Chapter 3
Polypropylene/Polystyrene/clay nanocomposites: Effect of different modifications of kaolin clay

Abstract
Nanoclay composites based on polypropylene (PP)/polystyrene (PS) blends were prepared by melt mixing in a Thermo Haake Rheocord mixer. The effect of modified clays on the properties of nanocomposites has been studied. The degree of dispersion and morphology of nanocomposites were evaluated from X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning electron microscopy (SEM). Nanocomposites prepared from modified clays show improved tensile strength and modulus as compared to those prepared from unmodified clay. Vinyl silane and dialkyl silane modified nanocomposites show considerable improvement in mechanical properties. Thermogravimetric analysis (TGA) shows improved thermal stability of PP/PS/clay nanocomposites. The dynamic mechanical analysis reveals higher storage moduli over a temperature range of 40–125°C for nanocomposites and the extent of increase in the storage modulus is dependent on the type of clay. Transmission electron microscopic (TEM) observations show that vinyl silane modified nanoclay layers are intercalated on the polymer matrix and are located at the interface between the two polymers and dialkyl silane modified nanoclay layers are partially exfoliated on the polymer matrix and were located at the interface and also on the PP phase.

3.1 Introduction

Nanotechnology promises revolutionary technological changes for a wide range of applications in traditional industry and advanced materials. Nanostructured materials have the potential to significantly impact on the growth at every level of the world economy in the 21st century. 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, gas and water vapor impermeability, 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.

Polypropylene (PP) and Polystyrene (PS) are two of the most widely used commercial polymers and hence the hybridization of PP/PS blends with nanostructured fillers may be useful in generating a variety of useful materials [3]. PP and PS used in this study are immiscible, which leads to the formation of multiphase system with different morphology that depends on the composition of the blend, viscosity ratio of the components, interfacial tension between the two phases and processing condition of the blends. Especially PP/PS blends exhibit low impact strength, low wear resistance and high friction [4]. Several problems of these blends may be caused by poor compatibility of the components. These features can be improved by using compatibilizers. As PP and PS are immiscible, a considerable amount of work on compatibilizing PP and PS has been done.
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by using compatibilizers such as Styrene Butadiene block copolymer (SBS), Styrene Ethylene Butylene styrene copolymer (SEBS), Styrene-Ethylene/Propylene Diblock Copolymer (SEP) and PP-g-PS [5]. Sani Amril Sasudin et al. studied the effect of SEBS on the impact strength and flexural modulus of PS/PP blends and they found that the addition of SEBS increased the impact strength of the blends but reduced the flexural strength and flexural modulus [6]. Chang–jiang You et al. studied the effect of Styrene-Ethylene/Propylene Diblock Copolymer (SEP) on the compatibilization of PP/PS blend. The results showed that SEP diblock copolymer could act as compatibilizer in PP/PS immiscible blends which increased the mechanical properties [5]. Studies on the reactive compatibilization of PP/PS blend have been reported because of the lack of functional groups in both PP and PS. Dicumyl peroxide (DCP) was employed by Xie and Zheng in order to generate in-situ PP-g-PS graft copolymer in one step extrusion process and the dispersed particle size was greatly reduced [7].

In recent years, the possible application of relatively cheap organoclays as modifiers is getting significant attention. Organoclays are being widely used as an attractive alternative to conventional fillers. The first demonstration of polymer clay nanocomposites was reported by Kojima and co-workers [8, 9]. Since the early 1990 polymer blends have been used as the matrices of polymer nanocomposites. Much of the work in this area has focused on montmorillonite. Yun Zhu et al. found out that MMT clay can plays a significant role in reducing the dispersed domain sizes in PP/PS blend. The results showed that the organoclay platelets tend to form knife like structure in the PS domain under the shear stress of the continuous PP phase during compounding [10]. Kyunyl Kim et al. successfully prepared PP/PS clay
nanocomposites by continuous compounding with high intensity ultrasonic waves during extrusion process which enhanced the interfacial interaction between the immiscible polymer blend [11]. Suprakas Sinha Ray et al. studied the role of Cloisite 20 A (C20A) as an interfacial modifier in PS/PP or PS/PP-g-MA blends. The results clearly indicated that C20A simultaneously acts as nanofiller and modifier [12].

Hence, in this study kaolin nanoclay with a 1:1 type layered structure with chemical composition Al₂Si₂O₅(OH)₄ is proposed to be used. It is a layered silicate mineral with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. The layers are held together via hydrogen bonds, dipolar interactions and Van der Waals forces, which result in a low intrinsic inner surface reactivity. Because of the hydrophilic character of kaolin and hydrophobic properties of polymer the modification of kaolin is necessary [13, 14]. Modification was done by coupling of organosilane compounds, with 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 [15]. The silane grafting of clay has received much attention in recent years, both in the industry and academy. Silane modified kaolin nanoclay has many applications; it is used in paper, paint, rubber, plastics, and ceramic industries.

A comparative study of Nanocaliber 100 (unmodified kaolin nanoclay) along with four types of commercially available modified nanoclays viz. Nanocaliber 100 V (vinyl silane modified kaolin nanoclay) Nanocaliber 100 A (amino silane modified kaolin nanoclay), Nanocaliber 100 M (mercapto
silane modified kaolin nanoclay) and Nanocaliber 100 Z (dialkyl silane modified kaolin nanoclay), on the static and dynamic mechanical properties of Polypropylene/Polystyrene blends has proposed to be investigated. The morphological and thermal properties of PP/PS blend have also been explored.

3.2 Methodology

3.2.1 Materials

The details of the polymers and nanoclay types used for the study are discussed in Chapter 2 (sections 2.1.1, 2.1.2 & 2.1.3).

3.2.2 Methodology

3.2.2.1 Nanocomposite preparation

PP/PS (80/20) and the nanoclays Nanocaliber 100 V, Nanocaliber 100, Nanocaliber 100M, Nanocaliber 100Z and Nanocaliber 100 A 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 the mixing time is 8 min for each sample. After mixing the melt was pressed in a hydraulic press, cut into pieces and injection molded in a DSM Micro 10cc Injection Molding Machine, with barrel temperature of 190°C.

3.2.2.2 Characterization

The details of the characterization techniques used for the study are given in the section 2.2.3. Transmission electronic microscopy (TEM) was performed on a JEM2100 at an acceleration voltage of 200 KV. In order to assess resistance of the tensile samples to aging, samples were UV–irradiated
using a low pressure mercury vapor discharge lamp (TUV 30 W, $\lambda = 253.7$ nm) in air atmosphere at room temperature for 360 hours. Samples were mounted on racks positioned 5 cm from the lamps and the temperature in the cabinet was maintained at $30^\circ \pm 2^\circ C$. The UV irradiated samples were then subjected to tensile test.

### 3.2.3 Theoretical modeling of tensile modulus

In the present study Halpin-Tsai model, Takayanagi model, Hui-Shia, Voigt upper bound model and Reuss lower-bound prediction models for elastic moduli of filled polymers are used to predict the elastic- mechanical response.

Halpin and Tsai developed a well-known composite theory for predicting the stiffness of unidirectional composites as a function of aspect ratio. The Halpin–Tsai model is chosen in this work because of its effectiveness in predicting the stiffness of glass fiber reinforced composites, their adaptability for different filler geometries, particularly disks and for their prevalence in the literature [16]. Halpin-Tsai equations are widely used to estimate the reinforcing effect of filler in the composites. The elastic modulus of composite materials reinforced by fibers or flake like fillers can be predicted by Halpin- Tsai equation [17, 18]. The equation theoretically predicts Young’s modulus of a composite material. The Halpin-Tsai model may be expressed as:

$$\frac{E_c}{E_m} = \frac{(1 + \zeta \eta \phi_f)}{(1 - \eta \phi_f)}$$  \hspace{1cm} \text{(3.1)}

where $\eta = \left( \frac{E_f}{E_m} - 1 \right) / (E_f/E_m + \xi)$
where $E_c$, $E_f$ and $E_m$ are Young’s moduli of composites, filler and polymer matrix respectively, $\phi_f$ is the filler volume fraction and $\zeta$ is the shape parameter dependent on filler geometry, orientation and loading direction. In a particular direction, $\zeta = 2(l/d)$ for fibers or $2(l/t)$ for disk-like platelets where $l$, $d$ and $t$ are the length, diameter and thickness of the dispersed fillers. A 2-D disc-like clay platelets contribute less to modulus than 1-D fiber-like fillers. So a modulus reduction factor (MRF) is introduced to modify the Halpin-Tsai model and the corresponding equation is represented as [19]:

$$E/E_m=1+ \{\zeta (MRF) \eta \phi_f / 1-\eta \phi_f \} \quad \text{.................................(3.2)}$$

MRF might lie in the range between 0.167 and 1 for randomly disposed short fibers and in a special case of platelet fillers, MRF = 0.66 has been shown to well predict the tensile moduli of rubber/clay nanocomposites over a wide range of clay volume fractions [20].

By assuming fibers as aligned and both the fibers and matrix are under the uniform strain in the fiber direction, $\zeta \to \infty$ the Halpin-Tsai model predictions concerning the elastic modulus reach the upper-bound. Then the theory is referred as Voigt rule of mixtures (ROM) [21, 22] and the equation may be stated as:

$$E_c=\phi_f E_f + (1-\phi_f) E_m \quad \text{.................................................(3.3)}$$

Reuss [23] applied the same uniform stress on the fiber and matrix in the transverse direction (normal to the fiber direction) and got the effective modulus in the transverse direction. In such case $\zeta \to 0$, the Halpin-Tsai
model equation reaches at the lower bound elastic modulus value corresponding to the elastic response. Then the theory is referred to as Reuss inverse rule of mixtures (IROM) [24] and the equation may be stated as:

\[ \frac{1}{E_c} = \varphi_f / E_f + (1 - \varphi_f) / E_m \] ................................. (3.4)

If the effects of interface are neglected (t=0), the well-known Ji’s model for tensile modulus prediction reduces to the two-phase model of Takayanagi [25, 26]. The Takayanagi model prediction underestimates the Young’s modulus as the effect of interfacial contribution which plays a functional role in stress-transfer mechanism is neglected.

\[ E = E_0 \left(1 - \beta\right) + \beta / \left(1 - \beta\right) + \beta E_f / E_0 \right)^{-1} \] ............................ (3.5)

where \( \beta = \sqrt{\varphi_f} \), \( \varphi_f \) is the volume fraction of the platelets.

Hui-Shia model (H-S model) [27, 28] was developed to predict the tensile modulus of composites with the simple assumption of perfect interfacial bonding between the polymer matrix and clay is given by:

\[ \frac{E_c}{E_m} = 1 / \left\{1 - \varphi_f / \left(1 + 3/\zeta\right) - 3/\zeta^+\right\} \] ................................. (3.6)

Where \( \zeta = \varphi_f + E_m / E_f - E_m + 3 \left(1 - \varphi_f\right) \left\{1 - (g) \left(\alpha^2 - g/2\right) / \alpha^2 - 1\right\} \)

\[ g = \pi / 2 \alpha \]

\[ = \left(1 - \varphi_f\right) \left\{3(\alpha^2 + 0.25) g - 2 \alpha^2 / (\alpha^2 - 1)\right\} \]
where $\alpha$ is the inverse aspect ratio of dispersed fillers and $\alpha = t/l$ for disk-like platelets ($\alpha \leq 0.1$).

### 3.2.3.1 Effect of aspect ratio on the modulus ratio of PP/PS/clay nanocomposites

Figures 3.1 and 3.2 depict the effect of aspect ratio on the modulus in Equations (3.1) and (3.6) respectively. The figures show that the modulus ratio increases with increasing aspect ratio. Thus at high aspect ratios, the level of reinforcement is predicted to be higher for the nanocomposites. In general, both theories emphasize the strong effects of filler modulus and aspect ratio. Dispersion of nanoclay layers of high aspect ratios into the matrix is considered as the major contributor to the enhancement of stiffness in clay nanocomposites.
3.3 Results and Discussion

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction is extremely useful to analyze the structure and morphology of polymer nanocomposites. The change in interlayer spacing of clay gives more information about the formation of nanocomposites. The formation of an intercalated structure should result in a decrease in $2\theta$, indicating an increase in the d-spacing. The interlayer d-spacing observed by XRD for polymer-clay nanocomposites has been used to describe the nanoscale dispersion of clay in the polymer matrix [29].
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Figures 3.3 & 3.4 depict the XRD patterns of N100, N100V, N100Z, N100M, N100A, PP/PS pure blend and its nanocomposites reinforced with the five types of modified nanoclays at 3wt %. Diffraction peaks that appear at 2θ = 15° - 20°corresponds to the monoclinic α form of the PP (Figure 3.3(a)) [30, 31]. The PP/PS/clay nanocomposites have slightly different intensity of reflections than PP/PS blend and this indicates the modification of the crystalline nature of PP in the PP/PS/clay nanocomposites. The original basal reflection peak for N100 is 12.54° having an intergallery spacing of 7.05 nm and the peaks for N100V and N100A are at 12.44° and at 12.28°, respectively, and have an intergallery spacing of 7.11 and 7.20 nm.
Figure 3.4 XRD patterns of (a) N100A (b) blend+N100A (c) N100Z (d) blend+N100Z (e) N100M and (f) blend+N100M

For the PP/PS/N100V nanocomposite, the characteristics peak of N100V is shifted to \(2\theta = 12.08^\circ\), corresponding to a d-spacing of 7.32 nm, which indicates that some PP/PS molecular chains are intercalated between the nanoclay galleries, forming an intercalated structure. Characteristic peak for PP/PS/N100A nanocomposite is at \(12.74^\circ\) having a d-spacing of 6.99 nm and peak for PP/PS/N100 is at \(12.67^\circ\) having a d-spacing of 6.99 nm. The XRD does not show any shift in the diffraction peak for the PP/PS/N100A and PP/PS/N100 nanocomposites. The characteristic peak for N100M is at \(12.19^\circ\) having an intergallery spacing of 7.25 nm. PP/PS/N100M nanocomposite shows the characteristic peak at \(12.76^\circ\) and has a d-spacing of 6.93 nm. This shows that these blends can be considered as conventional micro composites. The
basal reflection peak for N100Z is 12.18° having an intergallery spacing of 7.26 nm. There is a broadening of peak and reduction of intensity is observed in the case of PP/PS/N100Z modified clay nanocomposite. This shows an improved dispersion of nanoclay layers in the polymer matrix and it confirms partial exfoliation of nanoclay in the nanocomposite. When nanoclay exfoliates, there will be a decrease in the intensity of the diffraction peaks due to a reduction in the degree of crystallinity of the silicate sheets.

The extent of nanoclay intercalation in a polymer nanocomposite depends on three important factors: clay–clay interaction, polymer–surfactant interaction and polymer–clay interaction. Surfactants can weaken clay–clay interaction so as to allow polymer interaction between clay layers; these same surfactants can also sterically hinder the access of polymer chains to the nanoclay surface. Hence, the selection of an appropriate surfactant for the polymer of interest is of utmost important in melt processing [32]. By incorporating surfactant with hydrophobic tails on the nanoclay surface will efficiently reduce clay–clay interaction. During melt blending, the presence of vinyl silane groups and dialkyl silane groups enhances the ability of the PP/PS chains to intercalate between the nanoclay galleries. This is due to the increased nanoclay gallery distance and favorable interactions between the surfactant and the polymer molecule. Vinyl silane and dialkyl silane modified nanoclays are found to be more suitable for PP/PS blend [33]. N100V and N100Z modified nanoclays exhibits a maximum basal spacing which is probably due to the difference in structure of the surfactants used in the modification of unmodified kaolin nanoclay.
3.3.1.1 Relative Interaction of Nanocomposites

Relative interaction (RI) of the nanocomposites has been computed as a percentage increase in d-spacing according to the following equation [34]:

$$RI = \frac{(d-d_0)}{d_0} \times 100$$ ...................................................... (3.7)

where $d_0$ and $d$ are the d-spacing of the nanoclay and corresponding nanocomposites respectively.

As the nanocomposite with N100Z is showing a broad peak due to partial exfoliation, it is impossible to calculate RI in accordance with the above equation. The nanocomposite with N100V only shows intercalated structure and its RI (%) value is 3.017 %.

3.3.1.2 Number of Crystallites of PP/PS/clay nanocomposites

When the polymer molecules exist in a nanoclay gallery, the d-spacing value is usually high and when the molecules do not exist in a gallery, the d-spacing value is expected to be lower. The d-spacing of nanocomposites is the average value of the different d-spacing between the platelets of a clay crystallite. According to the Daumas–Herold model, [35] the stage structure of clay nanocomposites were determined as follows.

Crystallite thickness can be calculated by using the Scherrer equation:

$$t = \frac{(K \times \lambda)}{B \cos \theta}$$ ......................................................(3.8)

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

$\theta = $ diffraction angle
The number of platelets in a clay crystallite can be calculated by the following formula:

\[ N = \frac{t}{d_{001}} + 1 \]  \hspace{1cm} (3.9)

where \( N \) = no. of clay platelets (stacks) in a clay crystallite and \( d_{001} \): d-spacing of corresponding nanocomposites

### Table 3.1 Number of crystallites of PP/PS/clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite thickness(nm)</th>
<th>No of clay platelets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend +3wt % N100</td>
<td>24.57</td>
<td>4.52</td>
</tr>
<tr>
<td>Blend +3wt % N100A</td>
<td>24.58</td>
<td>4.54</td>
</tr>
<tr>
<td>Blend +3wt % N100M</td>
<td>18.16</td>
<td>3.62</td>
</tr>
<tr>
<td>Blend +3wt % N100V</td>
<td>18.13</td>
<td>3.42</td>
</tr>
<tr>
<td>Blend +3wt % N100Z</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Crystalline thickness and the number of clay platelets of PP/PS nanocomposites containing five clays (N100, N100A, N100M, N100Z and N100V) measured using equations 3.8 and 3.9 are listed in Table 3.1. From the table it can be observed that the nanocomposites with N100 and N100A shows crystallite thickness of 25 nm but in the case of N100V modified nanocomposite it reduced to 18nm. This decrease in the crystallite thickness or number of stacks in the N100V based nanocomposites can be due to the possible exfoliation of a few layers from the end of the stacks into the melt.

### 3.3.2 Transmission electron microscopy (TEM)

The dispersion and location of organoclay in the polymer blends has a significant influence on the morphological development of the blends as well as on the effect of organoclay as a modifier. Transmission electron
microscopy is an effective method to find out the location of nanoclay particles in polymer.

Figure 3.5  Low magnification transmission electron microscopic image of PP/PS/3wt% N100V

The low magnification TEM image of PP/PS/3wt%N100V and PP/PS/3wt%N100Z nanocomposites are illustrated in the Figures 3.5 & 3.6 respectively. The figure shows a bright field TEM image of nanoclay-filled PP/PS blend that gives a general view of the dispersed PS domains (ellipsoid) in the PP matrix. Besides, the nanoclay particles (dark lines) are easily visualized in the TEM photographs. In PP/PS/3wt%N100V nanocomposite, the nanoclay particles are located in the PP/PS interface; thereby it acts as a modifier. But in the case of PP/PS/3wt%N100Z nanocomposite the nanoclay particles are present both in PP/PS interface and also in PP phase. Therefore the nanoclay particles act as modifier and also as reinforcing filler.
TEM analysis was carried out to localize the nanoclay particles in the blend and to have more insight into nanoclay interfacial activity. TEM bright field images of PP/PS/N100Z nanocomposites with 3 and 5wt% loadings are displayed in Figures 3.7(a) and 3.7(b). The bright phase of the picture is the matrix phase and the dark phase the particle phase. In the TEM photographs (Figure 3.7(a)) most of platelets appear to be well-dispersed and are in a random distribution. There are few locations in which the nanoclay platelets are appeared to be agglomerated in the matrix [36]. The nanoclay particles are found to be agglomerated in PP/PS blend having 5 wt% of nanoclay loading.

TEM bright field images of PP/PS/N100V nanocomposites with 3 and 5wt% loadings are shown in the Figures 3.8(a) and 3.8(b). The bright phase of the picture is the matrix phase, and the dark phase is the particle
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phase. The dark entities are the cross section of intercalated nanoclay layers. The intercalation of the modified kaolin nanoclay by the polymer blend is further evidenced in Figure 3.8(a). The polymer molecules separate the clay particles into individual layers of nanometer thickness.

Figure 3.7 Transmission electron microscopic bright field images of (a) PP/PS/3 wt% N100Z nanocomposite and (b) PP/PS/5 wt% N100Z nanocomposite

Figure 3.8 Transmission electron microscopic bright field images of (a) PP/PS/3 wt% N100V nanocomposite and (b) PP/PS/5 wt% N100V nanocomposites
The intercalation of the modified kaolin nanoclay by the polymer blend is further evidenced by the TEM analysis and it supports the results obtained from XRD. TEM image of PP/PS/N100V nanocomposite with 5 wt% clay loading is shown in Figure 3.8(b). Nanoclay particles are found to be agglomerated in PP/PS blend at higher filler loadings which is in good agreement with the mechanical properties discussed in section 3.3.7.

3.3.2.1 Determination of aspect ratio of clay platelets

In order to model the modulus of nanocomposites, the aspect ratio of nanoclay platelets must be determined. TEM photographs are used to analyze the length and thickness of the clay platelets for the determination of aspect ratio. The silicate layers have good plane orientation. Therefore, the aspect ratio of nanoclay platelets should be directly calculated by measuring the length and thickness of the dark lines in TEM photographs at different magnifications. The statistical data of the aspect ratio for the clay nanocomposites are shown in the Figures 3.9(a) & 3.9(b). These data were obtained by measuring TEM photographs of nanocomposites at different magnifications [17]. The average aspect ratio for PP/PS/N100Z (Figure 3.9(a)) nanocomposite is found to be 36 and for PP/PS/N100V (Figure 3.9(b)) nanocomposite is 30.
Figure 3.9(a) Histogram of the aspect ratio of clay platelets in PP/PS/N100Z nanocomposites

Figure 3.9(b) Histogram of the aspect ratio of clay platelets in PP/PS/N100V nanocomposite
3.3.3 Scanning electron microscopy (SEM)

The changes in the phase morphology of PP/PS blend with different types of nanoclay modifications at 3wt% are shown in the Figure 3.10. On the basis of the morphology of organoclay, we can explain how the silane modification of the nanoclay edges affects the dispersion process of clay nanoparticles in a polymer matrix. The morphology of the fractured cross sections of the tensile samples is illustrated in Figure 3.10. PP/PS blend (Figure 3.10 (a)) exhibits a morphology in which spherical domains of PS phase are surrounded by the continuous PP phase. The interface between the spherical domains and the PP matrix shows weak interfacial adhesion between two phases.

The PP/PS/N100 nanocomposite (Figure 3.10(b)) contains aggregates of micro sized particles, which shows weak interfacial interaction. SEM analysis shows that the nanoclays are dispersed in the polymer matrix in the form of large and small aggregates in PP/PS/N100A nanocomposites (Figure 3.10(c)). The weak interface between the dispersed phase (PS) and the continuous phase (PP) results in reduction of properties in PP/PS/N100A nanocomposite. A similar result obtained for PP/PS/N100M nanocomposite also explains the reduction in mechanical properties (Figure 3.10 (d)).
Figure 3.10 SEM images of (a) PP/PS blend, (b) PP/PS/N100, (c) PP/PS/N100A, (d) PP/PS/N100M (e) PP/PS/N100V and (f) PP/PS/N100Z

SEM photograph of a typical homogeneous dispersion is observed in the N100V modified clay nanocomposite and in N100Z modified clay nanocomposite (Figures 3.10(e) & 3.10(f)). Addition of N100V and N100Z clays improve adhesion between two components giving a homogeneous morphology. Thus the improved homogeneity increases the tensile and flexural properties. This result is in complete agreement with the observed mechanical properties (section 3.3.7) and corroborates the XRD results (section 3.3.1). The nanocomposites prepared using vinyl silane and dialkyl silane modification exhibits better dispersion of nanoclay layers within the polymer matrix than the unmodified as well as amino silane modified kaolin nanoclay and mercapto silane modified kaolin nanoclay.

3.3.4 Thermogravimetric analysis (TGA)

In most cases the incorporation of nanoclay into the polymer matrix is found to enhance the thermal stability. The thermal stability of
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nanocomposites has been investigated using TGA; Table 3.2 presents the results of TGA of PP/PS nanocomposites. The temperature at which 50\% degradation occurs (T_{50}), a measure of the onset of degradation (T_0), maximum degradation temperature (T_{max}) and the fraction of material that remains at 600°C (denoted as residues) are recorded. It is also observed that all five types of clay nanocomposites (3wt \%) show higher degradation temperature than pure PP/PS. Figures 3.11 & 3.12 show the TG and DTG curves of neat PP/PS (80/20) and nanocomposites with different modified kaolin nanoclays at 3wt \%.

Figure 3.11 TG curves of PP/PS blend, PP/PS/N100, PP/PS/N100V, PP/PS/N100A, PP/PS/N100M and PP/PS/N100Z. The inset shows their TG curves in temperature range 410-480°C
The maximum decomposition temperature of the clay nanocomposites increases in the order N100, N100M, N100A, N100Z and N100V. Pure blend shows an onset degradation temperature of 370.5°C. For the unmodified clay this temperature shifts to 390.8°C, the corresponding value for vinyl, dialkyl, mercapto and amino modified clay nanocomposites are 397.3°C, 393.2°C, 394.6°C and 395.1°C, respectively. Improved thermal stability of nanocomposites may be due to the formation of highly charred carbonaceous silicate cumulating on the nanocomposites surface. The charred surface layer formed during decomposition shields the thermal shock due to heat penetration to the underlying material; on the other hand such cumulative char layer tends to retard diffusion of volatile products.
through nanocomposites [37-39]. The temperature at which weight loss reaches 50% shifts to higher temperatures on the addition of nanoclay.

The oxidation index values for PP/PS/clay nanocomposites can be observed from the Table 3.2. Higher the values of oxidation index (OI), higher will be the thermal stability [40, 41].

Table 3.2 Results from DTG curve of PP/PS/clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>50% mass loss (°C)</th>
<th>T onset (°C)</th>
<th>Tmax (°C)</th>
<th>Residue at 600 °C (%)</th>
<th>OI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS blend</td>
<td>426.6</td>
<td>370.5</td>
<td>434.4</td>
<td>0.46</td>
<td>0.032</td>
</tr>
<tr>
<td>Blend +3wt % N100</td>
<td>440.1</td>
<td>390.8</td>
<td>450.1</td>
<td>1.5</td>
<td>0.104</td>
</tr>
<tr>
<td>Blend +3wt % N100A</td>
<td>445.0</td>
<td>395.1</td>
<td>456.8</td>
<td>1.09</td>
<td>0.076</td>
</tr>
<tr>
<td>Blend +3wt % N100M</td>
<td>444.0</td>
<td>394.6</td>
<td>453.7</td>
<td>1.76</td>
<td>0.122</td>
</tr>
<tr>
<td>Blend +3wt % N100V</td>
<td>446.4</td>
<td>397.3</td>
<td>460.7</td>
<td>1.77</td>
<td>0.124</td>
</tr>
<tr>
<td>Blend +3wt % N100Z</td>
<td>446.4</td>
<td>393.3</td>
<td>458.8</td>
<td>2.10</td>
<td>0.146</td>
</tr>
</tbody>
</table>

3.3.4.1 Kinetic analysis of thermal decomposition

Kinetic parameters were evaluated from TGA curves using the plots of Horowitz-Metzger (HM) method, Broido’s method (BR) and Coats Redfern (CR) methods.

Table 3.3 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 +3wt % N100</td>
<td>185</td>
<td>212</td>
<td>184</td>
</tr>
<tr>
<td>Blend +3wt % N100A</td>
<td>193</td>
<td>213</td>
<td>187</td>
</tr>
<tr>
<td>Blend +3wt % N100M</td>
<td>190</td>
<td>221</td>
<td>195</td>
</tr>
<tr>
<td>Blend +3wt % N100V</td>
<td>196</td>
<td>228</td>
<td>196</td>
</tr>
<tr>
<td>Blend +3wt % N100Z</td>
<td>194</td>
<td>223</td>
<td>196</td>
</tr>
</tbody>
</table>
The CR, BR and HM plots for the thermal degradation of PP/PS/ clay nanocomposites with different modified kaolin nanoclay at 3wt % from the onset degradation temperature to the maximum degradation temperature are shown in the Figures 3.13(a), 3.13(b) & 3.13 (c) respectively. The activation energy (Ea) calculated using each method is given in Table 3.3. The respective concurrency value (R²) close to unity is chosen. BR, HW and CR methods gave comparable values of Ea.

Figure 3.13 Kinetic plots for the determination of activation energy of PP/PS blend, PP/PS/N100, PP/PS/N100V, PP/PS/N100A, PP/PS/N100M, and PP/PS/N100Z using (a) Coats-Redfern equation (b) Broiido’s method (c) Horowitz-Metzger equation
From Table 3.3 it is clear that \( E_a \) values are higher for nanocomposites compared to pure blend. The improvement in thermal stability and \( E_a \) values of the nanocomposites are attributed to the dispersion of nanoclay particles in the polymer matrix which restricts the easy diffusion of volatiles from the bulk [42].

Lower \( E_a \) of pure blend may be due to the presence of different kinds of polymer di-radicals produced due to the bond scission and unzipping during degradation process. In the nanocomposites the nanoclay platelets confine the radicals and prevent the decomposition reaction [40, 42]. In nanocomposites the nanoclay layers delay the volatilization of the products originated by carbon-carbon bond scission in the polymer matrix [43]. The influence of modified kaolin nanoclays is higher than that of unmodified clay. The modified kaolin nanoclays can make layered silicates disperse more homogeneously in the polymer matrix. As can be seen from the Table 3.3, the nanocomposites with N100V and N100Z clays show higher \( E_a \) values.

3.3.5 Dynamic mechanical analysis (DMA)

DMA is used to study the relaxation in polymers. DMA measurement consists of the observation of time-dependent deformation behavior of a sample under periodic mostly sinusoidal deformation force with very small amplitudes. Thus, it is possible to calculate storage modulus \( E' \) and loss factor \( \tan \delta \) as a function of temperature and deformation frequency. The analysis of storage modulus and \( \tan \delta \) curves is very useful in ascertaining the performance of the sample under cyclic stress and temperature
Table 3.4 Storage moduli and \( T_g \) values of PP/PS bend, PP/PS/N100, PP/PS/N100V, PP/PS/N100A, PP/PS/N100M, and PP/PS/N100Z.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage modulus</th>
<th>( T_g ) (°C) from tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45°C 80°C 100°C 120°C</td>
<td></td>
</tr>
<tr>
<td>PP/PS blend</td>
<td>1007 525.3 374.1 159.0</td>
<td>114.95</td>
</tr>
<tr>
<td>Blend +3wt % N100</td>
<td>1101 599.7 431.8 182.8</td>
<td>114.67</td>
</tr>
<tr>
<td>Blend +3wt % N100A</td>
<td>1162 647.5 481.7 207.6</td>
<td>114.35</td>
</tr>
<tr>
<td>Blend +3wt % N100M</td>
<td>1005 590.3 447.0 187.0</td>
<td>114.49</td>
</tr>
<tr>
<td>Blend +3wt % N100 V</td>
<td>1369 792.7 573.6 245.6</td>
<td>114.35</td>
</tr>
<tr>
<td>Blend +3wt % N100 Z</td>
<td>1175 709.1 503.2 217.8</td>
<td>113.46</td>
</tr>
</tbody>
</table>

Figure 3.14 compares dynamic storage modulus curves of nanocomposites with different modified kaolin nanoclays at 3 wt% and PP/PS pure blend. PP/PS/clay nanocomposites exhibit higher storage moduli over the entire temperature range of the study (40–125°C). It is evident from the Figure 3.14, the nanocomposites with vinyl silane modified nanoclay and dialkyl silane modified nanoclay shows noticeably higher values of storage modulus over the range of temperature. This further show the overall superiority of the vinyl silane modified and dialkyl silane modified kaolin nanoclays in improving the mechanical behavior of the blend. This observation clearly illustrates the effect of intercalation of the polymer in clay layers, leading to the dispersion of nanoclay platelets in the polymer matrix. The enhancement of storage modulus strongly depends on the aspect ratio of the dispersed nanoclay particles and the intercalation of the polymer chains inside the nanoclay galleries [44-46]. When a polymer matrix is reinforced with rigid filler particles, the polymer interface adjacent to the nanoclay particle is highly restrained mechanically. Active surface area of the filler increases because of the intercalation of the polymer chains inside the nanoclay galleries.
Polymer chains inside the nanoclay galleries are immobilized and the effective immobilization of these chains is responsible for the enhancement of the hydrodynamic storage modulus. The variation of tan $\delta$ [ratio of loss and storage modulus ($E''/E'$)] plotted as a function of temperature is shown in Figure 3.15. The tan $\delta$ curves represent the ratio of dissipated energy to stored energy and relates to the $T_g$ of the polymer. Tan $\delta$ is useful in determining the occurrence of molecular mobility transitions such as $T_g$. From the figure it can be noticed that there is a slight decrease in $T_g$ with the addition of nanoclays. The reduction is attributed to the plasticizing action of the various surfactants of organically modified clays. Such plasticizing action may be responsible for the improved mobility of polymer chains which cause reduction in $T_g$ [47]. Table 3.4 shows the $T_g$ values obtained for the pure PP/PS blend and the modified nanocomposites from the tan $\delta$ curves.
In order to clarify the effect of nanoclay addition in enhancing the blend properties, the relative storage moduli of PP/PS/nanoclay composites to those of PP/PS blend is plotted in Figure 3.16. The relative storage moduli of PP/PS/clay nanocomposites were higher than those of the respective PP/PS matrix at all temperature range. In Figure 3.16, “hump like curves” are observed which may be attributed to the hindrance of polymer chain movement due to the presence of nanoclay particles [48-50]. This “hump like curves” could be attributed to the resistance of the applied stress as a result of development of polymer-nanoclay network.
3.3.5.1 Calculation of the activation energy

The nanocomposites with N100 V and N100 Z show higher storage modulus over the range of temperature. So the nanocomposites with N100V and N100Z are used to study the effect of frequency on the dynamical mechanical properties. In order to investigate the effect of frequency on the dynamical mechanical properties of PP/PS clay nanocomposites, DMA tests were performed over a temperature range of 40 to 125°C and at five different frequencies (0.1, 1, 3, 5 and 10 Hz). The temperature dependence of tan δ for PP/PS/5wt%N100Z nanocomposite and PP/PS/5wt%N100V nanocomposite at the five frequencies studied is shown in the Figures 3.17(a) and 3.17(b). From the figure it can be seen that the relaxation peak shifts to higher temperature as the frequency increases from 0.1Hz to 10 Hz. Weixia Zhong et al. obtained similar observation in their studies. They reported that the relaxing unit of PP chain segments shift to higher temperature as the
frequency increases [51]. From the relaxation peaks; obtained from tan \( \delta \) curves at different measuring frequencies, the activation energy of the PP/PS/clay nanocomposites was calculated using the Arrhenius equation [52]:

\[
f = f_0 \exp \left( \frac{-E_a}{RT} \right)
\]

where \( f_0 \) is a constant and \( f \) the frequency of the test, \( R \) is the gas constant, \( E_a \) is the activation energy, and \( T \) is the temperature corresponding to the maximum of the tan \( \delta \) curve in Kelvin scale.

**Table 3.5 Activation energies of PP/PS/ clay nanocomposites**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy (E( _a )) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PS blend</td>
<td>533</td>
</tr>
<tr>
<td>Blend +1wt % N100Z</td>
<td>622</td>
</tr>
<tr>
<td>Blend +3wt % N100Z</td>
<td>638</td>
</tr>
<tr>
<td>Blend +5wt % N100Z</td>
<td>657</td>
</tr>
<tr>
<td>Blend +1wt % N100V</td>
<td>645</td>
</tr>
<tr>
<td>Blend +3wt % N100V</td>
<td>700</td>
</tr>
<tr>
<td>Blend +5wt % N100V</td>
<td>716</td>
</tr>
</tbody>
</table>

**Figure 3.17** Effect of frequency on DMA curves of (a) PP/PS/5wt%N100Z clay nanocomposite (b) PP/PS/5wt%N100V clay nanocomposite
Figure 3.18 Representative Arrhenius plots for the activation energy of
(a) PP/PS blend (b) PP/PS/5wt%N100Z nanocomposite (c) PP/PS/5wt%N100V nanocomposite
A plot of log $f$ versus $1/T$ gives a straight line and the activation energies for the nanocomposites are calculated from the slope of this line (Figure 3.18). Activation energies calculated according to equation 3.10 are given in Table 3.5. From the table it can be observed that the activation energy of the nanocomposites is higher than that of the PP/PS blend. The restricted flow and the enhanced temperature sensitivity of the nanocomposites may be attributed to the increased interfacial adhesion between modified kaolin clays and the polymer matrix [53]. This result is also attributed to the better dispersion of clay platelets in polymer matrix [54].

### 3.3.6 Differential scanning calorimetry (DSC)

DSC measures the amount of energy absorbed or released by a sample as it is heated cooled or held at a constant temperature. The crystallization temperature ($T_c$), the apparent melting temperature ($T_m$) and the corresponding enthalpies ($\Delta H$) are shown in the Table 3.6. The DSC melting and cooling curves for PP/PS blend and nanocomposites with different modified kaolin clays at 3 wt % are shown in the Figure 3.19.

**Table 3.6 DSC parameters of PP/PS blend, PP/PS/N100, PP/PS/N100V, PP/PS/N100M, PP/PS/N100Z and PP/PS/N100A**

<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>Blend+3wt%N100</td>
<td>114.1</td>
<td>45.0</td>
<td>159.2</td>
<td>21.0</td>
</tr>
<tr>
<td>Blend+3wt%N100V</td>
<td>114.4</td>
<td>63.3</td>
<td>160.2</td>
<td>40.0</td>
</tr>
<tr>
<td>Blend+3wt%N100A</td>
<td>112.8</td>
<td>56.7</td>
<td>160.7</td>
<td>27.9</td>
</tr>
<tr>
<td>Blend+3wt%N100M</td>
<td>113.7</td>
<td>62.1</td>
<td>159.0</td>
<td>39.9</td>
</tr>
<tr>
<td>Blend+3wt%N100Z</td>
<td>113.9</td>
<td>63.7</td>
<td>161.1</td>
<td>40.5</td>
</tr>
</tbody>
</table>
Crystallization temperature of all nanocomposites is increased with increase in nanoclay loading as given in the Table 3.6. The crystallization temperature of PP/PS blend is 111.8°C and the presence of nanoclay increases $T_c$ up to 114°C. This increase in $T_c$ indicates the nucleating effect of nanoclays in the polymer matrix [55]. The extent of increase in crystallization temperature varies slightly with the type of nanoclays. The order of magnitude of $T_c$ for the different nanoclays is as shown: Blend/N100V ≈ Blend/N100 ≈ Blend/N100Z ≈ Blend/N100M ≈ Blend/N100A ≈ PP/PS Blend. The melting temperatures of the studied samples of the nanocomposites were increased, in comparison to pure polymer matrix. This increase in $T_m$ values signifies that the crystal structure in nanocomposites is more perfect than in polymer matrix. The increase in $\Delta H_m$ values of the nanocomposites [Blend/N100Z & Blend/N100V] than that of the neat polymer matrix indicates a higher thermal stability of the nanocomposites [56].
3.3.7 Mechanical Analysis

(a) Tensile properties

The tensile strength and tensile modulus as a function of increasing filler loading of unmodified and modified nanocomposites are depicted in Figures 3.20 and 3.21, respectively. Tensile properties increase initially with increasing filler loading reaches an optimum and then decreases. The insertion of the polymer chains inside the silicate layers leads to an increase in the surface area of interaction between the nanoclay and polymer matrix thereby resulting in an increase in strength and modulus. The increment in tensile strength and modulus is also attributed to the reinforcing characteristics of dispersed nanoclay layers. Nanoclay platelets present in the polymer matrix act as an efficient stress transfer agent in nanocomposite, inducing plastic deformation into the base polymer [57]. The mechanical properties of the compatibilized polymer blends are likely to be improved compared to corresponding uncompatibilized ones because of the lower interfacial tension and enhanced interfacial adhesion, which results in more efficient stress transfer between the phases during fracture [7]. Sanjay K Nayak et al. reported that the increase in tensile modulus was due to the resistance exerted by the nanoclay layers against the plastic deformation of the polymer and the stretching resistances of polymer chains with an extended conformation in the gallery [34]. The decrease in tensile properties at higher loadings may be due to the agglomeration of nanoclay particles. The stress acting on a small part of the material surface would be much greater than the average stress applied to the test specimen in the presence of nanoclay agglomerates.
Figure 3.20 Variation of tensile strength with clay loadings

Figure 3.21 Variation of tensile modulus with nanoclay loadings

(b) Flexural properties

Effect of organoclay type on flexural properties of nanocomposites is presented in Figures 3.22 and 3.23, respectively. The increase in flexural
strength and modulus indicates that the nanocomposites have become more rigid and less flexible. The enhancement in the mechanical properties is more pronounced in PP/PS blend with N100V and N100Z loadings. From the result it can be concluded that vinyl silane modified kaolin nanoclay (N100V) and dialkyl silane modified kaolin nanoclay (N100Z) have better interaction with the matrix.

Figure 3.22 Variation of flexural strength with nanoclay loadings

Figure 3.23 Variation of flexural modulus with nanoclay loadings
(c) Impact strength

The effect of nanoclay modification on the impact strength with increasing clay loadings is given in the Figure 3.24.

![Figure 3.24 Variation of impact strength with nanoclay loadings](image)

The impact strength increases with clay loading after reaches a maximum value thereafter decreases. The enhancement of impact strength is due to the dispersion of stress by intercalated nanoclay layers. Thus the intercalated clay layers in the nanocomposite play a role in hindering the crack path caused by impact. When the interaction between the polymer and the clay layers increases the stress transfer is more prominent [58]. The stress distribution is dominant in the nanocomposites with the addition of vinyl silane and dialkyl silane modified nanoclays.

(d) Hardness

Hardness is a measure of resistance to indentation. Surface hardness indicates the degree of compatibility and crosslink density [59]. Figure 3.25
gives the variation of hardness with increasing clay loading. The surface hardness of the nanocomposites increases with increase in nanoclay content and reaches a maximum and thereafter shows a reverse trend. The improvement in hardness is due to the presence of intercalated and exfoliated nanoclay platelets in polymer matrix. The intercalated or exfoliated nanoclay platelets restrict indentation and increase the hardness of the nanocomposites. At higher nanoclay loading, the reinforcing effect of clay gets decreased due to agglomeration [60].

![Figure 3.25 Variation of hardness with clay loadings](image)

**Figure 3.25 Variation of hardness with clay loadings**

### 3.3.8 Theoretical modeling of tensile modulus

Figures 3.26 and 3.27 exhibit the comparison between the experimental data and the results provided by various theoretical models fit tensile moduli for PP/PS/ modified kaolin nanoclay nanocomposites with N100Z and N100V respectively. By considering that $E_0 = 569.38$ MPa (Figure.3.21) and $E_1 = 12$ GPa [61], the tensile modulus prediction tends to follow a trend with the experimentally determined values.
Among all the model fits the predicted moduli based on modified Halpin-Tsai (with a modulus reduction factor) and Hui-Shia model shows the closest proximity to the experimentally determined tensile modulus values at lower nanoclay loading up to 3 wt%. But at higher loadings the magnitude of the tensile modulus is converged to Takayanagi model in the case of PP/PS/N100Z nanocomposites (Figure.3.26). Lower bound and upper bound model stay largely deviated from the predicted moduli. The predicted moduli by Halpin-Tsai equation are higher than the experimental data. This could be attributed to the contribution of plate-like clay to the tensile modulus which is less than a fiber like dispersed phase. The morphology differences between the plate–like filler (two dimension) and fiber like filler (one dimension) which is neglected in the composite theories are taken into account in the modified Halpin-Tsai model. MRF is related to the morphology and aspect ratio of the filler [17]. The experimental results also shows close proximity to the Hui-Shia model which indicates a perfect interfacial bonding between nanoclay and the polymer matrix as per the assumptions of the model. An imperfect interface reduces the reinforcing efficiency of the nanoclay platelets as it is implied that the interface in nanocomposites plays an important role in the effective load transfer from the matrix to the fillers. At higher nanoclay loadings, the clay clusters act as a stress concentrates which results in deviation of the experimental result from the Hui-Shia model. In Takayanagi model the effect of interfacial contribution which plays a functional role in stress-transfer mechanism is neglected.
Figure 3.26 Theoretical modeling of tensile modulus as a function of filler loadings using various models of PP/PS/N100Z nanocomposites.

Figure 3.27 Theoretical modeling of tensile modulus as a function of filler loadings using various models of PP/PS/N100V nanocomposites.
In the case of PP/PS/N100V nanocomposites (Figure 3.27) the experimentally determined tensile modulus values is converging towards the modified Halpin-Tsai (with a modulus reduction factor) and Hui Shia model but at higher loadings it shows close proximity to the Takayanagi model.

### 3.3.9 Effect of UV aging on the tensile properties

The effect of UV aging on the tensile strength and tensile modulus of PP/PS/clay nanocomposites are given in the Figures 3.28 and 3.29. Figures depict the variation of tensile strength and tensile modulus with nanoclay loading after UV aging. From the figure it is observed that the tensile properties decreases after aging when compared to before aging (Figures 3.20 & 3.21).

![Figure 3.28 Effect of UV aging on the tensile strength of PP/PS/clay nanocomposites](image-url)
Figure 3.29 Effect of UV aging on the tensile modulus of PP/PS/clay nanocomposites

The photodegradation of polystyrene is initiated by the absorption of UV radiation by the aromatic ring which results in scission of the C-H bond from the main chain carbon bonded to the aromatic ring. The free radical thus produced has low reactivity due to resonance stabilization. Photodegradation of PS is further accelerated by acetophenone, a chromophore with strong UV absorption which is formed in the primary photodegradation step [62]. Sandrine Morlat et al. reported that the photodegradation of polypropylene is by the formation of hydroperoxides, which can decompose to produce alkoxy radicals, which abstract hydrogen on the polymeric backbone or undergo a β-scission [63]. According to Walter et al. degradation in polymer blend is very complex depending upon the variety of interactions between the blend components. In PP/PS blend, PS domain acts like a UV radiation trap. Photo degradation of PS is accelerated by acetophenone (formed as a product of primary photo degradation step) and it interacts with PP domains and form more reactive tertiary carbon radicals [64]. In
PP/PS/clay nanocomposites the nanoclay accelerates the photo degradation of PP/PS blend. Generally, nano particles have greater acceleration effect than micro particles due to its smaller size and greater interfacial area [65, 66].

3.3.10 Melt Flow Index (MFI)

The measurement of melt flow index (MFI) is a simple way to estimate the chain mobility of polymer materials. Effect of nanoclay type on the MFI value with increasing nanoclay loading is shown in the Figure 3.30. From the figure it is clear that the MFI value of all nanoclay types decreases with increasing clay loading. The clay particles act as fillers causing an increase in viscosity (decrease in MFI value [67]. The N100V and N100Z modified nanocomposites shows low MFI values.

Figure 3.30 Variation of MFI with nanoclay loadings

Ke Wang et al. suggested that the decrease in MFI with nanoclay loading is also due to the formation of nanoclay network at higher loadings. The orientation and flow of polymer chains would be retarded if the polymer chains were confined in narrow spacing between nanoclay particles, resulting in the decrease of melt fluidity [68].
3.4. Conclusions

The effect of kaolin nanoclay modification on the mechanical, thermal and morphological behavior of PP/PS blend is described. In Nanocaliber100V modified nanocomposite system, the clay layers are delaminated as thin platelets in the matrix as evidenced by the shifting of diffraction peaks to lower angle in XRD region and in Nanocaliber100Z modified nanocomposite, there is a reduction of intensity which confirms a partial exfoliation of nanoclay layers in polymer matrix. TEM results show that N100V can be act as an interfacial modifier and N100Z can act as both interfacial modifier and as reinforcing filler and it corroborates the results obtained from XRD. Thermogravimetric analysis shows improved thermal stability of PP/PS/clay nanocomposites caused by the partial exfoliation of the nanoclay in the nanocomposites. The dynamic mechanical analysis reveals higher storage moduli over a temperature range of 40–125°C for nanocomposites, and the extent of increase in the storage modulus is dependent on the type of nanoclay. N100V and N100Z modified nanocomposites show maximum improvement in mechanical properties, suggesting that it provides better interfacial interaction. Hui-Shia and modified Halpin-Tsai models show close proximity to the experimental values till 3 wt%. This confirms the presence of a perfect interface between matrix and nanoclay platelets. SEM photograph shows better dispersion for PP/PS/N100V and for PP/PS/N100Z nanocomposites and the dispersion of the particles in polymer matrix is influenced by the strength of interaction between polymer and filler and also the type of modification. The dispersion of nanoclay particle is also found to improve with proper modification.
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