

Ultrasonic properties of composites of polymers and inorganic nanoparticles

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The temperature dependencies of ultrasonic velocity and attenuation were measured in composites of inorganic nanoparticles with two types of polymers, poly(urea) elastomer with inorganic $\text{Mo}_6\text{S}_4\text{I}_6$ nanowires and poly(ϵ -caprolactone) (PCL) with $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires. Below room temperature large ultrasonic relaxation attenuation maxima and velocity dispersion were observed. It was found that the attenuation peak in the elastomer shifted to higher temperature after doping with nanoparticles and this behavior was related to the shift of glass transition temperature. The ultrasonic attenuation data was fitted to a relaxation equation with a single temperature

dependent relaxation time. The thermal activation energy of the relaxation process, which was calculated from ultrasonic data, was found to increase in the poly(urea) elastomer doped with MoSI nanowires. The low temperature ultrasonic velocity increased in the poly(urea) with nanowires added and is determined by the increase in elastic modulus. Similar ultrasonic behavior was obtained for PCL composites with inorganic MoSI nanowires. In this case, the increase in elastic modulus was smaller in comparison to the composites of poly(urea) and nanowires. Therefore, reinforcement of PCL was less pronounced.

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1 Introduction Recently, it has been demonstrated that the formation of fullerene-like and nanotube structures is not specific to carbon, but is a generic property of (2D) layered materials, such as MoS_2 . Such inorganic nanotubes can be used for fabrication of various composites with polymer materials as the matrix. Multi-functional materials produced from composites of polymers containing inorganic nanotubes, which can be designed at the nanoscale, are expected to have great impact on industrial applications in the future. New electrically conductive, high strength and thermally conductive polymer composites may exhibit highly enhanced properties. Studies on composites of inorganic nanotubes/nanowires and polymers are relatively few, but significant contributions in this field have been already reported [1–3]. Therefore, it was of interest to investigate the elastic properties of composites of polymers with inorganic nanotubes and nanowires. Ultrasonic methods and mechanical spectroscopy are non-destructive testing techniques and can be used to determine the elastic

properties of polymer composites. Composites of acrylonitrile–butadiene–styrene (ABS) reinforced with carbon nanotubes have been investigated by elastic studies using mechanical spectroscopy in Refs. [4–6] and showed improvements in strength and a higher elastic modulus. Other authors have established that in PMMA– SiO_2 composites with a modified layer of the polymer at the surface of the silica particles can influence the polymer glass transition temperature and kinetics [7]. Recently, the influence of inorganic nanofillers on low frequency dynamic elastic properties and the glass transition temperature was demonstrated in iPP/INT [2], poly(urea) [8], and poly(ϵ -caprolactone) (PCL) [9] composites. Earlier we performed preliminary studies of poly(urea) composites with inorganic MoS_2 nanotubes at ultrasonic frequencies [10]. In the present work, the results of more extensive investigations of the temperature dependencies of ultrasonic velocity and attenuation in poly(urea) and PCL composites with inorganic MoSI nanowires are reported.

2 Experimental procedure Composite of poly (urea) [11] with inorganic MoSI nanowires were produced at ETH, Zurich, Switzerland. The doping was about 0.1 wt%. Nanowires acting as crosslinkers were embedded in a chemical elastomeric network using technology presented in Ref. [11, 12]. In this case evidence of good quality of the dispersion and distribution of the nanofillers was already demonstrated using silica-coated hematite in the same poly (urea) elastomers [12]. Composites of PCL with $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires (which were provided by Mo6 Ltd., Slovenia) has been prepared via melt mixing in a twin screw extruder. Chin et al. showed by SEM studies that nanowires are well dispersed and distributed in polymer matrix. More detailed information about the preparation and morphology can be found in Ref. [9]. In our investigation we used the same set of samples. Measured specimens had dimensions of $4\text{ mm} \times 4\text{ mm} \times 1\text{--}3\text{ mm}$.

Ultrasonic measurements were carried out using methods which we previously developed for such measurements for layered ferroelectrics [13, 14]. A pulse-echo automatic time-of-flight technique was applied. The flow chart in Fig. 1 illustrates the operational arrangement of our measurement process.

All equipment works according to a transmission scheme with one lithium niobate piezoelectric transducer, T_1 functioning as transmitter and another one, T_2 as receiver. The quartz buffers (QBs) are used for time delay of ultrasonic signals as well as sample holders. The excitation radio frequency pulse causes the piezoelectric transducer to oscillate sending an ultrasonic wave through the sample material placed between the buffers. The transducer T_2 converts the ultrasonic wave back to an electric radio frequency pulse. This electrical signal is amplified and displayed on the screen of a digital oscilloscope, and also converted to digital format and recorded by a computer. Analysis program controls the temperature and records the amplitude and time delay of the received signal at any temperature. Silicone oil was used to make acoustic bonds for excitation of longitudinal ultrasonic waves. It is necessary to note that the sticky elastomer by itself makes an acoustic bond with the QB. The absolute values of

ultrasonic velocity and attenuation were measured at room temperature. For this, two identical samples of each composite with the same thickness, L were placed between the buffers. The amplitude, A_1 and delay time, τ_1 of the first transmitted radio frequency pulse were measured. After that one sample was taken away and in this case we measured the amplitude, A_2 and delay time, τ_2 when a polymer sample with a thickness of only half of the former sample was placed in the system. Then values of ultrasonic attenuation α and velocity V for sample of thickness L can be directly obtained as

$$\alpha = \frac{1}{L} \ln \frac{A_2}{A_1} \quad (1)$$

and

$$V = \frac{L}{\tau_2 - \tau_1}. \quad (2)$$

At any other temperature the amplitude and delay time were measured automatically relative to room temperature values. The accuracy of relative time measurements was better than 0.3 ns. The amplitude of received signal was measured with an accuracy of 0.2 mV. This gives the estimated relative velocity and attenuation resolution better than 10^{-4} and 0.3 dB cm^{-1} , respectively.

3 Results and discussion Ultrasonic investigations were performed for several poly(urea) elastomers with various mechanical properties which were tuned over a broad range by varying the molecular weight of the components and MoSI nanowire loading.

The ultrasonic studies revealed large, nanoparticle dependant, attenuation maxima below room temperature, and elastic reinforcement of poly(urea) composites with nanoparticles similar to that presented earlier [10]. Here, we present the most characteristic temperature dependencies of ultrasonic velocity and attenuation in pure poly(urea) (JD) and composite with MoSI nanowires. Measurements were performed slowly changing temperature (at a rate of 0.1 K min^{-1}) for both heating and cooling cycles. No pronounced temperature hysteresis effects were observed, showing that in the ultrasonic frequency range the thermal equilibrium is always reached.

The temperature dependencies of ultrasonic attenuation are shown for the elastomer with nanowires and the reference sample at 10 MHz frequency (Fig. 2). After addition of 0.1 wt% MoSI nanowires to the elastomer the ultrasonic attenuation peak clearly shifts to higher temperature. The longitudinal ultrasonic attenuation values at room temperature are almost independent of nanowire doping level. The temperature dependencies of ultrasonic velocity in the composite and reference sample are shown in Fig. 3. These dependencies were obtained from variation of delay time in mechanical system after subtracting the known part of delay variation in the QBs.

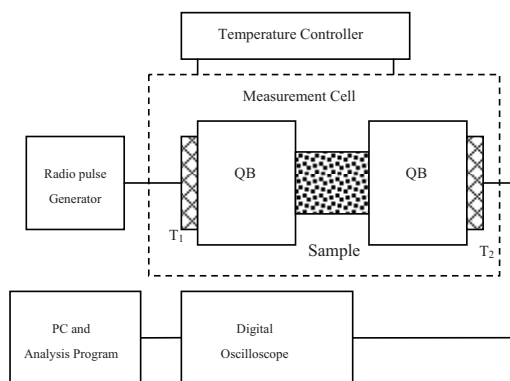


Figure 1 Block diagram of ultrasonic measurement assembly.

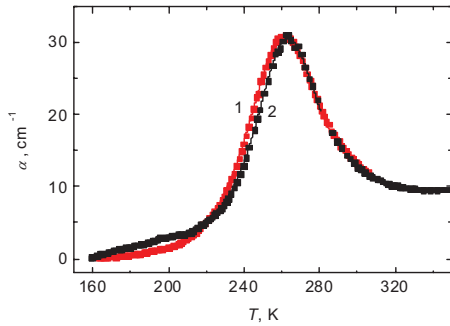


Figure 2 Temperature dependence of ultrasonic attenuation in poly(urea) elastomer JD composites: (1) reference, (2) with $\text{Mo}_6\text{S}_4\text{I}_6$ nanowires. Solid curves are fits according Eq. (3) combined with Eq. (6).

The steepest velocity dispersion region corresponds to attenuation maxima. The shift of attenuation and velocity curves to higher temperatures ($\Delta T \approx 5\text{--}6\text{ K}$) is clearly seen especially in the low temperature attenuation wing. This behaviour can be attributed to a shift of the glass transition temperature for the composite with nanowires. A similar shift was observed using dynamic mechanical analysis at low frequencies for the same poly(urea) samples [8] and was explained by attractive interactions between the polymer and nanoparticles [8, 15]. In this study, the shift of glass transition is not the only effect of nanowire addition on the dynamic ultrasonic properties – another feature observed is the decrease in peak width. This ultrasonic attenuation peak can be described using the relaxation theory of elasticity (see, e.g. [16]). Expressions for the ultrasonic attenuation α and velocity, V for a single relaxation process with relaxation time τ can be written in the form:

$$\alpha = A \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}, \quad (3)$$

$$V^2 = V_\infty^2 - \frac{V_\infty^2 - V_0^2}{1 + \omega^2 \tau^2}. \quad (4)$$

Here, ω is the angular frequency of ultrasonic wave, V_0 and V_∞ are the low and high frequency values of ultrasonic velocity. The parameter A can be estimated from the

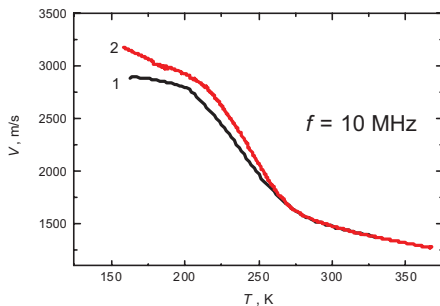


Figure 3 Temperature dependencies of ultrasonic velocity in poly(urea) elastomer JD composites: (1) reference, (2) with $\text{Mo}_6\text{S}_4\text{I}_6$ nanowires.

attenuation peak

$$A = \frac{V_\infty^2 - V_0^2}{2V_0^3} = 2\alpha_{\max}/\omega, \quad (5)$$

where α_{\max} is the peak ultrasonic attenuation value. The relaxation process can be related to re-arrangements in the polymer network, interpreted as a glass transition [17, 18]. Over a wide temperature range, a single relaxation time of a thermally activated process can be described by the Arrhenius law

$$\tau = \tau_0 \exp(\Delta E/kT), \quad (6)$$

where τ_0 is a pre-factor usually supposed as attempt time, and ΔE is the activation energy of the thermally activated process. In order to obtain relaxation parameters the ultrasonic attenuation was fitted with the attenuation expression (3), where τ is expressed by Eq. (6). After a fitting procedure the following parameters were obtained: $\omega\tau_0 = 2.5 \times 10^{-7}$ for the composite with nanowires, and $\omega\tau_0 = 8.5 \times 10^{-7}$ for the reference sample, $\Delta E = 0.36\text{ eV}$ for sample with 0.1 wt% MoSI nanowires and $\Delta E = 0.32\text{ eV}$ for the reference sample; $A = 9 \times 10^{-7}\text{ s m}^{-1}$ for both samples.

The increase in the activation energy for sample with nanowires can be related to elastomer–nanowire interaction at the surface layer and modification of the glass transition. As mentioned above, the ultrasonic velocity temperature variation is quite large.

This also supports the idea that longitudinal velocity dispersion in this temperature region is mostly determined by the glass transition. At room temperature the ultrasonic velocity is of order 1500 m s^{-1} for both the reference sample and composite. The earlier transient grating experiments in similar poly(urea) composites also did not reveal velocity changes at room temperature [19].

Similar ultrasonic investigations were carried out for PCL composites with different MoSI nanowire loading. Three samples, 1, 3, and 5 wt% were chosen from the same composite range described in Ref. [9]. The temperature dependencies of ultrasonic attenuation are shown for the PCL/MoSI composites and unfilled PCL as a reference at the frequency of 10 MHz, see Fig. 4.

The temperature dependencies of longitudinal ultrasonic velocity are shown in Fig. 5. At low temperatures, $V=f(T)$ dependencies are presented in Fig. 6 for PCL with different MoSI content, over the zoomed scale.

We propose that the ultrasonic velocity and attenuation behavior in PCL is also associated with the glass transition, T_g as in the case for low frequency elastic studies performed by the dynamic mechanical analysis [9], where T_g was found to be $\approx 221\text{ K}$. In our study the change of slope in $V=f(T)$ dependence appears in the same temperature range. Although the nanowire content in PCL was higher than in the case of the poly(urea) composites their influence on PCL was considerably smaller. The shift of T_g caused by nanowire addition to PCL is difficult to estimate from Fig. 4,

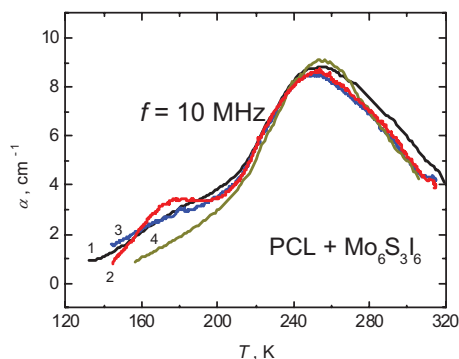


Figure 4 Temperature dependencies of ultrasonic attenuation in PCL composites: (1) reference, (2) with 1 wt%, (3) 3 wt%, and (4) 5 wt% $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires.

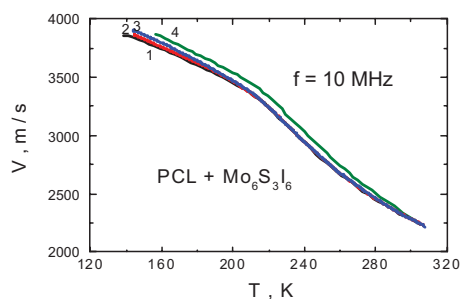


Figure 5 Temperature dependencies in ultrasonic velocity for PCL composites: (1) reference, (2) with 1 wt%, (3) 3 wt%, and (4) 5 wt% $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires.

because at low temperatures additional attenuation caused by other relaxation processes are clearly seen. It is necessary to note that at low temperature ultrasonic velocity in pure PCL and its composites with nanowires showed a linear dependence with temperature.

The onset of deviation appears near the glass transition temperature. The variation of longitudinal ultrasonic velocity with MoSI nanowire content can be best approximated by a linear fit (Fig. 7). However, the increase

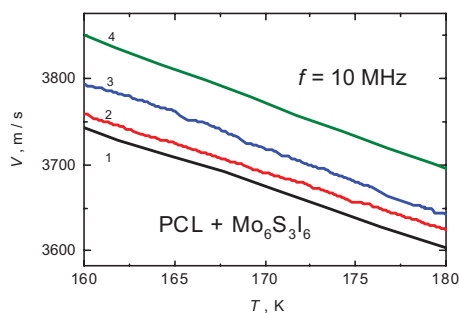


Figure 6 Low temperature part of ultrasonic velocity as a function of temperature for PCL composites: (1) reference, (2) 1 wt%, (3) 3 wt%, and (4) 5 wt% $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires.

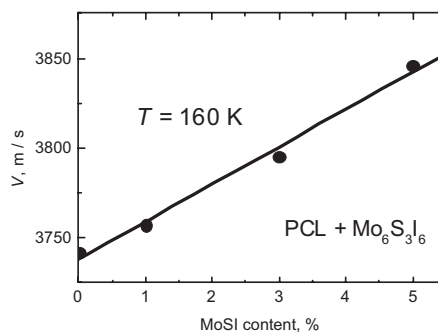


Figure 7 Ultrasonic velocity in PCL as a function of MoSI nanowire content at 160 K.

in ultrasonic velocity, in comparison with the poly(urea) based composites, is small (<2%).

The temperature dependencies of longitudinal ultrasonic velocity and attenuation in PCL composites can be also described using relaxation of some internal degrees of freedom which are also responsible for the glass transition process in pure PCL. As mentioned previously, and from Figs. 4 and 5, it is difficult to describe ultrasonic attenuation and velocity dependencies using only one relaxation time. In this instance a distribution of relaxation times must be taken into account. It is known that in PCL there are several relaxation processes [20]. The existence of α , β , and γ relaxations in PCL introduces a complication with regard to the relationship between local and segmental modes in the polymer.

Also, the abundance of modes makes the analysis of this semi-crystalline polymer complicated as the temperatures where the modes are isolated are practically unseen at the experimental frequency used (10 MHz).

It is interesting to compare reinforcement phenomenon between the poly(urea) and PCL composites with MoSI nanowires (Fig. 8).

The most interesting feature from comparing the ultrasonic behavior of the two polymers doped with MoSI nanowires is the different influence on the low temperature ultrasonic velocity. For the poly(urea) composites, addition

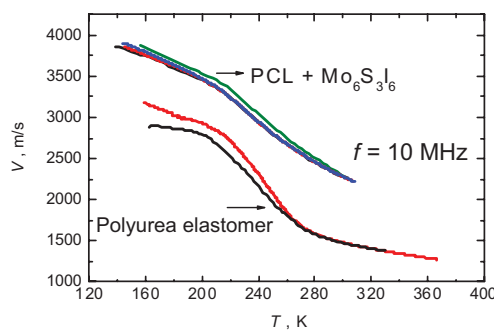


Figure 8 Comparison of the ultrasonic velocity for poly(urea) elastomer and PCL composites with MoSI nanowires.

of a small amount = 0.1 wt% nanowires resulted in a significantly larger change of ultrasonic velocity compared to PCL with 5 wt% nanowires added. Therefore, the simple “rule of mixtures” for different polymer matrices and filler having different elastic properties with respect to their volume fractions is not always valid. Of course the increase in ultrasonic velocity shows that reinforcement of the polymer depends not only on the volume fraction, but also on polymer–nanoparticle interaction as well as filler geometry and orientation of these particles with respect to applied ultrasonic wave stress [21]. Therefore, further studies on the other polymer/nanowire composite materials with a larger range of filler doping and different particle orientations are needed in order to clarify the ultrasonic behavior of such composites.

4 Conclusions Ultrasonic measurements of longitudinal velocity and attenuation in composites of poly(urea) elastomer and PCL with MoSI nanowires at 10 MHz in the 150–300 K temperature range have been presented. A large ultrasonic attenuation peak and velocity dispersion have been observed in these composites. It was shown that the relaxation maxima were affected by addition of inorganic MoSI nanowires. Adding nanoparticles to a poly(urea) elastomer matrix resulted in an increase in glass transition temperature. The experimental data for the poly(urea) composites were compared with ultrasonic relaxation theory involving a single relaxation time of a thermally activated process. It was concluded that the activation energy increased in the composite with addition of nanowires. At low temperatures the increase of longitudinal ultrasonic velocity related to viscoelastic properties was observed in poly(urea) and PCL composites with MoSI nanowires. The increase in velocity caused by elastic reinforcement from nanowires was larger for poly(urea) composites when compared to PCL based composites.

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