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What is This?

Effect of soft segment and clay volume fraction on rate dependent damping of polyurethane and polyurethane-clay nanocomposites

Trisha Sain[1], Bongjun Yeom[2], Anthony M Waas[3] and Ellen M Arruda[4]

Abstract

Amorphous polymers have been extensively used for energy dissipative applications due to their relatively low density and controllable rate dependent damping. In general, molecular mobility depends on the rate of applied loading and the ambient temperature, and results in a wide variety of mechanical properties. The variation in the macromolecular chain dynamics can be obtained by altering the chemical architecture and morphology of the constituent monomers. The present study is focused on finding a correlation between the chemical structure of the constituent monomer and the rate dependent viscous damping of the macromolecules. Polyurethane (PU) made up of isophorone diisocyanate (IPDI) and polycaprolactone diol (PCL) is considered to estimate the effect of soft segments (diol content) on damping property of PU. A linear viscoelastic mathematical model (based on standard-linear solid (SLS) model) is used to extract the rate dependent relaxation time constants for the materials. It is found that increasing the soft segment content in the PU does not improve damping limitlessly. Beyond a critical percentage of soft segment content, characteristic relaxation times have a significant drop. Further, the analysis is extended for PU-clay nanocomposites and a correlation between the clay volume fraction and relaxation constants is established. The study will help to choose and design PU and volume percentage of clay nanoparticle for manufacturing PU-clay nanocomposites with desired damping property.

Keywords

Polymer nanocomposites, viscoelasticity, rate dependent damping, characteristic relaxation times

Introduction

The concept of integrated computational material design relies on developing a computational tool to predict the correlation between the constituent property and macroscopic response of the materials. In the present study, a computational model is developed to extract the relation between morphology of the chemical constituents of polyurethane (PU) and PU-clay nanocomposites and their rate dependent viscoelastic property.

To control the physical properties of a polymer by altering their constituent monomers and crosslinking agents, is an active research topic of the material research community.[1–4] Numerous publications pertaining to the structure–property relationships of the polymers have been reported in polymer

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chemistry literature. Damping property of a polymer is essentially governed by different relaxation process within the macromolecular network and several mechanisms can influence the rate dependent nature of these relaxations. Hence, to interpret the change in damping due to the change in morphology of the polymers and the applied strain rate, it is useful to track the change in relaxation times which can be measured or determined macroscopically. In an ongoing study[5] on designing an impact proof helmet using layered materials, it has been shown that an oncoming blast wave can be attenuated or trapped effectively using viscous materials with extremely fast relaxation time constants. Similar studies focusing on a specific application of polymeric materials demand the usefulness of constituent optimization to maximize or attenuate certain mechanical properties. In order to manufacture such materials this study focusses on how the variation in chemical constituents (relative weight fractions of the monomers and the volume fractions of clay nanoparticles) alter the rate dependent relaxation behavior of the polymer or polymer based nanocomposites.

In particular, PU possesses a distinct microdomian structure which is phase separated due to the thermodynamic incompatibility between the soft and hard segments. The soft segments, having a very low glass transition ($T_g < T_{room}$) forms a rubbery disordered matrix state, in addition to hard segments that are below their T_g at operating condition and have a crystalline or semicrystalline microstructures. The degree of microphase separation influences the mechanical and viscoelastic properties of the PU. If two domains are well phase separated, T_g of the PU will coincide with T_g of the soft domain ($T_g << T_{room}$) and therefore the material can behave like a viscous fluid at room temperature. In order to design a PU with high enough viscous damping and simultaneously useful for mechanical application, T_g of the resulting material should be near or around room temperature. For high rate applications, the objective is to arrest stress waves generated due to an impulse. Therefore, as mentioned in Rahimzadeh et al.'s[5] study, characteristic relaxation times of the polymers have to be much faster for the material to be effective in energy dissipation at a faster rate. In order to identify or optimize the constituent properties to result in a superior macroscopic response, the present study focusses on a particular type of PU with various percentages of soft segment content (W_s). PUs are assumed to have multiple relaxation processes governed by various molecular movements depending on the time scales involved in the deformation and each of these relaxation process is characterized by a relaxation time (τ_j) and an associated modulus (G_j). Considering standard-linear solid model which is a physical model to describe viscoelastic relaxation,[6,7] a

spring (with shear stiffness G_j) representing bending and stretching of the intermolecular bonds is used in conjunction with a viscoelastic dashpot (viscosity modeled with relaxation time τ_j) to represent the intra-chain sliding. The PU samples with various W_s content has been tested in a dynamic mechanical analyzer (DMA) under frequency sweep condition to measure frequency dependent storage modulus and $\tan\delta$. The relaxation times are then extracted using these experimental DMA data through a nonlinear least-square curve fitting approach as explained later.

It is observed that beyond a critical weight percentage of W_s, damping in the PU drops and correspondingly relaxation times also increase. There is a significant change in relaxation characteristics for PU with higher W_s. Furthermore, to observe the effect of clay volume fraction on the PU-Montmorillonite (PU-MTM) nanocomposites behavior, PU-MTM samples are prepared with three different clay volume fractions and experimentally characterized. To explain the fundamental mechanism responsible for the improvement in PU-MTM nanocomposite properties, the effect of clay on microphase separation of PU has been investigated by several researchers and the current state of art remains inconclusive.[8,9] It was reported that the degree of microphase separation in the hard segments decreased with increasing amount of clay, but reached a plateau at 5%wt of MTM concentration. However, Dai et al. found that the degree of microphase separation first increased with the clay ratios in the PU matrix and then decreased. The present observation suggests a trend of decreasing degree of microphase separation as the volume fraction of clay increases, which was manifested by a drop in damping measurement at room temperature. However, it is also seen that the trend saturates beyond a critical percentage of clay volume fraction with an irregular increase in characteristic relaxation times. The phenomenon has been explained with the argument of binding of the clay particles with the PU segments. In order to validate the proposed study, more experiments related to high loading rates and thermal characterization of the materials are currently underway.

Experimental and numerical characterization of PU and PU/MTM nanocomposites

In the present study, several forms of PU are manufactured by changing the relative weight fractions of the constituent monomers by reacting diisocyanate with alcohol (or macrodiols). The diols are essentially the long chain macromolecules and considered as soft segments, whereas the diisocyanates are the hard segments which form physical crosslinks within the soft

segments. In the present case, isophorone diisocyanate (IPDI, a small molecule organic compound, sometimes found in semicrystalline form) is used with polycaprolactone diol (PCL with an average molecular weight of Mw = 530 and $T_g \approx -60°C$). Ethylene diamine (EDA) is used as chain extender and *N*-methyl diethanolamine (NMDA) is used to functionalize IPDI to increase the crosslinking points. The variation in weight percentage of the chemical constituents is as given in Table 1.

By changing the relative weight percentage of the soft segments (W_s) results in an alteration of the macroscopic stiffness of the PU and also the relaxation characteristics of the macromolecules. Typically, the soft segments provide elasticity and flexibility while hard segments offer physical crosslink sites and prevent whole scale macroscopic viscous flow in the

Table 1. Details of the chemical constituents used to manufacture samples of PU.

Name of the sample	Molar ratio of the constituents (IPDI:PCL:NMDA:EDA)	% weight of soft segment (W_s)
PN1	4.3:1:2.3:1	27.1
PN2	5:2:2:1	42
PD1	4.5:2:1.5:1	46
PN3	4:2:1:1	48.4
PN4	6:4:1:1	57.4

macromolecules. Hence, it might appear obvious that by increasing soft segment weight percentage one can improve the flexibility of the chains and amplify the viscous flow of the polymer. However in the present study, experimental measurements of damping (tan δ) show a critical percentage of soft segment beyond which no significant improvement in damping was observed. Figure 1(a) shows the experimental measurements of tan δ as a function of frequency for all the PU samples. It is seen that tan δ values do not improve with increase in soft segment content beyond $W_s = 48.4\%$. Assuming linear viscoelasticity prevails in the material response, following SLS formulation the complex shear modulus as a function of sinusoidal loading frequency (ω) is given by:

$$G^*(\omega) = (G_0 - G_\infty) + \sum_{j=1}^{N_b} \frac{G_j i\omega\tau_j}{1 + i\omega\tau_j} \quad (1)$$

In the above equation, N_b represents the total number of molecular mechanisms involved in viscous damping triggered over frequency range ω. Theoretically $N_b \rightarrow \infty$ for a macromolecule's response to represent accurately. However depending on the rate of deformations extremely fast and slow relaxations never get activated during a mechanical stress bearing application of the polymer. Moreover, depending on the range of frequency measured in DMA only a finite range of
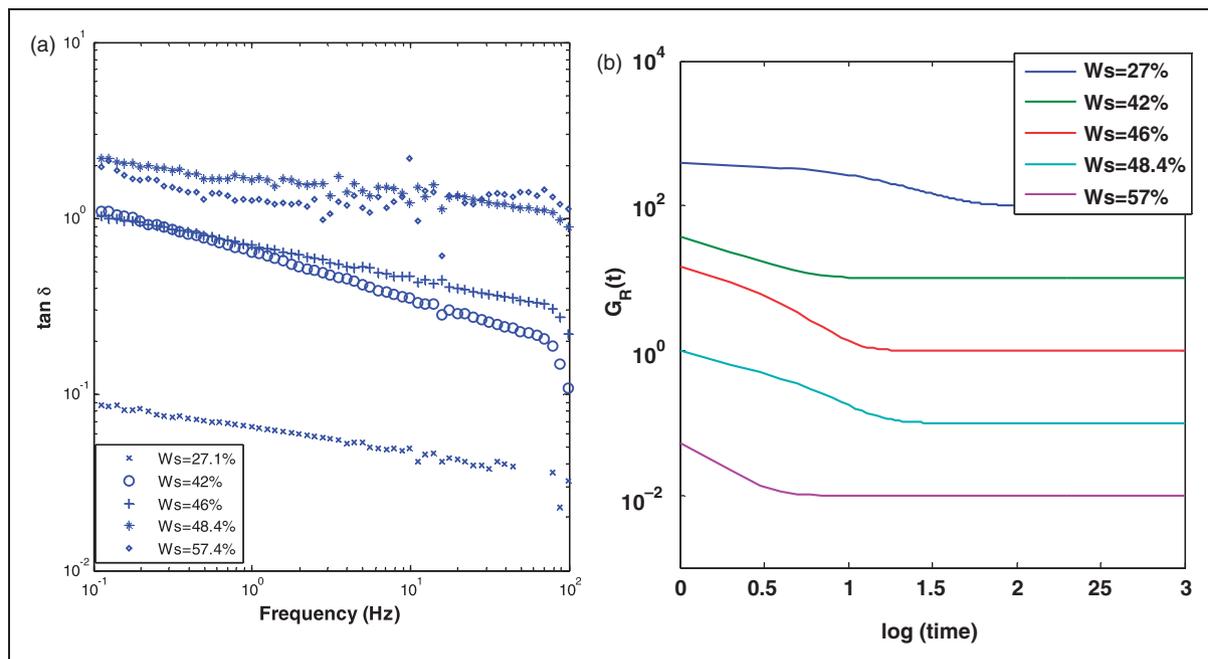

Figure 1. (a) Experimental frequency sweep measurement of tan δ at room temperature for PUs with different soft segment content, (b) relaxation modulus for all the PU's with various soft segment content.

relaxation characteristics can be extracted in a physical experiment. Hence in the present study N_b is assumed to be finite and its specific value is considered by assuming a statistical criterion of good fit as explained later.

Following equation (1), viscoelastic loss factor ($\tan\delta$) can be written as

$$\tan\delta = \frac{\text{img}(G^*(\omega))}{\text{Re}(G^*(\omega))} \qquad (2)$$

Hence the loss factor can be expressed as a function of τ_j's and G_j's. A nonlinear least squares curve fitting approach is used between experimental frequency sweep measurement of $\tan\delta$ and equation (2) to determine τ_j's and G_j's. To assess the goodness of fit and decide an exact value for N_b, the sum of the squared of the residual (R^2) is calculated and compared with a user specified tolerance as

$$R^2 = \sum_{i=1}^{m} \left(\tan\delta_i - \tan\delta_f\right)^2 \le \text{tol}$$

where $\tan\delta_i$ is the experimentally measured value and $\tan\delta_f$ is the fitted value; m is the total data counts and tol is the user specified tolerance assumed to be 1% in the present study. By using the least squares fitting approach, the relaxation time constants (τ_j) and the associated moduli (G_j) have been found from experimental DMA data.

For a linear viscoelastic material, the frequency domain complex modulus $G^*(\omega)$ can also be expressed in a time domain representation by using inverse fourier transform.[7] In the time domain representation, the viscoelastic relaxation modulus in shear ($G_R(t)$) is given as:

$$G_R(t) = (G_0 - G_\infty) + G_j \exp\left(\frac{-t}{\tau_j}\right)$$

The relaxation modulus physically represents the time dependent stiffness variation of a viscoelastic polymer in a stress relaxation experiment. Figure 1(b) represents the relaxation modulus for all the PU considered. It is seen that the predicted rate of relaxation is much faster for PU with higher soft segments. However, no definite conclusions are drawn at this stage, as more experimental measurements (FTIR, stress relaxation tests or creep tests) are necessary to confirm this finding. Using linear viscoelasticity correspondence principle to a standard-linear solid model, the (viscous) shear strain rate can be inversely related to the relaxation time constants as:

$$\dot{\gamma}_d \propto \frac{1}{G_j \tau_j}$$

Table 2. Relaxation constants and associated moduli for various PUs with different $W_s\%$.

PUs	G_j (MPa) and τ_j (s)				
PN1	G_j 51.54	26.96	21.77	29.6	295.53
	τ_j 0.0032	0.04	0.153	0.6	17.07
PN2	G_j 189.27	131.9	101.4	67.05	36.68
	τ_j 0.004	0.026	0.114	0.43	1.85
PD1	G_j 115.5	60.5	43.4	25.97	15.96
	τ_j 0.003	0.02	0.08	0.41	2.63
PN3	G_j 4.1e5	80.29	27.83	6.96	1.65
	τ_j 1.23e−7	0.003	0.017	0.09	0.53
PN4	G_j 15.21	1.48	0.47	0.15	
	τ_j 8.3e−4	0.011	0.113	0.81	

For polymers with multiple relaxation times, the rate of viscous dissipation will also be very different depending on the applied loading. Hence to increase damping at a given strain rate, the product $G_j\tau_j$ has to be small. For high rate blast/impact events (durations of the events are often in milliseconds), only the fastest time constants (τ_j is of the order of t_{event}) influence the material response as ($\tau_j > t_{event}$) it will not produce any significant influence in the viscous damping. To characterize the rate dependent damping behavior one needs to determine all the relaxation time constants present within the polymer. As explained earlier by using the least square fit, the relaxation time constants are found for the considered PU's. The corresponding G_j and τ_j are listed in Table 2. Our current least square fitting code converges accurately with five pairs of (G_j,τ_j) unknowns. Figure 2(a) shows the comparison between the fitted $\tan\delta$ and experimentally measured frequency dependent $\tan\delta$. As mentioned earlier, to capture the frequency dependent variation of $\tan\delta$ multiple relaxation times are required. In the molecular level, one typical molecular movement gets activated at a particular frequency or applied strain rate. At higher strain rates (for impact or blast loading) where the loading events are usually of millisecond duration, only the faster relaxation constants are active in material response. Similarly at quasi-static strain rates, where the entire deformation occurs in a much longer time scale (multiple of seconds) slower relaxation constants will govern the viscoelastic dissipation.

As mentioned earlier, slower time constants ($\tau_{j,max}$) are active in polymer response within quasi-static or moderate rate experiments ($t_{test} > 10$–$20\,s$), whereas faster time constants ($\tau_{j,min}$) influence the material behavior at high rates. As seen in Figure 2, ($1/G_j\tau_{jmax}$) starts increasing as the soft segment weight percentage
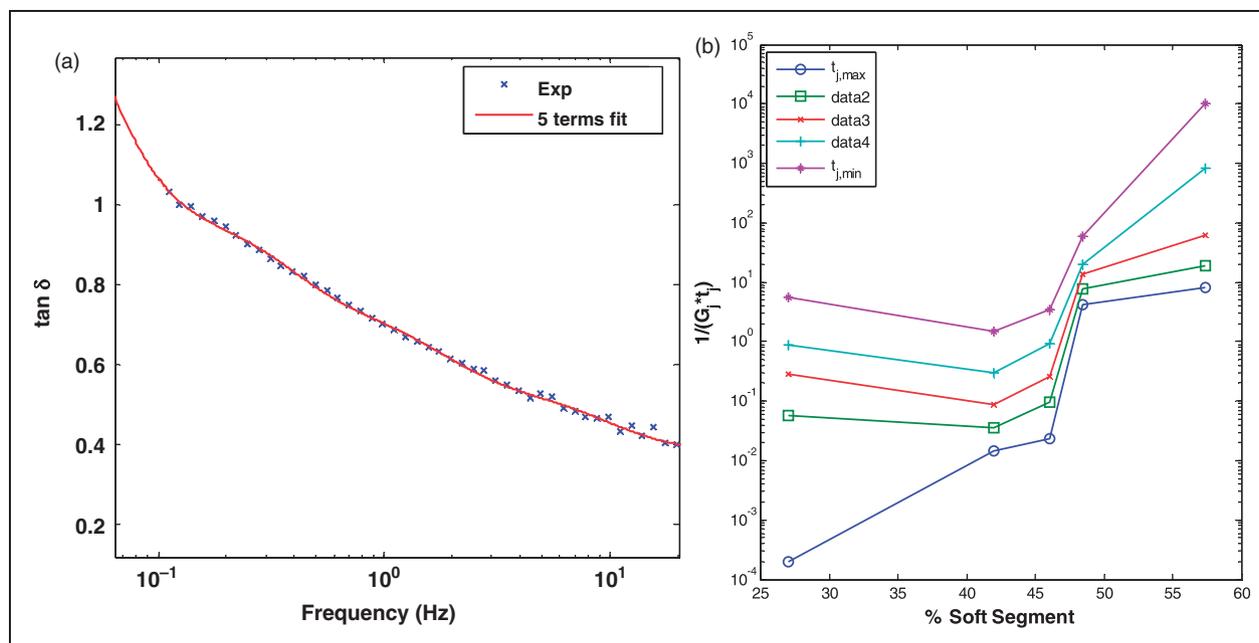
Figure 2. (a) Experimental tan δ and numerical fitting of the data as a function of frequency, (b) variation of relaxation time constants $(1/G_j\tau_j)$ as a function of soft segment weight percentage.

increases within the PU, which indicates the increase in viscous dissipation at slow rate as W_s goes up. However $(1/G_j\tau_{j,min})$ does not increase until $W_s = 46\%$, which indicates no significant improvement in damping at higher rates as a function of soft segment increase. Beyond 46% the faster time constants change more rapidly than τ_{jmax}, which indicates higher damping at relatively high rates. This is depicted in the experimental tan δ plot also. As seen in Figure 1(a), beyond 42–46% of W_s, tan δ increases as a function of W_s in the high frequency regime. Also the absolute value of the relaxation constants has a significant drop in value beyond $W_s = 46\%$. As reported in Table 2 for PN3 and PN4, $\tau_{j,max} < 1$ s and $\tau_{j,min} < 1$ µs. Hence it is important to choose a particular polymer as a constituent depending on which time scale phenomenon will affect the material response.

To explain the saturation in damping beyond a certain W_s percentage, the phase separated molecular structure of PU and time-temperature correlation can be used. By changing the relative weight fraction of the soft and hard phases, the glass transition temperature (T_g) of PU can be altered. At a certain W_s percentage, T_g coincides with room temperature resulting in highest tan δ value for the material measured at T_{room}. At $W_s = 45$–46% the microphase separation of PU is optimized in such a manner that T_g nearly equals to T_{room}.

Currently, experiments are underway to determine the T_g of several PU samples for validating the above argument.

In addition to the effect of soft segment variation, the present study also considers how the volume fraction of clay nanoparticles influences the chain dynamics in the formation of PU nanocomposites. MTM clay nanoparticles at three different volume fractions $f = 4\%$, $f = 9\%$, and $f = 12\%$ are used to manufacture PU-MTM nanocomposites using a PU sample with $W_s = 46\%$. The samples are tested under frequency sweep DMA at room temperature. As seen in Figure 3 the tan δ decreases for PU-MTM nanocomposites as the clay volume fraction increases.

It is well known[10,11] that addition of nanoparticles alters mobility of the polymer matrix surrounding the inclusions with the formation of an interphase region. Considering the clay nanoparticle as a rate independent elastic material, one needs to determine the relaxation behavior of the interphase (modified polymer chains) and how it changes as the clay volume fraction increases. In order to determine the relaxation time constants associated with the interphase region, the PU storage and loss modulus are subtracted from the PU-MTM data. A least square fit is then performed over $(\tan \delta)_{interphase}$ to determine the stiffness and relaxation coefficients for the interphase. The relaxation time constants and associated stiffness moduli are tabulated for the interphase for PU-MTM with three different volume fractions, as shown in Table 3.

By comparing the relaxation time constants for three different volume fractions (f) of clay, it is seen with increasing f, the relaxation times (slowest) that are
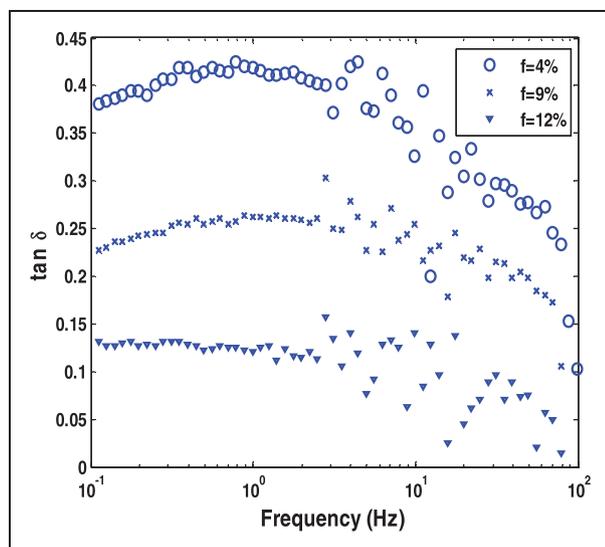
Figure 3. Experimental tan δ measurement of frequency sweep DMA for PU-MTM nanocomposites with different clay volume fractions.

Table 3. Relaxation time constants and associated moduli for PU-MTM nanocomposites for three different clay volume fractions.

f	i	1	2	3	4	5
4%	τ_i (s)	4.435	0.456	0.145	0.025	0.0028
	G_i (MPa)	124	67	103	224	288
9%	τ_i (s)	10.85	0.42	0.084	0.023	0.0034
	G_i (MPa)	754	270	282	356	586
12%	τ_i (s)	17.07	0.6	0.153	0.04	0.003
	G_i (MPa)	295.5	29.6	21.77	26.96	51.5

significant to the test duration at quasi-static range increased (τ_{j1}), resulting in a loss in viscosity of the nanocomposites. The stiffness enhancements and reduction in damping of these nanocomposites are highly dependent on the phase location where the nanoparticles are located. If the nanoparticles are associated with soft segments, then increasing volume fraction will alter the flexibility of the soft segments. Montmorillonite with its lateral dimensions (70–200 nm) being larger than typical hard domains (of the order of 25 nm), at higher volume fractions always influences the soft segment mobility. Hence the viscous dissipation reduces in the nanocomposites with increasing f. Another important point to be noted is the change in associated moduli as the clay volume fraction increases. It is observed that an increase of f from 4% to 9% results in an increase in the associated moduli, but from 9% to 12% there is a decrease in the

associated moduli. In fact, as the rate of damping is a combined effect of ($G_j*\tau_j$), the slowest relaxation part shows an improvement in rate of damping at 12% compared to 9%. The reason behind such an unusual finding can be explained in light of already published literature on nanocomposites. In particular, recent works[10–13] on PU-MTM nanocomposites show, beyond a critical volume fraction of clay (10–12%), it is hard to achieve uniform dispersion of nanoparticles within the matrix and hence mechanical properties get altered in an undesired fashion. Reduction in damping for PU-MTM at room temperature indicates decrease in phase separation within the PU as a function of clay volume increases. Hence the present study also is in line with the finding reported in Tien and Wei,[14] with a saturation observed near or around 12%.

To understand the micro-mechanics involved, a more detailed experimental study is currently underway. This is done by manufacturing PU-MTM nanocomposites at different volume fractions within the 4–12% range, and finding the critical value for f. The present study opens many avenues for designing polymer or polymer nanocomposites with desired damping and relaxation characteristics. As presented here, for PU with $W_s = 46\%$, and clay volume fraction exceeding 4%, damping drops down. Clearly one needs to determine how the PU-MTM properties get altered by changing the base PU with higher soft segments ($W_s = 48\%$ or more). The present study indicates a base PU with higher W_s has a better inherent damping, and to have the same amount of damping reduction in the nanocomposite, one needs to add more clay particle as the base polymer has higher volume of soft segments within the representative volume element. As explained in literature,[8,9] degree of microphase separation in PU and influence of clay nanoparticle are the main reasons for stiffness and damping alteration in PU-MTM nanocomposites. Hence it is important to study further how different values of f alter the behavior of PU with different W_s.

Conclusions

In order to identify a PU with desired damping property for designing application specific materials, it is important to note the various relaxation mechanisms involved in the material response. The present study focusses on characterizing multiple relaxation times present within a particular type of PU and how those relaxation times can be altered either by changing the soft segment content within the PU itself or by adding clay nanoparticle at different volume fractions. It is observed that by increasing the soft segment content, relaxation characteristics of the PU can be changed dramatically with an improved damping behavior

until a critical percentage is reached. Beyond a soft segment weight content of 46% the damping drops down at room temperature. The phenomena has been explained in light of the time–temperature relationship of polymer. Nearly 46% of soft segment content of the T_g of the chosen PU coincides with the measured room temperature and damping is maximum. Hence to design a PU with desired damping characteristics, the selection has to be made based on the operational temperature and the time scale on which the material response is predominant.

For the PU-MTM nanocomposites, it is observed the characteristic relaxation rates drop down with a decrease in viscous damping as a function of increasing clay volume fraction. Addition of nanoparticles changes the relaxation characteristics of the soft segment of the base PU by constraining the relative sliding of the macromolecules chains. Hence resulting stiffness increase in the nanocomposites is always accompanied by reduction in damping. In future, further experimental studies are planned to establish a sounder conclusion in terms of time–temperature correlation and high loading rates.

Conflict of interest

None declared.

References

1. Skarja GA and Woodhouse KA. Structure-property relationships of degradable polyurethane elastomers containing an amino acid based chain extender. *J Appl Polym Sci* 2000; 75: 1522–1534.
2. Saini A, Daunch WA, Verbeke H, et al. Origin of multiple melting endotherms in high hard block content polyurethane, 1 thermodynamic investigation. *Macromolecules* 2001; 34: 9059–9068.
3. Koberstein JT and Galambos AF. Multiple melting in segmented polyurethane block copolymers. *Macromolecules* 1992; 25: 5618–5624.
4. Bruins PF. *Polyurethane technology*. New York: Interscience Publishers, 1969.
5. Rahimzadeh T, Wass AM, Thouless MD, et al. Design of materials for blast resistant armour. Manuscript under preparation.
6. Wei Y, Cheng F, Li H, et al. Thermal properties and micromorphology of polyurethane resins based on liquefied benzylated wood. *J Sci Ind Res* 2005; 64: 435–439.
7. Wineman AS and Rajagopal KR. *Mechanical response of polymers: an introduction*. Cambridge University Press, 2000.
8. Velankar S and Cooper SL. Microphase separation and rheological properties of polyurethane melts: effect of block length. *Macromolecules* 1998; 31: 9181–9192.
9. Xia H, Song M, Zhang Z, et al. Microphase separation, stress relaxation, and creep behavior of polyurethane nanocomposites. *J Appl Polym Sci* 2007; 103: 2992–3002.
10. Dai XH, Xu J, Guo XL, et al. Study on structure and orientation action of polyurethane nanocomposites. *Macromolecules* 2004; 37: 5615–5623.
11. Li Y, Wass AM and Arruda EM. The effects of the interphase and strain gradients on the elasticity of layer-by-layer polymer/clay nanocomposites. *Int J Solids Struct* 2011; 48: 1044–1053.
12. Nguyen QT and Baird DG. Preparation of polymer-clay nanocomposites and their properties. *Adv Polym Technol* 2006; 25: 270–285.
13. Plaseied A and Fatemi A. Tensile creep and deformation modeling of vinyl ester polymer and its nanocomposite. *J Reinf Plast Compos* 2009; 28: 1–14.
14. Tien YI and Wei KH. Hydrogen bonding and mechanical properties in segmented montmorillonite/polyurethane nanocomposites of different hard segment ratios. *Polymer* 2001; 42: 3213–3221.

Appendix

Notation

f	volume fraction of clay
$G(.)$	shear modulus
G_0	initial modulus
G_∞	long term modulus
$\tan\delta$	viscous damping
T_g	glass transition temperature
T_{room}	room temperature
W_s	percentage weight of the soft segment content
γ_d	viscous shear strain rate
τ_j	relaxation time
ω	cyclic frequency (Hz)