Nanofiller reinforcement of elastomeric polyurea

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ABSTRACT

The effects of multiwall carbon nanotubes (MWCNT), nanolayered silicate (nanoclay), and trisilanolphenyl-functionalized polyhedral oligomeric silsesquioxane (POSS) on the rheology and mechanical properties of an oligomeric polydiamine and the polyurea formed by its reaction with isocyanate were measured. The MWCNT and nanoclay increase the viscosity of the polydiamine and form a flocculated filler network at very low concentrations (<1%). This network imparts a strong strain-dependence to the dynamic modulus. These effects are absent with POSS, which primarily affects the polyurea chemistry. The tensile modulus of the cured polyurea is higher for all three additives, with POSS significantly toughening the material, provided adjustments to the stoichiometry are made.

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1. Introduction

Polymers often include a significant amount of carbon black, silica, or other reinforcing filler, to improve their mechanical properties. Optimal performance requires good dispersion and substantial transfer of stress through interfacial regions [1–3]. Non-reinforcing fillers such as calcium carbonate, talc, conventional clays, and other mineral fillers are also used, generally to reduce cost and improve properties such as Young's modulus and processability (e.g., less swelling of extrudates). A more recent development is the use of nanoparticles, which are smaller than conventional fillers and thus give rise to confinement or other effects specific to nm length scales. Their key attribute is an enormous specific surface area, which overcomes generally weaker interactions with the polymer [4]. Substantial improvements in the mechanical properties can be obtained with a few percent or less of nanofiller [5–7]. A problem with nanofillers is achieving good dispersion. Relying on hydrodynamic forces during mixing to overcome the cohesive forces holding particle agglomerates together is usually inadequate, and recourse to chemical modification of the particles is often necessary [8–10].

An interesting aspect of nano-reinforcement is the effect of physical confinement on the material properties. Large surface to volume ratios and the presence of an external dimension commensurate or smaller than the polymer coil size (tens of nm)

can perturb the molecular shape and potentially change the behavior. For example, sufficiently small filler particles have been reported to enhance the segmental mobility of polymers [11–18], relevant to applications involving very high strain rates [19–21].

Polyureas (PU) are not obvious candidates for nanofillers, since they are intrinsically reinforced by their morphology. PU self-assemble into a continuous rubbery matrix with dispersed rigid domains. These domains are well-connected to the rubbery phase and have nanoscale dimensions; thus, the system represents an ideal filler-polymer composite. The hydrogen bonding within the soft phase confers additional toughness. Nevertheless, it is of interest to study the effect of added nanoparticles that have different geometry and interactions with the soft PU domains. Previously polyurea with nanofillers has been investigated for fire retardancy [22] and fouling-release properties [23].

We study three nanofillers herein, nanolayered silicate (nanoclay), multiwall carbon nanotubes (MWCNT), and polyhedral oligomeric silsesquioxane functionalized with trisilanolphenyl (POSS); these have respectively one, two, and three dimensions that are of nm size. The use of these fillers in polymers generally and rubber specifically continues to grow [1,24,25]. The present study was undertaken to better understand nanoparticle reinforcement of an elastomer having a complex morphology like PU, and compare the behavior of these three nanofillers.

2. Experimental

The polyurea herein was the reaction product of a modified methylene diphenyl diisocyanate (Isonate 143L from Dow

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Chemical Co.) and polytetramethylene oxide-di-*p*-aminobenzoate (Versalink P1000 from Air Products) in a 1:4 ratio. The multiwall carbon nanotubes were NC3100 from Nanocyl, having a mean length = 1.5 μm and diameter = 9.5 nm. The MWCT were processed using a ball mill to obtain a very fine powder prior to their mixing with the polydiamine. The latter was first dissolved in methanol, followed by addition of the MWCNT with stirring (the solvent was necessary to reduce the viscosity). The methanol was then removed in vacuum at 50 °C. (Ultrasound agitation of the methanol dispersion was also tried, but resulted in samples having equivalent properties.) The clay was Cloisite 10A, montmorillonite ($Na(Mg_xAl_{2-x})(AlSi_3O_{10})(OH)_2$) modified with a quaternary ammonium salt. It was dispersed in the diamine by mechanical mixing at moderate speeds; the mixture becomes very viscous as the clay incorporates. Trisilanolphenyl POSS was obtained from Hybrid Plastics. A solid at room temperature, the POSS and the diamine were dissolved in a common solvent, ethanol, which was subsequently removed using a rotary vacuum, followed by additional drying in vacuum at 50 °C for several days. For all samples both the P1000 and isocyanate were degassed, at 50 °C for the former to remove crystallinity, prior to reaction to form the polyurea.

Rheology measurements on the diamine mixture were done with an ARES rheometer using a cone and plate configuration. Different radii (2.5–4 cm) were used depending on the sample viscosity. For the PU samples a parallel plate geometry was employed, with disks ~2 mm thick and having a 4 mm radius.

Uniaxial strain measurements employed an Instron 5500R with optical extensometer. Glass transition temperatures were measured by differential scanning calorimetry (DSC) using a TA Q100 calorimeter. A heating rate of 10 C/min was imposed after quenching the melted sample to prevent crystallization.

3. Results

3.1. Multiwall carbon nanotube composites

We first assess the effect of MWCNT on the precursor polydiamine, which is the main component of the rubbery phase of the cured PU. Concentrations by volume, ϕ, from 0.06 to 1.22% were mixed into the polydiamine. Fig. 1 shows that low levels of MWCNT dramatically alter both the elastic and viscous components of the mechanical response. The Newtonian behavior of the low molecular weight polymer is lost, the response becoming more solid-like. At all concentrations the MWCNT inhibit chain motions over extended length scales. The value of the storage modulus at a given fixed frequency exhibits power law behavior, e.g., $G' \sim \phi^{3.0}$ at 0.1 Hz, although the accuracy of this exponent is poor, since the abscissa spans less than two decades.

If the data in Fig. 1 are plotted versus linear MWCNT concentration (Fig. 2), a qualitative change of behavior is evident at a critical volume fraction equal to 0.0036. This value $\phi^* = 0.36\%$ is intermediate between the percolation threshold concentrations reported for carbon nanotubes in other polymers [1,26–28]. However, since large changes in the shear modulus and viscosity are observed for concentrations well below 0.36% (Fig. 1), the threshold must be at lower levels of the nanotubes. Assuming random orientation and distribution, the concentration for overlap of the MWCNT depends only on their aspect ratio, f [29,30]

$$\phi^* = \frac{\pi}{4} f^{-2} \tag{1}$$

Using $f = 160$ (as reported by the supplier) in Eq. (1) gives $\phi^* = 0.003\%$, which is less than the lowest concentration of MWCNT
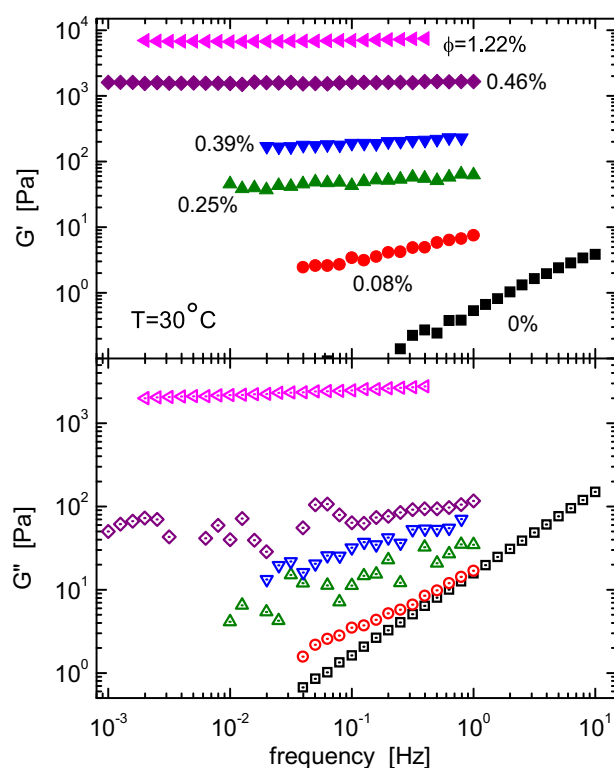

Fig. 1. The storage (upper panel) and loss (lower panel) shear modulus as function of frequency of the polydiamine/MWCNT mixtures having different concentrations of MWCNT. The concentrations are given for G′ (solid symbols), with the same symbols (open) used for the corresponding G″ data.
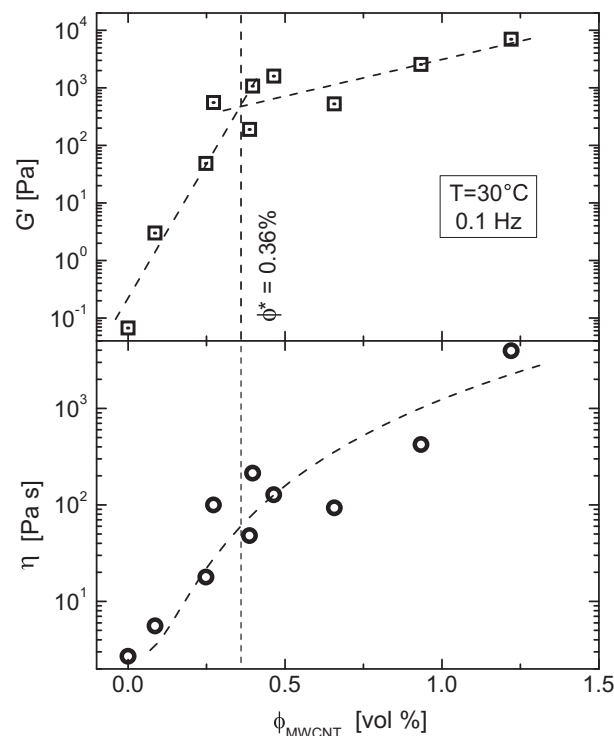

Fig. 2. Storage modulus (upper panel) and dynamic viscosity (lower panel) at fixed frequency (0.1 Hz) of the polydiamine/MWCNT mixtures as a function of MWCNT concentration.
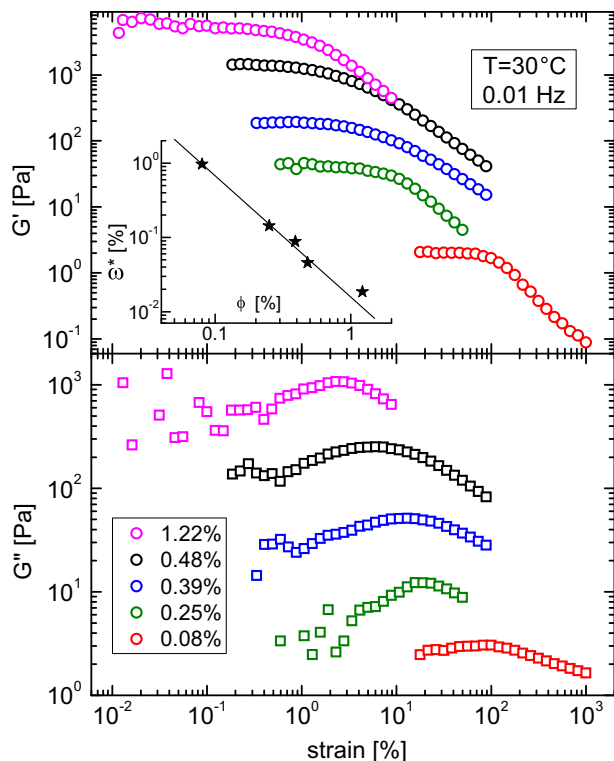
Fig. 3. Variation of the storage and loss modulus of MWCNT filled polydiamine with dynamic strain amplitude. The inset shows the variation in the strain associated with the peak in $G''(\varepsilon)$ with filler concentration.

herein, consistent the presence of a particle network at all the investigated concentrations herein. Using $\phi^* = 0.36\%$ in Eq. (1), we obtain an "effective" aspect ratio equal to only 15; thus, the qualitative change of behavior at $\phi^* = 0.36\%$ in Fig. 2 is ascribed to aggregation of the flocculated particles [28–37], rather than to the formation of a particle network.

It has been found that ϕ^* for carbon nanotubes is affected by the polymer matrix and method of mixing [34], reflecting the importance of particle dispersion. The Einstein equation

$$\eta = \eta_{\phi=0}\left(1 + 0.67\phi + 1.62f^2\phi^2\right) \qquad (2)$$

describes the purely hydrodynamic effect (strain amplification) of inextensible particles in the regime of very high dilution (below percolation). Fitting Eq. (2) to the viscosity data for all concentrations (dotted line in lower panel Fig. 2), gives a reasonable fit to the data for $f = 21$, which again is lower than the known aspect ratio. This is further evidence of agglomeration of the particles.

A flocculated particle network would give rise to a yield stress [30,31], often referred to as the Payne effect [38]. Strain sweeps (Fig. 3) are consistent with breakup of the flocculated structure with increasing strain amplitude. The minimum strain necessary to effect this breakup, ε^*, defined as the strain of the maximum in the loss modulus (breakup of interparticle contacts dissipates energy), varies with filler concentration according to $\varepsilon^* \sim \phi^{-1.6}$ (inset to Fig. 3). Such power law behavior for the yield strain is typical of

Table 1
Effect of MWCNT on T_g. (heating at 10 K/min following quenching).

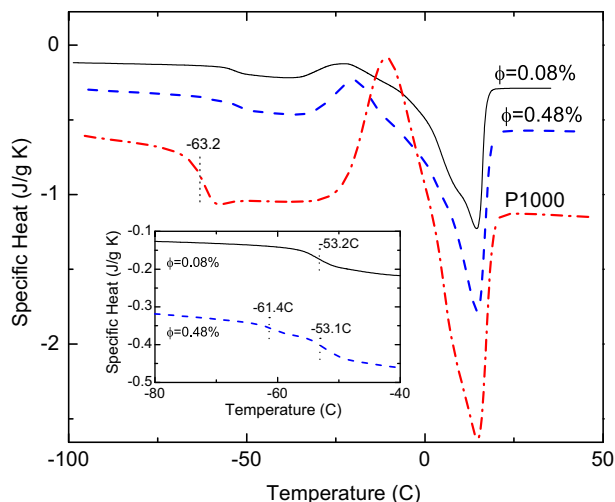|	Neat	$\phi = 0.08\%$	$\phi = 0.48\%$
P1000	−61.2 (±0.2) °C	−53.2 ± 0.5 °C	−61.4 °C, −53.1 (±0.9) °C
Polyurea	−68.7 °C	–	−63.2 °C

Fig. 4. DSC heating curves for neat polydiamine and two mixtures with MWNCT. The inset shows the glass transition region on an expanded scale; note the presence of two T_g's for the higher concentration of filler.

fractal networks. Note this Payne effect is observed for all ϕ, even those below ϕ^* determined from the data in Fig. 2. The network structure remains intact during the frequency sweep experiments, because of the low strain amplitude; hence, the plateau in G' is observed, consistent with solid-like behavior.

Unlike flocculated carbon black particles [39,40], recovery of the MWCNT network was essentially instantaneous for all ϕ; that is, reducing the strain below ε^* immediately reproduces the prior, low strain behavior. We also note that the maximum in the loss modulus in Fig. 3 does not occur at a constant value of the strain energy; that is, unlike results for conventional filled systems [40], strain energy is not the control parameter governing breakup of the particle network.

Although a MWCNT network forms in the polydiamine, the cured polyurea showed no Payne effect, and in fact the storage modulus was unchanged from that of the neat PU. However, as discussed below, an effect of the MWCNT on PU becomes apparent at large strain.
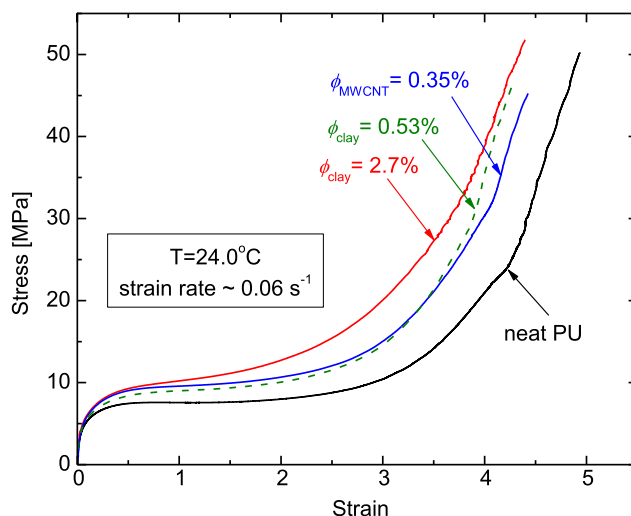

Fig. 5. Stress during uniaxial straining of the polyurea, neat and reinforced with the indicated concentrations of MWCNT or nanoclay.

Table 2
PU PU/MWCNT mechanical properties (tensile strain rate ~ 0.06 s^{-1}).

ϕ (%)	Tensile strength	Failure strain	Toughness (MJ/m^3)
0	50 ± 3 MPa	490 ± 10%	69 ± 10%
0.74 MWCNT	45 ± 3 MPa	440 ± 10%	68 ± 10%
0.53% cloisite	46 ± 3 MPa	430 ± %	62 ± 10%
2.7% cloisite	52 ± 3 MPa	440 ± 10%	82 ± 10%

An important application of elastomeric polyureas involves high strain rates [19–21], which involve the segmental dynamics; thus, we measured the effect of MWCNT on the glass transition. The transition temperatures, T_g, of both the precursor diamine and cured polyurea are listed in Table 1. Unlike for the neat diamine, it was not possible to quench the MWCNT-reinforced diamine without some crystallization. So, for example, during DSC heating following cooling, the melting enthalpy was larger than the area under the crystallization peak for the MWCNT mixtures (Fig. 4). For the lowest concentration ($\phi = 0.08\%$), a single T_g was observed, 8° higher in temperature than for neat P1000. Higher concentrations (e.g., $\phi = 0.48\%$) exhibited two T_g's, with the lower T_g corresponding to the transition of the neat P1000 (Fig. 4). The cured PU exhibits only a single T_g, which was significantly higher in the presence of the MWCNT.

Not only did cooling to ambient temperature induce some crystallization of the polydiamine mixed with MWCNT, the subsequently formed PU had detectable crystallinity (i.e., the crystallites remain intact during reaction with the isocyanate). In principle this could affect the mechanical properties, in addition to the direct effect of the nanotubes. Fig. 5 compares the stress-strain response at low strain rate (nominally 0.06 s^{-1}) for the neat PU and $\phi = 0.48\%$, which is above the threshold ϕ^*. The filled sample has a yield stress that is about 20% higher, but lower failure properties (Table 2). Previous work found that functionalization [26] or orientation [41] of carbon nanotubes in the polymer matrix is necessary for optimization of the toughness. Moreover, the high viscosity of the P1000/MWCNT mixture increases the possibility of defects due to entrapped (but undetected) air in the sample, which would lower the measured strength. Comparing the toughness (area under the stress-strain curve), the value for PU/MWCNT is lower than for neat PU due to the larger failure strain of the latter, even though the presence of the MWCNT raised the yield stress. *In*
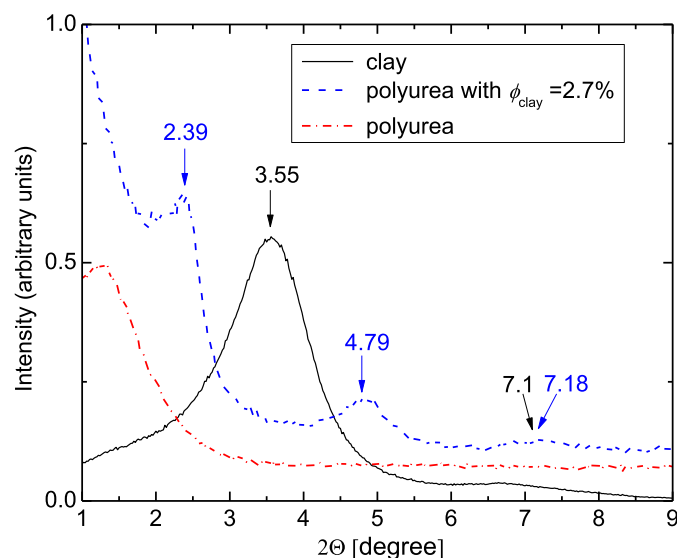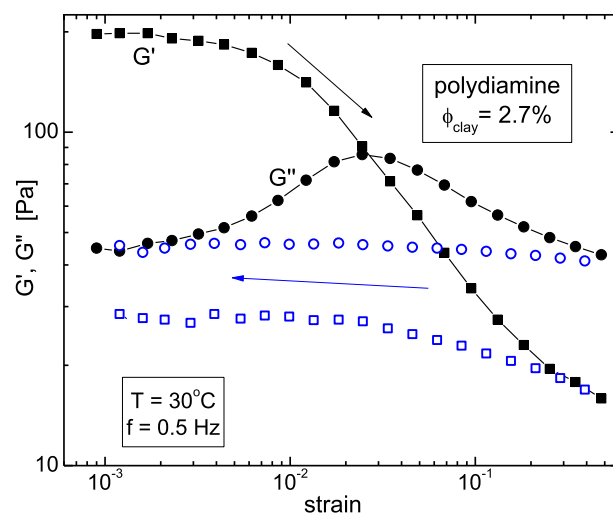

Fig. 7. Dynamic moduli of PU with $\phi = 2.7\%$ nanoclay as a function of strain. The peak in the loss modulus indicates the breakup of the flocculated particle network. The moduli on decreasing the amplitude (hollow squares) are similar to the values at high strains, reflecting the retarded reformation of the network structure.

toto, these data give no cause to expect better failure performance for PU reinforced with the MWCNT.

3.2. Nanoclay composites

Nanoparticles of layered mineral silicates have been used to improve the mechanical properties of various elastomers, including nitrile rubber [42,43], styrene-butadiene copolymer [44], poly-isoprene [8], and polyurethane [45]. Improvements in mechanical properties require intercalation (matrix chains residing within the clay galleries) or exfoliation (complete separation of the silicate layers). Such dispersion of the nanoclay can be deduced from X-ray diffraction measurements, since the regularity of the interlayer gap gives rise to a diffraction peak at an angle corresponding to the silicate d-spacing. As polymer segments enter the galleries, the layer spacing increases; for the PU herein, the peak shifted from
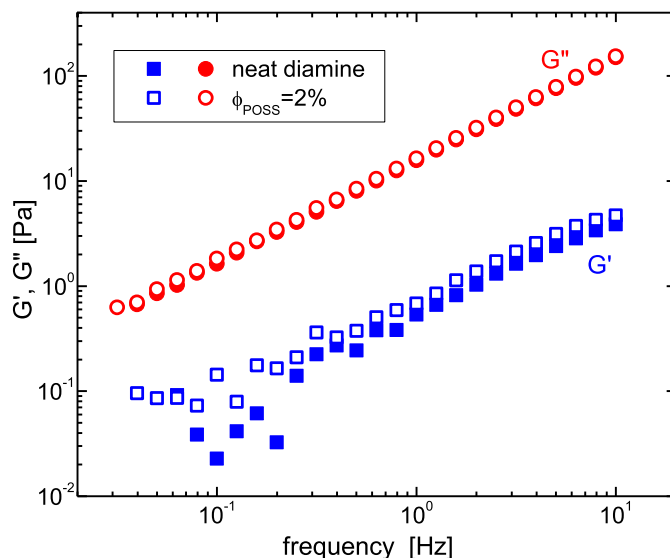

Fig. 6. Wide-angle X-ray diffraction pattern of unfilled PU, nanoclay, and their mixture.

Fig. 8. Frequency dependence of the storage and loss moduli of the polydiamine, neat and with $\phi = 2\%$ POSS.
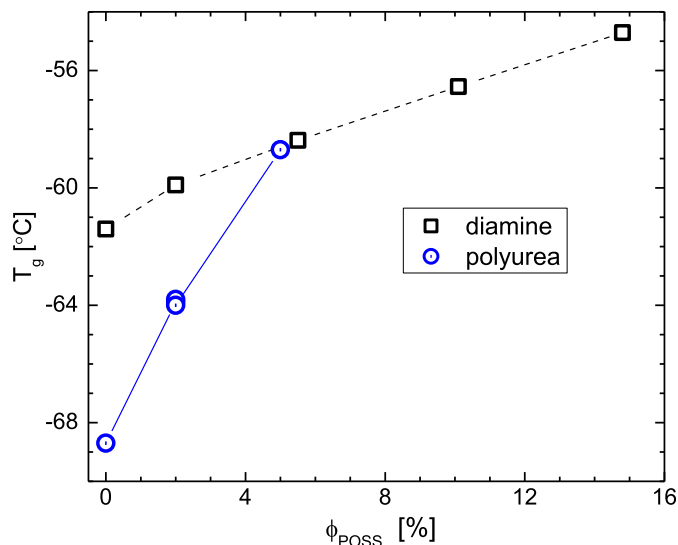
Fig. 9. Calorimetric glass transition temperature of the precursor diamine and the cured PU as a function of POSS content. Variations in stochiometry had a negligible effect on T_g.

3.55° (dry, neat clay) to 2.39° (Fig. 6), corresponding to an increase in spacing from 25 Å to 37 Å. This indicates significant penetration of the polydiamine into the layers; however, we were unable to achieve exfoliation, which would cause the disappearance of the diffraction peak. (Note the spacing of the neat clay is larger than reported previously [46], likely due to incomplete drying.)

The viscosity of the P1000/nanoclay is more than an order of magnitude higher than for the neat diamine; however, at equal concentrations η is smaller and less concentration-dependent than for the MWCNT-reinforced diamines. This smaller viscosity enhancement is advantageous for processing, including mixing with the isocyanate. The polydiamine/nanoclay exhibits the Payne effect (Fig. 7), similar to the data in Fig. 3 for MWCNT. However, unlike for the latter, recovery of the clay particle network is slow, requiring many hours. Although the expectation might be that the viscosity of the matrix would govern the timescale of the recovery, the required adjustments in particle position and orientation to reform the network are very local and presumably very sensitive to particle shape, in particular the aspect ratio.
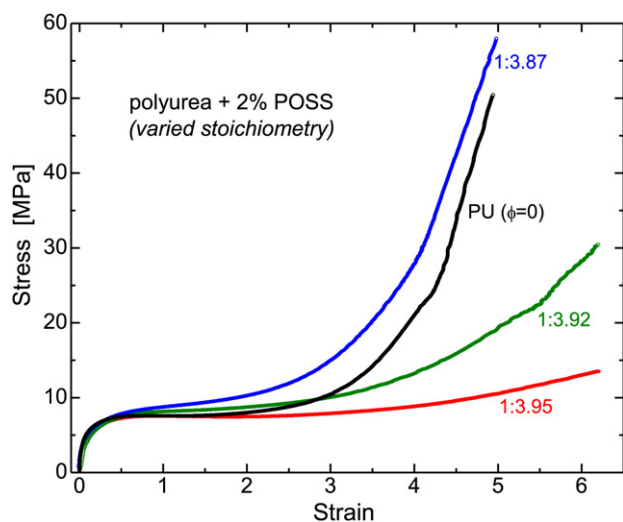

Fig. 10. Stress during uniaxial straining of the PU with $\phi = 2\%$ POSS and varying stochiometry.

Table 3
Summary of nanofiller effects.

Filler	P1000 viscosity	Payne effect	PU T_g	PU modulus	PU toughness
MWCNT	Increased	Yes	~7 K increase	Higher	Negligible change
Nanoclay	Increased	Yes	No change	Higher	Negligible change
POSS	Negligible change	No	~10 K increase	Higher[a]	20% improvement[a]

[a] For optimized stoichiometry.

Both calorimetry and dielectric relaxation measurements gave no indication of a change in T_g, either for the precursor diamine or the polyurea. The Payne effect was absent for the nanoclay/PU samples (unlike for the polydiamine with nanoclay), and the dynamic moduli were equal to that of neat PU. Despite this lack of any effect of the nanoclay on the shear properties of the cured polyurea, the tensile stress-strain behavior was markedly different. Included in Fig. 5 is the stress-strain curves for PU with $\phi = 0.53\%$ and 2.7% nanoclay. Similar to the results for PU with MWCNT, there is a substantially higher yield stress and comparable failure stress. However, there is some decrease in the strain at failure, and thus any changes in toughness are negligible.

3.3. Polyhedral oligomeric silsesquioxane composites

POSS, often with amine or hydroxyl functionality, has been incorporated into polyurethanes to give materials with higher modulus and higher T_g [24,47–53]. The POSS used herein has the generic formula $RSi_7O_9(OH)_3$, where R is a phenyl group. The pendant hydroxyl groups affect the crosslinking chemistry (as known for reaction of POSS with epoxies [54]), reacting with the isocyanate to incorporate into polyurethane [55–57] or polyurea, as well as hydrogen bonding with the subsequent network.

Frequency sweeps of the precursor polydiamine with 2% POSS showed no appreciable change (Fig. 8), the storage modulus of the neat diamine being marginally lower. However, as found generally for POSS/polymer composites [24,58], the T_g of both the precursor diamine and the PU increased with increasing POSS concentration (Fig. 9). Although T_g doesn't become constant at higher POSS concentrations, above 5% POSS the mixtures with diamine become unstable, with phase separation transpiring over time (days). This gives rise to a second glass transition corresponding to that of the pure polydiamine. We also observed from the DSC measurements that the presence of the POSS reduced the crystallization tendency of the P1000.

Stress-strain curves for PU with 2% POSS are shown in Fig. 10. The stochiometry (relative concentration of the diamine and isocyanate) was adjusted to 1:3.87, 1:3.92 and 1:3.95 (by weight), to account for the reaction of the isocyanate with the hydroxyl groups on the POSS. With optimized stoichiometry (reduced P1000 concentration to compensate for these hydroxyl groups), the PU with 2% POSS had higher strength and elongation, corresponding to 20% increase in energy to break (toughness). These improvements might be attributed at least in part to the presence of urethane linkages, which are more flexible than the urea bonds.

4. Summary

For two of the three nanofillers examined herein the reinforcement was much more significant on the precursor polyamine than on the cured polyurea. This is unsurprising, since the latter has substantial isocyanate-enriched nanodomains, which function as a particulate reinforcement. These results are summarized in Table 3.

While generally small filler particles maximize the interfacial area and provide greater reinforcement, this is not the case for POSS, notwithstanding its diminutive size extending to three dimensions. POSS does not function as a conventional filler, but rather is a chemically reactive additive. The MWCNT and nanoclay both enhance mechanical properties in the manner of conventional fillers, but at much lower levels than for carbon black, silica, etc. The nanofillers significantly increase the modulus and viscosity of the prepolymer, and form a percolated structure evident in a strong dependence of properties on the dynamic strain amplitude (Payne effect). However, only the POSS, which has three nm dimensions, toughens the cured polyurea; the layered silica and MWCNT, nm sized in one and two dimensions respectively, do not. The limited effectiveness of these two fillers in increasing the toughness of PU may stem, at least in part, from the increased viscosity of the prepolymer, which makes the final polymer more prone to defects (inhomogeneous distribution of reactants, entrapped air, etc.). The toughening of the PU by POSS largely results from its effect on the chemistry and consequent structure of the PU, rather than from any physical effect in the manner of conventional fillers. Whether these changes in the isocyanate reaction could be achieved as effectively by other means remains to be determined. Previously we showed that adjustment of the relative amount of diamine and isocyanate cannot provide increases in both the yield stress and the failure strain [59].

Acknowledgments

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