CHAPTER 6:
DYNAMIC MECHANICAL PROPERTIES

ABSTRACT

Blends of nanoclay filled thermoplastic polyurethane (TPU) / polypropylene (PP) were evaluated for dynamic mechanical properties such as storage modulus ($E'$), loss modulus ($E''$) and dissipation factor ($\tan \delta$). The dynamic mechanical properties for the various blend nanocomposites were plotted as a function of temperature, at different frequencies of 1, 10 and 20 Hz over a temperature range of -100°C to 200°C. Attempts were made to correlate the observed viscoelastic properties of the blends with morphology. Various models were used to model the dynamic mechanical data.

A part of the results of this chapter has been published in J.Mater.Sci., 45(4),1078-1085 (2010).
6.1 Introduction

Dynamic mechanical analysis has proved to be an effective tool especially for characterizing the dual viscous and elastic nature of polymeric materials. In an oscillatory field, the viscoelastic material shows a phase lag between the imposed dynamic strain and the dynamic stress response or vice versa. Since the stress and strain are generally not in phase, modulus and phase angle can be determined. Dynamic mechanical results are generally given in terms of complex modulus, $E^*$ which can be represented as

$$E^* = E' + iE''$$

where $E'$ is the real part of the modulus and $E''$ is the imaginary part of the modulus. $E'$ is the storage modulus due to the stored elastic energy in the material and $E''$ is the loss modulus due to viscous dissipation. The angle that reflects the time lag between the applied stress and strain is $\delta$ and is defined by $\tan \delta = E'' / E'$.

The main purpose of the present study is to analyze the dynamic mechanical properties of nanoclay filled TPU/PP blends. The properties including storage modulus ($E'$), loss modulus ($E''$) and dissipation factor (tan $\delta$) were investigated as a function of temperature and frequency. The area under the loss curve is evaluated to investigate the damping behavior. The parameters of interest in this study are the respective loss factor peak heights and the loss factor peak locations to assess the blend miscibility and phase continuity. The dynamic mechanical properties like $E'$, $E''$ and tan $\delta$ of polymer blends are sensitive not only to different molecular motions but also to various transitions, relaxation process, structural heterogeneity, extent of crosslinking and the morphology of multiphase systems. The damping in the system or energy loss per cycle can be measured from the
tangent of the phase angle. DMA is a very powerful technique to investigate the heterogeneity of polymeric materials, since materials are often subjected to cyclic stressing during service [1-3]. In DMA, miscibility is ascertained by considering the $T_g$ values of virgin polymers and their blends. A single $T_g$ for the blends is an indication of miscibility; while two separate $T_g$'s indicate immiscibility in the system. Experimental evidence of miscibility is often found when a single and a sharp glass transition temperature, $T_g$, is observed [3-5] in between the $T_g$'s of the individual components. In the glass transition region of linear polymers, the storage modulus usually decreases by three to four orders of magnitude over a temperature range of 20-30°C. Also, in the glass transition region, $E''$ and $\tan \delta$ go through maxima. The quantities $E''$ and $\tan \delta$ can be utilized in mechanical damping applications to reduce mechanical vibrations and noise emission [6-8].

Brahimi et al. [9] studied the effect of diblock copolymer on dynamic mechanical properties of PS/PE blends. They reported a reduction in phase separation and improvement in interfacial adhesion on compatibilisation. George et al. [10] reported the viscoelastic properties of blends of polyethylene and nitrile rubber based on the effect of blend ratio and reactive compatibilisation. Influence of two reactive compatibilisers namely phenolic modified polypropylene and maleic modified polypropylene were compared and enhancement in storage modulus were correlated with change in domain size of dispersed NBR particles. Many citations are available in literature regarding the importance of both theoretical and experimental approaches of dynamic mechanical properties [11-17]. Varkey et al. [18] investigated the viscoelastic properties of NR/SBR blends at different frequencies and temperatures.
The phase behavior of the blends was evaluated using Cole-Cole plots. All the NR/SBR blends showed two distinct glass-transition temperatures, indicating the immiscibility of the system. In a recent report, the effect of blends ratio and reactive compatibilisation on dynamic mechanical properties of high density polyethylene/ethylene vinyl acetate copolymer (HDPE/EVA) blends has been made by John et al.[19] Guo et al.[20] studied dynamic mechanical properties of polyamide6/polystyrene (PA6/PS) blend by addition of a copolymer poly(styrene-b-ethylene oxide) (SBEO). It has been reported that compatibility and mechanical properties of the blends PA6/PS (80/20 wt/wt) can be improved by addition of SBEO copolymers. Tjong et al. [21] reported dynamic mechanical data of blends of polybutylene terephthalate/high impact polystyrene with and without compatibilisers. Zhang and He [22] studied viscoelastic properties of polysulphone/thermotropic liquid crystalline polymer. Ferrer et al. [23] showed an improvement of the thermomechanical properties for blends of styrene-butadiene-styrene triblock copolymer and isotactic polypropylene when i-PP was the dispersed phase. Many citations are available in literature reporting on the viscoelastic properties of polymer blends [24-31].

In the present study, investigations are carried out on nanoclay filled both ester- and ether-based TPU/PP blend with compatibilizer to get overall best performance. Preparation of ester- and ether-based TPU/C10A nanocomposites by direct melt blending, using 3 wt% Cloisite 10A (organically modified montmorillonite clay) as the nanoscale reinforcement. Nanocomposites with PP using MA-g-PP as the compatibiliser were prepared by melt blending. Nanocomposites performances have been studied with emphasis on sequence on nanoclay addition.
6.2 Results and discussion

6.2.1 Uncompatibilised blends

Figures 6.1(a), (b), (c) and (d) show the wide temperature range DMA measurements [storage modulus, log storage modulus, loss modulus and loss tangent factor (tan δ)] for TPU/PP blends at 10 Hz. TPU records the minimum and intermediate values for the compatibilised blends. At low temperature, since the polymers are in the glassy state, effect of temperature on modulus improvement could not be observed for all compositions. The highest damping value is seen for TPU. Damp value decreases upon incorporation of PP, as seen in the figure and have higher loss tangent values.

The damping is low below T_g because the chain segments are frozen in. Below T_g, the deformations are thus mainly elastic and molecular slip resulting in viscous flow is low. As temperature increases, damping goes through a maximum near T_g, in the transition region and then a minimum in the rubbery region. Above T_g where rubbery region exists, the damping is also low because molecular segments are very free to move about and there is very little resistance for flow. Thus, when the segments are either frozen in or are free to move, damping is low. The T_g due to TPU is seen at -60°C. There is change in T_g value due to TPU phase, on the addition of PP into TPU. The T_g due to TPU transitions obtained from E"_max and tan δ_max are given in Table 6.1 and 6.2 for ester – and ether- based TPU blends respectively. There is considerable change in T_g value due to TPU phase, on the addition of PP into TPU.
Table 6.1. T\textsubscript{g} of uncompatibilised ester-TPU/PP blends

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>T\textsubscript{g} from Loss Modulus (°C)</th>
<th>T\textsubscript{g} from tan delta (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP 100/0</td>
<td>-36</td>
<td>-24</td>
</tr>
<tr>
<td>TPU/PP 70/30</td>
<td>-34</td>
<td>-22</td>
</tr>
<tr>
<td>TPU/PP 50/50</td>
<td>-24</td>
<td>-16</td>
</tr>
<tr>
<td>TPU/PP 30/70</td>
<td>-20</td>
<td>-7 &amp; 103 (T\textsubscript{a})</td>
</tr>
<tr>
<td>TPU/PP 0/100</td>
<td>-11</td>
<td>3 &amp; 108 (T\textsubscript{a})</td>
</tr>
</tbody>
</table>

Table 6.2. T\textsubscript{g} of uncompatibilised ether-TPU/PP blends

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>T\textsubscript{g} from Loss Modulus (°C)</th>
<th>T\textsubscript{g} from tan delta (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP 100/0</td>
<td>-44</td>
<td>-30</td>
</tr>
<tr>
<td>TPU/PP 70/30</td>
<td>-39</td>
<td>-25</td>
</tr>
<tr>
<td>TPU/PP 50/50</td>
<td>-32</td>
<td>-21</td>
</tr>
<tr>
<td>TPU/PP 30/70</td>
<td>-28</td>
<td>-14 &amp; 101(T\textsubscript{a})</td>
</tr>
<tr>
<td>TPU/PP 0/100</td>
<td>-11</td>
<td>3 &amp; 108 (T\textsubscript{a})</td>
</tr>
</tbody>
</table>
Figure 6.1 (a). Storage modulus (b). Log storage modulus of ester-TPU based uncompatibilised blends

Figure 6.1. (c). Loss modulus (d). Tan δ of ester-TPU based uncompatibilised blends
Figure 6.2(a). Storage modulus (b). Log storage modulus of ether-TPU based uncompatibilised blends

Figure 6.2. (c). Loss modulus (d). tanδ of ether-TPU based uncompatibilised blends
Figures 6.1(a), 6.1(c), 6.2(a), and 6.2(c) upper and lower curves show the temperature dependence of storage and loss modulus of the uncompatibilised samples from -100 to 200°C. The effects of temperature on tan δ values of the blends are evident in Figure 6.1(d) and 6.2(d). At very low temperature modulus of the blends are high. The modulus decreased with increase in temperature and finally levels off at high temperature. The storage and loss moduli values of TPU are high at low temperature and decreased sharply around -60°C indicating distinct transition from glassy to rubbery region. TPU rich blend [TPU/PP(70/30)] also shows same trend. At low temperature, the molecules are frozen in and exhibit very high modulus. Some secondary relaxations occur after the glassy transitions. TPU exhibits very low modulus in the rubbery plateau. The modulus values finally levels off as temperature increases. The decrease in modulus above PP T_g is more pronounced in PP rich blends. Around the glass transition temperature of TPU the blends are in the glassy state and the modulus is high.

The E’ intensity nearly follows the composition. Thus it can be concluded that the stiffness of the samples decreases with TPU content. A high modulus observed in [TPU/PP(70/30)] is mainly due to major contribution from PP. A sharp increase in damping value in [TPU/PP(70/30)] blend is due to the major contribution of TPU phase. It is observed that at room temperature, the storage and loss moduli of PP are greater than those for TPU due to the high brittleness of PP because of its high T_g. Thus the unmodified TPU/PP show typical behavior for immiscible blends. The above results are very much in agreement with that of systems based on blends of polypropylene and ethylene propylene diene monomer (PP)/EPDM studied by Papke and Karger-Kocsis[32-33].
The chain mobility of the polymer can be understood from the area under the loss modulus versus temperature curve [34]. As expected, loss modulus increases up to transition zone, until they reach a maximum and then decreases with temperature. The damping behaviour of the blends increases with increase in concentration of TPU.

McGrum and colleagues [35] have demonstrated that the tan δ curve of PP exhibits three relaxations localized in the vicinity of -80 (γ), 10 (β) and 108 °C (α). However DMA analysis [Figure 6.1(d) and 6.2(d)] do not show any clear separate tan δ peak corresponding to the β relaxation [glass transition temperature of PP (T_g)], but more definite tanδ peak was observed corresponding to T_α at approximately at 108 °C. The tanδ value at around 108°C, corresponding to the α transition (T_α), is believed to be the result of molecular motions which resist the softening effect of the applied heat. While T_g reflects mobility within the amorphous regions, T_α dictates the onset of segmental motion within the crystalline regions [36–38]. Clear tan δ peak was observed corresponding to the α relaxation for the TPU/PP blend composition of 0/100 and 30/70, but not in the case of 50/50, 70/30 and 0/100. The tanδ peak corresponding T_α for TPU/PP (0/100) and (30/70) blend composition are given in Table 6.1 and 6.2. Increase of TPU portion eliminates the β relaxation in the blend system.

6.2.2 Modulus –composition models

Various models exist for predicting elastic properties of polymeric materials. Different models like parallel, series, Halpin- Tsai, Kerner, Davies and Budiansky were used to predict the mechanical behavior of the blends. The two simple models are the so-called parallel and series models, which could represent the upper and lower bounds of the tensile strength.
predictions. The highest upper bound parallel model is given by the rule of mixtures discussed in equation 4.1. This model is applicable to materials in which the components are connected parallel to one another so that the applied stress elongates each component to the same extent. In the lowest-lower bound series model, the blend components are arranged in series (Reuss prediction) perpendicular to the direction of the applied force. The modulus prediction is given by the inverse rule of mixtures discussed in equation 4.2. For both these models, no morphology is required, but strain or stress can be continuous across the interface, and Poisson’s ratio is the same for both phases.

The phase continuity and phase inversion in polymer blends can be studied by relating the dynamic mechanical moduli to modulus-composition models [39]. A general mixing equation, which often successfully predicts certain properties of composites with two continuous phases, has been presented by Nielsen [40]. \( P \) is a property such as elastic modulus and \( n \) is a function of the morphology of the system. For \( n = 1 \), the ordinary rule of mixtures results, whereas for \( n = -1 \), the inverse rule of mixtures. The logarithmic rule of mixtures arises when \( n = 0 \). The Davies equation [41-42], which Hourston and Zia [43] class as a special solution to the Nielsen [40] equation, is designed for systems in which both components are present as continuous phases. It is discussed for systems in which both components are present as continuous phases.

Kerner [44] proposed expressions for gross bulk and shear moduli of multi component systems for spherical particulate filled isotropic composites. Mazich et al.[45-46], Bandyopadhyay et al.[47], George et al.[48] have applied these models for predicting dynamic properties of rubber-rubber blends. Oommen et al.[49] did theoretical modeling on
viscoelastic properties of natural rubber/poly(methyl methacrylate) blends (NR/PMMA) System. Kerner model is described in equation 4.11. This equation was found to represent dynamic data for a variety of systems of the type soft inclusion / hard matrix reasonably well. Poisson ratio for homopolymers was assumed to be 0.48 for TPU and 0.40 for PP.

Figure 6.3(a) and (b) gives a comparison of theoretical and experimental values of storage modulus of the ester- and ether-TPU based blends as a function of volume fraction of PP at 10°C and frequency of 10 Hz. The experimental values are in between series and parallel models. The predictions of these theories have been made with $E_1 = 293$ for ester, $E_1 = 331$ for ether and $E_2 = 6028$ MPa for the storage modulus for TPU and PP respectively.
Figure 6.3. TPU based blends theoretical model of (a) Ester based blends (b) Ether based blends as a function of volume fraction of PP at 10°C; TPU/PP (70/30) theoretical model of (c) Ester based blends (d) Ether based blends as a function of temperature
6.2.3 Effect of compatibilisation with nanoclay

Preparation of ester- and ether- TPU/C10A nanocomposites by direct melt blending [50-57], using 3 wt% Cloisite 10A (organically modified montmorillonite clay) as the nanoscale reinforcement. Nanocomposites with PP using MA-g-PP as the compatibiliser were prepared by melt blending.

Low temperature DMA measurements on few selected samples of the compatibilised blends were carried out at a frequency of 10 Hz. The effect of temperature on storage modulus, log storage modulus, loss modulus and $\tan \delta$ of MA-g-PP compatibilised blends are shown in Figure 6.4.(a),(b),(c),(d) and 6.5(a),(b),(c),(d) respectively. Indication of miscibility; while two separate $T_g$ s indicate immiscibility of the system. Experimental evidence of miscibility is often found when a single and a sharp glass transition temperature, $T_g$, is observed in between the $T_g$ s of the individual components. In the glass transition region of linear polymers, the storage modulus usually decreases by three to four orders of magnitude over a temperature range of 20-30°C [59-64]. Also, in the glass transition region, $E''$ and $\tan \delta$ go through maxima. The quantities $E''$ and $\tan \delta$ can be utilized in mechanical damping applications to reduce mechanical vibrations and noise emission. $T_g$ from $E''_{\text{max}}$ and $\tan \delta_{\text{max}}$ are given in Table 6.3 and 6.4.

Similar to the uncompatibilised blends, the compatibilised blends show a decrease in modulus with temperature. The dynamic mechanical parameters (storage modulus) for the various blend nanocomposites are plotted as a function of temperature, at a constant frequency of 10 Hz [Figures 6.4(a)and 6.5(a)]. The storage moduli at -50 °C, 0 °C, 20 °C and 30 °C are shown in Table 6.5 and 6.6.
The storage modulus at -40 °C of ester-TPU/PP blends, without nanoclay and compatibilized with the same wt% of MA-g-PP, prepared under identical conditions, is reported to be 7.23 GPa [58]. Thus, a 3 wt% C10A reinforcement increased the storage modulus of the blend by ~ 40%. At room temperature, the storage modulus value of the ester-TPU (nano)/PP/MA blend nanocomposite is more than that of the other blends. It is possible that well-dispersed clay platelets resulted in an increase of storage modulus.

The dissipation factor (tanδ) of the materials is presented as a function of temperature in Figure 6.4(d) and 6.5 (d). The tanδ peak is associated with the soft segment glass transition temperature and the peak positions are given in Table 6.3 . The temperature corresponding to the tanδ peak increases in the order- ester-TPU/PP < ester-TPU/PP/MA-g-PP < ester-TPU(nano)/PP/MA. This is attributed to the increasing order of dispersion for the blends. In DMA testing, one way of calculating Tg is based on tan delta. Each tan delta peak temperature indicates the Tg of TPU soft segment for that particular composition. A shift in this peak indicates an effect on the dispersion level of blend system. The temperature corresponding to the tan delta peak increases in the order: TPU / PP < TPU / PP / MA-g-PP < TPU / PP(nano) / MA-g-PP < TPU (nano) / PP / MA-g-PP (-22 0°C < -15 0°C< -11 0°C < -7 0°C for ester and -25 0°C < -18 0°C< -14 0°C < -10 0°C for ether). The same order was observed in DSC experiment also (-61.5 0°C < -59.3 0°C < -53.5 0°C). The Tg may have different numerical values but it follows the same order. DMA and DSC experiments are based on different concepts and hence the numerical values may not match. Ether based blends also shows same type of trend with less shift in Tg values.
Table 6.3. $T_g$ of compatibilised ester TPU/PP (70/30) blends

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>$T_g$ from Loss Modulus (°C)</th>
<th>$T_g$ from tan delta (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP 70/30</td>
<td>-34</td>
<td>-22</td>
</tr>
<tr>
<td>TPU/PP/MA-g-PP</td>
<td>-26</td>
<td>-15</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP</td>
<td>-24</td>
<td>-11</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP</td>
<td>-19</td>
<td>-7</td>
</tr>
</tbody>
</table>

Table 6.4. $T_g$ of compatibilised ether- TPU/PP (70/30) blends

<table>
<thead>
<tr>
<th>Material Composition</th>
<th>$T_g$ from Loss Modulus (°C)</th>
<th>$T_g$ from tan delta (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP 70/30</td>
<td>-39</td>
<td>-25</td>
</tr>
<tr>
<td>TPU/PP/MA-g-pp</td>
<td>-34</td>
<td>-18</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP</td>
<td>-32</td>
<td>-14</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP</td>
<td>-27</td>
<td>-10</td>
</tr>
</tbody>
</table>

Table 6.5. Storage modulus of compatibilised ester-TPU based blends

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Storage modulus, $E’$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-50°C</td>
</tr>
<tr>
<td>TPU/PP</td>
<td>7101</td>
</tr>
<tr>
<td>TPU/PP/MA-g-PP</td>
<td>7605</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP</td>
<td>8206</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP</td>
<td>10173</td>
</tr>
</tbody>
</table>
Figure 6.4 (a). Storage modulus (b). Log storage modulus of compatibilised ester-TPU based blends

Figure 6.4(c). Loss modulus (d). Tanδ of compatibilised ester-TPU based blends
Table 6.6. Storage modulus of compatibilised ether-TPU based blends

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>Storage modulus, $E'$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-50°C</td>
</tr>
<tr>
<td>TPU/PP</td>
<td>5489</td>
</tr>
<tr>
<td>TPU/PP/MA-g-PP</td>
<td>6116</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP</td>
<td>6613</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP</td>
<td>7763</td>
</tr>
</tbody>
</table>

Figure 6.5 (a). Storage modulus (b). Log storage modulus of compatibilised ether-TPU based blends
All the blends showed a sharp decrease in $E'$ around -60°C. The MA-g-PP compatibilised blends show an increase in storage and loss modulus at 5% compatibiliser loading compared to the uncompatibilised counterpart TPU/PP (70/30) at the same temperature. The higher value for storage modulus observed at this composition can be due to the increased interaction between TPU and PP phases upon the addition of compatibiliser. Thus it is important to note that there is a sharp increase in modulus with very small amount of the compatibiliser followed by a marginal decrease, as the copolymer content is increased above the equilibrium concentration. Thus addition of compatibiliser makes the blend technologically compatible, but molecular level miscibility is not achieved. At higher loading of compatibiliser, modulus value decreases. This is due to the formation of agglomerates of the compatibiliser molecule. This is in agreement with morphological observations seen in Figures 3.7 (a to d).
There is change in $T_g$ values due to TPU on adding MA-g-PP to the blend system. The two-step curves in the figure for the blends, is due to two-phase morphology indicating immiscibility. Thus the transitions due to TPU and PP phases indicate that addition of compatibilisers do not make the system single phase (Table 6.3). Or compatibiliser addition could not promote molecular level miscibility. This observation is in agreement with conclusions made by Paul [35] that if two polymers are far from being miscible, then no compatibiliser is likely to make the system single phase. In a completely immiscible system, the main role of the compatibiliser is to act as an interfacial agent. The effect of temperature on the storage modulus, loss modulus and $\tan\delta$ of MA-g-PP compatibilised blends is shown in Figure 6.4 and 6.5.

The $T_g$ corresponding to TPU transition is shifted to higher temperature upon compatibilisation. MA-g-PP with nanoclay compatibilised blends showed maximum shift. Nanoclay reinforcement, besides giving substantial increase in modulus and tensile strength, also functions as a surface modifier for TPU hard segments. The reduction in surface energy of hard segments is confirmed by AFM tests and contact angle measurements. The reduced interfacial tension between the thermoplastic polyurethane and the polypropylene due to the incorporation of nanoclay gives better compatible blends. Compatibilisation effect is further improved by introducing functionalised PP (MA-g-PP) in the nanoclay containing blends. At room temperature, the storage modulus value of the ester-TPU blend nanocomposite is more than that of the ether-TPU blend nanocomposite. As mentioned in the introductory chapter, the high polarity difference between thermoplastic polyurethane and polypropylene limits the miscibility of their blends. Nanoclay was used to reduce the surface energy of the TPU hard
segments and makes them more compatible with the non-polar PP. More miscible blends have been obtained by using MA-g-PP as the compatibiliser. Better dispersion of organoclay may be attributed to two reasons. Firstly, maleic anhydride forms hydrogen bonds with the hydroxyl groups of the silicate layers. Secondly, there is a possible chemical reaction between maleic anhydride and the urethane linkages in the TPU hard segments. Compared to the ether-TPU based blend nanocomposites, the ester-TPU blends show better miscibility as confirmed by DMA analysis. The clear difference between ester-TPU and ether-TPU is that ester-TPU has carbonyl groups both in the polyol segments as well as the TPU hard segments. This may lead to more extensive hydrogen bonding in the blend system thus improving the miscibility.

6.2.4 Effect of sequence of nanoclay addition on TPU/PP blend

In sequence I, TPU/C10A nanocomposites were prepared and subsequently blended with PP using MA-g-PP as compatibiliser. In sequence II, nanoclay was added to PP by similar extruder melt blending and subsequently melt blended with TPU using MA-g-PP as compatibiliser.

Compared to sequence II blend nanocomposites, the sequence I shows better miscibility. The clear difference between sequence I and sequence II is that the effect of nanoclay is fully utilized for changing the surface tension of TPU hard segment in sequence I. The hydroxyl group of silicate layers forms hydrogen bonding with the carbonyl group of TPU and maleic anhydride moieties leading to reduction in surface tension of TPU hard segment from 45 dynes/cm to 30 dynes/cm [50]. This change in surface tension favours for better dispersion of PP in TPU material, and also the hydroxyl group of the silicate layers forms hydrogen bonds with the carbonyl
groups of TPU and maleic anhydride moieties. In the case of sequence II, the
dispersion and the reaction of nanoclay with TPU was reduced since
nanoclay was first added to PP.

Table 6.7. Effect of sequence of nanoclay addition on $T_g$

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ (°C) from E”</th>
<th>$T_g$ (°C) from Tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP(nano)/MA-g-PP (Ester)</td>
<td>-22</td>
<td>-9.0</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP (Ester)</td>
<td>-19</td>
<td>-7.0</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP (Ether)</td>
<td>-29</td>
<td>-12.0</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP (Ether)</td>
<td>-27</td>
<td>-10.0</td>
</tr>
</tbody>
</table>

(a) Ester-TPU storage modulus  
(b) Ester-TPU loss modulus
Figure 6.6. Effect sequence of nanoclay addition on compatibilised TPU/PP blends

6.2.5 Cole-Cole plot

The Cole-Cole plot mapping dynamic mechanical data is a useful way for miscibility characterisation. This kind of plot was introduced by Han [65] in 1983 and later on was named as modified Cole-Cole plot by Harrel
and Nakayama [66-67]. G'' vs. G' representation in a complex plane gives a circular arc for a miscible blend [68-71].

Figure 6.7. The Cole-Cole Plot of different TPU/PP blends at a frequency of 10Hz.

Figure 6.7 shows the Cole-Cole plot that maps the relative contribution of the G'' response to that of G'. The curves of uncompatibilised as well as compatibilised blends drift from a semicircle due to the multiphase structure. It is seen that the compatibilised blends exhibits the highest values for G'. Similar reports have been made by Jafari et al. for in polyamide 6 (PA6)/styrene acrylonitrile (SAN) blends compatibilised by SAN-MA [72-74].

6.2.6 Degree of entanglement density

Degree of entanglement density (n) between polymer chains can be obtained from storage modulus data using the equation,
\[ n = \frac{G'}{6RT} \]  

(6.2)

where, \( G' \) is the storage modulus obtained from the plateau region of storage modulus versus temperature curves. \( R \) is the universal gas constant and \( T, \) is the absolute temperature. The values for degree of entanglement density between TPU and PP obtained at 10Hz. and 25°C are presented in Table 6.8. Addition of compatibiliser usually increases the entanglement between the homopolymers. This can be due to better adhesion between the blend components as a result of compatibilisation resulting in decrease of interfacial tension.

**Table 6.8.** Entanglement density of blends (moles/m²) measured at 25°C

<table>
<thead>
<tr>
<th>Blends</th>
<th>Entanglement Density (moles/m²)</th>
<th>Blends</th>
<th>Entanglement Density (moles/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU/PP 70/30 (Ester)</td>
<td>45</td>
<td>TPU/PP 70/30 (Ether)</td>
<td>44</td>
</tr>
<tr>
<td>TPU/PP/MA-g-PP (Ester)</td>
<td>175</td>
<td>TPU/PP/MA-g-PP (Ether)</td>
<td>60</td>
</tr>
<tr>
<td>TPU/PP(nano)/MA-g-PP (Ester)</td>
<td>221</td>
<td>TPU/PP(nano)/MA-g-PP (Ether)</td>
<td>78</td>
</tr>
<tr>
<td>TPU(nano)/PP/MA-g-PP(Ester)</td>
<td>270</td>
<td>TPU(nano)/PP/MA-g-PP(Ether)</td>
<td>130</td>
</tr>
</tbody>
</table>

Oommen et al.[45] reported that the entanglement density increases as a result of compatibilisation. Both the compatibilised blend series showed improvement in entanglement density values.
6.3 Conclusion

Dynamic mechanical analysis measurements were done on TPU/PP blends. The storage modulus of the blend decreased with increase in TPU content. Dynamic mechanical analyses were also performed to evaluate the nanoclay effect and MA-g-PP compatibiliser action in incompatible TPU/PP blends. Compatibilisation increased the storage modulus values of the system which is due to the fine dispersion of PP domains in the TPU matrix providing an increased interfacial interaction. Very specifically storage modulus, loss modulus and $\tan\delta$ were carefully measured for the systems and changes could be observed in these values for the systems compatibilised with MA-g-PP and nanoclay incorporation. The $\tan\delta$ curve of the blends showed a peak corresponding to the $T_g$ of TPU, which indicate that the glass transition temperature of TPU is affected by blending with PP using MA-g-PP as a compatibiliser and nanoclay incorporation. Ester-TPU(nano)/PP/MA blend nanocomposite was found to have very good overall performance and is a potential candidate for cost-effective, high strength applications of thermoplastic polyurethane. This is because maleic anhydride undergoes chemical reaction with the urethane groups in the TPU hard segments and also forms hydrogen bonds with the silicate layers of C10A. Ester-TPU with carbonyl groups both in the polyol segments and urethane hard segments, has more extensive hydrogen bonding than ether-TPU.

Various composite models were used to fit the experimental viscoelastic data. The kerner model was found closely suitable to fit with the experimental data. An improvement in entanglement density values showed better compatibilising action upon copolymer addition. Homogeneity of the blends was looked into by Cole-Cole analysis.
6.4 References


32. N. Papke and J. Karger-Kocsis, Polymer, 42, 1109 (2001)
36. R.H. Boyd, Polymer, 26, 1123 (1985)
54. F. Chavarria and D. R. Paul, Polymer, 47, 7760 (2006)


