drying, they condense to siloxane structures and chemically bond to the surface.

The reaction of hydrolyzed coupling agents with glass fibre surface hydroxyl is accepted as an essential element of the theory of bonding by silane coupling agents in composites. A simplified picture of the bonding mechanism that silane coupling agents act at the interface between inorganic (such as glasses, metals and minerals) and organic materials (such as polymers, coatings and adhesives) to bond together is shown in Figure 2.5. Additionally, silanols may condense on the substrate to form polysiloxane structure. The amount of knowledge gained on the chemistry of coupling agents is considerable through their use in glass fibre reinforced composites. This knowledge has helped significantly the development of hybrid materials and is twofold, arising from the dual character of the organosilicon alkoxide molecule.

The adhesion mechanisms between silane coupling agents and polymeric matrices have been proposed by Pleuiddmann \(^{50}\) and most of them may be categorized in three different ways.

In the first category, highly crosslinked polysiloxane is form first and matrix polymer will not be able to diffuse into polysiloxane phase, in other words, they will be a sharp boundary. In this type of adhesion, the bond strength is in
part, dependent on the surface free energy. The bond strength of this type of adhesion is generally weak. Fairly strong bonding can be expected for chemically reacted interfaces, even if this has a sharp boundary.

In the second category, the silane coupling agent and the thermoplastic polymer matrix interdiffuses into each other and they form a graded interphase structure. Both molecules interdiffuse into each other thermodynamically, resulting in the improvement of mechanical properties. The extent of interdiffusion is due to the solubilities of the matrix polymer with silane coupling agent\(^{(53)}\). Therefore, this type of interphase can be dealt in the same manner, which have been done for partially miscible polymer blends. The bond strength is expected to be improved compared with the first category.

\[
R' - Si - (OR)_3 \xrightarrow{\text{Solvent}} \xrightarrow{\text{Catalyst}} R' - Si - (OH)_3
\]

Figure 2.5: Structure formula of silane hydrolyzate.
In the third category, both the silane and the crosslinkable polymer interdiffuse into each other and then crosslink. Composites consisting of a silane and a thermosetting resin belong to this type. In most cases, crosslink is accompanied by chemical reactions between the organofunctionallity of silane and crosslinkable polymer. These chemical reactions and IPN formation make the interphase structure so complex, and many studies have focused on this complexity.

The silane coupling agents most used in thermoset applications are the amines (APS), epoxy (GPS) and methacrylate (MPS) functional silanes. MPS was invented in 1962 (Plueddemann, et al. (52)) and is still the standard silane for unsaturated polyester resins because of the reactivity of the methacrylate double bond, the ease of use, and resultant improvement in physical properties. APS are the silanes, which are used commercially in the largest volume in phenolics, acrylics, some epoxies, polyurethane, PVC, and in thermoplastics such as polyamides and polyolefins. GPS is used in acrylics, polyurethanes, polysulfides, epoxy resins, and many other systems.

2.1.4 APPLICATIONS OF SOL-GEL PROCESS.

The first step in assessing the suitability of sol-gel derived glasses and ceramics to any particular application is to investigate the mechanical and physical properties pertaining to that material. Sol-gel products normally retain a large degree of microporosity even after sintering. Therefore, this immediately suggests the suitability toward the manufacture of membranes, filters and substrates for catalytic converter. Leenaars et al. (54) produced alumina membranes with approximately 50% porosity with pore dimension between 3 to 4 nanometers. These membranes were successfully tested in
the filtration of various solutions and it was believed that gas separation would also be possible \(^{(55)}\).

It is difficult to produce dense monolithic glasses within an economically viable time scale, due to excessive shrinkage of the sol-gel products during densification, which causes cracking on the product. With the exception of optical fibre preforms \(^{(56)}\), most sol-gel applications are as thin films and coating. Anti-reflection coating based on controlled leaching of single layers of silicates and borosilicates have been developed \(^{(57)}\). Anti-reflection coating has also been applied to polymeric materials such as polycarbonates and acrylics \(^{(58)}\).

The ability to produce dense thin films at low temperatures has permitted the incorporation of organic species into the glassy sol-gel derived networks, thus creating the possibility to produce a myriad of new optical materials \(^{(59)}\).

2.1.5 ORGANIC-INORGANIC HYBRID MATERIALS.

a) General Introduction.

The incorporation of organic material, specifically functionalized oligomer and polymers has lead to the development of a new class of materials, generally known as organic-inorganic hybrids. These new class materials have been called Nanocomposites, Ormocers, Ormosils and Ceramers.

Organic-inorganic hybrids represent a creative alternative to conventional synthetic methods for the production of new materials. The possibility of combining the properties of organic and inorganic compounds in a single material is an old challenge that started with the beginning of the industrial
Ishak Manaf

Chapter 2: Literature Survey

era. Some of the oldest mixtures of organic-inorganic materials come from the paint industry. In this industry, an inorganic pigment such as TiO$_2$, is suspended in organic mixtures of solvents, surfactants and other ingredients. However, the concept of "hybrid organic-inorganic" materials emerged less than 15 years ago, as a result of a desire to produce sophisticated materials with a higher added value $^{(60,61)}$. In more recent years organic-inorganic hybrids also called "Ceramers", has become an expanding field of investigation $^{(62,63)}$.

These new materials are very promising for new applications in many fields such as optics, electronics, ionics, mechanics and biology $^{(64-69)}$. These materials are considered as biphasic materials, where the organic and inorganic phases are mixed at the nanometre to sub-micron scales.

It is obvious that the properties of ceramer materials are not just the sum of the individual contribution from organic and inorganic phases $^{(70)}$. The major features of the organic and inorganic phases are generally preserved in ceramer materials. However, the main physical, mechanical and optical properties of these composite materials are strongly dependent on phase continuity, average phase size, molecular mixing at the phase boundaries and intrinsic properties of constitutive components.

The choice of polymer is usually guided by their mechanical and thermal properties. Properties such as hydrophobic/ hydrophilic balance, chemical stability, biocompatibility, optical the electronic properties and chemical functionalities must also be considered in the choice of the organic precursor.

b) Ceramers Development.

Many attempts to produce new ceramer materials through sol-gel process have been made by several scientists since mid-1980. These are typically
produced by the incorporation of functionalized oligomeric species within a hydrolyzed metal alkoxides solution\(^{71-76}\). Examples of these include a study by Huang et al. \(^{72}\) involving a polyurethane-based poly (tetramethylene oxide) (PTMO) oligomer in TEOS silica. In this study, it was found that the component miscibility improved with an increasing number of triethoxysilane (TES) functional groups on the backbone\(^{72,75}\). It was concluded that ceramer system produced with a base catalyst displays similar periodicity of SiO\(_2\) domains to those of acid-catalyzed system, but the former suffers higher phase separation between the matrix and the domains.

Several researchers\(^{77-79}\) have demonstrated the production of ceramers by acid-catalyzed polymerisation of TEOS within poly (vinyl acetate) (PVAc) and poly (methyl methacrylate) (PMMA) matrices. PVAc showed superior properties particularly dynamic mechanical properties, above the glass transition temperature, as compared to fine particle filled materials. The interaction between fine polymer-silica network is hydrogen bonding between the uncondensed hydroxyl groups at the surface of silica and carbonyl groups in the polymer\(^{79}\).

More challenging work on the production of ceramers with high performance properties such as high temperature resistance, mechanical properties and dimensional stability has been reported. Polyimides have been used for the production of high temperature ceramers as they are already widely used in much advanced technology such as microelectronics and composites. Yano et al.\(^{80}\) has produced the first polyimide-inorganic hybrids by intercalating clay with aqueous solutions of dodecylamine (HCl salt) or with n-decyl trimethoxyl ammonium chloride. Polyamic acid was used to prepare the polyimide/ sol-gel silicate ceramers. The polyamic acid was formed by the reaction of 4,4 diaminodiphenylether and pyromellitic dianhydride in dimethylacetamide (DMAC) which is a solvent for preparation of polyimides.
Ceramers obtained from this system exhibited a thermal expansion coefficient much lower than the monocomponent polyimide film produced in the same way and with the same curing process.

The first attempt to produce polyimide-silica hybrids by sol-gel process was made by Morikawa et al. (81). They have successfully produced a ceramer by the hydrolysis and condensation of TEOS in poly (amic acid) (PAA) solution. A ceramer solution containing a mixture of TEOS, water and PAA was stirred for six hours and then cast as thin film on glass plates. The films were then dried for 12 hours at 60°C and thermally treated at 260°C for another 3 hours under nitrogen atmosphere.

Kioul and Mascia (82) have investigated the effects of alkoxy silane coupling agents on polyimide-silica ceramers. Different ceramers morphology were obtained by varying the alkoxy silane solution composition and mixing parameters, γ-Glycidyloxypropyltrimethoxysilane (GOTMS) proved to be the most effective coupling agent. This was believed to result from epoxy groups in GOTMS reacting or strongly interactions with the carboxylic groups in PAA. The coupling agent has a vital role in changing the morphology from a typical dispersed microstructure to fine interpenetrating heterophase co-continuous phase morphology. This was found to give better high temperature stability and lower thermal expansion, while a fine particulate structure was seen to give maximum ductility. This phenomenon was also supported by Menoyo et.al. (83) Whose found that high level of co-continuity in the final polyimide-silica ceramer was achieved due to the decomplexing action of coupling agents, such as GOTMS or 3-isocyanatopropyltriethoxysilane (ICTES), for the removal of the associated solvent within the PAA.
c) Biodegradable and Biocompatible Ceramers.

Since the concept of ceramers is based on organic-inorganic hybrids, therefore it is possible to produce a biodegradable and biocompatible ceramers by choosing the suitable biodegradable and biocompatible polymer precursor. The sol-gel process has the potential of combining valuable properties into a novel type of ceramer, such as non-toxicity for living organisms, adsorption after an appropriate period of implantation time and good ultimate mechanical properties. These hybrid ceramers may be envisaged as a novel types of degradable bioglass. They could also be used as coating materials for bone implants and prosthetic devices. They could also be used as supports for enzyme immobilisation. The nano-porosity of the silica phase can permit the penetration of living organisms to achieve better biocompatibility.

Dubois et al.\(^{(84)}\) produced the first biodegradable and biocompatible ceramers by the conversion of the hydroxyl end-groups of poly (ε-caprolactone) (PCL) into triethoxysilane end-groups. A co-continuous interpenetrating network of the inorganic component (silica) and organic polymer (PCL) have been achieved when the weight composition is close to 50% (SiO\(_2\)/PCL). As a result, a transparent hybrid material was exhibited. The high level of SiO\(_2\) required achieving continuity of phases, that is probably due to the fact that coupling agents were not used. In-vitro cell culture and biodegradation tests have confirmed that these new ceramer materials are novel biomaterials endowed with biodegradable and biocompatible property\(^{(85)}\).
d) Poly(ethylene oxide)/ Silica Hybrids

There are not many recorded attempts to produce new ceramer materials through sol-gel process using the PEO as a base material. Wojcik et al. \(^{(28)}\) prepared the PEO-silica hybrids and studied the influence of preparation conditions on their physical and optical properties. They used TEOS in an aqueous solution of PEO under acidic condition. The PEO content in the hybrids system were 1.7% and 6.5% weight to weight ratio with two different molecular weights of PEO i.e. 100,000 and 300,000 respectively. They also studied the effect of water-to-alkoxy ratio (i.e. the volume of water was either water-to-alkoxy group ratio (R) equal to 3 or 8, for each concentration of PEO and each molecular weight) on the hybrids and concluded that, the water-to-alkoxy ratio has an important effect on properties of the final hybrid materials. Hybrids with less stoichiometric water (R=3), where the ratio between water and TEOS is equal to 3, gave lower shrinkage and exhibited decreasing densities as a consequence of higher amounts of organic component. However, they were more homogeneous in structure, had lower porosity, gave better transparency and showed no sign of phase separation.

Park et al. \(^{(86)}\) studied the structure characteristics of the silica-PEO hybrid thin films produced by sol-gel process using NMR spectroscopy. The epoxide polymerization of GOTMS was confirmed by using FTIR. They found out that the homogeneous and crack free silica-PEO hybrid films could be obtained by spin coating of the ceramer solution.
2.2 POLYETHYLENE OXIDE (PEO)

2.2.1 INTRODUCTION.

These are divided into two classes of PEO, differentiated by molecular weight, i.e.
(a) Low molecular weight polymers (known also as polyethylene glycols) with an average molecular number \( M_n \) of 600-20,000 and
(b) High molecular weight PEO with \( M_n = 100,000 - 8,000,000 \).

With the increases of molecular weight, the crystallinity of PEO increases and they change from viscous liquids to soft solids to flexible/ductile solids. PEO possesses very low toxicity \(^{87}\) and is neither a skin nor an eye irritant \(^{88}\).

PEO polymers have common structure of \((\text{O-CH}_2\text{-CH}_2)_n\). The presence of the ether linkages (oxygen atom in every third position of the backbone) is responsible for the unique properties of these polymers. PEO is a tough ductile, highly crystalline thermoplastic and is readily soluble in water. The polymer exhibits a well defined monoclinic crystal structure; the unit cell consists of two ethylene oxide polymer chains, probably present in the form of parallel helixes.

High molecular weight PEO homopolymers are sold as free flowing white powders \(^{89}\), and they are commercially available with \( M_n \) values ranging from 100,000 to 8,000,000 from Union Carbide Corporation (i.e. Polyox), Meishi Chemical Work Ltd. (Alkox), Seitetsu Kagaku Co., Ltd. i.e. (PEO), and Neochim Company i.e. (Badimol) \(^{90}\).
2.2.2 PROPERTIES.

a) General Properties

In general, PEOs are soluble in water at room temperature in all percentage. Solutions of the higher \( M_n \) grades are "stringy" at 2% concentration. Solutions of higher concentration are elastic gels. Close to the boiling point of water, the water solubility decreases and a cloudy liquid phase form. The solution structure of the PEO chain in water can be interpreted as an association between each ether oxygen and two water molecules. PEO dissolves readily in common solvents.

The melting point variation of PEO with molecular weight is shown in Table 2.4. The melting point increases with \( M_n \) up to about 15,000, and then it remains approximately constant \(^{(91)}\).

<table>
<thead>
<tr>
<th>( M_n )</th>
<th>Melting Point (°C)</th>
<th>( M_n )</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-15 to -8</td>
<td>3,000</td>
<td>54-58</td>
</tr>
<tr>
<td>400</td>
<td>4-8</td>
<td>6,000</td>
<td>59-61</td>
</tr>
<tr>
<td>600</td>
<td>20-25</td>
<td>8,000</td>
<td>60-63</td>
</tr>
<tr>
<td>800</td>
<td>24-29</td>
<td>14,000</td>
<td>61-67</td>
</tr>
<tr>
<td>1000</td>
<td>37-40</td>
<td>300,000</td>
<td>62-67</td>
</tr>
<tr>
<td>1450</td>
<td>43-46</td>
<td>2,000,000</td>
<td>65-67</td>
</tr>
</tbody>
</table>

The density calculated from structural x-ray data is 1.33 g/cm\(^3\) at 20°C; the experimentally determined value is 1.15 to 1.25 g/cm\(^3\). The extrapolated melt density data gives a value of 1.13 g/cm\(^3\), equivalent to that for amorphous phase \(^{(92)}\). The crystalline phase contains chains with seven structural units, -CH\(_2\)CH\(_2\)-O-, in two helical turns for each identity period. The melting fraction
of PEO over the Mn range of 3,500 to 5,000,000 has been studied by thermal analysis (93-94) by Sung et al. When heated above the crystalline melting point, it can be processed by conventional methods to produces film. These films are flexible, strong, heat-sellable and readily dissolved: filler can be added in them (95). The glass transition temperatures are reported to be in the region of -90 to 17°C (96-97). Union Carbide Chemical Company reported that the PEO undergoes some deterioration in air at temperature above 50°C (98).

Charlesby (99) studied the effect of radiation on PEO and discovered that it undergoes crosslinking. This phenomenon was also supported by Pearson (100), who irradiated PEO in the air and vacuum. In vacuo crosslinking is easily measured but in air, it is very difficult due to oxidative degradation. It was noted that when PEO was irradiated in air, crosslinking occurred at doses as low as 1 Mrads, after which oxidation of the gel caused rapid degradation. Infrared studies showed the development of carbonyl group and vinylidene double bonds during the degradation (100).

Smith et al. (101) reported that the PEO tensile properties are not effected significantly by contact with relative humidity conditions below 70°C. At 90% relative humidity, the yield strength and modulus drop appreciably.

Table 2.5: Some Mechanical Properties of Medium/ High Mw PEO (101)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>12.6-16.8</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
<td>7.0-10.5</td>
</tr>
<tr>
<td>Ultimate elongation (%)</td>
<td>700-1200</td>
</tr>
<tr>
<td>Extension at yield (%)</td>
<td>5-30</td>
</tr>
<tr>
<td>Tensile modulus, stiffness (MPa)</td>
<td>210-490</td>
</tr>
<tr>
<td>Izod impact strength</td>
<td>Sample bent, did not break</td>
</tr>
<tr>
<td>Shore hardness (A scale)</td>
<td>99</td>
</tr>
</tbody>
</table>
b) Solution Technique.

The preparation techniques of PEO resins influence the viscosity values of the resin solutions. The decrease in viscosity with increasing shear rate is reversible except when high shearing forces actually break apart the longest molecules. Therefore, if maximum viscosity is desired, high speed agitation must be avoided during the dissolution process.

High molecular weight PEO is soluble in many common solvents such as ethylene dichloride, carbon tetrachloride, benzene, toluene xylene, etc \(^\text{(69)}\). With a number of solvents, such as methanol, the solvent action is very slow at room temperature, as indicated in Table 2.6. The only true non-solvents are aliphatic hydrocarbons, some glycols, and glycerine. Small quantities of water in any of these solvents markedly increase the effectiveness of the solvent for a PEO resin.

c) Solution Properties

i. **Solubility in Water**

All grades of PEO resins are completely soluble in water with highly progressive thickening as the concentration increases. When placed in water, PEO particles swell and pass into solution as the long polymer chains disentangle and become hydrated. PEO resin solutions have almost no surface activity and their concentrated solutions are slightly hazy to moderate opaque. The hazy solution is due to small amounts of inorganic residues left from the polymerization process and not to undissolved resin. In order to get clear solutions; organic or mineral acids can be used to acidify the PEO solution to a pH between 5 to 6.
PEO resins precipitate from solution at high temperatures. The temperature depends upon the concentration of the resin in solution and upon the molecular weight of the polymer, as shown in Figure 2.6 (90). Above $M_w$ of about 50,000 and a resin concentration of about 0.3% in water, the precipitation temperature becomes insensitive to both $M_w$ and resin concentration.

![Figure 2.6: Solubility-Temperature Relationship of PEO](image)

ii. Aqueous Solution Stabilization.

It is well known that aliphatic ethers react with oxidising agents such as oxygen and hydrogen peroxides, to form hydroperoxides. These peroxides subsequently can decompose in a variety of ways depending upon the conditions; generally, chain scission is involved. For example, the C-O bond in diethyl ether can be broken to give acetaldehyde and ethanol (102). The C-C bond in 1,2-bisethers and glycol can be broken to give formic acid and
formaldehyde \(^{(103)}\). In view of these facts, it is not surprising that PEO is very susceptible to similar oxidizing agents and therefore, the solution viscosity decreases rapidly in the presence of these materials. Table 2.8 illustrates the effect of certain chemical agents on the solution viscosity of PEO. Solution containing traces of certain transition metal ion such as ferrous, copper and silver gave PEO solution with lower viscosities and poor long term stability.

PEO solutions can be stabilized by a variety of agents. Allyl alcohol, isopropanol, ethanol, ethylene glycol or propylene glycols are very effective stabilizers when they are at 5 to 10\% by volume (based on total volume).

iii. Light Stability

PEO solutions were very sensitive to light exposure. The decrease in solution viscosity is particularly marked in the case of strong UV light and is significant for exposures to small quantities of incident fluorescent light. McGary, Jr. \(^{(104)}\) reported the aqueous solution viscosities of PEO decreased 4 and 42\% respectively when storage in the dark for 12 days and in the shaded window. Exposure to the sun lamp resulted even more drastic effects. UV stabilizers, such as salicylates can stabilize this effect.
### Table 2.7: Solubility of POLYOX Water Resins (approx. 1% by weight) in Selected Solvent (90)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature at which POLYOX Resin Precipitates on Cooling, °C</th>
<th>Temperature at which POLYOX Resin Dissolves on Heating Above 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stay in Solution at 0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Below 0</td>
<td>-</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>Below 0</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene Dichloride</td>
<td>Below 0</td>
<td>-</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>Below 0</td>
<td>-</td>
</tr>
<tr>
<td>Methylene Dichloride</td>
<td>Below 0</td>
<td>-</td>
</tr>
<tr>
<td>Stay in Solution at Room Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Isopropanol, 91%</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Must Be Heated to Dissolve</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Xylene</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Acetone</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Methanol</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Cellosolve Acetate</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Anisole</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>4</td>
<td>40</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>26</td>
<td>40</td>
</tr>
<tr>
<td>Dimethyl Cellosolve</td>
<td>27</td>
<td>40</td>
</tr>
<tr>
<td>Cellosolve Solvent</td>
<td>28</td>
<td>45</td>
</tr>
<tr>
<td>Ethanol, 200 proof</td>
<td>31</td>
<td>45</td>
</tr>
<tr>
<td>CARBITOL Solvent</td>
<td>32</td>
<td>50</td>
</tr>
<tr>
<td>Butanol</td>
<td>33</td>
<td>50</td>
</tr>
<tr>
<td>Butyl Cellosolve</td>
<td>33</td>
<td>50</td>
</tr>
<tr>
<td>Butyl Acetate</td>
<td>34</td>
<td>50</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>37</td>
<td>50</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>Diethyl Cellosolve</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>Water Miscible Non-Solvents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3 Butanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropanol Anhydrous</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note: Values are approximate and may vary depending on the specific conditions and concentration of POLYOX resins.*

40
Table 2.7: The Effect of Some Chemical Agents on the Viscosity of Aqueous Solutions of PEO \(^{(104)}\)

<table>
<thead>
<tr>
<th>Chemical agents (^a)</th>
<th>Viscosity Loss, (^%)^ (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peracetic acid</td>
<td>99</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>97</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>96</td>
</tr>
<tr>
<td>Bromine</td>
<td>92</td>
</tr>
<tr>
<td>Ferrous sulfate</td>
<td>96</td>
</tr>
<tr>
<td>Cuprous chloride</td>
<td>81</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>64</td>
</tr>
<tr>
<td>Zinc chloride</td>
<td>9</td>
</tr>
<tr>
<td>Cupric chloride and hydrogen peroxide</td>
<td>98^c</td>
</tr>
</tbody>
</table>

\(^a\) Chemical agent, 0.01 g; PEO, 1.00 g; and water, 100 g.

\(^b\) Initial viscosities were 15 MPa. s before additions of agents, final viscosities were determined after approximately 2 days.

\(^c\) Loss observed immediately after the addition.

iv. Normal Aging

McGary, Jr \(^{(104)}\) demonstrated that the extent of viscosity loss upon aging PEO solutions is dependent upon the history of the solid polymer. Obviously, during preparation, PEO may be exposed to certain agents such as air and metallic residues. Table 2.9 illustrates the correlation of PEO stability with regard to prolonged aging and aging in the presence of CuCl\(_2\) and UV light. It is concluded that the primary reason for long term instability of PEO solution is
related to the presence of small amount of hydrogen peroxide or related substances in the initial polymer.

v. Effects of Stabilizers.

Table 2.8 illustrates the stabilizing effect of isopropyl alcohol on aqueous polymer solutions toward long-term aging, UV light, oxidizing agents, and metallic ion initiators. Clearly, all of these phenomena can be rationalized by assuming a free radical mechanism in the degradation of PEO solutions. It is noteworthy that, isopropyl alcohol stabilized the polymer solution toward strong acids, indicating that simple hydrolysis is not involved. It is assumed by Seubold et al. \(^{(106)}\), that hydroperoxides present in the polymer, undergo ionic rearrangement in the polymer to give chain scission.

Primary and secondary alcohols are very effective in retarding the decrease in PEO solution viscosity. (Table 2.10). The effectiveness of the alcohols is in the order of allyl alcohol \(>\) isopropyl alcohol \(>\) ethanol \(>\) methanol \(^{(105)}\). These data suggest that some oxidizable materials such as primary and secondary alcohols compete favorably with PEO for peroxides and free radicals, and are oxidized selectively.
Table 2.8: The Effect of Various Degrading Agents on PEO Solutions in Isopropyl Alcohol (106).

<table>
<thead>
<tr>
<th>Degrading Agent</th>
<th>Aging Time</th>
<th>Alcohol-water$^a$</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>7 weeks</td>
<td>0.5</td>
<td>34</td>
</tr>
<tr>
<td>UV light</td>
<td>50 hrs.</td>
<td>10</td>
<td>64</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>6 days</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>Cupric chloride</td>
<td>4 weeks</td>
<td>1.5</td>
<td>43</td>
</tr>
<tr>
<td>Ferrous sulfate</td>
<td>5 days</td>
<td>6.6</td>
<td>96</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 4.0</td>
<td>5 days</td>
<td>0.4</td>
<td>61</td>
</tr>
<tr>
<td>pH 1.2</td>
<td>5 days</td>
<td>8.2</td>
<td>95</td>
</tr>
</tbody>
</table>

$^a$Equal part of isopropyl alcohol and water by volume

Table 2.9: Effect of Alcohol on the Stability of Aqueous PEO Solutions (105).

<table>
<thead>
<tr>
<th>Alcohol $^a$</th>
<th>Viscosity Loss, $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl</td>
<td>7.6</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>10.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.5</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>20.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>50.0</td>
</tr>
<tr>
<td>Tert Butanol</td>
<td>61</td>
</tr>
</tbody>
</table>

$^a$ Alcohol content: 10% vol. % in solvent

$^b$ After exposure to UV light for 50 hours.
2.2.3 PEO BLENDS.

PEO has been found to be miscible with many other polymers. Studies of PEO with thermosetting resins such as epoxy resins (107-110) and unsaturated polyester (111), have been reported by Zhang et al. (112). Most of the known miscible blends are composed of polymers with functional groups, which are capable of forming strong interactions with PEO, one such interaction is hydrogen bonding. This is the basis for miscibility of PEO blends with other polymers as reported for many polymeric blends (113-118). It has been well reported that the presence of ether linkages, (oxygen atom in every third position of the backbone), is an excellent proton-accepting polymer which make the hydrogen bonding interaction possible in blends of PEO with proton donor polymers containing OH group. FTIR, DSC and optical microscopic analysis (119) have demonstrated this interaction between polymers through hydrogen bonding.

An aromatic copolymer containing amide and enaminonitrile groups gave miscible blends with PEO up to 60% weight PEO. The basis for the miscibility is most likely due to hydrogen bonding interactions between the proton donor from tertiary amide group (enaminonitrile) and proton accepting sites of PEO (120).

The kinetics of spherulite radial growth and the morphology of the compatible system PEO/PVC have been studied by Iragarri et al. (121) by optical microscopy. He reported the usual spherulite radial growth behaviour for miscible blends with PEO content more than 70% PEO. At lower concentrations, distortion of the usual spherulite morphology was observed, meaning that the blend is partially miscible.
A simple and useful method to analyse the polymer blends miscibility is by determining the glass transition temperature $T_g$ as a function of composition \(^{(122-123)}\). A single $T_g$ point is the most commonly used criterion for establishing any miscibility of a polymer blend. Conversely, immiscible blends exhibit the $T_g$ of each component. Partially miscible blends exhibit two $T_g$ but different from each polymer. Chen-Chi et al. \(^{(124)}\) have reported the complete miscibility, due to strong associations with novolac-type phenolic resins, which results in the positive deviation of the $T_g$, from the law of mixtures.

### 2.2.4 COMMERCIAL APPLICATIONS.

Most applications of PEO polymers are based on water solubility, solution rheology, low toxicity, thermoplasticity, and flocculant ability \(^{(125)}\). PEGs are used in ceramics as binders, cosmetics, lubricants, metal working, pharmaceuticals, polyurethanes, rubber chemicals, electronics and other applications.

Viscosity and rheology are important for the thickening of acid cleaners. The chemical stability in the present of acid gives these polymers a distinct advantage over natural and cellulose polymers.

The sensitivity of viscosity to shear is important in many applications. Waterborne paint thickened with these polymers exhibit high viscosity under low shear, and therefore sag is reduced. Solution of these polymers can be used to stabilize foams, by their thickening and pseudoplastic behaviour; a content of a few ppm is sufficient. At concentrations of 5 to 50 ppm, PEO reduces turbulence at the interface of solid surface and flowing liquid phase. This friction reduction ability is also used to reduce drag on an object moving through water. The variety of uses includes slurry transport and fire fighting.
Due to its ability to form gels and its low toxicity, PEO is applied in dental adhesives where a thick cushioning fluid holds dentures in place while protecting the gums. The biologically inert nature of PEO helps to reduce unpleasant odours and tastes.

High molecular weight PEOs are able to flocculate finely dispersed solids (coal and silica suspensions, phosphate slimes, uranium ore slimes, and clays such as the bentonite, monmorillonite, and kaolin). The addition of few hundred ppm or less, results in more rapid settling and filtration times and a tough floc. The strong interactions of PEO with surfaces of minerals help to wet the surface and provide lubricity. This is important in systems with high mineral content such as concrete and ceramics. Therefore, PEO is used for plaster walls, stabilisers for plaster compositions, and is a drying retardant for cements in the building materials field.

PEO films are used for water-soluble packaging of harmful and difficult-to-handle products, such as pesticides, herbicides, and dyes. PEOs are also use as soil conditioners and stabilizers, protective root coatings, crop mulches, and seed coatings. The seed tape, marketed under the Evenseed trademark, which dissolves after being planted leaving uniformly spaced seeds, has been developed.

PEO is widely used as a material for "solid" polymer electrolytes and especially in rechargeable lithium batteries (126). The unique combination of properties makes PEO useful in a seemingly endless variety of ways.
2.3 CERAMER BLENDS

2.3.1 INTRODUCTION

It is well known that blending polymers with finely divided inorganic fillers or fibres does not produce high performance materials because of the low efficiency with which stresses are transferred.

However, blending of fine co-continuous organic-inorganic hybrid materials such as ceramer could produce high performance new materials. The polymer used in the blends should be miscible with the organic precursor used in the production of the ceramers. Therefore, PEO-SiO₂ ceramer can be blended with many polymers such as poly (vinyl chloride) (PVC), polyamide, poly (vinyl acetate) (PVAc) and epoxy resins, which are miscible with the PEO. The author has found no references to research of such blends and related organic-inorganic hybrid materials.

In this study, nano-composite polymeric alloys will be using PEO as a carrier for the silica phase. If PEO is fully miscible when the PEO-SiO₂ hybrid precursor is mixed with these polymers, the PEO may migrate from the silica phase and these polymers form miscible moiety, leaving behind a preformed continuous silica phase. Alternatively a system containing domains of PEO-SiO₂ hybrids diffused in the matrix polymer will result.
2.3.2 POLY (VINYL CHLORIDE).

a) Introduction

Poly (vinyl chloride) is a major, highly versatile thermoplastic for many important applications, notably as insulation and jacketing for electrical wires and cables. It is also widely used in the medical field, such as connectors and tubings. Nowadays, ready-made PVC compounds are available in great variety and profusion, formulated to meet the need not only of the main processes and applications, but also of individual process and application variants.\(^{(127)}\)

PVC materials incorporating significant amounts of plasticizers are known as plasticized PVC (PPVC). Flexible and soft PVC formulation contain plasticizers in proportions high enough to impart these properties to the material in substantial degree. On the other hand, unplasticised PVC (uPVC) contain no plasticizers, the term is often referred as rigid PVC. Rigid and semi-rigid PVC exhibit more rigid properties.

b) Properties of PVC

For commercial resins, the degree of polymerization 'n' may have values between 500 and 2000, giving the molecular weights in the region of 30,000 to 100,000. The chains are branched with an estimated degree of branching between 0.2 and 2.0 branches per 100-carbon atom.\(^{(127)}\) Commercially grades normally give a diffuse x-ray diffraction spectra, and based on this infrared spectral evidence, they are considered to be substantially amorphous even though they do possesses a low level of crystallinity. Table 2.10 shows some of the typical properties of commercial PVC products.
Table 2.10: Some of the important properties of the PVC.

<table>
<thead>
<tr>
<th></th>
<th>Unplasticized</th>
<th>Plasticized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.4</td>
<td>Down to about 1.25</td>
</tr>
<tr>
<td>Water absorption</td>
<td>&lt;0.5%</td>
<td>Up to 0.5%</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>~60 MPa</td>
<td>Down by a factor of 4 or more</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>1.5-3.0 GPa</td>
<td>Down by a factor of 100 or more</td>
</tr>
</tbody>
</table>

The glass transition temperature ($T_g$) of rigid PVC is about 80°C. Plasticization generally lowers the effective $T_g$ temperature, and hence the softening point of the polymer.

2.3.3 EPOXY RESINS.

a) Introduction

Epoxy resins were first prepared by Pierre Casten in Switzerland and S.C. Greenlee in the United State in the late 1930s\(^{(128)}\). Epoxy resins were first offered commercially in 1946\(^{(129)}\). Epoxy resins are chemically characterized by a three members ring, called alternatively the epoxide, epoxy and ethylene oxide or oxirane group.\(^{(129,130)}\)

The most important commercial intermediate epoxy resin oligomers are products of epichlorohydrin and bisphenol A.\(^{(129,131)}\). The general formula for the epoxy resin is shown below. Shell Chemicals Company and Union Carbide Corp. began research in the commonly used bisphenol A based epoxy resins in the late 1940s.
In order to convert epoxy resins to hard, infusible thermoset networks, it is necessary to use crosslinking agents. These crosslinkers, (hardener or curing agents as they are widely known), promote crosslinking or curing of epoxy resins. Curing can occur by either homopolymerization initiated by a catalytic curing agent or a polyaddition/copolymerization reaction with a multifunctional curing agent.

b) Curing Agents for Epoxy Resins

Curing agents may be classified in the following broad categories \(^{(130)}\) i.e. aliphatic amines, modified aliphatic amines, aromatic amines, acid anhydrides and catalytic curing agents. Since only the aromatic amine was used in this study, only this group of curing agent will be described.

Polyfunctional amine containing more compact and rigid group would provide greater heat resistance. This is indeed the case, for the aromatic amines are the best for use in higher temperature applications. Three commonly employed aromatic amines are meta-phenyline diamine (MPDA), 4,4'-methyleneedianiline (MDA) and diaminodiphenyl sulfone (DADPS). Mixing of these curing agents with the epoxy resin at temperature of 150°C to 200°C, leads to useful properties of the resin.
c) Properties of Epoxy Resins.

Epoxy resins are thermosetting materials. When converted by curing agent, they become hard, infusible systems. Cured epoxy resins exhibit good engineering properties, such as high stiffness and strength, creep resistance and chemical resistance. In common with all thermoset plastics however, they are intrinsically brittle. To alleviate this deficiency, epoxy resins are frequently modified by dissolving in the liquid resin system, a small proportion of liquid rubber (about 10 to 20%) containing reactive groups and allowing the precipitation of crosslinked rubbery particles during curing \(^{(132)}\). It is preferable that the impact modifying agent is a low molecular weight polymer, to ensure that the viscosity of the resin is not increased excessively, so that the processability of the system is not impaired \(^{(133)}\).

Another weakness of conventional epoxy resins is their relatively large level of water absorption, which causes a large reduction in glass transition temperature \(^{(134-135)}\) and deterioration in mechanical properties \(^{(136-137)}\). The high affinity of epoxy resins towards water is explained by the presence of highly polar groups in the epoxy network.

Despite the above weaknesses, the thermosetting epoxy resins possess a number of unusually valuable properties, immediately amenable to use in the formulation of adhesives, sealing liquids, cold solders, castings, laminates, and coating. The more important of these properties are:

i. Versatility

The epoxy resins are compatible with a wide variety of curing agent \(^{(128)}\). Hence the properties of the cured epoxy resin systems can be engineered to widely diverse specifications.
ii. Good Handling Characteristics

Many epoxy systems can be worked at room temperature, while those which cannot require only moderate heat to melt during mixing. The ratio of curing agent incorporated in the epoxy resins is not as critical as with some thermosetting materials. In general, a few percent error in the incorporation of curing agent may be tolerated in most applications and some curing agents permit even wider margins.

iii. Toughness

Cured epoxy resins are approximately seven times tougher than cured phenolic resins\(^\text{(128)}\). This is attributed to the distance between crosslinking points and the presence of integral aliphatic chains.

iv. High adhesive properties.

Epoxy resins have high adhesive strengths arising from the polarity of aliphatic hydroxyl and ether group (R-O-R), present in the initial resin chain and in the cured system\(^\text{(128, 138-139)}\). The polarity of these groups serves to create electromagnetic bonding forces between the epoxy molecule and the adjacent surfaces. This make epoxy resins useful as adhesives to bond with various substrates, such as many plastics, metals, rubbers and wood\(^\text{(139)}\).

v. Low shrinkage.

The cured shrinkage of an unmodified epoxy resin is of the order of 2% or less\(^\text{(128)}\). Therefore, it can be moulded to reproduce accurate shapes and dimensions without requiring expensive machining or other finishing\(^\text{(139)}\).
vi. Chemical Resistance

Cured epoxy resins are very inert chemically \(^{128, 130}\). The ether groups in the benzene rings and, when present, the aliphatic hydroxyls in the cured epoxy system are virtually invulnerable to caustic attack and extremely resistant to acids.
CHAPTER 3

EXPERIMENTAL

3.1. PEO-SiO₂ CERAMERS.

3.1.1. MATERIALS.

a) Poly (ethylene oxide)-PEO

Poly (ethylene oxide) used in the study was supplied by Union Carbide Corporation under the trade name of Polyox Resin. Two types of Polyox resins were used, to cover the number molecular weight range of 100,000 to 8,000,000, Polyox WSRN-10 and WSR-301 respectively. They have melting points in the region of 62 to 67°C, and can be dissolved in water at room temperature in all proportion.

b) Alkoxysilane-Silicate Precursor Solution

The alkoxysilane precursor used in this study is tetraethylorthosilicate (TEOS) supplied by Fluka Chemie AG. It is 98% pure and a transparent liquid having a specific gravity of 0.933, and the boiling point in the range of 163 to 167°C. The remaining 2% are reported to be a mixture of ethanol, stabilizers and a pH indicator. The indicator will turn pink from its original colourless if hydrolysis takes place during storage. In this study, TEOS was used without further purification.
c) Coupling Agents

Compatibilisation of the alkoxy silane phase and PEO was achieved with the use of a coupling agent. The coupling agents investigated are:

i. γ-Glycidyloxypropyltrimethoxysilane (GOTMS)

γ-Glycidyloxypropyltrimethoxysilane (GOTMS) supplied by Fluka Chemie AG. It is a transparent liquid with a boiling point of 260°C. The chemical structure is:

\[
\begin{align*}
\text{O} & \quad \\
\text{H}_2\text{C} & \quad \text{C} \quad \text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3
\end{align*}
\]

ii. an Adduct of GOTMS with Chlorendic anhydride (CA)

1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride (CA) is a white powder with a melting point of 235 to 239°C. and has the following structure:

Adducts were obtained by reacting GOTMS and CA at various molar ratios.
d) Solvent and Water.

The water used in alkoxysilane solution was distilled in the laboratory. HPLC grade ethanol was used as a miscibilizer for the alkoxysilane/water system. Tetrahydrofuran (THF), HPLC grade, was also used for the preparation of solutions. Fisher U.K Scientific Ltd supplied both solvents.

e) Catalyst.

Hydrochloric acid (HCl) was used as catalyst for the alkoxysilane solution, a 32% by weight solution from Fluka Chemie AG. In order to gain a better control of the acidity of alkoxysilane and polymer solutions immediately after preparation, the original HCl was diluted to 5% w/w with distilled water.

3.1.2. PREPARATION AND EVALUATION OF THE SOL-GEL PRECURSORS.

(a) Polymer solution

The PEO solution was prepared by dissolving in water at room temperature, stirring until it completely dissolved, which normally took about 5 to 10 minutes. The concentrated solutions are hazy due to the small amounts of inorganic residue left from the polymerization. Clear solutions were obtained by acidifying to a pH 5 or less.

(b) Alkoxysilane solution

Different types of alkoxysilane solutions were prepared in this work. These solutions were based on TEOS or TEOS/silane coupling agents mixtures, i.e.
with and without coupling agents. The detail formulations are shown in Table 3.1 below:

Table 3.1: The formulation of alkoxy silane solutions

<table>
<thead>
<tr>
<th>Component</th>
<th>TEOS</th>
<th>GOTMS</th>
<th>C₂H₅OH</th>
<th>Water</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of moles</td>
<td>1</td>
<td>0.12</td>
<td>1.13</td>
<td>3.2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The actual percentage of silica present in the material is related to the amount of TEOS used initially, but will also depend on the amount of the PEO resin used and the amount of volatilization of various substances during the curing process. The HCl is referred to as being 100% in the above table because the water contained in the 5% HCl (w/w) that was actually used is accounted for in the entry above for water.

The order of addition of the components to TEOS that is first GOTMS followed by ethanol, water and HCl. The solution was shaken in a closed cylindrical container (25mm diameter), to achieve miscibilization of the reactants. During mixing heat evolution was noted, which indicated that the exothermic hydrolysis reactions had occurred. The pH of the solution was about 2. The alkoxy silane solution was matured for about 10 minutes before the preparation of the ceramer solutions. This formulation was named “CG” and was used as the basic starting point for silica synthesis by the sol-gel process.

In the case where the alkoxy silane precursor was prepared without any coupling agent, the alkoxy silane formulation will be referred as a “C” solution. The “C” solution is similar to the “CG” solution, with respect to the molar proportions of alkoxy groups, ethanol and HCl to water.
When coupling agents other than GOTMS were used for the preparation of silicate precursor solutions, they were generally added to TEOS in the same way as the "CG" formulation. Again the molar ratios of the alkoxy groups, ethanol and HCl to water were kept constant.

(c) The effect of pH on polymer solution viscosity

The Haake Viscometer Model CV20 was used for the measurements of PEO solutions viscosities. This is a cone and plate rotational viscometer, which can be used to measure the torque as function of the rotational speed and the test temperature. As the torque is proportional to the shear stress ($\tau$) and the rotation speed for the shear rate ($\gamma$), the viscosity ($\eta$) of resins at given test temperature can be calculated from the above formula:

$$\eta = \frac{G \times \tau}{\gamma}$$

where $G$ is the instrument calibration factor.

The effect of pH on PEO viscosity was carried out in order to determine its stability towards acid. This is important due to the use of HCl in the formulation of ceramics using sol-gel process.

Viscosity measurement was carried out at room temperature using the solution of PEO prepared from Polyox WSRN-10, as mentioned in Section 3.1.2 (a). Since the initial pH of the solution is in the range of 9.0, a 2% w/w HCl solution in water was used to adjust the pH in the ranges of 0.5-9.0. PEO solutions with different pH values were prepared and their viscosities measured at different shear rates at room temperature.
3.1.3. PREPARATION OF THE PEO-SiO₂ CERAMERS MATRIX.

(a) Introduction

Different types of ceramers were prepared.

i. PEO/TEOS (uncompatibilized system)
ii. PEO/TEOS/coupling agent (compatibilized system)
iii. PEO containing the same amount of acid as in the alkoxy silane solutions above.

The amount of silica used in the formulation was 25%, 35% and 50% by weight PEO. The alkoxy silane precursor solutions were mixed in a closed conical flask at 60°C for about 1 hour with stirring starting an initial pH value of ~2. The solutions were then cooled at room temperature to eliminate the bubbles entrapped during the mixing, and then cast on the Mylar film and glass slides, and dried in an air-circulating oven for 24 hours at 60 °C (i.e. just below the Tₘ of PEO). Figure 3.1 shows the schematic diagram of the Sol-Gel process for the production of the PEO-SiO₂ ceramers.

(b) Effect of pH on Gelation Time of ceramer solutions

Ceramer solutions C25 and CG 25 (i.e. 25% silica in the solid ceramer) were prepared as in Section 3.1.3 (a). The gel time of the ceramer solutions was followed, as function of pH at 60°C, starting with an initial pH was subsequently increased by adding triethylamine. On the other hand, to reduce the pH, a 2% w/w HCl solution was added.
(c) Effect of maturation time on viscosity of the ceramer solutions.

Different types of ceramer solutions were prepared for this study. These were:

i. A control formulation based only on PEO
ii. A formulation based only on PEO acidified with HCl
iii. A formulation based on (ii) with coupling agent (GOTMS) added.
iv. A formulation based on (ii) with TEOS/GOTMS added.

All these solutions were kept in the oven at 60°C for different maturation time ranging from 1 to 6 hours. After each interval time, the solution viscosity of each formulation was measured using the Haake Viscometer CV20.
Figure 3.1: Schematic diagram of the sol-gel process for the production of PEO-SiO$_2$ ceramers.

1. **Alkoxide**
2. **Solvent + Acid**
3. **Clear Viscous**
4. **PEO Precursor pH~2.1**
   - Maturation/hydrolysis (10 minutes).
   - Mixing at 60°C for 1 hour in an oil bath.
5. **Ceramer Solution**
6. **Cast on Mylar Films**
   - Evaporation of water and other solvents at 60°C for 24 hours.
   - (Air circulating oven)
7. **Solid PEO-SiO$_2$ ceramer**
3.1.4. MORPHOLOGICAL STUDIES OF PEO-SiO$_2$ CERAMERS.

(a) Effect of silica content

PEO based precursor solutions yielding different concentrations of silica (25 to 50% w/w) were prepared and visual appearance were recorded of the cast and cured films.

(b) Effect of mixing time

In this series of experimental work, the precursor solutions were heat treated at 60°C with different mixing times, in order to determine the optimum mixing time for the production of PEO-SiO$_2$ ceramers. The ceramer solutions, with and without GOTMS coupling agent, containing 35% silica were mixed in a closed container for 60, 180 and 300 minutes. Visual observations of the film appearance were recorded.

(c) Effect of mixing temperatures

Precursor solutions giving 35% silica, with and without GOTMS coupling agent, were prepared at various mixing temperatures. This experiment was designed to assess the effect of mixing temperature on the film morphology. The mixing temperatures used were 60, 80 and 100°C. To avoid irreversible water/solvent evaporation; the mixing of both precursors was done in a closed container. In order to maintain the temperature of the system, an oil bath was used and it was ensured the level of the solution in the flask was always below the oil level in the heating bath.
The PEO-SiO₂ ceramer solutions were then cooled to room temperature after 60 minutes mixing, in order to eliminate the air bubbles formed during stirring. The solutions were then cast as films on Mylar film and dried at 60°C overnight (~24 hours) in an air circulating oven and visual observations of the film were recorded.

(d) Effect of the amount of GOTMS coupling agent

Ceramer solutions giving 35% silica were prepared at 60°C with different amounts of GOTMS coupling agent, to examine the effects on the ceramer film morphology. The TEOS: GOTMS molar ratios used are shown in Table 3.2.

Table 3.2: The TEOS: GOTMS ratios in the ceramer solution formulations.

<table>
<thead>
<tr>
<th>Samples</th>
<th>TEOS/GOTMS Weight of TEOS (g)</th>
<th>Weight of GOTMS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG 0.06 35</td>
<td>1:0.06</td>
<td>7.35</td>
</tr>
<tr>
<td>CG 0.12 35</td>
<td>1:0.12</td>
<td>6.93</td>
</tr>
<tr>
<td>CG 0.24 35</td>
<td>1:0.24</td>
<td>6.10</td>
</tr>
<tr>
<td>CG 0.36 35</td>
<td>1:0.36</td>
<td>5.27</td>
</tr>
</tbody>
</table>

(e) Effect of other coupling agents

The use of other coupling agents in producing ceramer solutions, was investigated to examine any morphological changes that may arise. The total theoretical silica content of the ceramer film was 35% w/w. The molar ratio of TEOS to coupling agents in each experiment was 1:0.12 (i.e. equal to the standard molar ratio in the ceramer solutions formulation with GOTMS coupling agent). The coupling agents examined were bis-γ-trimethylsilylpropyl
amine (A 1170), mercaptopropyltrimethoxysilane (A 189), and the reaction product of GOTMS with chlorendic anhydride at two molar ratios (1:0.25 and 1:0.50). The reaction conditions for the preparation of the GOTMS-CA adducts are given in Section 3.1.4 (g).

(f) The solvents effect.

A comparative study for PEO-SiO₂ ceramers prepared using different types of solvent, was carried out in order to investigates the structural changes in the ceramer morphology. The PEO precursor was prepared by dissolving the PEO in THF (15% in the solvent) by stirring at about 50°C. A solution of HCl (2% w/w) was used to adjust the pH of the solution to about 2. PEO-SiO₂ ceramer solutions, giving 35% w/w silica with and without GOTMS coupling agent, were prepared as in Section 3.1.3 (a). The ceramer films were obtained by casting the solutions on Mylar films, which were dried as described in Section 3.1.3 (a).

(g) Preparation and characterisation of GOTMS-CA adducts

The reaction of GOTMS and chlorendic anhydride (CA) was carried out to produce acid functionalized derivatives in the coupling agent as shown in Figure 3.2.

Test samples for the analysis were prepared as follow:

i. Pure GOTMS in solution;
ii. Pure CA powder;
iii. Adduct of GOTMS and CA with two different molar ratios, 1:0.5 and 1:0.25, prepared by mixing the reactants in a closed container and heat treated for 3 hours at 60°C.
Figure 3.2: Expected reaction between the oxirane ring of epoxide compounds such as GOTMS and chlorendic anhydrides (CA) are:

In presence of water.

\[
\text{[abbreviation (OC-CA-CO)O]} \quad \xrightarrow{\text{Step I}} \quad \text{[abbreviation (OC-CA-CO)O] + CA} \quad \xrightarrow{\text{Step II (less likely without catalyst)}}
\]

65
In absence of water

(i) $\text{CA} + \text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$

This would partially hydrolyze upon addition of water, to produce acid groups as in Scheme (a).

(ii) $\text{CA} + \text{MeO-Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$

Upon addition of water hydrolysis would take place with the elimination of CA.
Sample preparation

One or two drops of pure GOTMS were placed in the centre of a sodium chloride plate from a pipette and sandwiched between a second plate in order to spread the solution into a thin layer film. The plates were placed in sample holder and located in the sample beam of the FTIR spectrometer (Pye Unicam SP3) in the transmittance mode.

A KBr disc was prepared by weighing about 2mg of pure CA powder and grinding it in a small agate mortar with 300 to 400 mg of pure spectroscopic grade KBr and place in the die of a press. This results in the formation of a very fragile translucent sample disc, which can be removed from the die with tweezers and placed it in the sample beam of the FTIR spectrometer.

Adducts of GOTMS and CA samples were prepared by following the same procedure as that for GOTMS, since they were liquids.

3.1.5. CHARACTERISATION OF THE PEO-SiO₂ CERAMERS.

(a) Appearance of the PEO-SiO₂ ceramer films

The dried ceramer films were removed from the oven and the morphology of the solid ceramers were established. Visual appearance of each of the PEO-SiO₂ ceramer films was used to classify the ceramers. The ceramers were classified as transparent or opaque.
(b) Microscopically Study

i. Introduction

Microscopically studies give invaluable information about the morphology of any polymeric composites such as size and type of spherulites, size and dispersion of insoluble components such as colourants, fillers or other additives. The morphology is interrelated with the processing conditions as well as mechanical and other properties. An understanding and knowledge of these structure-morphology interrelationships, will enable us to implement any improvement in the product properties.

A wide range of microscopically technique have becomes available in recent years in order to perform morphological studies in the polymeric composite field. The differences between the various systems arise, either from the type of radiation employed to interact with the specimen, or from the type of instrumental devices incorporated in the microscope, to process those interactions, and render the image interpretably by the human eye.

Common light, polarized light and scanning electron microscope are widely used in the study of polymer composites. Microscopy involves enlarging the image to a visible range.

In this study, SEM was used to study the particle sizes and phase characterization of the PEO-SiO₂ ceramics. TEM was also used to examine the particle sizes of the particles in the organic-inorganic hybrid systems.
ii. **Scanning Electron Microscope (SEM)**

Scanning electron microscope (SEM) is widely used with polymeric samples. SEM can give some insight into topographic features of a fracture surface. In the electron microscopy, the radiation that interacts with the specimen is a beam of high energy electrons, produced from a filament and accelerated by a high voltage. Three imaging signals can be used, back scattered electrons, secondary electrons and x-rays. Characteristic x-rays have well defined energies for different atoms. Thus, analytical information can be obtained from an x-rays spectrum. Back scattered electrons are primarily beam electrons which have been elastically scattered by the nuclei in the sample and escape from the surface. Thus, they can be used to obtain compositional contrast in the sample. Secondary electrons are emitted with low energy from the top few nanometers of the materials. This technique yields topographic images of the sample surface. Due to its great depth of field, SEM images have an almost three dimensional appearance, and have a much higher resolution.

Damage of the polymer by the electron beam is one of the principal shortcomings of electron microscopy. Grubbs et al. review of works on radiation damage and electron microscopy of organic polymers, indicates that three effects, namely, loss of crystallinity or mass, contrast artifacts and distortion, can lead to great changes in the image formed in the microscope. In order to minimize these, the surface of a specimen is coated with an electrically conducting thin layer of gold or gold/palladium alloy.

Dried ceramer films of PEO-SiO₂ were used in more detailed visual assessment. After the specimen was glued to a stub with colloidal silver and a thin layer of gold was sputtered on the specimen to ensure conductivity, a
Leica Cambridge Instruments Ltd. Stereoscan 360 equipment was used for topographic observation of the brittle fracture areas.

iii. Transmission Electron Microscope (TEM)

Electron microscopy is a powerful tool in elucidating the morphology of the multiphase materials such as polymer composites. TEM has been used in many instances in order to determine the miscibility and phase segregation of polymer network and polymer blends. The information about the continuous phase and the size and shape of the domains and their distribution in the composites materials, can be investigated. At high magnifications, domains in order of 1 nanometer scan are investigated. The preparation of the samples for TEM analysis can be difficult since an ultra-thin section of the materials has to be cut.\(^{(143,144)}\)

A more detailed visual assessment of the phases characteristics of the PEO-SiO\(_2\) ceramer films were conducted with a Joel 100CX instrument. The instrument was run with an accelerating voltage of 10kV with sample magnifications at 10000 times. The sample preparation was difficult due to the character of the PEO-SiO\(_2\) ceramer films, which were brittle at room temperature after drying. Thus, prior to sectioning, the films were embedded with a suitable epoxy resin to increase the hardness. An ultra-thin section of 100nm thickness was cut using a LKA Bromma 8800 Ultratome III ultramicrotome.

(c) Differential Scanning Calorimetry (DSC)

Different scanning calorimetry is extensively used to measure transitions in polymers and polymers blends. In semi-crystalline thermoplastic based
composites, crystalline features such as degree of crystallinity, are important parameters effecting the mechanical properties.

DSC technique relies upon the change at endothermic and exothermic transitions and shows changes in the heat capacity when the polymer undergoes a secondary transition. Reference and sample pans are scanned through a pre-set time-temperature programme. Heat is transferred through the disc to the sample and reference. Differential heat flow is monitored by thermocouples located beneath the disc. The quantity of heat (joules) or a measurement of heat-flow (calories/unit time) is obtained by dynamically heating a sample and an inert reference. The energy difference that is necessary to keep the specimen at equal temperature with the reference, is plotted again the temperature, the area beneath the exothermic or endothermic peaks is proportional to the total enthalpy change in the specimen. The rate at which the specimen absorbs or gives off heat is proportional to it specific heat, as this is the amount of energy needed to change the specimen temperature by a given amount. The heat of fusion ($\Delta H_f$) is the amount of energy necessary to transform a polymer from a crystalline to a completely disordered amorphous state. It is measured by calculating the area under well defined thermogram traces.

Accuracy of the DSC results can be affected by several factors such as the precision of sample weight, calibration and assessment of peak area, and the most important factor is to determine the actual content of the silica ($SiO_2$) in the specimen. In this study, the silica contents in the specimens were kept constant in the ranges of 25 to 70% (w/w).

In this experiment, ceramer films weighing about 10 to 12 mg were cut and put into the aluminium pan. These pans were sealed properly to avoid thermal mismatches. A Du Pont 910 Differential Scanning Calorimeter combined with
the Du Pont 2000 Thermal Analysis System, was used for this study. The samples were run from room temperature (approximately 25°C), to 100°C at a heating rate of 10°C/min and purged with nitrogen gas at a flow rate of 60cm³/min.

(d) Thermogravimetric Analysis (TGA)

i. Introduction

A thermobalance is an instrument that permits the continuous measurement of a sample’s weight as the temperature and/or time is changed. The thermobalance in TGA system is used to denote a balance system, which is capable of following the sample over a range of temperature. Weight losses at high temperatures for PEO and PEO-SiO₂ ceramics were measured by a TA instrument high-resolution modulated TGA 2950 thermogravimetric analyser. Tests on the specimens were carried out in an air atmosphere at a heating rate of 10°C per minute. Test samples for the thermogravimetric analysis were prepared as follow:

ii. PEO samples

PEO resin solutions were prepared by dissolving the Polyox-WSRN-10 in water at room temperature. Hydrochloric acid at 5% concentration w/w in water was used to adjust the pH of the solution to a value of 2. This solution was then heated in an oil bath for 1 hour at 60°C. After that the solution was subjected to another heat treatment at 60°C in an air circulating oven for about 24 hours. The same procedure was also applied to PEO dissolved in THF.
iii. PEO-SiO$_2$ ceramer samples.

PEO-SiO$_2$ ceramers samples were prepared by mixing the PEO polymer precursor and alkoxy silane solution in a closed container at 60°C for 1 hour. The ceramer solutions were then cast as films on Mylar film and dried at 60°C for overnight (~24 hours) in an air circulating oven.

(e) Surface Area Measurement (N$_2$ Adsorption Study)

i. Introduction

When surface area or pore volume distribution of solid materials is altered, drastic changes occur in the properties of those materials. It is well known that nitrogen adsorption at 77K is a convenient and powerful method to evaluate specific surface area, pore volumes, and pore size distribution of porous solids$^{(145-149)}$. Measurements of surface area and pore size are based upon physisorption, i.e. the physical adsorption and desorption of gas, (typically nitrogen, argon or krypton), at the surface and in the pores of the solid samples.

When a clean solid is exposed to a gas, it will attract gas molecules onto its surface in an attempt to satisfy the imbalance of surface atom forces. A gas may be thought of as molecules moving along straight paths. Numerous collisions change the directions and speeds of the molecules. When a molecule collides with a surface, it may be either bounce off or it may be adhere to the surface for a certain period of time. The length of time that a gas molecules stays on a surface depends upon a number of factors such as the actual point on the surface to which the molecule is attached, the nature of both the surface, the molecule, and the temperature of the surface.
The application of the nitrogen adsorption technique for surface characterization has become easier than before, due to the commercial availability of adsorption instruments capable of performing measurements starting from relative pressure as low as $10^{-7}$ atmosphere. Various kinds of porous materials such as non-grafted carbon black \(^{(150)}\), grafted carbon black \(^{(151)}\), and porous inorganic oxide (silica, alumina, titania and zirconia) \(^{(152)}\) exhibit markedly different low pressure nitrogen adsorption properties.

Gas pressure is expressed as the force exerted by molecules colliding with a surface unit area. If the molecules collide more often (due to an increase in population) or at higher speed due to an elevation in the gas temperature, pressure will increase. Gas molecules, which leave the bulk of gas to adsorb onto a surface, cause the average number of molecules in the gas to decrease; therefore, the pressure decreases. By combining the decrease in pressure with the temperature of the gas and the volume of the container, it is possible to determine the number of molecules adsorbed. Brunauer-Emmet-Teller (BET) equation is used to calculate the surface area of the system by special software available in the interface computer system and the nitrogen adsorption equipment.

ii. Materials

PEO-SiO\(_2\) ceramer film containing 35% w/w silica was prepared both with and without GOTMS coupling agent. Ceramer films of C35 and CG35 were used in this study. Silica from TEOS was also used as control as well as a mixture of TEOS/GOTMS coupling agent. After 60 minutes of mixing at 60°C, the ceramer solutions were coated on Mylar film and dried at 60°C for about 24 hours in an air circulating oven, followed by 2 hours drying at 120°C. All
ceramer films produced were then heated at 500°C in an oven for 3 hours, before they were crushed into small particles.

iii. Characterisation Method

Nitrogen adsorption-desorption isotherms at 77K were measured in the relative pressure range of 0.05 to 0.02 on a Micromeritics model ASAP 2010 (Nacross, GA, USA) adsorption analyzer. Prepurified grade nitrogen was used. Prior to the analysis, the ceramer samples were outgassed (degas) for at least 24 hours, until the vacuum pressure gauge was reading 15mmHg to 20mmHg, then the degas stage was usually completed. After all the necessary steps were taken in the analysis procedures, the samples were put onto the analysis port and the nitrogen adsorption analysis started.

BET surface area of PEO-SiO₂ ceramers were calculated using the standard BET method by special software available in the interface computer system.
3.2. PEO-SiO₂ CERAMER BLENDS.

3.2.1. PEO-SiO₂ CERAMER BLENDS WITH PVC.

3.2.1.1. Materials

(a) PVC resin

The European Vinyl Corporation (EVC) supplied PVC, with the trade name of EVIPOL used in this study. It is a suspension homopolymer with the trademark and grade codes of SH6030. PVC SH 6030 has a density of 53 kg/m³ and the K-value of 60. It is a white odourless powder.

(b) Plasticiser

Di-2-ethylhexyl phthalate (DOP) was used as a plasticizer for PVC. DOP is a general-purpose plasticizer for PVC products and it is colourless liquid with the molecular weight of 390. Its boiling point temperature is 230°C at 5 mmHg and it has a density of 98 kg/m³.

Compatibilized PEO-SiO₂ ceramer, containing 50% silica, was used in the blend.

3.2.1.2. Blend Preparation

Solution blending was performed using tetrahydrofuran (THF) as a common PVC solvent. First, the compatibilized PEO-SiO₂ ceramers solution was prepared as mentioned in Section 3.1.3 (a). This solution was then blended with the PVC solution, dropwise in a closed container. The mixing process was carried out for about 4 hours at 60°C until the solution mixture became
transparent. THF solvent was removed by evaporating the blend in an air circulating oven at 60°C. Thin films of about 0.5mm in thickness or less, formed by solvent casting on the Mylar film, were dried at 60°C for 24 hours followed by 2 hours vacuum dried at 80°C at 30 bar pressure. Details of the blend formulations are shown in below:

Table 3.3: The PEO-SiO₂/PVC Ceramer Blend Formulations.

<table>
<thead>
<tr>
<th></th>
<th>PEO-SiO₂/PVC-0</th>
<th>PEO-SiO₂/PVC-20</th>
<th>PEO-SiO₂/PVC-40</th>
<th>PEO-SiO₂/PVC-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (pph)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>DOP (pph)</td>
<td>0</td>
<td>20</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>PEO (pph)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>SiO₂ (pph)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

Blends between PEO/PVC were also prepared as control with different amount of DOP plasticizer content as shown in Table 3.4.

Table 3.4: The PEO/PVC Blend Formulations.

<table>
<thead>
<tr>
<th></th>
<th>PEO/PVC-0</th>
<th>PEO/PVC-20</th>
<th>PEO/PVC-40</th>
<th>PEO/PVC-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC (pph)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>DOP (pph)</td>
<td>0</td>
<td>20</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>PEO (pph)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>
3.2.1.3. Characterization of the PEO-SiO$_2$ Ceramers Blends with PVC.

a) Differential Scanning Calorimetry (DSC)

Thermal properties of the PVC/PEO-SiO$_2$ ceramers blends were examined by differential scanning calorimetry (DSC). Samples from thin films were weighted about 10 to 12 mg and placed in a small aluminium pan with a lid, and a similar empty pan, together with its lid, was used as a reference. To ensure a uniform history, the blend samples were first heated to 100°C from room temperature and the cooled down by passing the air through the samples. The samples were then heated to 150°C at scanning rate of 20°C per minute under nitrogen gas atmosphere (i.e. ~50 cm$^3$/minute flow rate).

b) Scanning Electron Microscope (SEM)

Phase characterization of PVC / PEO-SiO$_2$ ceramers blends were achieved by scanning electron microscopy (SEM). Samples from the thin films were used in this study and all the procedures on the analysis were follows as mentioned in Section 3.1.5(b)(ii).

c) Transmission Electron Microscope (TEM)

A more detail visual assessment of the phase's characteristic of the PEO-SiO$_2$ ceramer/PVC blends was investigated by following the procedure in Section 3.1.5(b)(ii).

d) Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is an invaluable tool capable of providing information about the mechanical properties of a polymeric material as a function of temperature.
and frequency by measuring the response to an oscillating force, usually in the range 0.1 to 100 Hz. During the dynamic testing, an oscillatory (sinusoidal) strain / (or stress), is applied to the material and the resulting stress or strain developed in the material is measured. These properties include the two components of dynamic modulus, i.e. $E'$ and $E''$ and the mechanical loss tangent or phase lag between the sample strain and applied stress, known also as $\tan \delta$.

Modulus is defined as the ratio of stress to strain (stress/strain), the resultant stress generated in a viscoelastic material subjected to a sinusoidal strain, can be used to calculate the dynamic modulus $E^*$ (or complex modulus). The complex modulus is a measure of the material's resistance to deformation. It encompasses both elastic and viscous responses.

The elastic modulus, or storage modulus ($E'$) and the viscous modulus, or loss modulus ($E''$), can be calculated directly from the elastic and viscous stress respectively. Summaries of the calculation are as follows.

Complex Modulus, \[ E^* = E' + iE'' \]

Where \[ E^* = \text{dynamic modulus} \]
\[ E' = \text{storage modulus} \]
\[ E'' = \text{loss modulus} \]
\[ i = \text{complex number} \]

\[ \tan \delta = \frac{E''}{E'} \]

$\tan \delta$ is the ratio of the loss modulus to storage modulus. This ratio is a measure of the damping ability of a material. Apart from providing valuable information on the mechanical behaviours of the material, DMTA is also use
to determine the transition temperatures of samples (e.g. glass transition temperature, $T_g$) as the temperature at which $\tan \delta$ goes through a maximum while the storage modulus decreases rapidly.

Dynamic mechanical test was carried out using the TA Instrument Dynamic Mechanical Analyser, Model DMA 2980. The DMA 2980 works in conjunction with a TA Instrument Controller and associated software to make-up a thermal analysis system. The fundamental measurement of DMA 2980 is sample stiffness. Sample stiffness is defined as force applied to the sample, divided by the amplitude of deformation. The stiffness of a material is dependent on its geometry (i.e. physical dimension). The modulus of material, however, is independent of its geometry. A good understanding of sample stiffness is important for understanding geometry selection when conducting the DMTA measurement.

The blend samples in the form of thin films were cut into rectangular shape with the size ranging from 30mm length, up to 0.5mm in thickness and up to 6.5 mm in width. The samples were clamped to the film tension clamp. Figure 3.2 show the tension clamp. The samples were subjected to an oscillating frequency of 1 Hz with 20 $\mu$m amplitude (i.e. strain) in the temperature range from $-100^\circ$C to 140$^\circ$C, at a heating rate of 3$^\circ$C per minute. Since the film tension clamp was used in this study, a minimal static force of 0.010 N was applied to the sample. The force from the applied tension is recorded as a function of the magnitude and phase of the sample displacement. The signal were automatically used to calculate the dynamic storage modulus ($E'$), loss modulus ($E''$) and the loss tangent ($\tan \delta$) which were plotted as a function of temperature. The $\tan \delta$ peak was taken as the glass temperature ($T_g$) of the sample.
e) Tensile Test.

Stress-strain measurement is amongst the most widely used, basic measurement of the mechanical properties of polymers \(^\text{(154)}\).

In the present study, the tensile test was conducted using a Lloyd 2000R tensile testing machine equipped with a 500N load cell. A crosshead speed of 2 mm/minute was employed. Small size dumbbells with a gauge length of 30mm were used throughout this study. Tests were conducted at 23°C ± 1°C and the reported values of all properties were the average of at least 4 to 5 determinations. The properties investigated were the tensile strength, \(T_s\) (stress at break) and the elongation at break, \(\varepsilon_b\) (strain at break).

Figure 3.2: The tension clamp for DMTA \(^\text{(153,155)}\)
3.2.1.4 Morphology stability of the PEO-SiO₂/PVC blends.

The PEO-SiO₂/PVC blends were subject to further studies by melt blending in the Haake Rheocon 90, for about 20 minutes at 180°C. The entire PEO-SiO₂/PVC blends were used in equal weight to suit the Haake Rheocon blending machine. The resulting melt blends were then made into test plaques using compression moulding. The plaques were produced using a "frame type" mould between steel plates. The appropriate amount of material (10% excess) was placed in the mould; the mould was loaded in the press and preheated at 180°C for about 3 minutes. A pressure of 15 tonnes was then applied for another 5 minutes and the mould was transferred to a cold press and allowed to cool with running water in the platen for about 5 minutes under the same pressure, in order to avoid deformation of the plaques.

The above samples were then fracture in the liquid nitrogen and subjected to the SEM analysis. This experimental work was done in order to investigate the structure morphology stability of the blends.

3.2.2. PEO-SiO₂ CERAMERS BLEND WITH EPOXY RESIN.

3.2.2.1. Materials

(a) Epoxy Resin

An unmodified liquid bisphenol A epichlorohydrin epoxide resin, namely Epikote 828 supplied by Shell Chemicals UK Ltd, was used. Its has number average molecular weight of less than 700 with a density at 25°C of 1160 kg/m³ Neville et al. (128). Epikote 828 has medium viscosity, measured to ASTM D445, of 12 to 14 Pa.s, and can be used at room temperature without solvent diluent.
Epikote 828 is stable under normal use conditions. It reacts with strong oxidising agents, polymerizing exothermally with amines, mercaptans, Lewis acids at ambient temperature and above. It is used in many applications with various curing agents at ambient temperatures, for example, in the electrical and electronic industries, as adhesives, casting, surface coatings, laminating, and civil engineering composites and coatings\(^{(128)}\).

(b) Curing Agent

Di-amino-diphenylamine, also known as 4,4'-methylene dianiline 97% supplied by Across Organic, Fisher Scientific UK, was used as the only epoxy curing agent in this study. It is an aromatic amine and it is a polyfunctional amine containing more compact and rigid group, which can provide greater heat resistance.

3.2.2.2. Blend Preparations and Characterizations.

PEO-SiO\(_2\) ceramer containing 50% (w/w) was used for the blend. The previous blending procedures described in Section 3.2.1.2, were used. Two blend formulations were prepared using the aromatic amine curing agent. Amine curing agent was added to the epoxy resin in THF solvent before the blending process with the PEO-SiO\(_2\) ceramer solution was carried out. This was called Blend A. On the other hand, the addition of amine curing agent was done after the blending process of the two components was completed and continuous with the mixing for about 5 minutes, before it was cast as film. This blend was called Blend B. The blend was then made into thin film by casting on Teflon film and dried at 60°C for 24 hour followed by 150°C for 3 hours in an air circulating oven.
The amount of acid used in the preparation of the alkoxy silane solution was considered to be too small to have any significant effect on the hardener used for the curing of the epoxy resins.

The film samples were then subjected to the blend characterizations such as SEM, TEM and DMTA, as described in Section 3.2.1.3. However, due to the brittleness of the samples, mechanical tests could not be carried out.
CHAPTER 4

RESULTS

4.1. PEO-SiO\textsubscript{2} CERAMER SYSTEM

4.1.1. PREPARATION AND EVALUATION OF THE SOL-GERL PRECURSORS.

a) Solubility study of the PEO polymer in water

Table 4.1 shows the PEO solubility in water at room temperature. It is completely soluble at room temperature in all proportion. However, Polyox WSR-301 (i.e. the high molecular weight PEO), formed an elastic gel at about 5% concentration in water whereas Polyox WSRN-10 (i.e. lower molecular weight) formed a viscous solution. Both concentrated solutions were slightly hazy to moderately opaque due to a small amount of inorganic residue left behind from the polymerization operation process and not to undissolved resin.

Table 4.1: Solubility of Polyox Resin WSR-301 (high molecular weight PEO) at Room Temperature

<table>
<thead>
<tr>
<th>WSR-301 (%w/w)</th>
<th>Water (part)</th>
<th>Ethanol (part)</th>
<th>32%w/w HCl (part)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>PEO completely soluble after 4-5 hours with hazy solution and very high in viscosity (almost form gel)</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
<tr>
<td>1</td>
<td>75</td>
<td>25</td>
<td>-</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>0.1</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.5</td>
<td>0.1</td>
<td>All soluble in water and the viscosity was very high (gel) especially with the highest percentages of polymer.</td>
</tr>
</tbody>
</table>
Table 4.1b: Solubility of Polyox Resin WSRN-10 (lower molecular weight PEO) at Room Temperature

<table>
<thead>
<tr>
<th>WSRN10 (part)</th>
<th>Water (part)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100</td>
<td>PEO completely soluble with hazy solution due to the small amount of inorganic residue left from the polymerization operation.</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

b) The effect of pH on PEO polymer solution viscosity.

The effect of pH on PEO solution viscosity was carried out in order to determine its stability towards acid. This is important due to the used of HCl as a catalyst in the formulation of the ceramer solutions for the production of ceramer by the sol-gel process.

Figure 4.1 (see page 110) shows the effect of pH on PEO solution viscosity. The solution viscosity reduced significantly below pH 2. Above pH 2, the PEO solution is very stable and its viscosity does not change. From this observation, it can be concluded that at low pH, a large reduction in viscosity takes place in PEO solution. Furthermore, PEO is known to be stable with respect to hydrolysis even in highly acidic environment, as reported by Wojcik et al. (28). However, the PEO solution can be stabilized with respect to hydrolysis by a variety of agents such as isopropanol, ethylene glycol, and ethanol when they are present at 5 to 10% by volume, (based on total volume)
4.1.2. PREPARATION OF CERAMER SOLUTIONS.

a) The effect of pH on gelation time of ceramer solutions.

Gelation time data for ceramer solutions CG25 and C25, which contained about 25% silica equivalent and based on Polyox WSRN-10 polymer, are shown in Figure 4.2. The curves follow "S" shape behaviour, which is similar to the findings of Iler (19) for the condensation of colloidal silica and by Coltrain et al. (156) for the gelation of TEOS and TMOS in the presence of different acids, having different pKa values. Kioul (157) has also supported this finding in his study on polyimide-silica ceramers.

It is noted that gelation times for compatibilized ceramer, CG25 are much shorter than those are without compatibilization agent included. The maximum gelation time for the ceramer solution was observed near pH 2.1, and is attributed to the isoelectric point of silicate, as reported by Iler and Coltrain (19,156). A minimum in gelation time of ceramer solutions, against pH, is observed around pH 6. Iler has also observed a gelation time around pH 2 to 3 and a minimum near pH 6. The small differences from these experimental results were probably due to the alkoxy silane precursor and the catalyst used in this study.

b) The effect of maturation time on viscosity of ceramer solutions.

The ceramer solution, CG25, containing coupling agent, exhibit a large increase in viscosity after 3 hours maturation times at 60°C, followed by gelation as shown in Figure 4.3 (see page 111). This drastic jump in viscosity values compared to the other ceramer solution without coupling agent, which was associated with gelation could also be due to reactions taking place
between epoxy groups themselves in the presence of water and HCl leading to homopolymerization of GOTMS, as was proposed by Dislich [18]. It was also probably due to the condensation of silanol groups formed by hydrolysis of alkoxy silane groups on the silane molecules with epoxide group, if present, to form an alkoxy silane Si-O-R bond [158]. On the other hand, solution viscosities of all other ceramers did not change at all, even after 6 hours maturation time.

4.1.3. MORPHOLOGY OF CERAMERS.

a) The effect of silica content

Table 4.2 (see page 112) shows the effect of silica content on the optical appearance of the resulting ceramer films after drying and curing for 24 hours at 60°C, in an air circulating oven. It shows that increasing silica content produces greater transparency of the ceramer film. It was also noted that the incorporation of compatibilizing agent in the silica gives higher transparency to the ceramer films. Ceramer films without the coupling agent were opaque, indicating that precipitation of larger particles had occurred.

Conversion to silica was increased by treatment of the ceramer films at 120°C for 2 hours. The film appearance, however, did not change with respect to the corresponding dried ceramer. This indicated that the morphology of PEO-SiO₂ ceramer films developed during the drying and curing stages, did not change when heated further. However, most of the films appeared to be brittle and the degree of transparency was increased in comparison with ceramer films cured at 60°C.

The PEO-SiO₂ ceramer films were fractured in liquid nitrogen and observed by scanning electron microscope (SEM). Figure 4.4 (see page 120) shows the
ceramer films without coupling agent. It is observed that these films appeared to contain a particulate morphology having large diameters. It's seemed to have an agglomeration of particles, which explain why these films were opaque. In contrast, a co-continuous fine morphology was present in the PEO-SiO₂ ceramer films containing GOTMS coupling agent. Figure 4.5 (page 121) shows the morphology of compatibilized ceramers, for mixing time of 60 minutes at 60°C was very fine. The levels of transparency between them were increased as the silica content increased.

b) The effect of mixing time at 60°C.

Table 4.3 (see page 113) shows the effect of mixing time at 60°C on PEO-SiO₂ ceramer films optical appearance. It is revealed that by increasing the mixing time to more than three hours for compatibilized systems at 35% silica, resulted in the formation of opaque films, indicating precipitation of larger particles had taken places in the ceramer system.

Ceramer films without compatibilization were always opaque in their appearance. Therefore, it is concluded that the existence of a particulate morphology with particles having larger diameters was confirmed for visually opaque film as shown in the SEM analysis (Figure 4.6 in page 122). A co-continuous fine morphology of PEO-SiO₂ ceramer films is apparent in the ceramer CG35 (i.e. ceramer containing 35% w/w silica with GOTMS coupling agent) as shown in Figure 4.7a and Figure4.7b (page 123). However, greater than three hours mixing times, then agglomeration of particles was observed as shown in Figure 4.7c.
c) The effect of mixing temperature.

Table 4.4 (see page 114) shows the effect of mixing temperature on the optical appearance of the resulting ceramer films containing 35% w/w silica content. The formation of transparent ceramer films only appeared with the PEO-SiO$_2$ solutions containing GOTMS, when they were mixed at 60°C for an hour.

SEM image of the ceramer revealed that ceramer CG35 has developed a very fine morphology, which exhibited a high degree of co-continuity phase, as shown in Figure 4.9a in page 125. It was shown that the mixing for an hour was sufficient to impart a semi-IPN structure to the CG35 ceramer. Mixing the PEO-SiO$_2$ precursor solution above 60°C gave an opaque film due to large particles, as shown in Figure 4.9b and Figure 4.9c in page 125. This finding was in agreement with Mascia and Kioul ($^{144}$) and supported by Menoyo ($^{145}$) in their studies involving the production of polyimide-silica ceramers. On the other hand, ceramer C35 exhibited a particulate phase with coarsening in its structure as can be seen in Figure 4.8 (see page 124). Slightly better morphology for this ceramer was found, when the mixing temperature was 80°C.

d) The effect of the amount of epoxy coupling agent, GOTMS

Table 4.5 (see page 115) shows the effect of changing the TEOS: GOTMS molar ratios on the optical appearance of PEO-SiO$_2$ ceramer film (CG35) containing 35% w/w silica. It is noted that the optimum molar ratio of 1:0.12 between TEOS and GOTMS gives transparent ceramer films. This observation of the appearance of the films was in agreement with Mascia and Kioul ($^{82-83}$), and supported by Xenopoulos et al. ($^{159}$).
The morphologies observed by SEM analysis of the above ceramer films were similar with a very fine co-continuous structures. Figure 4.10 (see page 126) shows increases in the amount of GOTMS more than the threshold (0.12 molar ratio), to a greater amounts, has an effect on the ceramer films appearances. The ceramer films were became opaque due to an agglomeration of the particles, and hence the particle sizes of the system were increased to larger diameters. This finding was supported by the shorter gelation time of the ceramer solution, as shown in Figure 4.11 in page 127. The ceramer solutions were became cloudy during the mixing when the molar ratio between TEOS/GOTMS was greater than 0.12.

e) The effect of other coupling agents

The most significant role of coupling agents that make them necessary in the production of organic-inorganic hybrids is that of compatibilization, by means of miscibilising the components phases. Besides GOTMS, several coupling agents had been used, in order to find the most suitable coupling agents for the production of ceramer from water-soluble polymer of ethylene oxide. These were bis- (γ-trimethoxysilylpropyl) amine (i.e. Silane A1170), mercaptopropyltrimethoxysilane (i.e. Silane A 189) and phenylaminopropyltrimethoxysilane (i.e. Silane Y 9669).

There were two different methods of ceramer preparation. The addition of coupling agent to TEOS according to the formulation, as described in the Section 3.3, and by the addition of coupling agents to polymer precursor of PEO. The method of coupling agent incorporation in TEOS is the most favourable for compatibilization using GOTMS where in all cases; the ceramer films were transparent. The results had not been achieved with other coupling agents.
The addition of Silane A 1170 to TEOS resulted in the alkoxy silane precursor produces phase separation, which is due to the basic nature of the silane solutions. After hydrolysis of TEOS solution containing Silane A 1170 in 1: 0.12 molar ratio, the precipitation of small globules in the solution took place. Gelation of the solution was also immediately took place. Since the use of Silane A 1170 promoted almost an instant gelation of the alkoxy silane solution, the molecular structure of the bridge between the hydrolyzed alkoxy groups seemed to be less important, than the rapid gelation promoted by the co-condensation of those groups with neighbouring silane-terminated molecules.

The same observation was also made with Silane Y 9669. It was impossible to produce a ceramer solution with alkoxy silane solution containing 1: 0.12 molar ratio of TEOS: Y9669 due to a rapid gelation of the alkoxy silane solution. This rapid gelation was caused by the catalytic effect of Silane Y9669 in the condensation reaction of TEOS.

A reaction between GOTMS and CA was used in order to produce an acid functionalized derivative in the coupling agent. Two molar ratios were used as compatibilization agents, which were 1: 0.5 and 1: 0.25. The mixture was prepared by heating the appropriate amount of GOTMS and CA in a closed container at 60°C, with constant stirring for about 3 hours. Higher mixing temperature was not used due to polymerization reactions leading to gelation.

Table 4.6 (see page 116) shows the effect of a mixture of GOTMS-CA coupling agent on the optical appearance of PEO-SiO2 ceramer containing 35% w/w silica. All the films were opaque, indicating the existence of a particulate morphology, with particles having bigger diameters. By incorporation of GOTMS: CA mixture into silane solution, the agglomeration of particles took place, as shown in Figure 4.12 (see page 128). The
agglomeration of larger particles could have been due to the crystallization of PEO in the ceramer system as shown in the DSC analysis in Figure 4.27 in page 140.

f) The solvent effect on PEO-SiO$_2$ ceramers.

Table 4.7 (see page 117) shows the comparison on the optical appearances of the resulting PEO-SiO$_2$ ceramer films containing 35% w/w silica content prepared with different type of solvents for the PEO precursor i.e. water and THF. It can be seen that the ceramer films prepared using THF as a solvent, gave a better optical appearance and they were more transparent.

SEM images on these ceramer films (i.e. C50, C70, CG35, CG50 and CG70) have developed a very fine morphology, which exhibited a high degree of cocontinuity of phases, as shown in Figure 4.16 c, Figure 4.16 d, and Figure 4.17 a, b and c in pages 132 to 134 respectively. Ceramer films containing less than 35% w/w silica were opaque.

4.1.4. INTERACTION OF THE GOTMS COUPLING AGENT WITH CHLORENDIC ANHYDRIDE (CA)

a) Infrared spectroscopy study on GOTMS/CA interaction.

Figure 4.15 (see page 131) shows the FTIR spectra of the resulting solution between GOTMS and CA, reacted at 60°C for about 3 hours at molar ratios of 1:0.5 and 1:0.25 respectively. Both spectra show similar peaks and the only difference between them is the size of peaks, appear in the regions of 3500-2500cm$^{-1}$, 1800-1600cm$^{-1}$, 1400-1000cm$^{-1}$ and 1000-600cm$^{-1}$. These
differences were proportional to the molar ratio of GOTMS and CA in the solution.

In the spectral region between 1800 cm\(^{-1}\) and 1600 cm\(^{-1}\), two sharp and strong peaks could be observed respectively at 1751 cm\(^{-1}\) and 1604 cm\(^{-1}\), corresponding to the carbonyl stretching, C=O, and C-H stretching respectively. However, in the pure CA spectrum, these two peaks appeared to merge with each other. These differences between the spectra of the binary combinations of GOTMS/CA and that of pure GOTMS, can be attributed to the presence of the substitution of a halogen groups on the carbon molecules, that caused the C=O absorption bands to shift to slightly higher wave number location. Therefore, in this spectrum, the C=O absorption band was shifted from 1701 cm\(^{-1}\) to 1751 cm\(^{-1}\) as shown in Figure 4.15.

A broad peak at 3200-2500 cm\(^{-1}\) corresponded to the C-H stretching absorption as shown in Figure 4.13, of the CA has generated three clear and distinct peaks at 3500 cm\(^{-1}\), 2900 cm\(^{-1}\) and 2843 cm\(^{-1}\), as shown in Figure 4.15. These peaks correspond to aliphatic COOH absorption from the ring opening of the CA, the CH stretching of the aliphatic chain of GOTMS, Si-O-CH\(_3\) stretching from GOTMS.

The epoxy ring for GOTMS produced a strong broad band at 916 cm\(^{-1}\), as shown in Figure 4.14, but in the binary reacted system GOTMS/CA, only a combined broad peak at 821 cm\(^{-1}\) appeared, corresponding to O-Si-O stretching absorption. According to Comyn et al. \(^{(160)}\) the epoxy bands are reported in the regions 736-864 cm\(^{-1}\), 863-950 cm\(^{-1}\), and 1260 cm\(^{-1}\), but due to the multiplicity of bands that occur in these regions, band assignments are difficult. The possible reaction between the epoxy group of GOTMS and anhydride group of CA would have probably produced acid functionalized
derivatives (i.e. carboxylic acid), characterized by very strong peaks at 3500-3000cm$^{-1}$.

The OH stretching absorption from CA at 1604cm$^{-1}$ was more intense in the spectrum of GOTMS/CA binary solution with 1:0.5 molar ratio. The intensities of the other peaks such as C=O stretching absorption at 1753cm$^{-1}$, Si-O-Si stretching at 1195cm$^{-1}$ and 1089cm$^{-1}$, O-Si-O stretching at 821cm$^{-1}$ and also the stretching absorption of COOH groups at 3500-300cm$^{-1}$ resulted from the reaction between GOTMS and CA.

The functionalization of the GOTMS with CA, takes place through the ring opening of the anhydride group from the CA and the epoxide group of GOTMS to form acid functionalized carboxylic acid group, COOH. Infrared measurements showed that the epoxy band at 916cm$^{-1}$ for GOTMS, disappeared in the GOTMS/CA binary system (Figure 4.15), corresponds to the hydroxyl group OH, formed as a result of the epoxy ring opening during the reaction. The binary GOTMS/CA solution is became more viscous with higher molar ratio of CA, probably due to the reaction possibility of Step II taking place to form longer chains and COOH functionalized groups.

4.1.5. DIFFERENTIAL SCANNING CALORIMETRY (DSC).

Figure 4.18 and Figure 4.19 show the comparison on the effect of silica content on PEO-SiO$_2$ ceramer films (water as solvent), with and without compatibilization of GOTMS mixed at 60°C for one hour respectively. It can be observed that all the opaque ceramer films, presented a sharply defined melting peak. For the ceramer containing 35% w/w silica with GOTMS coupling agent, CG35 and CG50 ceramer films containing 50% w/w silica, the melting peak were disappeared. These two ceramer films were transparent.
With the ceramer film containing 50% silica but without coupling agent, C50, its appearance was opaque even though its melting peak was diminished. However, CG35 ceramer film was intact. On the other hand CG50 film was very brittle.

The melting peak was smaller, in comparison to the thermograms corresponding to PEO-SiO₂ ceramer films, containing silica without coupling agent, and instead a broad band was decreased.

Figure 4.20 and Figure 4.21 (see page 127) show the effect on the DSC thermograms of the mixing time on PEO-SiO₂ ceramer films heat treated at 60°C. These revealed that the two ceramer films, with and without GOTMS coupling agent, gave a totally different DSC thermograms. It was observed that the opaque ceramer films of C35, corresponding to particulate morphology, display a very broad band. On the other hand, the transparent ceramer film of CG35, displayed a smaller broad band in DSC thermograms. It was therefore concluded that ceramer films containing 35% w/w silica compatibilized with GOTMS, can be produced by mixing the PEO precursor and the alkoxysilane solutions at 60°C for one hour or less. One hour mixing time is gave the best results on ceramer films.

The opaque PEO-SiO₂ ceramer films, (i.e. without coupling agent), were compared to a clear ceramer film having an equivalent TEOS: GOTMS molar ratio equal to 1: 0.12 in the solution, heat treated at 60°C at different temperatures, is shown in Figure 4.22 and Figure 4.23 (see page 138). Opaque ceramer film showed a strong melting peak as compare to slightly smaller and broad peak exhibited by the transparent film.

The consequence of this experiment was to confirm that the presence of sharp endothermic peak, is always associated with an opaque PEO-SiO₂.
ceramer films. On the contrary, transparent PEO-SiO$_2$ ceramer films exhibited a small broader endothermic peak.

Figure 4.24 (see page 139) shows the effect of changing the TEOS: GOTMS molar ratios on the DSC thermograms of PEO-SiO$_2$ ceramer films, CG35. An increase in the amount of GOTMS to more than 0.12 molar ratio has an effect on the DSC thermogram peaks. The melting peak is increasing proportionally to the amount of GOTMS in the ceramer solutions. However, ceramer films containing more than 1:0.12 molar ratio of TEOS: GOTMS gives opaque films as shown in Table 4.5.

Figure 4.25 and Figure 4.26 (see pages 139 and 140) shows the effect of organic solvent on the DSC thermograms of PEO-SiO$_2$ ceramer films. Figure 4.27 (see page 140) shows the effect of binary coupling agent between GOTMS and CA on the DSC thermogram of PEO-SiO$_2$ ceramer films.

DSC tests were also used to investigate the effect of silica content in the PEO-SiO$_2$ ceramer films on melting point temperatures ($T_m$), heat of fusion ($\Delta H_{f100}$) and degree of crystallinity.

The degree of crystallinity ($X_c$) can be calculated by the following equation:

$$X_c = \frac{\Delta H_f \text{ sample} \times 100}{\Delta H_{f100}}$$  \hspace{1cm} (13)

Where $\Delta H_f$ is heat fusion of the ceramer film, $\Delta H_{f100} = 205 \text{ J/g}$ the heat fusion of 100% crystalline PEO $^{(161)}$. However, heat of fusion from the DSC thermograms need to be corrected in order to take into account for the presence of silica in the PEO-SiO$_2$ ceramer films.
\[ \Delta H_{\text{corrected}} = \frac{\Delta H_{\text{f sample}}}{\% \text{ PEO in the ceramer}} \]  

(14)

Therefore, the degree of crystallinity \((X_c)\) can be calculated by the following equation:

\[ X_c = \frac{\Delta H_{\text{corrected}} \times 100}{\Delta H_{f100}} \]  

(15)

It can be seen from Table 4.2 that the melting point temperature \((T_m)\) of the PEO-SiO\(_2\) ceramer films (with and without GOTMS coupling agent), decreases with increasing silica content. However, a significant reduction on the heat of fusion \((\Delta H_f)\) and the degree of crystallinity for both ceramers can be observed. The degree of crystallinity for PEO-SiO\(_2\) ceramer films without GOTMS coupling agent only decreased slightly with increasing silica content. Significant decreases in the degree of crystallinity can be observed in the ceramer films containing 50% w/w silica, as well as the compatibilized ceramer films containing even 35% w/w silica. The crystallinity was absent in ceramer films containing more than 50% w/w silica. From the above observation, it can be concluded that the degree of crystallinity of PEO-SiO\(_2\) ceramer films is disturbed significantly by the presence of GOTMS coupling agent.

A significant reduction in the heat of fusion and the degree of crystallinity can be observed on the PEO-SiO\(_2\) ceramer films containing GOTMS coupling agent, prepared with different mixing time at 60°C. On the other hand, PEO-SiO\(_2\) ceramer films without GOTMS coupling agent, were only slightly affected by the mixing time. Table 4.3 (see page 113) shows the effect of mixing time on melting point temperature, heat of fusion and the degree of crystallinity of PEO-SiO\(_2\) ceramer films.
From the above preparation conditions for PEO-SiO₂ ceramer films, it can be concluded that the melting point temperature of the compatibilized ceramer films with GOTMS coupling agent, had less effect than the uncompatibilized ceramer films.

Table 4.4 (see page 114) shows the effect of mixing temperature on melting point temperature, heat of fusion and the degree of crystallinity for PEO-SiO₂ ceramer films cured at 60°C for 24 hours. The melting point temperature, heat of fusion and the degree of crystallinity all increase with increasing the mixing temperature from 60°C to 80°C and 100°C. On the other hand; compatibilised PEO-SiO₂ ceramer films exhibit the opposite properties. The melting point temperature also decreased as the mixing temperature increased. However, both heat of fusion and degree of crystallinity were reduced significantly, compared to the ceramer without GOTMs coupling agent.

The amount of GOTMS coupling agent in the formulation of PEO-SiO₂ ceramer films plays a vital role in determining the melting point temperature and the degree of crystallinity of the ceramer as shown in Table 4.5 (see page 115). The molar ratio between TEOS and GOTMS at 1:0.12 is the optimum ratio to produce the ceramer films having a higher melting point temperature and heat of fusion. It also reduced significantly the degree of crystallinity of the ceramer films.

A significant reduction in the heat of fusion and the degree of crystallinity can be observed in the PEO-SiO₂ ceramer films containing GOTMS coupling agent, as shown in Table 4.2 (see page 112).
4.1.6. THERMOGRAVIMETRIC ANALYSIS (TGA).

a) PEO samples.

Figure 4.28 (see page 141) shows the thermogravimetric analysis for PEO resin dissolved in different types of solvents and undergone different treatments. It can be observed that the degradation of virgin PEO took place at a higher temperature, compared to the PEO dissolved in water or dissolved in THF. Both samples degraded at slightly lower temperature due to earlier degradation of the polymer during the heat treatment and drying processes. The solvent had removed the heat stabiliser from the PEO solution. It was also noticeable that some small ashes residues were left behind in the final burning process. This is probably due to the small amount of inorganic residues left from the original polymerisation of the PEO resin.

b) PEO-SiO₂ ceramer films.

Figure 4.29 (see page 142) shows the thermogravimetric analysis of particulate ceramer films. Initially, a progressive increase in weight loss from PEO film to the maximum content of silica in the PEO-SiO₂ ceramer films had took place. Some weight losses for all the ceramer films took place below 100°C due to the evaporation of solvents. The significant weight loss on the ceramer films took place at different temperatures, depending on the silica content. After the initial reduction in decomposition temperature caused by the presence of the PEO phase, the ceramer films containing higher amount of silica becomes more thermally stable.
On the other hand, compatibilised PEO-SiO₂ ceramer films exhibited different behaviour with respect to the thermal stability, as shown in Figure 4.30 (see page 143). It was observed that ceramer film containing a large amount of silica, started to lose weight earlier than that with a smaller silica content. This was a consequence of the condensation of silanol-silica group present in the dried film and the subsequent loss of water and other solvents. Thermal stability of ceramer films with 50% w/w silica was higher than that of PEO and other ceramer films containing less silica. This was probably due to the accumulated volatiles entrapped within the porous silica domains during the thermogravimetric analysis process was in progress at high temperature. Therefore, the rate of weight loss (degradation) is reduced as a result of the reduced diffusion of gases. The same phenomena were also observed with the ceramer films prepared using THF as solvent, for the PEO precursor as shown in Figure 4.31 and Figure 4.32 (see page 144 and 145 respectively).

Table 4.8 (see page 118) shows the measured weight losses between the initial weight losses started until full pyrolysis completed at about 600°C. From these data, we can estimate that the contribution of silica to the total weight of ceramer, by taking the residue at 600°C as silica content in the hybrid system.

The initial degradation of the ceramer does not vary much from sample to sample for both PEO-SiO₂ ceramers, prepared using water or THF as solvent for the PEO precursor. However, weight losses of the ceramer containing GOTMS coupling agent occurred at about 150°C, which is slightly lower than for the uncompatibilised ceramer system, which took place at about 160°C, as can be seen in Table 4.8. The more hygroscopic character of the binary sample containing GOTMS, could be responsible for the low temperature weight loss in the PEO-SiO₂ ceramer, through desorption of moisture. This finding is in agreement with the study done by Xenopoulos (145).
Both compatibilised and uncompatibilised PEO-SiO₂ ceramers displayed increasing thermal stability with the increase in the silica content.

4.2. SURFACE AREA MEASUREMENT.

Table 4.9 (page 119) shows the BET surface area for PEO-SiO₂ ceramer samples. Compatibilised PEO-SiO₂ ceramer samples exhibited higher BET surface area compared to uncompatibilised ones. Silica produced by hydrolysis and condensation of TEOS, displayed a similar trend with high BET surface area.

Transparent ceramers exhibit higher BET surface areas probably due to high energy adsorption sites, which can strongly interact with nitrogen probe molecules. Due to this, therefore, the gas molecules colliding with a surface unit area is more often due to increases in the population. This will results in the increase of the pressure of the system and hence, the amount of gas adsorbed onto the surface of the molecules was increased.
4.2. **BLENDS OF PEO-SiO$_2$ CERAMERS WITH OTHER POLYMERS.**

4.2.1. **BLENDS OF PEO-SiO$_2$ CERAMERS WITH PVC.**

*a) Differential Scanning Analysis (DSC).*

DSC analysis was carried out in order to investigate the miscibility of the blend components. Figure 4.33 and Figure 4.34 (see page 146) show the DSC thermogram of the PEO-SiO$_2$ ceramer blends with PVC, containing different amount of DOP plasticiser in the PVC phase. The degree of crystallinity of PEO decreased and became equal to zero when silica was present to form the corresponding ceramer. However, these blends produced opaque films due to the precipitation of the PEO-silica phase as large discrete particles, which were between 5 to 10 µm in diameter, as can be seen by the SEM and TEM analyses, and the micrographs in Figure 4.40 and Figure 4.41 respectively (see pages 153 to 156).

*b) Dynamic Mechanical Thermal Analysis (DMTA)*

Figure 4.35 (see page 147) shows the dynamic mechanical properties of the pure PEO, unplasticised-PVC (U-PVC) and plasticised-PVC (P-PVC) respectively. It was noted that the presence of DOP plasticiser in the PVC phase caused a decrease in storage modulus, as well as that of the glass transition temperature ($T_g$). Even the present of 20 pph DOP, $T_g$ was shifted from about 90°C to 53°C.

Figure 4.38 (see page 150) shows the dynamic mechanical properties of the PEO-SiO$_2$ ceramer blended with PVC, containing different amount of DOP plasticiser. The relative concentration of DOP in the PEO-SiO$_2$ ceramer phase and PVC, reflects that of the original plasticised PVC formulation used for
each ceramer composition. It is noted that the storage modulus and tan δ were shifted to lower temperatures, in proportion to the relative concentration of DOP plasticiser. It was revealed that the present of the PEO-SiO₂ ceramer phase in PVC phase, caused a decrease in storage modulus E’ of the system. Two broad transition peaks were observed for all blends with different amount of DOP plasticiser. However, at higher DOP contents, the blends display only one peak. Small shoulders were observed at slightly higher temperatures in blends containing less DOP plasticiser. Figure 4.39 (see page 152) shows the glass transition temperatures (T_g) for the blends.

The dispersion at higher temperature is associated with the α-peak of PVC, while the peak at the lower temperature was probably from the PEO in the PEO-SiO₂ ceramer phase. The β-transition of the PVC also appears at almost the same temperature with the tan δ of pure PEO. However, these peaks are superimposed on each other in the blend of PEO/PVC and also blends of PEO-SiO₂ ceramer/PVC, as shown in Figure 4.36 (see page 150). The intensity of the PEO peak decreases with the increasing amount of DOP in the blend. The magnitude of each peak is characteristic of the relative concentrations of PVC and PEO-SiO₂ ceramer. This behaviour is found whether the phases were dispersed or continuous (162-163). The curve of tan δ as a function of temperature, shows two peaks, each peak is characteristic of the glass transition temperature of one of the phases. The two glass transition temperatures are characteristic of immiscible two or three phase systems. Therefore, the PEO-SiO₂/PVC ceramer blend can be deemed to be immiscible or semi-miscible. This result is in agreement with the solvent-cast film appearance, which was opaque.

Similar behaviour was also observed for the PEO/PVC blends containing different amounts of DOP plasticiser. Figure 4.37 (see page 151) shows that both relaxation, the β-peak of PEO and the α-peak of PVC, persist, although
they move closer to each other. Overall, the spectra are characteristic of limited component miscibility. Broadening the relaxation was also observed, and this is usually attributed to local compositional inhomogeneity, i.e. mixed phases at the interphase. The same effect on $T_g$ was due to relative concentrations of PEO and PVC in the blend. The presence of PEO phase in PVC matrix also lead to lowering the glass transition temperature, as well as a reduction in the tan $\delta$ values. However, these blends produced higher storage modulus $E'$, as compared to the plasticised PVC. The PEO-PVC blends seemed to be miscible at higher DOP content (i.e. 60 pph DOP), where only one single $T_g$ was observed. This result is in agreement with the studies done by Margaritis et al. They concluded that the miscibility of the PVC/PEO blend could be achieved when the PEO content in the blend is relatively small.

The presence of DOP plasticiser in the PEO-SiO$_2$/PVC and PEO/PVC blends caused the decrease in glass transition temperatures $T_g$, compared to the blends without plasticiser. This can be seen in Figure 4.38 (A) (see page 151 respectively. The presence of silica in the blends does not effect the $T_g$. The glass transition temperature of the PEO-SiO$_2$/PVC blends without DOP plasticiser, is similar to the U-PVC, i.e: 90$^\circ$C as shown in Figure 4.38 (A). However, the presence of silica and with higher DOP plasticiser content in the blends, produced single glass transition temperature for the blends.

c) Scanning Electron Microscopy (SEM)

SEM micrographs of solvent cast films from the PEO/PVC blends, as shown in Figure 4.40 (see page 153 and 154), revealed slight morphology differentiation, such as the coarsening structure of the blends with increasing DOP plasticiser content. The two components form micro-domains. A coarse
structure was formed in all the blends. This result is in agreement with the studies by Margaritis et al. (164). They studied blends of high molecular weight PEO with PVC containing dibutyl tin dilaurate. They found out that at low PEO contents, the two components formed micro-domains and continuous interconnected phases. However, they revealed that phase separation and morphology differentiation occurred with increasing PEO content.

Totally different micrographs can be seen for the PEO-SiO₂/PVC ceramer blends, as shown in Figure 4.41 (see page 155 and 156). PEO-SiO₂ ceramer particles are embedded in the PVC matrix. These become increasingly more distinct as the DOP content was increased. All the films produced were opaque due to large particles of the ceramer inclusions, which were between 5 to 10 μm in diameter. The dispersive x-rays analysis carried out with SEM examination, revealed that the dominant element in the precipitated particles was silicon, as can be seen in Figure 4.46 (see page 161), indicating that the particles indeed contain silica domains. In the x-rays dispersive spectra, there are 3 major peaks, these are Cl from the PVC, Si from the PEO-SiO₂ ceramer and Au which was used in the coating the sample, for the purpose of SEM analysis.

d) Transmission Electron Microscopy Analysis (TEM)

The PEO-SiO₂ ceramer blends with PVC were subject to further morphological studies by TEM examinations. Comparing the morphologies in Figure 4.42 (see page 157 and 158), it is possible to see that an increase in the amount of DOP plasticiser in the blends, has the effect of coarsening the particles, as well as the areas of the encircled materials around the silica particles. The particle sizes have an average diameter between 6 to 10 μm, whereas the thickness of the shell around the particles is in the region of ~1μm.
e) Tensile Tests

Tensile tests were carried out on the PEO-SiO\(_2\) ceramer blends with PVC. Figure 4.43 (see page 159) shows a reduction in elongation at break of the PEO-SiO\(_2\) ceramer/PVC blends as compared to PEO/PVC blends. In all cases with increasing in the amount of DOP plasticiser, there is an increase in elongation at break. Furthermore, tensile strength and tensile modulus data are given, in Figure 4.44 and Figure 4.45 respectively (see pages 159 and 160). The tensile strength and tensile modulus of the PEO-SiO\(_2\) ceramer/PVC blends increased with increasing amounts of both PEO and SiO\(_2\).

f) Morphology stability of the PEO-SiO\(_2\)/PVC blends.

Figure 4.47 (see page 162) show the SEM micrographs of the PEO-SiO\(_2\) ceramer blends after being re-blended using Haake Rheocond 90 at 180°C, in order to examine the structure morphology stability of the blend for higher temperature processing. It was found out that the morphology of the blends was unaffected by the process temperature. The silica particles after melt blending, were similar to those shown in Figure 4.40 for solution processed blends.

4.2.2. BLENDS OF PEO-SiO\(_2\) CERAMERS WITH EPOXY RESIN.

a) Dynamic Mechanical Thermal Analysis (DMTA)

The presence of PEO-SiO\(_2\) ceramer inclusions in the epoxy resin shows a significant effect on the dynamic mechanical properties of the cured epoxy resin. It revealed that the ceramer phase caused an increase in the storage
modulus $E'$, as can be seen in Figure 4.48 (see page 163). Blend B, in which the amine curing agent was added after blending was completed, displayed a reduction in the storage modulus compared to blend A. Blend A represents the blend of PEO-SiO$_2$/epoxy, where the curing agent was added to the epoxy resin solution before the blending process was carried out. Blend B was opaque whereas Blend A was transparent. Both blends have a single glass transition temperature.

Figure 4.48 shows the viscoelastic behaviour of the PEO-SiO$_2$ ceramer/epoxy cured with aromatic amine. A single, sharp tan $\delta$ peak was identified for each cured blend, which corresponded to their glass transition temperatures. In addition to the major transition, a pronounced secondary transition usually designated as $\beta$-relaxation in the range of -100°C to 0°C, was also exhibited. The reinforcement provided by the presence of ceramer phase in epoxy matrix for blend B, lead to a reduction of the height of the tan $\delta$ peak at $T_g$, as well as a significant drop in $T_g$ from 150°C to 107°C. For Blend A, however, the presence of the ceramer phase in the resin caused a reduction of the $T_g$ from 152°C to 130°C.

b) Scanning Electron Microscopy Analysis (SEM).

Figure 4.49 (see page 164) shows the SEM micrographs of cured epoxy resin and blends of PEO-SiO$_2$ with epoxy resin (Epikote 828). Almost a similar feature that is observed in the cured epoxy resin appeared in Blend B. Distinct fracture line characteristic of brittle resins was found in Blend B, as can be seen in Figure 4.49b. Large particle size also appeared in the micrographs, measuring approximately between 4.0 to 8.0 µm in diameter, which was the reason why the films were opaque.
On the other hand, a fine co-continuous structure morphology can be seen in Blend A (Figure 4.49c). No dispersed particles were observed in the micrographs. However, distinct fracture lines characteristics of brittle resins were visible.

c) Transmission Electron Microscopy Analysis (TEM).

Figure 4.50 (see page 165) show the TEM micrographs of the cured epoxy resin for Blend A and Blend B. It was revealed that phase separation had taken place for Blend B, that had fairly large particles size. Phase separation was also observed in Blend A, but the particle size was much smaller compared to Blend B and hence it produced transparent films.
Figure 4.1: The effect of pH on the viscosity of PEO solution in water.

Figure 4.2: Gelation time of PEO-SiO$_2$ precursor ceramer solutions containing 25% (w/w) silica as a function of pH at 60°C.

C25 = formulations without coupling agent.
CG25 = formulation containing GOTMS coupling agent (TEOS/GOTMS=1.0:0.12 moles)
Figure 4.3: The effect of maturation time on viscosity of the PEO-SiO₂ precursor ceramer solutions

**Legend:**
- **PEO** = PEO solution dissolved in water
- **PEO/HCl** = PEO solution dissolved in water and acidified with HCl
- **C25** = Ceramer solution precursor without coupling agent
- **CG25** = Ceramer solution precursor with GOTMS coupling agent.
Table 4.2: The effect of silica content on films appearance, $T_m$, $\Delta H_f$ and degree of crystallinity ($\chi$) for PEO-SiO$_2$ ceramer films cast at 60°C and cured at 60°C for 24 hours (mixing time = 60 minutes)

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Silica content (%w/w)</th>
<th>Film appearance</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PEO</td>
<td>0</td>
<td>Opaque</td>
<td>68</td>
<td>95</td>
<td>46</td>
</tr>
<tr>
<td>a) C25</td>
<td>25</td>
<td>Opaque</td>
<td>62</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td>C35</td>
<td>35</td>
<td>Opaque</td>
<td>59</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>C50</td>
<td>50</td>
<td>Opaque</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>b) CG25</td>
<td>25</td>
<td>Opaque</td>
<td>65</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>CG35</td>
<td>35</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>CG50</td>
<td>50</td>
<td>Transparent</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

a) Formulation without GOTMS coupling agent
b) Formulations containing GOTMS coupling agent (TEOS:GOTMS = 1.00:0.12 Molar ratio)
c) N/A = not available i.e. Zero.
Table 4.3:  The effect of mixing time at 60°C before casting into films on appearance, $T_m$, $\Delta H_f$ and degree of crystallinity ($\chi$) for PEO-$SiO_2$ ceramer cast at 60°C, obtained from the PEO-$SiO_2$ solutions containing 35% silica cured at 60°C for 24 hours.

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Mixing time (minutes)</th>
<th>Solution appearance</th>
<th>Film appearance</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) C35</td>
<td>60</td>
<td>Transparent</td>
<td>Opaque</td>
<td>59</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>Transparent</td>
<td>Opaque</td>
<td>63</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>Transparent</td>
<td>Opaque</td>
<td>63</td>
<td>29</td>
<td>22</td>
</tr>
<tr>
<td>b) CG35</td>
<td>60</td>
<td>Transparent</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>Transparent</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>Cloudy</td>
<td>Opaque</td>
<td>55</td>
<td>24</td>
<td>18</td>
</tr>
</tbody>
</table>

a) PEO-$SiO_2$ ceramer films without GOTMS coupling agent
b) PEO-$SiO_2$ ceramer with GOTMS coupling agent.
Table 4.4: Effect of mixing temperature on films appearance, $T_m$, $\Delta H_f$ and degree of crystallinity ($\chi$) for PEO-SiO$_2$ ceramer cast at 60°C (35% w/w silica cured at 60°C for 24 hours, one hour mixing time).

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Mixing temperatures(°C)</th>
<th>Film appearance</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) C35</td>
<td>60</td>
<td>Opaque</td>
<td>59</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Opaque</td>
<td>61</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Opaque</td>
<td>64</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>b) CG35</td>
<td>60</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>Opaque</td>
<td>60</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Opaque</td>
<td>54</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

a) PEO-SiO$_2$ ceramer films without GOTMS coupling agent
b) PEO-SiO$_2$ ceramer with GOTMS coupling agent.
Table 4.5: Effect of the amount of GOTMS coupling agent on films appearance, $T_m$, $\Delta H_f$ and degree of crystallinity ($\chi$) for PEO-SiO$_2$ ceramer cast at 60°C, (35%w/w silica cured at 60°C for 24 hours (One hour mixing time at 60°C).

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Molar ratio of TEOS:GOTMS</th>
<th>Film appearance</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG$_{0.12}$ 35</td>
<td>1:0.12</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>CG$_{0.24}$ 35</td>
<td>1:0.24</td>
<td>Opaque</td>
<td>59</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>CG$_{0.36}$ 35</td>
<td>1:0.36</td>
<td>Opaque</td>
<td>54</td>
<td>14</td>
<td>11</td>
</tr>
</tbody>
</table>

PEO-SiO$_2$ Ceramer films containing 35%w/w silica with different molar ratios between TEOS and GOTMS.

a) CG$_{0.12}$ 35 = 1:0.12
b) CG$_{0.24}$ 35 = 1:0.24
c) CG$_{0.36}$ 35 = 1:0.36
Table 4.6: Effect of the amount of GOTMS/CA adduct coupling agent on films appearance, $T_m$, $\Delta H_f$, and degree of crystallinity ($\chi$) on PEO-SiO$_2$ ceramer cast at 60°C (35% w/w silica cured at 60°C for 24 hours, one hour mixing time at 60°C).

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Molar ratio of GOTMS:CA</th>
<th>Film appearance</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG 0.12 35</td>
<td>1:0.00</td>
<td>Transparent</td>
<td>63</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>CGCA 0.25 35</td>
<td>1:0.25</td>
<td>Opaque</td>
<td>59</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>CGCA 0.50 35</td>
<td>1:0.50</td>
<td>Opaque</td>
<td>54</td>
<td>17</td>
<td>13</td>
</tr>
</tbody>
</table>

CG 0.12 35 = PEO-SiO$_2$ Ceramer films containing GOTMS coupling agent (TEOS/GOTMS= 1: 0.12 moles)
CGCA 0.25 35 = PEO-SiO$_2$ Ceramer films containing GOTMS/Chlorendic Anhydride adduct (GOTMS/CA= 1: 0.25 moles)
CGCA 0.50 35 = PEO-SiO$_2$ Ceramer films containing GOTMS/Chlorendic Anhydride adduct (GOTMS/CA= 1: 0.50 moles)
Table 4.7: Effect of organic solvent on films appearance, $T_m$, $\Delta H_f$, and degree of crystallinity ($\chi$) on PEO-SiO$_2$ ceramer cast at 60°C, containing different amount of silica cured at 60°C for 24 hours, (THF used as solvent).

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Silica content (%w/w)</th>
<th>Film appearance</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H_f$ (Joule/g)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C25</td>
<td>25</td>
<td>Opaque</td>
<td>61</td>
<td>62</td>
<td>41</td>
</tr>
<tr>
<td>C35</td>
<td>35</td>
<td>Opaque</td>
<td>53</td>
<td>26</td>
<td>19</td>
</tr>
<tr>
<td>C50</td>
<td>50</td>
<td>Opaque</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>C70</td>
<td>70</td>
<td>Transparent</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CG25</td>
<td>25</td>
<td>Translucent</td>
<td>62</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CG35</td>
<td>35</td>
<td>Transparent</td>
<td>61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CG50</td>
<td>50</td>
<td>Transparent</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>CG70</td>
<td>70</td>
<td>Transparent</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

a) C25 = PEO-SiO$_2$ ceramer film containing 25% w/w silica without coupling agent.
b) CG25 = PEO-SiO$_2$ ceramer film containing 25% w/w silica with GOTMS coupling agent
c) N/A = not available i.e. zero.
Table 4.8: Thermogravimetric Analysis data for PEO-SiO$_2$ Ceramers.

<table>
<thead>
<tr>
<th>Ceramer samples</th>
<th>Initial Weight loss $T_i$(°C)</th>
<th>Weight loss at ~600°C $W_i$ (%)</th>
<th>% Residue at 600°C (regarded as silica content of the ceramer)</th>
<th>Theoretical silica content (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water as solvent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C25</td>
<td>159</td>
<td>94</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>C35</td>
<td>158</td>
<td>95</td>
<td>31</td>
<td>35</td>
</tr>
<tr>
<td>C50</td>
<td>159</td>
<td>94</td>
<td>43</td>
<td>50</td>
</tr>
<tr>
<td>CG25</td>
<td>149</td>
<td>100</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>CG35</td>
<td>151</td>
<td>97</td>
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<td>35</td>
</tr>
<tr>
<td>CG50</td>
<td>150</td>
<td>97</td>
<td>48</td>
<td>50</td>
</tr>
<tr>
<td><strong>THF as solvent</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C25</td>
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<td>97</td>
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<td>C35</td>
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<td>96</td>
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<td>35</td>
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<tr>
<td>C50</td>
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<td>95</td>
<td>43</td>
<td>50</td>
</tr>
<tr>
<td>C70</td>
<td>225</td>
<td>92</td>
<td>65</td>
<td>70</td>
</tr>
<tr>
<td>CG25</td>
<td>149</td>
<td>100</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>CG35</td>
<td>151</td>
<td>97</td>
<td>33</td>
<td>35</td>
</tr>
<tr>
<td>CG50</td>
<td>153</td>
<td>97</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>CG70</td>
<td>213</td>
<td>95</td>
<td>68</td>
<td>70</td>
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Table 4.9: BET Surface Area of the PEO-SiO₂ Ceramers

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m²/g)</th>
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<tbody>
<tr>
<td>TEOS</td>
<td>135</td>
</tr>
<tr>
<td>TEOS/GOTMS</td>
<td>192</td>
</tr>
<tr>
<td>C35</td>
<td>784</td>
</tr>
<tr>
<td>CG35</td>
<td>898</td>
</tr>
</tbody>
</table>

TEOS = Hydrolysed Tetraethylorthosilicate
TEOS/GOTMS = Hydrolysed TEOS containing GOTMS coupling agent
C35 = PEO-SiO₂ ceramer without coupling agent.
CG35 = PEO-SiO₂ ceramer with GOTMS coupling agent.
Figure 4.4: Scanning electron micrographs for non-compatibilised PEO-SiO$_2$ ceramer films cured at 60°C for 24 hours, silica content (%w/w) of (a) 25% (b) 35% and (c) 50% (precursor solutions matured at 60°C for one hour).
Figure 4.5: Scanning electron micrographs for compatibilised PEO-SiO$_2$ ceramer films (containing TEOS/GOTMS with 1:0.12 molar ratio) cured at 60°C for 24 hours, silica content (%w/w) of (a) 25% (b) 35% and (c) 50% (precursor solutions matured at 60°C for one hour.)
Figure 4.6: Scanning electron micrographs for cured PEO-SiO₂ ceramer films containing 35% w/w silica produced from precursor solutions matured at 60°C for (a) 1 hour (b) 3 hours and (c) 5 hours.
Figure 4.7: Scanning electron micrographs for PEO-SiO₂ ceramer films with 35% w/w silica (containing TEOS/GOTMS with 1:0.12 molar ratio) produced from precursor solutions matured at 60°C for (a) 1 hour (b) 3 hours and (c) 5 hours.
Figure 4.8: Scanning electron micrograph for cured PEO-SiO$_2$ ceramer films containing 35% w/w silica produced from precursor solutions mixed for one hour at (a) 60°C (b) 80°C and (c) 100°C.
Figure 4.9: Scanning electron micrograph for cured PEO-\(\text{SiO}_2\) ceramer films containing 35% w/w silica produced from precursor solutions with molar ratio of 1:0.12 between TEOS/GOTMS mixed for one hour at (a) 60°C (b) 80°C and (c) 100°C
Figure 4.10: Scanning electron micrograph for cured PEO-SiO\textsubscript{2} ceramer films containing 35\% w/w silica produced from precursor solutions mixed at 60\(^\circ\)C for one hour containing different molar ratio between TEOS/GOTMS (a) 1:0.12 (b) 1:0.24 and (c) 1:0.36
Figure 4.11: Effect of the amount of TEOS/GOTMS molar ratio on the gelation time of PEO-SiO₂ ceramer solution containing 25% w/w silica heat treated at 60°C for one hour.
Figure 4.12: Scanning electron micrograph for cured PEO-SiO₂ ceramer films containing 35% w/w silica produced from precursor solutions, mixed at 60°C for one hour containing different molar ratio between GOTMS/CA adduct (a) 1:0.25 and (b) 1:0.5
Figure 4.13: FTIR spectra of Chlorendic Anhydride (CA)

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C=O stretching vibration</td>
<td>Two strong bands at 1701 cm(^{-1}) and 1601 cm(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>C-O-C stretching vibration</td>
<td>Strong absorption between 1332-1064 cm(^{-1}).</td>
</tr>
<tr>
<td>3</td>
<td>C-O-C stretching vibration</td>
<td>Additional strong absorption due to the five-membered cyclic anhydride at 895 cm(^{-1}).</td>
</tr>
<tr>
<td></td>
<td>C-Cl stretching vibration</td>
<td>736 cm(^{-1})</td>
</tr>
<tr>
<td>4</td>
<td>C-H stretching</td>
<td>3000 cm(^{-1})</td>
</tr>
</tbody>
</table>
Figure 4.14: FTIR spectra for the pure solution of GOTMS coupling agent.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Assignments</th>
<th>Wavenumber(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si-O-C aliphatic group</td>
<td>Strong peak at 1089 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Si-O-Si stretching</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si-CH(_3) aliphatic group</td>
<td>1194 cm(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>Si-C stretching absorption</td>
<td>1467 cm(^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>O-Si-O stretching vibration</td>
<td>821 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Epoxy stretching</td>
<td>910 cm(^{-1})</td>
</tr>
<tr>
<td>4</td>
<td>C-H aliphatic stretching</td>
<td>2943 cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Si-O-CH(_3) stretching</td>
<td>2843 cm(^{-1})</td>
</tr>
</tbody>
</table>
Figure 4.15: FTIR spectra for the resulting solutions between GOTMS/CA, heat treated at 60°C for 3 hours with different molar ratio (a) 1:0.25 and (b) 1:0.50.
Figure 4.16: Scanning Electron Micrograph for non-compatibilized PEO-SiO$_2$ ceramer films cured at 60°C for 24 hours. Silica content (%w/w): (a) 25% (b) 35% (c) 50% and (d) 70% produced from precursor solutions matured at 60°C for one hour. THF was used as solvent for the PEO precursor.
Figure 4.17: Scanning Electron Micrograph for compatibilized PEO-SiO$_2$ ceramer films (containing TEOS/GOTMS with 1:0.12 molar ratio) cured at 60°C for 24 hours. Silica content (%w/w): (a) 25% (b) 35% (c) 50% and (d) 70% produced from precursor solutions matured at 60°C for one hour. THF was used as solvent for the PEO precursor.
Figure 4.18: DSC thermogram for cured PEO-SiO₂ ceramer films (without GOTMS coupling agent). Silica content (%w/w): (a) 0% (Pure PEO with acid treatment) (b) 25% (c) 35% and (d) 50% produced from precursor solutions matured at 60°C for one hour.

Figure 4.19: DSC thermogram for cured PEO-SiO₂ ceramer films (containing GOTMS coupling agent). Silica content (%w/w): (a) 0% (Pure PEO with acid treatment) (b) 25% (c) 35% and (d) 50% produced from precursor solutions matured at 60°C for one hour.
Figure 4.20: DSC thermogram for cured PEO-SiO$_2$ ceramer films (without GOTMS coupling agent) formulated to have 35% final silica content (%w/w), precursor solutions mixed at 60°C for (a) 1 hour (b) 3 hour and (c) 5 hours.

Figure 4.21: DSC thermogram for cured PEO-SiO$_2$ ceramer films (with GOTMS coupling agent) formulated to have 35% final silica content (%w/w), precursor solutions mixed at 60°C for different times (a) 1 hour (b) 3 hour and (c) 5 hours.
Figure 4.22: DSC thermogram for cured PEO-SiO$_2$ ceramer films (without GOTMS coupling agent) formulated to have 35% final silica content (%w/w). Precursor solutions mixed for one hour at (a) 60°C (b) 80°C and (c) 100°C.

Figure 4.23: DSC thermogram for cured PEO-SiO$_2$ ceramer films (with GOTMS coupling agent) formulated to have 35% final silica content (%w/w). Precursor solutions mixed for one hour at (a) 60°C (b) 80°C and (c) 100°C.
Figure 4.24: DSC thermogram for cured PEO-SiO₂ ceramer formulated to have 35% final silica content (%w/w) with different molar ratio of TEOS/GOTMS in the precursor solutions mixed for one hour at 60°C (a) 1:0.12 (b) 1:0.24 and (c) 1:0.36.

Figure 4.25: DSC thermogram for cured PEO-SiO₂ ceramer films (without GOTMS coupling agent) formulated to have different amount of silica content (%w/w) prepared from ceramer solutions precursors dissolved in THF mixed for one hour at 60°C (a) Pure PEO (b) 25% (c) 35% (d) 50% and (e) 70%.
Figure 4.26: DSC thermogram for cured PEO-SiO$_2$ ceramer films (with GOTMS coupling agent) formulated to have different amount of silica content (%w/w) prepared from precursor solutions in THF mixed for one hour at 60°C: (a) 25% (b) 35% (c) 50% and (d) 70%.

Figure 4.27: DSC thermogram for cured PEO-SiO$_2$ ceramer films (with GOTMS coupling agent) formulated to have 35% silica (%w/w) prepared from precursor solutions mixed for one hour at 60°C with different molar ratio of (a) 1:0.12 TEOS/GOTMS (b) 1:0.25 GOTMS/CA and (c) 1:0.50 GOTMS/CA.
Figure 4.28: Thermogravimetric curves for (a) Pure PEO (b) PEO dissolved in water (acid treated) and (c) PEO dissolved in THF. Test conducted in an air atmosphere (I) Linear weight (II) Derivative weight variation with temperature.
Figure 4.29: Thermogravimetric curves for cured PEO-SiO$_2$ ceramer films (without GOTMS coupling agent) formulated to have different amount of silica content (%w/w). Prepared from precursor solutions mixed for one hour at 60°C (a) PEO in H$_2$O (b) 25% (c) 35% and (d) 50%. Test conducted in an air atmosphere (I) Linear weight (II) Derivative weight variation with temperature.
Figure 4.30: Thermogravimetric curves for cured PEO-SiO₂ ceramic films (with GOTMS coupling agent) formulated to have different amount of silica content (% w/w) (a) PEO in H₂O (b) 25% (c) 35% and (d) 50%, prepared from precursor solutions mixed for one hour at 60°C. Test conducted in an air atmosphere (I) Linear weight variation with temperature.
Figure 4.31: Thermogravimetric curves for cured PEO-SiO₂ ceramer films (without GOTMS coupling agent) formulated to have different amount of silica content (% w/w) (a) 25% (b) 35% (c) 50% and (d) 70%, prepared from precursor solutions, mixed for one hour at 60°C. Precursors were dissolved in THF. Test conducted in an air atmosphere (I) Linear weight (II) Derivative weight variation with temperature.
Figure 4.32: Thermogravimetric curves for cured PEO-SiO₂ ceramer films (with GOTMS coupling agent) formulated to have different amount of silica (%w/w): (a) 25% (b) 35% (c) 50% and (d) 70%, prepared from precursor solutions, mixed for one hour at 60°C. Precursors were dissolved in THF. Test conducted in an air atmosphere (I) Linear weight (II) Derivative weight variation with temperature.
Figure 4.33: DSC thermograms for the (a) Pure PEO, (b) PEO/PVC Blend (50:50 w/w \%) and (c) PEO-SiO$_2$ ceramics/PVC blends containing different amount of DOP plasticiser.

Figure 4.34: DSC thermograms for (a) Plasticised PVC (20pph DOP) and PEO-SiO$_2$ ceramer/PVC blends containing (b) 0 pph (c) 20pph (d) 40 pph and (e) 60 pph DOP plasticiser.
Figure 4.35: DMTA spectra of (a) Pure PEO, (b) Unplasticised PVC and (c) Plasticised PVC (20pph DOP)
Figure 4.36: Detail of the DMTA spectra of (a) Pure PEO (b) Unplasticised PVC and (c) Plasticised PVC (20pph DOP).
Figure 4.37: PEO/PVC blends with different amount of DOP plasticiser (a) 0 pph (b) 20 pph (c) 40 pph and (d) 60 pph
Figure 4.38: PEO-SiO$_2$ ceramer/PVC blends with different amount of DOP Plasticiser
(a) 0 pph (b) 20 pph (c) 40pph and (d) 60pph
Figure 4.38 (A): Tan delta of (a) PEO/PVC- without DOP (b) PEO-SiO$_2$/PVC-without DOP (c) PEO/PVC-40pph DOP and (d) PEO-SiO$_2$/PVC-40pph DOP in the blends.

Figure 4.38 (A): Tan delta of (a) PEO/PVC- 20pph DOP (b) PEO-SiO$_2$/PVC-20pph DOP (c) PEO/PVC-60pph DOP and (d) PEO-SiO$_2$/PVC-60pph DOP in the blends.
Figure 4.39: Glass transition temperature ($T_g$) of the PEO/PVC blends and PEO-SiO$_2$/PVC ceramer blends with different amount of DOP Plasticiser.

PEO/PVC = Blend of PEO and PVC containing different amount of DOP plasticiser
PEO-SiO$_2$/PVC = Blend of PEO-SiO$_2$ ceramer with PVC containing different amount of DOP Plasticiser and 25% SiO$_2$. 

\[
\begin{align*}
\text{Glass Transition Temperatures (C)} & \\
\text{DOP Content (pph)} & \\
0 & 10 & 20 & 30 & 40 & 50 & 60 & 70
\end{align*}
\]
Figure 4.40: Scanning electron micrograph for PEO/PVC Blend (50:50 %w/w) with different amount of DOP Plasticiser (a) 0 pph (b) 20 pph (c) 40 pph and (d) 60 pph
Figure 4.41: Scanning electron micrographs for the PEO-SiO₂ ceramer/PVC blend with different amount of DOP Plasticiser a) 0 pph (b) 20 pph (c) 40 pph and (d) 60 pph
Figure 4.42: TEM micrographs for the PEO-SiO_{2}/PVC Blends (a) without DOP (b) 20pph DOP (c) 40pph DOP and (d) 60pph DOP
Chapter 4: Results

(c) 200nm

(d) 200nm
Figure 4.43: Comparison of elongation at break for the PVC/PEO blends and PVC/PEO-SiO$_2$ ceramer blends with different amount of DOP plasticiser content.

![Graph showing elongation at break vs. DOP content](image)

Figure 4.44: Comparison of tensile strength of the PVC/PEO blends and PVC/PEO-SiO$_2$ ceramer blends with different amount of DOP plasticiser content.

![Graph showing tensile strength vs. DOP content](image)
Figure 4.45: Comparison of tensile modulus of the PEO/PVC blends and PEO-SiO$_2$ ceramer/PVC blends with different amount of DOP plasticiser.
Figure 4.46: Dispersive x-rays analysis of the PEO-SiO₂/PVC Ceramer Blends.

Si = Silicone peak from the PEO-SiO₂ ceramer
Au = Gold peak from the thin layer of gold sputtered on the specimen and,
Cl = Chlorine peak from PVC.
Figure 4.47: SEM micrographs of PEO-SiO$_2$ ceramer blend with PVC in Haake Rheocord 90 at 180°C for 20 minutes (a) low magnification and (b) high magnification.
Figure 4.48: DMTA spectra of PEO-SiO₂ ceramer blend with Epoxy cured at 60°C for 24 hours followed by 150°C for 3 hours (a) Cured Epoxy Resin (b) Blend A and (c) Blend B
Figure 4.49: Scanning electron micrograph of PEO-SiO<sub>2</sub> ceramer blend with epoxy cured at 60°C for 24 hours followed by 150°C for 3 hours (a) Cured Epoxy Resin (b) Blend B and (c) Blend A.
Figure 4.50: Transmission electron micrographs of PEO-SiO2 ceramer blend with Epoxy cured at 60°C for 24 hours followed by 150°C for 3 hours (a) Cured Epoxy Resin (b) Blend B and (c) Blend A.
CHAPTER 5

DISCUSSION

5.1. PEO-SiO$_2$ CERAMERS.

5.1.1. Gelation of the PEO-SiO$_2$ precursor solutions

Gelation of the PEO-SiO$_2$ precursor solutions, yielding 25% (w/w) silica in the final product, was studied at 60°C as a function of pH. This produced an S-shaped curve similar to that reported by Iler (19) and also by Coltrain et al. (156), for the condensation of colloidal-silica, for the gelation of TEOS and TMOS in the presence of acids having different pKa values. This phenomenon has also been reported by Kioul and Mascia (157) in their study on polyamide-silica ceramers.

In the PEO-SiO$_2$ ceramer solutions, the maximum gelation was observed at pH 2.1, is attributed to the isoelectric-point (IEP) of silicates (19,156). The IEP is defined as the point where there is no electrical mobility of silica particles in the system, which corresponds to the silanol monomers reacting at the slowest rate among themselves to form dimers. A gelation time for the PEO-SiO$_2$ ceramer solutions was observed at pH 6. Iler has also observed a maximum gelation time at around pH 2 to 3 and a minimum near pH 6, for TEOS solution without PEO. The small differences from the results of this study were probably due to the alkoxyisilane precursor and the catalyst used in this study.

It was noted that the gelation time for compatibilized ceramer solutions CG25 was much shorter, than the values obtained without compatibilization agent in the formulations. However, the positions of the maximum in relation to pH had
not changed. The addition of GOTMS coupling agent only accelerated the gelation process, but did not alter the mechanism. The gel time decreased with the addition of GOTMS, up to the amount corresponding to a pH at 2.1. Comparing the curves for the PEO-SiO₂ ceramer solutions with and without GOTMS coupling agent, uncompatibilized ceramer solutions were much slower to gel, as shown in Figure 4.2.

Compatibilized ceramer solutions tend to gel faster due to the involvement of the epoxy GOTMS coupling agent. Since the ceramer solution was acidic, there was a possibility of acid catalyzed hydrolysis of the epoxide group in the GOTMS, via ring opening reactions (165-168) to form 1,2 diols. This was possible even at room temperature with a pH of 1 (167), or at moderately high temperatures, around 90°C with a pH of 3.5 (168). These conditions were approximately those at the initial and intermediate stages of the reactions in this experimental procedures. Polyaddition of the diol phase to form poly (glycol ethers), with or without participation of unhydrolyzed epoxide groups could also take place to different degrees. However, the possible homopolymerization of the epoxy groups in GOTMS, was probably the factor for the increase in viscosity, which can slow down the rate of phase separation in the PEO-SiO₂ ceramer system. This has been suggested by Mascia and Kioul (169) in their studies involving the PMDA-ODA/TEOS-derived silica system. Interactions of the GOTMS coupling agent, which enabled it to act as a link between the organic and inorganic components, has also been discussed by those authors. It is also possible that the 1,2 diols could have reacted with =Si-(OCH₃) to form a hybrid network.
Dislich (19) had proposed a reaction path for epoxy group in GOTMS in the presence of water and acid catalysts as shown below:

\[
\begin{align*}
\text{CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3\text{-Si(OCH}_3\text{)}_3 & \quad \text{(a)} \\
& \xrightarrow{\text{H}^+\text{/H}_2\text{O}} \\
\text{CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3\text{-Si(OH)}_3 & \quad \text{(b)} \\
\text{OH} & \quad \text{OH} \\
& \xrightarrow{} \\
\text{CH-CH}_2\text{-O-CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3\text{-Si(OH)}_3 & \quad \text{(c)} \\
\text{OH} & \quad \text{OH} \\
& \xrightarrow{} \\
\text{CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3\text{-O-Si(OH)}_2\text{-O-CH}_2\text{-CH-CH}_2 & \quad \text{(d)} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

Adhesion mechanisms between silane coupling agents and polymeric matrices have been proposed by Pleuddmann (50). The silane coupling agents act at the interface between inorganic and organic materials to bond together, as shown in Figure 2.5. Mascia et al. (170) discovered that silane-grafted polyolefins exhibited a strong adhesion towards epoxy resins. Therefore, it
can be suggested that strong interactions or chemical reactions are possible between silanol and epoxy groups, as shown in reaction (d) above.

Since water was used to dissolve the PEO resin in the ceramer preparation, an excess of water was present in the ceramer system. Therefore, full hydrolysis of the TEOS presented more opportunities for interaction between silanol groups in the silica and ether oxygen on the PEO solution through hydrogen bonding. This hypothesis is supported by the findings of Wojcik et al. (28) in their studies on the effect of water-to-alkoxy ratio on the final structure of the PEO-Silica hybrid. They found that the skeletal density for the PEO-silica hybrids containing more water-to-alkoxy ratio, was increased with the increasing PEO content and decreased for the system with less water.

In the light of the above facts, therefore, it can be deduced that the overall gelation rate of the PEO-SiO<sub>2</sub> ceramer solution containing GOTMS coupling agent, should become greater with higher concentration of the coupling agent. The fact that in this work, for the standard molar ratio of 1:0.12 GOTMS:TEOS, the gelation time was actually increased rather than decreased, with respect to the pH of the ceramer solution. A minimum gelation time was observed at the initial pH at 2. A possible explanation for this observation is that for GOTMS, the molar concentration of 0.12 in the solution was at a critical point, below which the GOTMS was likely to affect the gelation rate by homopolymerization and interacting with the rest of the solution. Therefore, the solution viscosities increased.

Following this argument, for greater than the standard molar ratio of 0.12 for TEOS: GOTMS, the effectiveness of the coupling agent would be compromised by the fact that the catalysts that promote the homopolymerization reaction, would be diminished. The amount of GOTMS that did not actively take part in the sol-gel reaction (171-172) or polymerize (173),
would act as a diluent within the reaction medium, and so would decrease the rate of reaction. Based on this, it may be predicted that a further increase in the GOTMS concentration in the ceramer system, could lead to a decrease in gelation time because of dilution.

5.1.2. Viscosity of the ceramer solutions.

Ceramer solution CG25 (i.e. which contained GOTMS coupling agent and 25% w/w silica), exhibited a large increase in viscosity after 3 hours maturation time at 60°C, followed by gelation, as shown in Figure 4.3. It is noted in Figure 4.3 that all ceramer solutions and PEO displayed a minimum viscosity at around 1 hour maturation time. On the other hand, virgin PEO and PEO solutions containing water and HCl displayed an almost constant viscosity (i.e. plateau), throughout the six hours maturation time. No changes in the viscosity for both solutions were observed due to PEO solution stability with respect to hydrolysis, even in highly acidic conditions.

Uncompatibilized PEO-SiO₂ ceramer C25, (i.e. containing 25% w/w silica) displayed only a very small increase in the viscosity during maturation, which was probably due to solvent loss. For ceramer solutions, condensation reactions of some silanol groups probably also contributed to the viscosity increases.

The compatibilized ceramer solution CG35, (i.e. containing epoxy-coupling agent GOTMS) showed a large increase in viscosity, compared to ceramer solutions without compatibilization. This could be due to a reaction taking place between epoxy groups in the presence of water and HCl, leading to homopolymerisation of GOTMS. Thomas et al. (158) found that the epoxy functionality of GOTMS readily undergoes hydrolysis in acidic solutions to
form principally a solution of vicinal diol and silanol groups. The reaction of GOTMS in acid may also lead to the formation of enols, alkenes, low concentrations of carbonyl compounds ether, due to molecular condensation between diols. The silanol groups formed by the hydrolysis of the alkoxysilane groups on the silane molecules, can also condense with epoxide groups, if present, to form an alkoxysilane Si-O-R bond \((174-178)\). The Si-O-R bond for long chain organic group R, has been found to be relatively stable in water compared to that Si \((OCH_3)_3\) group, due to steric effects. The general chemical reactivity of epoxides towards other functional groups has been review by several authors \((179-181)\), including the reactivity to silanol groups. Relative reaction rates towards epoxy groups has been summarised as \(RSH>RNH_2>R_2NH>RCOOH>SiOH>>ROH>H_2O\) \((174-182)\).

The condensation reaction of GOTMS resulting in homopolymerization has also proposed by Dislich \((18)\):

\[
\begin{align*}
\text{CH}_2\text{-CH-CH}_2\text{-O} \quad \text{(CH}_2\text{)}_3\text{-Si(OCH}_3)_3 \\
\text{O} \\
\text{H}^+/\text{H}_2\text{O} \\
\text{CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3\text{-Si(OH)}_3 \\
\text{OH} \quad \text{OH} \\
\text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O} \\
\text{CH}_2 \\
\text{O} \\
\text{(CH}_2\text{)}_3 \\
\text{Si} \\
\text{CH}_2 \\
\text{O} \\
\text{(CH}_2\text{)}_3 \\
\text{Si}
\end{align*}
\]
5.1.3. PEO-SiO$_2$ ceramer morphology

The GOTMS/PEO interaction leading to the PEO-SiO$_2$ ceramer compatibilization, was one of the objectives of this study. The presence of GOTMS coupling agent in the TEOS solution, together with the heat treatment of the ceramer solution for a certain period of time, has previously been found to be essential for the compatibilization of the polyamide-silica ceramers (82,157,169). Therefore, it could be necessary to study the same effect on the PEO-SiO$_2$ ceramer systems, in order to gain a better understanding of the compatibilization mechanism of these systems. Apart from the scientific interests in gaining a better understanding of the compatibilisation mechanism, there are few other reasons for this. All grades of PEO resins, for instance, are completely soluble in water. However, at higher temperatures, PEO resin precipitate from solution. The precipitation temperature depends upon the concentration of the polymer in solution and upon the molecular weight of the polymer, as can be seen in Figure 2.6.

The procedure for the production of the PEO-SiO$_2$ ceramer had to be optimised in terms of time, temperature and the amount of GOTMS coupling agent for the compatibilization.

a) The effect of silica content.

Table 4.2, shows that the transparency of the PEO-SiO$_2$ ceramer film increased with increasing silica content in the systems. This is attributed to hydrogen bonding interactions between the PEO and silica domains in the ceramer systems, containing GOTMS coupling agent. This evidence is supported by differential scanning analysis, as can be seen in Figure 4.19. It is noted that the melting peak of PEO does not appear for the PEO-SiO$_2$...
ceramer samples containing PEO less than 50%, denoting the complete absence of crystallization. For the PEO-SiO₂ ceramer containing more than 50% PEO (or less silica), a well defined PEO melting peak appeared, indicating that a fair amount of PEO was not associated to the silica phase, forming PEO crystalline domains. Due to the presence of large amounts of PEO in the system, there were no sufficient sites for hydrogen bonding in the silica, and therefore crystallization took place. The agglomeration of larger particles from the crystalline phase of PEO, was the reason why the films were opaque. The melting peak for PEO-SiO₂ ceramer without GOTMS coupling agent is quite pronounced, as shown on Figure 4.18.

In the PEO- SiO₂ ceramer, prepared using water as solvent for the PEO precursor, adsorption of PEO involved a competition between H₂O and -(CH₂-CH₂-O- CH₂-CH₂) unit for the silica surface sites. Rubio et al. (183) suggested that isolated silanol groups provide the best adsorption sites, acting as proton donors in hydrogen bonding to ether oxygens.

\[
\text{\hspace{1cm} -Si-OH \quad \text{\rightarrow} \quad O-(CH₂-CH₂)}
\]

Howard and McConnell (184) also suggested this hypothesis for low molecular weight PEO, and also Fontana (185) for a copolymers of ethylene oxide and methyl methacrylate. Klein et al. (186) have also found out in their studies of the mechanical properties of soluble polymer (PEO)/silica hybrids, that the interactions between the polymer and the silica network occur largely through hydrogen bonding between ether oxygen in PEO and silanols. Nor should it be excluded, that there is a possibility at the high silica contents in the ceramer system, will produce more silanol groups, (brought together for condensation reaction), thus forming networks which will more readily entrap PEO chains, to produce IPN system. These findings were supported by the work of Nakhisi and Soga (187) for their studies on the morphology of
polyacrylic acid (HPAA)-silicate (based on TEOS) ceramers by the SEM analysis. They noted that with increasing silica content in the ceramer solutions, a more highly interconnected structure is obtained.

The above mentioned facts, show that the silica content is playing an important role in producing a fine co-continuous morphology of the PEO-SiO₂ ceramer film. GOTMS coupling agent produced more sites for hydrogen bonding between the silanol/ hydroxyl groups from the silica precursor and ether groups from the PEO solution in the ceramer system.

b) The effect of mixing time and temperatures.

Figure 4.6 to Figure 4.9 show the effect of mixing time and temperatures on the PEO-SiO₂ ceramer morphology. It can be seen that the heat treatment at 80°C and 100°C for the duration of 1 to 5 hours, can severely affect the PEO, which was evident from the brittleness of the resulting ceramer films.

As the temperature was increased for the mixing stage, the PEO-SiO₂ precursor solution became cloudy, and the final ceramer films were opaque, as shown in Table 4.3 and Table 4.4. This was due to the precipitation of the PEO as the temperature rose, since the solubility of PEO in water decreased (188). The upper temperature limit or the precipitation temperature of the PEO used in this study, is between 90 to 100°C, as shown in Figure 2.6. The inverse solubility-temperature relationship was due to the association of the ether oxygen atoms of the PEO with water, which is unique to the PEO structure. An explanation could be that the heat destroyed the hydrogen bond interaction between the ether oxygen in PEO and the silanol groups in silica, resulting in the phase separation in the PEO-SiO₂ ceramer. Therefore, the
agglomeration of larger particles in the ceramer occurred through the precipitation of the PEO and hence the films were opaque.

It is noteworthy that certain combinations of mixing time and temperature will have produced a co-continuous fine morphology, such as that shown in Figure 4.9(a). In this system of the PEO-SiO₂ ceramer, the ideal combination of mixing time and temperature was one hour and 60°C.

c) The effect of amount of GOTMS coupling agent and other coupling agent.

The presence of GOTMS coupling agent is always necessary to achieve compatibilisation of a ceramer system, as reported by Kioul, (157) Menoyo, (169) and Xenopoulos (159), in their studies on the polyimide-silica ceramers. They found out that without GOTMS coupling agent in the ceramer, phase separation occurred to form fairly large silicate domains, and hence produced opaque films. PEO-SiO₂ ceramers follow the same trend, as can be seen in Table 4.2 and Figure 4.5 respectively.

An interpretation of the compatibilisation mechanism may be that a suitable coupling agent will increase the rate of gelation of the silica phase, so that the spinodal decomposition is prevented through the entrapment of the PEO chain by means of direct interaction between the epoxide groups of GOTMS and the ether oxygen of PEO. It has been found (190) that the addition of GOTMS to a pre-hydrolysed TEOS solution has the effect of increasing the rate of gelation of a ceramer solution. This is attributed to the fact that a larger amount of reactive epoxy groups from the GOTMS coupling agent, are available for the reactions mentioned earlier.
The amount of the GOTMS coupling agent in the PEO-SiO₂ ceramer is also affecting the final structure morphology of the films. This can be seen in Table 4.5 and Figure 4.10. This finding was also supported by the DSC analysis, see Figure 4.24. The threshold value for the compatibilisation of the PEO-SiO₂ ceramer was 1:0.12 (TEOS: GOTMS molar ratio). An increase in the amount of GOTMS above the standard formulation value had the opposite effect on the ceramer structure, which made the films opaque. This was due to the ceramer solution becoming cloudy before casting the film, as a result of premature precipitation of silica particles from the solution.

There are no references in the literature concerning the use of mercapto-functional silane (Silane A 189), bis- (γ-trimethoxysilylpropyl) amine (Silane A 1170) and phenyl-aminopropyl trimethoxysilane (Silane Y9669) as coupling agents for PEO-SiO₂ ceramers. The addition of Silane A 1170 to TEOS resulted in the alkoxysilane precursor undergoing phase separation, which was due to the basic nature of this silane coupling agent. Due to an increase in pH that results from this coupling agent, the gelation of the alkoxysilane precursor took place earlier. This result was in agreement with the effect of pH on the gelation of the PEO-SiO₂ ceramer solution, shown in Figure 4.2.

The high viscosity and subsequent precipitation of PEO from water solution with the addition of Silane A 1170 coupling agent is most probably attributed to a rapid condensation reactions, caused by NH₂ group present in the amine coupling agent.

The use of acid functionalized derivatives, (eg. carboxylic acid) as an adducts from the reaction between GOTMS and CA, did not improve the compatibilization of the PEO-SiO₂ ceramer films, as can be seen in Figure 4.27. The agglomeration of larger particles was due to the inability of the acid groups formed, to interact with the hydrolysed TEOS. This was a surprising
result since it was expected that the acid group would interact with the ether oxygen of the PEO, in line with the finding of Smith et al. \(^{(191)}\), who reported an association between PEO and polymeric poly (carboxylic acid). They discovered that an insoluble complex formed had a very high intermolecular order, resembling crystallinity. A high crystallinity for the PEO-SiO\(_2\) ceramer-containing GOTMS-CA adducts as coupling agent, was also obtained in this study, as shown in Figure 4.27.

Therefore, it can be concluded that polymer complex formation of PEO with carboxylic acid from the functionalised GOTMS with CA, contributes to the agglomeration of larger particle sizes in the PEO-SiO\(_2\) ceramer.

d) The solvent effect on PEO-SiO\(_2\) ceramer.

A comparison study on the solvent effect between PEO-SiO\(_2\) ceramer system and PEO, in water and that in tetrahydrofuran (THF) medium, was carried out. It was found that the solvent that caused the strongest interaction with the reactants through hydrogen bonding (i.e. from water in this system), exerted the greatest stearic hindrance for the sol-gel reaction between PEO and silica. This steered the system towards the formation of more branched species \(^{(192)}\), thereby creating larger particles size and higher pore volume. Therefore, in the absence of GOTMS, the PEO-SiO\(_2\) ceramer films were opaque. It is noted however, that the trend in the variation of the degree of crystallinity \((X_c)\) with the PEO content for the PEO-SiO\(_2\) ceramer system obtained from the ceramer system in water and from the ceramer system in THF, was considerably alike. A similar phenomenon, from the basis of the melting point depression behaviour for the two systems, can also be seen in Figures 4.18, 4.19, 4.25, and 4.26. The melting temperatures decreased as the amount of silica increased.
The use of water as the solvent for the PEO precursor in the production of PEO-SiO₂ ceramer system, had the effect of coarsening the structure of the final ceramer. This effect was more pronounced in the hybrids without GOTMS coupling agent, as can be seen in Figure 4.5 and Figure 4.6. This is probably due to the silicate, which was already in an advanced state of condensation when it was mixed with the PEO. On the other hand, a ceramer produced from PEO dissolved in THF, was likely to be more resistant to coarsening. A co-continuous fine structure of PEO-SiO₂ ceramer can be achieved from a ceramer solution containing GOTMS coupling agent, as shown in Figure 4.17.

Another factor that makes the PEO-SiO₂ ceramer, prepared from the PEO precursor dissolved in THF, more transparent (i.e. a fine co-continuous structure morphology), is due to the different solvent affinity for the silica surface. Water clearly is a moderately good solvent for PEO and undoubtedly is attracted to a silica surface. Therefore, the removal or replacement of hydroxyl groups at the silica surface leads to a net reduction in polymer adsorption to silica. Due to this, PEO molecules becoming dominant in the ceramer solution and hence the precipitation or agglomeration of larger particles takes place. This hypothesis is in agreement with the findings of Howard et al. (193), in their studies on the adsorption of polymers at the solution-solid interface for PEO on silica. They found out that the extent of adsorption depended strongly upon the solvent, in a manner which can be rationalized from both the polymer-solvent interactions, and the competition between polymer segments and solvent molecules for surface sites.

From the above observations, it may be concluded that the effect of the solvent in the sol-gel process for PEO-SiO₂ ceramer system, seems to be very important to produce a co-continuous fine morphology.
5.1.4. Surface Area Measurement of the PEO-SiO₂ ceramers.

Compatibilized PEO-SiO₂ ceramer exhibit higher BET surface area compared to uncompatibilized one, as shown in Table 4.9. Silica produced from the hydrolysis and condensation of TEOS, also displayed a high BET surface area than those without GOTMS coupling agent.

Nitrogen adsorption for the PEO-SiO₂ ceramer was measured on samples outgassed at the lowest temperature from a series of measurements for each sample. The uptake of nitrogen by the ceramer samples proceed as monolayer-multilayer adsorption, followed by instantaneous filling of pores with nitrogen gas (absorbate), in the relative pressure range of 0.05 to 0.02. Compatibilized PEO-SiO₂ ceramers display higher BET surface area than those without compatibilizer. It appears that the thermal treatment of the porous PEO-SiO₂ ceramer removes adsorbed species from their surface, most likely physically and/ or chemically adsorbed water. Therefore, exposing high energy adsorption sites, which can strongly interact with the nitrogen, probe molecules, and hence resulting in higher surface area.

The more hydrophobic character of the compatibilised ceramer containing GOTMS coupling agent could be responsible for the higher desorption of moisture. This, therefore, would create high adsorption sites for nitrogen gas molecules when the samples were subjected to thermal treatment during the BET surface area measurement.
5.2. BLENDS OF PEO-SiO₂ CERAMERS WITH OTHER POLYMERS.

5.2.1. Blends of PEO-SiO₂ Ceramer with PVC.

The results obtained from DSC and DMTA analyses of the PEO-SiO₂ ceramer blends with PVC, show that the blends were immiscible. This can clearly be seen in Figure 4.38 where each blend gives two glass transition temperatures (T_g). However, the glass transition temperatures were decreased with an increasing amount of DOP plasticiser content in the blends.

The solvent cast films from the PEO-SiO₂ ceramer blend with PVC, were opaque. This was due to larger particle sizes of the blends, which were between 5 to 10µm in diameter, as can be seen in the SEM and TEM analysis (Figures 4.41 and 4.42 respectively).

An increase in the elongation at break of the PEO-SiO₂/PVC ceramer blends was also observed, as the amount of DOP plasticiser increased. This was due to better chain mobility in the PVC phase, as a result of the addition of plasticiser. On the other hand, a reduction in the tensile strength was observed in the blends as the DOP plasticiser increased. The presence of larger particles, acting as filler is believed to be the major cause for the observed changes in the blend properties. This can be seen in both SEM and TEM analyses at fracture surfaces from liquid nitrogen.

One of the objectives of this study was to blend the PEO-SiO₂ ceramer with a polymeric system in order to reinforce the polymer. The PEO-SiO₂ ceramer blend with plasticised PVC showed a better tensile strength and modulus, compared to the blend of PVC/PEO. This enhancement of the modulus was due the higher resistance of the PEO-SiO₂ ceramer particles against the plastic deformation. This finding is in agreement with the studies by Lim et.al
They studied the incorporation of organophilic montmorillonite (OMMT) into the PEO/PMMA blends to produce the PEO/PMMA/OMMT nanocomposites. They use the PEO/PMMA blends in their studies because these materials showed miscibility or compatibility, in spite of the fact that one of the components has a strong tendency to crystallize out.

In their studies, a polymer/clay nanocomposites based on the blend of PMMA and PEO were used, instead of a single polymer. The blending of monmorillonite, PMMA and PEO was carried out in solution. They found out that x-ray analyses of these nanocomposites showed peaks, one due to the clay interlayer and the other to the crystallinity of PEO. The intensities of the PEO crystalline peaks decreased monotonically with an increase in the PMMA. Tensile modulus and elongation of these new types of nanocomposites were higher than the PEO/PMMA blend without clay.

5.2.2 Blend of PEO-SiO₂ Ceramic with Epoxy Resin.

PEO-SiO₂ ceramic/epoxy blends cured with di-amino-diphenylamine (DDA) seemed to be miscible. This was demonstrated by DMTA studies. DMTA spectra shows single, sharp major relaxation peaks of tan δ. The results indicate that the presence of the PEO-SiO₂ ceramic phase in the epoxy system, lowered the T_g values, and became between the T_g of the pure PEO and epoxy resins. As the PEO-SiO₂ ceramic was blended with the epoxy system, it progressively resulted in an incomplete curing reaction, due to steric hindrance in the highly viscous system. Therefore, an imperfect semi-IPN was formed, with lower T_g values. The probability of contact between the epoxide ring and amine group will have decreased due to dilution effect of the PEO-SiO₂ ceramic used as a miscible inactive diluent, and therefore, the
curing reaction does not go to completion because of steric hindrance in the standard curing condition \(^{(199)}\).

A greater effect on the \(T_g\) appeared in Blend B, compared to Blend A. As the curing agent was added at the end of the blending process, the probability of contact between the epoxide ring and amine group will decrease even more due to dilution effect of the PEO-SiO\(_2\) ceramer phase. Larger particles were found to be formed and hence the blend film becomes opaque.

It has been shown by IR spectra \(^{(196)}\) that there were hydrogen-bonding interactions involving amine-crosslinked epoxy resins. In this case, the cured blend could also possess hydrogen bonding interactions between the amine-crosslinked Epikote 828 and PEO. The hydrogen bonding occurred between hydroxyl groups, which were generated from the reaction of the amine hydrogen and epoxide group, and ether bond of PEO.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

6.1. CONCLUSIONS

In the Discussion section on the preparation of ceramers from the water soluble polymer of poly (ethylene oxide) using water as solvent, has lead to several conclusions. The main conclusions that can be drawn from this study in relation to the main aspects of the work are outlined below:

1. The gelation time of compatibilized PEO-SiO₂ ceramer solutions is shorter than that of the corresponding ceramer without compatibilization. The addition of GOTMS coupling agent accelerates the gelation time of the solution.

2. It has been shown that water can be used as solvent for the production of the PEO-SiO₂ ceramer. Compatibilization at the nanometres scale of the PEO-SiO₂ ceramer can be achieved exclusively by the addition of appropriate amounts of GOTMS coupling agent. In addition to the above, the influence of several reaction parameters, such as pH, catalyst, the amount of silica contents, mixing time and temperature, drying and curing steps play an important role in the production of a co-continuous fine structure morphology.

3. It is well known that silica has an enormous affinity for PEO due to the very strong hydrogen bonds between the silanol groups and ether linkages. Compatibilised PEO-SiO₂ ceramer systems bring about a drastic reduction
in the degree of crystallisation of the PEO phase even at silica concentration as low as 20%.

4. An acid functionalised coupling agent obtained from the reaction between GOTMS and chlorendic anhydride (CA) did not improve the compatibilization of the ceramer.

5. Compatibilized PEO-SiO₂ ceramer displays larger BET surface area compared to uncompatibilized ceramer.

6. The use of PEO-SiO₂ ceramer as “in-situ generated filler” with plasticised PVC is possible for all the blends containing different amounts of DOP plasticizer. All blends produced opaque films which were due to the larger particles size diameter of the ceramer acting as a filler.

7. There was an improvement in tensile strength and modulus of the PEO-SiO₂ ceramer blends with PVC, compared to the blend of PVC/PEO only. It is also observed that the PEO-SiO₂ ceramer blended with PVC were stable towards heat and processing at 180°C, as their morphologies did not changed.

8. The PEO-SiO₂ ceramer blend with Epikote 828 (epoxy resin) seemed to be miscible, as can be seen from a single glass transition temperature (T₉). However, Blend B, where the addition of amine curing agent was made after the mixing process was completed, produced an opaque film compared to Blend A, for which the amine curing agent was added in the epoxy resin solution before the blending process was carried out.
6.2. RECOMMENDATIONS FOR FURTHER STUDIES.

To get a more thorough understanding of the ceramer system studied here, it is suggested that the following work should be carried out.

1. Determine the mechanism by which the GOTMS coupling agent compatibilised between the PEO-silicate system. This could be achieved by infrared spectroscopic analysis of the PEO-SiO₂ ceramer system, to establish the interaction/bonding between the various components.

2. Further studies should be carried out on the ceramer blends with PVC. Ways to reduce the particle sizes of blends should be investigated, in order to make the blend miscible and hence the reinforcement effect on the blend can be improved. The reinforcement effect of the different amounts of the ceramer phase in the PVC should also be studied further.

3. Further studies should also be done on the melt blending of the PEO-SiO₂ ceramer with PVC, especially in morphological stability towards heat during the processes.

4. Studies should also be made on the ceramer blends with epoxy resins. The reinforcement effect of different amounts of ceramer phase in the epoxy resin should be pursued, in order to know the effectiveness of the ceramer enhancement to the structure morphology and physical properties of the blends.
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