CHAPTER 5

UNSATURATED POLYESTER / POSS NANOCOMPOSITES

In this chapter the preparation of unsaturated polyester (UP) based nanocomposites by incorporation of nano cube Polyhedral Oligomeric Silsesquioxane (POSS) through covalent bonding formation using radial polymerization in the presence of benzoyl peroxide as free radical initiator have been studied and discussed.

5.1 UNSATURATED POLYESTER / OCTAMALEIMIDO PHENYL SILSESQUIOXANE (OMPS) NANOCOMPOSITES

Nanosilica in the form of POSS is incorporated into the unsaturated polyester resin system via covalent bonding through in situ polymerization method. In this chapter, the synthesized octamaleimidophenyl silsesquioxane (OMPS) was incorporated into unsaturated polyester resin system through in situ polymerization by covalent interaction between the organic (UP) resin and inorganic POSS. The formation of nanocomposites was confirmed through physico chemical characterizations, further the data resulted from thermal, mechanical and morphological studies were also discussed in this chapter.

For the past few decades an intense research has been carried out for the development of organic-inorganic hybrid polymer nanocomposites. Functionalised polyhedral oligomeric silsesquioxane (POSS) has been used as nano crosslinker in the preparation of organic-inorganic hybrid polymer nanocomposites. Both mono functional and multifunctional POSS have been incorporated into the thermoplastic and thermostetting materials using
standard chemical methods via covalent bonding, copolymerization, grafting or blending. Uniform dispersion of inorganic POSS components into the organic polymer matrices at the nanoscale level synergistically improved the bulk properties. Multifunctional POSS derivatives were used as nanocrosslinker for epoxy resin, vinyl ester (Fu et al 2001), polyurethanes, polyimides (Tamaki et al 2003; He et al 2004), acrylates, phenolics (Liang et al 2005), cyanate esters (Liang et al 2006) and optical organic polymers (Yand et al 2006). Due to its rigid cage like structure and nanoscale dimension (0.53nm) it offers excellent thermal and mechanical stabilities (Martuscelli et al 1993).

In the present work, multifunctional POSS with eight maleimide functional groups [octamaleimidophenylsilsesquioxane (OMPS)] is used as nanocrosslinker for unsaturated polyester (UP) to improve its characteristic properties. UP resins are among the most widely used thermosetting materials because of their characteristic properties such as lightweight and reasonably good mechanical properties (Crosbie and Phillips 1985) and competitive cost. They are largely employed as matrices for composites in automotive applications. Properties like brittle behaviour, low shrinkage during curing restricts their utility for number of high performance applications. Hence, modifications of unsaturated polyester resin with suitable chemical and/or polymeric intermediates are warranted.

Fracture properties can be improved by blending with reactive liquid rubber (Martuscelli 1996). Thermoplastic additives such as polymethyl (methacrylate) or polyvinyl (acetate) are used to achieve low shrinkage. Musto et al (1996) upgraded the UP resin by reactive blending with the comonomer bismaleimide (BMI) and also studied its cure kinetics, and yield stress, Young’s modulus and thermal properties. Dinakaran et al (2002) studied the modification of UP resin using epoxy and vinyl ester by forming an intercrosslinked matrix with the comonomer BMI, and reported that the
introduction of BMI into UP resin alters the thermal, thermomechanical properties according to their percentage concentration. Recently Josephine (2007) et al reported the modification of UP resin with vinyl ester and organically modified montmorillonite clay and reported the mechanical, thermal and thermomechanical properties. In the present work it is proposed to use OMPS as a nanocrosslinker, with utilization of its reactive maleimide group to modify unsaturated polyester and to study the physicochemical, thermal and morphological properties using FTIR, NMR, WAXD, SEM, DSC and TGA analysis.

5.1.1 Preparation of UP-POSS hybrid nanocomposites

A typical OMPS incorporated unsaturated polyester matrices were prepared as follows; Fixed amount of UP resin (100g) and benzoylperoxide (BP) (2 wt%) and varying weight percentages of OMPS (1, 3, 5 and 10 wt%) were mixed at 90 °C for 10 minutes with constant stirring. Then the resulting product was subjected to vacuum to remove the entrapped air and then cast into a preheated mould at 70 °C. The product was cured at 70 °C for 12 hours and then post cured at 100 °C for 2 hours. A similar curing procedure was adopted for the unmodified UP resin and is used as reference material.

5.2 RESULTS AND DISCUSSION

5.2.1 Molecular structure

The molecular characterization of OMPS was discussed in the preceding chapters. The FTIR spectrum (Figure 5.1) of OMPS showed complete disappearance of N-H stretching band of the primary amine at 3360 cm⁻¹ and the appearance of band at 3100 cm⁻¹, corresponding to the H-C= vibration, 1610 cm⁻¹ represents conjugated C=C stretch of the imide ring and 1710 cm⁻¹ represents conjugated C=O stretch of the imide ring. The
tentative molecular structure of unsaturated polyester resin and their FTIR spectra of uncured and cured using benzoylperoxide (BP) is presented in Figure 5.2.

5.2.2 Preparation and characterization

POSS-UP hybrid nanocomposite matrices were prepared using different weight percentages (1%, 3%, 5% and 10%) of OMPS, by dissolving OMPS in UP at 90 °C. The formation of network structure between POSS moiety and UP skeleton takes place through radical polymerization involving maleimide groups of POSS and unsaturation sites present in UP. The resulting POSS-UP hybrid nanocomposites displayed a good transparency after curing. Wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM) studies confirmed the nano-level homogeneous dispersion of POSS molecules into the unsaturated polyester matrices.

5.2.3 Spectral analysis and cure behaviour

Reactive maleimide functional groups present in POSS were used to form an intercross linked network structure within unsaturated polyester resin to obtain hybrid unsaturated polyester/POSS nanocomposites. It is well known that UP-maleimide blends have three different reactive sites, i.e. fumarate double bonds, styrene double bonds and maleimide unsaturations. The consumption of double bonds during curing was monitored through FTIR spectrum. The utilization of styrene double bonds was ascertained from the decrease in peak intensity at 914 cm$^{-1}$ due to the out-of-plane bending mode of the $\equiv$CH$_2$ group (Figure 5.2). The decrease in peak for the polyester unsaturation was observed at 1645 cm$^{-1}$ corresponds to C=C stretching mode (Figure 5.2). Maleimide double bonds present a typical absorption at 3097cm$^{-1}$ which is generally employed to monitor the progress of the curing reaction, though this peak appears relatively with a low intensity because of
low maleimide-POSS content in the blends. However the appearance of band at 830 cm\(^{-1}\) has been reported for several maleimide moieties due to an out-of-plane bending of the \(\equiv\text{C-H}\) group.

![FTIR spectrum](image)

**Figure 5.1** FTIR spectrum of octaaminophenyl silsesquioxane (OAPS) and octamaleimidophenyl silsesquioxane (OMPS)

![FTIR spectrum](image)

**Figure 5.2** FTIR spectrum of (a) uncured UP, (b) OMPS incorporated BP cured UP and (c) BP cured UP
FTIR spectra of uncured unsaturated polyester (UP), OMPS incorporated benzoylperoxide (BP) cured UP, BP cured UP are presented in Figure 5.2. The peak representing for polyester unsaturation and styrene double bonds at 1645 cm\(^{-1}\) and 914 cm\(^{-1}\) disappeared completely after curing. Similarly, the peak 3430 cm\(^{-1}\) representing terminal OH groups of UP completely disappeared and this confirms complete curing. Figure 5.3 shows the FTIR spectra of unmodified UP, 3 wt%, 5wt% and 10 wt% octamaleimide-POSS modified BP cured UP systems. From Figure 5.3 it is observed that all the OMPS modified UP hybrids exhibit peak at 1124 cm\(^{-1}\) corresponds to the cubic Si-O-Si linkage, which confirms that during curing, the cube structure is not disrupted.
Further, the double bonds present in the maleimide groups of OMPS showed a peak at 3097 cm$^{-1}$ when it is incorporated into the UP resin due to its low concentration, the peak appeared at 3097 cm$^{-1}$ was not much intense hence the peaks at 830 cm$^{-1}$ has been assigned for maleimide out-of-plane bending of =C-H group and 1735 cm$^{-1}$ for maleimide C=O group. Since the disappearance of peaks at 830 cm$^{-1}$ and 3097 cm$^{-1}$ show that the maleimide groups react with unsaturated double bonds of styrene and fumarate double bonds present in the UP resin. During curing, the maleimide radicals are formed easily in the presence of radical initiator and thus they may expected to interact faster with other unsaturated sites present in the system readily rather than homopolymerization, thus causing the reactive mixture to undergo cross linking to result homogeneous product. FTIR of cured (Figure 5.3) UP-POSS hybrids indicated the disappearance of peaks representing styrene units at 912 cm$^{-1}$ (vinyl =CH$_2$ wagging) and 992 cm$^{-1}$ (trans –HC=CH- wagging).

The complete disappearance of peaks at 1645 cm$^{-1}$ (C=C stretching) and 982 cm$^{-1}$ (trans –HC=CH- wagging) of fumarate double bonds of UP resin and the existence of peak at 1124 cm$^{-1}$ of Si-O-Si cube, 1735 cm$^{-1}$ of C=O stretching of maleimide group indicates the successful reinforcement of POSS unit at nano-level into the unsaturated polyester resin with high intercross linking density.
Scheme 5.1 Intercrosslinked network structure of octamaleimide-POSS modified unsaturated polyester resin hybrid nanocomposites
5.3 THERMAL AND THERMOMECHANICAL PROPERTIES

5.3.1 Differential scanning calorimetry

The values of $T_g$ obtained from the DSC analysis for unmodified UP and OMPS (1, 3, 5 and 10 wt %) modified unsaturated polyesters are presented in Table 5.1. The $T_g$ values observed from Figure 5.4 are increased with increasing the percentage incorporation of OMPS into the UP matrices and consequent increase in crosslink density compared with that of the unmodified UP resin. The $T_g$ values for 1 wt% and 3 wt% of OMPS modified UP resins are 136 °C and 140 °C respectively which are slightly higher when compared with that of unmodified UP (i.e. 133 °C) whereas for 5 % and 10 wt% of OMPS modified UP hybrids impart higher $T_g$ values of 148 °C and 157 °C respectively.

The increase in $T_g$ values is attributed due to the high crosslinking resulted from the incorporation of octafunctional POSS units (OMPS) and the bulky structure of POSS units which retard the segmental motion of polymer chain in addition to the presence of higher amount of UP resin with rigid aromatic structure. In the cases of 5 % and 10 wt% OMPS incorporated systems, the values of $T_g$ are higher due to enhanced crosslink density arises because for high percentage incorporation of POSS, which provides more number of maleimide groups to react with the unsaturated double bonds present in UP and the styrene double bonds. The formation of intercross linked network structure is presented in Scheme 5.1. The single $T_g$ value obtained for all the samples of POSS-UP hybrids confirmed that the hybrid sample is a single chemical entity.
Figure 5.4  DSC thermograms of unmodified, 1%, 3%, 5% and 10 wt% OMPS modified unsaturated polyester nanocomposites

5.3.2 Dynamic mechanical analysis

Storage modulus of the unmodified, 1, 3, 5 and 10 wt% POSS modified UP resin are presented in Figure 5.5. The values of storage modulus of the hybrid nanocomposites were found to increase with increase in wt% of POSS into the UP resin compared with that of the unmodified system. The values of storage modulus for nanocomposite systems are 7794 MPa, 8435 MPa, 8534 MPa and 7557 MPa for the POSS content of 1, 3, 5 and 10 wt% respectively. The improvement in storage modulus is due to the presence of molecular level dispersion of POSS cubes in the polyester matrix, and also due to the perfect bonding without any aggregation of POSS into UP resin matrices.
Figure 5.6 shows the variation of damping factor (tan $\delta$) for unmodified and POSS (1, 3, 5 and 10 wt%) modified UP nanocomposite systems. The damping factor increases on addition of inorganic POSS cube. The stiffness variation between the nanocube and polymer matrix might have caused internal damping, resulting in increased damping factor for nanocomposite systems. Glass transition ($T_g$) corresponds to the peak tan $\delta$ value in dynamic mechanical analysis curve. Thus on increasing the wt% of POSS, the $T_g$ values are increased due to enhanced cross linking density of the nanocomposites because of the octafunctionalised POSS, which undergoes intercross linking to result in an highly rigid network structure and is represented in Scheme 5.1 The peak of the nanocomposites are broad when compared with that of the unmodified UP. The peak height is decreased and shifted to the higher temperature on increasing the POSS content and is due to increased cross linking density.

Further the improvement in $T_g$ suggested that POSS nanocube stiffens the polymer matrix at high temperatures. The larger surface area of the POSS cube (octa functionality) results in an efficient interaction with POSS cube through covalent bonding which inturn prevents segmental motion of the polymer chains. Hence at higher temperature, polymer chains will not experience softening behaviour due to rigid barrier phase. A similar trend was observed from the DSC thermograms of the nanocomposites.
Figure 5.5 Storage modulus of unmodified, 1%, 3%, 5% and 10 wt% OMPS modified unsaturated polyester matrices

Figure 5.6 Tan δ of unmodified, 1%, 3%, 5% and 10 wt% OMPS modified unsaturated polyester matrices
5.3.3 Thermogravimetric analysis

Thermal stability and degradation behaviour of the POSS-UP nanocomposites were analyzed using TGA (Table 5.1). Figure 5.7 depicts the thermal degradation curves of unmodified UP, 1%, 3%, 5% and 10 wt% of OMPS modified unsaturated polyester hybrid matrices. Thermal stability of hybrids increased with an increase in the wt% of OMPS into the UP resin compared with that of unmodified UP resin system. The initial degradation temperature and the temperature required for 5% weight loss for all the hybrid samples are presented in Table 5.1. The initial degradation temperature was increased with increase in the percentage incorporation of OMPS. The delay in degradation is due to the thermally stable aromatic heterocyclic nature of maleimide group and also due to the highly intercross linked network structure formed due to the nanoreinforcement of octamaleimide functionalised POSS with the unsaturated polyester resin. Thus, the nanoscale dispersion of octafunctional POSS results in highly cross linked network structure at higher POSS loading of 10 wt% into the UP matrix resin.

![Figure 5.7 Thermal behavior of unmodified, 1%, 3%, 5% and 10 wt% OMPS modified unsaturated polyester matrices](image)

Figure 5.7  Thermal behavior of unmodified, 1%, 3%, 5% and 10 wt% OMPS modified unsaturated polyester matrices
The char yields of POSS-UP hybrids at 800 °C under nitrogen are higher when compared with that of unmodified UP resin. The char yield obtained for 1, 3, 5 and 10 wt% OMPS modified UP hybrids are 8%, 10.7%, 15.2% 17.4% and 22.3% respectively. Higher values of the char yield obtained for POSS-UP is due to the presence of thermally stable silsesquioxane fraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (°C)</th>
<th>(T_d) (°C)(^a)</th>
<th>5% wt loss (°C)</th>
<th>Char Yield at 800°C (wt %)</th>
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<tbody>
<tr>
<td>UP-0 % OMPS</td>
<td>133</td>
<td>384</td>
<td>389</td>
<td>8</td>
</tr>
<tr>
<td>UP-1 % OMPS</td>
<td>136</td>
<td>386</td>
<td>393</td>
<td>10.7</td>
</tr>
<tr>
<td>UP-3 % OMPS</td>
<td>140</td>
<td>391</td>
<td>400</td>
<td>15.2</td>
</tr>
<tr>
<td>UP-5 % OMPS</td>
<td>148</td>
<td>394</td>
<td>402</td>
<td>17.4</td>
</tr>
<tr>
<td>UP-10 % OMPS</td>
<td>157</td>
<td>397</td>
<td>403</td>
<td>22.3</td>
</tr>
</tbody>
</table>

\(^a\) Decomposition temperature

5.4 MECHANICAL PROPERTIES

The improvement in mechanical properties is due to the presence of well dispersed nano POSS at molecular level with in the polymer matrix, as well as on the rigid nature of the POSS cube.

5.4.1 Tensile properties

The values of tensile strength of unsaturated polyester and UP modified OMPS with different weight percentages are presented in Figure 5.8a and Table 5.2. The introduction of 1%, 3%, 5% and 10 wt% of OMPS into UP resin increased the tensile strength by 7.2%, 12.8%, 23.1% and 31.5%
respectively when compared with that of the unmodified UP resin. The increase in the values of tensile strength is due to the higher degree of intercross linked network structure formed between the OMPS molecule and UP chains (Scheme 5.1). On increasing the weight percentage of OMPS the reactive sites increased resulted in a higher cross linked network density and rigidity of the UP nanocomposites.

The values of tensile modulus obtained for unmodified UP and UP modified with different weight percentages of OMPS were also presented in Figure 5.8b and Table 5.2. They exhibited a similar trend as in the case of tensile strength of OMPS modified UP system.

5.4.2 Flexural properties

The observed values of flexural strength of unmodified UP and different weight percentage of OMPS modified UP systems are presented in Figure 5.8c and Table 5.2. The introduction of 1%, 3%, 5% and 10 wt% of OMPS into UP resin increases the flexural strength by 4.5%, 12.8%, 22.8% and 33.4% respectively when compared with that of the unmodified UP. The enhancement in the values of flexural strength according to their nature and percentage content of OMPS into the UP nanocomposites. Due to the presence of higher number of reactive sites in the OMPS obtained from higher percentage of OMPS enhanced the crosslink density and rigidity and in turn improved the flexural properties.

A similar trend was observed for the flexural modulus of the OMPS/UP nanocomposites and the values are presented in Table 5.2 and Figure 5.8d. The enhancement is influenced by the synergistic effect of toughening and rigidity imparted by OMPS units.
Figure 5.8  Effect of OMPS content (wt %) on
   (a)  Tensile strength of UP nanocomposites
   (b)  Tensile modulus of UP nanocomposites
   (c)  Flexural strength of UP nanocomposites
   (d)  Flexural modulus of UP nanocomposites
Table 5.2  Mechanical properties of OMPS modified unsaturated polyester

<table>
<thead>
<tr>
<th>UP/OMPS</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (MPa)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural Modulus (MPa)</th>
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</thead>
<tbody>
<tr>
<td>100/0</td>
<td>32.0</td>
<td>1023.0</td>
<td>42.1</td>
<td>780.0</td>
</tr>
<tr>
<td>99/1</td>
<td>34.3</td>
<td>1150.6</td>
<td>44.2</td>
<td>821.7</td>
</tr>
<tr>
<td>97/3</td>
<td>36.1</td>
<td>1198.3</td>
<td>47.5</td>
<td>910.2</td>
</tr>
<tr>
<td>95/5</td>
<td>39.4</td>
<td>1258.1</td>
<td>51.7</td>
<td>980.4</td>
</tr>
<tr>
<td>90/10</td>
<td>42.1</td>
<td>1353.0</td>
<td>56.2</td>
<td>1037.5</td>
</tr>
</tbody>
</table>

5.5  WATER ABSORPTION BEHAVIOUR

Water absorption behaviour of unmodified and POSS modified UP nanocomposite systems are shown in Figure 5.9. The water absorption resistance behaviour of nanocomposite systems are better when compared to that of the unmodified UP system. Water absorption resistance was increased with the enhanced addition of POSS up to 5wt %, beyond 5wt% it decreased, but the value is found to be well above the limit compared to that of the unmodified UP resin. The inorganic silicone POSS cube present in the unsaturated polyester matrix act as barrier and increases the mean effective path for the water molecules to travel, and also lead to an increase in water absorption resistance.
5.6 MORPHOLOGICAL STUDIES

Morphology of the POSS-UP hybrid nanocomposites were studied by wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM) analysis. Nanoreinforcement of octamalelimide-POSS into the unsaturated polyester matrix is observed form the WAXD and SEM micrographs. Figure 5.10 presents the XRD pattern of OMPS, 3% and 10 wt% OMPS modified UP resins. For OMPS, a high-intensity peak was observed at $2\theta = 5.3^\circ$, corresponding to 1.7 nm and a peak was observed at about $2\theta = 20^\circ$. No sharp and narrow peaks were observed due to the presence of meta and para isomeric mixture of OMPS. Further, the peak at $5.3^\circ$ is absent in the case of diffraction patterns of both 3% and 10 wt% of OMPS modified UP hybrid systems. The intensity of the peak appeared at about $2\theta = 20^\circ$ in the case of hybrid OMPS indicated that the OMPS is well dispersed in unsaturated polyester network in the form of single chemical entity.
Figure 5.10 XRD patterns of OMPS, 3 wt% OMPS/UP and 10 wt% OMPS/UP cured hybrid nanocomposites

In addition to WAXD measurements, scanning electron microscopy (SEM) was used to investigate the morphology of unmodified UP resin and 3% and 10 wt% OMPS modified UP hybrid systems (Figure 5.11). The SEM micrographs of the fractured surface of the unmodified unsaturated polyester system (Figure 5.11a) indicated a smooth, glassy and homogeneous microstructure without any plastic deformation. Similarly, the fractured surfaces of the OMPS modified (1, 3 and 10 wt%) UP hybrid systems (Figures 5.11c, 5.11e and 5.11g) also indicate the homogeneous morphology without any apparent phase separation. Further, in the case of POSS incorporated systems, the fractured surface seems to be rough with fine siloxane particles, this proved the formation of strong bonding between the POSS and the unsaturated polyester resin. These data further confirmed the nanoreinforcement of POSS units into the unsaturated polyester resin in the form of covalently bonded UP-POSS hybrid nanocomposites.
Figure 5.11 SEM images of (a,b) unmodified UP, (c,d) 1 wt% OMPS/UP, (e,f) 3 wt% OMPS/UP and (g,h) 10 wt% OMPS/UP nanocomposites
Figure 5.12  Transparent sample of 3 wt% OMPS modified UP hybrid nanocomposite
Octamaleimide-POSS (OMPS) was synthesized and confirmed through spectral analysis. OMPS was used as nanocrosslinker and chemical modifier for unsaturated polyester resin through radical polymerization. OMPS was successfully incorporated into the UP resin through intercross linked network producing a transparent and homogeneous non-phase separated hybrid nanocomposites with varying (1, 3, 5 and 10 wt %) OMPS concentration in the UP resin. The intercross linked network structure was confirmed by FTIR analysis and the nanocrosslinked homogeneous morphology was confirmed by WAXD and SEM analysis. The values of $T_g$ and thermal stability of UP-POSS hybrids are increased with increasing percentage incorporation of OMPS into UP when compared with those of the unmodified UP and was explained due to the formation of higher degree of cross linking density. The char yield also increased with increase in OMPS content due to the presence of thermally stable inorganic POSS moieties. The dynamic mechanical analysis indicated the higher storage modulus on increasing the POSS content both above and below the $T_g$. The higher storage moduli obtained for 5 wt% of POSS-UP (8534 MPa) and tan $\delta$ peak for the nanocomposites are decreased and increasing the temperature due to the highly cross linked network structure. This also results an increased glass transition value for 10 wt% POSS loaded UP nanocomposites (157 °C i.e. 15% and is higher than that of unmodified UP resin matrix). Similarly nanocomposites possess less water absorption characteristics than that of the unmodified UP system to due the incorporation of hydrophobic silsesquioxane (POSS) moiety.