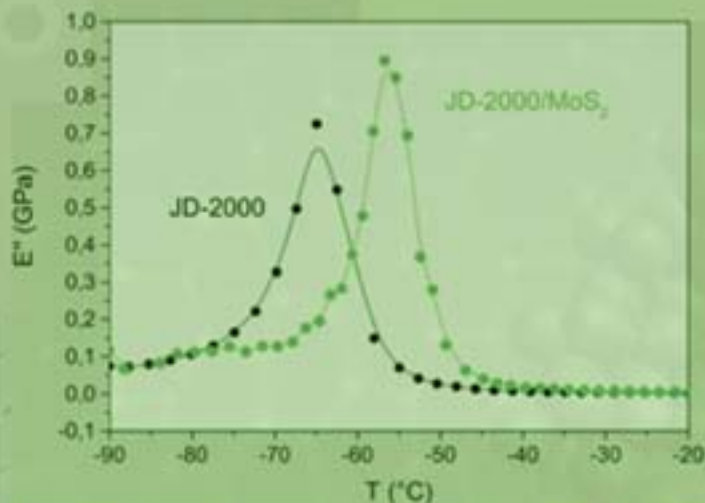
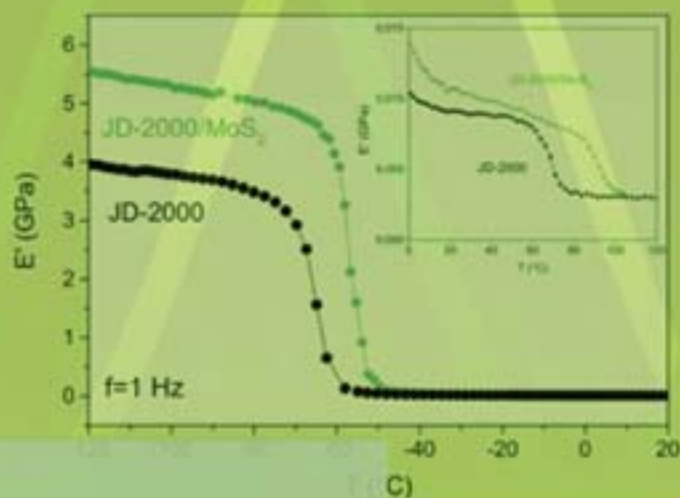


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# Influence of inorganic nanoparticles on the glass transitions of polyurea elastomers

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Received 10 May 2013, revised 7 August 2013, accepted 9 August 2013

Published online 9 September 2013

**Keywords** composites, elasticity, glass transitions, inorganic materials, nanoparticles, polymers

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The properties of polymers can be significantly changed by incorporating nanoparticles, which yields a great potential for applications. In the present study, we use nanocomposites of new polyurea elastomers filled with 0.1, 0.5, and 1 wt.% MoS<sub>2</sub> nanotubes. Using dynamic mechanical analysis (DMA) measurements we show, that the glass transition temperatures

$T_g$  of the nanocomposites are increased by small amounts of inorganic nanotubes. In line with results from computer simulations of polymer melts with nanoscopic particles, we explain the observed shift of  $T_g$  to be due to a gradual slowing down of polymer chain dynamics in the proximity of nanotubes.

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**1 Introduction** Composites of nanoparticles (NPs) and polymers are attractive materials with a high potential for applications [1], due to their flexibility and superior electrical, magnetic, mechanical, thermoelectric, and optical properties, etc. [2]. The properties of polymers can be tuned by adding NPs of different shapes, i.e., spheres, tubes, or sheets. Since NPs have large surface areas their performance depends strongly on the properties of the interfacial regions between the polymer and the NPs, i.e., on the type of interaction (attractive or repulsive) between the NPs and the polymer matrix, the degree of dispersion of the NPs, etc.

Polyurea networks synthesized by sol/gel chemistry [3] are relatively new elastomers with extreme resistance to chemical abrasion and service temperatures between  $-60$  and  $+200$  °C.

In the present work, we have to deal with a problem of many scales of length (and time) for the following reason. Polyurea elastomers exhibit a phase separated structure [3] with rigid urea domains (hard domains) embedded in a matrix of flexible polymer chains (soft domains). The

average size of the hard domains is of the order of several nanometers and the same holds for the average distance between them [3]. As we shall show below, the average distance between MoS<sub>2</sub> nanotubes is of the order of several micrometers, i.e., thousand times larger.

The mechanical properties of polyurea elastomers can be tuned by the relative amount of hard and soft domains – average molecular weight between crosslinking points – and also by the loading with NPs [4]. Pure polyurea elastomers exhibit two glass transition temperatures at  $T_{g1} \approx -65$  °C and  $T_{g2} \approx T_{g1} + 25$  °C [9] attributed to cooperative motions of molecular segments in the soft domains of pure polyurea ( $T_{g1}$ ) and to regions near the hard nanodomains ( $T_{g2}$ ).

Although there are several techniques available to evaluate  $T_g$ , one of the most sensitive techniques is dynamic mechanical analysis (DMA). Here we present new DMA experiments where the presence of inorganic MoS<sub>2</sub> nanotubes [5] in different PU elastomer nanocomposites influences the polymer chain dynamics and the glass transition temperatures of the polymer network.

## 2 Experimental

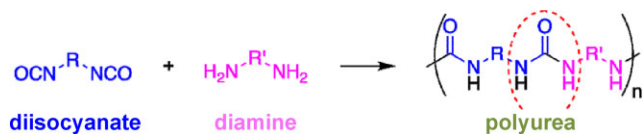
**2.1 Samples** For the present study, the linear hydrophobic diamino-terminated polyetheramine Jeffamine D-2000 ( $M_n = 2060 \text{ g mol}^{-1}$ ,  $\rho = 991 \text{ kg m}^{-3}$ ) and the hydrophilic Jeffamine ED-2003 ( $M_n = 2300 \text{ g mol}^{-1}$ ,  $\rho = 1068 \text{ kg m}^{-3}$ ), from Huntsman International LLC, and the triisocyanate crosslinker Basonat HI-100 ( $m_w = 504 \text{ g mol}^{-1}$ ,  $\rho = 1174 \text{ kg m}^{-3}$ ), from BASF SE, were used as received. Details of the synthesis of these PU elastomers are well described in the literature [4].

PU polymers are formed by the chemical reaction between a diisocyanate and a diamine to build urea moieties, as shown in Scheme 1. When one of these components – the isocyanate- or amino-containing chemicals – has more than two reacting groups, then networks are obtained.

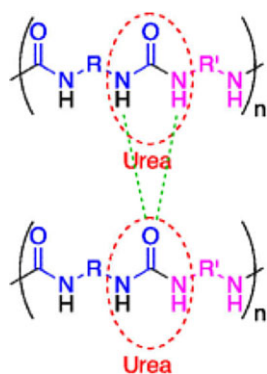
In these PU networks, intermolecular hydrogen bonds are formed between the active hydrogen atoms from one urea group ( $-\text{NH}-$ ) and the oxygen coming from the carbonyl group ( $>\text{CO}$ ) from another urea moiety (Scheme 2), bringing additional properties to the system.

At room temperature polyurea shows microphase segregation, with hard segments dispersed in a soft matrix (Fig. 1). From SAXS and WAXS experiments [4], the average size of the hard domains and the distance between them were determined for the Jeffamine D-2000-based PU network, with values in the order of few nanometers and 6.4 nm, respectively.

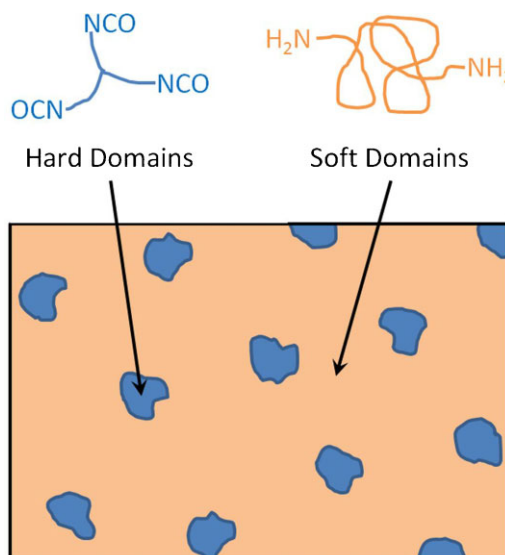
Two reference elastomeric samples JD-2000 and JED were synthesized when crosslinking the two linear diamino-terminated polyetheramine Jeffamine D-2000 and Jeffamine



**Scheme 1** Chemical reaction between a diisocyanate and a diamine yielding the corresponding polyurea compound (in the red oval, the urea moiety is shown).



**Scheme 2** Intermolecular hydrogen bonds between two urea motifs.



**Figure 1** Phase separated structure of polyurea elastomers.

ED-2003, respectively, with the triisocyanate crosslinker Basonat HI-100. The volume fraction of hard domains for both PU systems was  $\phi_x = 0.12$ .

A first PU nanocomposite containing around 1 wt.% of  $\text{MoS}_2$  nanotubes (JD-2000/ $\text{MoS}_2$ ) was synthesized after crosslinking the corresponding Jeffamine D-2000 [8, 9]. Moreover, two sets of nanocomposites filled with 0.1, 0.5, and 1 wt.% of  $\text{MoS}_2$  multiwall-nanotubes ( $\text{MoS}_2/170$ : 80–100 nm diameter, 10  $\mu\text{m}$  length) obtained from the desulfurization of  $\text{MoS}_7$  nanotubes (JED-C1-X) and of  $\text{MoS}_2$  multiwall-nanotubes ( $\text{MoS}_2/628$ : 250 nm diameter, 100  $\mu\text{m}$  length) obtained from the decomposition of multiwall  $\text{Mo}_6\text{S}_2\text{I}_8$  nanowires (JED-C2-X) were prepared after crosslinking the Jeffamine ED-2003.

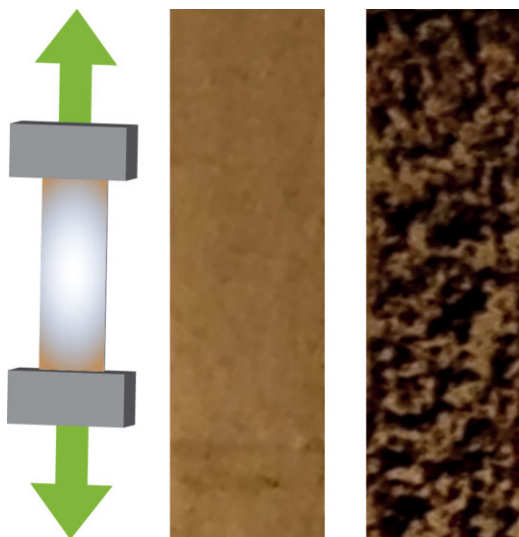
**2.2 Experimental methods** DMA is a technique to measure the low frequency elastic moduli and damping of materials [7]. A static force  $F_{\text{stat}}$  is sinusoidally modulated by a dynamic force  $F_{\text{dyn}} \exp(i\omega t)$  at a chosen amplitude and frequency. The elastic and anelastic response of the sample leads to a change in length  $u$  and phase shift  $\delta$  between force and amplitude, which is registered via inductive coupling. Normal resolutions for the length and phase shift are  $\Delta u \approx 10 \text{ nm}$  and  $\Delta \delta \approx 0.1^\circ$ , respectively. The knowledge of the sample length  $u$  and the phase shift  $\delta$  allows determining the real and imaginary parts of a certain component of the complex elastic compliance tensor  $S'_{ii}$

$$S_{ii} = S'_{ii} \cos \delta \text{ and } S''_{ii} = S'_{ii} \sin \delta. \quad (1)$$

The corresponding storage ( $E'$ ) and loss modulus ( $E''$ ) are defined as  $E' := 1/S'_{ii}$  and  $E'' := 1/S''_{ii}$ , respectively.

DMA experiments were performed on a Perkin Elmer DMA 7 or on the Perkin Elmer Diamond DMA. In both setups the complex elastic compliance can be measured in



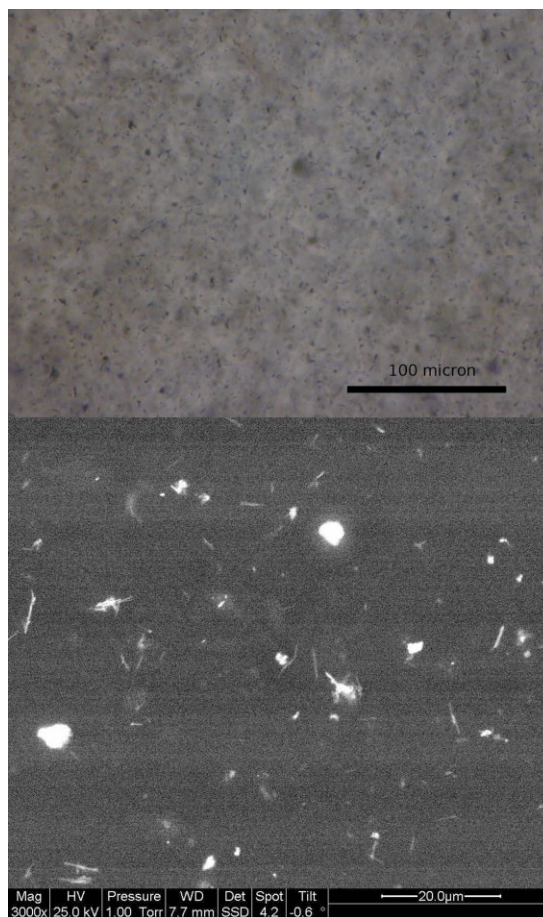


**Figure 2** Tensile stress measurement geometry (left). The two right-hand pictures show two JED samples with 0.1 and 0.5 wt.% MoS<sub>2</sub>, respectively. Sample size is about 2 mm × 9 mm and 0.2 mm.

a frequency range between 0.01 and 100 Hz, and for temperatures between 80 and 850 K. The minimal force that can be applied is 10<sup>-3</sup> N with a resolution of 10<sup>-5</sup> N. The maximal forces are 2.5 N for DMA 7 and 10 N for the Diamond DMA. In both instruments the force is transmitted via a quartz- (DMA 7) or steel- (DMA 7 and Diamond DMA) rod, which also probes the sample size. The present experiments were performed in tensile stress (TS) geometry (Fig. 2). For more details concerning the DMA method, see, e.g., Ref. [7]. Typical sample size was  $l = 9$  mm,  $b = 2$  mm, and  $t = 0.2$  mm. The samples were cooled down to about -183 °C and heated again with a heating rate between 0.5 and 2 °C min<sup>-1</sup>. Up to five heating/cooling cycles were performed. In the present work, we always compare data for pure and filled samples that were taken from the same heating sequence.

**3 Results and discussion** In Figs. 3–5, optical and scanning electron microscopy images of polyurea JD-2000 filled with ≈1 wt.% MoS<sub>2</sub> (Fig. 3) and JED-C1 filled with 0.1 wt.% MoS<sub>2</sub>/170 (Fig. 4) and 0.5 wt.% MoS<sub>2</sub>/170 (Fig. 5) are shown for comparison.

The nanotubes are well dispersed, with an average distance between the NPs of several micrometers (Figs. 3 and 4), i.e., several tens of the diameter (≈100 nm) of a multiwall-nanotube. The JED-C1 samples filled with 0.5 wt.% show “clouds” of agglomerated nanotubes with regions between where the NPs are relatively well dispersed (Fig. 5). A similar inhomogeneous distribution of NPs was also observed for the 1 wt.% JED-C1 samples. For comparison, pristine MoS<sub>2</sub> nanotubes usually form bundles or ropes of up to 10<sup>6</sup> individual tubes [5] which can be up to many tens of micrometers long.



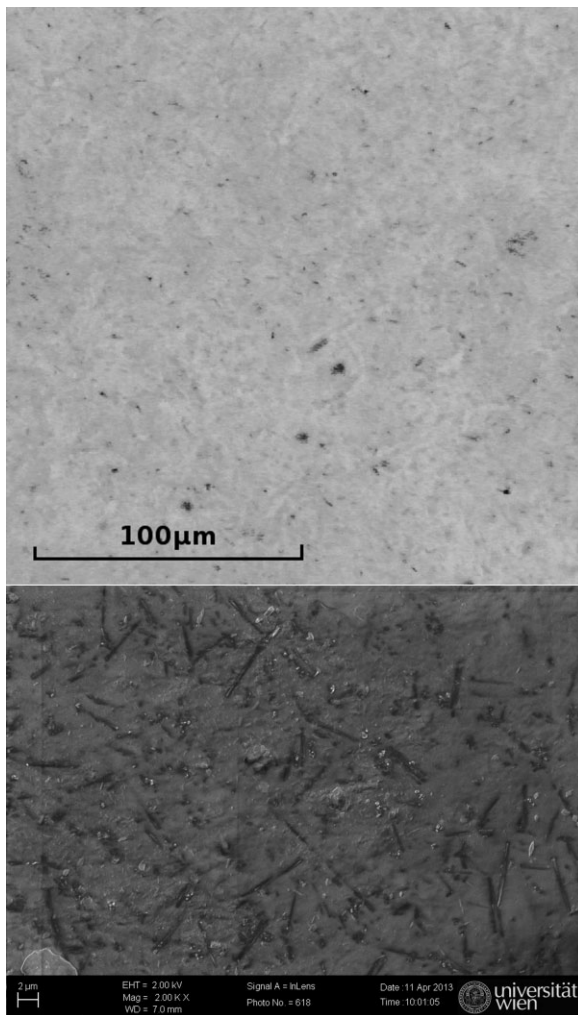
**Figure 3** Optical (top) and scanning electron microscopy (bottom) [6] images of JD-2000 filled with ≈1 wt.% MoS<sub>2</sub>.

In order to study the effect of NPs in the polymer matrices, DMA experiments as a function of temperature and frequency were performed.

Figure 6 displays the temperature and frequency dependencies of  $\tan \delta = E''/E'$  of pure polyurea JD-2000, showing two glass transitions at  $T_{g1} \approx -65$  °C and  $T_{g2} \approx T_{g1} + 25$  °C.

The glass transition at  $T_{g1}$  is attributed to the regions in the soft domains whereas the higher  $T_{g2}$  originates from regions near the hard domains [9]. Such a two glass transition behavior can be observed when sufficiently strong particle enthalpic interactions lead to a permanent attachment of chain segments to the NPs [24], which obviously is the case in the vicinity of the hard domains in polyurea. A discussion of this two glass transition behavior as well as detailed measurements for polyureas with different molecular weight of the polyetheramines (soft domains) will be the subject of a forthcoming paper.

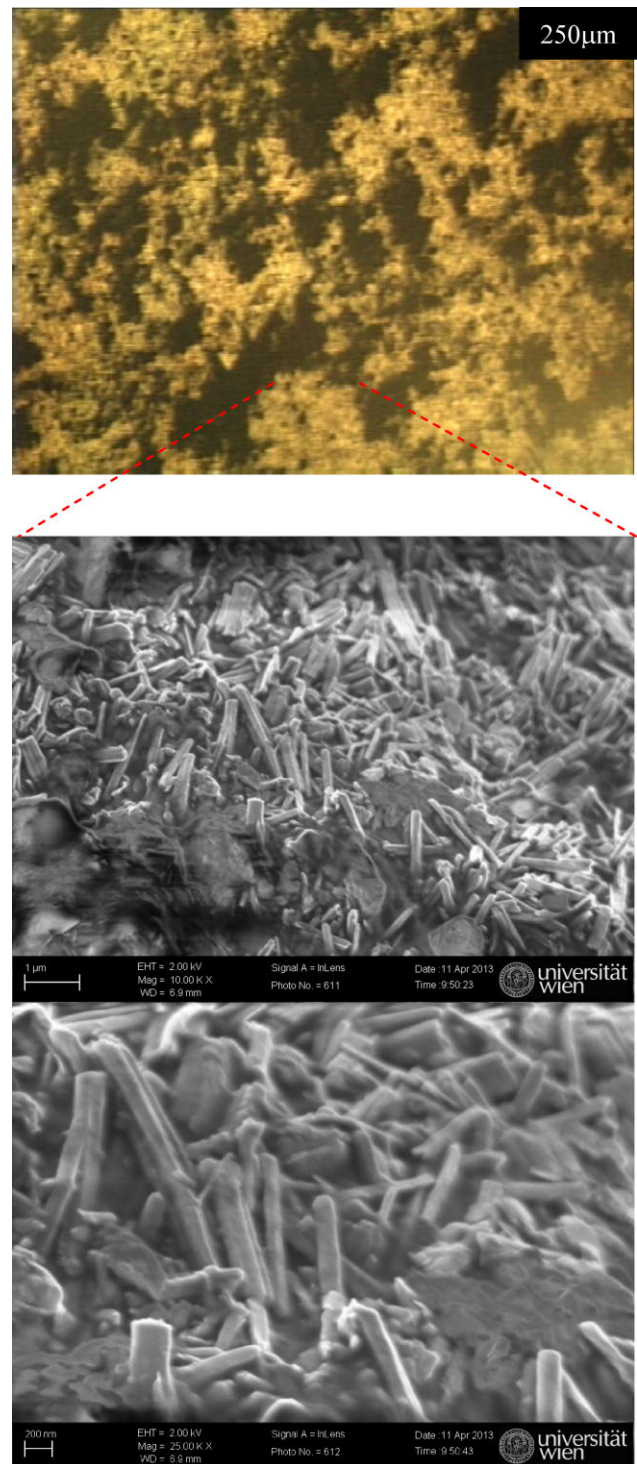
The storage  $E'$  and loss  $E''$  moduli and  $\tan \delta$  as function of temperature are compared for the pure polyurea elastomer JD-2000 and the elastomeric nanocomposite JD-2000/MoS<sub>2</sub> (≈1 wt.% of MoS<sub>2</sub>) in Fig. 7. Several methods are



**Figure 4** Optical (top) and scanning electron microscopy (bottom) of JED-C1 filled with 0.1 wt.% MoS<sub>2</sub>/170. On the SEM picture separated multiwall-nanotubes are visible as “sticks” of about 10 μm length.

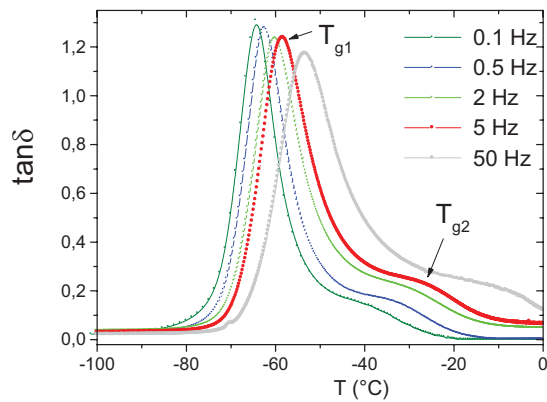
commonly used to determine the glass transition temperature  $T_g$  from DMA measurements [10]. They either relate  $T_g$  to the onset-temperature of  $E'$  or to the temperature of the  $E''$ -peak or the  $\tan \delta$  peak, respectively. Irrespectively which method we use to locate  $T_g$ , we obtain a shift of  $T_{g1}$  to higher temperatures by the addition of the inorganic NPs. For 1 wt.% MoS<sub>2</sub> we obtain a shift of  $T_{g1}$  of about +8 °C (Fig. 7). Averaging ten successive temperature scans for pure and filled JD-2000, respectively we obtain  $\Delta T_{g1} = 8 \pm 3$  °C. For JD-2000 filled with 0.1 wt.% MoS<sub>2</sub> the change in  $T_{g1}$  was smaller than 0.8 °C. In contrast,  $T_{g2}$  is not affected by the presence of inorganic NPs.

It is important to note, that all these measurements shown here were performed on samples that were not annealed at high temperatures, i.e., the intermolecular hydrogen bonds between polyurea chains were not removed. Starting from room temperature they were cooled down to



**Figure 5** Optical microscopy (top) and SEM (bottom) images of JED-C1 filled with 0.5 wt.% MoS<sub>2</sub>, showing “clouds” of MoS<sub>2</sub> aggregates (top) with relatively well-dispersed regions in between (bottom). Individual multiwall-nanotubes of about 100 nm thickness and 10 μm length are perfectly discernible.

low temperatures and then heated until the hydrogen network broke down.



**Figure 6** Temperature and frequency dependence of  $\tan \delta$  of the pure polyurea elastomer JD-2000. The measurements were performed at a heating rate of  $dT/dt = 1 \text{ }^\circ\text{C min}^{-1}$ .

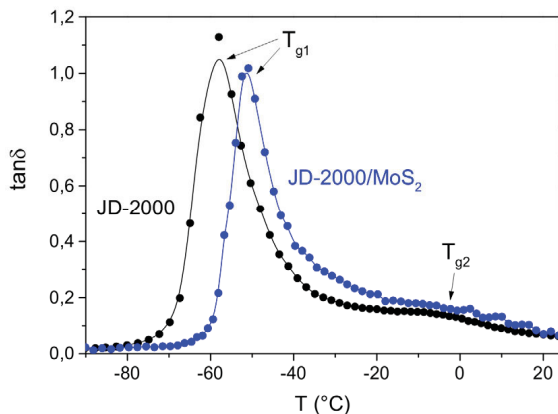
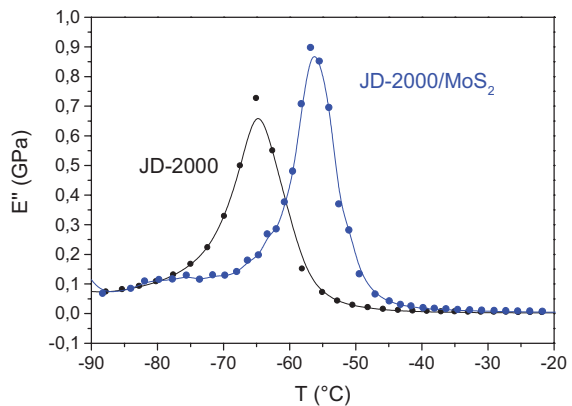
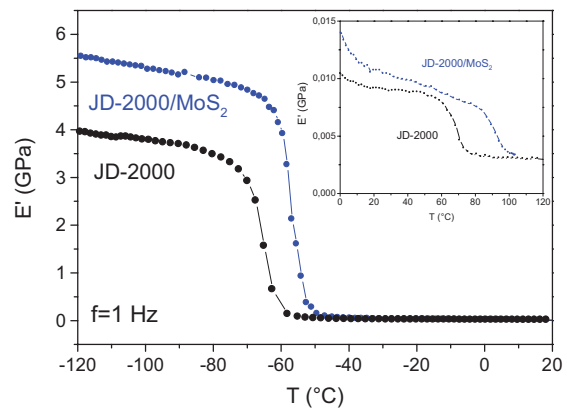
The inset of Fig. 7 displays the high temperature part of  $E'(T)$  drawn on a larger scale to show the changes in Young's moduli due to the breakdown of the hydrogen bonded network. One clearly observes an increase of the annealing temperature due to the presence of  $\text{MoS}_2$  NPs.

On the other hand, samples that were annealed at about  $80 \text{ }^\circ\text{C}$  for at least 2 h prior to measurements, did not show any significant effects of NPs on  $T_g$ .

To study the influence of inorganic nanofillers for another polymer we have performed DMA measurements of the elastomer JED (empty as reference system) and JED filled with 0.1, 0.5, and 1 wt.%  $\text{MoS}_2/170$  (called JED-C1) and  $\text{MoS}_2/628$  (called JED-C2). Pure JED exhibits a glass transition around  $T_g \approx -51 \text{ }^\circ\text{C}$ . Similar as for JD-2000 we found an increase of the glass transition for increasing concentration of  $\text{MoS}_2/170$  NPs. (Fig. 8) for not annealed samples. Also here the effect of NPs on  $T_g$  vanishes with annealing.

The maximum shift of  $T_g = +7 \text{ }^\circ\text{C}$  was observed in not annealed samples for 1 wt.% of  $\text{MoS}_2$ .  $\Delta T_g \approx +3 \text{ }^\circ\text{C}$  for 0.1 wt.% and  $+4 \text{ }^\circ\text{C}$  for 0.5 wt.% of  $\text{MoS}_2$ . For the samples filled with larger nanotubes (JED-C2) no significant shift in  $T_g$  was observed (Fig. 9). In both types of composites (JED-C1 and JED-C2) an increase in  $E'$  (reinforcement) was observed at least at temperatures above  $T_g$  (inset of Figs. 8 and 9). It is also notable that in both composites the annealing temperature for removing the hydrogen bonds is influenced by the presence of nanotubes. With increasing concentration it shifts to higher temperatures by an amount up to  $5 \text{ }^\circ\text{C}$  for 1 wt.% nanotubes (inset of Figs. 8 and 9). For JD-2000 the shift was more than  $20 \text{ }^\circ\text{C}$  (inset of Fig. 7).

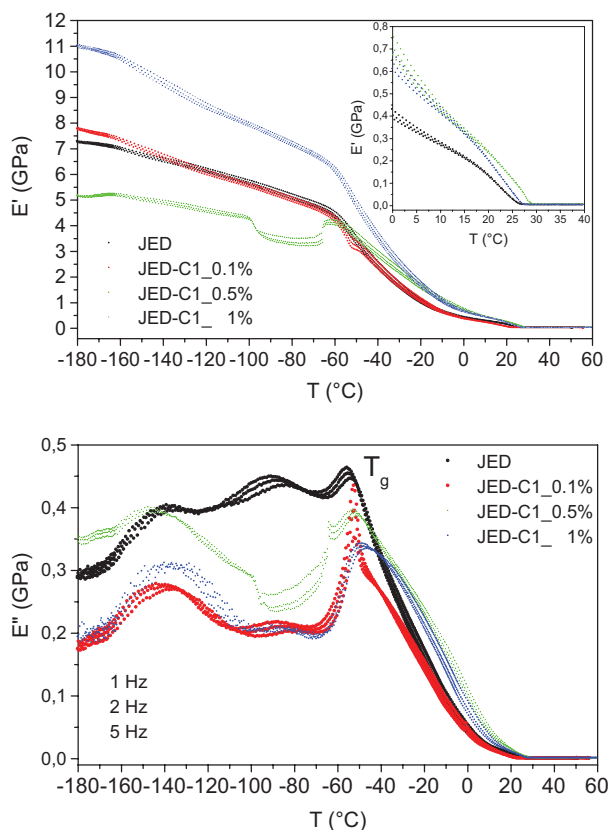
Such changes of  $T_g$  in nanocomposites are not unusual. It is well established, that many properties of polymer nanocomposites depend crucially on the polymer-NP interface [11, 13]. For example, Bansal et al. [12] have shown, that the thermomechanical properties of polymer nanocomposites are critically affected by the polymer-NP wetting behavior. They used  $\text{SiO}_2$  NPs with a diameter of



**Figure 7** Storage  $E'$ , loss  $E''$  moduli and  $\tan \delta$  of pure polyurea JD-2000 compared with the nanocomposite JD-2000/ $\text{MoS}_2$  (1 wt.% of  $\text{MoS}_2$ ). The measurements were performed at the heating rate  $dT/dt = 1.5 \text{ }^\circ\text{C min}^{-1}$  and frequency of 1 Hz.

$14 \pm 4 \text{ nm}$  dispersed in a polystyrene matrix. For untreated silica surfaces, which are non-wetting to polystyrene, they found a rather moderate decrease in  $T_g$ . For 1 wt.%  $\text{SiO}_2$  they obtain  $|\Delta T_g(1\%)| \approx 1.5 \text{ K}$ , for 5 wt.% the shift is about 4 K. For silica NPs grafted with dense polystyrene brushes ("hairy" NPs), silica surfaces provide intimate surface-polymer contact and  $T_g$  is shifted to higher temperatures, i.e., up to 4 K for 5 wt.% of grafted (wetting) NPs.



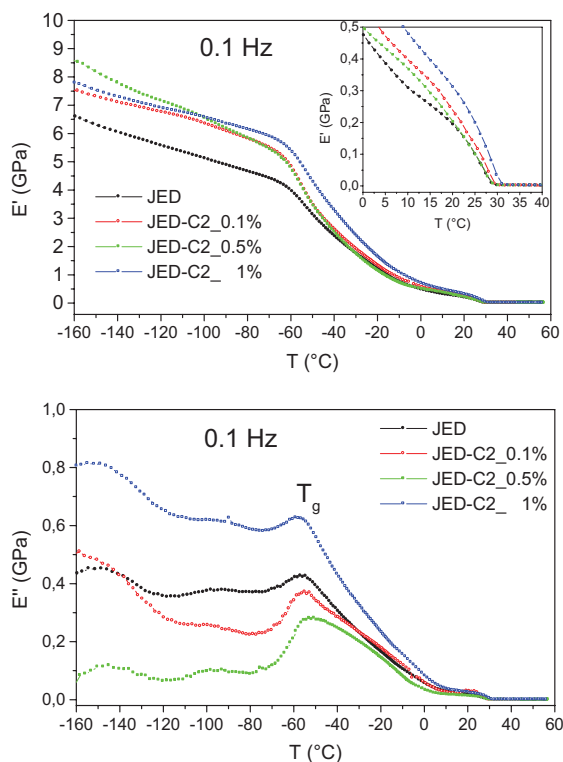


**Figure 8** Storage  $E'$  and loss modulus  $E''$  of pure elastomer JED compared with JED filled with 0.1, 0.5, and 1 wt.% MoS<sub>2</sub>/170. The measurements were performed at the heating rate  $dT/dt = 1\text{ °C min}^{-1}$  with frequencies of 1, 2, and 5 Hz.

The details of the mechanisms giving rise to the changes of  $T_g$  measured in polyurea–NP composites are difficult to resolve, since the glass transition mechanism itself is not yet fully understood [16–20]. A possibility to explain the observed increase of  $T_g$  is based on the results of extensive molecular dynamics simulations of polymers with nanoscopic particles [15]. According to these results the polymer dynamics is affected in the proximity of the NPs. Depending on the type of interaction between the NPs and the polymers, the chain relaxation dynamics can accelerate (for non-wetting conditions, i.e., repulsive interactions) or slow down considerably (for attractive interactions, i.e., wetting or for neutral interfaces).

In the present case, the prevalent polymer–nanotube interaction is most probably attractive [28] occurring due to bonding of the hydrogens with the S-atoms of MoS<sub>2</sub> [14] (Fig. 10).

Because the size of CRRs increases for  $T \rightarrow T_g$ , the dynamics of polymer chains at certain distances away from the NP surface will slow down, which then will reduce the dynamics of the whole sample, rationalizing the observed increase of the glass transition temperature. This picture is in good agreement with our observations (Fig. 7), showing that only the glass transition in the soft domains at  $T_{g1}$  is



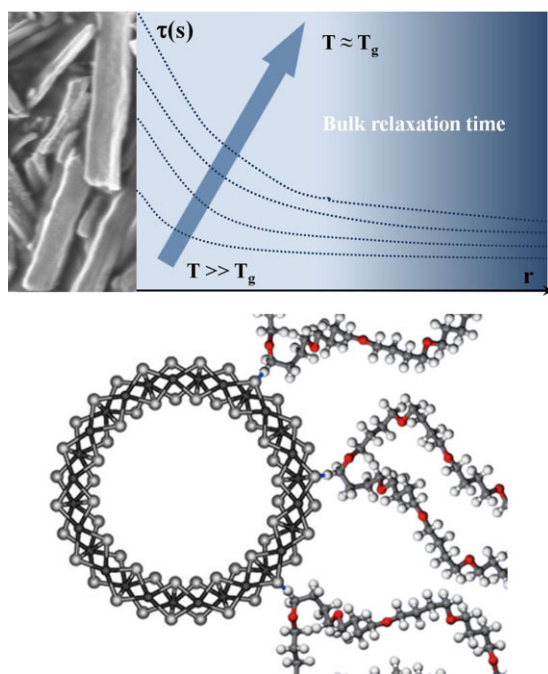
**Figure 9** Storage  $E'$  and loss modulus  $E''$  of pure elastomer JED compared with JED filled with 0.1, 0.5, and 1 wt.% MoS<sub>2</sub>/628. The measurements were performed at a heating rate of  $dT/dt = 1.5\text{ °C min}^{-1}$ .

influenced by the addition of inorganic NPs, whereas the regions near the hard domains yield a glass transition at  $T_{g2}$  that is independent of the presence of NPs: the molecules near the hard domains are already strongly (chemically) attached, so that their dynamics is substantially slowed down and thus  $T_{g2}$  is not expected to be much influenced by the interaction with inorganic NPs.

A similar decrease of mobility was recently observed in natural rubber–silica nanocomposites [21]. Even in the absence of specific polymer–filler interactions, polymer segments within a few nanometers of the filler particles exhibit relaxation times up to 2–3 orders of magnitude slower leading to an increase of the glass transition temperature of few Kelvin compared to bulk natural rubber.

In PMMA–C60 nanocomposites with NPs up to 6 wt.% a maximal increase of  $T_g$  of about 4 K was detected [22], and was also explained in terms of slowed down interfacial polymer/NP regions.

This picture of slowed down interfacial regions near MoS<sub>2</sub> NPs may be complemented by the observation, that the annealing temperatures for removing the hydrogen bonds are increased with increasing NP concentration (Figs. 7–9). It suggests that the NPs support the formation of intermolecular hydrogen bonding between the polymer chains (Scheme 2). Such an increase in cross-links between polyurea chains could explain the observed increase in



**Figure 10** Top: Polymer chain relaxation time  $\tau(r)$  as a function of distance  $r$  from the nanoparticle surface, at various temperatures approaching  $T_g$ . The arrow indicates the spatial increase of the slowed down regions due to the increase of correlation length with  $T \rightarrow T_g$ . Bottom: Schematic illustration of the bonding between the hydrogen atoms of polyurea chains and the sulfur atoms of MoS<sub>2</sub> nanotubes as proposed in Ref. [28].

tensile strength and would also explain the observed reduced chain mobility in the vicinity of NP induced crosslinking points and the resulting increase in  $T_g$ . Similar observations have been made very recently by Dodiuk et al. [27]. The authors have studied the influence of WS<sub>2</sub> NPs on the thermo-mechanical and adhesive peel properties of polyurethane. They also came to the conclusion, that the WS<sub>2</sub> NPs may induce formation of intermolecular hydrogen bonding within the polyurethane.

An interesting observation has been made recently by Taschin et al. [6] with transient grating experiments of polyurea JD-2000 filled with  $\approx 1$  wt.% MoS<sub>2</sub> nanotubes. An intermediate dynamics was clearly detected at room temperature at the time scale of  $\tau \approx 5 \times 10^{-5}$  s. Since this signal was absent in the pure samples, the authors argued that the effect is coming from the interfacial polymer chains in the vicinity of the nanotube surfaces. Taking into account that the relaxation time  $\tau_\alpha$  of the alpha-relaxation in pure polyurea [21] is of the order of  $\tau_\alpha \approx 10^{-7}$  s at room temperature, one could speculate that the observed intermediate dynamics becomes visible in the filled samples due to an increase of local relaxation times from  $10^{-7}$  s in the bulk to  $10^{-5}$  s close to the NPs. This explanation is in good agreement with our findings. However, to draw more specific conclusions detailed investigations, like, e.g., temperature dependent transient grating experiments or

local dielectric spectroscopy measurements [26] have to be performed on polyurea/MoS<sub>2</sub> nanocomposites.

**4 Conclusions** We have presented extensive DMA measurements of pure polyurea elastomers and nanocomposites of polyurea filled with various concentrations of inorganic nanotubes MoS<sub>2</sub>. An upshift of  $T_g$  of several °C was observed together with a slight increase of the Young's moduli of the composites. The increase of  $T_g$  is explained in terms of slowing down of local polymer chain dynamics, i.e., for polymer chains in the vicinity of the nanotubes. A clear cut analytic theory concerning such a suppression of dynamics is still missing. However, molecular dynamics simulations [15, 25] have shown a gradual slowing down of the polymer dynamics approaching the surface of NPs, that do interact with the polymer matrix. In the present case, such an interaction between polyurea chains and MoS<sub>2</sub> NPs could be mediated via hydrogen bonding. Indeed, recent computer simulations [23] have shown that hydrogen may form stable chemical bonds with some low Miller-indexed edges of MoS<sub>2</sub>. First principles calculations on a MoS<sub>2</sub> monolayer [28] yielded that hydrogen atoms prefer to bond to S atoms with a length of 1.41 Å and a formation energy of 1.91 eV. Although the detailed local geometry of the polymer–nanotube interface cannot be resolved at the moment, it seems clear, that the observed slowing down comes from such an interaction between the hydrogen atoms and sulfur atoms of MoS<sub>2</sub> nanotubes. Also our observation, that for annealed samples (hydrogen bonds are removed) the effect of nanotubes on  $T_g$  vanishes, is in accordance with such a picture.

As we have shown here, in the absence of permanent attachments of the polymer chains to the MoS<sub>2</sub> NPs the system yields a single, but larger average  $T_g$ , due to the increase of the longest relaxation time. On the other hand, polyurea opens a unique possibility to study also the effect of very strong NP/chain enthalpic interactions. Due to its phase separated nanostructure into so called hard and soft domains (Fig. 1), two glass transitions appear which are related to cooperative motions of molecular segments in the soft domains ( $T_{g1}$ ) and to regions near the hard nanodomains ( $T_{g2}$ ), respectively. Due to the strong attractive NP–polymer chain interactions the polymer chain motions near the hard nanodomains are considerably slowed down and as a result  $T_{g2}$  turns out to be much larger than  $T_{g1}$ .

More detailed results on the corresponding two glass transition behavior (Fig. 3) in polyureas with various molecular weights of the polyetheramines will be presented in a forthcoming paper.

**Acknowledgements** The present work was performed in the frame of the COST Action MP0902 (COINAPO – Composites of Inorganic Nanotubes and Polymers). Financial support by the Austrian Science Fund (FWF) P23982-N20 is gratefully acknowledged. Support from Prof. R. Mezzenga (member of the COINAPO Swiss team) is greatly appreciated. We sincerely thank S. Puchegger (Faculty Center for Nanostructure Research, University of Vienna) for providing the SEM images.



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