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Ultrasonic and Dielectric Studies of Polyurea Elastomer Composites with Inorganic Nanoparticles

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The temperature dependence of ultrasonic velocity and ultrasonic attenuation were measured in polyurea elastomer composites with inorganic nanoparticles. The decrease in the ultrasonic velocity along with an attenuation maximum was observed above the glass transition temperature, T_g. The shape and position of this peak are directly proportional to the amount of embedded nanoparticles. In addition, the sharp anomalies in the ultrasonic velocity and ultrasonic attenuation were observed above the glass transition temperature in semicrystalline polyurea elastomers. These anomalies are related to the corresponding first order phase transition of these crystalline domain-containing networks. The ultrasonic attenuation peak related to glass transition is considerably smaller in these polyurea networks showing a small influence of the soft domains below the melting temperature, T_m. The first order phase transition in the semicrystalline polyurea elastomers shows a large temperature hysteresis of more than 10 K, which was confirmed by dielectric investigations. The addition of small amounts of inorganic nanoparticles resulted in a shift of the first order phase transition temperature in semicrystalline nanocomposites.

Keywords Elastomers; polyurea; nanocomposites; phase transitions; ultrasonic properties

Introduction

Inorganic MoS_2 nanotubes [1] and $Mo_6S_4I_6$ nanowires [2] can be used for the fabrication of nanocomposites when combined with polymeric matrices, exhibiting a good dispersability in the final composite material. Multifunctional materials produced out of polymers containing inorganic nanotubes/nanowires that can be designed at the nanoscale are expected to have a great impact on industrial applications in the future. A new family of such composites consists of polyurea elastomer composites with inorganic MoS_2 nanotubes or $Mo_6S_4I_6$ nanowires. Polyureas are a new kind of materials with higher performance than polyurethanes [3]. The enhancement of mechanical, chemical and thermal properties is due to the presence of hydrogen bonds between the urea motives, which can

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be reversibly erased at high temperature and soften the elastomeric network. Thus, the final polymer network could be considered as a chemical and physical network at room temperature, and as a conventional rubber above the temperature where such hydrogen bonds break down [4]. Such materials are a combination of a polymer melt and a cross-linker that connect the polymer chains into a single macromolecule. The fast reaction between poly(isocyanates) (rigid crosslinkers) and poly(etheramines) (flexible chains) results on the formation of such polyurea networks, which exhibit a phase separated structure with rigid urea domains (hard domains) embedded in a matrix of flexible polymer chains (soft domains) [4–5]. The elastic properties of polyurea nanocomposites can be tuned over a broad range by varying the molecular weight of the components, the relative amount of hard and soft domains, and the loading of nanoparticles.

Ultrasonic methods, as non-destructive techniques, can be used for the characterization of elastomers and nanocomposites. At room temperature a large ultrasonic relaxation attenuation maximum and ultrasonic velocity dispersion related to the glass transition were observed in polyurea elastomers [6–7]. The position of the ultrasonic attenuation peak and the corresponding activation energy of the relaxation process strongly depend on the segmental molecular weight between crosslinking points, M_c, and on the nature of the crosslinker in the polymer network [7]. Recently, it was shown by ultrasonic and mechanical spectroscopy experiments that small amounts of MoS_2 nanotubes or $Mo_6S_4I_6$ nanowires embedded in polyurea matrices shifted the ultrasonic attenuation peak. This behavior was related to the shift of the glass transition towards higher temperatures [8–11].

The reinforcement of polyurea and polycaprolactone polymers by the addition of small amounts of inorganic nanoparticles (0.1 to 5 wt-%) was also observed by ultrasonic velocity measurements [11], confirming the results obtained in previous studies where ellipsoidal silica-coated hematite nanoparticles were dispersed into a polyurea matrix [12–13]. In this way, we present the temperature dependence of the longitudinal ultrasonic velocity and the ultrasonic attenuation of these new polyurea elastomer composites with inorganic nanoparticles.

Sample Preparation and Experimental Procedure

The MoS_2 nanotubes and $Mo_6S_4I_6$ nanowires were synthesized as described below. Briefly, bundles of $Mo_6S_4I_6$ nanowires were fabricated from elements sealed in evacuated quartz ampoule. This ampoule was placed in two zone furnace and annealed at chemical transport reaction conditions [14]. The $Mo_6S_2I_8$ nanowires were directly synthesized from elements at 1050°C at uniform temperature conditions [15]. The prolonged reaction time (3 days) resulted in several-millimetre-long needles with diameters from several tens to few hundred nanometres. The obtained nanowires were used also as the precursor material for transformation into MoS_2 nanotubes by annealing in the reactive gas mixture composed of 98 vol-% of Ar, 1 vol-% of H_2S, and 1 vol-% of H_2. The morphology of the nanowire bundles was preserved. Thinner MoS_2 nanotubes (from $Mo_6S_4I_6$) [14] were obtained with diameters around 100 nm and lengths up to several micrometers, and thicker MoS_2 nanotubes (from $Mo_6S_2I_8$) [15] with diameters up to several micrometers and lengths up to several hundred of micrometers.

Two types of polyurea elastomers and nanocomposites have been investigated: i) a first set of samples (JSD) obtained by using the hydrophobic elastomer matrix synthesized when crosslinking the poly(etheramine) Jeffamine→ SD-2001 with the triisocyanate crosslinker Basonat→ HI-100, and ii) a second set of samples (JED) which are related to

the hydrophilic elastomer matrix synthesized when crosslinking the poly(etheramine) Jeffamine→ ED-2003 with the same triisocyanate molecule (for the chemical description and preparation of the sample we refer to [4,12–13]). For obtaining the JSD nanocomposite samples, 0.1 wt-% of MoS_2 multiwall nanotubes (MoS_2/170, 100 μm diameter), 0.1 wt-% of MoS_2 multiwall nanotubes (MoS_2/628, 250 μm diameter), and 0.1 wt-% of $Mo_6S_4I_6$ multiwall nanowires were dispersed into the hydrophobic matrix. The JED polyurea nanocomposites were prepared when the hydrophilic matrix was filled with 0.1, 0.5 and 1.0 wt-% of MoS_2/170 nanotubes, and when filled with 0.1, 0.5 and 1.0 wt-% of MoS_2/628 nanotubes. Large samples with a thickness of about 5 mm were obtained for ultrasonic measurements, and smaller cut in a prism of dimensions $4 \times 4 \times 2$ mm^3. Silicone oil was used as a bond for longitudinal ultrasonic waves.

The ultrasonic measurements were carried out using the methods that we previously developed for such measurements for layered ferroelectrics [16–17]. Pulse-echo automatic time-of-flight technique was applied at 10 MHz frequency. At first, the ultrasonic velocity and attenuation values were measured at room temperature. After that, the temperature variation of amplitude and time-of-flight were measured. From these data the temperature dependencies of ultrasonic velocity and ultrasonic attenuation were obtained.

Dielectric measurements were carried out from 100 to 320 K temperature and from 1.2 kHz to 1 MHz frequency interval. Aluminum contacts were deposited on the surfaces of the elastomers. The capacity and lost tangent were measured with a HP4284A LCR-meter.

Experimental Results and Discussion

The temperature dependence of the longitudinal ultrasonic velocity and ultrasonic attenuation in JSD elastomer and nanocomposites with different types of nanoparticles are depicted in Figures 1 and 2, respectively. The longitudinal ultrasonic velocity shows a linear behavior at high temperatures, *i.e. T > 275 K*. The 3% precision in the absolute ultrasonic velocity measurements in small samples did not allow us to ascertain the impact of the different nanoparticles used at room temperature. Therefore, the absolute ultrasonic
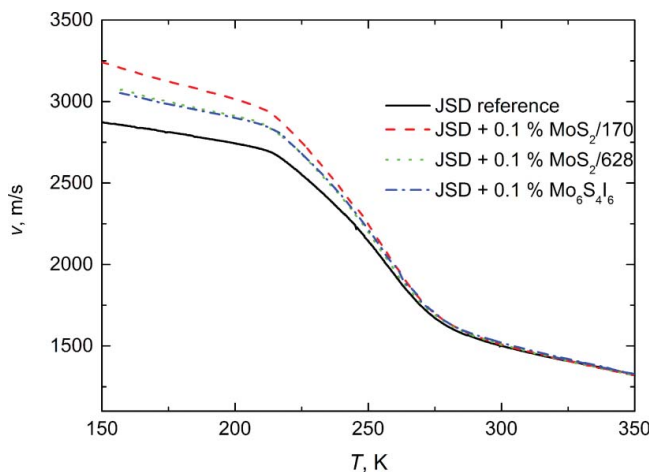

Figure 1. Temperature dependence of the ultrasonic velocity for the JSD polyurea elastomer and the JSD nanocomposites.

velocity was set to be the same at room temperature for all JSD nanocomposites. The relative ultrasonic velocity measurement precision was high enough, therefore near room temperature, the temperature dependence of the ultrasonic velocity $v = f(T)$ shows the same slope for all samples (Figure 1). Below this region, the ultrasonic velocity showed some dispersion associated with the glass transition, and the slope depends on the nature of the nanoparticles dispersed in the polymer matrix. The increase of the longitudinal velocity vs. the type of nanoparticle in the low temperature region is associated with the change in the elastic modulus of the nanocomposite. The different types of nanotubes/ nanowires harden the elastomeric network below the glass transition temperature, T_g. The reinforcement of this polymer nanocomposite depends on the interactions between polymer and nanoparticle interfaces, the elastic modulus and shape of the filler, as well as the orientation with respect to the applied stress [18]. It is known that the elastic modulus of MoS_2 nanotubes [19] is a lot higher than polyurea elastomers, therefore the elastic modulus of the resulting nanocomposite increases. The different impact to the ultrasonic properties of the different nanoparticles probably comes from the interfaces between the nanoparticles and the polymer matrix. Smaller $MoS_2/170$ nanotubes can be distributed more homogenously in polyurea elastomer matrix, whereas larger $MoS_2/628$ nanotubes and $Mo_6S_4I_6$ nanowires tend to be in bundles [2]. In this case, the change in the ultrasonic velocity can be attributed to the small surface of the interface with the elastomer.

The temperature dependence of the longitudinal ultrasonic attenuation (Figure 2) brings information about the impact of the presence of nanostructures to the glass transition dynamics of the elastomers, and polymers in general. Usually, the ultrasonic attenuation peak is observed in the vicinity of T_g. Such peak was observed in all JSD nanocomposites although no significant increase in the peak height was observed. The only visible feature was a small shift in the ultrasonic attenuation peak to higher temperatures with the addition of nanoparticles (mostly for $MoS_2/170$ nanotubes). This shift is due to a change of polymer dynamics in the presence of nanoscale structures that affect the glass transition temperature [20–22]. For attractive interactions between the polymer and the nanoparticles, the chain relaxation time is increased and leads to higher T_g values relative to the pure polyurea matrix [8–11]. It should be noted that the relaxation strength
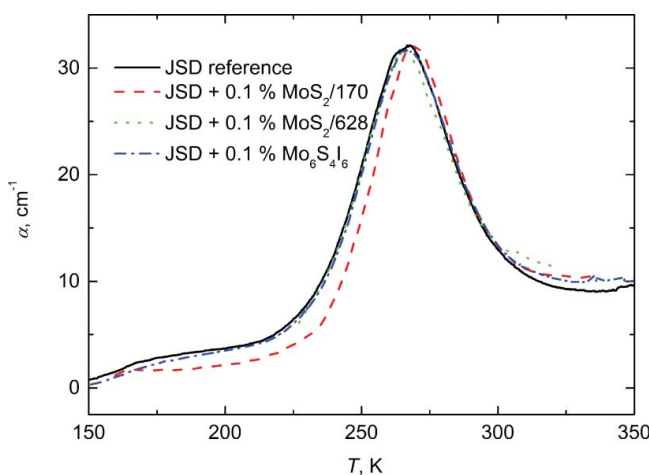

Figure 2. Temperature dependence of the ultrasonic attenuation for the JSD polyurea elastomer and the JSD nanocomposites.
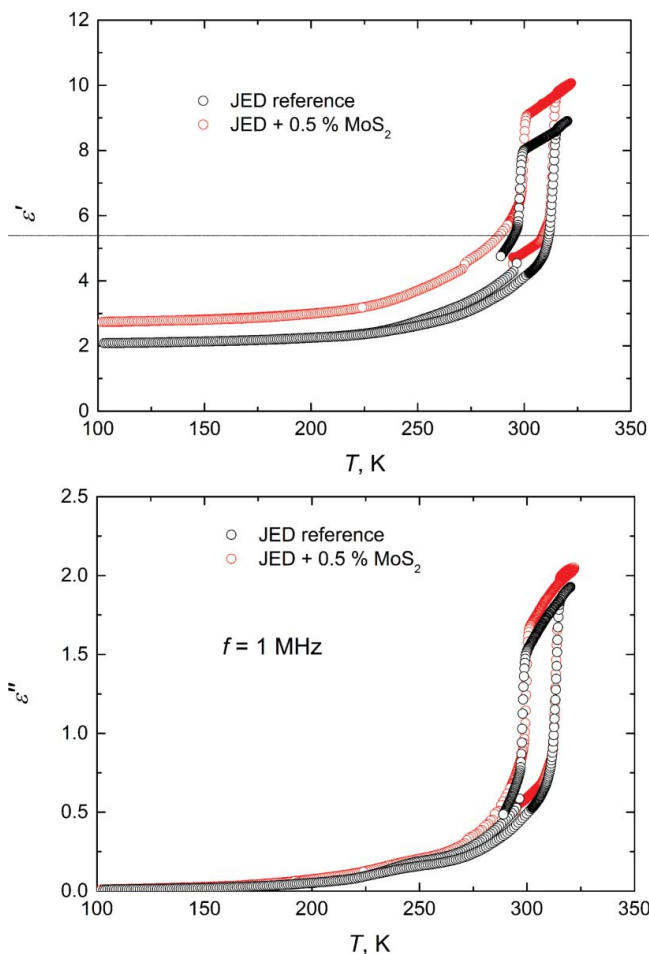
Figure 5. Temperature dependences of the real and imaginary parts of the dielectric permittivity for the JED polyurea elastomer and the 0.5 wt-% MoS_2/170 containing JED nanocomposite.

heating/cooling cycle. Thus, these jumps of the ultrasonic attenuation and ultrasonic velocity cannot be fully reproduced in the following cooling run. The temperature maxima and velocity dispersion near the phase transition can be qualitatively explained by the Landau's mean field dynamic theory of sound behavior in the vicinity of T_m [24], which implies the critical anomaly of relaxation time of the order parameter determined by long-range crystalline order. It is not clear which fraction of the elastomer sample is in the crystalline phase below T_m, therefore the numerical description of ultrasonic anomalies is difficult to determine. Nevertheless, the influence of nanotubes/nanowires to the first order crystalline-to-amorphous phase transition indicates a decrease in the melting temperature upon increasing the loading of nanoparticles as evidenced in Figure 3 and 4.

The main part of ultrasonic attenuation and ultrasonic velocity dispersion below T_m is attributed to the glass transition corresponding to the amorphous fraction of the polyurea elastomer nanocomposites. The impact of the nanofiller on the glass transition for all JED nanocomposites is not as obvious as for JSD samples, as shown in Figures 3 and 4. The ultrasonic attenuation peak (Figure 3) slightly shifts towards higher temperatures when

increasing the filler content, but the 1.0 wt-% sample shows a completely different behavior, *i.e.* the attenuation peak moves to lower temperatures – even lower than the reference sample without nanoparticles. This behavior might be due to the inhomogeneous dispersion of the fillers with the corresponding formation of clusters or aggregates at such a high concentration. Figure 4 shows that the longitudinal ultrasonic velocity change due to the presence of nanoparticles is not as significant as for JSD samples, effect attributed to the small fraction of amorphous polymer backbone in JED elastomer. The evidence of the former statement comes from the attenuation peak which is almost two times smaller compared to JSD samples. The dispersion is observable in these nanocomposites but the change of ultrasonic velocity for the different nanoparticles is insignificant at low temperatures.

The temperature dependence of the complex dielectric permittivity (Figure 5) perfectly illustrates the presence of the melting process and the glass transition. The dielectric permittivity was measured during cooling and heating cycles. These plots show the reversibility of the samples after heating and cooling, but accompanied by a quite large hysteresis of about ~10 K. The temperature dependence of the loss tangent (Figure 5) shows another anomaly which is located between 220 and 275 K, and could be related to the glass transition of the elastomeric matrix. The amount of nanofiller in the composites was not enough to see the influence in the crystalline-to-amorphous phase transition or any lower temperature anomaly. Thus, no significant shifts were observed in dielectric permittivity vs. temperature plots.

In order to ascertain the impact of the fillers to the first order phase transition in JED nanocomposites, the electrostrictive response of the elastomer films was measured. When the DC BIAS field was applied to the thin sample, the film worked as an ultrasonic transducer, and the amplitude of the detected signal was measured. This signal is proportional to the electrostrictive tensor component, and Figure 6 represents the results for a pure JED matrix and the corresponding nanocomposite with $MoS_2/170$ nanotubes during a heating run. These measurements revealed that the maximum of the detected signal shifts towards lower temperatures when adding nanotubes, showing that the dielectric
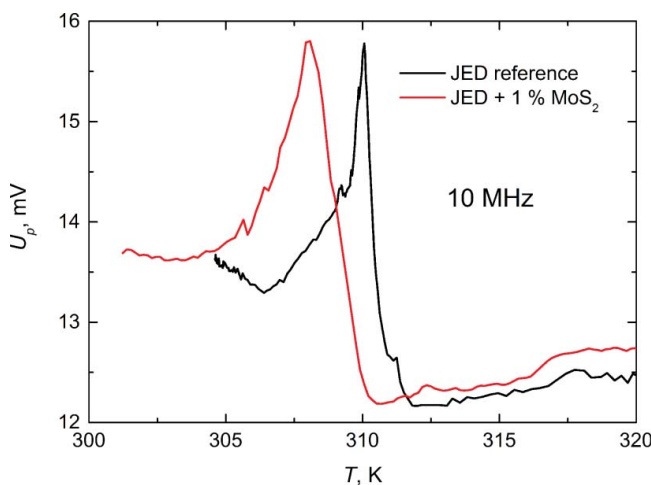

Figure 6. Temperature dependence of the ultrasonically detected electric signal for the JED polyurea elastomer and the 1.0 wt-% $MoS_2/170$ containing JED nanocomposite.

measurements are not that sensitive as ultrasonic techniques are for revealing the impact of inorganic nanoparticles to the properties of polymers.

Conclusions

Measurements of longitudinal ultrasonic velocity and ultrasonic attenuation in composites of polyurea elastomer with MoS_2 nanotubes and $Mo_6S_4I_6$ nanowires at 10 MHz frequencies between 150 and 330 K temperature have been performed. A large ultrasonic attenuation peak and ultrasonic velocity dispersion related to the glass transition have been observed in these nanocomposites. Adding nanoparticles to a polyurea elastomers matrix leads to an increase in the glass transition temperature. At low temperatures the increase of longitudinal ultrasonic velocity related to viscoelastic properties was observed in such polyurea nanocomposites with inorganic MoS_2 and $Mo_6S_4I_6$ nanoparticles. In semicrystalline polyurea elastomer nanocomposites above the glass transition temperature, the ultrasonic anomalies related to the crystalline-to-amorphous phase transition were also observed, and at high nanofilller concentration the melting temperature slightly decreased due to the presence of aggregates or clusters.

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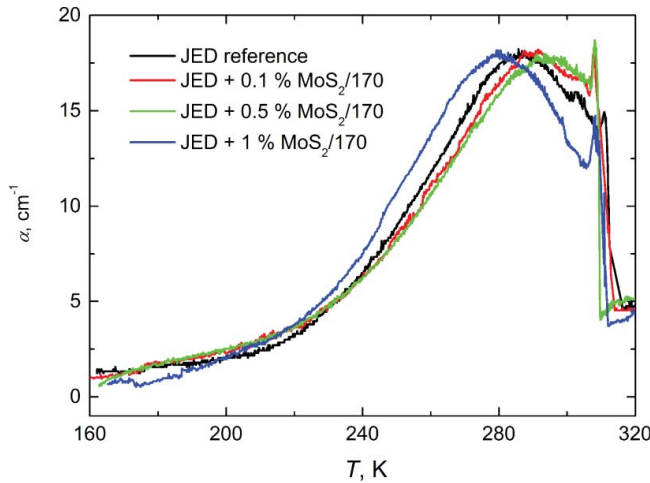
Figure 3. Temperature dependence of the ultrasonic attenuation for the JED polyurea elastomer and the $MoS_2/170$ containing JED nanocomposites.

can be attributed mainly to the polymer matrix because the ultrasonic attenuation peaks are almost the same for all JSD nanocomposites.

JED elastomer and nanocomposites, in addition to the glass transition, have a phase transition coming from the melting of the crystalline domains in the semicrystalline polymer, *e.g.* poly(ethylene oxide) [23]. This phase transition sequence is observable in both ultrasonic (Figure 3 and 4) and dielectric measurements (Figures 5). When the elastomer approaches the melting temperature, T_m, it gets softer and the crystalline domains start melting, which is manifested as a narrow peak and a downward jump in the temperature dependence of the ultrasonic attenuation (Figure 3). It is important to note that the first order crystalline-to-amorphous phase transition ($T_m = 312$ K, upon heating) was accompanied by a large hysteresis, and the elastomer itself changed its dimensions after
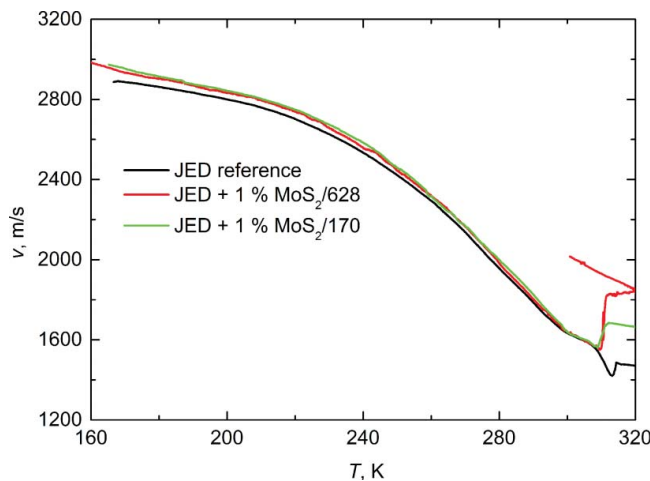

Figure 4. Temperature dependence of the ultrasonic velocity for the JED polyurea elastomer, and the 1.0 wt-% $MoS_2/170$ and $MoS_2/628$ containing JED nanocomposites.

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