

# Ultrasonic studies of polymer composites with inorganic nanotubes

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**Abstract**—The temperature dependencies of longitudinal ultrasonic attenuation and velocity in several groups of new polyurea elastomers and poly( $\epsilon$ -caprolactone) composites were measured. In region of the glass transition the large ultrasonic attenuation maxima were observed. These peaks have relaxation behavior and can be approximated by temperature dependant relaxation time described by Arrhenius equation. The position of ultrasonic attenuation maxima and activation energy of relaxation process depends on the structure of the polyurea network. The ultrasonic relaxation peak in poly( $\epsilon$ -caprolactone) is also related to glass transition. The influence of inorganic nanotubes and nanowires in polyurea elastomers and poly( $\epsilon$ -caprolactone) is also discussed.

**Keywords**; ultrasonic attenuation; inorganic nanotubes; polymer nanocomposites

## I. INTRODUCTION

During last years it has been demonstrated that formation of fullerene-like and nanotube structures is not specific to carbon, but is a generic property of layered materials, such as MoS<sub>2</sub>. Such inorganic nanotubes can be used for fabrication of various composites based on polymer materials. Composite materials made of polymers with inorganic nanofillers can become a perspective alternative for conventionally used materials in industry and science. Ultrasonic waves as non-destructive testing technique are usually used for determination of elastic properties of polymer composites. Ultrasonic spectroscopy allows to observe and evaluate processes that govern polymer elastic behaviour and to describe variation of these processes because of the change of the filler concentration. In this contribution we present the temperature measurements of ultrasonic velocity and attenuation in two types of polymer composites with inorganic nanotubes: polyurea elastomers and poly( $\epsilon$ -caprolactone) (PCL). Polyurea elastomers are a new kind of materials with higher performance than polyurethanes [1-2]. PCL is an important biodegradable polymer used in medicine [3].

Ultrasonic experiments showed a change in the slope for the ultrasonic velocity and attenuation peak above the glass transition temperature  $T_g$  in both types of polymers. This relaxation maximum strongly depends on the segmental

molecular weight of the polymer chains between crosslinking points and on the nature of the crosslinkers in the network in polyurea elastomers. The addition of inorganic nanofillers resulted in the increase of ultrasonic velocity in composites and change of ultrasonic relaxation parameters in the material.

## II. EXPERIMENTAL PROCEDURE

Polyurea polymer samples were produced in ETH, Zurich, Switzerland. We investigated several types of hydrophobic elastomers with small (JD-400), medium (JD-2000) and high (JD-4000) linear molecular weight polymer backbone having only crosslinking points from triisocyanate (for polymer chemical description and preparation we refer to ref. [1]). Two solutions in acetone were prepared as described in literature [2]: one containing the diamino-terminated polymer, and the other the trifunctionalized crosslinker with or without inorganic MoS<sub>2</sub>/628 nanotubes. After solutions gently mixed and dried [2] the pure polyurea and composite with nanoparticles were obtained. The preparation and other properties of composites of poly( $\epsilon$ -caprolactone) (PCL) with Mo<sub>6</sub>S<sub>3</sub>I<sub>6</sub> nanowires have been described previously [3]. For ultrasonic studies we used the same set of samples as described in [3]. The procedure of attenuation and velocity measurement was presented earlier [4]. For ultrasonic measurements, samples of dimensions 4 mm × 4mm × 1-3 mm were prepared. The temperature dependencies of longitudinal ultrasonic velocity and attenuation in pure polyurea elastomer and composite with nanoparticles were measured slowly changing temperature (rate of 0.1 K/min) in heating and cooling cycles. No pronounced temperature hysteresis effects were observed, showing that in the ultrasonic frequency range the thermal equilibrium was always reached.

## III. RESULTS AND DISCUSSION

Temperature dependencies of longitudinal attenuation for JD elastomers are shown in Fig. 1. From all these graphs it is clearly seen that there are attenuation peaks related to relaxation processes. Low temperature hog of the curves correlate with the glass transition temperature which was

earlier presented in [1, 5]. Maxima of attenuation shift towards higher temperatures when molecular weight decreases in the polyurea elastomers. The peak also narrows with increasing of molecular weight.

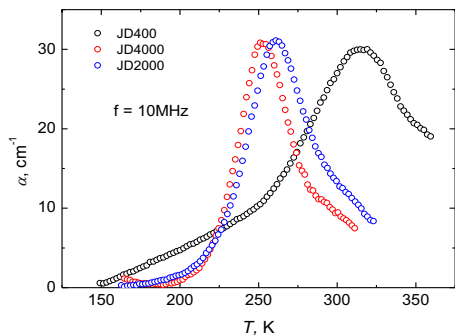


Figure 1. Temperature dependencies of longitudinal ultrasonic attenuation in JD400, JD2000 and JD4000 polyurea elastomers.

We can conclude that ultrasonic properties of JD elastomers are strongly dependant on molecular structure. The same shift of relaxation maximum was observed after addition of MoS<sub>2</sub> nanotubes in these polyurea elastomers as well.

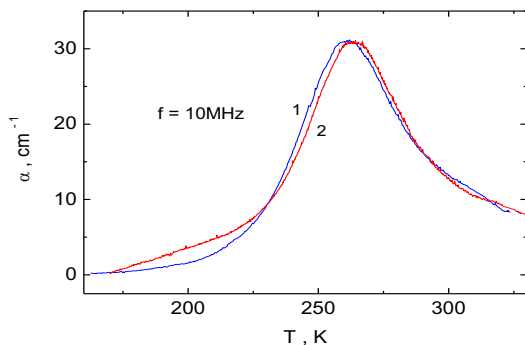


Figure 2. Temperature dependencies of longitudinal ultrasonic attenuation in JD2000 (1) and JD2000 with MoS<sub>2</sub> nanotubes (2) polyurea elastomers.

As an example in Fig. 2 we present the temperature dependencies of ultrasonic attenuation for JD2000 elastomer (pure and with MoS<sub>2</sub> nanotubes). The amount of nanotubes was no more than 1%. It is clearly seen that relaxation peak is shifted by 3 K. The shift is related to the impact of fillers to glass transition temperature and correlate to the results obtained by low frequency mechanical analysis method [5]. The ultrasonic attenuation in polymers can be explained simply by relaxation process with single temperature dependant relaxation time described by Arrhenius equation [4]. In this case the peak width is related to the activation energy of this process. Decrease of width of the peak shows that the activation energy increased in elastomers with MoS<sub>2</sub> nanotubes.

Similar results were obtained for polycaprolactone polymer with MoSI nanowires (Fig. 3). Here we also see narrowing of ultrasonic attenuation peak in composite with nanowires as

well as a little shift of peak position to higher temperatures. In this case the maximum attenuation is considerably smaller than for polyurea elastomers.

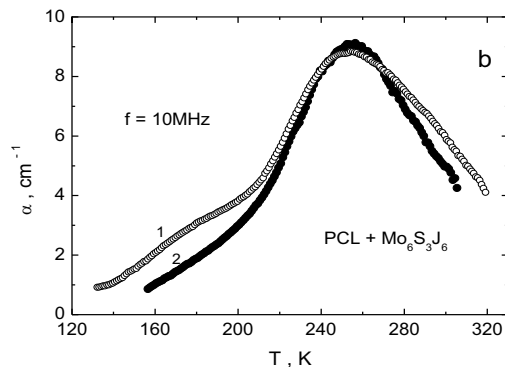


Figure 3. Temperature dependencies of longitudinal ultrasonic attenuation for PCL polymers: reference (1) and PCL with 5% MoSI nanowires (2).

It is necessary to note that in both types of polymer composite with inorganic nanoparticles ultrasonic velocity increases, especially at low temperatures, and it is consequence of the reinforcement of such composite, because elastic coefficients of inorganic nanotubes are considerably larger.

#### IV. CONCLUSIONS

The temperature dependencies of longitudinal ultrasonic attenuation and velocity in polycaprolactone and polyurea elastomer composites with MoS<sub>2</sub> nanotubes and MoSI nanowires were measured. The large ultrasonic attenuation peak and velocity dispersion have been observed related to glass transition. This ultrasonic relaxation can be described by relaxation theory involving single relaxation time of thermally activated process. At low temperatures the increase of longitudinal ultrasonic velocity related to viscoelastic properties was observed in PCL and polyurea composites with nanoparticles.

*Acknowledgements:* The work was supported by the COST Action MP0902 and Lithuanian Research Council under project MIP-068/2012.

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