Effect of Cloisite and modified Laponite clays on the rheological behavior of TPU–clay nanocomposites

A. K. Mishra · S. Mushtaq · G. B. Nando · S. Chattopadhyay

Abstract The effect of nanoclays (modified Laponite and Cloisite) on the dynamic modulus, dynamic viscosity, and relaxation time of thermoplastic polyurethane (TPU)-based nanocomposites is studied by using the dynamic mechanical rheometer in strain, temperature, frequency sweeps, and stress relaxation experimental modes. Cloisite 20A preferentially associates to the soft domains and dodecyl amine-modified Laponite RD favors the hard domains of the TPU, whereas cetyl trimethyl ammonium bromide-modified Laponite RD does not show any preference and gets distributed both in the hard and soft domains randomly. Cloisite-based nanocomposites, having longer diskette size, possess greater dynamic modulus and viscosity than Laponite-based ones. The change in modulus and viscosity of the nanocomposites over the range of frequencies registers a completely different behavior at different temperature regimes depending on the size of diskettes of the nanoclays and their distribution (before and after the softening of the hard domains). Addition of clay is found to increase the elastic component of stress relaxation of the TPU at 120°C. This behavior is more prominent in the case of Cloisite-based nanocomposites as compared to their Laponite-based counterparts. The morphology correlates well with the dynamic rheological properties of these nanocomposites.

Keywords Thermoplastic polyurethane · Nanocomposite · Morphology · Viscoelasticity and rheology

Introduction

Thermoplastic polyurethane (TPU) is a highly versatile polymer composed of hard and soft blocks. The hard and soft blocks become incompatible at lower temperatures and create phase separation to form hard and soft domains. The use of dynamic rheological techniques to investigate the phase transition behavior of polymeric systems has gained increasing interest. The rheological and viscoelastic measurements on TPU are important at least for two reasons. Firstly, rheological techniques can be used as noninvasive experimental tools (though indirect) for the investigation of the rich phase transition/relaxation behavior of this class of polymers. Secondly, rheology could be useful to investigate the effect of phase transition or relaxations on the processibility of TPU nanocomposites. Generally, TPUs show a low soft-segment glass transition temperature, a rubbery plateau, and finally the hard segment glass transition or crystalline melting above which final flow occurs. Most viscoelastic property measurements of TPUs at higher temperatures have employed temperature sweep mode of dynamic mechanical analysis (Kajiyama and MacKnight 1969; Bogart et al. 1983). However, the limitation involved in this experiment is that it ends when the sample begins to flow. Investigation of the rheological properties in the heating and cooling processes is important for polymer processing operations because TPU is mostly processed under
high temperature followed by slow cooling to shape the final product.

A direct consequence of the incorporation of nanofillers in molten polymers is the significant change in their viscoelastic properties. Since the linear dynamic rheological behavior of nanocomposites is sensitive to the structure, particle size, shape, and surface characteristics of the silicate phase, the rheological tool is intensively used to assess the state of dispersion of nanoparticles in the molten state.

Literature survey reveals that studies on polyurethane–clay nanocomposite involve the synthesis and characterization of the nanocomposite involving montmorillonite clay or its modified versions (Cloisite). A number of publications can be found involving the rheology of the TPU system as such (Lu and Kalyon 2003; Nichetti and Cossar 2005; Florez et al. 2005). However, a detailed study on the rheology of TPU–clay nanocomposite (TPUCN) is strikingly small in number.

The three varieties of nanoclay used in this work differ from each other in terms of size and type of modifier. Cloisite 20A (C) is a modified montmorillonite (a natural hectorite clay modified with dimethyl, dehydrogenated tallow, and quaternary ammonium chloride), but Laponite RD (L) is a synthetic hectorite. The chemical compositions of unmodified montmorillonite and L are $M_x(A_{14-x}Mg_x)Si_8O_{20}(OH)_4$ and $M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$, respectively. The length of the major axis of individual elliptical platelet or diskette of C varies from 150 to 250 nm, whereas it is nearly 25 to 30 nm in the case of L. The thickness of individual diskettes is approximately 1 nm for both varieties of unmodified clays. In this study, Laponite RD is modified by dodecylamine hydrochloride and cetyl trimethyl ammonium bromide (CTAB) to prepare two different types of modified Laponite clays. These three varieties of clay differ in the extent of modification and hard/soft segment preference as well.

This article focuses mainly on the effect of these three varieties of clays on the dynamic rheological properties of TPU with respect to strain, temperature, frequency, and time.

**Experimental**

**Materials**

Desmopan KU2 8600E (specific gravity of 1.11), which is a polyether-based TPU prepared from 4,4'-methylene bisphenyl diisocyanate, polytetramethylene glycol, and 1,4-butanediol, was kindly provided by Bayer Materials Science Pvt Ltd, Chennai. Laponite RD and Cloisite 20A were supplied by Rockwood Additives Ltd., UK. Cloisite 20A was used as received. However, Laponite RD was modified by two types of surfactants. Dodecyl amine and cetyl trimethyl ammonium bromide (used to modify Laponite clays) were obtained from Sigma-Aldrich, USA, and used without any further purification. Tetrahydrofuran (THF) and concentrated hydrochloric acid (Reagent Grade, Merck, Germany) were used as received.

**Modification of Laponite clay**

Laponite RD (L) was modified with cetyl trimethyl ammonium bromide (c) and dodecyl ammonium chloride (d) (prepared from the reaction between dodecyl amine and concentrated HCl), by using the standard ion exchange process to increase the hydrophobicity of the clay and also to increase the interlayer spacing of the clay platelets. The process of modification was reported in details elsewhere (Mishra et al. 2008). Laponite RD modified by “c” and “d” are designated by cL and dL, respectively. Cloisite 20A is designated as C. The amounts of modifier present in the modified clays (as calculated by thermogravimetric analysis) are 32.9%, 14.8%, and 12.6% for C, dL, and cL, respectively.

**Preparation of TPU–clay nanocomposite**

A 20% solution of TPU was prepared in THF. Calculated amount of clay (C, dL, or cL) was mixed with THF and sonicated for 30 min (subjected to ultrasonic vibration of frequency 30 kHz and power of 250 W) and then added slowly to the TPU solution maintaining gentle stirring. Stirring was continued for another 15 min. The mixture was then sonicated for 15 min to make homogeneous dispersion of clay into the TPU matrix. It was then casted on a flat petridish and allowed the solvent to evaporate at room temperature. After complete removal of the solvent at room temperature, sample was kept in a vacuum oven at 70°C till constant weight was achieved. Control TPU sample was prepared by following the same procedure without the addition of clay to accomplish a better comparison, and it is designated as T0. The nanocomposites so prepared are designated as Txy, where T stands for TPU, x stands for weight percent of clay used (1–5%), and y stands for type of clay incorporated (C, dL, and cL).

In general (without mentioning weight percent of clay used), the nanocomposites prepared with C, dL, and cL are designated as TC, TdL, and TcL, respectively.
Characterization

Transmission electron microscopy

Transmission electron microscopy (TEM) of the solution-casted film and the annealed samples (equilibrium phase-separated morphology) was performed in a high-resolution TEM of Jeol JEM 2100 make, Japan, after microtoming the samples (~50-nm section) using Leica Ultracut UCT (Austria) microtome, equipped with a diamond knife. The annealed TPU–clay nanocomposite samples were kept at 140°C for overnight in a vacuum oven and slowly cooled down to room temperature for another 8 h under nitrogen atmosphere to ensure the development of equilibrium morphology.

Dynamic rheological measurements using RPA

Dynamic rheological behaviors of the samples under sinusoidal shear deformation were studied on a rubber process analyzer (RPA), RPA-2000 of Alpha Technologies, USA. The details about the instrument have been described elsewhere (Hui et al. 2009).

Strain sweep experiment was carried out at 40°C and 140°C at 0.5-Hz frequency. Strain sweep at 40°C was performed for evaluating the changes in linear viscoelastic properties due to the addition of modified clay particles, whereas strain sweep at 140°C was carried out only to measure the linear viscoelastic region (LVR). The percent error associated with this experiment was within ±2%. Forward temperature sweep experiment was carried out within a temperature range of 130°C to 220°C to access the dynamic rheological behaviors at a constant frequency of 0.5 Hz and 1% strain. The average variation in storage modulus and viscosity was within ±3%. Frequency sweep (0.033–30 Hz) was carried out at two different temperatures (140°C and 170°C) at 1% strain, which was found to be within the LVR for the matrix (Fig. 1). The two temperatures were selected relying on the differential scanning calorimetry thermogram (corresponding to the destruction of the short range and long range ordering; semicrystalline melting and final hard-segment melting, respectively; Mishra et al. 2008). The percent errors associated with the dynamic viscosity or storage modulus measurements were within ±1% and ±2% at 140°C and 170°C, respectively. Stress relaxation experiment was carried out at 120°C to access the elastic to viscous response of the nanocomposites at the temperature close enough for the destruction of the short range ordering in the hard domain. In stress relaxation, the samples were deformed by 69.75% shear strain, and the stress decay was monitored over 120 s (with a preheat time of 60 s). The percentage errors associated with the stress relaxation experiment were within ±2%.

In stress relaxation experiment, RPA measures the absolute torque (stress) response after a step in strain (Soltani and Sourki 2005).

In all the cases, the samples were loaded once the required temperature is reached, and samples were equilibrated before the specific test.

Results and discussion

Transmission electron microscope

Figures 2 and 3 represent the TEM photomicrographs of the original solvent-casted samples and annealed samples, respectively. Figure 2 shows that TC follows a more exfoliated structure compared to other varieties of clay. TdL and TcL exhibited a combination of a loosely aggregated to intercalated structure throughout the matrix. At higher clay content (more than 5%), the size scales of the aggregates increase in the case of dL, whereas it remains nearly indifferent with cL. Distribution of C and dL with the soft and hard domains, respectively, is already reported in our earlier communication (Mishra et al. 2008). The same is further confirmed from the TEM photomicrographs of the annealed samples (as a result of the self-organization of the hard domains). In Fig. 3, the spherical gray-colored structures represent the ordered hard domain, the darker (black) spherical structures represent the hard domain with clay platelets, and the linings reveal the distributed clay platelets. It is observed that dL preferentially associates with the hard domain, C
Fig. 2  TEM photomicrographs of the solution-casted TPUCNs a T5C, b T3dL, and c T3cL.

associates with the soft domain, whereas cL gets distributed in both the hard and soft domains randomly.

Thus, the generalized morphologies of the TPU nanocomposites are as depicted in Scheme 1.

Fig. 3  TEM photomicrographs of the annealed TPUCNs a T5C, b T3dL, and c T3cL.

Strain sweep

The amplitude-dependent decrement of the dynamic storage modulus of filled polymers (at low dynamic
The Payne effect (Payne 1965) is often referred as the Payne effect (Payne 1965). In case of the neat TPU, storage modulus shows considerable strain dependencies even at lower strains (nonlinearity due to a polymer structure), whereas several factors, like polymer–filler interaction, filler–filler interaction, available surface area of filler in the matrix, etc., can affect the strain dependencies of polyurethane–clay nanocomposite (TPUCN; Fröhlich et al. 2005). Percentage drops in modulus values at different strain percent (1, 7, 20, 70, and 100) are compared with the initial modulus for the neat TPU and TPUCNs (Table 1).

![Scheme 1 Morphology of modified clay in TPU matrix](image)

The greater amount of drop in modulus in the case of TC as compared to those of TdL and TcL can be ascribed to the soft segment preference of C in combination with its greater diskette size. However, the stronger Payne effect of the TcL as compared to those of TdL is probably due to their random distribution in both hard and soft domains (Fig. 3). This is in agreement with our earlier explanation as given in Section “Transmission electron microscope”.

A schematic representation explaining the decrement in the modulus of neat TPU at different strain levels is shown in Scheme 2. However, the effect of strain for various nanocomposites is represented in Scheme 3. The increase in strain level from low to high mainly transfers the stress from soft segment to the hard domain, respectively (Scheme 1).

![Table 1 Percentage decrease in modulus value as compared to the initial modulus at different strain levels at a frequency of 0.5 Hz](image)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% drop in modulus value at different strain %</th>
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<tr>
<td></td>
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</tr>
<tr>
<td>T0</td>
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</tr>
<tr>
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<td>6.2</td>
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<td>T1dL</td>
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<td>T3dL</td>
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<td>T5dL</td>
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<tr>
<td>T1cL</td>
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<td>T3cL</td>
<td>12.8</td>
</tr>
<tr>
<td>T5cL</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Drop in modulus increases with the increase in C content in the TPU matrix, and the percentage drop in modulus is independent of strain at higher levels (>20%). The maximum decrease in modulus value is observed with T5C. The decrease in modulus with the increase in amount of filler is a quite obvious phenomenon and observed by many researchers (Lion
A gradual increase in percent decrement in modulus at higher strain levels for all samples indicates that other mechanisms of deformation as mentioned above gradually contributes over filler structure breakdown. For dL, maximum decrement in modulus is observed with T3dL. It is due to the greater amount of filler–filler and polymer–filler interactions at this particular clay content. The decrement in modulus value in the case of T5dL is even less than the neat TPU. This is possibly due to the combined accomplishment of the ball bearing action (spherical aggregate formation, which can lead to rolling effects in shear deformation) and the hard domain preference of dL (due to the hard domain preference, the clay aggregate destroys the partial crystallinity in the hard domain, as revealed from the wide angle XRD section in our earlier publication; Mishra et al. 2008). In the case of TcL, the decrement in modulus value remains nearly the same uncaring of clay content. This is due to the similar size scale of aggregation at lower and higher clay contents and the random distribution of cL in hard and soft domains (as observed in the equilibrium bulk morphology of such composites).

Temperature sweep

The temperature range of 130°C to 220°C was chosen to understand the effect of clay on the modulus–temperature behaviors at higher temperature regions. The study was carried out at a heating rate of 6°C/min. In all the cases, there is a drastic reduction in both storage ($G'$) and loss ($G''$) modulus values from 140°C to 170°C followed by a comparatively slower and monotonous reduction up to 220°C (Fig. 4). The drastic reduction in modulus value is ascribed to the transition from the rubbery plateau to flow behavior, and the terminal plateau corresponds to the restriction in flow.
It is observed that all the nanocomposites possess lower storage modulus compared to neat TPU for 1% clay content (Table 2) at the range of temperatures studied here (130–220°C). This is possibly due to the change in molecular relaxation due to which shear thinning events dominates at lower clay content. However, an increasing trend in modulus values with the increase in clay content in all the cases is also noticed.

Figure 4 shows the storage and loss modulus values of neat TPU and TPUCN with 3 weight percent of various clays. Overall, TC possesses higher storage and loss modulus values as compared to their Laponite counterparts at the whole range of temperatures. Highest modulus value of T3C at the lower temperature region is possibly due to the longer diskette size, greater exfoliated structure (resulting in a greater polymer–filler interaction), and soft domain preference of C (due to the combined effect of inorganic and organic hard domains). Among the Laponite-based nanocomposites, T3cL registers higher storage modulus values as compared to T3dL at low temperature regions (up to 170°C). This is again due to the combined effect of organic and inorganic hard domains present in the case of TcL (which is absent in the case of dL along with the destruction in crystallinity of the hard domain; Mishra et al. 2008). However, at the higher temperature region, no significant change in modulus is observed. This is due to the complete melting of the hard domain due to which TPU looses its stiffness.

Frequency sweep

The changes in dynamic storage moduli and complex viscosity values with angular frequency were monitored. A monotonous decrease in complex viscosity (η*) and a monotonous increase in dynamic storage modulus (G′) are observed with the increase in frequency, independent of the temperatures studied here (140°C and 170°C). In general, two different sorts of behavior are encountered at two different temperatures. At 140°C, G′ > G″, whereas at 170°C, G″ > G′, for
Effect on complex viscosity at 140°C

From the time sweep experiment of T0, T3C, T3dL, and T3cL at 140°C (Fig. 6a), it is evident that the modulus values of T0 remain nearly the same with respect to time. However, the modulus values increase up to an order of 30–40 kPa for the filled systems. The effect is more prominent in the case of T3C as compared to T3dL and T3cL. This is possibly because of the mutual reorganization of nanoclays and TPU molecules thereby enabling optimum secondary interactions between the filler and polymer. However, time sweep above 150°C (not shown) shows nearly marginal change in the modulus values with respect to time. Thus, beyond 150°C (Fig. 6b), equilibrium reorganization is subdued.

Figure 7a–c displays the complex viscosity vs. frequency plots at 140°C. It is observed that the complex viscosities ($\eta^*$) of TC, TdL, and TcL are of the same order of magnitude with those of the neat TPU up to 3% clay content (Fig. 7a–c). However, they are always higher than those of the neat TPU for 5% clay content.
Fig. 7  a Complex viscosity vs. frequency plot of TPUCNs with 3% clay content at 140°C and 1% strain. b Complex viscosity vs. frequency plot of TC at 140°C and 1% strain. c Complex viscosity vs. frequency plot of TdL at 140°C and 1% strain.

The η* values of T1C are always greater than those of T1dL and T1cL (e.g., η* values of T1C, T1dL, and T1cL at 3.33 Hz are 14,917, 12,263, and 13,134 Pa-s, respectively). However, at 3% and 5% clay content, the η* values of TC are lower than those of TdL up to a frequency of 1.67 Hz, and the corresponding values are greater at higher frequencies. Similarly, the η* values of TC at 3% and 5% clay content are lower than those of TcL up to 3.33 Hz, and the values are greater at higher frequencies. The greater η* value of T1C as compared to that of T1dL and T1cL is mainly due to the more exfoliated morphology (also due to soft segment preference and greater size), resulting in higher polymer–filler interaction. However, the frequency-dependent decrease of initial viscosity also stems from the local segmental dynamics. However, the increased modulus values at a higher-frequency region are due to the mutual reorganization of C and TPU molecules. The increased η* value at higher clay content is mainly due to the greater aggregation tendency of dL and cL as compared to that of C (as described in Section “Transmission electron microscope”).

The η* values of TcL are greater as compared to their TdL counterparts at lower clay content (up to 3%). However, the reverse is true at 5% clay content. The effect at lower clay content is ascribed to the hard domain preference of dL. However, the increased η* value at higher clay content is possibly due to the reduced degree of preference of dL to hard segments at higher clay content.

Scheme 4 represents the effect of frequency on neat TPU at 140°C. At a low-frequency region, sufficient time is allowed for the stress to elongate the soft domain to a maximum extent. However, at a high-frequency region, due to unavailability of time, stress gets concentrated mostly on the hard domain regions. Similarly, for the nanocomposites, at a low-frequency region, sufficient time is allowed for the stress to elongate the soft domain to a maximum extent (Scheme 5). At a high-frequency region, due to paucity of time, stress gets concentrated mostly on the hard domain regions, and clay aggregates. Thus, a frequency-dependent spectrum has been obtained especially at 140°C. The shear thinning event especially at lower clay content can be explained based on the presence of the more exfoliated structure and the presence of the modifier.

independent of the frequency range studied here (0.033 to 30 Hz). The lower η* value at lower clay content is ascribed to the contribution of the shear thinning event due to the change in molecular relaxation (this is in agreement with our earlier observations in Section “Temperature sweep”). However, greater η* value at 5% clay content is due to the increased state of aggregation. At higher clay content, the extent of intercalated structures possibly diminishes and the shear thinning events are restricted by preponderance of larger scale aggregated structures (Ray 2006). The slight increase in complex viscosity value in the case of T3C as compared to that of the neat TPU at a higher-frequency region may be due to the mutual reorganization of nanoclays and TPU molecules, thereby enabling optimum secondary interactions between the filler and polymer in the case of C (as seen in the time sweep experiment).
on the clay surface. TC registers a higher $\eta^*$ value as compared to its Laponite-based counterparts possibly due to the greater diskette size of clay and restoration of the hard domain ordering to maximum extent. However, lowest complex viscosity in case of TdL can be ascribed to the destruction of the hard domain ordering (due to the hard domain preference of clays, Mishra et al. 2008, XRD section).

**Effect on complex viscosity at 170°C**

Figure 8a, b displays the complex viscosity vs. angular frequency plots at 170°C of the nanocomposites. At 170°C, $\eta^*$ values of TPUCNs follow an increasing trend with the increase in clay content independent of the type of clay used. At 170°C, the long range ordering in the hard segment softens. Hence, most of the contributions toward the viscosity and modulus are attributed to the amount of fillers present in the matrix, following the Guth–Gold equation (hard or soft domain preference should not matter anymore).

At this temperature, $\eta^*$ values of TC are higher than those of Laponite-based nanocomposites with equivalent clay content. This can be ascribed to the greater size of individual diskette of C as compared to that of Laponite. On an average, the $\eta^*$ values for TcL are higher as compared to those for TdL at this temperature. This is possibly because of the greater state of aggregation of dL as compared to that of cL. At 170°C, polymer chains are much labile, and the presence of hard domain is also diminished. Application of even small amount of stress would enable the clay particles to move closer to each other. Thus, the size of clay particles and their mutual degree of affinity are much more influential at this temperature.

The flow behavior index ($n$) was calculated by using the power law model,

$$\eta^* = k \gamma^{n-1}$$

where, $\eta^*$ is the complex viscosity, $k$ is the consistency index, and $\dot{\gamma}$ is the shear rate.

Therefore Eq. 1 can be rewritten as

$$\log \eta^* = \log k + (n-1) \log \dot{\gamma}$$

The slope of log$\eta^*$ vs. log$\dot{\gamma}$ plot gives the value of $n$. The values are given in Table 3.

A pseudoplastic behavior is observed in all the cases. The $n$ value is always higher than the neat TPU in all the nanocomposites irrespective of the type of clay and amount of clay. This shear thinning behavior can be ascribed to the assistance in relaxation due to the presence of modifiers on the clay surface. A similar trend in shear thinning behavior is already mentioned earlier (Sections “Temperature sweep” and “Effect on complex viscosity at 140°C”). The $n$ value is found to follow the order TC > TcL > TdL at 140°C. This can be ascribed to the hydrophobicity of the modifiers present on the clay surface. However, $n$ values of the nanocomposites are comparable at 170°C. The consistency index $k$ (not shown) is found not to follow any particular trend at both the temperatures.

**Effect on modulus at 140 and 170°C**

Figure 9a, b shows the storage modulus vs. frequency plots of the 3% clay-filled nanocomposites at 140°C and 170°C, respectively. It is observed that the storage moduli of TC, TdL, and TcL at 140°C are lower or at the same order of magnitude than those of the neat TPU up to 3% clay content (Fig. 9a). However, they are always higher than those of the neat TPU for 5% clay content.
independent of frequency range studied here (0.033 to 30 Hz). Overall, at 170°C, the value of the storage modulus of the nanocomposites is higher than that of the neat TPU (Fig. 9b). An increasing trend in the storage modulus value is observed with the increase in the clay content, and this behavior is independent of the temperature. Here, also similar reasons are applicable as already mentioned in earlier sections (Sections “Effect on complex viscosity at 140°C” and Effect on complex viscosity at 170°C).

Stress relaxation

Stress relaxation experiment was carried out at 120°C (the temperature close enough for the destruction of the short range ordering in the hard domains, Mishra et al. 2010).

A brief theoretical background on stress relaxation

To realize the behavior of stress relaxation, the Maxwell model (e.g., a spring of modulus $G$ and a dashpot of viscosity $\eta$ in serial combination) is frequently used. However, this model is not adequate to describe the molecular relaxations (e.g., glass transition or Brownian motion etc.), especially in the case of a system like TPU because of complex combinations of the several contributing units.

The Maxwell model describes the stress relaxation behavior of simple amorphous polymers qualitatively (for a singular relaxation). The expression for the stress relaxation in shear using the simple Maxwell model is

$$G = G_0 e^{-t/\tau}$$  \hfill (3)
Fig. 8  a Complex viscosity vs. frequency plot of TPUCNs with 3% clay content at 170°C and 1% strain. b Complex viscosity vs. frequency plot of TC at 170°C and 1% strain.

where \( G = \) storage modulus at time \( t \) in seconds and \( G_0 = \) initial storage modulus and

\[ \nu = \frac{1}{\tau} \]  \hspace{1cm} (4)

where \( \tau \) is the characteristic relaxation time and \( \nu \) is the relaxation frequency.

Even a particular relaxation process of a simple amorphous polymer does not occur at a singular time, but it happens over a distribution of time. The generalized Maxwell model (as depicted below) can be applied to such systems for qualitative analyses as:

\[ G = n \sum_{i=1}^{\infty} G_i e^{-t/\tau_i} \]  \hspace{1cm} (5)

Various \( G_i \)'s can be replaced by a continuous function, \( G(\tau) \), of the relaxation time (to integrate the process), where this function is called a distribution of relaxation times. In addition to the distribution \( G(\tau) \), one often refers to \( H(\tau) \), which is defined as:

\[ H(\tau) = \tau G(\tau) \]  \hspace{1cm} (6)

However, for this study, the simple Maxwell model has been used to capture the instantaneous stress relaxation time only (due to poor \( R^2 \) value at longer time).

**Table 3** Flow behavior index \( (n) \) at 140°C and 170°C

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Flow behavior index ( (n) ) at</th>
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<tr>
<td></td>
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<tr>
<td>T0</td>
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<tr>
<td>T1C</td>
<td>0.20</td>
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<tr>
<td>T3C</td>
<td>0.26</td>
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<td>T5C</td>
<td>0.23</td>
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<tr>
<td>T1dL</td>
<td>0.19</td>
</tr>
<tr>
<td>T3dL</td>
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<td>T3cL</td>
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<tr>
<td>T5cL</td>
<td>0.21</td>
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</table>

Fig. 9  a Storage modulus vs. frequency plot of TPUCNs with 3% clay content at 140°C and 1% strain. b Storage modulus vs. frequency plot of TPUCNs with 3% clay content at 170°C and 1% strain.

Instantaneous (0.1 s) and 30-s stress relaxation times at 120°C

The \( \tau \) value was calculated from the plot of time vs. modulus (Fig. 10), by using Eq. 3. A very good correlation coefficient (\( R^2 \) value > 0.90) is observed up to
0.1 s time of relaxation. For longer time of relaxation, equation could not be fitted with the experimental result. Hence, the $\tau$ value was calculated up to 0.1 s and is given in Table 4. Although the $\tau$ value within the fraction of a second (0.1 s) does not provide a clear picture of the flow behavior of the TPU as a whole, rather it gives insight about the instantaneous relaxation (equivalent to the running extrudate swell in steady-state capillary rheology). However, to study the effect upon prolonged time (equivalent to the equilibrium extrudate swell; Hui et al. 2009), the $\tau$ value at 30 s was calculated. The values so obtained are given in Table 4 ($R^2$ values of the relaxation time at 30 s are not tabulated, as the values are calculated directly by using Eq. 5, considering the initial modulus to be $G_0$ and the modulus value at 30 s to be $G$). It is observed that both instantaneous relaxation time and the relaxation time after 30 s are higher with the neat TPU as compared to those of the nanocomposites (Table 4).

This suggests that addition of nanoclay increases the elastic component of viscoelastic behaviors at 120°C. $\tau$ values are marginally lower in case of Cloisite-based nanocomposites as compared to their Laponite-based counterparts. However, the values are nearly similar in the case of TdL and TcL. Relaxation time at 30 s also follows a similar trend. The higher $\tau$ values for the Laponite-based TPU nanocomposites as compared to those for TC can be ascribed to the longer length scale of aggregation. This phenomenon is in accordance with the precedent results on longer time-dependent mechanisms of relaxation of Laponite-based dispersions (Pignon et al. 1998; de Bruyn et al. 2008) that have been ascribed to aggregation phenomena at different length scales from nanometer to micrometer length scales. For TC, its preference to the soft segments and more exfoliated morphology in the TPU matrix increase the elastic component of relaxation leading to diminished $\tau$ values.

### Conclusions

The dynamic rheological behaviors of TPU–clay nanocomposites have been explained on the basis of equilibrium morphology obtained from TEM observations. Cloisite-based nanocomposites register greater decrement in modulus as compared to their Laponite counterparts, over the percent strain owing to the greater size and soft segment preference of Cloisite. Among the Laponite RD-based nanocomposites, the CTAB-modified Laponite RD-based TPU nanocomposites display stronger Payne effect as compared to the dodecyl ammonium-modified counterparts due to the hard segment preference of the dodecyl ammonium-modified Laponite. In frequency sweep experiment, it is found that $G' > G''$ at 140°C, whereas $G'' > G'$ at 170°C, for all the nanocomposites (irrespective of the frequency). Cloisite-based nanocomposites register greater $\eta^*$ values as compared to Laponite RD-based counterparts irrespective of the temperatures. This is again ascribed to the greater size and greater polymer–filler interactions. Hard/soft segment preference of nanoclays is highly reflected at 140°C, but aggregation tendency of clay prevails at 170°C. The addition of clay is found to increase the elastic component of stress relaxation for the TPU at 120°C. This behavior is more prominent in the case of Cloisite-based nanocomposites as compared to their Laponite-based counterparts. Overall, the size of nanoclay and morphology of the nanocomposites play vital roles in determining the rheology of TPU–clay nanocomposites.

### Table 4

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Instantaneous relaxation time (s) (fitted up to 0.1 s)</th>
<th>Equilibrium relaxation time (s) (at 30 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>0.27 (0.91)</td>
<td>24.9</td>
</tr>
<tr>
<td>T1C</td>
<td>0.22 (0.93)</td>
<td>21.9</td>
</tr>
<tr>
<td>T3C</td>
<td>0.20 (0.93)</td>
<td>20.0</td>
</tr>
<tr>
<td>T5C</td>
<td>0.19 (0.92)</td>
<td>19.3</td>
</tr>
<tr>
<td>T1dL</td>
<td>0.24 (0.93)</td>
<td>22.0</td>
</tr>
<tr>
<td>T3dL</td>
<td>0.24 (0.93)</td>
<td>22.5</td>
</tr>
<tr>
<td>T5dL</td>
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</tr>
<tr>
<td>T1cL</td>
<td>0.24 (0.93)</td>
<td>23.4</td>
</tr>
<tr>
<td>T3cL</td>
<td>0.23 (0.94)</td>
<td>21.9</td>
</tr>
<tr>
<td>T5cL</td>
<td>0.23 (0.93)</td>
<td>21.8</td>
</tr>
</tbody>
</table>

*Values given in the parenthesis represent the correlation coefficients*
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References


