

Ultrasonic Characterization of Dynamic Elastic Properties of Polymer Composites with Inorganic Nanotubes

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Abstract: The temperature dependencies of ultrasonic velocity and attenuation were measured in pure polyurea elastomer and doped with inorganic MoS₂ nanotubes. Below room temperature the large ultrasonic relaxational attenuation maxima and velocity dispersion were observed. It was found that the attenuation peak in elastomer shifted to lower temperature after doping with nanotubes. The ultrasonic attenuation data were fitted to relaxation equation with temperature dependent relaxation time. The thermal activation energy of relaxation process, which was calculated from ultrasonic data, was found to increase in polyurea elastomer doped with MoS₂ nanotubes. The low temperature ultrasonic velocity increases in polymer with nanotubes and it is determined by the increase of elastic modulus. *Copyright © 2011 IFSA.*

Keywords: Ultrasonic attenuation, Ultrasonic velocity, Elastomer composite with inorganic nanotubes, Thermal activation energy.

1. Introduction

During last years it was demonstrated that formation of fullerene-like and nanotube structures is not specific to carbon, but is a generic property of (2D) layered materials, such as MoS₂. Such inorganic nanotubes can be used for fabrication of various composites based on polymer materials, because they exhibit a good homogeneity and solubility of the composite material. Multifunctional materials produced from composites of polymer 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. The research of inorganic nanotube-polymer composites is just beginning. Therefore, it is

of interest to investigate elastic properties of polymer composites with inorganic nanotubes. Ultrasonic method and mechanical spectroscopy are non-destructive testing techniques and can be used for the determination of elastic properties of polymer composites. Composites such as acrylonitrile-butadiene-styrene (ABS) reinforced with carbon nanotubes have been already investigated by elastic studies and mechanical spectroscopy in [1-3] and showed improved strength and higher elastic modulus. Other authors have demonstrated that in PMMA –SiO₂ composites a modified layer of the polymer at the surface of silica particles can influence the polymer glass transition temperature and kinetics [4]. To our knowledge there are no similar studies of elastic properties of polymers doped with inorganic nanotubes. Therefore it is of interest to perform ultrasonic investigations of the polyurea elastomer composites containing MoS₂ nanotubes. In present work we carried out the temperature measurements of ultrasonic velocity and attenuation in such composites. Below room temperature the large ultrasonic attenuation maxima, affected by inorganic nanotubes, were observed.

2. Experimental Procedure

Composite material samples of polyurea with inorganic MoS₂ nanotubes fillers were produced in ETH, Zurich, Switzerland. The MoS₂ addition was 0.1 wt%. The large samples with the thickness of about 1 mm were obtained. For ultrasonic measurements the samples of dimensions 4 mm × 4 mm × 1 mm were prepared.

The ultrasonic measurements were carried out using the methods, which we previously developed for such measurements for layered ferroelectrics [5-6]. Pulse-echo automatic time-of-flight technique was applied. The flow chart in Fig. 1 illustrates the operation principles of our measurement assembly.

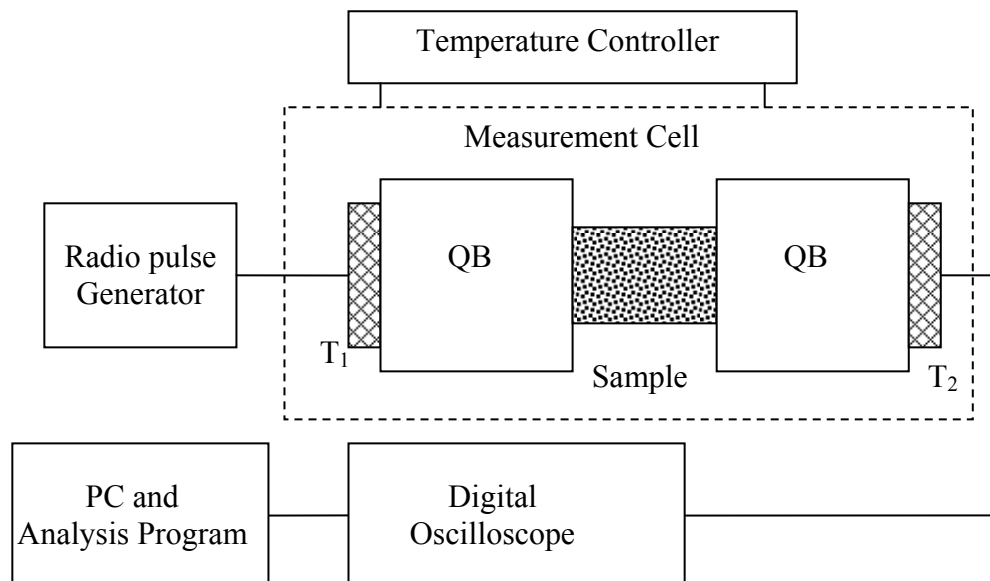


Fig. 1. Block diagram of ultrasonic measurement assembly.

All equipment works according to through transmission scheme with one lithium niobate piezoelectric transducer T₁ functioning as sender and another one T₂ as receiver. The quartz buffers QB are used for time delay of ultrasonic signals as well as for sample holders. The excitation radio frequency pulse causes the piezoelectric transducer to oscillate sending an ultrasonic wave through the sample material placed between buffers. The transducer T₂ converts ultrasonic wave back to electric radio frequency

pulse. This electrical signal is amplified and displayed in the screen of digital oscilloscope, also this signal is converted to digital format and is recorded by the computer. Later this signal is automatically processed. Analysis program controls the temperature and records the amplitude and time delay of 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 sticky elastomer by itself makes acoustic bond with quartz buffer. The absolute values of ultrasonic velocity and attenuation were measured at room temperature. For this, two identical samples of elastomer with the same thickness L were put between 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 in system was polymer sample with a thickness of only half of former sample. The values of ultrasonic attenuation α and velocity V for sample thickness L can be straightforwardly estimated as: $\alpha = \frac{1}{L} \ln \frac{A_2}{A_1}$ and $V = \frac{L}{\tau_1 - \tau_2}$. At any other temperature the amplitude and delay time

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

3. Results and Discussion

The temperature dependencies of ultrasonic velocity and attenuation in pure polyurea elastomer (JSD) and composite with MoS₂ nanotubes (JSD-C1) 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 is always reached. The temperature dependencies of ultrasonic attenuation are shown for elastomer with nanotubes and for reference sample in Fig. 2 at 10 MHz frequency. After addition of 0.1 % MoS₂ nanotubes to an elastomer the ultrasonic attenuation peak shifted to lower temperature and become narrower. The change of the longitudinal ultrasonic relaxation attenuation at room temperature is also clearly seen. The temperature dependencies of ultrasonic velocity in composite and reference samples are shown in Fig. 3. These dependencies were obtained from delay time variation after subtracting the known part of variation in quartz buffers. The steepest velocity dispersion regions correspond to attenuation maxima. Therefore it shows that possibly almost only one relaxation process is involved in this temperature range. From the general theory of elasticity it is easy (see e.g. [7]) to get expressions for the ultrasonic attenuation α and velocity V for single relaxation process with relaxation time τ in form:

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

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

Here ω is the angular frequency of ultrasonic wave, V_0 and V_∞ are low frequency and high frequency values of ultrasonic velocity. Parameter $A = \frac{V_\infty^2 - V_0^2}{2V_0^3} = 2\alpha_{max}/\omega$, where α_{max} is peak ultrasonic

attenuation value. The relaxation process can be related to rearrangements in polymer network, interpreted as a glass transition [8-9]. Over a comparatively small temperature range relaxation time of thermally activated process can be described by Arrhenius law:

$$\tau = \tau_0 \exp(\Delta E / kT), \quad (3)$$

where τ_0 is the prefactor, and ΔE is the activation energy of thermally activated process. In order to obtain relaxation parameters the ultrasonic attenuation was fitted to relaxation attenuation expression (1). After fitting procedure the following parameters were obtained: $\tau_0 = 2.5\text{E-}9$ s for sample with nanotubes, and $\tau_0 = 1.43\text{E-}7$ s for reference sample, $\Delta E = 0.45$ eV for sample with 0.1 % MoS₂ nanotubes and $\Delta E = 0.34$ eV for reference sample, parameter A was chosen to be almost the same for both materials, because peak attenuation values are quite close. Furthermore, parameter A is related to low frequency and high frequency values of ultrasonic velocity what it is difficult to measure by pulse-echo method especially in thin samples. The increase of activation energy for sample with nanotubes was observed, and this can be related to elastomer and nanotube interaction at a surface layer and modification of glass transition.

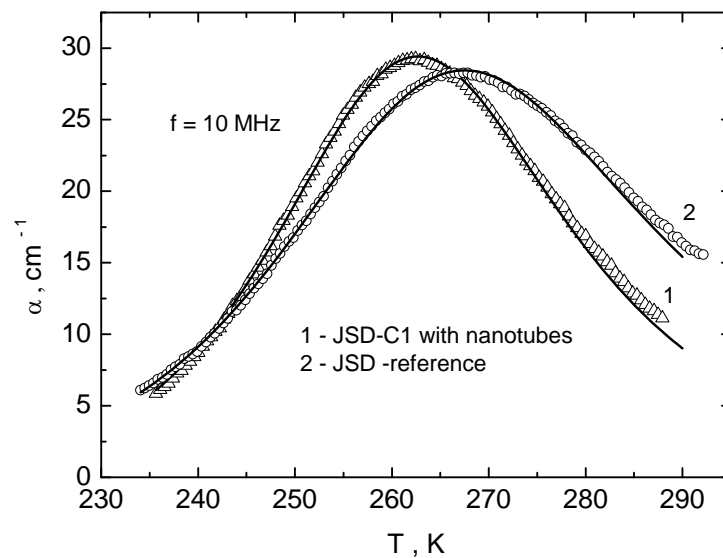


Fig. 2. The temperature dependencies of longitudinal ultrasonic attenuation in JSD polymer with MoS₂ nanotubes (1) and in reference JSD sample (2). The full lines are obtained after approximation to Eq.1.

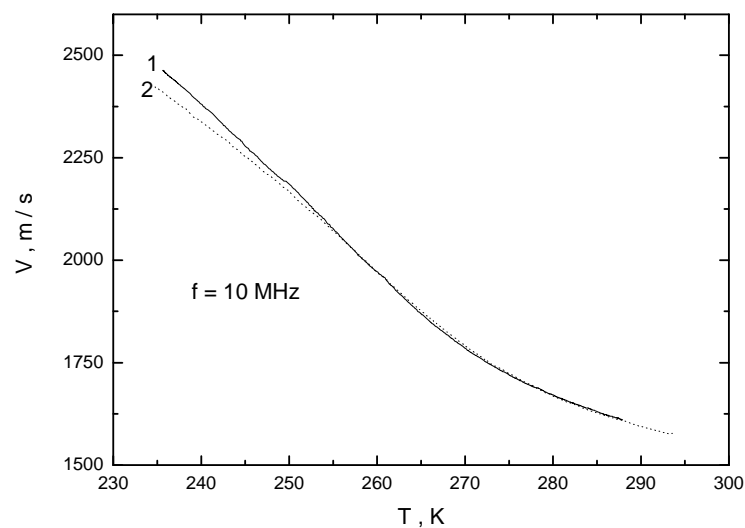


Fig. 3. The temperature dependencies of longitudinal ultrasonic velocity in JSD polymer with MoS₂ nanotubes (1) and in reference JSD sample (2).

As it was mentioned above, the ultrasonic velocity temperature variation is quite large. This also supports the idea that longitudinal velocity dispersion in this temperature region is determined by glass transition. It is necessary to note that at room temperature the ultrasonic velocity is of order 1600 m/s and almost do not depend on nanotube addition. At low temperature the longitudinal ultrasonic velocity increases in polymer with nanotubes what is determined by an increase in the elastic modulus composite. Such reinforcement could be due to elastomer and nanotube interaction at a surface layer adhering the nanotubes.

4. Conclusions

The temperature dependencies of longitudinal ultrasonic velocity in polyurea elastomer composite with MoS₂ nanotubes and in pure reference elastomer were measured at 10 MHz frequency in 230-300 temperature interval. The large ultrasonic attenuation peak and velocity dispersion have been observed in these elastomer samples. It was shown that the relaxation maxima were affected by addition of inorganic MoS₂ nanotubes. The experimental data were compared with ultrasonic relaxation theory involving single relaxation time of thermally activated process. It was concluded that activation energy increased in composite material with nanotubes. At low temperatures the increase of longitudinal ultrasonic velocity related to viscoelastic properties was observed in composite with MoS₂ nanotubes.

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References

- [1]. D. Mari, R. Shaller. Mechanical spectroscopy in carbon nanotube reinforced ABS, *Materials Science and Engineering A*, Vol. 521-522, 2009, pp. 255-258.
- [2]. M. L. Shofner, F. J. Rodriguez-Maclas, R. Vaidyanathan, E. Bareira. Single wall nanotube and vapor grown carbon fiber reinforced polymers processed by extrusion freeform fabrication, *Compos. Part A: Appl. Sci. Manuf.*, Vol. 34, 2003, pp. 1207-1217.
- [3]. K. Zheng, L. Chen, Y. Li, P. Cui, Preparation and thermal properties of silica-graft acrylonitrile-butadiene-styrene nanocomposites, *Polym. Eng. Sci.*, Vol. 44, 2004, pp. 1077-1082.
- [4]. P. Rittigstein, R. D. Priestley, L. J. Broadbelt J. M. Torkelson, Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites, *Nat. Mater.*, Vol. 6, 2007, pp. 278-282.
- [5]. V. Samulionis, J. Banys, Y. Vysochanskii, Piezoelectric and elastic properties of layered materials of Cu(In, Cr)P₂(S, Se)₆ system, *J. Electroceram.*, 2009, Vol. 22, pp. 192-197.
- [6]. V. Samulionis, J. Banys, Y. Vysochanskii, Linear and nonlinear elastic properties of CuInP₂S₆ layered crystals under polarization reversal, *Ferroelectrics*, 2009, Vol. 379, pp. 293-300.
- [7]. V. Valevicius, V. Samulionis, J. Banys, Ultrasonic dispersion in the phase transition region of ferroelectric materials, *J. Alloys and Compounds*, 1994, Vol. 211/212, pp. 369-373.
- [8]. P. A. O'Connell, G. B. Mc Kenna, Arrhenius type temperature dependence of the segmental relaxation below T_g, *J. Chem. Phys.*, 1999, Vol. 110, pp. 11054-11061.
- [9]. G. Li, P. Lee-Sullivan, R. W. Thring, Determination of the activation energies for glass transition of an epoxide adhesive using dynamic mechanical analysis, *Journal of Thermal Analysis and Calorimetry*, 2000, Vol. 60, pp. 377-383.