SILOXANE MODIFIED HYBRID MATERIALS BY THE SOL-GEL PROCESS

by

Saikat Sutej Joardar

Dissertation submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Materials Engineering Sciences

APPROVED:

T. C. Ward, Chairman

G. L. Wilkes

J. E. McGrath

S. B. Desu

H. W. Gibson

September, 1992

Blacksburg, Virginia
SILOXANE MODIFIED HYBRID MATERIALS BY THE SOL-GEL PROCESS

by

Saikat Sutej Joardar

Committee Chairman: Thomas C. Ward

(ABSTRACT)

The first part of this research constituted the study of oligomeric incorporation into an inorganic network leading to the formation of a hybrid material by the sol-gel process. The oligomeric species chosen was silanol terminated poly(dimethylsiloxane) (PDMS) and the inorganic oxide precursor chosen was titanium tetra-isopropoxide (TIP). The rationale for choosing these materials stemmed from the desire to make materials for optical filters since a gradient of optical properties can be derived based on the composition and the initial reaction conditions. \(^{29}\text{Si NMR}\) studies were conducted to investigate the incorporation process which led to the conclusion that the PDMS chains were being degraded by the TIP. This problem led to the synthesis of TIP endcapped PDMS which was then used as the oligomeric component in the hybrid materials. The endcapping changed the functionality of the oligomer to six, and more importantly, its reactivity which was now closer to that of the TIP. Also, having the same functionality at the ends as the precursor affects the compatibility of the two components.

Hybrid materials in the form of free standing films were fabricated from varying TIP/PDMS compositions and different initial reaction conditions. The hybrid materials synthesized were then subjected to a systematic structure-property relationship study. The degree of phase mixing or the encapsulation of the siloxane phase by the inorganic oxide
increases with higher TIP content. This behaviour was seen by both the dielectric and dynamic mechanical studies. The modulus and the stress to break increased with higher TIP content while the strain to break decreased. At the 50/50 TIP/PDMS composition there was an abrupt change in the mechanical properties which signified a morphological change in these materials. The refractive indices of the materials also showed a trend similar to that of the mechanical properties. Three different cure procedures, viz., room temperature, thermal cure at 70 °C and microwave cure at 70 °C were utilized to fabricate the films. More phase separation occurred in the microwave cured over the thermally cured materials as evident from dielectric and dynamic mechanical studies. However, the effect diminished with higher TIP content in the materials. Changing the initial reaction conditions by varying the initial water and acid content changed the properties observed in the final products. Dielectric and dynamic mechanical studies showed that the phase separation was higher with increased water content. Also, the modulus of the materials made with increased water content was higher. Decreased acid content led to better dispersion of the two components as shown by the dielectric and dynamic mechanical experiments. The effect of using a less reactive inorganic component tetra-ethyl orthosilicate (TEOS), instead of TIP was also studied. The TEOS/PDMS materials showed more phase mixing than the TIP/PDMS materials, although, the dielectric tan δ peak maxima appeared at a lower temperature. The TEOS/PDMS materials were also less stiff than the TIP/PDMS materials.

Structural studies were conducted by means of solid-state NMR, electron microscopy and small angle x-ray scattering (SAXS). With few exceptions, these studies correlated very well with the properties observed in these materials. The spin-lattice relaxation times obtained from the solid-state NMR correlated with the better phase mixing observed in the TEOS/PDMS materials relative to the TIP/PDMS materials. Electron microscopy in the backscattered mode showed the presence of microphase separation in these materials. At the 50/50 TIP/PDMS composition connectivity of the inorganic oxide
phase was complete, perhaps encapsulating the siloxane phase totally. Microstructural differences were observed due to the variation in the cure modes. The domain sizes of the oxide phase were finer in the thermally cured as compared to the room temperature cured materials. Higher water content led to a very different microstructure when compared to materials made with lower water content. Smaller spherical particulate type structures were observed in the material made with higher water content. The domain sizes of the oxide phase in the TEOS/PDMS material were bigger than those in the TIP/PDMS material of equivalent composition. These differences may be intimately related to the reactivity difference between TIP and TEOS. The SAXS data supported the microstructure seen by electron microscopy and the properties observed by dynamic mechanical, dielectric and mechanical studies.


Acknowledgments

First of all, I would like to acknowledge my advisor Prof. Ward for his patience and support during my stay here. Although, the freedom he gave me was very trying in the early part of my research endeavour, the opportunity helped me develop into a more confident and an independent scientist. His brilliant teaching and simplistic breakdown of most difficult topics made my learning process a joy indeed. I thank Prof. Wilkes for all the time, help and interest in my research progress. His insight and curiosity as well as advice led to a number of experiments which formed an integral part of my thesis. The devious morphology and rheo-optics tests were thought provoking and fun to take. I acknowledge Prof. Desu for the encouragement during the most difficult part of my research work, viz., when I was trying to focus on my research topic. His idea of optical filters prompted the choice of the precursors I ultimately used to make hybrid materials. Prof. McGrath inspired me to work hard and I thank both him and Prof. Gibson for imparting me knowledge in Polymer Synthesis, and also, for being on my committee. Prof. Marand was very kind to substitute as my committee member on very short notice.

I am indebted to numerous people for technical help. Dr. Ramji Srinivasan and Venkat Sekharipuram helped with initial setup for synthesis experiments as well as teaching me moisture free chemical handling techniques. I express gratitude to Prof. Wilkes to allow the use of SAXS equipment and Chinmay Betrabet for running the samples. Steve McCartney showed extraordinary patience with the STEM experiments and also, considerable expertise in obtaining excellent micrographs of the hybrid materials. I thank Tom Glass for the solid-state NMR experiments. My colleagues in the Polypkem group were an excellent group to work with and the presence of Taigyou Park has been entertaining and with whom numerous adventures in the laboratory has been very fruitful. I would also like to express appreciation to Esther, Joyce, Bonnie, Millie and Laurie from the office for all the help they gave me.

I thank my wife, Vinita, for her support as well as typing and proofreading portions of my thesis. Her influence has also helped me become a more disciplined and responsible person! I have had the fortune of having a number of good friends and colleagues who have helped me in various facets of my graduate student life. Some of them are Milind, Bharat and Venkat from my college days in Bombay, Joysula, Sanjay and Shantanu from Stony Brook, and Hemanshu, Rajesh, Dinesh, Mia, Steve, Mike, Joyce, Park, George and Button from Blacksburg. Lastly, but most importantly, I would like to thank my parents who have been the motivation for whatever I have achieved in my life so far.
Dedicated to

my father, Sutej Chandra Joardar

and

my mother, Dipali Joardar

who lacked the opportunity for higher education but sacrificed a lot so that I could get

one

and

my wife, Vinita

whose being with me has made graduate studies a very pleasant experience
# TABLE OF CONTENTS

**Chapter 1**  INTRODUCTION AND RESEARCH OBJECTIVES  
1

**Chapter 2**  LITERATURE REVIEW  
6  
2.1 Sol-gel Process  
6  
2.1.1 Introduction  
6  
2.1.2 Reaction Mechanisms  
7  
2.1.3 Governing Parameters  
10  
2.2 Inorganic-Organic Hybrid Materials  
20  
2.2.1 Introduction  
20  
2.2.2 ORMOSILS  
21  
2.2.3 CERAMERS  
27  
2.2.4 Other Hybrid Materials  
33  
2.3 Microwave Curing Of Materials  
37

**Chapter 3**  OLIGOMER INCORPORATION STUDIES AND SYNTHESIS OF TIP ENDCAPPED PDMS  
40  
3.1 Introduction and Objectives  
40  
3.1.1 Oligomer Incorporation Studies by $^{29}\text{Si NMR}$  
40  
3.1.2 Synthesis of TIP endcapped PDMS  
41  
3.2 Experimental  
43  
3.2.1 Oligomer Incorporation Studies by $^{29}\text{Si NMR}$  
43  
3.2.2 Synthesis of TIP endcapped PDMS  
46  
3.2.3 $^{29}\text{Si NMR solution technique}$  
48  
3.2.4 $^{1}\text{H NMR technique}$  
48  
3.2.5 Vapor Phase Osmometry  
49  
3.2.6 Intrinsic Viscosity Experiment  
49  
3.3 Results and Discussion  
49  
3.3.1 Oligomer Incorporation Studies by $^{29}\text{Si NMR}$  
49  
3.3.2 Synthesis of TIP endcapped PDMS  
57  
3.4 Conclusions  
62

**Chapter 4**  FABRICATION OF HYBRID MATERIALS AND THEIR PROPERTIES  
63  
4.1 Introduction and Objectives  
63
4.2 Experimental
   4.2.1 Fabrication of free standing films 65
   4.2.2 Thin Film Fabrication 66
   4.2.3 Dielectric Thermal Analysis 67
   4.2.4 Dynamic Mechanical Thermal Analysis 67
   4.2.5 Differential Scanning Calorimetry 67
   4.2.6 Stress-strain Experiments 68
   4.2.7 Optical Properties 68
4.3 Results and Discussion 68
   4.3.1 Relaxation studies by DETA and DMTA 68
      4.3.1.1 General Features of the spectra 68
      4.3.1.2 Effect of TIP content 74
      4.3.1.3 Effect of Cure modes 84
      4.3.1.4 Effect of the PDMS molecular weight 93
      4.3.1.5 Effect of the water content 93
      4.3.1.6 Effect of the acid content 96
      4.3.1.7 Effect of the sol aging time 99
      4.3.1.8 Effect of the Metal Alkoxide type 102
   4.3.2 Differential Scanning Calorimetry 112
   4.3.3 Mechanical Properties 113
   4.3.4 Optical Properties 120
4.4 Conclusions 126

Chapter 5 STRUCTURAL CHARACTERIZATION OF
THE HYBRID MATERIALS 128
5.1 Introduction and Objectives 128
5.2 Experimental
   5.2.1 Solid-state NMR spectroscopy 129
   5.2.2 Scanning Transmission Electron Microscopy 129
   5.2.3 Small angle x-ray scattering 129
5.3 Results and discussion 133
   5.3.1 Solid-state NMR spectroscopy 133
   5.3.2 Electron Microscopy 136
      5.3.2.1 Effect of TIP content 136
      5.3.2.2 Effect of cure modes 142
      5.3.2.3 Effect of water content 147
5.3.2.4 Effect of the Metal Alkoxide type 149

5.3.3 Small angle x-ray scattering 153
   5.3.3.1 Effect of TIP content 153
   5.3.3.2 Effect of cure modes 164
   5.3.3.3 Effect of acid content 167
   5.3.3.4 Effect of the water content 170
   5.3.3.5 Effect of the metal alkoxide type 170

5.4 Conclusions 170

Chapter 6 SOME POTENTIAL APPLICATIONS OF 174
   THE HYBRID MATERIALS
   6.1 Introduction and Objectives 174
   6.2 Experimental 176
   6.3 Results and Discussion 177
   6.4 Conclusions 180

Chapter 7 CONCLUSIONS AND RECOMMENDATIONS 181
   7.1 Conclusions 181
   7.2 Recommendations 186

REFERENCES 188

VITA 195
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Positive partial charge for various metals ($\delta(M)$) in different alkoxides</td>
<td>11</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Molecular Complexity (Number of Metal atoms per Osmotic Molecule) of some Transition Metal Ethoxides as a function of Metal Size</td>
<td>12</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Charge Distribution in Ti and Si n-alkoxides</td>
<td>13</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>Influence of the hydrolysis ratio 'h' upon the charge distribution in monomeric precursors</td>
<td>14</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>Charge distribution according to the partial charge model within a titanium oxo-polymer</td>
<td>19</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Description of the solutions studied by $^{29}$Si NMR</td>
<td>45</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Activation energies of the glass transition from the dielectric data for various compositions cured by all three techniques</td>
<td>82</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Activation energies of the PDMS glass transition from the dynamic mechanical data for various compositions cured by all three techniques</td>
<td>83</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>$T_g$ by DSC of various compositions cured at room temperature</td>
<td>108</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Mechanical Properties of TIP/PDMS materials</td>
<td>117</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Mechanical properties of 40/60 TIP/PDMS materials with initial water content of 0.5 cured at room temperature</td>
<td>118</td>
</tr>
<tr>
<td>Table 4.6</td>
<td>Mechanical properties of TEOS/PDMS materials studied</td>
<td>119</td>
</tr>
<tr>
<td>Table 4.7</td>
<td>Calculated thicknesses of the thin films cured thermally and by microwave</td>
<td>125</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>$T_1$ values of the $^{29}$Si and $^{13}$C for TIP/PDMS and TEOS/PDMS materials</td>
<td>135</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Fractal dimension of the TIP/PDMS compositions cured at room temperature</td>
<td>163</td>
</tr>
</tbody>
</table>
List of Figures

Fig. 1.1 Outline of the Project 4
Fig. 2.1 Examples of ionic and coordinative crosslinking points between an inorganic and organic component (32) 22
Fig. 2.2 Examples of reactions of network formers (32) 23
Fig. 2.3 Morphological model of a Ceramer (44,46) 31
Fig. 3.1 Structure of the precursors, TIP, and silanol terminated PDMS 44
Fig. 3.2 Reaction to form TIP endcapped PDMS 47
Fig. 3.3a $^{29}$Si NMR spectrum of neat silanol terminated PDMS 50
Fig. 3.3b $^{29}$Si NMR spectrum of solution of silanol terminated PDMS in isopropanol 50
Fig. 3.4 $^{29}$Si NMR spectra of solution A 52
Fig. 3.5 $^{29}$Si NMR spectra of solution B 53
Fig. 3.6 $^{29}$Si NMR spectra of solution C 54
Fig. 3.7 $^{29}$Si NMR spectra of solution D 55
Fig. 3.8 $^{29}$Si NMR spectra of solution E 56
Fig. 3.9 $^{29}$Si NMR spectra of the reaction performed under neat conditions 58
Fig. 3.10 $^{29}$Si NMR spectrum of the reaction product made in toluene 60
Fig. 3.11 $^1$H NMR spectrum of the reaction product made in toluene 61
Fig. 4.1 Structures of the precursors for the hybrid materials 64
Fig. 4.2 Dielectric spectra of 50/50 TIP/PDMS cured at room temperature (first run) 69
Fig. 4.3 Dielectric spectra of 50/50 TIP/PDMS cured at room temperature (second run) 70
Fig. 4.4 DMTA spectra of 40/60 TIP/PDMS cured thermally 73
Fig. 4.5 Dielectric tan δ of various compositions cured thermally 75
Fig. 4.6 DMTA spectra at 1 Hz for various compositions cured thermally 76
Fig. 4.7 Dielectric tan δ of various compositions cured by microwave processing 78
Fig. 4.8 DMTA spectra at 1 Hz of various compositions cured by microwave processing 79
Fig. 4.9  Dielectric tan δ of various compositions cured at room temperature
Fig. 4.10  DMTA spectra at 1 Hz of various compositions cured at room temperature
Fig. 4.11  DMTA spectra at 5 Hz of 30/70 TIP/PDMS cured thermally and by microwave processing
Fig. 4.12  Dielectric tan δ spectra at 5 kHz of 30/70 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.13  DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.14  DMTA spectra at 1 Hz of 50/50 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.15  Dielectric tan δ of 40/60 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.16  Dielectric tan δ of 50/50 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.17  DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured thermally at 70 °C and 45 °C
Fig. 4.18  DMTA spectra at 1 Hz of 50/50 TIP/PDMS cured thermally; molecular weight of PDMS used are 2600 and 4200 g/mol
Fig. 4.19  Dielectric tan δ at 5 kHz of 50/50 TIP/PDMS cured at room temperature with two different initial water content
Fig. 4.20  Dielectric tan δ at 10 kHz of 50/50 TIP/PDMS cured thermally with three different initial acid content
Fig. 4.21  DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured at room temperature with three different periods of prehydrolysed sol aging
Fig. 4.22  Dielectric tan δ at 10 kHz of 50/50 TEOS/PDMS cured at room temperature (first and second run)
Fig. 4.23  DMTA spectra at 1 Hz of 50/50 TEOS/PDMS cured at room temperature (first and second run)  

Fig. 4.24  Dielectric tan δ at 10 kHz of 50/50 TEOS/PDMS and 50/50 TIP/PDMS cured at room temperature  

Fig. 4.25  DMTA spectra at 1 Hz of 50/50 TEOS/PDMS and 50/50 TIP/PDMS cured at room temperature  

Fig. 4.26  DMTA spectra at 1 Hz of 40/60 TEOS/PDMS and 50/50 TEOS/PDMS cured at room temperature  

Fig. 4.27  DMTA spectra at 1 Hz of 50/50 TEOS/PDMS cured at room temperature with two different initial water content  

Fig. 4.28  DSC scans of 0/100 TIP/PDMS (M_n = 2600 g/mol) a) first heat 
b) after isothermal hold at -75 °C for three hours  

Fig. 4.29  DSC scans of 10/90 TIP/PDMS (M_n = 2600 g/mol) a) first heat 
b) after isothermal hold at -75 °C for three hours  

Fig. 4.30  DSC scans of 30/70 TIP/PDMS cured thermally and by microwave processing after isothermal hold at -75 °C for three hours  

Fig. 4.31  Stress-strain behaviour of various TIP/PDMS compositions cured at room temperature  

Fig. 4.32  Stress-strain behaviour of various TIP/PDMS compositions cured thermally  

Fig. 4.33  Stress-strain behaviour of various TIP/PDMS compositions cured by microwave processing  

Fig. 4.34  Transmittance spectrum of 50/50 TIP/PDMS thin film cured thermally  

Fig. 4.35  Refractive indices as a function of wavelength for various TIP/PDMS compositions cured in the microwave  

Fig. 4.36  Refractive indices as a function of wavelength for various TIP/PDMS compositions cured thermally  

Fig. 5.1  $^{29}$Si NMR spectrum of 50/50 TIP/PDMS material cured at room temperature  

Fig. 5.2  $^{29}$Si NMR spectrum of 50/50 TEOS/PDMS material cured at room temperature  

Fig. 5.3  $^{29}$Si NMR spectrum of 50/50 TEOS/PDMS material cured at room temperature  

Fig. 5.4  Electron micrographs of various TIP/PDMS composition cured at room temperature
<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Electron micrographs of various TIP/PDMS composition cured at room temperature</td>
</tr>
<tr>
<td>5.6</td>
<td>Electron micrographs of various TIP/PDMS composition cured by microwave processing</td>
</tr>
<tr>
<td>5.7</td>
<td>Electron micrographs of various TIP/PDMS composition cured by thermal processing</td>
</tr>
<tr>
<td>5.8</td>
<td>Electron micrographs of 30/70 TIP/PDMS composition cured by thermal, microwave and room temperature processing</td>
</tr>
<tr>
<td>5.9</td>
<td>Electron micrographs of 40/60 TIP/PDMS composition cured by thermal, microwave and room temperature processing</td>
</tr>
<tr>
<td>5.10</td>
<td>Electron micrographs of 50/50 TIP/PDMS composition cured by thermal, microwave and room temperature processing</td>
</tr>
<tr>
<td>5.11</td>
<td>Electron micrographs of 40/60 TIP/PDMS composition cured at room temperature with two different initial water content</td>
</tr>
<tr>
<td>5.12</td>
<td>Electron micrographs of 50/50 TIP/PDMS and 50/50 TEOS/PDMS compositions cured at room temperature</td>
</tr>
<tr>
<td>5.13</td>
<td>Schematic phase diagrams of silica-organic polymer system for a) weak segregation strength b) moderate segregation strength c) strong segregation strength (97)</td>
</tr>
<tr>
<td>5.14</td>
<td>SAXS profiles as a function of varying TIP content cured at room temperature</td>
</tr>
<tr>
<td>5.15</td>
<td>Computer simulated structures using various kinetic growth models (1)</td>
</tr>
<tr>
<td>5.16</td>
<td>Fractal dimension determination from log intensity vs. log S plot for 20/80 TIP/PDMS material cured at room temperature</td>
</tr>
<tr>
<td>5.17</td>
<td>Fractal dimension determination from log intensity vs. log S plot for 30/70 TIP/PDMS material cured at room temperature</td>
</tr>
<tr>
<td>5.18</td>
<td>Fractal dimension determination from log intensity vs. log S plot for 40/60 TIP/PDMS material cured at room temperature</td>
</tr>
<tr>
<td>5.19</td>
<td>Fractal dimension determination from log intensity vs. log S plot for 50/50 TIP/PDMS material cured at room temperature</td>
</tr>
<tr>
<td>5.20</td>
<td>Fractal dimension determination from log intensity vs. log S plot for 50/50 TEOS/PDMS material cured at room temperature</td>
</tr>
<tr>
<td>5.21</td>
<td>SAXS profiles of 30/70 TIP/PDMS composition cured by thermal, microwave and room temperature processing</td>
</tr>
<tr>
<td>5.22</td>
<td>SAXS profiles of 40/60 TIP/PDMS composition cured by thermal, microwave and room temperature processing</td>
</tr>
</tbody>
</table>
thermal, microwave and room temperature processing

Fig. 5.23  SAXS profiles of 50/50 TIP/PDMS composition cured thermally with acid catalyst and without acid catalyst  168

Fig. 5.24  SAXS profiles of 50/50 TIP/PDMS composition cured by microwave processing with acid catalyst and without acid catalyst  169

Fig. 5.25  SAXS profiles of 40/60 TIP/PDMS composition cured at room temperature with two varying initial water contents  171

Fig. 5.26  SAXS profiles of 50/50 TIP/PDMS and TEOS/PDMS compositions cured at room temperature  172

Fig. 6.1  Absorption curves for 30/70 TIP/PDMS and 40/60 TIP/PDMS materials doped with Coumarin 153  178

Fig. 6.2  FTIR spectrum of silica-titania thin film  179
Chapter 1 --- Introduction and Research Objectives

The sol-gel process is a unique low temperature solution route for the formation of inorganic glasses. Metal alkoxides have by far been the predominant precursors used because of their solubility in a variety of organic solvents (mostly alcohols). The formation of metal oxides from metal alkoxides can be represented in a highly simplified form by the two reactions shown below:

\[
M(OR)_n + nH_2O \longrightarrow M(OH)_n + nROH
\]

\[
M(OH)_n \longrightarrow MO_{n/2} + (n/2)H_2O
\]

\(M\) represents a metal in the above reactions. The first step is the hydrolysis of the metal alkoxide to metal hydroxide with the release of alcohol. The second step represents the condensation reactions which lead to the formation of metal-oxygen-metal bridging bonds. Once hydrolysis occurs, condensation reactions may start concurrently. The reactions taking place are, however, much more complicated than what is shown here and will be discussed in more detail in the literature review (Chapter 2). The advantages of the sol-gel process over traditional ceramic processes are many. However, the major complication of the sol-gel process is the significant mass and volume loss associated with the transformation of the metal alkoxide to the oxide. The resulting large inherent stresses thus generated make it very difficult to obtain monolithic pieces or thick films. This has been one of the major motivating factors for the development of novel hybrid materials where the inorganic oxides are chemically reacted with the organic moieties. Schmidt and coworkers have developed a variety of hybrid materials where the choice of the organic moieties have been based upon specific application needs. More discussion of the materials made by them is presented in Chapter 2.
The idea of incorporating functionalised oligomeric species in the developing inorganic structure was first put forward by Prof. G. L. Wilkes (44). The function of the oligomeric species was to impart flexibility to the inorganic network and therefore make possible the fabrication of monolithic pieces. The first oligomeric species used by Wilkes et al. was silanol terminated PDMS with the inorganic component precursor being tetra-ethyl orthosilicate (44). Successful hybrid materials were made using these precursors and since then a variety of hybrid materials have been reported by them using titanium alkoxides, zirconium alkoxides, aluminum alkoxides and mainly PTMO as the oligomeric component (42-47, 50, 51).

The primary objective of this research was to make hybrid materials by the sol-gel process based on silanol terminated PDMS as the oligomeric component and titanium tetra-isopropoxide (TIP) as the inorganic component. The approach to making these materials was to be similar to that developed by Wilkes et al. The rationale for choosing these precursors was to develop hybrid materials for applications as optical filters. TIP is a precursor for high refractive index metal oxide and PDMS is a low refractive index material. Therefore the combination of these two materials in varying compositions should result in systematic changes in the optical properties of these materials. PDMS is a highly flexible polymer with a very low glass transition temperature (-120 °C) and therefore should toughen the inorganic network. Titanium oxide containing PDMS has been reported by Mark et al. (58,123,124). However, these materials were prepared by swelling the crosslinked sheets of PDMS in the metal alkoxide followed by their hydrolysis and condensation to achieve the precipitation of the metal oxides. Mark et al. (58) have also reported siloxane modified by TIP made by a method similar to that used by Wilkes et al. but the level of incorporation was less than 1 weight percent of titanium oxide. These factors became the motivation for developing TIP/PDMS hybrid materials with varying composition and initial reaction conditions which have not yet been reported.
The first objective was to study the incorporation process of the PDMS into the inorganic network by $^{29}$Si NMR. The formation of the Si-O-Ti bond should be seen distinct from the other silicon peaks which should then give information on the incorporation process. The conclusions from this research was that the PDMS was being degraded by TIP. Therefore, the objective of synthesizing TIP endcapped PDMS was undertaken. This would increase the functionality of the PDMS to six and also the reactivity of the PDMS would be closer to that of TIP. Gelation will occur faster and the probability of the incorporation will be much higher.

The new approach of utilising TIP endcapped PDMS as the oligomeric species is fundamentally different from the other hybrid materials reported so far which have been synthesized from triethoxysilyl endcapped oligomeric species. The higher reactivity of TIP compared to TEOS was anticipated to lead to materials with different structures and, therefore, properties. The next step was to fabricate materials utilising TIP endcapped PDMS as the oligomeric species and TIP as the inorganic component. The objective now was to do a systematic structure-property relationship study on the hybrid materials prepared as a function of a number of different variables. An outline of the project is shown in fig. 1.1. The variables used for the fabrication of the hybrid materials are all shown in the categories of synthesis and processing mode. The TIP content is the factor governing the stiffness of the materials. Also, the morphology of the materials will be dictated by it. The catalyst and water content are important external variables in the sol-gel process which affect the reaction kinetics. This results in different microstructure of the materials and, therefore, different properties. Besides room temperature curing, microwave curing was also used to fabricate the hybrid materials. Hybrid materials were also made by thermal curing at the same temperature to compare the properties and structure obtained to those cured in the microwave. Microwave processing shortens the cure time and enhances
Fig. 1.1 Outline of the Project
the reaction kinetics. Also, the structures and the properties have been shown to be different from the thermally cured materials (72).

Dynamic mechanical and dielectric studies were conducted to observe the phase mixing characteristics of the materials as judged by their tan δ behaviour. The mechanical properties were evaluated by stress-strain studies. The optical property primarily investigated was the refractive index as a function of the varying TIP content. Limited differential scanning calorimetry was used to support certain conclusions based upon the dynamic mechanical and dielectric studies. The structural studies were mainly done by solid-state NMR, electron microscopy and small angle x-ray scattering (SAXS). Solid-state NMR was done to obtain the spin-lattice relaxation times (T₁) of ²⁹Si and ¹³C in the hybrid materials. These values give information about the silicon and carbon environment and hence indirectly indicative of the morphology of the phase separated systems. Electron microscopy was used to see the microphase separation in these materials and also to study the systematic variation in the microstructure as a function of the different synthetic and processing variables. SAXS was mainly used to support the microstructure observed by electron microscopy and also to help explain some of the properties exhibited by the hybrid materials.

A general review on the principles of the sol-gel process of mainly the transition metal alkoxides is presented in chapter 2. A discussion of the various reported hybrid materials is also presented in chapter 2. The oligomeric incorporation study and the synthesis of TIP endcapped PDMS are described in chapter 3. The fabrication and the evaluation of the properties of the hybrid materials are presented in chapter 4. Structural characterization of the hybrid materials is presented in chapter 5. Finally, the potential of using the hybrid materials as matrix for laser dye dopants and also as precursor for silica-titania films is presented in chapter 6.
Chapter 2 --- Literature Review

2.1 Sol-Gel Process

2.1.1 Introduction

Sol is defined as a dispersion of colloidal particles or polymeric species in a solvent. Gel is a continuous solid network surrounding and supporting a continuous liquid medium. The sol to gel transition is driven by covalent crosslinking or by Van der Waal's forces (1). This process is an ancient technique; gels of silica were prepared as early as in 1864 by T. Graham (2). However, it was rediscovered in 1956 by R. Roy (3) and thereafter used in the field of ceramics for synthesis of homogenous powders. The technique gained familiarity in the materials community with the work of B. E. Yoldas in 1975 (4) after which there has been an explosion of research activity in this area. The research activity prior to 1990 has been very well documented in the book by C. J. Brinker and G. W. Scherer (1). There are a number of good reasons for this intense research activity in this area. Some of them are:

1) High purity glasses can be made (1).

2) Multicomponent oxides in exact proportions are easier to make (5).

3) Lower firing temperature of the gels as compared to traditional ceramics making process (6).

4) The sols or gels allow the formation of fibers, films, or composites by either spinning (7), dip coating (8), or impregnation (9).

Metal alkoxides have by far been the most popular precursors in the sol-gel process due to their ease of hydrolysis and solubility in a variety of organic solvents. The sol-gel processing of silicon alkoxides to silicates has been the most extensively studied system
primarily due to its lower hydrolysis and condensation rates compared to those of the transition metal alkoxides. The difference between these two systems arise due to:

a) Higher electrophilic character of the transition metal due to its lower electronegativity.

b) The ability of most transition metals to exhibit several coordinations and therefore allowing coordination expansion (10).

These effects lead to much higher reactivity of the transition metal alkoxides when compared to silicon alkoxides. For example, the hydrolysis rate constant for Si(OEt)$_4$ is about $5 \times 10^{-9}$ M$^{-1}$s$^{-1}$ at pH = 7, whereas an approximate estimate for minimum possible hydrolysis rate constant of Ti(OR)$_4$ at pH = 7 is $10^{-4}$ M$^{-1}$s$^{-1}$ (1). Also, the condensation rate constant for Si(OEt)$_4$ is $10^{-4}$ M$^{-1}$s$^{-1}$ (11); the condensation rate constant for Ti(OEt)$_4$ is 30 M$^{-1}$s$^{-1}$ (12). The higher reactivity necessitates stricter control of moisture exposure and also makes fundamental kinetic studies harder to perform.

2.1.2 Reaction Mechanisms

The sol-gel process involving the formation of metal oxides from metal alkoxides goes through two chemical processes: hydrolysis and condensation. The overall hydrolysis reaction is shown in eq. 2.1.

\[
M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH
\]  

2.1

However the reaction is much more complex than is shown. Once hydrolysis begins, condensation reactions occur concurrently. A three step mechanism is proposed for the hydrolysis by Sanchez et. al. (13) which is shown in eq. 2.2. The first step involves the nucleophilic addition of water to the electrophilic metal atom M, thereby increasing the
coordination number. The second step involves a proton transfer from the entering nucleophile to the negatively charged oxygen of the OR group to form an intermediate.

\[
\begin{align*}
H \quad O: + M-OR & \quad \rightarrow \quad H \quad O: \quad M-OR \\
H \quad \quad \quad & \quad \rightarrow \quad \rightarrow \\
\end{align*}
\]

2.2

\[
\begin{align*}
HO-M \quad O \quad R & \quad \rightarrow \quad M-OH + ROH \\
H \quad \quad \quad & \quad \rightarrow \\
\end{align*}
\]

The third step is the departure of the better leaving group to give metal hydroxide and an alcohol.

Condensation is also a complex process and starts as soon as hydroxyl groups are generated. There are three mechanisms for condensation depending upon the experimental conditions. They are (10):

a) **Alcoxolation**: This reaction, shown as eq. 2.3, forms bridging oxo group through the elimination of an alcohol molecule.

\[
\begin{align*}
M \quad O: + M-OR & \quad \rightarrow \quad M \quad O: \quad M-OR \\
H \quad \quad \quad & \quad \rightarrow \quad \rightarrow \\
\end{align*}
\]

2.3

\[
\begin{align*}
M-\quad O-M \quad O \quad R & \quad \rightarrow \quad M-O-M + ROH \\
H \quad \quad \quad & \quad \rightarrow \\
\end{align*}
\]

The mechanism is the same as for hydrolysis with the metal replacing the proton in the entering group. Therefore the thermodynamics and kinetics of the reaction are dependent upon the same parameters as for the hydrolysis step.
b) *Oxolation*: This reaction follows the same mechanism as alcoxolation except that the R group of the leaving group replaces the proton.

\[
\begin{align*}
M_{\text{O}} + M_{-\text{OH}} & \rightarrow M_{\text{O}} - M_{-\text{OH}} \\
M_{-\text{O}} & \rightarrow M_{-\text{O}} + M_{\text{H}_2\text{O}}
\end{align*}
\]

Therefore the leaving group from this reaction is a water molecule.

c) *Olation*: The reactions shown in eq. 2.5 occurs when the full coordination sphere of the metal atom is not satisfied in the alkoxide. Bridging hydroxo groups can be formed via the elimination of water or alcohol molecule.

\[
\begin{align*}
M_{-\text{OH}} + M_{\text{O}} & \rightarrow M_{-\text{O}} + \text{ROH} \\
M_{-\text{OH}} + M_{\text{O}} & \rightarrow M_{-\text{O}} + \text{H}_2\text{O}
\end{align*}
\]

These nucleophilic substitution reactions are strongly favored when the nucleophilic character of the entering group and the electrophilic strength of the metal are high.

Overall, these four reactions, hydrolysis, alcoxolation, oxolation and olation determine the transformation process of metal alkoxides into oxide networks. These reactions and their relative rates therefore determine the structure and morphology of the final product formed. The governing factors for these reactions are:

a) Nature of the Metal atom, M
b) Nature of the alkyl groups, R

c) Water/alkoxide ratio (h)

d) Catalyst

e) Concentration

f) Solvent

g) Temperature.

2.1.3 Governing Parameters

a) Nature of the Metal atom: Transition metal alkoxides are more electropositive than silicon alkoxides and thus more easily hydrolysed. This effect can be quantified in terms of the partial charge model. The combination of two atoms results in charge transfer, each atom thereby acquiring a partial positive or negative charge. This is the basis for the partial charge model which therefore does not account for the precise electronic structures and the changes in the coordinations of the reactant species. However, it can be adequately utilised for an insight into the reaction pathways. The positive partial charge of the metal atom, \( \delta(M) \), for various metal ethoxides which quantifies the electropositivity is shown in table 2.1 (10). This is precisely the reason for higher rate constants mentioned in section 1.1.1. Also, the molecular complexity of the metal alkoxides are dependent on the nature of the metal atom. The size of the metal atom determines the molecular complexity as is evident from table 2.2 (10) which lists the size as we go down the same group of the periodic table.

b) Nature of the alkoxy ligand: For silicon alkoxides, the rate of hydrolysis decreases with increasing alkyl group size (14, 15, 16, 17). These results can be extended to transition metal alkoxides and have been rationalised on the basis of the partial charge model. The partial charge distribution and the associated hydrolysis rate constants are shown in table 2.3 (10). As the positive partial charge of the metal atom decreases with
Table 2.1 Positive partial charge for various metals ($\delta$(M)) in different alkoxides (10)

<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>$\delta$(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(OEt)$_4$</td>
<td>+0.65</td>
</tr>
<tr>
<td>Ti(OEt)$_4$</td>
<td>+0.63</td>
</tr>
<tr>
<td>Nb(OEt)$_5$</td>
<td>+0.53</td>
</tr>
<tr>
<td>Ta(OEt)$_5$</td>
<td>+0.49</td>
</tr>
<tr>
<td>VO(OEt)$_4$</td>
<td>+0.46</td>
</tr>
<tr>
<td>W(OEt)$_6$</td>
<td>+0.43</td>
</tr>
<tr>
<td>Si(OEt)$_4$</td>
<td>+0.32</td>
</tr>
</tbody>
</table>
Table 2.2 Molecular Complexity (Number of Metal atoms per Osmotic Molecule) of some Transition Metal Ethoxides as a function of Metal Size (10)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ti(OEt)₄</th>
<th>Zr(OEt)₄</th>
<th>Hf(OEt)₄</th>
<th>Th(OEt)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent radii (Å)</td>
<td>1.32</td>
<td>1.45</td>
<td>1.44</td>
<td>1.55</td>
</tr>
<tr>
<td>Molecular Complexity</td>
<td>2.9</td>
<td>3.6</td>
<td>3.66</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Table 2.3 Charge Distribution in Ti and Si n-alkoxides (10)

<table>
<thead>
<tr>
<th>R</th>
<th>$\delta$(Ti)</th>
<th>$\delta$(OR)</th>
<th>$\delta$(H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>+0.66</td>
<td>-0.16</td>
<td>+0.12</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>+0.63</td>
<td>-0.16</td>
<td>+0.10</td>
</tr>
<tr>
<td>n-C$_4$H$_9$</td>
<td>+0.61</td>
<td>-0.15</td>
<td>+0.09</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{13}$</td>
<td>+0.60</td>
<td>-0.15</td>
<td>+0.08</td>
</tr>
<tr>
<td>n-C$<em>9$H$</em>{19}$</td>
<td>+0.59</td>
<td>-0.15</td>
<td>+0.07</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R</th>
<th>$\delta$(Si)</th>
<th>$\delta$(OR)</th>
<th>$\delta$(H)</th>
<th>$k_h 10^2$ M$^{-1}$s$^{-1}$[H$^+$]$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>+0.36</td>
<td>-0.09</td>
<td>+0.14</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>+0.32</td>
<td>-0.08</td>
<td>+0.11</td>
<td>5.1</td>
</tr>
<tr>
<td>n-C$_4$H$_9$</td>
<td>+0.30</td>
<td>-0.08</td>
<td>+0.09</td>
<td>1.9</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{13}$</td>
<td>+0.29</td>
<td>-0.07</td>
<td>+0.08</td>
<td>0.83</td>
</tr>
<tr>
<td>n-C$<em>9$H$</em>{19}$</td>
<td>+0.28</td>
<td>-0.07</td>
<td>+0.08</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Table 2.4 Influence of the hydrolysis ratio 'h' upon the charge distribution in monomeric precursors (10)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>h</th>
<th>$\delta$(OPr$^i$)</th>
<th>$\delta$(OH)</th>
<th>$\delta$(Pr$^i$OH)</th>
<th>$\delta$(H$_2$O)</th>
<th>$\delta$(Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(OPr$^i$)$_4$</td>
<td>0</td>
<td>-0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti(OPr$^i$)$_4$(OH$_2$)</td>
<td>1</td>
<td>-0.08</td>
<td>-0.38</td>
<td>+0.01</td>
<td>-0.28</td>
<td>+0.62</td>
</tr>
<tr>
<td>Ti(OPr$^i$)$_3$OH</td>
<td>1</td>
<td>-0.08</td>
<td>-0.38</td>
<td>+0.02</td>
<td>-0.28</td>
<td>+0.62</td>
</tr>
<tr>
<td>Ti(OPr$^i$)$_3$(OH)(OH$_2$)</td>
<td>2</td>
<td>-0.00</td>
<td>-0.36</td>
<td>+0.10</td>
<td>-0.26</td>
<td>+0.64</td>
</tr>
<tr>
<td>Ti(OPr$^i$)$_2$(OH)$_2$</td>
<td>2</td>
<td>+0.04</td>
<td>-0.36</td>
<td>+0.15</td>
<td>-0.25</td>
<td>+0.64</td>
</tr>
<tr>
<td>Ti(OPr$^i$)$_2$(OH)$_2$(OH$_2$)</td>
<td>3</td>
<td>+0.13</td>
<td>-0.34</td>
<td>+0.25</td>
<td>-0.22</td>
<td>+0.65</td>
</tr>
<tr>
<td>Ti(OPr$^i$)(OH)$_3$</td>
<td>3</td>
<td>+0.28</td>
<td>-0.32</td>
<td>+0.41</td>
<td>-0.18</td>
<td>+0.67</td>
</tr>
<tr>
<td>Ti(OPr$^i$)(OH)$_3$(OH$_2$)</td>
<td>4</td>
<td>+0.38</td>
<td>-0.30</td>
<td>+0.52</td>
<td>-0.16</td>
<td>+0.68</td>
</tr>
<tr>
<td>Ti(OH)$_4$</td>
<td>4</td>
<td>-</td>
<td>-0.19</td>
<td>-</td>
<td>+0.01</td>
<td>+0.76</td>
</tr>
</tbody>
</table>
alkyl chain length, the sensitivity of the alkoxide towards hydrolysis decreases. Steric hindrance is also utilised in explaining the reactivity of the metal alkoxides. For a series of isomeric titanium butoxides, the hydrolysis rate observed is in the order tertiary > secondary > normal (18). The condensation rate also decreases with increasing alkyl length size. (19).

c) Hydrolysis ratio (h): One of the main external parameters for control of the sol-gel reaction is the hydrolysis ratio, h, defined as

\[ h = \frac{[H_2O]}{[M(OR)_{n}]}. \]

Livage et al. (10) have divided this factor up into three domains for a rough qualitative analysis

i) \( h < 1 \)

Condensation in this domain is mainly thought to proceed by alcoxolation and olation. Gelation or precipitation does not occur as long as hydrolysis is carefully controlled and an infinite network is seldom formed. Olation and alcoxolation lead to molecular transition metal oxo-alkoxides which have been isolated as single crystals from solution (20).

ii) \( 1 \leq h \leq z \)

\( Z \) here is the coordination number of the metal atom. Calculations based on the partial charge model by Livage et al. (10) is shown in table 2.4 for different values of the hydrolysis ratio. It is evident that the first two steps of hydrolysis are facile since \( \delta(OR) < 0 \) and \( \delta(Ti) > 0 \). Alcoxolation is the favored reaction pathway as \( \delta(\text{IPrOH}) \) is positive leading to chain polymers shown in the simplified scheme shown in eq. 2.6. Such chain polymers were reported to have been synthesized by Boyd (21) with titanium n-butoxides.
A similar method was used by Kamiya et al. to make spinnable sols to enable TiO₂ fibers to be drawn (22). As hydrolysis progresses, positive partial charge of the alkoxide group increases making the proton transfer the rate limiting step. Therefore hydrolysis usually does not go to completion even with \( h = 4 \). The fourth alkoxy group has been proved to be difficult to remove via hydrolysis or alcoxolation (21,23). For silicon alkoxides where the full coordination is already satisfied, oxolation becomes more competitive whereas for transition metal alkoxides olation becomes the preferred reaction. Solvent release upon aging via syneresis proves that olation is the preferred pathway for transition metal alkoxides in this region.

iii) \( h > z \)

Excess water results in very rapid kinetics and usually particulate gels or precipitates are obtained in this domain. Also, the mean size and weight of the macromolecules depend on the hydrolytic ratio in this domain (24,25).

d) **Catalyst Factor**: This is the second external parameter that can be used by the experimentalist to control hydrolysis and condensation reactions which ultimately govern the structure of the final product. Two major types of catalysis can be done; acidic and basic.

The action of an acid catalyst such as HCl or HNO₃ is shown below in eq. 2.7.
The negatively charged alkoxy group is easily protonated by $\text{H}_3\text{O}^+$ and hence the prototropic transfer along with the removal of the leaving group is no longer the rate limiting step. Therefore in the presence of sufficient water, all alkoxy groups are hydrolysable. In general, hydrolysis rates increase using acid catalyst for all alkoxides. This has been proven for silicon alkoxides (14, 15, 27) and for titanium alkoxides (28). The action of acid catalyst on condensation can be seen by considering a partially hydrolysed polymer shown below in eq. 2.8.

\[
\begin{align*}
\text{(A)} & \quad \text{(B)} & \quad \text{(C)} & \quad \text{(D)} \\
\text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR} \\
\text{HO} & \quad \text{Ti} & \quad \text{O} & \quad \text{Ti} & \quad \text{O} & \quad \text{Ti} & \quad \text{O} & \quad \text{Ti} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR} & \quad \text{OR}
\end{align*}
\]

Livage et. al. (10) performed partial charge calculations for the sites A-D, the results of which are shown in table 2.5. The electron donating power of the ligands decrease in the order $D \gg A > C >> B$ and therefore the ease of protonation decreases in that order. Hence condensation takes place preferentially at the chain ends rather than the chain middles leading to more extended and less branched polymers. The synthesis of monolithic gels (25) and spinnable sols (22, 29) via acid catalysis and low $\text{pH}$ values provides rationalization to the previous argument. At higher acid concentration ($[\text{H}^+] = [\text{Ti}]$), condensation is severely retarded.

Strong nucleophiles are produced by base catalysis as shown in eq. 2.9 (10).

\[
\text{M-OH} + \text{B} \rightarrow \text{M-O}^- + \text{BH}^+ \quad 2.9
\]
B, for example, is a species like OH⁻ or NH₃. Referring to table 2.5 showing partial charge calculations for a partially hydrolysed polymer, it is seen that the order of reactivity towards nucleophilic attack would decrease in the order B >> C ~ A > D. Therefore in this case the condensation and hydrolysis are directed toward the middle of the chain rather than the ends and hence more compact, highly branched species are produced. This has been experimentally shown for tetraethyl orthosilicate (TEOS) system by Briaker et. al. (30). Though it has been shown that base catalysis promotes hydrolysis for silicon alkoxides (14,15), hydrolysis rate for titanium sec-butoxide in the presence of NaOH catalyst was less compared to neutral or acidic conditions (28).

e) Concentration Factor: The main effect of the solvent concentration used is the control of interaction between reacting species. The sol-gel transition time can then be controlled by dilution. Yoldas working with titanium alkoxides demonstrated that the gelation time was dependent upon the starting concentration. He showed that under the same conditions a 2 percent solution gelled in 24 hours whereas 1 percent solution did not gel at all. He also showed that the densification and crystallization rate of the TiO₂ samples were dependent upon the dilution factor. The change in density as the materials were sintered was more for the diluted precursor case compared to the undiluted system.

f) Solvent: Proper choice of solvent for sol-gel process is an important external parameter since it affects kinetics and the resulting structure (10). Some alkoxy bridges are more stable towards hydrolysis than associated solvent molecules. Kundu and Biswas (31) demonstrated that when Zr(OPr)₅ is dissolved in n-PrOH, a polar, protic solvent, precipitation occurs. However when dissolved in cyclohexane, a non-polar, aprotic solvent, homogenous gels are obtained. Alcohol association occurs when n-PrOH is used resulting in rapid hydrolysis and condensation leading to precipitation. When cyclohexane is used as solvent, controlled hydrolysis occurs since alkoxy bridging takes place.
**Table 2.5** Charge distribution according to the partial charge model within a titanium oxo-polymer (10)

<table>
<thead>
<tr>
<th>Site</th>
<th>$\delta$(OR)</th>
<th>$\delta$(Ti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.01</td>
<td>+0.70</td>
</tr>
<tr>
<td>B</td>
<td>+0.22</td>
<td>+0.76</td>
</tr>
<tr>
<td>C</td>
<td>+0.04</td>
<td>+0.71</td>
</tr>
<tr>
<td>D</td>
<td>-0.08</td>
<td>+0.68</td>
</tr>
</tbody>
</table>
Therefore, solvent in this case affects the molecular complexity of the starting alkoxides thereby controlling the sol-gel reactions that takes place leading to the final product. Use of high dielectric constant solvents like formamide etc. have rather subtle effects since they may induce different pathways for hydrolysis and condensation through the cleavage of polar M-O-C bonds (10).

g) **Temperature**: The effect of temperature is usually to increase both the hydrolysis and condensation rate (10). For example, Colby et al. have shown the gelation time for TEOS systems catalyzed by HCl to be 380, 70, and 20 hours at 25°C, 50°C and 70°C respectively (66). The dramatic differences in the gelation times are primarily due to the greater hydrolysis and condensation rates.

### 2.2 Inorganic-Organic Hybrid Materials

#### 2.2.1 Introduction

The impetus for commercially important novel materials is always driven by demands and needs of the society. For glasses, these demands have been mainly in the areas of optical and mechanical properties (32). Combination of materials is usually done to achieve a special purpose, a function which the individual materials on their own may not possibly be capable of. Good examples are fiber reinforced composites and other types of composites materials.

The basic passion for the development of inorganic-organic hybrid materials are derived mainly from these three difficulties of sol-gel processing (1):

a) Thick coatings (> 1 μm) are difficult to fabricate and crack easily.

b) The films are generally quite brittle.
c) High temperatures are required for getting optimum properties.

The soft chemical route (temperature wise) of the sol-gel process where organic incorporation is therefore possible makes this route to hybrid materials very attractive. Additionally, this process allows the use of chemistry to control reactions, the formation of pre-inorganic networks in solutions, the densification to inorganic solids at low temperatures and the potential to form new glass compositions (36). In this section review of work done on the innovations and development of hybrid materials like ORMOSILS, ORMOCERS and Ceramers will be discussed.

### 2.2.2 ORMOSILS

The approach of combining inorganic and organic structures at an atomic level to make products on a large scale was developed by H. Schmidt (32). Most of the work done was based on silicates and hence the name ORMOSIL which is an acronym for Organically Modified Silicates. For non-silicate structure, he generalized this term to ORMOCER which stands for Organically Modified Ceramic.

Combination of inorganic and organic networks by distribution of the individual networks in a random fashion without any chemical links between them is possible only by means of having the network formation of each to occur on the same time scale. This is not an easy task since the two networks' hydrophilicity may be very different leading to inhomogenieties like phase separation. Schmidt's idea was to introduce crosslinking points between the two networks which could be in the form of ionic, coordinative or covalent bonding (32). These crosslinked products would then lead to better defined structures. Ionic bonds were proposed to form via mixed salt structures as shown in fig. 2.1 (32). Also shown in fig. 2.1 is the proposal of using transition metal oxides with complex
Fig. 2.1 Examples of ionic and coordinative crosslinking points between an inorganic and organic component (32)
Polymerization

Addition

Condensation

Fig. 2.2 Examples of reactions of network formers (32)
ligands like cyclopentadiene. However, Schmidt and coworkers adopted the use of covalent crosslinking points especially by means of the -O-Si-C bonds. This was chosen due to the good thermal and hydrolytic stability of O-Si-C. Further, the organic component used was divided into two categories; network formers and network modifiers.

The network formers have functionalities such that they could be polymerizable either by addition or condensation reactions as shown in fig. 2.2 (32). The wide variety of choices is immediately apparent which can be implemented by using a spectrum of organic reactions and metal alkoxides. Copolymerization of pure organic monomers also becomes feasible and therefore adds to the choices.

Network modifiers are formed when one or more of the substituents on the Si atom is replaced with a non-reactive substituent. This then decreases crosslinking density and affects the properties of the final products. Also, the nature of the substituents affects the structure and hence the properties. A representative scheme of such a polymer is shown in eq. 2.10

\[
\cdots \text{Me}^n - \text{O-Si-O-Si-O-Me}^n - \text{O-Si} \cdots \\
\text{R} \quad \text{R}
\]

\[2.10\]

\[R = \text{CH}_3, \text{C}_6\text{H}_5 \text{ etc.}\]

The use of different organic substituents can be chosen to impart tailored properties to materials. For example, the properties could be acidic or basic functions, hydrophillic functions, ligands for complex formations etc. (32). Also, the processing properties of the polymers could be changed by varying the substituent. For example, substitution of -CH\(_3\) by -C\(_6\)H\(_5\) led to products being soluble in most organic solvents which was attributed to
lesser degree of crosslinking due to the phenyl group's steric hindrance (32). These basic foundations led to the development of number of novel materials tailored for specific applications by Schmidt and coworkers as well as by others. Some of these examples are discussed next.

One of the first hybrid materials prepared was polymethylmethacrylate incorporated silicon and titanium alkoxides materials for applications as contact lenses (33). Initially, the materials were prepared form epoxy silane and silicon alkoxides or titanium alkoxides. The alkoxides were primarily used for densification purposes. Good mechanical properties of the materials prepared from these precursors were not achieved which therefore led to the use of methacrylates. Methacryloxysilane ((CH₃O)₅Si(CH₂)₃OOC(CH₃)=CH₂) which has polymerizable as well as condensable components has been chosen which would in principle act as a "hook" between the siliceous network and the methacrylate. The methacrylates used were methyl methacrylate or 2-hydroxyethyl methacrylate. The materials were prepared by a two step process. The nonhydrolytic condensation of the starting materials with alcoholic HCl preserves the epoxide moiety as shown in eq. 2.11.

$$2\equiv \text{Si-OR'} + \text{HCl} \longrightarrow \equiv \text{Si-O-Si} \equiv + \text{R'OH} + \text{R'Cl} \quad 2.11$$

R' = alkyl

This step was followed by hydrolytic condensation and polymerization to give the dense desired products. Thus a mixture of epoxysilane, methacryloxysilane and titanium alkoxide was condensed by the two-step process after which the monomeric methacrylate was added. This mixture was polymerized with a peroxide catalyst. The materials prepared had excellent properties required for contact lens like oxygen permeability, contact angle with water and the requisite mechanical properties.
Another example of ORMOSIL developed was for use as hot melt adhesives for sealant purposes. The generalized reaction scheme for such a material is shown in eq. 2.12

\[
\text{Ti(OR)}_4 + \text{Si(OR)}_4 + R_1'R_2'Si(OR)_2 + \frac{\text{H}_2\text{O}}{-\text{ROH}} \rightarrow -\text{O}-\text{Ti}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O} - \frac{R_1'}{R_2'}
\]

\[2.12\]

\[
R_1' = \text{CH}_3 \quad R_2' = (\text{CH}_2=\text{CH})
\]

During the thermal curing step crosslinking also takes place via the vinyl group which determines the viscosity behaviour of the cured material. Therefore the temperature dependence of the viscosity and the sealing strength of the material can be tailored. The materials prepared in this fashion had excellent sealant strength and moisture resistance.

A new family of ORMOSILS were developed by Ravaine et. al. for applications as solid state ionic conductors (35). Tetramethyl orthosilicate or tetraethyl orthosilicate was reacted with polyethylene glycol (PEG) and to this solution lithium containing salts were added. Transparent materials with bridging PEG were reported. The conductivities obtained were much higher than the materials obtained in the vitreous state by conventional melting (35).

Many more ORMOSILS (ORMOCERS) have been synthesized by Schmidt and co-workers for applications especially in optics, functional and protective coatings (36-41). These materials cover a wide spectrum of metal alkoxides used and varied organic modification of silanes for tailoring the properties for specific applications. These would be discussed to some extent in the Applications chapter.
2.2.3 Ceramers

The idea of utilising functionalised organic oligomeric species to co-condense with inorganic based metal alkoxides led to the development of novel hybrid materials also termed "Ceramers" (42). Prof. Wilkes and co-workers who pioneered this area have made a number of novel materials using different metal alkoxides and oligomeric species. In this section, a brief review of their contribution to the area of hybrid materials is presented.

The first ceramer was made with tetraethyl orthosilicate (TEOS) as the inorganic precursor and silanol terminated polydimethyl siloxane (PDMS) as the oligomeric species. The molecular weights of the PDMS used were 1700 g/mol and 3400 g/mol. The materials were prepared by addition of desired amount of water and HCl to the solution of the two reactants in an inert solvent medium. This mixture was refluxed for 30 minutes at 80 °C and then poured into molds. The films obtained were flexible, depending on the inorganic content and optically clear (42). Hence, successful incorporation of the oligomeric species into the siliceous network was achieved with the absence of macrophase separation. An idealized reaction scheme for the synthesis of this material is shown in eq. 2.13 and 2.14 (42).

The TEOS content, acid content, molecular weight of PDMS, and the water content were varied to give a spectrum of materials which were subjected to structure-property relationship study (42-45). The dynamic mechanical analysis of these materials revealed bimodal tan δ behaviour with the two loss maxima occurring at ca. -106 °C and ca. -30 °C. The lower transition temperature results from the glass transition process of the PDMS and the higher transition process which had a broad distribution was ascribed to the relaxations of the PDMS which was well mixed with the silicate phases. Increasing the acid content led to decreasing modulus and higher elongation to break. The authors attributed
this effect to different morphologies produced due to the increased hydrolysis and condensation rates with higher acid content. Self condensation of silanols of the PDMS constituted the early

\[ \text{Si(OR)}_4 + 4\text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{Si(OH)}_4 + 4\text{ROH} \]  

\[ \text{Si(OH)}_4 + \text{HO} \left( \begin{array}{c} \text{CH}_3 \\ \text{Si} \\ \text{CH}_3 \end{array} \right)_x \xrightarrow{\text{OH}} \left( \begin{array}{c} \text{CH}_3 \\ \text{Si} \\ \text{CH}_3 \end{array} \right)_x \]

part of the reaction resulting in molecular weight buildup and hence phase separation. Ultimately, the slowly hydrolysed TEOS would condense with the silanol of the PDMS. Therefore Huang et. al. inferred that the systems were better dispersed with increased acid content. This was confirmed by performing Small Angle X-ray Scattering (SAXS) on the materials. The SAXS profile is a plot of the scattered intensity as a function of the angular vector \( s \) ((2sin\( \theta \))/\( \lambda \)) where \( \theta \) is half the radial scattering angle and \( \lambda \) is the wavelength of the X-ray scattering source. The scattered intensity results from the fluctuations in the electron density of the sample. For a periodic fluctuation of the electron density, a peak or a shoulder is observed in the scattering intensity plot. As the electron density fluctuation increases, so does the scattered intensity whereas if the system is well mixed, the scattered intensity decreases. Huang et al. (44) observed decrease in the scattered intensity with
increasing acid content which lends validity towards a better dispersed system. However, increasing acid content and the conditions of synthesis (80 °C) could lead to degradation of the siloxane chains offering alternate explanations of the results. Higher TEOS content increased the plateau storage modulus and led to a decrease in magnitude of the tan δ behaviour.

Ceramers using polytetramethylene oxide (PTMO) instead of PDMS were also made by Huang et al. (45). Uncertainty about the degradation of the PDMS chains and better mechanical properties of the PTMO led to its choice as the organic modifier. Also, PTMO was endcapped with triethoxysilane thereby increasing the effective functionality to six. The parameters examined were metal alkoxide to oligomer weight ratio, acid to metal alkoxide ratio, solvent media, aging and molecular weight of the oligomeric species. The loss behaviour from dynamic mechanical studies showed broad unimodal dispersion as compared to the bimodal dispersions from the TEOS/PDMS materials. The glass transition temperature increased with higher TEOS content. Two types of motional restrictions were cited to account for this behaviour:

a) Type I : The effect of bonding the ends of the chains into the network.

b) Type II : The effect of mixing of the PTMO segments with the highly condensed TEOS species or the encapsulation of the PTMO segments by the silicate species.

Significant differences in the TEOS/PTMO ceramers as opposed to those based on TEOS/PDMS were ascribed to the increased functionality of the oligomers in the former materials. Also, aging effects were observed in the TEOS/PTMO ceramers at ambient or at elevated temperatures for a short time period. Condensation of unreacted silanol and/or alkoxides in the gels were explanations given for the aging behaviour. Titanium tetra-isopropoxide (TIP) was also incorporated in the TEOS/PTMO hybrid materials and aging
was also observed in these materials (46). Aging in all these materials were attributed to diffusion limited curing of the TEOS based species.

A morphological model of these hybrid materials was proposed to account for the observed structure-property behaviours (44, 46). The model as applied to TEOS/PTMO hybrids is illustrated in fig. 2.3. The three schematic regimes in this model are:

a) The PTMO rich region
b) The silicate rich region
c) The PTMO/silicate mixed region

These regions are expected to change with different composition and molecular weight of the oligomers used. Appropriate modifications of this model with respect to the varying parameters have helped account for the mechanical properties and the scattering behaviour of the hybrid materials. The distance between the silicate regions is obtained from the reciprocal of the 's' (angular vector) value corresponding to the maxima in the SAXS intensity profile.

Noël et. al. utilised functionalised poly (arylene ether ketone) (PEK) with TEOS to make another series of novel hybrid materials (47). The major differences with respect to the other ceramers were that the molecular weight of the PEK was higher and its glass transition temperature (ca. 150 °C) was much higher. The higher glass transition temperature apparently has the effect of leading the system to early vitrification and hence limited extent of reaction. However, subjecting the material to higher temperatures solved this problem and better properties were achieved. The structure-property relationship could be explained on a basis similar to the earlier ceramers.

Spiau et. al. (48, 49) incorporated methoxysilyl terminated PDMS into silicate networks formed from tetramethyl orthosilicate (TMOS) in the absence of catalysts. A
Fig. 2.3 Morphological model of a Ceramer (44,46)
broad range of compositions were studied and efficient incorporation of the PDMS into the inorganic networks were achieved. Also, the overall extent of conversion of the glassy component was affected by the PDMS modifier as proved by $^{29}$Si solid state NMR.

Spinu et al. (48, 49) also synthesized hybrid materials by replacing the PDMS with functionalized polyimides. However, unsatisfactory extent of crosslinking at temperatures below the glass transition temperature led to inefficient incorporation. As in the case with PEK modified silicates, this effect was attributed to the vitrification of the network before the glass transition of the polyimide was reached.

Brennan made TEOS/PTMO ceramers with poly (styrene sulfonic acid) (PSS) instead of HCl as the acidic catalyst (50). The structure-property relationships of these materials were similar to ceramers made with the HCl catalyst. However, extent of reaction in the PSS catalysed ceramers was postulated to be higher.

Also, novel materials incorporating TIP and zirconium tetra-n-propoxide into silane functionalised PTMO were synthesised by Brennan et al. (50, 51). The dispersion loss obtained from the dynamic mechanical analysis of these materials was significantly different from TEOS/PTMO hybrids. The loss maxima temperature at ca. -70 °C was much lower than that observed for TEOS/PTMO hybrids which occurred at ca. -10 °C. Therefore the level of phase mixing between the two phases in these new materials was much lower. The mechanical properties of these materials were also superior to those of the TEOS/PTMO hybrids. SAXS study of these materials indicated a microphase separation morphology similar to that of the TEOS/PTMO hybrids. The correlation length 'd' ranged from 10 to 17 nm for these new materials. The higher reactivity of titanium and zirconium alkoxides and the apparent higher extent of reaction according to Brennan lead to little or no evidence of aging in these materials (50).
Kohjiya et al. have also prepared hybrid materials following similar methods used for making ceramics (60). The oligomeric species used were hydroxyl terminated PDMS, hydroxyl terminated PTMO and triethoxysilyl terminated PTMO while the inorganic precursor was TEOS. Soxhlet extraction studies were done to see the efficiency of incorporation of the oligomeric species into the inorganic network. Hydroxyl terminated PTMO showed very poor incorporation efficiency. Both triethoxy silyl terminated PTMO and hydroxyl terminated PDMS showed good incorporation, the former being more efficient.

2.2.4 Other Hybrid Materials

Major contributions have been made by J. E. Mark et al. for reinforcing elastomers with mostly silica fillers generated in-situ by the sol-gel process (52-58). The main thrust was to generate fillers by precipitation within a polymer after the polymer is cured into a network structure. This method proves to be advantageous over traditional methods of introducing fillers which happens to be a time consuming and energy extensive process. Also, premature gelation and control of structure are difficult in the conventional mixing process (53). The general procedure for making in-situ filler reinforced elastomers was to swell the elastomeric network in TEOS. The weight percent of the fillers to be incorporated could be controlled by this process. After this process, and phase transfer catalysts were added to the system which resulted in the generation of in situ precipitation of SiO₂ (53). Mark et al. went on to study the effect of various catalysts (54,57) and bimodal distribution of the elastomeric network (55). Elastomers containing large mole fraction of short chain linked with large chains, resulted in superior mechanical properties. Simultaneous curing and filling was achieved by mixing hydroxyl terminated PDMS, TEOS and the catalyst after which they were poured into molds for casting. Water required for hydrolysis was
allowed to be absorbed via humidity in air (56). Elastomeric networks of PDMS
crosslinked with titania fillers were also made (58). The characterization of these networks
were mainly done by stress-strain analysis which proved that this new technique of
incorporation of fillers was efficient and resulted in better elastomeric properties when
compared to those made by conventional mixing process.

incorporation of acrylate polymers into SiO₂ networks to give novel hybrid
materials has been reported by Wei et al. (59). Poly(allyl methacrylate) (PAMA) and
poly(allyl methacrylate -co- methyl methacrylate) (PA-MMA) were prepared by group-
transfer polymerization which has been demonstrated to be a living polymerization
process. The carbonyl conjugated vinyl groups in the monomers get polymerized leaving
the allylic groups intact.

\[
\begin{align*}
\text{MeO} & \quad \text{O} \quad \text{O} \\
\text{CH}_2\text{CHCH}_2\text{O} & \quad \text{CH}_2\text{CHCH}_2\text{O} \\
\text{Me} & \quad \text{Me} \\
\text{CH}_2\text{C} & \quad \text{CH}_2\text{C} \\
\text{COOMe} & \quad \text{COOMe} \\
\text{COOCH}_2\text{CH} & \quad \text{COOCH}_2\text{CH} \\
\text{Me} & \quad \text{Me} \\
\text{CH}_2\text{C} & \quad \text{CH}_2\text{C} \\
\text{COOMe} & \quad \text{COOMe} \\
\text{COOCH}_2\text{CH} & \quad \text{COOCH}_2\text{CH} \\
\end{align*}
\]

PAMA (x = 0) or PA-MMA

Then triethoxysilyl groups are introduced into the polymers by hydrosilation of the allylic
vinyl groups. These polymers are then combined with TEOS with acid catalysed hydrolysis
and polycondensation to give transparent, monolithic materials.
Nandi et al. used the concept of site isolation to synthesize polyimide matrices which trapped very small sized SiO₂ and TiO₂ clusters (61). They prebind the oxide precursors (TEOS, titanium tetra-ethoxide) with the polymer before the final curing step. This is thought to be achieved by the reaction of the precursor with the carboxylic acid of the polyamic acid, thereby preventing the agglomeration of the inorganic species. The water released during the imidization step is then utilised for the hydrolysis of the metal alkoxides, eventually generating small sized clusters in the polyimide matrix. Mostly golden yellow, transparent, and flexible films were obtained. The TiO₂ polyimides' 10 weight percent degradation temperature was lowered compared to the undoped polyimide while that of the SiO₂ doped materials was higher (61).

Long et al. (62) synthesized trimethoxysilyl terminated polystyrene via the living polymerization route, the structure of which is shown below in eq.2.16.

\[
\text{CH}_3\text{CH}_2\text{CH} - \left(\text{CH}_2 - \text{CH}\right)_n \text{CH}_2 - \text{Si(OCH}_3)_3
\]

The single terminal reactive group provides the coupling center for these macromonomers via hydrolysis of the trimethoxysilyl end groups. The final products obtained by this coupling are high molecular weight, completely soluble starshaped polymers which were characterized by size-exclusion chromatography (63). Although this material’s inorganic content is small (molecular weight dependent), it has the potential of being utilised with tetra-alkoxyxysilyl monomers to form higher inorganic content hybrid materials.

The field of optics has been one of the major beneficiaries of the sol-gel process. The need for materials in the form of films or fibers with large second order optical nonlinearities is immense which has led to the development of several hybrid materials. The
discussion would be done in more detail in the Applications chapter. However, two examples would be discussed here to complete the spectrum of organic/inorganic hybrid materials.

Prasad et al. have prepared hybrid materials of conjugated optically nonlinear polymer and inorganic oxides from metal alkoxide precursors (64). For example, a sulfonium salt of poly p-phenylene vinylene (PPV) is homogeneously mixed with the metal alkoxide in a common solvent. The film is cast and heat treated to give the final conjugated polymer (eq. 2.17).

\[
\begin{align*}
\text{CH} & \text{-CH}_2 \\
\text{S} & \text{Cl} \\
\end{align*} \quad T = 220 \degree C \quad \begin{array}{c}
\text{CH} \\
\text{S} \\
\end{array} + \text{HCl} + \text{S} \quad 2.17
\]

The final material is transparent with good waveguiding capability. However, the morphology and the microstructure of these materials have not yet been investigated.

Another approach is to have the organic optically nonlinear chromophore directly attached to the metal as in N-(3-triethoxysilyl) propyl-2,4-dinitrophenylamine shown in eq. 2.18.

\[
\begin{array}{c}
\text{Si} \\
\text{CH}_2 \quad \text{NO}_2 \\
\text{EtO}_3 \\
\end{array} \quad 2.18
\]

This precursor along with the metal alkoxides are subjected to the usual hydrolysis and condensation after which they were poled at 120 \degree C by a corona discharge technique (65). The properties obtained by this method were superior to the materials made by doping.
Novak et al. have developed a route for making hybrid materials without any shrinkage in the drying stages (126-128). Tetraalkenyl orthosilicates were used instead of TEOS to form the SiO₂ matrix while the unsaturated alcohol released was polymerised in situ using free radical techniques. Such a scheme is shown in eq. 2.19 below (127).

This approach solves the problem of incompatibility between the two components and also eliminates the shrinkage problem associated with drying. Novak et al. (128) have recently used silicic acid oligomers to increase the glass content in these materials and achieved in making transparent monolithic hybrid materials. Variety of co-solvent monomers have been used to make materials which ranged from being rubbery in nature to stiff at room temperature.

2.3 Microwave Curing of Materials

One of the research objectives mentioned earlier was to process the hybrids in the presence of electromagnetic field and compare the properties of the product with the thermally cured ones. Therefore a brief discussion of microwave processing is presented in this section as a part of the literature review.

The ability of a material to heat is dependent upon the effective dielectric loss factor of the material which in turn is directly related to its structure. An easily polarisable material
has a high loss factor and therefore heats readily under an electromagnetic field. The power absorbed is directly related to the dielectric loss as shown below

\[ P_a = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E^2 V \]

where \( P_a \) is the power absorbed, \( \omega \) is the frequency, \( V \) is the volume in m\(^3\), \( E \) is the electric field strength, \( \varepsilon_0 \) is the permittivity of vacuum and \( \varepsilon_{\text{eff}} \) is the effective dielectric loss factor of the material. The polarising field alternating directions at high frequency causes the molecule to agitate. This agitation generates friction amongst the molecules which in turn causes the material to heat. Thus, heat is generated from within the material. Thermal heating of material proceeds by conduction and convection, thereby being independent of the structure of the material. The advantage of microwave heating is then immediately apparent since it can induce selective heating as compared to the thermal process. Many polymeric materials possess lossy functional groups like nitrile, hydroxyl, amine or epoxy. The concentration of such groups basically determine the heatability of the materials and also the heating rate (67).

The effect of microwave radiation on reactions has been studied for many systems and the major conclusion has been that the reaction rates are accelerated. Cure of epoxy and modified epoxy systems by microwaves has been studied extensively. Accelerated cure rates were achieved but the mechanical properties do not differ significantly from the thermally cured materials (68, 69, 70). However, the morphology of the thermoplastic modified epoxy showed a lower degree of phase separation (70). These differences apparently resulted from the differences in viscosity during the cure which affects the phase separation kinetics.

The room temperature curing of Ceramers is a long process (2-3 days). Therefore Rodrigues et al. (71) utilised microwave radiation to cure these materials and in some
formulations, the gelation times were reduced from 144 hours to 20 minutes. TEOS/PTMO
cermers catalysed by acid in a reaction medium of differing proportions of dimethyl
formamide (DMF) to isopropanol (IPA) were subjected to microwave radiation at 2.45
GHz and initial power of 10 watts. The structure-property relationship were studied by
dynamic mechanical analysis, stress-strain response and SAXS. Besides the shortening of
cure times, the microwaved samples had remarkably different properties than those cured
thermally at the same temperature. The modulus and the extent of curing and densification
(concluded from SAXS) of the microwave cured samples were higher. However, the
morphologies of the oven and microwave cured materials were deemed to be to be similar.
Rodrigues (72) concluded that the phase separation characteristics are set almost at the time
reaction begins and hence cannot be significantly altered by the mode of curing. TIP/PTMO
cermers were also made by microwave curing by Rodrigues (72). The differences in these
cermers cured thermally and by microwaves were not as great as observed in the
TEOS/PTMO systems. The faster reaction rate of the titanium alkoxides is believed to be
the responsible factor. However, the reaction rate was influenced by microwave radiation
since a higher degree of phase separation was seen in the microwave cured materials by
dynamic mechanical analysis. Zirconium propoxide/PTMO cermers were also processed
by microwave curing but virtually no differences in the structure-property relationships
were obtained compared to the thermally cured samples. This was attributed to the lack of
water used for the reaction. The lack of water results in low amounts of hydrated metal
oxides which have higher dielectric loss factor than the alkoxides (72).
Chapter 3 --- Oligomer Incorporation Studies and Synthesis of TIP end capped PDMS

3.1 Introduction and Objectives

3.1.1 Oligomer Incorporation Studies by $^{29}$Si NMR

The primary objective of this research was to study the formation of Si-O-Ti bond as a result of the linkage of a titanium oxide network and a silanol terminated PDMS. The crucial point in the formation of an inorganic-organic hybrid material is this bond formation and hence generated strong interest. The other reason which stems from the processing aspect will become clearer after a brief discussion of the rationale for choosing the starting precursors, titanium tetra-isopropoxide (TIP), and silanol terminated PDMS.

Titanium oxide containing PDMS has been reported by Mark et al. (58). However, the level of inorganic content was very small (< 1 weight percent). Also, their primary objective was to make toughened elastomeric networks which therefore limited the extent of the inorganic content. The characterization was primarily restricted to stress-strain analysis of the materials and the synthetic technique employed to make these materials were very different. Parkhurst et al. (73) have reported PDMS modified SiO$_2$-TiO$_2$ materials which were characterized by thermal analysis. But PDMS modified TiO$_2$ material has not yet been reported using a variety of different compositions and the effect of different variables of the sol-gel process. This was one of the driving factors for initiating this research. Also, PDMS was a low refractive index material and TIP is a precursor to high refractive index oxide which opened up the possibility of making optical filters. The refractive index of the material would be dependent upon the
composition and therefore would allow the generation of materials with tailored optical properties.

Optical characterization meant depositing thin films which brings out the importance of the Si-O-Ti bond formation from the processing point of view. The maximization of the incorporation of the PDMS into the inorganic network would be determined by the Si-O-Ti bond formation, the magnitude of which we can predict based on the molecular weight of the PDMS. It would be optimum to deposit the solution when the incorporation is at the maximum in order to obtain good properties of the final product. In addition to these reasons, any study of this nature by $^{29}$Si NMR spectroscopy has not yet been reported.

The $^{29}$Si NMR technique was selected because it is very sensitive and has a good dispersion with the changing environment around the Si atom (84). Though there are no reported literature values for the chemical shift of the Si-O-Ti bond in this specific chemical environment, it was felt that the signal from it would be fairly displaced from that of the silanol silicon and the backbone silicons. The determination of the chemical shift could then establish the basis for the characterization of these hybrid materials by the solid state NMR technique.

### 3.1.2 Synthesis of TIP endcapped PDMS

The results from the incorporation studies proved degradation of the siloxane chains. Therefore a different approach had to be used to make successful hybrid materials based on TIP and PDMS. A good way of avoiding the degradation of the siloxanes would be to have the gelation occur as fast as possible and to have the Si-O-Ti bond already formed in the oligomeric species, making incorporation into the growing inorganic network
automatic. One way of achieving these objectives is to use titanium tri-isopropoxide endcapped PDMS instead of the silanol terminated PDMS. The Si-O-Ti bond is resistant to hydrolysis (80) and therefore would not be detrimental to the incorporation process. Also, the functionality of the PDMS would be increased to six thereby tremendously raising the probability of the incorporation. Besides the advantages of faster gelation and minimization of the degradation of the PDMS, the reactivity of the two vastly different components would become very similar. Basil et al. (77) have shown the homocondensation rates of the silanols to be higher than the heterocondensation rate to form Si-O-Ti in a TEOS-titanium tetra-ethoxide system. As mentioned previously in chapter 2, the kinetics of the titanium system is orders of magnitude higher than that of the silicon system. Therefore the approach of having TIP endcapped PDMS has fundamental implications on the kind of structure and morphology the hybrid materials would possess.

There have been numerous reports on the synthesis of compounds containing the Si-O-Ti bonds, some of which are referenced here (78-82). Most of the work was done by Andrianov and co-workers in the period between 1950-1965 and have appeared mostly in Russian journals and have been well reviewed in references 81 and 82. Reaction between titanium alkoxides and silanol terminated polysiloxanes were done mainly in mole ratios of ca. 4:1 to synthesize elastomers (83). However, structural and synthetic details in most of these literature are sketchy at the best.

The first method to incorporate TIP at the ends of the PDMS was based on the conditions employed in the reaction between butyl titanate and a, w - polyorganosiloxane diol (82). The synthesis required heating at 150 °C for 3 hours in nitrogen atmosphere followed by 30 minutes at 200 °C and reduced pressure. The second method involved the slow addition of silanol terminated PDMS solution in toluene to a boiling dilute solution
of TIP in toluene, thereby, allowing continuous removal of the alcohol formed. This method was based on the technique used by Bradley et al. (79) to make tetrakis(trimethyl siloxy) titanium at 100 percent yield and Zeitler et al. (78) to make tetrakis(triphenyl siloxy) titanium.

3.2 Experimental

3.2.1 Oligomer Incorporation Studies by $^{29}$Si NMR

The structure of the starting materials TIP and PDMS are shown in fig. 3.1. TIP (98 percent purity) was obtained from Aldrich while PDMS was obtained from Petarch. The molecular weight of the PDMS was ca. 1800 g/mol. Both these materials were stored under dry argon. Isopropanol used as solvent was obtained from Fisher, distilled over magnesium and iodine to remove traces of moisture and stored under argon. Acid catalyst, whenever used, was 10 N HCl and distilled water was used for the hydrolysis and condensation reactions.

The composition utilised for this study was fixed at 50:50 by weight percent of TIP to PDMS. The acid catalyst, whenever used, was fixed at [HCl]/[alkoxide] ratio of 0.06. The water used was fixed at [H$_2$O]/[alkoxide] ratio of 0.25. The variables changed to make different solutions are listed in table 3.1. A generalised scheme for making the solutions will now be described. As was mentioned before, TIP is an extremely moisture sensitive compound. Therefore care was taken to avoid any traces of moisture in the glassware used by flame drying under argon purge. The appropriate amount of PDMS and TIP were syringed into two 50 ml flasks respectively after which a fifty percent solution of both was made in isopropanol. The water and acid (whenever used) was diluted with appropriate amount of isopropanol and was then added to the TIP solution.
Fig. 3.1 Structure of the precursors, TIP, and silanol terminated PDMS
Table 3.1 Description of the solutions studied by $^{29}$Si NMR

<table>
<thead>
<tr>
<th>Solution Code</th>
<th>Reaction Temp.</th>
<th>Nature of TIP</th>
<th>Acid Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>room temp.</td>
<td>undistilled</td>
<td>yes</td>
</tr>
<tr>
<td>B</td>
<td>room temp.</td>
<td>undistilled</td>
<td>no</td>
</tr>
<tr>
<td>C</td>
<td>reflux temp.</td>
<td>undistilled</td>
<td>no</td>
</tr>
<tr>
<td>D</td>
<td>room temp.</td>
<td>distilled</td>
<td>no</td>
</tr>
<tr>
<td>E</td>
<td>reflux temp.</td>
<td>distilled</td>
<td>no</td>
</tr>
</tbody>
</table>
drop by drop via the cannula technique while stirring vigorously. After the addition was over, the solution was stirred for another 1-2 minutes after which the PDMS solution was added to it. This solution was then maintained at room temperature or subjected to reflux conditions (ca. 82 °C). Portions of this solution were then taken at appropriate intervals for $^{29}$Si NMR spectroscopy. The distillation of TIP was carried out under reduced pressure at a temperature of ca. 50 °C. The initial and final fractions were rejected, the middle fraction was collected and stored under argon.

3.2.2 Synthesis of TIP endcapped PDMS

The reaction for making TIP endcapped PDMS is shown in fig. 3.2. TIP was added to PDMS in a 2:1 mole ratio in a clean and dry flask. Once again, all precautions were taken to maintain the moisture free nature of the apparatus used. The temperature was raised to 150 °C and the reaction flask subjected to vacuum to remove the isopropanol formed. $^{29}$Si NMR spectra were recorded at every hour for 3 hours to monitor the reaction.

The second method involving the use of toluene as co-solvent for the synthesis is described here. The apparatus consisted of a four necked reaction flask with a magnetic stir bar in it. Each of these necks were attached to an argon line, addition funnel, Dean-Stark trap to which a condenser is attached, and a temperature probe for monitoring the reaction temperature respectively. A heat tape was wrapped around the arm of the Dean-Stark trap to prevent condensation of the distillate on its sides. This apparatus once setup was flame dried under vacuum 3 times to remove all traces of moisture. The flask was then kept under argon atmosphere. Typically about 0.03 moles (60 gms) of silanol terminated PDMS was weighed into a dry flask which was then subjected to vacuum with stirring for 2 hours to remove dissolved air. The PDMS was then dissolved in equivalent
Fig. 3.2 Reaction to form TIP endcapped PDMS
volume (60 ml) of toluene and transferred to the addition funnel. The toluene used was distilled over calcium hydride to remove moisture from it and then stored under argon. About 250 ml of toluene was transferred to the reaction flask and the requisite amount of TIP (0.06 moles) added to it. The transferring of all the reagents was accomplished by the cannula technique. Heating of the reaction flask was commenced and after 20 minutes toluene started to collect in the Dean-Stark trap. The temperature stabilised at ca. 110 °C and after some time (~ 10 minutes) the PDMS solution from the addition funnel was added drop by drop. The isopropanol formed in the reaction along with the toluene collected in the Dean-Stark trap and was removed at regular time intervals. After the addition is over, the reaction was continued for another half hour at 120 °C. At this point most of the toluene had been removed from the system. The heating was stopped and the flask is then subjected to vacuum at room temperature for 4 hours to remove any traces of toluene. The reaction product was then stored under argon and was characterized by $^{29}$Si NMR, $^1$H NMR, Vapor Phase Osmometry (VPO) and intrinsic viscosity.

### 3.2.3 $^{29}$Si NMR solution technique

The $^{29}$Si NMR study was done on 400 MHz Varian Spectrometer at a frequency of 79.459 MHz. 5 mm NMR tubes with septa which were flame dried under argon were used as sample holders. The experiments were carried out with acquisition time of 1.2 seconds, relaxation delay of 20 seconds, pulse width of 20 mseconds and number of repetition of a minimum of 120 times. The spectrum acquired was then fourier transformed with a line broadening of 1 Hz.

### 3.2.4 $^1$H NMR technique

$^1$H NMR spectroscopy was done on 400 MHz Varian spectrometer with acquisition time of 3.744 seconds, relaxation delay of 1 second and pulse width of 0.5 msec. The number of repetitions was sixteen.
3.2.5 Vapor Phase Osmometry

Vapor phase osmometer, model 233-200, made by Wescan Instruments was used to determine the molecular weights of both the silanol terminated PDMS and the TIP endcapped PDMS. The experiments were carried out at 50 °C and the solvent used was toluene. The calibration curve was determined using narrow molecular weight distribution polystyrene standards whose molecular weights spanned the expected molecular weights of the PDMS. For each concentration an average of four runs was used for the calculations.

3.2.6 Intrinsic Viscosity Experiment

The intrinsic viscosity was estimated by the time required for a specified volume of a known polymer solution concentration to flow through a capillary tube compared to the time required by the pure solvent at a temperature of 25 °C. An Ostwald-Fenske type viscometer was used for these experiments. Four concentrations of each oligomer were used. The solvent used was toluene. The inherent and the reduced viscosities were calculated and the intrinsic viscosity determined by double extrapolation method.

3.3 Results and Discussion

3.3.1 Oligomer Incorporation Studies by $^{29}$Si NMR

The $^{29}$Si NMR spectrum of neat PDMS is shown in fig. 3.3a. Also shown in fig. 3.3b is the spectrum of the same PDMS in isopropanol. The peak at the lower chemical shift is due to the silanol silicon whereas the peaks at ca. -22 - -23 ppm are due to the backbone silicons. Taking the ratio of the integrated peak area, the number average
Fig. 3.3a $^{29}\text{Si}$ NMR spectrum of neat silanol terminated PDMS

Fig. 3.3b $^{29}\text{Si}$ NMR spectrum of solution of silanol terminated PDMS in isopropanol
molecular weight ($M_n$) was determined to be 1900 g/mol. This was confirmed by VPO which showed the molecular weight to be 1923 g/mol.

The results from the bond formation studies were anticipated to be a new signal due to the Si-O-Ti bond and that the magnitude or the ratio of the integrated peak area to that of the backbone silicon would approach a value similar to that observed for the precursor PDMS. Fig. 3.4 shows the results for solution A. We observe a new peak emerging at -15.6 ppm as opposed to the silanol peak seen at -14.4 ppm for the PDMS solution. We attribute this new peak at -15.6 ppm to the Si-O-Ti bond, which is justified on the basis of group electronegativity. More importantly, this assignment is proved by the results which are presented in this section as well as by the NMR spectra presented in the TIP endcapped PDMS section. Prediction of $^{29}$Si NMR shift based on the sum of the group electronegativity of the substituents on the silicon atom of interest was first put forward by Oldfield et al. (74). Electronegativity is basically the ability of an atom in a molecule to attract electrons to itself. Oldfield et al. regarded the polyatomic groups (the substituents) as pseudoatoms and termed their electronegativity as 'group electronegativity'. The group electronegativity was correlatable to the $^{29}$Si chemical shifts. For example, the chemical shift of the silicon in trimethyl siloxy group of tetrakis trimethylsiloxy titanium ([((CH$_3$)$_3$SiO)$_4$Ti]) is 13.0 ppm, and for tetrakis (trimethylsiloxy) silicon ([((CH$_3$)$_3$SiO)$_4$Si]), it appears at 8.0 ppm (75). The Pauling electronegativity of Al and Ti have the same value of 1.5 (76). Based on this we can assume OAl and OTi to have the same group electronegativity which is 3.73 (76). The group electronegativity of OSi is ca. 3.9 which then explains the upfield shift in the case of tetrakis trimethylsiloxy silicon compared to tetrakis (trimethylsiloxy) titanium. The group electronegativities for OH, OAl and OSi are 3.59, 3.73 and 3.9 respectively. Therefore the Si-O-Ti peak should appear somewhere between the silanol and the backbone silicon peaks. This certainly seems to be the case for the $^{29}$Si NMR spectrum of solution A. However, it should be
Fig. 3.4 $^{29}$Si NMR spectra of solution A
Fig. 3.5 $^{29}$Si NMR spectra of solution B
Fig. 3.6 $^{29}\text{Si}$ NMR spectra of solution C
Fig. 3.7 $^{29}\text{Si}$ NMR spectra of solution D
Fig. 3.8 $^{29}\text{Si}$ NMR spectra of solution E
noted that the group electronegativity concept is only an approximate one since the structural complexity is not really accounted for in this approach. But it does give an approximate idea of the chemical shifts and therefore definitely is of some predictive utility. This new peak at -15.6 ppm grows beyond the magnitude that we would expect it to relative to the signal from the backbone silicons. Therefore we conclude that the siloxane chains are being degraded in solution with time. Also, there is another peak around -8.6 ppm which could be due to the D₃ cyclic species. Hence, this solidified the belief that the PDMS chains were definitely degrading and the possible reason could be the HCl catalyst. Degradation of the siloxane chains under the influence of acid has been reported before (73). Therefore solution B was made without the acid catalyst but the results remained the same. The spectrum for solution B is shown in fig. 3.5. The Si-O-Ti peak grew disproportionately with time. The reaction was carried out at elevated temperature (82 °C) to increase the efficiency of the incorporation in a shorter time. This was solution C for which the results are shown in fig. 3.6. The results remain the same and perhaps in this case the degradation is faster. The conclusion reached was that maybe the impurity in TIP is TiCl₄ which on reaction with water would release HCl which in turn would degrade the siloxane chains. Also, the TIP obtained from Aldrich was yellowish as opposed to being colorless. Therefore the TIP was distilled and used to make solutions D (room temp.) and E (reflux temp.) without the acid catalyst. The results are shown in fig. 3.7 and fig. 3.8 respectively and show the same trend as was seen before. Therefore the conclusion was that TIP itself was responsible for the degradation of the siloxane chains.

3.3.3 Synthesis of TIP endcapped PDMS

The ²⁹Si NMR spectra of the reaction based on the first method using neat precursors at elevated temperature to make TIP endcapped PDMS is shown in fig. 3.9.
Fig. 3.9 $^{29}$Si NMR spectra of the reaction performed under neat conditions
A new peak emerges at -16.4 ppm which is in the vicinity of the Si-O-Ti peak seen in the previous discussion. The slight shift is attributed to the solvent effect in the previous spectra. This peak grows with time and eventually reaches the magnitude it is expected to determining the end of the reaction. Also, the backbone silicon peaks are seen at approximately -22 ppm where the smaller peaks are due to the silicons closer to the terminal group. The chemical shifts of these peaks are affected by the incorporation of TIP at the ends of the siloxane chains. Therefore it was concluded that TIP endcapped PDMS could be made by this technique. However, the possibility of the side reaction of homocondensation of the silanols and the drastic reaction conditions were definite disadvantages. These factors led to the use of boiling toluene as a common solvent for the reaction. If a dilute solution of silanol is added to a very dilute boiling solution of TIP, then the disadvantages of the neat reaction are minimised to a great extent. The reaction occurring in boiling toluene provides an effective means of removal of the isopropanol formed in the reaction and also lessens the probability of silanol homocondensation. The reaction conditions are also milder than the previous technique. The reaction product, on a qualitative basis seemed to have similar flow characteristics in comparison to the PDMS precursor and was also colorless. Fig. 3.10 shows the $^{29}$Si NMR spectrum of the titanium tri-isopropoxide endcapped PDMS made by this method. The area ratio of the Si-O-Ti peak to those of the backbone silicons are in good agreement with that obtained from the PDMS precursor. The $^1$H NMR spectrum of the reaction product is shown in fig. 3.11. The two sets of doublets arise from the protons of the methyl groups of the isopropoxide. The upfield set is due to the isopropoxide of the TIP endcapper attached to the PDMS while the downfield set belongs to unreacted TIP. The multiplet at 4.0 ppm is due to the methine proton of the isopropoxide of the TIP endcapper. From these results we can conclude that efficient endcapping of the PDMS with TIP is achieved. Molecular weight studies by VPO were done to confirm the possible effect of chain extension. The $M_n$ of the precursor, silanol terminated PDMS was found out to be 1923 gms/mol while
Fig. 3.10 $^{29}$Si NMR spectrum of the reaction product made in toluene
Fig. 3.11 $^1$H NMR spectrum of the reaction product made in toluene
that of the TIP endcapped PDMS was 2202 g/mol. Though no presence of cyclics were seen in the NMR spectra, intrinsic viscosity studies were done to confirm this aspect. The intrinsic viscosity of the silanol terminated PDMS was 0.0349 dl/g while that of the TIP endcapped PDMS was 0.0369 dl/g. Therefore these studies proved that no significant chain extension or cyclics formation takes place during the reaction. This synthetic technique was therefore the method of choice for making the TIP incorporated PDMS for use in making the hybrid materials.

3.4 Conclusions

The Si-O-Ti $^{29}$Si peak assignment for this specific chemical environment was -15.6 ppm. The Si-O-Ti peak grows disproportionately and exceeds the expected theoretical magnitude. Therefore, we concluded that the siloxane chains are being degraded and that the primary cause of the degradation is TIP, contrary to earlier expectations that HCl was the cause.

An efficient synthesis technique for TIP incorporated PDMS was achieved. The structural studies by both $^{29}$Si and $^1$H NMR proved this fact. The molecular weight determined by VPO was in agreement with the expected values. The intrinsic viscosity was also very close to that of the starting silanol terminated PDMS.
Chapter 4 ---- Fabrication of Hybrid Materials and Their Properties

4.1 Introduction and Objectives

The structure of the precursor TIP and TIP end-capped PDMS used for making the hybrids are shown in fig. 4.1. Also shown in the figure is the structure of tetra-ethyl orthosilicate (TEOS) which was used instead of TIP in certain cases. The first objective was to fabricate free standing films to enable evaluation of their properties. Three different cure techniques were employed to make these films which were designated room temperature, thermal (70 °C), and microwave (70 °C) processing. The other variables were composition (weight percent inorganic/oligomeric content), acid content, water content, molecular weight of the PDMS and the prehydrolysed sol aging period. Predominantly, materials were made with $M_n = 2600$ g/mol although some were made with $M_n = 4200$ g/mol to study the effect of molecular weight. Hybrid materials were also made using TEOS instead of TIP to probe the changes in the properties due to the big reactivity difference between them.

The second objective was to evaluate the properties of these ceramics. Relaxation studies were done by Dynamic Mechanical Thermal Analysis (DMTA), Dielectric Thermal Analysis (DETA) and solid-state NMR spectroscopy. Discussion of the solid state NMR results will be found in the structural characterization chapter. The first two techniques served the purpose of giving information about the PDMS glass transition process based on which the phase mixing between the inorganic and the oligomeric components of the materials was ascertained. The shape and the position of the tan δ behaviour was used to judge this effect. Differential scanning calorimetry studies were done to obtain the $T_g$ of the materials and also to study certain crystallization aspects of
Fig. 4.1 Structures of the precursors for the hybrid materials
the materials. Mechanical properties were evaluated by performing stress-strain experiments. Also, thin films were deposited on quartz substrate to enable optical evaluation of the hybrid materials. The primary interest in the optical characterization was the refractive index.

The differences in these TIP ceramers and the ones reported to date by Brennan et al. (50,51) primarily are:

a) PDMS is being used instead of PTMO.
b) PDMS is endcapped with a more reactive TIP instead of TEOS.

These differences in the oligomeric component and its reactivity necessitated fundamental investigations of the properties of these materials. The differences in the properties due to the variables affecting the sol-gel reactions are also investigated in this chapter.

4.2 Experimental

4.2.1 Fabrication of free standing films

The procedure for making the solutions is the same as described in 3.2.1. Unless mentioned otherwise, PDMS of \( M_n = 2600 \) g/mol was used for making all the hybrid materials. Distilled TIP and isopropanol were used. The water to alkoxide mole ratio used was 0.25 while the acid to alkoxide mole ratio used was 0.06. In certain cases different water and acid contents were used and these will be pointed out in the appropriate sections. Once again, all precautions were taken to ensure prevention of moisture from the atmosphere. After the addition of the PDMS solution to the prehydrolysed sol, stirring was continued for 5 minutes. Then it was poured into polystyrene petridishes for casting films. The room temperature cure consists of subjecting the solution in the petri-dish to
70 °C in a convection oven for 10 minutes after which they are kept at room temperature. The solution gels and a transparent film is formed which is then tested after a week from the period it was cast. The thermal cure consists of subjecting the petri-dish containing the solution to a temperature of 70 °C in a convection oven for a period of 24 hours. Microwave curing was done in a cylindrical cavity at a frequency of 2.45 GHz. The initial input power was 10 W and the cavity was tuned continuously to achieve a reflected power of zero. About 6-7 minutes were required before the temperature reached 70 °C which was then maintained for additional 23-24 minutes by varying the input power and the cavity dimensions. The total curing time was 30 minutes for all the samples. The temperature of the sample was monitored by a Fluoro-opticR temperature probe using a detection system made by Luxtron. All these materials were also transparent and the thickness of the films ranged from 0.2 - 0.4 mm. The materials prepared by thermal and microwave curing were tested a week after they were cast.

**4.2.2 Thin Film Fabrication**

Thin films on quartz were deposited by spin coating of the same solutions mentioned in 4.2.1 at a speed of 2000 rpm over a period of 15 seconds. The fused quartz substrate was 1/16 inch thick and 1 inch in diameter and was obtained from ESCO products. The substrate with the film was then cured in the microwave with initial power of 10 W for 10 minutes. The temperature of the films while being cured in the microwave could not be monitored. Thermal curing of the substrates with films was done at a temperature of 70 °C in a convection oven for a period of 24 hours. The thin films appeared clear and transparent after these processing techniques.
4.2.3 Dielectric Thermal Analysis (DETA)

Polymer Laboratory Dielectric Thermal Analyser was used for the dielectric studies of the ceramics. The diameter of the electrodes used was 20 mm. A strip of the hybrid material big enough to cover the plates was used for the analysis. Dry nitrogen purge was maintained inside the cell to exclude the condensation of moisture from the air. The temperature was varied from -150 °C to 150 °C at a heating rate of 1 °C/minute. The frequencies tested were 1, 5, 10, 50 and 100 kHz.

4.2.4 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical analysis was performed on a Polymer Laboratory Mark II Dynamic Mechanical Thermal Analyser in the bending mode. The geometry used was a single cantilever beam and the maximum nominal displacement the sample was subjected to was 40 microns. The temperature was varied from -140 °C to a maximum of 150 °C (less in most cases) at a heating rate of 1 °C/minute. Three frequencies were used for the tests which were 0.1, 1 and 10 Hz or 1, 5 and 10 Hz.

4.2.5 Differential Scanning Calorimetry (DSC)

Subambient DSC experiments were carried out on a Perkin Elmer DSC 7. The sample was subjected to a heating rate of 10 °C/minute from -150 to 25 °C for the determination of the Tg. For crystallization studies, the samples were subjected to -75 °C in the cell for a period of 3 hours after which they were quenched to -150 °C. Then they were subjected to a regular run at a heating rate of 10 °C/minute.
4.2.6 Stress-strain Experiments

Mechanical evaluation of the hybrid materials were carried out on a Polymer Laboratory Miniature Materials Testing equipment. 10 mm gauge length dogbones were cut from the materials with the help of a die. The dogbone samples were then tested at a crosshead speed of 2 mm/minute.

4.2.7 Optical Properties

The transmittance spectra of the thin films on the quartz substrate were obtained on a Perkin-Elmer 330 spectrophotometer. The data was collected in the wavelength range of 200-2000 nm at a speed of 20 nm/minute.

4.3 Results and Discussion

4.3.1 Relaxation Studies by DMTA and DETA

4.3.1.1 General Features of the spectra

A general explanation of the spectra collected by DMTA and DETA will be attempted in this section to facilitate the discussion to follow in the later sections. The nomenclature, 40/60 TIP/PDMS, means 40 weight percent of the precursor to 60 weight percent of PDMS. This nomenclature has been used throughout the dissertation. The dielectric spectrum of 50/50 TIP/PDMS cured at room temperature with initial water content of 0.5 is shown in fig. 4.2. Tan δ and the dielectric storage, E', are plotted as a function of temperature for the five different frequencies. At -150 °C, the dielectric storage (dielectric constant) values for all the frequencies are almost the same. At this
Fig. 4.2 Dielectric spectra of 50/50 TIP/PDMS cured at room temperature (first run)
Fig. 4.3 Dielectric spectra of 50/50 TIP/PDMS cured at room temperature (second run)
temperature the mobility of the system is frozen. As the temperature is increased, dipolar mobility increases and the dielectric constant goes through a step. This step is due to the \( T_g \) transition or the glass transition process of the PDMS. With increased dipolar mobility, reorientation polarization increases thereby allowing the material to store more energy. The curve shifts to higher temperature with increased frequency as expected. After the \( T_g \), there is a slight decrease in the values with increasing temperature. For the whole temperature range, the dielectric constant is higher for the lower frequency data. In the temperature region between 40 \(^\circ\)C and 100 \(^\circ\)C, the dielectric constant increases. The explanation for this behaviour will be clear when examining the \( \tan \delta \) behaviour. The \( \tan \delta \) values are very low at -150 \(^\circ\)C for all the frequencies since dipolar mobility is at a minimum. As the temperature is increased, the \( \tan \delta \) behaviour goes through a peak which is due to the \( T_g \) process of the PDMS (86). Again, the peak maxima is shifted to higher temperature with increased frequency as expected. The peak maxima lies in the range of -130 \(^\circ\)C to -110 \(^\circ\)C which is close to the values obtained from the DSC (-120 \(^\circ\)C). Adjachi et al.'s (85) dielectric study of PDMS is one of the first reported in the literature. Neat PDMS of \( M_v = 83500 \) g/mol was studied. The \( T_g \) determined by the \( \tan \delta \) peak maxima in their work also appears at ca. -120 \(^\circ\)C. However, the \( T_g \) values obtained from the peak maxima in our studies were expected to be higher. The anamolous shift of the glass transition process of the PDMS studied by means of dielectric analysis has been reported for PDMS-polycarbonate block co-polymers which were microphase separated (87). The anamolous decrease in the \( T_g \) of the PDMS as measured by dielectric spectroscopy was thought to be due the six-times higher thermal expansion coefficient of the PDMS relative to the polycarbonate. As the temperature is increased further, there is another peak in the region of -70 \(^\circ\)C to -50 \(^\circ\)C which is due to the dipolar losses of water (92). Higher than room temperature, the lower frequency values start to increase very sharply and go through a big peak centered around 70 \(^\circ\)C. The peak maxima are frequency independent suggesting ionic conductivity to be the reason. This behaviour is
probably a combination of ionic impurities and Maxwell Wagner Sillars (MWS) type relaxations. This type of behaviour has been reported for TIP/PTMO ceramics by Rodrigues (72). These relaxations typically occur at the interface of a two phase system and are more marked at low frequencies. This mechanism may be intimately related to any water or isopropanol present in the material. Fig. 4.3 shows the dielectric spectrum of the same material which was heated upto 150 °C. Clearly the small peak in the region of -50 °C present in the first run has disappeared and so has the MWS effect at 70 °C. Therefore these transitions are definitely related to the residual water and alcohol left in the material. However, ionic conductivity does come into the picture from around 50 °C which could be due to impurities in the material. Heating the material to 150 °C did not affect the tan δ behaviour at the glass transition region significantly. The behaviour described so far is quite representative of all the TIP/PDMS hybrid materials.

A typical dynamic mechanical spectrum of a hybrid material obtained from DMTA is shown in fig. 4.4. The hybrid material was 40/60 TIP/PDMS cured thermally. The data was collected for three different frequencies which are 1, 5 and 10 Hz. The plot shows tan δ and the log E' (storage modulus) as a function of temperature. The log E' values for all the frequencies at -140 °C is ca. 9.6 which is typical for a material in the glassy state since molecular mobility is very low in this region. As the temperature is increased the storage modulus drops by about a decade as the material goes through the glass transition process of the PDMS phase. As in the dielectric spectrum, the higher frequency data shifts to a greater temperature which is typical of a viscoelastic material. The log rubbery plateau storage modulus is ca. 8.4 which is higher than most rubbery materials. The tan δ values peak at about -105 °C which is higher than the values obtained from the DSC. This peak is due to the glass transition process of the PDMS resulting from the segmental motions of the chains. The broad tan δ peak indicates a multitude of relaxation times for the PDMS. Again, with increasing frequency the tan δ
Fig. 4.4 DMTA spectra of 40/60 TIP/PDMS cured thermally
peak shifts to higher temperature. Using the PDMS glass transition peak position at a particular frequency, an Arrhenius plot can be made to calculate the energy of activation. The same procedure can be done with the dielectric tan δ behaviour. Having discussed the general features of the dielectric and dynamic mechanical spectra, we will now see the comparisons as a function of the different variables studied.

4.3.1.2 Effect of TIP content

Increasing the TIP content in the materials was expected to result in profound changes in the properties of the final product. Gelation times would be shortened and the crosslink density would increase. The materials made were transparent and their flexibility was dependent upon the percentage of TIP. Qualitatively, the materials seemed brittle at a composition of 50/50 TIP/PDMS with the lower TIP compositions being flexible. This was true for all the materials processed by room temperature, thermal and microwave processing.

Fig. 4.5 displays the tan δ behaviour obtained from dielectric analysis at a frequency of 10 kHz. The compositions displayed are 30/70, 40/60 and 50/50 TIP/PDMS cured thermally. Increasing the TIP content results in lower magnitude of the tan δ peak as expected. However, there is a shift of the peak to higher temperature and the breadth of the transition also increases. Based on the morphological model suggested by Huang (45) which was discussed in chapter 2, two types of restrictions to the mobility of the oligomeric chains were cited in the ceramics. They are:

Type 1 - Having both ends of the oligomeric chain connected to the inorganic network.

Type 2 - Mixing of the oligomeric species with lightly branched and condensed inorganic species or being encapsulated in the inorganic network.
Fig. 4.5 Dielectric tan δ of various compositions cured thermally
Fig. 4.6 DMTA spectra at 1 Hz for various compositions cured thermally
The morphological model with minor modifications has certainly proved to be representative for the ceramers reported by Wilkes et al. (42-47, 50, 51,71, 72). The results shown in fig. 4.5 indicate increasing restriction of the mobility of the PDMS with increasing TIP content. Also, the breadth of the transition would indicate broader distribution of the relaxation times with increasing TIP content. The DMTA spectra collected at a frequency of 1 Hz for the same materials are shown in fig. 4.6. The storage modulus in the glassy state at -140 °C are similar. However, the onset of the glass transition behaviour is shifted to a higher temperature and also the decrease is more gradual with increasing TIP content. The plateau rubbery storage modulus, an indicator of the stiffness of the materials, is higher with increasing TIP content. The inorganic species being stiffer than the PDMS moiety would explain this behaviour. The mechanical tan δ behaviour is similar to that seen in the dielectric spectra. The peak shifts to a higher temperature and is very broad for the 50/50 TIP/PDMS material. Similar dynamic mechanical and dielectric behaviour is seen in the microwave and room temperature cured materials as seen in fig. 4.7-4.10.

The position of the tan δ peak maxima for the 30/70 and 40/60 TIP/PDMS materials indicate little phase mixing between the titanium oxide and the PDMS phase. However, the materials were transparent. Thus the size of the phases must be very small. Brennan (45) has observed bimodal tan δ behaviour in the TIP/PTMO ceramers and ascribed them to the Type 1 and Type 2 restrictions discussed earlier in this chapter. Though the bimodal behaviour is not very discernable in the DMTA results presented here, the tailing portion in the higher temperature region of the tan δ behaviour could be due to the Type 2 restrictions. The sharper peak observed in the lower region could then be due to the PDMS rich phase in the materials. Increasing TIP content leads to a decrease in the magnitude of the sharp peak with the eventual disappearance in the 50/50 TIP/PDMS composition. Therefore, the general behaviour indicates better phase mixing
Fig. 4.7 Dielectric $\tan \delta$ of various compositions cured by microwave processing
Fig. 4.8 DMTA spectra at 1 Hz of various compositions cured by microwave processing
Fig. 4.9 Dielectric tan δ of various compositions cured at room temperature
Fig. 4.10 DMTA spectra at 1 Hz of various compositions cured at room temperature
Table 4.1 Activation energies of the glass transition from the dielectric data for various compositions cured by all three techniques

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thermal (kcal/mol)</th>
<th>Microwave (kcal/mol)</th>
<th>Room Temp. (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/70 TIP/PDMS</td>
<td>22</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>23</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>24</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>60/40 TIP/PDMS</td>
<td></td>
<td></td>
<td>28</td>
</tr>
</tbody>
</table>
Table 4.2 Activation energies of the PDMS glass transition from the dynamic mechanical data for various compositions cured by all three techniques

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thermal (kcal/mol)</th>
<th>Microwave (kcal/mol)</th>
<th>Room temp. (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/70 TIP/PDMS</td>
<td>63</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>43</td>
<td>43</td>
<td>54</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>40</td>
<td>47</td>
<td>48</td>
</tr>
</tbody>
</table>
or encapsulation of the PDMS by the titanium oxide phase as the level of TIP is increased in these materials. The activation energies of the glass transition process from the DETA and DMTA experiments are listed in table 4.1 and table 4.2 respectively. The activation energies obtained from the dynamic mechanical experiments do not show any trend with composition. Also, the values may not be very accurate as only three frequencies were used for the experiments. The peak maxima for the 50/50 TIP/PDMS composition are hard to pinpoint as the transitions are very broad. The activation energies obtained from the DETA experiments are in the range of 20 -27 kcal/mol which are slightly higher than the reported value of 18 kcal/mol for pure PDMS of $M_n = 85000$ g/mol (85). This may be due to the restrictions imposed on the PDMS by the titanium oxides. There is a trend of increasing activation energies with increased TIP content, which would support the above argument.

4.3.1.3 Effect of Cure Modes

The DMTA spectra at a frequency of 5 Hz for 30/70 TIP/PDMS materials cured thermally and in the microwave are shown in fig. 4.11. This particular spectrum was acquired in the tensile mode as opposed to all the other DMTA spectra shown in this thesis which were acquired in the bending mode. The plot in fig. 4.11 shows tan δ and the storage modulus ($E'$) as a function of temperature. The peaks observed in the region of -110 °C are due to the PDMS phase undergoing the glass transition process. However, the region of interest is between -90 °C and -50 °C. A broader tan δ behaviour is seen for the microwave cured material compared to the thermally cured material. Also, the drop in the storage modulus from the glassy region to the rubbery region is more for the microwave cured material. Fig. 4.12 shows the dielectric tan δ behaviour at 5 kHz of the 30/70 TIP/PDMS material cured thermally, at room temperature and by the microwave process. The big peak in the vicinity of 0 °C is due to adsorbed water (91). In this figure too, there
Fig. 4.11 DMTA spectra at 5 Hz of 30/70 TIP/PDMS cured thermally and by microwave processing
Fig. 4.12 Dielectric tan δ spectra at 5 kHz of 30/70 TIP/PDMS cured thermally, at room temperature and by microwave processing.
is found similar behaviour of the microwave cured material when compared to the thermally cured material. Also, the magnitude of the tan δ is higher for the microwave cured material. The broad tan δ behaviour is concluded to be due to the melting of the crystallized PDMS chains in the material. This crystallization process probably occurs when the material is cooled down to -150 °C from room temperature for the experiments. Though the type 2 restrictions could certainly contribute to this behaviour, the effect is negligible since it is not predominant in the materials cured thermally or at room temperature as evident from the DETA spectra. Therefore, it can be concluded that the microwave cured material is definitely more microphase separated when compared to the thermally cured material or the room temperature cured material. This certainly seems to be true for the 30/70 TIP/PDMS materials, but the effect seems to diminish as the level of TIP content increases. The DMTA spectra at 1 Hz for 40/60 and 50/50 TIP/PDMS cured by all three techniques are shown in fig. 4.13 and 4.14 respectively. The storage moduli data for the 50/50 TIP/PDMS is not totally reliable since at this composition the material is quite brittle and proper clamping of the sample is difficult. The microwaved material in the case of 40/60 TIP/PDMS composition does show similar trend as in the 30/70 TIP/PDMS case. The magnitude of tan δ is higher and the drop in the storage modulus is also more compared to the thermally cured material. However, for the 50/50 TIP/PDMS composition, the tan δ behaviour is very similar for the materials cured by the three different techniques. The dielectric tan δ behaviour of the 40/60 and 50/50 TIP/PDMS materials is shown in fig. 4.15 and 4.16 respectively. The tan δ peak maxima are in the order: microwave < thermal < room temperature. The shifting of the tan δ curves to higher temperature for the room temperature cured material suggests better phase mixing of the PDMS with the titanium oxide phase. Fig. 4.17 shows the DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured thermally at 70 °C and 45 °C. Here again, the relaxation shifts to higher temperature with decreased cure temperature indicating better phase mixing. Increased temperature would result in faster kinetics of the sol-gel reactions, leading to
Fig. 4.13 DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured thermally, at room temperature and by microwave processing.
Fig. 4.14 DMTA spectra at 1 Hz of 50/50 TIP/PDMS cured thermally, at room temperature and by microwave processing.
Fig. 4.15 Dielectric $\tan \delta$ of 40/60 TIP/PDMS cured thermally, at room temperature and by microwave processing.
Fig. 4.16 Dielectric tan δ of 50/50 TIP/PDMS cured thermally, at room temperature and by microwave processing
Fig. 4.17 DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured thermally at 70 °C and 45 °C
more separation of the two phases. The morphology of these materials will be discussed in the chapter on structural studies. Also, the differences in the morphology between microwave and thermal cure leading to somewhat varied relaxation properties will be discussed in the structural characterization chapter. Therefore, no further speculation as to the reasons between the differences will be attempted here.

4.3.1.4 Effect of the PDMS molecular weight

Hybrid materials with PDMS of Mn = 4200 g/mol were also made to compare the effects chain length would have on the structure-property relationships. The TIP endcapped PDMS was synthesized in the same fashion as was described before for the PDMS of M_n =2600 g/mol. Increasing molecular weight is expected to lessen the possibility of siloxane phase to be encapsulated by the inorganic oxide phase and also, phase separation would be increased. Fig. 4.18 shows the DMTA spectra at 1 Hz for 50/50 TIP/PDMS with the two different molecular weight PDMS cured thermally. The tan δ behaviour clearly demonstrates better mixing between the two phases in the case of the hybrid materials made with the smaller chain length PDMS. The onset of the relaxation process is delayed for the 2600 g/mol case as seen by the storage moduli behaviour. Therefore, the extent of phase separation increases with increasing molecular weight of the PDMS as expected. The microstructure of the materials can thus be controlled by the molecular weight of the oligomeric component. Similar behaviour was observed for the TEOS/PDMS hybrid materials made by Huang (44).

4.3.1.5 Effect of the water content

As was already mentioned in chapter 2, the amount of water critically controls the final structure of the gel. The initial water content affect the kinetics of the
Fig. 4.18 DMTA spectra at 1 Hz of 50/50 TIP/PDMS cured thermally; molecular weight of PDMS used are 2600 and 4200 g/mol
Fig. 4.19 Dielectric tan δ at 5 kHz of 50/50 TIP/PDMS cured at room temperature with two different initial water content
hydrolysis and the condensation reactions leading to different structures and properties of the final product. Therefore, initial water content which was kept at 25 percent of the alkoxide content was increased to 50 percent to see the resultant changes in the properties of the material. This correlates to changing the hydrolysis ratio from 1 to 2. Fig. 4.19 shows the dielectric tan δ behaviour at 5 kHz for 50/50 TIP/PDMS cured at room temperature. The material with more initial water content shows lesser phase mixing. This behaviour is confirmed by the DMTA also. Higher initial water content would lead to faster kinetics of the sol-gel reactions perhaps leading to formation of the oxide domains which are better defined than in the case of lower water content. If this is the case, then the process of phase mixing would definitely be lower resulting in the properties as seen by DETA and DMTA. Discussion on this effect also will be done in more detail in the structural characterization chapter.

4.3.1.6 Effect of the acid content

The acid content effects are expected to result in similar behaviour as with the water content. Lowering the acid content would result in slower kinetics of the sol-gel reactions. The dielectric tan δ behaviour at 10 kHz for 50/50 TIP/PDMS materials cured thermally with three different initial acid content is shown in fig. 4.20. The magnitude of the tan δ peak decreases and also shifts to higher temperature with lower acid content. Similar behaviour is seen in the microwave cured films when analysed by DMTA. This implies better phase mixing as the amount of acid catalyst used decreases. The behaviour seen here is contrary to that observed for TEOS/PDMS hybrids made by Huang (44). Better dispersion with increased acid content was observed in those materials. More discussion on the effect of acid content on the morphology of TIP/PDMS materials follows in chapter 5.
Fig. 4.20 Dielectric $\tan \delta$ at 10 kHz of 50/50 TIP/PDMS cured thermally with three different initial acid content
Fig. 4.21 DMTA spectra at 1 Hz of 40/60 TIP/PDMS cured at room temperature with three different periods of prehydrolysed sol aging.
4.3.1.7 Effect of sol aging time

All the materials were prepared by adding TIP endcapped PDMS solution in isopropanol to freshly prepared prehydrolysed titania sol. However, in this experiment the effect of aging the prehydrolysed sol for a certain period of time before adding the PDMS solution to it was investigated. Cerqua et al. (90) have shown that compressive stresses result in titania and silica thin films deposited on a substrate when the sol was aged compared to tensile stresses when the films were deposited from a freshly prepared sol. More thoroughly reacted sols were concluded to be the reason for this behaviour. Also, redissolution and formation of bigger particles cannot be ruled out in the aging process of the sol. Fig. 4.21 displays the DMTA spectra at 1 Hz for 40/60 TIP/PDMS cured at room temperature. The comparisons are for materials made with fresh sol, sol aged for 3 days and sol aged for 7 days. Though the effect on the dynamic mechanical properties is not great, the trend is quite definite. However, the sol was still clear and no particulates were seen. With increased aging of the sol, the phase mixing between the PDMS and titanium oxide phase decreases. The onset of the glass transition process of the PDMS as evidenced by the drop in the storage modulus shifts to a lower temperature and the magnitude of the decrease is also larger with increased aging of the sol. The magnitude of the tan δ and the peak maxima shift to lower temperatures with increased aging of the sol supporting the conclusion that increased phase separation takes place with longer aging of the prehydrolysed sol. The aged sol after a period of 7 days was slightly yellowish in color. Titanium alkoxides are known to form pentacoordinate and hexacoordinate complexes in the presence of water (125), which may be the reason for the color. The dynamic mechanical behaviour suggests bigger sized oligomeric species of the titanium oxides with increased aging. Bradley et al. (28) have proposed several structures for the oligomers of the metal oxides based on the hydrolysis ratio. Though no experimental proof of the existence of these structures are furnished, the basic idea of
Fig. 4.22 Dielectric tan δ at 10 kHz of 50/50 TEOS/PDMS cured at room temperature (first and second run)
Fig. 4.23 DMTA spectra at 1 Hz of 50/50 TEOS/PDMS cured at room temperature (first and second run)
condensation taking place between these well defined oligomers has been postulated to be qualitatively right (1). Therefore, it is conceivable that bigger domains of the titanium oxides are formed with increased sol aging period which will then result in more phase separated materials.

4.3.1.8 Effect of the Metal Alkoxide type

Using TIP endcapped PDMS presented an opportunity to use a different metal alkoxide with lower reactivity to study the effect of the differences in the reactivity of the two components in a hybrid material on its structure and the resulting properties. Tetra-ethylorthosilicate (TEOS) was chosen because of the vast difference in the reactivity compared to TIP. Also, the hybrid materials synthesized with TEOS made possible direct comparison with the first ceramers made by Huang et al. (42-44). The compatibility between PDMS and TEOS is expected to be better than PDMS with TIP. This would be mainly due to the similarity in the Si-O-Si structure forming in the silicates from the TEOS and the siloxane bonds of the PDMS. However, it should be noted that even though a lot of analogies are drawn between silicon alkoxides and titanium alkoxides, the growth process and reactions from these two can be very different. The TEOS/PDMS hybrids are made in an analogous fashion to the TIP/PDMS materials. Fig. 4.22 shows the dielectric tan δ behaviour at 10 kHz of a 50/50 TEOS/PDMS material run the first time to 100 °C and then the same film run the second time up to 150 °C. The differences between the two runs are similar to the TIP/PDMS materials with the water peak being observed at -70 °C in the first run and then notably being absent in the second run. However, the MWS effect is seen at a lower temperature (ca. 50 °C) as compared to the TIP/PDMS material. This might be related to the differences in the structures of the two materials due to the different metal alkoxide type as speculated by Rodrigues (72). The tan δ peak becomes a little broader in the second run suggesting further reactions on
Fig. 4.24 Dielectric tan δ at 10 kHz of 50/50 TEOS/PDMS and 50/50 TIP/PDMS cured at room temperature
Fig. 4.25 DMTA spectra at 1 Hz of 50/50 TEOS/PDMS and 50/50 TIP/PDMS cured at room temperature
Fig. 4.26 DMTA spectra at 1 Hz of 40/60 TEOS/PDMS and 50/50 TEOS/PDMS cured at room temperature
Fig. 4.27 DMTA spectra at 1 Hz of 50/50 TEOS/PDMS cured at room temperature with two different initial water content
heating the material up to 100 °C. DMTA spectra at 1 Hz for the same material taken up to 150 °C and then taken again back to the same temperature are shown in fig. 4.23. Beyond room temperature there is a decrease in the storage modulus and the tan δ spectra appears noisy. However, on the second run this behaviour is absent. This therefore suggests that there are volatiles present in these systems similar to what was seen for the TIP/PDMS materials.

Fig. 4.24 displays the dielectric tan δ behaviour at 10 kHz of 50/50 Metal Alkoxide/PDMS cured at room temperature where the metal alkoxides are TIP and TEOS. The peak maxima in the TEOS/PDMS material appears at a lower temperature relative to the TIP/PDMS material. Also, the peak is broader and lower in magnitude. The activation energy for TEOS/PDMS system is 12 kcal/mol while that of the TIP/PDMS material was 24 kcal/mol. This is indicative of shorter relaxation times for the PDMS in the TEOS/PDMS material. Dynamic mechanical behaviour at 1 Hz shown in fig. 4.25 is also similar. A very broad tan δ behaviour between the range of -115 °C to 0 °C is seen. Also, the storage modulus drop at the glass transition process was very gradual in the TEOS/PDMS relative to the TIP/PDMS material. Better phase mixing of the silicate with the PDMS is anticipated in the TEOS/PDMS material resulting in a partial explanation of the above behaviour. However, the tan δ maxima from both the dielectric and dynamic mechanical experiments appear at a lower temperature in the TEOS/PDMS materials compared to the TIP/PDMS materials. The TIP endcapped PDMS is more reactive than the TEOS and therefore more homocondensation of the PDMS may result in the TEOS/PDMS materials. Therefore, more siloxane rich phase may be expected in these materials. The effect of increased TEOS content is similar to the behaviour seen in the TIP/PDMS materials. The DMTA spectra at 1 Hz for 40/60 and 50/50 TEOS/PDMS cured at room temperature with initial water content of 50 percent of the alkoxide groups are shown in fig. 4.26. The tan δ behaviour shows more siloxane rich phase for the 40/60
Table 4.3 $T_g$ by DSC of various compositions cured at room temperature

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100 TIP/PDMS</td>
<td>-120</td>
</tr>
<tr>
<td>10/90 TIP/PDMS</td>
<td>-119</td>
</tr>
<tr>
<td>45/55 TIP/PDMS</td>
<td>-107</td>
</tr>
</tbody>
</table>
Fig. 4.28 DSC scans of 0/100 TIP/PDMS a) first heat b) after isothermal hold at -75 °C for three hours
Fig. 4.29 DSC scans of 10/90 TIP/PDMS (M_n = 2600 g/mol) a) first heat b) after isothermal hold at -75 °C for three hours
Fig. 4.30 DSC scans of 30/70 TIP/PDMS cured thermally and by microwave processing after isothermal hold at -75 °C for three hours
TEOS/PDMS compared to the 50/50 TEOS/PDMS composition. However, the effect of increased water content was opposite to what was observed for the TIP/PDMS materials. Fig. 4.27 shows the DMTA spectra at 1 Hz of 50/50 TEOS/PDMS materials cured at room temperature with two different initial water contents. Increasing the water content results in a flattening of the tan δ behaviour as well as decreased drop in the storage modulus over the glass transition temperature regime. Higher water content in TEOS has been shown to produce more crosslinked network and also acceleration of the condensation rate (I). This explains the properties observed by the DMTA here.

4.3.2 Differential Scanning Calorimetry (DSC)

DSC studies were done to find the T_g of the PDMS in these hybrid materials. This task became difficult as the level of TIP in these materials increased. The transition becomes very broad and is increasingly difficult to see for compositions with higher TIP content. The T_g values for some of the compositions cured at room temperature obtained from the DSC are shown in table 4.3. The T_g of the PDMS increases with higher TIP content. This is due to increasing restrictions on the PDMS with higher TIP content as has been mentioned previously. However, DSC studies proved more valuable in doing some crystallization studies of these materials. PDMS is known to have melting transition at ca -50 °C (92). Fig. 4.28a shows the DSC trace of 0/100 TIP/PDMS cured at room temperature where the T_g is observed at -120 °C. However, no melting transitions are observed. When the same sample is held at -75 °C for 3 hours and then quenched rapidly to -150 °C, the melting transitions are then observed as shown in the DSC trace in fig. 4.28b. The sharper melting transition is observed at -43 °C and the ΔH for the melting transitions is 20 J/g. The absence of melting in the first run indicates the difficulty of the crystallizing the PDMS chains when in the crosslinked state. The DSC trace for the 10/90 TIP/PDMS is shown in fig. 4.29a where the T_g is observed at -119.5 °C and again no
melting transitions are observed. The melting transitions are observed when the sample is subjected to the same isothermal holding procedure, as shown in fig. 4.29b. The peak observed in 10/90 TIP/PDMS material is not as sharp as was seen in the 0/100 TIP/PDMS composition. The heat of melting for the 10/90 TIP/PDMS was 14 J/g. This therefore suggests that the addition of TIP is causing restrictions in the PDMS crystallization process. The 30/70 TIP/PDMS materials cured thermally and in the microwave were subjected to the same procedure as above. The DSC traces after the 3 hours of holding at -75 °C are shown in fig. 4.30. The melting transition though very small compared to 0/100 and 10/90 TIP/PDMS materials is nevertheless present in the microwave cured sample. The thermally cured as opposed to the microwave cured material does not show the melting transition. This confirms the DMTA and DETA spectra shown earlier for these materials and confirms the belief that the microwave cured material does tend to have more microphase separation relative to the thermally cured material.

4.3.3 Mechanical Properties

The mechanical properties of these hybrid materials were studied with stress-strain experiments. The general stress-strain behaviour for the materials with different compositions cured by the room temperature, thermal and microwave cured materials are shown in fig. 4.31, 4.32 and 4.33 respectively. The mechanical properties of these materials are tabulated in table 4.4. Increased TIP content leads to higher modulus, higher stress at break and lower strain percent at break. This trend is certainly true for the materials cured by all the three different techniques. The 50/50 TIP/PDMS composition cured by all the three different techniques is brittle and hence dogbone samples are difficult to cut. Also, these samples broke easily in the grips. Therefore, data for these materials were limited. The striking feature in these data is the jump in the modulus and
Fig. 4.31 Stress-strain behaviour of various TIP/PDMS compositions cured at room temperature
Fig. 4.32 Stress-strain behaviour of various TIP/PDMS compositions cured thermally
Fig. 4.33 Stress-strain behaviour of various TIP/PDMS compositions cured by microwave processing
Table 4.4 Mechanical Properties of TIP/PDMS materials

<table>
<thead>
<tr>
<th>Composition</th>
<th>Modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80 TIP/PDMS</td>
<td>8.2</td>
<td>1.1</td>
<td>18</td>
</tr>
<tr>
<td>25/75 TIP/PDMS</td>
<td>13.0</td>
<td>1.3</td>
<td>17</td>
</tr>
<tr>
<td>30/70 TIP/PDMS</td>
<td>35.1</td>
<td>1.9</td>
<td>13</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>98.1</td>
<td>3.6</td>
<td>6</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>ca. 700</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Mechanical Properties of Room Temperature Cure Materials

<table>
<thead>
<tr>
<th>Composition</th>
<th>Modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80 TIP/PDMS</td>
<td>6.3</td>
<td>1.0</td>
<td>23</td>
</tr>
<tr>
<td>25/75 TIP/PDMS</td>
<td>18.8</td>
<td>1.2</td>
<td>18</td>
</tr>
<tr>
<td>30/70 TIP/PDMS</td>
<td>29.2</td>
<td>1.6</td>
<td>12</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>112.1</td>
<td>2.1</td>
<td>5</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Mechanical Properties of Thermally Cured Materials

<table>
<thead>
<tr>
<th>Composition</th>
<th>Modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80 TIP/PDMS</td>
<td>5.9</td>
<td>1.2</td>
<td>22</td>
</tr>
<tr>
<td>25/75 TIP/PDMS</td>
<td>12.0</td>
<td>1.5</td>
<td>22</td>
</tr>
<tr>
<td>30/70 TIP/PDMS</td>
<td>29.1</td>
<td>1.8</td>
<td>12</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>72.7</td>
<td>1.9</td>
<td>7</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Mechanical Properties of Microwave Cured Materials
Table 4.5 Mechanical properties of 40/60 TIP/PDMS materials with initial water content of 0.5 cured at room temperature

<table>
<thead>
<tr>
<th>Cure Mode</th>
<th>Modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at break (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>153.6</td>
<td>5.0</td>
<td>5</td>
</tr>
<tr>
<td>Thermal</td>
<td>249.3</td>
<td>4.5</td>
<td>6</td>
</tr>
<tr>
<td>Microwave</td>
<td>147.0</td>
<td>5.3</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 4.6 Mechanical properties of TEOS/PDMS materials studied

<table>
<thead>
<tr>
<th>Composition</th>
<th>Water Content</th>
<th>Modulus (MPa)</th>
<th>Stress at break (MPa)</th>
<th>Strain at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40/60 TEOS/PDMS</td>
<td>0.50</td>
<td>172.8</td>
<td>8.1</td>
<td>6</td>
</tr>
<tr>
<td>50/50 TEOS/PDMS</td>
<td>0.50</td>
<td>389.7</td>
<td>10.6</td>
<td>3</td>
</tr>
<tr>
<td>50/50 TEOS/PDMS</td>
<td>0.25</td>
<td>336.6</td>
<td>13.3</td>
<td>6</td>
</tr>
</tbody>
</table>
the general mechanical behaviour at the 50/50 TIP/PDMS composition. This definitely suggests a substantial change in the morphology of the materials where the inorganic species have probably achieved some kind of connectivity between them. The general differences between the cure modes for the same composition seem to be minimal, although the ultimate properties of the room temperature cured materials seem to be better. No big differences are seen between the thermally and microwave cured materials. The mechanical properties of 40/60 TIP/PDMS with initial water content of 0.5 cured by all the three techniques are shown in table 4.5. Increasing the water content leads to higher modulus, slightly higher stress to break and lower elongation to break. No explanation presented for the higher modulus of the thermally cured material compared to the microwave or room temperature cured material. The mechanical properties of the TEOS/PDMS materials are shown in table 4.6. The modulus of the 50/50 TEOS/PDMS material is lower than that of the TIP/PDMS material made under the same conditions. Better mechanical properties were reported for TIP/PTMO ceramers when compared to the TEOS/PTMO ceramers by Brennan et al. (51). Similar behaviour is noted here for the 50/50 Metal alkoxide/PDMS systems. However, for the 40/60 composition with higher initial water content, the behaviour is reverse. The moduli of the materials are fairly close, although the stress at break is higher. This might be due to higher extent of reaction of the TEOS in the TEOS/PDMS material whereas in the TIP/PDMS material a totally different morphology results due to the higher initial water content.

4.3.4 Optical Properties

The transmittance of light was measured for the thin films deposited on the quartz substrate by a spectrophotometer. A typical transmission spectrum is shown in fig. 4.34 where the composition of the film was 50/50 TIP/PDMS and was cured thermally. The interference pattern obtained then can be used for the calculation of the refractive index
Fig. 4.34 Transmittance spectrum of 50/50 TIP/PDMS thin film cured thermally
as a function of the wavelength and also the thickness of the thin film. The calculations are based on the method proposed by Manifacier et al. (93). The expressions used are for the case of weak absorption. An envelope is drawn connecting the $T_{\text{max}}$ and $T_{\text{min}}$ of the transmission spectrum as shown in fig. 4.34. The refractive index, $n$, can then be calculated for a particular wavelength by the equation shown below:

$$n = \left[ N + \left( N^2 - n_0^2n_1^2 \right)^{0.5} \right]^{0.5}$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1\frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}}T_{\text{min}}}$$

$n_0$ and $n_1$ are the refractive indices of air and the substrate. The refractive indices calculated can then be used to calculate the thickness, $t$, of the thin film as shown in the equation below:

$$t = \frac{M\lambda_1\lambda_2}{2(n\lambda_1)\lambda_2 - n(\lambda_2\lambda_1)}$$

$\lambda_1$ and $\lambda_2$ are the wavelengths representing two maxima or two minima and $M$ is the number of oscillations between them.

The refractive indices calculated for the region of 400 - 700 nm for TIP/PDMS materials of different compositions cured in the microwave are shown in fig. 4.35. The refractive indices range from 1.47 to 1.58. For each composition the refractive index decreases with the wavelength. The refractive index increases with increasing TIP content. The increase in the refractive index is systematic with higher TIP content and therefore shows the feasibility of designing optical filters and waveguides utilising these hybrid materials. The refractive indices of the materials cured thermally are shown in fig.
Fig. 4.35 Refractive indices as a function of wavelength for various TIP/PDMS compositions cured in the microwave
Fig. 4.36 Refractive indices as a function of wavelength for various TIP/PDMS compositions cured thermally
Table 4.7 Calculated thicknesses of the thin films cured thermally and by microwave

<table>
<thead>
<tr>
<th>Composition</th>
<th>Thickness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal Cure</td>
<td>Microwave Cure</td>
</tr>
<tr>
<td>30/70 TIP/PDMS</td>
<td>2187</td>
<td>2347</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>1683</td>
<td>1710</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>1361</td>
<td>1470</td>
</tr>
<tr>
<td>60/40 TIP/PDMS</td>
<td>1273</td>
<td>1177</td>
</tr>
</tbody>
</table>
4.36. The refractive indices range from around the low of 1.47 to a high of 1.55. The trend here is again similar to that seen for the microwave cured materials. Anomalous behaviour of the 60/40 TIP/PDMS material was observed. The refractive index of the 60 percent TIP content film increased with the wavelength. No explanation of this behaviour is given at this time. The refractive indices for the microwave cured material are generally lower than the ones cured thermally except for the 60/40 TIP/PDMS material where the opposite behaviour is seen. The thickness calculated from the data for both the microwave and thermal cured films are shown in table 4.7. The values decrease with increasing TIP content as expected.

4.4 Conclusions

Successful fabrication of the hybrid materials in the form of free standing films and thin films was achieved using novel TIP endcapped PDMS as the oligomeric component and TIP as the inorganic component. The properties of these films were then studied by dielectric analysis, dynamic mechanical analysis, stress-strain measurements, differential scanning calorimetry and optical measurements.

The relaxation behaviour as studied by DETA and DMTA suggests increased phase mixing or encapsulation of the PDMS by titanium oxide phase having higher TIP contents. The mechanical properties and the optical properties support the above inference. The modulus of the 50/50 TIP/PDMS material shows a big increase over lower TIP concentrations and so does the refractive index when compared to the 40/60 TIP/PDMS material. These property differences therefore indicates a significant change in the morphology when the TIP content is increased from 40 to 50 weight percent. The microwave cured materials showed more microphase separation as compared to those cured thermally. This was proved by crystallization studies done on a DSC. However,
the effect decreases with increasing TIP content. The external variables of the initial water and catalyst content result in hybrid materials with different dielectric, dynamic mechanical and mechanical properties. Higher water content leads to increased phase separation as observed by the dynamic mechanical and dielectric behaviour. The moduli of the higher water content materials are greater than those made with lower water content. Decreasing the initial acid content led to better phase mixing of the two components. The kinetics of the sol-gel reactions are decreased with lesser acid content thereby allowing better mixing. Aging the prehydrolysed sol before adding the PDMS to it results in increased phase separation between the two components. Bigger domains of the titanium oxide phases are probably formed with increased aging time thereby resulting in the above behaviour. The degree of phase separation is higher with an increase in the molecular weight of the oligomeric species. The effect of using TEOS instead of TIP results in materials exhibiting different properties. The broader dielectric and dynamic mechanical tan δ behaviour of the TEOS/PDMS materials indicate better phase mixing between the two components compared to the TIP/PDMS materials. However, the onset of the tan δ and the tan δ maxima appear at a lower temperature than that of the TIP/PDMS materials. This indicates the presence of more siloxane rich phase in the TEOS/PDMS materials. This probably results from the reactivity mismatch between the between the TIP endcapped PDMS and the TEOS. The effect of increasing the TEOS content is similar to that seen for the TIP/PDMS materials. The effect of water content is however contrary to that seen for the TIP/PDMS materials.
Chapter 5 --- Structural Characterization of the Hybrid Materials

5.1 Introduction and Objectives

It was clearly demonstrated in Chapter 4 that significant differences in properties of the hybrid materials were observed when the synthetic variables like the inorganic content, initial acid content and the water content were varied. Replacing the TIP in these hybrid materials with TEOS also resulted in the changes of the properties. Also, differences between microwave and thermal cured materials were clearly established at least for the lower inorganic content materials. These differences in the properties are obviously due to the changes in the structure of the materials which was systematically affected by these variables. The primary objective then was to see the differences in these structures with the help of electron microscopy, small angle x-ray scattering and solid-state NMR. The presence of microphase separation was obvious from the relaxation studies of these materials and therefore should be visually evident by electron microscopy. SAXS was used to confirm the microstructures seen by electron microscopy and also to calculate the fractal dimension. Solid-state NMR spectroscopy was used mainly to differentiate the structures obtained in the TIP/PDMS and TEOS/PDMS materials. This was done by obtaining the spin-lattice relaxation times of the $^{29}$Si and $^{13}$C nuclei. All this structural information obtained will be correlated in this chapter to the properties already discussed in chapter 4.
5.2 Experimental

5.2.1 Solid-State NMR Spectroscopy

$^{29}$Si solid-state NMR with magic angle spinning and proton decoupling on was performed on Bruker 300 MSL spectrometer. The $^{29}$Si $T_1$ values were obtained by using the spin inversion recovery technique while the $^{13}$C $T_1$ values were obtained using the cross-polarization method. Films of the hybrid materials were powdered in a wiggle-bug and used for the experiments.

5.2.2 Scanning Transmission Electron Microscopy (STEM)

The specimen preparation for STEM consisted of fracturing the samples in liquid nitrogen and then mounting it on a copper strip with silver paint. The sample was then gold coated to avoid charging problems. High resolution electron microscopy was carried out on Philips 420 T Electron microscope in the STEM mode utilising mostly the backscattered detector. Sometimes, the secondary electron detector was also used to obtain images of the fracture surface. However, only backscattered images are presented in this chapter.

5.2.3 Small Angle X-Ray Scattering (SAXS)

SAXS was performed with a Siemens-Kratky camera system. Braun position sensitive detector from Innovative Technologies Inc. was used to determine the angular dependence of the scattered intensity. X-rays from a Siemens Cu-W x-ray tube powered by Siemens Model 1726 Generator were used for the experiment. The experiments were carried out by Chinmay Betabet in Prof. Wilkes' laboratory in the Chemical Engineering department.
Fig. 5.1 $^{29}$Si NMR spectrum of 50/50 TIP/PDMS material cured at room temperature
Fig. 5.2 $^{29}\text{Si}$ NMR spectrum of 50/50 TEOS/PDMS material cured at room temperature
Fig. 5.3 $^{29}$Si NMR spectrum of 50/50 TEOS/PDMS material cured at room temperature
5.3 Results and Discussion

5.3.1 Solid-State NMR Spectroscopy

$^{29}$Si solid-state NMR was used to determine the presence of the Si-O-Ti peak seen in the liquid state for the TIP endcapped PDMS mentioned previously in Chapter 3. Fig. 5.1 shows the $^{29}$Si spectrum of a 50/50 TIP/PDMS cured at room temperature. The Si-O-Ti peak seen at ca. -16 ppm in the liquid state is present in this spectrum, although, in a very broad form. This behaviour is expected since the ends of the chain are part of the rigid titanium oxide network and therefore of very low mobility. This results in a very broad response in the $^{29}$Si NMR spectrum. The peak at ca. -22 ppm is due to the backbone silicons of the PDMS. Fig. 5.2 and 5.3 show the $^{29}$Si NMR spectrum of the 50/50 TEOS/PDMS cured at room temperature. There are differences between this material's spectrum and the one seen for the TIP/PDMS material which will be discussed next. The peaks appearing between -90 ppm and -120 ppm shown in fig. 5.3 are due to the Q$_3$ and Q$_4$ species of the silicon oxides, the Q$_4$ moiety appearing at the lower chemical shift (42,95). Q$_3$ represents species where only three of the four functionalities on the silicon have reacted and Q$_4$ represents species where all four have reacted. The small, sharp peak at ca. -90 ppm cannot be ascribed to any moiety in the material and is probably due to impurity in the rotor used. The siloxane backbone silicons peak appears at ca. -22 ppm as in the TIP/PDMS material. However, there is a slight downward shift of this peak relative to the one in TIP/PDMS material. Also, this peak is broader compared to the one in TIP/PDMS material suggesting better mixing of the siloxane with the titanium oxides. The Si-O-Ti peak appears at approximately the same chemical shift as in TIP/PDMS material although, because of the effects mentioned above, it appears as a left shoulder of the siloxane backbone silicons peak. From these spectra it was surmised that doing $T_1$ studies of the $^{29}$Si nucleus in these materials where the endgroup Si of the oligomer is present in a
different environment than the backbone silicons will be valuable on obtaining more information about the morphology of these systems.

The spin-lattice relaxation time, $T_1$, is influenced by molecular motions in the material. Therefore, these hybrid materials which consists of a rigid inorganic phase and rubbery siloxane phase should give different $T_1$ values for the nucleus being observed. The difference will be influenced by the degree of interaction between the two components. The $T_1$ values for $^{29}$Si nucleus for the 50/50 TEOS/PDMS and the 50/50 TIP/PDMS are listed in table 5.1. The $^{29}$Si peak corresponding to the Q$_4$ peak representing the rigid silicon oxide peak has a $T_1$ value of 32.2 seconds. The $T_1$ values of the backbone silicons of the PDMS in contrast is 20.2 seconds. $T_1$ values (ca. 27 seconds) have been reported for PDMS before by Levy et al. (96). The longer $T_1$ corresponding to the silicates silicon shows the rigidity of this phase and its low mobility. Likewise, shorter $T_1$ of the backbone silicons of the PDMS shows it to be relatively the more mobile phase. The difference between them shows that these components do exist in two different phases. The endgroup silicon’s $T_1$ for the TEOS/PDMS material is 29.8 seconds. The difference between this $T_1$ and the silicate silicon’s $T_1$ is very small indicating that the PDMS ends are part of the interface between the siloxane and the silicate. For the 50/50 TIP/PDMS system cured also at room temperature, the endgroup silicons have a $T_1$ of 20.6 seconds whereas the backbone silicons of the PDMS have a value of 14.9 seconds. This was surprising since the dielectric and the dynamic mechanical behaviour suggested better mixing in the TEOS/PDMS relative to the TIP/PDMS material. The difference between the $T_1$ values shown here indicates otherwise. Also, the $T_1$ values of the TIP/PDMS material are lower than their respective counterparts in the TEOS/PDMS material. The mechanical properties indicated stiffer properties when TIP was used as the inorganic precursor. Therefore, longer values of $T_1$ were expected for both the backbone as well as the endgroup silicons. This would be true if a stiffer inorganic network is formed in the material containing TIP.
Table 5.1 $T_1$ values of the $^{29}\text{Si}$ and $^{13}\text{C}$ for TIP/PDMS and TEOS/PDMS materials

<table>
<thead>
<tr>
<th>Nuclei</th>
<th>$T_1$ (sec), peak position</th>
<th>$T_1$ (sec), peak position</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{29}\text{Si}$ (backbone)</td>
<td>14.9, -21.5 ppm</td>
<td>20.2, -22.0 ppm</td>
</tr>
<tr>
<td>$^{29}\text{Si}$ (ends)</td>
<td>20.6, -16.1 ppm</td>
<td>29.8, -18.0 ppm</td>
</tr>
<tr>
<td>$^{29}\text{Si}$ (SiO$_2$)</td>
<td></td>
<td>32.2, -107.8 ppm</td>
</tr>
<tr>
<td>$^{13}\text{C}$ (backbone)</td>
<td>2.2, 1.4 ppm</td>
<td>2.5, 1.8 ppm</td>
</tr>
</tbody>
</table>
But the results from the $T_1$ experiments indicate otherwise, although the mechanical properties support the previous argument. $T_1$ of the $^{13}$C nucleus of the siloxane methyl groups were also determined. For the TIP/PDMS this was 2.2 seconds while for the TEOS/PDMS material it was 2.5 seconds. Better mixing of the siloxane with the metal oxides will result in longer $T_1$ values which is true here and supports the dynamic mechanical and dielectric behaviour. To summarise, the $T_1$ values for the most part do confirm the differences observed in the properties of the hybrid materials. However, the anomalous behaviour of the of the $^{29}$Si spin-lattice relaxation values in the TIP/PDMS material cannot be explained at this time. More discussion on the effect of varying the metal alkoxide component follows in the electron microscopy and SAXS sections.

5.3.2 Electron Microscopy

5.3.2.1 Effect of TIP content

Backscattered detector was primarily used for the microstructure studies, since it gives better image of a two component system where the electron density of each component is different. In this case, the titanium having higher atomic number than silicon results in the titanium oxides phase backscattering more electrons and therefore appears white in the images. The siloxane phase by the same reasoning should appear black. Fig. 5.4 and fig. 5.5 shows the backscattered images of the fractured surface of varying compositions of TIP/PDMS materials which were cured at room temperature. The top images on each figure are taken at 50000 magnification and 1 mm on these photographs presented here represents 340 A°. The bottom images were taken at 100000 magnification and 1 mm on the photographs presented here is 170 A°. This is true for all the images that are presented in fig. 5.4 - 5.10. The 0/100 TIP/PDMS shown in fig. 5.4 A and 5.4 D does not show any contrast suggesting a one phase system. Since this material does not contain
Fig. 5.4 Electron micrographs of various compositions cured at room temperature (A to C, marker bar = .56 μ, or 1 mm = 340 Å; D to F, marker bar = .56 μ, or 1 mm = 170 Å)
EFFECT OF VARYING COMPOSITION (ROOM TEMPERATURE CURED)
Fig. 5.5 Electron micrographs of various compositions cured at room temperature (A to C, marker bar = .56 μm, or 1 mm = 340 A°; D to F, marker bar = .56 μm, or 1 mm = 170 A°)
EFFECT OF VARYING COMPOSITION (ROOM TEMPERATURE CURED)
any added TIP, this behaviour is expected. The only titanium present in this system are on the ends of the PDMS chains. However, distinct microphase separation is noted for 20/80 TIP/PDMS system. In the lower magnification image, it seems as if the two components exist in a co-continuous morphology. However, at higher magnification, we clearly see that the titanium oxide phase exists as discrete sized particles fractal, in nature on a macroscopic scale. As the percentage of the TIP is increased, more of the white portions representing the titanium oxide phase is seen. This is clear from the images of 30/70 TIP/PDMS shown in fig. 5.4C and 5.4F. At the 40/60 TIP/PDMS composition, the titanium oxide phases appear to be becoming connected to each other. Also, the distances between these phases is getting closer with increasing TIP content. At the 50/50 TIP/PDMS composition (fig. 5.5B and 5.5E), the connectivity of the oxide phase seems complete. A network-like structure of this phase is formed which can be seen very clearly in fig. 5.5E. The siloxane phase (the black parts) seem to be totally encapsulated by the white phase at this composition. Also, the size of the white parts seems to be smaller than those seen in lower TIP content images and the structure seems more open. Finally, in fig. 5.5C and 5.5F are shown the images of pure titanium oxide gel without any PDMS. A network structure of the oxide phase is seen with very small distance separating the white parts. The black part of the image represents the porous nature of the gel. This general discussion on the features of these images will now be followed by a discussion on their correlation with the properties observed.

Increasing TIP content leads to lesser defined phases of the two components in the materials. This implies better phase mixing of the components and also we see encapsulation of the siloxane by the inorganic oxide network at 50/50 TIP/PDMS composition. The dynamic mechanical and dielectric studies of these systems showed behaviour concurrent with this trend. Especially, it should be recalled that the 50/50 TIP/PDMS material showed a flat and broadened dynamic mechanical tan δ behaviour. The mechanical properties also support the conclusions reached from seeing the morphology of
Fig. 5.6 Electron micrographs of various TIP/PDMS compositions cured by microwave processing (A to C, marker bar = .56 μ, or 1 mm = 340 Å; D to F, marker bar = .56 μ, or 1 mm = 170 Å)
Fig. 5.7 Electron micrographs of various TIP/PDMS compositions cured by thermal processing (A to C, marker bar = .56 µ, or 1 mm = 340 Å; D to F, marker bar = .56 µ, or 1 mm = 170 Å)
EFFECT OF VARYING COMPOSITION (THERMALLY CURED)

A) 30/70 TIP/PDMS (MAG. = 50000)
B) 40/60 TIP/PDMS (MAG. = 50000)
C) 50/50 TIP/PDMS (MAG. = 50000)

D) 30/70 TIP/PDMS (MAG. = 100000)
E) 40/60 TIP/PDMS (MAG. = 100000)
F) 50/50 TIP/PDMS (MAG. = 100000)
these materials. With increasing TIP content the modulus of the materials and the stress at break increased while the strain at break decreased. From the images it was surmised that with increasing TIP content, the connectivity of the titanium oxide phases increases until at the 50/50 TIP/PDMS composition the connectivity seems to be complete. This is exactly the point at which the mechanical properties of the material change abruptly. The materials have a very high modulus and are brittle at this composition. The fracture surfaces of the microwave and thermal cured materials also show a similar trend with increasing TIP content as shown in fig. 5.6 and 5.7 respectively, although not as clearly as in the room temperature cured materials. The optical properties of the microwave and room temperature cured thin films also concur with the conclusions about this morphological behaviour. The increase in the refractive index with higher TIP content and the abrupt change at 50/50 TIP/PDMS composition can also be rationalised based on the observed microstructure of these materials.

5.3.2.2 Effect of Cure Modes

The dynamic mechanical and the dielectric relaxation studies showed the presence of sharper microphase separation in the microwave cured materials relative to those cured thermally at the same temperature. This was at least convincing for the lower TIP content materials, and the effect diminished with increasing TIP content. Fig. 5.8 shows the fractured surface of the 30/70 TIP composition cured by all the three different techniques. One striking difference that is immediately apparent is the size of the titanium oxide domains in the microwave cured specimen which are much bigger relative to the thermally cured material. The average distances between the inorganic phases in the microwave and thermally cured materials may be the same, but bigger pockets of black portions representing the siloxane phase are notable in the microwave cured material. This helps explain the broad tan δ behaviour due to melting transitions in the dynamic mechanical and
Fig. 5.8 Electron micrographs of 30/70 TIP/PDMS compositions cured by thermal, microwave and room temperature processing (A to C, marker bar = .56 μ, or 1 mm = 340 Å; D to F, marker bar = .56 μ, or 1 mm = 170 Å)
EFFECT OF CURE MODES (30/70 TIP/PDMS)

A) MICROWAVE CURED (MAG. = 50000)

B) THERMALLY CURED (MAG. = 50000)

C) ROOM TEMP. CURED (MAG. = 50000)

D) MICROWAVE CURED (MAG. = 100000)

E) THERMALLY CURED (MAG. = 100000)

F) ROOM TEMP. CURED (MAG. = 100000)
Fig. 5.9 Electron micrographs of 40/60 TIP/PDMS compositions cured by thermal, microwave and room temperature processing (A to C, marker bar = .56 µ, or 1 mm = 340 Å; D to F, marker bar = .56 µ, or 1 mm = 170 Å)
EFFECT OF CURE MODES (40/60 TIP/PDMS)

A) MICROWAVE CURED (MAG. = 50000)
B) THERMALLY CURED (MAG. = 50000)
C) ROOM TEMP. CURED (MAG. = 50000)

D) MICROWAVE CURED (MAG. = 100000)
E) THERMALLY CURED (MAG. = 100000)
F) ROOM TEMP. CURED (MAG. = 100000)
Fig. 5.10 Electron micrographs of 50/50 TIP/PDMS compositions cured by thermal, microwave and room temperature processing (A to C, marker bar = .56 μ, or 1 mm = 340 A°; D to F, marker bar = .56 μ, or 1mm = 170 A°)
EFFECT OF CURE MODES (50/50 TIP/PDMS)

A) MICROWAVE CURED (MAG. = 50000)
B) THERMALLY CURED (MAG. = 50000)
C) ROOM TEMP. CURED (MAG. = 50000)

D) MICROWAVE CURED (MAG. = 100000)
E) THERMALLY CURED (MAG. = 100000)
F) ROOM TEMP. CURED (MAG. = 100000)
dielectric relaxation experiments. Also, the DSC experiment where more crystallization was seen in the microwave cured material relative to the thermally cured material can be explained. Bigger portions of PDMS rich phase will have less restrictions in the crystallization process. These morphological differences between the microwave and thermal processing can also be seen for the 40/60 TIP/PDMS composition shown in fig. 5.9. However, the contrast between the two phases is diminished in the thermally cured material relative to the 30/70 TIP/PDMS composition. The trends for the microwave and thermally cured materials are similar to what was seen for the 30/70 TIP/PDMS composition. The 50/50 TIP/PDMS composition cured by all the three different techniques are shown in fig. 5.10. Again, differences are seen in the morphologies of the microwave and thermally cured materials. The room temperature cured materials for all the three compositions appear somewhat different than the microwave and thermal cured materials. The sizes of the inorganic domains appear bigger especially in the 30/70 TIP/PDMS composition. The differences observed are obviously related to the curing temperature of these materials. Microwave energy coupling with the sol-gel reactions have been shown to create more phase separation in the TEOS/PTMO and the TIP/PTMO ceramers by Rodrigues (72). Rodrigues also observed that the dielectric loss of the hydrated metal alkoxides were higher than the metal alkoxides. However, the differences between microwave and thermal processing diminished in the case of TIP/PTMO ceramers relative to the TEOS/PTMO ceramers. This was postulated to be due to higher reactivity of TIP compared to TEOS. The observation of TIP/PDMS materials showing more microphase separation agree with the findings of Rodrigues. The TIP is prehydrolysed before mixing with the reactive PDMS solution. Therefore it is conceivable that a considerable amount of metal hydroxides are present in the solution before being subjected to the microwave curing. Microwave energy effectively couples with these hydroxides, perhaps increasing the reaction rates considerably. As a result, bigger domains of the oxide phase are formed which are probably quite porous. The porous nature of the pure titania gel has already been
seen in fig. 5.5C and 5.5F. There have been no reports on the effects of temperature on the reaction kinetics of titanium alkoxides. As was stated in Chapter 2, kinetic studies of these systems are very hard to perform due to their extremely high reactivities. Therefore any conclusions on the differences in the morphologies of room temperature and thermally cured materials observed here are difficult to diagnose.

5.3.2.3 Effect of Water Content

Significant differences in the properties were observed when the initial water content was varied keeping the rest of the reaction conditions the same. The relaxation dispersion shifted to lower temperatures as studied by DMTA and DETA, while the mechanical properties were stiffer. Fig. 5.11 shows the fracture surfaces of 40/60 TIP/PDMS compositions cured at room temperature with two different water contents. 1mm on these photographs represents 300 Å and 150 Å for 50000 and 100000 magnification respectively. This is true for both fig. 5.11 and fig. 5.12. A marked difference between the morphology of the two materials is apparent. The material with higher water content shows smaller spherical particulates of the titanium oxides. Bradley et al. (28) have proposed several structures of the oligomers of the metal oxides based on the hydrolysis ratio, h (water to alkoxide mole ratio). Although these structures are hypothetical without any experimental verification, it is postulated that condensation of these oligomeric structures leads to the basic building blocks in the final product. Also, as discussed in Chapter 2, chain or more linear polymers are postulated to form when the hydrolysis ratio is around one (21) which corresponds to the materials made with water content of 0.25. Water content of 0.5 corresponds to hydrolysis ratio of 2. This would then fall outside the regime where linear chain like growth takes place. Increased water content is going to result in rapid kinetics and it has been reported that the mean size and weight of the oligomers then
Fig. 5.11 Electron micrographs of 40/60 TIP/PDMS compositions cured at room temperature with two different initial water contents.

A to B, marker bar = .56 μm, or 1 mm = 300 Å; C to D, marker bar = .56 μm, or 1 mm = 150 Å. 
EFFECT OF WATER CONTENT (40/60 TIP/PDMS, ROOM TEMP. CURED)

A) h = 0.25 (MAG. = 50000)

B) h = 0.50 (MAG. = 50000)

C) h = 0.75 (MAG. = 100000)

D) h = 0.50 (MAG. = 100000)
depend on the hydrolysis ratio (25). The morphology seen here correlates very well the discussion presented.

### 5.3.2.4 Effect of the Metal Alkoxide Type

Significant differences in the properties were observed when TEOS was used instead of TIP to make the hybrid materials. The relaxation dispersion was broader and the maxima shifted to a lower temperature relative to the TIP based materials. The fracture surfaces of the 50/50 metal alkoxide/PDMS composition cured at room temperature under the same reaction conditions are shown in fig. 5.12. The electron density difference between the silicates and the PDMS is smaller, the silicates conceivably being more than the PDMS. Therefore, the contrast is not observed as well as in the TIP/PDMS materials. However, here too an interconnected silicate morphology is seen and the domain sizes are much bigger compared to the TIP/PDMS material. Also, bigger portions of the PDMS phase are observed in the TEOS/PDMS materials. This supports the hypothesis that homolcondensation probably occurs on a larger scale in the TEOS/PDMS material. The differences in the structures of these materials are thus related to the both the reactivity difference between TEOS and TIP, and better compatibility between TEOS and PDMS relative to TIP and PDMS.

After having seen the differences between the microstructure of the hybrid materials as a function of variables affecting the sol-gel reactions, curiosity arises about the mechanism of the microphase separation development. An interesting study has been recently reported by Nakanishi et al. (97,98) on the phase separation of a silica system containing polyacrylic acid. Interconnected gel morphologies developed in these systems on micrometer range dimensions which was postulated to have occurred by spinodal phase decomposition. Nakanishi et al. suggest that their system consisting of an originally polymeric and
Fig. 5.12 Electron micrographs of 50/50 TIP/PDMS and 50/50 TEOS/PDMS compositions cured at room temperature (A to B, marker bar = .56 μ, or 1 mm = 300 Å; C to D, marker bar = .56 μ, or 1 mm = 150 Å)
EFFECT OF INORGANIC PRECURSOR TYPE
Fig. 5.13 Schematic phase diagrams of silica-organic polymer system for a) weak segregation strength b) moderate segregation strength c) strong segregation strength
polymerizable species undergoes polymerization induced spinodal phase separation, the free energy change being driven by chemical reactions. Chemical bond formation is deemed to be equivalent to attractive interaction among constituents, which is then equivalent to physically cooling the system (quenching). Usually, for the alkoxy derived sol-gels, gelation occurs in a one phase state. But the addition of a polymer to the system increases the binodal temperature such that phase separation can occur along with the gel formation or before gelation. Hypothetical phase diagrams are shown in fig. 5.13 based on the segregation strength between the silica and the organic polymer, where the segregation strength varies from weak to strong (97). Also shown are the viscosities of the silica rich and the polymer rich phases (dashed curve) as a function of the quench depth. The segregation strength between the polymerizing silica and the organic polymer is influenced by the molecular weight, temperature and the coexisting solvent. The quench depth and the viscosity changes in the system are the controlling factors in the formation of the morphology. Using these arguments they have rationalised different morphologies observed as a function of composition, reaction temperature and solvent content. Application of the spinodal decomposition ideas above to the hybrid materials studied here is very speculative. The oligomeric component used has reactive ends making these systems more complicated than the ones of Nakanishi et al. This difference probably results in much smaller domain structure as observed by electron microscopy. Also, the only evidence of spinodal phase decomposition observed in the hybrid materials presented here are the microstructures observed by electron microscopy. Nakanishi et al. observed finer domain structures with increasing reaction temperature. Similar difference is noted in the microstructures of the hybrid materials studied here obtained by thermal and room temperature curing. They postulate that the polymerization rate increases with temperature which results in the quench depth being deeper at which the phase separation is initiated and shortens the duration allowed for coarsening. This therefore results in finer domains (98). This explanation would also help explain the larger domain sizes in the TEOS/PDMS
material relative to the TIP/PDMS cured material, TEOS being a lesser reactive material. However, the domain sizes of the titanium oxides in the microwave cured material were bigger than those cured thermally. Microwave curing has been postulated to increase the reaction kinetics. Therefore, the microstructure observed in the microwave cured materials is contrary to that expected from Nakanishi's hypothesis. Again, it is emphasized that this discussion is highly speculative, although it does help in explaining some of the microstructural differences in terms of polymerization rates and reactivities.

5.3.3 Small Angle X-Ray Scattering (SAXS)

5.3.3.1 Effect of TIP Content

As stated before, SAXS has been used extensively by Wilkes et al.(42-50) to study the microstructure of Ceramers. In the studies presented here, SAXS was utilised to confirm the microstructure observed by STEM and to help explain the structural differences in the materials as a function of different variables studied. All the SAXS profiles shown in this section are smeared data. Fig. 5.14 shows the effect of increasing TIP content in compositions cured at room temperature. The SAXS profiles are plotted in terms of scattered intensity as a function of the angular factor, s. Decreasing TIP content leads to a sharper SAXS profile with a higher scattered intensity observed at the maxima. The maxima correlates to an average characteristic spacing, d, between the center of the two phases of the same electron density. In the case of hybrid materials presented here, d would represent the dimensions which correlate with average spacing between the inorganic oxides phases. The maxima also shifts to smaller s values. The breadth of the SAXS profile increases with higher TIP content indicating greater distribution of the d values. Also, in the higher s region, the scattered intensity increases with higher TIP content. The behaviour so far described here is totally opposite of the behaviour seen in most ceramers
Fig. 5.14 SAXS profiles as a function of varying TIP content cured at room temperature
including TIP/PTMO ceramers reported by Brennan (50). In the ceramers reported by Wilkes et al., the d value was dependent on the molecular weight of the oligomer used. The inorganic oxide is postulated to be in the form of clusters which are present at the end of the PTMO chains. With increasing metal alkoxide content the cluster size increases thereby increasing the d spacing and also the scattered intensity. The intensity of scattered radiation from SAXS is described by the equation below

\[ I(s) = 4\pi i_e<\Delta \rho^2> V \int_0^\infty \gamma(r) \frac{\sin(2\pi sr)}{2\pi sr} r^2 dr \] (5.1)

where \( <\Delta \rho^2> \) represents the mean square electron density fluctuation, \( V \) is the illuminated sample volume, \( i_e \) is the Thomson scattering coefficient for an electron and \( \gamma(r) \) is the correlation function which represents the spatial inhomogeneity of the specimen. \( S_0 \) here again is the angular factor and is equal to \( 2\sin^2\theta \) where \( \theta \) is half the radial scattering angle and \( \lambda \) is the wavelength of the incident x-ray beam. The mean square electron density fluctuation for a sharp boundary two phase system is given by the relationship shown below:

\[ <\Delta \rho^2> = \phi_1 \phi_2 (\rho_1 - \rho_2)^2 \] (5.2)

where \( \phi_1, \phi_2 \) are the respective volume fractions of the two phases and \( \rho_1, \rho_2 \) are their respective electron densities. With this background information, an attempt to explain the SAXS behaviour observed will be discussed.

From the dynamic mechanical and dielectric relaxation studies, it was concluded that the degree of phase mixing increases with higher TIP content. The tan \( \delta \) behaviour of the 30/70 TIP/PDMS composition indicated less mixing of the two components. Also, for
the 20/80 TIP/PDMS composition, the boundary between the two phases appeared very sharp in the electron micrographs. Therefore, for the lesser TIP content materials, low scattered intensities at higher 's' values are expected. Also, the higher intensity at larger s values indicates less sharper boundary between the two phases with increased TIP content. This behaviour is also indicative of greater phase mixing between the two components with higher TIP content, which in fact was the conclusion from the relaxation studies.

The fractal dimension, \( d_f \), was calculated by determining the slope of the Porod region, when the SAXS data is plotted as log (scattered intensity) as a function of the log (s). These plots are shown in fig. 5.16-5.20. When a polyfunctional monomer forms bonds at random or aggregation of a particulate sol takes place, fractal structures are commonly formed. This is certainly true in the case of the hybrid materials presented here. Fractals are distinguished in two categories: mass fractals where

\[
m \propto r^{d_f}
\]

where \( m \) and \( r \) are the mass and the radius of the object. The second type is the surface fractal where

\[
S \propto r^{d_s}
\]

\( s \), being the surface area of the object. The mass fractal dimension lies between values of 0 and 3, while the surface fractal dimension is between 2 and 3(1). For mass fractal objects, the mass and surface dimension are equal (1). Computer simulated structures using various kinetic growth models with their respective fractal dimension are shown in fig. 5.15 (1). The structures generally become more open with decreasing values of the fractal dimension.
<table>
<thead>
<tr>
<th>MONOMER-CLUSTER</th>
<th>REACTION-LIMITED</th>
<th>BALLISTIC</th>
<th>DIFFUSION-LIMITED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDEN</td>
<td>VOLD</td>
<td>WITTEN-SANDER</td>
</tr>
<tr>
<td>D = 3.30</td>
<td>D = 3.00</td>
<td>D = 2.50</td>
<td></td>
</tr>
<tr>
<td>CLUSTER-CLUSTER</td>
<td>RLCA</td>
<td>SUTHERLAND</td>
<td>DLCA</td>
</tr>
<tr>
<td>D = 2.09</td>
<td>D = 1.85</td>
<td>D = 1.80</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5.15 Computer simulated structures using various kinetic growth models (1)
Fig. 5.16 Fractal dimension determination from log intensity vs. log S plot for 20/80 TIP/PDMS material cured at room temperature.
Fig. 5.17 Fractal dimension determination from log intensity vs. log S plot for 30/70 TIP/PDMS material cured at room temperature
Fig. 5.18 Fractal dimension determination from log intensity vs. log S plot for 40/60 TIP/PDMS material cured at room temperature
Fig. 5.19 Fractal dimension determination from log intensity vs. log S plot for 50/50 TIP/PDMS material cured at room temperature
Fig. 5.20 Fractal dimension determination from log intensity vs. log S plot for 50/50 TEOS/PDMS material cured at room temperature
Table 5.2 Fractal dimension of the TIP/PDMS compositions cured at room temperature

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fractal Dimension (d1)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80 TIP/PDMS</td>
<td>2.53</td>
</tr>
<tr>
<td>30/70 TIP/PDMS</td>
<td>2.39</td>
</tr>
<tr>
<td>40/60 TIP/PDMS</td>
<td>2.38</td>
</tr>
<tr>
<td>50/50 TIP/PDMS</td>
<td>2.21</td>
</tr>
</tbody>
</table>

* corrected for slit smeared intensity
The TIP/PDMS materials indicated mass fractal behaviour. The fractal dimension for the various TIP/PDMS compositions cured at room temperature are shown in table 5.2. The values for lower TIP content materials are higher suggesting denser structure of the inorganic metal oxides in the material. Similar values were obtained for the TIP/PTMO materials by Rodrigues (72). The fractal dimension decreases for the 50/50 TIP/PDMS composition suggesting a more open structure relative to the lower TIP content materials. The more open structure of the titanium oxides would have a better chance of encapsulating the PDMS, which agrees with the morphology seen in the electron micrograph of this particular composition shown in fig. 5.5 E.

5.3.3.2 Effect of Cure modes

The SAXS profiles for the 30/70 TIP/PDMS composition cured by all the three different techniques are shown in fig. 5.21. The conclusions based on the dynamic mechanical and dielectric spectroscopy was the presence of more microphase separation in the microwave cured relative to the thermally cured material. There is a big difference in the SAXS profile of the thermally processed material relative to the microwave cured material. The intensity is much less although the peak position may be almost at the same s value. Such differences have been reported by Rodrigues (72) in the TEOS/PTMO and TIP/PTMO materials and were explained on the basis of higher extent of reaction in the microwave cured material leading to higher scattered intensity at the peak maxima. However, the difference in the SAXS profiles is bigger than what was expected based on the results of the relaxation studies and electron microscopy. The SAXS profiles of the room temperature cured and thermally cured materials are similar with perhaps the room temperature cured profile being somewhat broader. The SAXS profiles for the 40/60 TIP/PDMS composition cured by all the three different techniques are shown in fig. 5.22.
Fig. 5.21 SAXS profiles of 30/70 TIP/PDMS composition cured by thermal, microwave and room temperature processing
Fig. 5.22 SAXS profiles of 40/60 TIP/PDMS composition cured by thermal, microwave and room temperature processing
There is virtually no difference observed between the microwave and thermally processed material for this composition. We had observed from the relaxation studies that the effect of microwave processing influencing different properties diminishes with higher TIP content. The room temperature cured material's profile has higher scattered intensity suggesting higher extent of reaction relative to the microwave or the thermally cured material.

**5.3.3.3 Effect of Acid Content**

The dielectric relaxation studies of the 50/50 TIP/PDMS materials cured thermally with decreasing acid content had showed better phase mixing. The slower reaction rates with lesser acid catalyst will probably generate smaller oligomers of the titanium oxide species leading to better mixing with the siloxane. Fig. 5.23 shows the SAXS profile for the 50/50 TIP/PDMS materials cured thermally with acid content of 0.03 and 0.0. The profile of the material with no acid is flatter and also the scattered intensity is lower relative to the material with acid. This behaviour suggests better mixing in the material with no acid and also lower extent of reaction. This conclusion supports the dielectric tan δ behaviour observed in these materials. The SAXS behaviour for the same materials cured in the microwave are shown in fig. 5.24. The differences observed between the material with acid and no acid is more in this case as compared to the thermally cured materials. Hydrolysis rates are generally known to increase with acid catalyst for the titanium alkoxides (28). Therefore, the sol made with no acid probably has lesser amount of hydrated metal oxides which are more lossy than the alkoxides. The extent of reaction in the microwave would then be considerably less. This would explain the behaviour seen for the microwave cured materials.
Fig. 5.23 SAXS profiles of 50/50 TIP/PDMS composition cured thermally with acid catalyst and without acid catalyst
Fig. 5.24 SAXS profiles of 50/50 TIP/PDMS composition cured by microwave processing with acid catalyst and without acid catalyst
5.3.3.4 Effect of the Water Content

Higher water content led to the shift of the relaxation dispersion of the PDMS to lower temperatures and also better mechanical properties. Significant differences were also observed by electron microscopy in the microstructure of the materials prepared with varying initial water content. The SAXS profiles for the 40/60 Ti/PDMS composition cured at room temperature with initial water content of 0.25 and 0.50 are shown in fig. 5.25. The results are surprising since the scattered intensity of the material prepared with more water is much lower. Higher extent of reaction is expected with more water leading to more scattered intensity. Also, the profile does not show any maxima. It is possible that the correlation distance d, is outside the range of the size being analysed in the SAXS.

5.3.3.5 Effect of the Metal Alkoxide type

The SAXS profiles for the 50/50 metal alkoxide/PDMS composition cured at room temperature is shown in fig. 5.26. Recalling equations 5.1 and 5.2, it is apparent that the electron density difference between the silicates and the siloxane phases would lead to small correlation and hence less scattered intensity. This is exactly the behaviour seen in fig. 5.26. The fractal dimension calculated for the TEOS/PDMS material was 1.80 which is typical of an acid catalysed TEOS system (1). The fractal dimension suggests loosely branched linear structure which is open in nature. The fractal dimension of the Ti/PDMS material is also similar with a value of 2.19.

5.4 Conclusions

In general the structural information correlated very well with the properties observed. Solid-state NMR spectroscopy showed the presence of the peak due the Si-O-Ti bond
Fig. 5.25 SAXS profiles of 40/60 TIP/PDMS composition cured at room temperature with two varying initial water contents
Fig. 5.26 SAXS profiles of 50/50 TIP/PDMS and TEOS/PDMS compositions cured at room temperature
which was observed and assigned in the solution studies. The spin-lattice relaxation time measurements of the $^{29}\text{Si}$ nucleus indicated phase separation in the hybrid materials. The degree of phase mixing was seen to be more in the TEOS/PDMS materials relative to the TIP/PDMS material by the $^{13}\text{C} \ T_1$ values.

The microstructure observed by STEM showed the presence of phase separation in the hybrid materials. The degree of phase mixing between the two components of the hybrid materials increases with higher TIP content. Increased encapsulation of the siloxane phase by the inorganic is observed as the TIP content in the hybrid material is increased. At the 50/50 TIP/PDMS composition, the connectivity of the inorganic domains is complete. This explains the significant changes observed in the mechanical and optical properties at this composition. Bigger oxide domains were observed in the microwave cured materials as compared to the thermally cured materials. The thermally cured materials contain finer oxide domains as compared to those made by room temperature cure. The microstructure of the titanium oxide gel was observed to be porous in nature. This suggests that porosity is present in the inorganic oxide phase of the hybrid materials. The initial water content determines the microstructure of the hybrid materials. The material made with initial water content of 0.25 shows linear like growth of the titanium oxide phase. However, when the initial water content of 0.5 is used, spherical and smaller particulate like structure of the titanium oxide are produced. The SAXS profiles for these set of materials did not conform to the structures observed by STEM. The initial acid content also affects the microstructure in a similar manner as the water content. Materials prepared with no acid showed lower scattering intensity than those made with acid, processed both thermally and by microwave. However, the difference observed in the microwave cured materials is more than those cured thermally. Limited extent of reaction in the microwave due to the lack of hydrated metal alkoxides in the material with no acid is probably the cause for this behaviour.
Chapter 6 --- Some Potential Applications of the Hybrid Materials.

6.1 Introduction and Objectives

In this chapter, some of the potential applications of the hybrid materials synthesized will be discussed. Sol-gel processing has been predominantly used to deposit thin films since the liquid state prior to gelation allows simple processes like spin coating, dipping or spraying for deposition. The most important advantage of the sol-gel process is the ability to control the microstructure of the deposited film (1). However, the popularity of the sol-gel process to deposit thin films is mainly due to the inability of the process to form thick monolithic materials. Even if the monolithic formation is successful, the process tends to be lengthy. This is one area where the hybrid materials can be potentially useful for successful applications.

The scope and the application areas for sol-gel processing are vast. These ideas and novel proposals have been a major part of the sol-gel literature, some of which are referenced here (99-101). Applications in the form of thin films have encompassed the areas of optical coatings (102-104), electronic coatings (105) and protective coatings (106).

It was already shown in chapter 4 that the refractive indices of the TIP/PDMS materials increase with higher TIP content. Also, the thickness of these films is controllable by the concentration of the solution, coating time and speed. Therefore, the feasibility of designing optical filters is immediately apparent for the TIP/PDMS materials. Multiple layers optical filters can then be designed with the appropriate tailored refractive index and thickness of each layer.
The objective of the research here was to utilise the hybrid materials developed for end use applications. Two areas of applications were probed which are: a) hybrid materials as hosts for laser active dyes and b) firing of the hybrid materials to form TiO₂-SiO₂ thin films.

The sol-gel process, being a solution technique in the preliminary stage, allows the incorporation of dopants which can be dispersed uniformly in the system. Generally, organic laser dyes are thermally unstable when the laser exposure time is long and are also difficult to handle (107). Most organic laser dyes are soluble in alcohols providing an easy route for their dispersion in sol-gel processed systems. The biggest advantage of using inorganic matrices for these laser dyes over organic polymeric matrices is in the higher photostability (108). Also, most of the inorganic matrices generated by the sol-gel process are transparent in the visible and the near infra-red region (109). A wide variety of successful laser dye doped sol-gel processed materials have been reported using mostly a silica matrix (107-117), and in some cases, organically modified silicate matrices (113-114). Hybrid materials have the potential for serving as efficient matrices and thicker films of these materials are much easier to fabricate than the conventional metal oxides from the sol-gel process. Therefore, experiments were carried out with Coumarin 153 as the laser dye dopant in the TIP/PDMS systems to explore the possibilities of these materials serving as efficient matrices for the laser dyes.

Titania-silica thin films are of great commercial importance since they possess good chemical stability, small and sometimes even a negative thermal expansion coefficient and a high refractive index (118). The correlation of microstructure and properties of these films over a range of compositions has been widely studied, some of which are cited here (119-122). The low temperature sol-gel route has been the method of choice since the degree of homogeneity in the binary component system is better over the materials prepared by the
conventional high temperature flame pyrolysis method. However, materials with a higher TiO₂ content made by the sol-gel process have shown a tendency to phase separate, and homocondensation of the individual components has been suggested as the reason for this behaviour (1). TIP/PDMS hybrid materials synthesized in the research presented here can be potential precursors for silica-titania films since the Si-O-Ti bond is already preformed at low temperature. Also, the control of the microstructure of these hybrid materials with variables like the molecular weight of the PDMS and initial hydrolysis conditions can lead to interesting material properties of the silica-titania films derived from them.

6.2 Experimental

Coumarin 153 was obtained from Eastman Kodak. The free standing film fabrication was done in a similar manner to the procedure described in Chapter 4. An appropriate amount of Coumarin 153 was dissolved in isopropanol and then added to the sol used for casting the free standing films. The concentration of the laser dye used was 10⁻³ M. Free standing films of 30/70, 40/60 and 50/50 TIP/PDMS compositions with the laser dye dopant were fabricated by room temperature, thermal and microwave processing techniques. The absorption due to the laser dye was then studied by using a tunable laser source and optical multichannel analyser.

A silica-titania thin film was fabricated on a silicon wafer. A 50/50 TIP/PDMS composition solution was deposited on the substrate by the spin coating technique. After one week at room temperature this film was subjected to a temperature of 700 °C to get rid of all the organics from the material. The resultant TiO₂-SiO₂ thin film was then analysed by FTIR spectrophotometry. A Nicolet 400 FTIR spectrophotometer in the transmission mode was used for this experiment. The thin film spectrum presented here is obtained by ratioing the spectrum of the thin film on the silicon wafer to that of the neat silicon wafer.
6.3 Results and Discussion

The materials made with the dopants were transparent with an orange color due to the dopant. The transparent nature of the materials proved the absence of any segregation of the dye molecules. Dispersion of the dye in the hybrid material matrix results in the dye-matrix interaction which affects the characteristics of the dye. Fig. 6.1 shows the absorption characteristics of the 30/70 TIP/PDMS and the 40/60 TIP/PDMS materials with the dopant cured by the three techniques. The absorption due to the laser dye is apparent from the data indicating that no significant deterioration of the dopant characteristics occurs on its dispersion in the TIP/PDMS matrix. The absorption $\lambda_{\text{max}}$ for Coumarin 153 in ethanol is 423 nm. However, in the data presented here the maxima has shifted to longer wavelengths. These red shifts have been observed for Coumarin dyes in silicate gels compared to pure ethanol. These shifts are attributed to the presence of water and alcohol in the system (114). The dye molecules in doped silica systems have been postulated to reside in the pores or within the rigid cages of the matrix and have, therefore, been used as a probe for the structural studies of the silicate gels (110,112). The red shift has also been seen by Harvey et al. (115) and the origin in this case is thought to be due to dopant-matrix interaction. Preliminary studies proved the feasibility of using these materials as hosts for Coumarin 153. A wide variety of dopants for optical, nonlinear optical and other specific applications exist which shows the different ways in which these materials can be used for pragmatic purposes.

The silica-titania film was obtained by subjecting a 50/50 TIP/PDMS material to 700 °C. However, lower temperature (<500 °C) can be used to get the organics out of the system. This film visually appeared transparent without any cracks in it. The FTIR spectrum of the silica-titania film is shown in fig. 6.2. Three noticeable peaks are observed in the spectra. The peaks at 460 cm$^{-1}$ and 1065 cm$^{-1}$ are due to the vibration modes of Si-
Fig. 6.1 Absorption curves for 30/70 TIP/PDMS and 40/60 TIP/PDMS materials doped with Coumarin 153
Fig. 6.2 FTIR spectrum of silica-titania thin film
O-Si bonds in the material (122). The shoulder at 1200 cm\(^{-1}\) is also due to the vibrational modes of the Si-O-Si bonds. The peak at 945 cm\(^{-1}\) is due to the Si-O-Ti bond which agrees well with the findings of Matsuda et al. (122). The Ti apparently exists in a four-fold coordination state.

6.4 Conclusions

Successful potential applications for the TIP/PDMS hybrid materials were shown in this chapter. The doping of a laser dye, Coumarin 153, was achieved in the TIP/PDMS materials without any segregation. The characteristics of the laser dyes were not hampered by the dispersion in these hybrid materials. Also, the potential for using these hybrid materials as precursors for the silica-titania films of different compositions was shown. The silica-titania film using the 50/50 TIP/PDMS material showed structural features similar to what has been reported in the literature. The use of these hybrid materials especially for higher titania containing silica-titania materials is definitely an interesting proposition.
Chapter 7 --- Conclusions and Recommendations

7.1 Conclusions

The first part of the research study involved silanol terminated PDMS as the oligomeric component and TIP as the inorganic component for the formation of hybrid materials. The oligomeric incorporation study done by $^{29}\text{Si}$ NMR proved that the degradation of the PDMS was occurring in solution and that TIP was responsible for it. This study was followed by observing the silicon of the Si-O-Ti bond and an assignment of -15.6 ppm in this specific chemical environment. A synthetic technique for endcapping PDMS with TIP was established. The use of TIP endcapped PDMS should increase the efficiency of incorporation and gelation should occur quite rapidly. Therefore, degradation of the PDMS chains will be avoided.

Hybrid materials, using the TIP endcapped PDMS and TIP, were successfully made. The materials obtained were transparent and their flexibility depended on the TIP content. Materials with a range of synthetic variables were fabricated. The variables were weight percent organic/oligomeric content, initial water content and the hydrochloric acid content. The materials were cured by room temperature cure, microwave cure and thermal cure at 70 $^\circ$C. Materials with TEOS instead of TIP as the oxide precursor were also prepared to study the effect of reactivity. All these materials, prepared with a wide range of variables, were subjected to a systematic structure-property relationship study. The properties were studied by dielectric analysis, dynamic mechanical analysis, and stress-strain experiments. Optical properties of the materials were also evaluated. Structural characterization was done by solid-state NMR, electron microscopy and small angle X-ray scattering.
The effect of increased TIP content in the materials results in enhanced phase mixing or encapsulation of the siloxane phase as shown by DMTA and DETA. The mechanical properties support these conclusions. The modulus and the stress to break increase while the strain at break decreases with higher TIP content. The mechanical properties undergo an abrupt change at the 50/50 TIP/PDMS composition suggesting a significant morphological change at this composition as compared to those with lower TIP content. The moduli of these materials are much higher than those seen for the lower TIP content compositions. The tan δ behaviour for this composition shows a broad and flat behaviour. These results suggested that connectivity of the oxide domains takes place at this composition resulting in encapsulation of the siloxane phase. The refractive indices of these materials showed a systematic increase with higher TIP content. The microstructure of these materials seen by STEM explained the properties exhibited as a function of varying TIP content. Microphase separation was seen in these materials. Also, the extent of encapsulation of the siloxane phase increases with increasing TIP content supporting the conclusions drawn from the properties studied. Connectivity of the oxide domains seems complete at the 50/50 TIP/PDMS composition which explains the abrupt changes in the mechanical properties. Such increased restriction of the siloxane phase by the oxide domains also explains the broad and flat tan δ behaviour at the 50/50 TIP/PDMS composition. The SAXS experiments confirmed the microstructure seen by the STEM. The distance between the inorganic phases decreases with increasing TIP content, which is seen by the scattered intensity maxima shifting to higher 's' values. This is observed in the microstructures obtained by STEM too. The scattered intensity in the SAXS profiles at larger 's' values increase with higher TIP content. This behaviour is indicative of increased phase separation as the level of TIP is decreased. The fractal dimensions calculated from the SAXS data decreased with increasing TIP content in the hybrid materials. The values obtained were in the range of 2.5-2.0 which basically shows loosely branched linear titanium oxides typical of an acid catalysed sol-gel material.
Microwave cured materials showed more phase separation than the thermally cured materials for lower TIP containing compositions. However, the effect diminishes with increasing TIP content. This behaviour is seen in the dynamic mechanical and dielectric studies. Evidence of increased phase separation in the 30/70 TIP/PDMS composition cured by microwave was also proved by crystallization studies by DSC. However, for the higher TIP containing materials the differences between thermal and microwave cure are difficult to explain. The dynamic mechanical studies showed similar spectra for both the thermal and microwave cured materials, while the dielectric results were different. The mechanical properties were generally equivalent for the materials cured by thermal and microwave processing. The refractive indices of the microwave cured materials were a little lower than the thermally cured materials with the exception of the 60/40 TIP/PDMS composition. The STEM studies consistently showed bigger oxide domains in the microwave cured as compared to the thermal cured materials. For the lower TIP content materials bigger pockets of siloxane phase were seen in the microwave cured materials providing an explanation for more phase separation seen by the dynamic mechanical and dielectric experiments. Higher scattered intensity at the maxima in the SAXS profile is seen for the 30/70 TIP/PDMS composition cured by microwave as compared to the same composition cured thermally. Higher extent of reaction coupled with more phase separation probably results in this behaviour. The thermal and microwave cured 40/60 TIP PDMS compositions, however, showed similar SAXS profiles. The differences in the microwave and thermal cured materials are obviously related to the reaction kinetics. Hydrated metal alkoxides have been shown to be more lossy (72) and therefore effective coupling of the microwaves with these species is expected, enhancing the reaction rate. Further studies are needed to completely understand the effect of microwave radiation on the structure-property behaviour of these materials.
The initial water content affects the structure and hence, the properties of the hybrid materials. A higher degree of phase separation was seen in the material made with a water content of 0.5 over that made with a water content of 0.25. This behaviour was clearly seen in the dielectric studies of these materials. The moduli of the materials prepared with a higher water content were larger than those of the materials with a lower water content. This behaviour is explained by the microstructure of these materials as seen by STEM. A spherical particulate type structure of titanium oxides was seen for the material with a water content of 0.5 whereas a more linear like structure was observed for the material with a water content of 0.25. However, the SAXS profiles did not correlate with the microstructure observed by STEM.

The initial acid content also affects the structures and, therefore, the properties of the hybrid materials. A lesser acid content resulted in better dispersion or mixing of the two components as observed by dielectric analysis. This conclusion was also reached by the analysis of the SAXS profiles of these materials. The materials made without any acid showed less scattered intensity at the maxima for both thermal and microwave cured materials. This behaviour confirmed the belief that increased phase mixing resulted by decreasing acid content. The slower hydrolysis and condensation rate due to lower acid content probably leads to smaller oligomeric species of hydrated titanium alkoxides and, therefore, to better mixing with the siloxane phase.

The aging of the prehydrolysed titania sol resulted in increased phase separation in the hybrid materials. This conclusion was based on the dynamic mechanical studies of the 40/60 TIP/PDMS materials. An increased aging period probably results in bigger oligomeric species of the oxides formed by the process of condensation. Therefore, the extent of phase separation will increase with the aging period as was observed here. The use of higher molecular weight PDMS to fabricate hybrid materials results in increased
phase separation compared to those made with lower molecular weight PDMS. Decreased
probability of siloxane encapsulation and bigger size results in this behaviour which was
observed by dynamic mechanical studies.

The TEOS/PDMS materials showed significantly different behaviour from the
TIP/PDMS materials. The better compatibility of the silicates with the siloxane resulted in
better phase mixing in these systems. However, the dielectric and dynamic mechanical tan
δ maxima appeared at a lower temperature compared to the equivalent TIP/PDMS
composition. This behaviour is indicative of PDMS rich phase regions which have
probably resulted from the higher reactivity of the TIP endcapped PDMS compared to the
TEOS component. The $^{29}$Si $T_1$ values obtained from the solid-state NMR also suggested
phase separation in these materials. However, the difference between the $T_1$ values of the
PDMS "chain ends" and the "chain middles" silicons was smaller for the TIP/PDMS
materials compared to that of the TEOS/PDMS materials. The absolute values were also
lower. A behaviour contrary to what is observed was expected. However, the $T_1$ values of
the carbon of methyl group suggested better phase mixing of the siloxane phase with the
silicates. The comparison of the SAXS profiles of the TEOS/PDMS and the TIP/PDMS
materials did not yield much information due to the lack of any correlation seen in the
former. The increase in the TEOS content resulted in behaviour similar to that seen when
the TIP content is increased in the TIP/PDMS materials. The dynamic mechanical
behaviour suggests the formation of a highly condensed structure of the silicates with
higher water content.

Finally, two areas of potential applications of these materials were explored.
Coumarin 153, a laser dye, doped hybrid materials were successfully fabricated. The
properties of the dye were retained even when dispersed into the hybrid material. Also, a
silica-titania thin film was successfully fabricated using a 50/50 TIP/PDMS hybrid material as the precursor.

7.2 Recommendations

There exists many unanswered questions which still need to be addressed. More research is needed to study the mechanism of phase separation. The kinetics of the sol-gel reactions of the titanium alkoxides being an unknown creates difficulties in the study of these materials. Also, the differences between the microstructure observed by STEM as a function of the cure mode and the metal alkoxide type should be further probed. At present no convincing explanation can be given for the differences in the domain sizes seen in these materials.

An extension of the present work can be undertaken by using base catalysis instead of the acid catalysis. It would be interesting to see the properties obtained, since base catalysis will generate a more compact oxide species in contrast to the more linear growth observed in the acid catalysed materials. The encapsulation of the siloxane phase may then be avoided resulting in interesting structure-property relationships. Also, a two step process may be worked out where the acid catalysis is the first step followed by base catalysis. Another possible extension of the work presented in this dissertation would be to use triethoxysilyl terminated PDMS as the oligomeric component with TIP as the oxide precursor to form hybrid materials. The comparison of this material's structure-property relationship with that of the TEOS/PDMS materials made here could give a better idea of the effect of the reactivity differences between two components of a hybrid material. Additionally, some information may be obtained about the reactivity of TIP itself.

There is a lot of scope for doing application oriented research with these hybrid materials. Two such areas were explored in the dissertation research here, but the potential
is virtually limitless. The fundamental information obtained from structure-property relationship studies can be used to develop materials that are better for specific applications than those available to the society.
References


50) A. Brennan. Ph. D. VPI & SU. 1990


Vita

Saikat Joardar was born in Balurghat, India. He attended St. Aloysius' High School in Bhusawal, India until tenth grade and graduated in his twelfth grade from Wilson College, Bombay in 1980. He obtained a Bachelor of Science degree in Chemistry from University of Bombay in 1983. He continued his studies at University of Bombay in the Institute of Science and received Master of Science degree in Analytical Chemistry in 1985. He joined the doctoral program in the Chemistry Department of SUNY at Stonybrook in 1985 and pursued research in atmospheric sciences. However, the desire to be a polymer scientist and an experimentalist influenced him to leave this program. He obtained a Master of Science degree in Chemistry from Stonybrook in 1987 and subsequently joined Virginia Polytechnic Institute and State University. He joined Prof. Ward's group in June, 1988 and worked in the area of hybrid materials by the sol-gel process. He defended and received his doctorate in October, 1992.