Chapter 5

Polypropylene/Polystyrene/clay nanocomposites: Effect of vinyltriethoxysilane modification

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Chapter 5

Part -A

Modification and characterization of kaolin nanoclay using vinyltriethoxysilane

Abstract

Functionalization of kaolin clay with vinyltriethoxysilane (VTES) was reported in this study. The intercalation was achieved using kaolin-Dimethylsulfoxide (DMSO) intercalate as a starting material. FTIR shows that VTES effectively displaced DMSO from the clay mineral interlayer. The resulting material was characterized by X-ray diffraction, thermal analysis and Infra-Red Spectroscopy. The X-ray diffractograms reveal the intercalation of DMSO, and subsequently by VTES. The thermogravimetric curves of the kaolin clay functionalized with VTES indicates that the material was thermally stable up to 515 °C.

1) Mechanical and morphological properties of Organomodified kaolin/Polypropylene/Polystyrene nanocomposites; Asha Krishnan K, Tresa Sunitha George; K.E. George; Pauline Journal of research and studies; Vol.1.No.1(2013)

5. A.1 Introduction

Polymer-clay nanocomposites are a class of hybrid materials composed of organic polymer matrix in which layered inorganic particles with nanoscale dimension is distributed. As a result of the nanometer-scale dispersion, nanocomposites exhibit markedly improved mechanical, thermal and physicochemical properties, decreased gas and water vapor permeability, resistance to flammability and thermal degradation as compared with the conventional composites [1-3]. These nanocomposites synergistically integrate the advantages of organic polymers and those of the inorganic filler.

Clays are commonly used as fillers because they are composed of layered silicates that can intercalate organic molecules. The clay consists of
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stacked aluminosilicate layers that can be separated and are held together by electrostatic forces which cannot be broken into separate layers by simple shear. Thus, organic modification of the clay is required to achieve the separation of the stacked clay layers [4]. Clay minerals interact with organic compounds by adsorption, intercalation and cation exchange. Many of the work in this area have focused on montmorillonite (MMT) clays. Montmorillonite is a valuable mineral used for industrial applications because of their high cation exchange capacities, large surfaces areas, surface reactivities, and adsorptive properties. Organic modifiers such as alkyl ammonium cations make them organophilic, which further extend their applications [5]. The aspect ratio of MMT is about 10-1000 and the surface area is in the range of 750 m²/g.

Kaolin clay which is found in hydrothermal, residual and sedimentary deposits is less studied as its cation exchange capacity (CEC) is less than 0.1meq/g. Now there is an increasing interest on organo modified nanokaolin as filler in polymer to reinforce the mechanical properties and to reduce the cost. Kaolin clay is a 1:1 dioctahedral aluminosilicate with two distinct basal layers. One of them consists of a tetrahedral siloxane surface formed by very chemically inert -Si-O-Si- bonds, while the other is constituted by an octahedral gibbsite sheet, Al(OH)₃. The neutral layered 1:1 structure can be disrupted and the broken bonds have the ability to accommodate -OH groups [6]. Because of the hydrophilic properties of kaolin and hydrophobic character of polymer, the modification of kaolin is necessary.

Kaolin nanoclay can interact with organic molecules by intercalation. The reactive guest molecules enter the interlamellar space, break up the
hydrogen bonds and form new ones resulting in a nano-layered material. The kind of guest species intercalated between the layers of kaolin is limited due to the hydrogen bonding between the octahedral side and tetrahedral side. Limited number of polar guest species such as N-methylformamide (NMF) [7], Urea [8], DMSO [9] can be directly intercalated. Intercalation of kaolin with guest species can be done by displacement reactions. The separation of kaolin results in particle size reduction and an increase of the specific surface area. A good kaolin clay modification results in better intercalation between filler and polymer matrix.

Weiss et.al classified the guest molecules as (a) Compounds that form strong hydrogen bonds with the silicate layers e.g.: urea, formamide etc. (b) Compounds form strong dipole interaction with silicate layers e.g. DMSO and (c) Alkali salts of strong fatty acids for e.g. acetic acid. Non-reactive molecules enter into the clay layers by displacing reactive guest molecules. Reactive molecules can be used as precursors for the intercalation of non-reactive organic molecules via the displacement of intercalated molecules. In addition to the formation of organo-clay nano-hybrid materials, intercalation can lead to the covalent grafting of organic molecules [10, 11]. Hence in this study guest-displacement method is used to modify the kaolin nanoclay.

5. A.2 Methodology

5. A.2.1 Modification of kaolin nanoclay

Kaolin nanoclay is characterized by two types of interlayer surfaces: a gibbsite type surface covered by aluminol groups and a siloxane surface. Adjacent layers are linked by Van der Waals and H-bonds, which induce restricted access to the interlamellar aluminol groups. The strong interaction
between the nanoclay layers prevents the insertion of most substances; a preceding expansion step is required. Kaolin can be expanded by intercalating small and highly polar molecules such as dimethylsulfoxide (DMSO). Modification of kaolin nanoclay is done in two steps. First step involves the intercalation of kaolin nanoclay by dimethylsulfoxide in order to expand the interlayer space. Second step involves the displacement of DMSO by vinyltriethoxysilane (VTES). Figure 5a.1 shows the schematic representation of the modification of kaolin nanoclay.

**Figure 5a.1 Schematic representation of the modification of kaolin nanoclay**

5. A.2.1.1 Intercalation of kaolin nanoclay by dimethylsulfoxide (DMSO) as precursor

The modification of kaolin nanoclay is done by guest displacement method. Kaolin was modified by treatment in solution with DMSO. 10 g of the clay fraction was suspended in DMSO, and the mixture was occasionally stirred at 80°C, using a magnetic stirrer for two months. After two months, the clay–DMSO complex was washed with 1,4-dioxane to remove excess DMSO. The contents were filtered using vacuum in a Buchner funnel. The filter cake was dried in an oven at 70°C. The dried clay was ground using a mortar and pestle to get a fine powder of DMSO intercalated kaolin (K-DMSO). The guest molecules enter the interlayer space and move apart the
silicate layers. Figure 5a.2 shows the intercalation of DMSO into the kaolin layers.

![Schematic representation of the intercalation of DMSO into the kaolin layers.](image)

**Figure 5a.2 Schematic representation of the intercalation of DMSO into the kaolin layers.**

**5. A.2.1.2 Modification by vinyltriethoxysilane**

The nanoclay was modified by hydrolysis followed by condensation reaction of vinyltriethoxysilane. The DMSO intercalated clay particles were sonicated (10g/100ml of methanol-water mixture) for 1 hour to get a homogeneous aqueous dispersion. The dispersion was acidified (3-5 pH) with 2N HCl and triethoxy vinyl silane (vinyltriethoxysilane in the methanol-water mixture) was added slowly. Then the mixture was stirred for 3 min at 70 °C for the hydrolysis reaction. NaOH solution (7-9 pH) was then added and the mixture was further stirred for 1 hour at 60 °C for condensation reaction. Reaction of the vinyltriethoxysilane with nanoclay is shown in the Figure 5a.3. Silanetriols are most stable at pH 3-6, but condense rapidly at pH 7-9 [12]. This was then filtered, washed with distilled water and dried to get fine particles of vinyltriethoxysilane modified kaolin nanoclay (K-VTES).
Schematic representation of the possible reactions between nanoclay and vinyltriethoxysilane is shown in the Figure 5a.4.

**Figure 5a.3 Reaction process of vinyltriethoxysilane with nanoclay**
Figure 5a.4 Schematic representation of the possible reactions between the nanoclay and the vinyltriethoxysilane

5. A.2.2 Characterization

The modified kaolin nanoclay was characterized by using various techniques such as SEM, XRD, FTIR and TGA. Surface area, bulk density and particle size of the vinyltriethoxysilane modified kaolin clay was determined using the procedure given below.

(a) BET studies

Surface area of vinyltriethoxysilane modified kaolin clay was measured using BET method. Measurements were carried out under nitrogen atmosphere using Autosorb iQ Station 1, surface area and porosity analyser, Surface area was determined using the equation,

\[ S_{BET} = 4.353 \ V_m \]

Where \( S_{BET} \) is the surface area in m\(^2\)/g and \( V_m \) is the molar volume of adsorbate gas (N\(_2\)) at STP.
(b) **Bulk density**

The bulk density of the material was determined as per ASTM D 1895-96. Bulk density is defined as the weight per unit volume of a material. It is primarily used for powders or pellets. The test can provide a gross measure of particle size and dispersion, which can affect material flow consistency.

**Procedure**

The small end of the funnel is closed with hand or a suitable flat strip and 115± 5 cm³ of samples are poured into the funnel. Open the bottom of the funnel quickly and allow material to flow freely into the cup. If caking occurs in the funnel, the material may be loosened with a glass rod. After the material has passed through the funnel immediately scrape of the excess on the top of the cup with a straight edge without shaking the cup. Weigh the material nearest to 0.1 g and determine the bulk density.

(c) **Particle size analysis**

Particle size analysis of the vinyltriethoxysilane modified kaolin clay was carried out in a particle size analyzer (Nanotrac equipment from Microtrac). The sample was sonicated prior to analysis.

**5.A.3 Results and Discussion**

**5.A.3.1 Fourier transform infrared spectroscopy**

The infrared absorption spectra of unmodified kaolin clay, DMSO modified kaolin nanoclay (KDMSO) and vinyltriethoxysilane modified kaolin
Figure 5a.5 FTIR spectrum of (a) Unmodified kaolin nanoclay (b) KDMSO (c) Vinyltriethoxysilane modified kaolin nanoclay (K-VTES)
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(K-VTES) are given in the Figure 5a.5. Kaolin nanoclay (Figure 5a.5 (a)) consists of three kinds of hydroxyl groups that is, inner-surface hydroxyl, inner hydroxyl, and absorbed water hydroxyl. Bands observed at 3691 and 3620 cm\(^{-1}\) are attributed to the phase vibration of the inner-surface hydroxyl and inner hydroxyl respectively, and the band at 3652 cm\(^{-1}\) is the characteristic vibration band of absorbed water [13]. The bands at 1134, 1034 and 910 cm\(^{-1}\) are attributed to the Si-O stretching vibrations [14]. The bands at 791, 750, and 667 cm\(^{-1}\) are due to the O-Al-OH stretching vibrations [15].

Kaolin nanoclay is modified by guest displacement method in which new guest species can be intercalated by displacing previously intercalated species. After the intercalation of kaolin with DMSO (Figure 5a.5 (b)), the additional bands at 3539 and 3501 cm\(^{-1}\) are observed, which are attributed to intercalation of DMSO molecules through hydrogen bonding with the interlamellar hydroxyls of the nanoclay (Si=O-OH). The vibrational band of kaolin clay at 3620 cm\(^{-1}\) has not been affected but the bands at 3691 cm\(^{-1}\) is shifted to 3695 cm\(^{-1}\) after the intercalation of DMSO. New bands appear at 2935 and 3022 cm\(^{-1}\) are assigned to the vibrations of the DMSO C–H groups. The band of 3662 cm\(^{-1}\) is attributed to the hydroxyl stretching vibration of inner-surface hydroxyl groups that are hydrogen bonded to the –S=O group of DMSO. The band at 910 cm\(^{-1}\) are due to the Si-O stretching vibrations and the O-Al-OH stretching vibrations at 667 cm\(^{-1}\) is shifted to 688 cm\(^{-1}\)[16,17].

Figure 5a.5(c) shows two peaks at 2857 and 2928 cm\(^{-1}\) which are due to the vibrations of C–H bonds introduced by the organic modifier. Peaks at
2928 cm$^{-1}$, due to CH$_3$ asymmetric stretching, and at 2857 cm$^{-1}$, due to CH$_3$ and CH$_2$ asymmetric stretching confirm the presence of silane in modified kaolin clay. In the region of 3700–3200 cm$^{-1}$, a number of sharp peaks at 3695, and 3620 cm$^{-1}$ are observed due to O–H stretching vibration of silanol groups. The predominant peak at 1015-1080 cm$^{-1}$ is due to the siloxane bonds (Si-O-Si). The peak observed at 915 cm$^{-1}$ is accredited to the Al-OH stretching vibrations. The peak observed at 1662 cm$^{-1}$ is ascribed to the C=C stretching vibrations. The absorption band observed at 1405 cm$^{-1}$ is due to the C – CH$_3$ symmetric bending vibration [18, 19].

5. A.3.2 X-ray Diffraction

The schematic representation of the functionalization of kaolin clay is shown in the Figure 5a.6. The XRD patterns of unmodified clay, DMSO modified kaolin clay (K-DMSO), vinyltriethoxysilane modified kaolin nanoclay (K-VTES) are depicted in the Figure 5a.7. The characterization peak for unmodified clay exhibit a $d_{001}$ reflection at $2\theta = 12.44^\circ$ having a basal spacing of 7.11 Å. After the intercalation of kaolinite with DMSO, the original peak of kaolin at $2\theta = 12.44^\circ$ is shifted to 7.961. The basal spacing of KDMSO expands from 7.11 Å to 11.07 Å. Thereafter intense intercalation of VTES is confirmed by the typical increase of $d$ spacing from 11.07 Å to 15.60 Å with a corresponding decrease in $2\theta$ value to 5.66. VTES displaced the guest molecule (DMSO), as shown by XRD patterns (Figure 5a.7) [16].
Crystallite thickness of the vinyltriethoxysilane modified kaolin clay can be calculated by using the Scherrer equation [20]:

\[ t = \frac{(K \times \lambda)}{B \cos \theta} \] ....................................................... (5a.1)

where  
- \( t \) = crystallite thickness
- \( K \) = a constant (0.91 for clay)
- \( \lambda \) = X-ray wavelength
- \( B \) = Full width half max (FWHM) of the diffraction peak

**Figure 5a.6 Schematic representation of the functionalization of kaolin nano clay**
\[ \theta = \text{diffraction angle} \]

The crystallite size found using the equation 5a.1 is 15.26 nm.

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5. A.3.3 Scanning electron microscopy

Figures 5a.8 (a) & 5a.8 (b) illustrate the surface morphology of commercial vinyl silane modified nanoclay and vinyltriethoxysilane modified kaolin nanoclay. Commercial kaolin SEM photograph reveal the platelet hexagonal structure of the kaolinite crystals. The vinyltriethoxysilane modified kaolin shows individual plates. The vinyltriethoxysilane modified kaolin exhibits a compact platelet morphology with delaminated layers which shows the presence of organic modification in kaolin nanoclay.
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Figure 5a.8 SEM images of (a) Commercial vinyl silane modified nanoclay (b) Vinyltriethoxysilane modified nanoclay

5A.3.4 BET surface area

The surface area obtained for different samples by BET adsorption method are given in Table 5a.1. Vinyltriethoxysilane modified nanoclay has higher surface area than that of commercial vinyl silane modified nanoclay.

Table 5a.1 Surface area of kaolin nanoclay samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area(m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial vinyl silane modified nanoclay</td>
<td>30.00</td>
</tr>
<tr>
<td>Vinyltriethoxysilane modified nanoclay</td>
<td>46.29</td>
</tr>
</tbody>
</table>

The surface area of the nanoclay particles is found to be higher as particle size decreases. The above table shows that vinyltriethoxysilane modified kaolin nanoclay has lower particle size than the commercial nanoclay. This confirms that the presence of vinyl silane group on the surface of nanoclay particles which decreases the adsorption of nitrogen. This indicates that nanoclay surface is effectively modified by vinyltriethoxysilane.

5A.3.5 Bulk density

The bulk density values of vinyltriethoxysilane modified nanoclay are compared with commercial vinyl silane modified nanoclay (Table 5a.2).
Bulk density of vinyltriethoxysilane modified nanoclay is found to be higher than the commercial vinyl silane modified nanoclay. This is due to the smaller particle size of vinyltriethoxysilane modified kaolin nanoclay compared to that of the other.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bulk density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial vinyl silane modified nanoclay</td>
<td>0.2</td>
</tr>
<tr>
<td>Vinyltriethoxysilane modified nanoclay</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 5. A.3.6 Particle size analysis

For both commercial vinyl silane modified nanoclay (Figure 5a.9 (a)) and vinyltriethoxysilane modified nanoclay (Figure 5a.9 (b)) the finest fraction lies < 0.5 μm in size. Particle size analysis data shows that volume weighted mean D of the commercial vinyl silane nanoclay is 283 nm and for vinyltriethoxysilane modified kaolin nanoclay is 253 nm.

![Figure 5a.9 Particle Size Distribution of (a) Commercial vinyl silane modified nanoclay (b) Vinyltriethoxysilane modified nanoclay](image)
5.A.3.7 Thermogravimetric analysis

The thermal decomposition of unmodified clay, KDMSO and K-VTES in nitrogen atmosphere is shown in the Figure 5a.10. Figures 5a.10 (a) & 5a.10 (b) depict the TG and DTG curves for unmodified clay, KDMSO, K- VTES. Thermogravimetry can be used as a proof of interactions between organic medium and inorganic nano platelet’s surface. The unmodified clay shows a maximum degradation temperature at 507.9°C. It corresponds to dehydroxylation of kaolinite and the formation of metakaolinite. The kaolin intercalated with DMSO (KDMSO) exhibits two mass losses in the TG curve, accompanied with two endotherms centered at about 154.3°C and 510.4°C. The former is attributed to the loss of the organic moiety, and the latter is due to the usual dehydroxylation step of kaolinite [13]. The vinyltriethoxysilane modified kaolin (K-VTES) depicts a degradation peak at 515.3°C. Maximum degradation peak increased from 507.9°C to 515.3°C. This shows that thermal stability of kaolin nanoclay is increased by the addition of vinyltriethoxysilane.
5A.4 Conclusions

The basal spacing of kaolin is expanded with the intercalation of DMSO into the interlayer sheets of kaolin. KDMSO is successfully displaced with vinyltriethoxysilane in the interlayer spaces of kaolin. XRD shows an increase in d-spacing of kaolin nanoclay from 7.11 Å to 15.60 Å after the addition of vinyltriethoxysilane. Further the evidence for the delamination of kaolin nanoclay by DMSO with subsequent substitution of vinyltriethoxysilane is also displayed in FTIR spectra. Thermal analysis shows that the modified nanoclay is thermally stable up to 515°C. The bulk density and surface area of vinyltriethoxysilane modified kaolin nanoclay is higher than that of commercially available vinyl silane nanoclay and this confirms the presence of modifying group on the surface of kaolin nanoclay.

References


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Part -B

Polypropylene/Polystyrene/Vinyltriethoxysilane modified clay nanocomposites

Abstract

Polypropylene (PP)/Polystyrene (PS)/clay nanocomposites were prepared by melt mixing in a Thermo Haake Rheochord mixer. The effect of vinyltriethoxysilane modified nanoclay on the properties of PP/PS (80/20) blend was studied. The major objective was to examine the static and dynamic mechanical properties of the nanocomposites. The clay mineral layer exfoliation in nanocomposites was monitored by XRD and SEM. Evaluation of thermal degradation kinetics of nanocomposites by three kinetic methods namely Coats Redfern, Broido’s and Horowitz Metzger was also a focus of the present study. XRD results reveal the exfoliation of both PP and PS in nanoclay galleries. TGA results show an improved thermal stability for nanocomposites than the pure blend.

5. B.1 Introduction

Polymer blend/clay nanocomposites represent a new class of hybrid materials that emerged as a subject of enormous scientific interest. This is because the compounding leads to a new kind of high performance material, combining the advantages of polymer blends and polymer nanocomposites. A great deal of work has been focused on studying the modifying effect of nanoclay in the immiscible polymer blends [1]. The use of nanoclay for enhancement of properties is possible only if agglomeration between the particles is reduced and good interfacial bonding between particle surfaces and polymer matrix is ensured. Much of the work in this area is focused on montmorillonite [2,3]. So kaolin nanoclay with a chemical composition Al₂Si₂O₅(OH)₄ and 1:1 type layered structure is proposed to be used in this study.
Individual layers of kaolin nanoclay consist of both tetrahedral sheets and octahedral in which one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina. The hydrophilic character of the kaolin nanoclay makes it ineffective for absorption of aliphatic and relatively hydrophobic substances [4]. Modification of nanoclay minerals with organic intercalates changes the hydrophilic nature of nanoclay mineral to hydrophobic and increases the interlayer distance [5]. They ensure better dispersion in the organic polymer matrix by virtue of expanded interlayer space.

The kind of guest species intercalated between the layers of kaolin is limited due to the hydrogen bonding between the octahedral side and tetrahedral side. Limited number of polar guest species such as N-methylformamide (NMF) [6], Urea [7], Dimethylsulfoxide (DMSO) [8] can be directly intercalated. Intercalation of kaolinite with guest species can be done by displacement mechanisms. Yasemin Turhan et al. studied the effect of modified kaolin clay in Poly (vinyl chloride). In their study kaolin clay was modified using succunimide by replacing DMSO. They found that the incorporation of nanoparticles in polymer results in an increase in thermal stability and UV transparency [9]. Rugmini Sukumar et al. modified the kaolin clay with sodium salt of rubber seed oil (SRSO) and studied the effect of modified kaolin clay in natural rubber. They observed that the mechanical properties is increased, indicating the probable role of SRSO-modified kaolin as a nanofiller in NR [10].

Organo functional alkoxysilanes like aminoalkoxysilane [11], methacrylatealkoxysilane [12] are employed for the functionalization
of kaolin clay. Ignas K. Tonlé et al. have reported the grafting of 3-aminopropyltriethoxysilane (APTES) onto the kaolin clay [13].

Organosilane compounds contain two kinds of reactive groups (inorganic and organic) in a single molecule. A chemical reaction between the functional groups (such as -OH) of filler and the alkoxy groups of silane is expected to occur, creating a silane-functionalized surface [14]. The chemical reactions between the functional groups of the silane-modified clay and the polymer matrix enhance the interaction between the components of the polymer/clay nanocomposites.

In this study, vinyltriethoxysilane has been used as a modifier of kaolin nanoclay which replaces a DMSO intermediate. The effect of modified filler on the mechanical, thermal and morphological properties of PP/PS blend is proposed to be studied.

5. B.2 Methodology
5. B.2.1 Materials

The details of the polymers used for the study are discussed in Chapter 2 (sections 2.1.1 & 2.1.2).

5. B.2.2 Nanocomposite preparation

PP/PS (80/20) and vinyltriethoxysilane modified kaolin nanoclay (K-VTES) in varying amounts (1-5 wt %) were prepared by melt mixing using an internal mixer (Haake Rheomix 600) at 180 °C with a rotor speed of 50 rpm, and a mixing time of 8 min for each sample. After mixing the melt is pressed in a hydraulic press, cut into pieces and injection moulded in DSM Micro 10cc Injection Molding Machine, with a barrel temperature of
The tensile properties, flexural properties, impact strength, hardness, dynamic mechanical properties, thermal properties and morphology of the nanocomposites were analyzed according to various standards as described in Chapter 2 (section 2.2.3). The details of the UV aging studies are described in Chapter 3 (section 3.2.2.2).

5. B.3 Results and Discussion
5. B.3.1 X-ray diffraction

The XRD patterns of vinyltriethoxysilane modified kaolin nanoclay (K-VTES) and PP/PS/modified clay nanocomposite (3wt %) is given in the Figure 5b.1

![XRD patterns of K-VTES and PP/PS/3wt% K-VTES modified nanocomposite](image)

Figure 5b.1 XRD patterns of (a) K-VTES (b) PP/PS/3wt% K-VTES modified nanocomposite

The characterization peak for K-VTES appears at 15.69 Å with a 2θ value of 5.66°. Reduced peak intensity at (001) plane of nanocomposite is attributed to the reduced number of layers in clay stacks. The shear of
mixing process is capable of opening the basal plane of nanoclay in order to intercalate polymer chains into the nanoclay layers. This observation suggests a better dispersion and lower tactoid for the modified kaolin nanoclay in polymer matrix.

5. B.3.2 Scanning electron microscopy

The morphology of tensile fracture surface of PP/PS blend and PP/PS/modified clay nanocomposites (1, 3 and 5 wt % nanoclay) is given in Figure 5b.2. PP/PS blend (Figure 5b.2 (a)) exhibits a morphology in which spherical domains of PS phase are surrounded by the continuous PP phase. When PP is mixed with PS, the polymer blend is characterized by phase separation due to the high immiscibility. Addition of 1 wt % of K-VTES (Figure 5b.2(b)) improves the adhesion between two components giving a more homogeneous structure at some regions indicating good but not complete intercalation of the modified nanoclay. After the addition of 3wt % vinyltriethoxysilane modified kaolin nanoclay (K-VTES) (Figure 5b.2 (c)) the adhesion between the two components is improved to form a homogeneous morphology throughout with a better degree of intercalation. This is also evidenced by mechanical properties (section 5.B.3.6) and the XRD measurements (section 5.B.3.1). Figure 5b.2 (d) depicts the surface morphology of PP/PS blend with 5wt% vinyltriethoxysilane modified kaolin nanoclay. The composite shows a weak interface between the dispersed phase (PS) and the continuous phase (PP) resulting in inferior properties. At higher clay content, melt viscosity is high which can hinder the complete dispersion of nanoclays during melt mixing resulting in improper distribution of nanoclays in the interface.
5. B.3.3 Thermogravimetric analysis

The thermal stability of the nanocomposites in nitrogen atmosphere has been investigated using TGA. Table 5b.1 gives the results from the DTG curves of PP/PS/modified clay nanocomposites. Figure 5b.3 shows the TG and DTG curves for PP/PS pure blend and PP/PS clay nanocomposite with 1, 3 & 5 wt% of vinyltriethoxysilane modified nanoclay.
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Table 5b.1 Thermal characteristics of PP/PS/clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>50% mass loss (°C)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;onset&lt;/sub&gt; (°C)</th>
<th>Residue 600°C (%)</th>
<th>Oxidation Index (OI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS blend</td>
<td>426.6</td>
<td>434.4</td>
<td>370.5</td>
<td>0.46</td>
<td>0.032</td>
</tr>
<tr>
<td>Blend+1wt% modified clay</td>
<td>443.0</td>
<td>441.5</td>
<td>371.6</td>
<td>0.75</td>
<td>0.052</td>
</tr>
<tr>
<td>Blend+3wt% modified clay</td>
<td>443.6</td>
<td>460.2</td>
<td>373.9</td>
<td>1.02</td>
<td>0.071</td>
</tr>
<tr>
<td>Blend+5wt% modified clay</td>
<td>454.9</td>
<td>462.1</td>
<td>399.5</td>
<td>2.92</td>
<td>0.203</td>
</tr>
</tbody>
</table>

Figure 5b.3 TG curves of PP/PS pure blend, 1, 3 & 5 wt. % modified clay nanocomposites. The inset shows their respective DTG curves

Pure blend shows a maximum degradation temperature (T<sub>max</sub>) of 434.4°C. The addition of 1, 3 & 5 wt % of vinyltriethoxysilane modified nanoclay has shifted this temperature to 441.5, 460.2 & 462.1°C respectively. Nanoclay when incorporated into the polymer matrix is found to improve the thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during combustion. It results in the formation of highly charred carbonaceous silicate cumulating on the surface of
nanocomposite [15]. The OI values show increment with increase in the clay content and it indicates that the PP/PS/clay nanocomposites are more thermally stable than PP/PS blend.

5. B.3.3.1 Kinetic analysis of thermal decomposition

Kinetic parameters for the thermal degradation of PP/PS blend and PP/PS/clay nanocomposites were evaluated from the TGA curves using Horowitz-Metzger (HM) method, Broido’s method (BR) and Coats Redfern (CR) methods.

Table 5b.2 Activation energy (J/mol) calculated by Horowitz-Metzger, Broido’s and Coats-Redfern methods of PP/PS/clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Coats – Redfern</th>
<th>Broido’s</th>
<th>Horowitz-Metzger</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS blend</td>
<td>174</td>
<td>181</td>
<td>175</td>
</tr>
<tr>
<td>Blend+1wt% modified clay</td>
<td>177</td>
<td>185</td>
<td>180</td>
</tr>
<tr>
<td>Blend+3wt% modified clay</td>
<td>180</td>
<td>189</td>
<td>191</td>
</tr>
<tr>
<td>Blend+5wt% modified clay</td>
<td>185</td>
<td>192</td>
<td>198</td>
</tr>
</tbody>
</table>

The plots of ln [-ln (1-\(\alpha\))] verses \(\theta\) (HM), log [-log (1-\(\alpha\))/T^2] verses 1/T (CR) and log [-log (1-\(\alpha\))] verses 1/T (BR) for vinyltriethoxysilane modified clay nanocomposites are exhibited in the Figure 5b.4 a-c. The activation energy for each method is given in Table 5b.2. PP/PS/clay nanocomposites show higher \(E_a\) than PP/PS blend. Thus, the addition of clay nanoparticles slows down the release rate of the decomposed byproducts and hence enhances the thermal stability of the nanocomposites [16].
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Figure 5b.4 Kinetic plots for the determination of activation energy of PP/PS blend and nanocomposites (1, 3 & 5 wt %) using (a) Coats-Redfern equation (b) Broido’s method and (c) Horowitz-Metzger equation

Lower activation energy of pure blend is due to the presence of different kinds of polymer di-radicals produced during the bond scission and unzipping processes occurring at degradation stage. In the nanocomposites the clay platelets restrain the radicals produced and prevent the decomposition reaction [17].

5. B.3.4 Dynamic mechanical analysis

Figures 5b.5 & 5b.6 depict the temperature dependence of storage modulus and tanδ for pure PP/PS blend and PP/PS/clay nanocomposites (1,
3 & 5 wt %). Table 5b.3 gives the $T_g$ values obtained for the pure PP/PS blend and the modified nanocomposites from the tan $\delta$ curves. PP/PS/clay nanocomposites show higher storage modulus than pure blend. This observation clearly indicates the effect of intercalation of the polymer in nanoclay layers, leading to dispersion of nanoclay platelets in the polymer matrix [18]. After the addition of 5 wt % of nanoclay particles there is a slight decrease in storage modulus and this may be due to the agglomeration of nanoclay particles at higher loading.

Table 5b.3 Storage moduli and $T_g$ values of PP/PS blend and PP/PS/nanoclay composites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage modulus</th>
<th>$T_g$ (C) from tan $\delta$ curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45 C</td>
<td>80 C</td>
</tr>
<tr>
<td>PP/PS blend</td>
<td>1007</td>
<td>525.3</td>
</tr>
<tr>
<td>PP/PS/1% modified clay</td>
<td>1144</td>
<td>618.7</td>
</tr>
<tr>
<td>PP/PS/3% modified clay</td>
<td>1196</td>
<td>661.8</td>
</tr>
<tr>
<td>PP/PS/5% modified clay</td>
<td>1055</td>
<td>583.7</td>
</tr>
</tbody>
</table>

Figure 5b.5 Storage modulus curves of PP/PS blend and PP/PS/clay nanocomposites
The tan δ curves represent the ratio of dissipated energy to stored energy and relates to the T_g of the polymer. Tan δ is useful in determining the occurrence of molecular mobility transitions such as T_g. The Figure 5b.6 clearly illustrates that there is a slight decrease in T_g with the addition of nanoclay. This reduction is attributed to the plasticizing action of the surfactant of organically modified clay which is responsible for the improved mobility of polymer chains [15].

![Figure 5b.6 Tan δ curves of PP/PS blend and PP/PS/clay nanocomposites](image)

The relative storage moduli of PP/PS/vinyltriethoxysilane modified kaolin clay nanocomposites to those of PP/PS blend (E’_{PP/PS/clay}/E’_{PP/PS}) are plotted in Figure 5b.7. The relative storage moduli of PP/PS/clay nanocomposites are higher than those of PP/PS blend at all temperature range. Nanocomposite with 3 wt % nanoclay shows the highest relative storage modulus and it increases with temperature. There are “hump like curves” at higher loadings and these may be attributed to the hindrance of
polymer chain movement due to the presence of clay nanoparticles [19, 20]. These “hump like curves” show the resistance to the applied stress as a result of development of polymer-nanoclay network. This network resistance increases with the nanoclay loadings and the size of the “hump” also increases.

![Graph showing relative storage modulus curves of PP/PS blend and PP/PS/clay nanocomposites.](image)

**Figure 5b.7** Relative Storage modulus curves of PP/PS blend and PP/PS/clay nanocomposites

5. B.3.5 Differential scanning calorimetry

DSC measures the amount of heat energy absorbed or released when the material is heated, cooled or maintained at a constant temperature. Figure 5b.8 illustrates the melting and cooling curves for PP/PS blend and blend containing 1, 3 & 5 wt % of modified nanoclay. The crystallization temperature (T$_c$), the apparent melting temperature(T$_m$) and the corresponding enthalpies are shown in the Table 5b.4. The T$_m$ and T$_c$ values for
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nanocomposites are shifted towards the higher temperature range. The $\Delta H$ values are also increased as compared to the pure polymer matrix (Table 5b.4). The significant change in $T_c$ is due to the effective nucleating action of clay nanoparticles [1, 21].

$T_m$ and $\Delta H_m$ follow the same trend as $T_c$ and $\Delta H_c$. Figure 5b.8 also shows that there is a slight increase in melting temperature ($T_m$) with increase in filler loading. This increase in $T_m$ values signifies that the crystal structure in nanocomposites is more perfect than in polymer matrix [22]. The results show that $\Delta H_m$ values of the nanocomposites are significantly greater than that of the neat polymer matrix. This indicates a higher thermal stability for the nanocomposites [23].

![Figure 5b.8 DSC curves for melting and crystallization curves of PP/PS/clay nanocomposites](image)

Figure 5b.8 DSC curves for melting and crystallization curves of PP/PS/clay nanocomposites
Table 5b.4 DSC parameters of PP/PS/clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_c ) (C)</th>
<th>( \Delta H_c ) (J/g)</th>
<th>( T_m ) (C)</th>
<th>( \Delta H_m ) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS blend</td>
<td>111.9</td>
<td>61.1</td>
<td>158.4</td>
<td>32.4</td>
</tr>
<tr>
<td>PP/PS/1% modified clay</td>
<td>114.0</td>
<td>71.5</td>
<td>159.9</td>
<td>38.7</td>
</tr>
<tr>
<td>PP/PS/3% modified clay</td>
<td>114.9</td>
<td>76.9</td>
<td>160.7</td>
<td>40.1</td>
</tr>
<tr>
<td>PP/PS/5% modified clay</td>
<td>119.3</td>
<td>77.0</td>
<td>160.9</td>
<td>41.0</td>
</tr>
</tbody>
</table>

5. B.3.6 Mechanical properties

(a) Tensile properties

The tensile strength and tensile modulus as a function of clay loadings are plotted in the Figure 5b.9. The tensile properties increases initially, reach a maximum and then fall at higher nanoclay loadings. After the addition of clay particles, the interfacial tension is lowered and results in the enhancement of interfacial adhesion of the compatibilized blends giving more efficient stress transfer between the phases during fracture [1].

![Figure 5b.9 Variation of tensile properties with nanoclay loadings](image-url)
The resistance exerted by nanoclay layers against plastic deformation of the polymer and the stretching resistance of polymer chains with an extended conformation in the nanoclay gallery also contributes to the enhancement of modulus in clay nanocomposites [24].

(b) **Flexural properties**

Effect of organoclay loadings on flexural properties of nanocomposites is presented in Figure 5b.10. The change of flexural strength of the samples with respect to organoclay content shows resemblance to tensile strength change. The increase in flexural strength and modulus indicates that the nanocomposites have become more rigid and less flexible.

![Figure 5b.10 Variation of flexural properties with nanoclay loadings](image)

(c) **Impact strength**

Figure 5b.11 depicts the change in impact strength with nanoclay loading. The maximum impact strength is found to be at 3 wt% of modified
nanoclay. The improvement is attributed to the increase in toughness of the composite with increasing nanoclay content.

**Figure 5b.11 Variation of impact strength with nanoclay loadings**

The increase in impact strength of the nanocomposites is due to the interdiffusion of polymer matrix through the interlayer galleries of the modified kaolin nanoclay.

**d) Hardness**

The effect of nanoclay loadings on hardness is shown in Figure 5b.12. An improvement of 33% in the hardness has been achieved by adding 3 wt % clay loading. The uniformly distributed clay layers improved the stiffness of nanocomposites. The presence of nanoclay platelets restricts the indentation and improves the hardness [25, 26].
Figure 5b.12 Variation of hardness with nanoclay loading

The decrease in mechanical properties at higher loadings is due to the agglomeration of nanoclay particles within the polymer matrix.

5. B.3.7 Effect of UV aging on the tensile properties of PP/PS/clay nanocomposite

Figure 5b.13 displays the effect of UV aging on tensile properties of PP/PS/clay nanocomposites. Figures 5b.13 (a) & 5b.13 (b) shows the variation of tensile strength and tensile modulus with nanoclay loading before and after UV aging. From the figure it is observed that the tensile properties decrease after aging.

The polymer blend degradation study is very complex in view of the variety of interactions between the blend components. Walter et al. reported that in PP/PS blend, PS domain acted like a UV radiation trap. Photo degradation of PS is accelerated by acetophenone (formed as a product of
primary photodegradation step) and it interacts with the PP domains and form more reactive tertiary carbon radicals.

Figure 5b.13 Effect of UV aging on the (a) tensile strength (b) tensile modulus of PP/PS/clay nanocomposites
In PP/PS/clay nanocomposites, the nanoclay particles accelerate the photodegradation of PP/PS blend. Generally, nano particles had greater acceleration effect than micro particles due to its smaller size and greater interface area [27]. Several studies have been reported about the catalytic activities of nanoclays [28-30].

5. B.3.8 Melt Flow Index

The variation of MFI with nanoclay loading is given in Figure 5b.14. It is clear from the figure that MFI values decrease with increasing nanoclay content. Low melt flow index indicates higher melt viscosity. The influence of nanoclay particles on MFI values can be envisaged by taking into consideration of two aspects and they are (i) the nanoclay particles act as fillers causing an increase in viscosity (ii) the dispersed nanoclay particles further prevent the flow of the polymer chains.
5. B.4 Conclusions

The study shows that vinyltriethoxysilane modified kaolin nanoclay can act as a modifier for PP/PS blend. XRD patterns reveal a partial nanoclay exfoliation in PP/PS blend. Crystallinity and thermal stability of PP/PS blend increases by the incorporation of vinyltriethoxysilane modified kaolin nanoclay. Three kinetic methods namely Horowitz-Metzger, Broido’s and Coats-Redfern are used to study the thermal degradation kinetics of PP/PS/clay nanocomposites. The studies show that activation energies increase with the addition of organo clays confirming higher thermal stability. The dynamic mechanical analysis reveals higher storage moduli for the modified clay nanocomposites over the entire temperature range (40-125°C). Mechanical properties are found to be maximum at loading of 3 wt% modified kaolin nanoclay.

References


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Chapter 5


