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Abstract. The ultrasonic and dielectric temperature investigations were performed in polydi-methylsiloxane (PDMS) with zinc oxide (ZnO) and onion-like carbon (OLC) nanocomposites. In the glass transition region, the ultrasonic velocity dispersion and large ultrasonic attenuation maxima were observed. The positions of ultrasonic attenuation peaks were slightly shifted to higher temperatures after doping PDMS with OLC and ZnO nanoparticles. The ultrasonic relaxation was compared to that of dielectric and such behaviour was described by Vogel-Fulcher law. The upshift of the glass transition temperature with addition of nanoparticles was confirmed by both methods. The additional increase of ultrasonic attenuation in composites doped with OLC and ZnO was observed at room temperature and such behaviour we attributed to ultrasound–nanofiller interaction in polymer matrix.

1. Introduction

In recent years, polymer nanocomposites and understanding their physical and chemical properties have attracted great attention [1, 2]. The presence of nanoparticles in polymer allows both properties from nanoparticles material and polymer matrix to be combined, thus obtaining advanced polymer nanocomposites with improved mechanical, electrical, and optical properties of the materials. Especially, nanoscale inclusions such as carbon nanotubes or onion like carbons have been used to reinforce polymer materials, metal oxide ZnO nanoparticles doped polymers have been studied as alternative materials for optical applications [3]. Polymers, such as polyurea elastomers and PDMS have been proved to be suitable matrices in the development of composite structures due to their ease of production and processing, good adhesion with reinforcing elements. Earlier, using ultrasonic method, we have studied relaxation processes that determine the nanocomposite elastic behaviour of polyurea elastomers with inorganic nanofillers [4, 5]. The PDMS/OLS composites were studied by dielectric and ultrasonic methods [6, 7]. In this contribution we present further ultrasonic and dielectric studies of PDMS with ZnO and OLC nanofilers. The nanofiller content dependent dielectric losses, ultrasonic attenuation and velocity dispersion have been observed above the glass transition temperature. It is shown that the maximum of dielectric losses and ultrasonic attenuation in PDMS nanocomposite can be described according to the Vogel-Fulcher law and the glass transition temperature increases with nanofiller concentration. The addition of ZnO and OLC nanoparticles in

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polymer resulted in the increase of ultrasonic velocity in low temperature region and the increase of attenuation at room temperature.

2. Experimental procedure

The OLC samples which were used to fabricate OLC/PDSM composites were prepared according procedure described in [6]. NanoDiamonds with appropriate aggregate size were heated in vacuum (10−2 Torr) at 850°C for 3 h providing the production of OLC with corresponding size of aggregates. Fractions of ZnO with aggregate sizes 30 nm were used as filler similarly as it was described in the literature [6]. The polydimethylsiloxane, Sylgard, was purchased from Dow-Corning as a two part material. When forming PDMS/OLC or PDMS/ZnO composites, an intermediate solvent was employed that served as a dispersion medium for the nanoparticles prior to mixing with the polymer matrix. The nanoparticles were dispersed in the solvent and sonicated to break up large agglomerates, then the suspension was mixed with uncured PDMS. The solvent was subsequently removed in vacuum. The PDMS-nanoparticle mixture was cured at 60°C for 2 hrs and 40°C overnight. Thick films with continuous nanoparticle distribution were obtained. The complex dielectric permittivity of PDMS/OLC or ZnO nanocomposites was measured as a function of frequency and temperature using a bridge setup with LCR meter HP4284A. The ultrasonic studies were carried out by means of automatic computer controlled pulse-echo ultrasonic system as described in [8]. The large dynamic range and large input ultrasonic power allowed the large ultrasonic attenuation values to be measured. The procedure of attenuation and velocity measurement in polymer composites was presented earlier [7]. Samples of dimensions 4 mm × 4 mm × 2-3 mm were cut from larger thick films. We used pulse transmission method, therefore the sample was held confined between two buffer rods. The temperature dependencies of longitudinal ultrasonic velocity and attenuation in pure PDMS and composites with nanoparticles were measured changing temperature (rate of 0.1 K/min) in heating and cooling cycles.

3. Results and discussion

The temperature dependencies of longitudinal ultrasonic attenuation at 10 MHz frequency for PDMS/ZnO composites are shown in figure 1 in cooling cycle. These graphs demonstrate that there
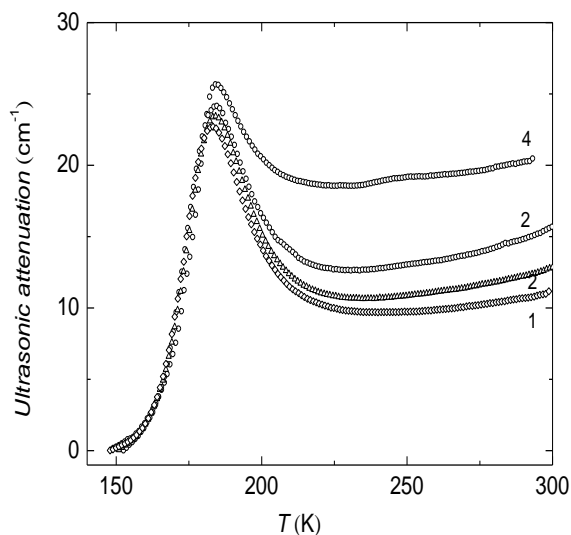
Figure 1. Temperature dependences of ultrasonic attenuation in composites PDMS /ZnO: 1 − 0, 2 − 2, 3 − 5, 4-10 wt% of ZnO nanoinclusions.
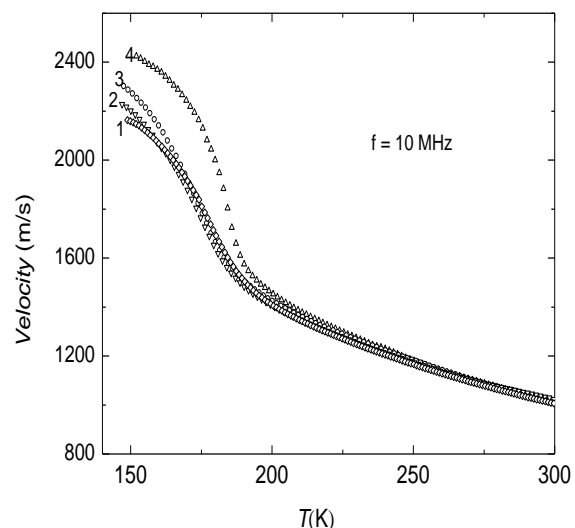
Figure 2. Temperature dependences of ultrasonic velocity in composites PDMS /ZnO: 1 − 0, 2 − 2, 3 − 5, 4 - 10 wt% of ZnO nanoinclusions.

are attenuation peaks characteristic for relaxation phenomena. Low temperature onset of the attenuation correlate with the glass transition temperature $T_g \approx 140$–160 K, known from earlier publications [6, 7]. The temperature dependences of ultrasonic velocity in the composites and reference sample are shown in figure 2. These dependencies were obtained from variation of delay time in mechanical system after subtracting the known part of delay variation in the quartz buffers. One can see that temperature dependencies of ultrasonic velocity in PDMS are also dependent on adding of ZnO nanoparticles. The steepest velocity dispersion region corresponds to attenuation maxima. The shift of attenuation and velocity curves to higher temperatures ($\Delta T \approx 2$-3 K) is clearly seen especially in the low temperatures attenuation wing. Such behaviour is related to a shift of the glass transition temperature in the composites with ZnO. An interesting hysteresis of ultrasonic properties we observed in composites with ZnO nanoparticles. This temperature hysteresis is merely noticeable in pure PDMS but it is more evident for nanocomposites with larger ZnO amount (figures 3 and 4). Such hysteresis can be attributed to the melting phase transition from semi-crystalline to pure amorphous phase which had been observed in PDMS near 220 K [9]. We suppose that ZnO nanoparticles serve as crystallization centres and at low temperatures the crystalline phase in PDMS with ZnO occupies higher volume. Therefore at the first order melting transition ultrasonic attenuation and velocity anomalies are more pronounced in composites with higher degree of crystallinity.
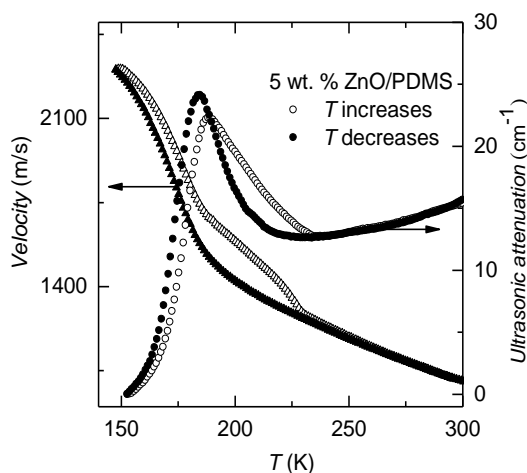
Figure 3. The ultrasonic attenuation and velocity temperature hysteresis in PDMS/ZnO composite with 5 wt % ZnO.
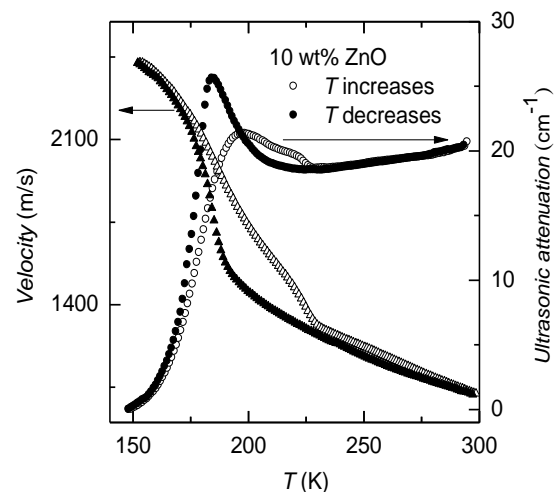
Figure 4. The ultrasonic attenuation and velocity temperature hysteresis in PDMS/ZnO composite with 10 wt % ZnO.

It is necessary to note that in PDMS/ZnO composites after addition of nanoparticles ultrasonic velocity increases, especially at low temperatures, and it is consequence of the reinforcement of PDMS polymer, because elastic coefficients of zinc oxide material are considerably larger. Dielectric measurements of PDMS/ZnO composites in the frequency range 500 Hz – 1 MHz have shown that dielectric relaxation appears in the same temperature region above glass transition and is similar to that of ultrasonic relaxation presented above. Temperature dependences of imaginary part of complex permittivity attributed to dielectric losses for pure PDMS and composites with 1 wt% and 5 wt% and 10 wt% of ZnO inclusions at frequency 1 MHz are shown in figure 5. It is clearly seen that the peak of dielectric loss maximum (T_{max}) also shifts to higher temperature values with increasing the concentration of ZnO nanoparticles in the same way as ultrasonic attenuation peaks (see figure 1). These frequency dependent maxima are caused by alpha relaxation as in pure PDMS matrix [10]. The temperatures T_m corresponding to dielectric loss peaks are also frequency f dependent (figure 6) and can be described by Vogel –Fulcher relationship [11]:

$$f = f_0 \exp(-E_f / k(T_m - T_0)) \tag{1}$$

where k is the Boltzmann constant, f_0 is the frequency in limit T_m - ∞, E_f is the parameter as activation energy, and T_0 is the glass transition temperature. Obtained parameters are summarized in table 1.
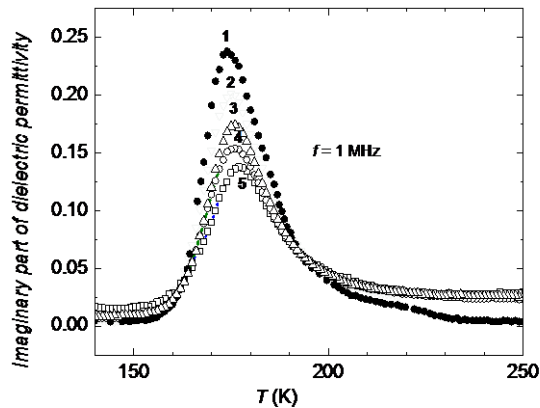
Figure 5. Temperature dependences of imaginary part of dielectric permittivity in composites PDMS/ZnO: 1 – 0, 2 – 1, 3 – 2, 4 – 5, 5-10 wt% of ZnO nanoinclusions.
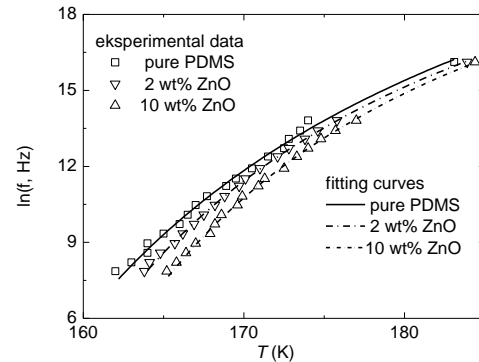
Figure 6. Measured frequencies f versus T_m of PDMS/ZnO composites 1 – 0, 2 – 2, 3 -10 wt% of ZnO nanoinclusions.

It is clearly seen in figure 5 that at low (up to 160 K) and high (210 K- 250 K) temperatures dielectric losses of pure polymer are lower than those of doped with ZnO nanoparticles. Moreover, the higher is the concentration of ZnO in the nanocomposite the higher is the imaginary part of the complex dielectric permittivity. Such differences in losses can be attributed to the impact of oxygen vacancies induced by ZnO inclusions on dielectric properties. Similar phenomenon in bulk $SrTiO_{3-x}$ and its local properties due to the gradient in the concentrations of oxygen vacancies from surface to surface has been observed and reported previously [12-14]. Hence, oxygen vacancies in the interface between ZnO particles and the ambient matrix can change the whole composite dielectric and electric properties.

The glass transition temperature is increasing with the ZnO filler concentration. It should be noted, that relaxation time $\tau = 1/2\pi f$ obtained from dielectric measurements was used to describe ultrasonic attenuation using equation for single relaxation time [5]. After fitting procedure the analogous to T_0 values of T_g and increase of glass transition temperature were verified, but parameters f_0 and E_f were different for elastic relaxation.

Table 1. Vogel- Fulcher fit parameters of dielectric relaxation in ZnO/PDMS nanocomposites.

Material	f_0 (THz)	E_a (eV)	T_0 (K)
Pure PDMS	9.0	0.063	129.4
2 % ZnO/PDMS	0.82	0.046	136.8
10 % ZnO/PDMS	0.89	0.046	140.8

Therefore, the most significant finding of the present investigation on ZnO/PDMS nanocomposites are the upshift of the glass transition temperature T_g with addition of nanoparticles. This upshift of T_g was observed earlier in polyurea elastomer composites with inorganic nanoinclusions and in PDMS/OLC nanocomposites [6, 15]. Molecular dynamics simulations have shown [16] that the presence of nanoscale structures in the polymer network affects the glass transition temperature due to a change of the polymer dynamics. In the case of attractive interactions between the polymer and the nanoparticles, the chain relaxation time is increased and leads to a higher T_g relative to the pure system. In our case, an attractive interaction between polymer chains and the ZnO nanoparticles can be then proposed to explain the observed increase in T_g relative to the pure PDMS polymer matrix. Moreover,

according to another theoretical calculation, the density of composite could be higher than the pure polymer density, and an increasing of the glass transition temperature with the filler concentration could be observed [17].

Earlier in polyurea elastomers, we explained the ultrasonic attenuation and velocity dispersion simply by relaxation process with single temperature dependent relaxation time described by Arrhenius equation [5]. In case of PDMS with ZnO and OLC nanoinclusions the attenuation peak is more asymmetric and at higher temperatures the ultrasonic damping is considerably higher than at T = 130 K. The high temperature wing is strongly dependent on doping.
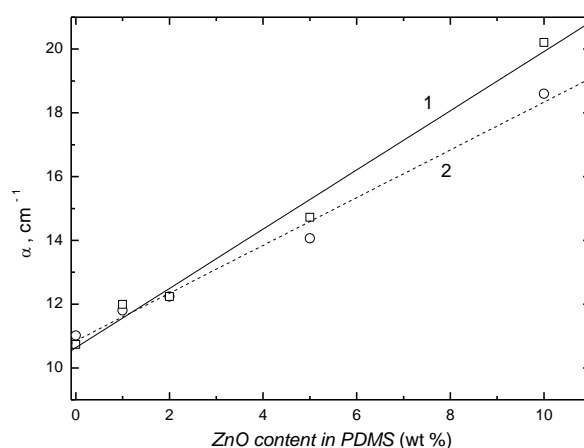
Figure 7. The ultrasonic attenuation dependences on OLC (1) and ZnO (2) content in PDMS composites. T = 290 K.

Figure 7 shows the longitudinal ultrasonic attenuation dependence of OLC and ZnO content at room temperature. It demonstrates that there is another mechanism involved in elastic dissipation process. Such behavior can be related to the ultrasound nanoparticle interaction in amorphous state of PDMS.

4. Conclusions

The temperature dependencies of longitudinal ultrasonic attenuation and velocity in polydimethylsiloxane/zinc oxide composites were measured. Near 180 K the ultrasonic attenuation relaxation maxima and velocity dispersion determined by glass transition in PDMS have been observed. Additionally, the ZnO content dependent ultrasonic attenuation has been observed at the high temperature region above T_g. At low temperatures longitudinal ultrasonic velocity increases with ZnO concentration and it shows that these PDMS polymers are reinforced by nanoparticles.

Acknowledgment

References
[1]   Godovsky D Y 2000 *Advances in Polymer Science* **153** 163-205
[2]   Kasim F A, Mahdi M A, Hassan J J, J Al-Ani S K and Kasim S J 2012 *International Journal of Nanoelectronics and Materials* **5** 57-66
[3]   Tachikawa S, Noguchi A, Tsuge T, Hara M, Odawara O and Wada H 2011 *Materials* **4** 1132-443
[4]   Samulionis V, Banys J, S ánchez-Ferrer A and Mezzenga R 2011 *Sensors & Transducers* **12**, 66-70

[5]   Samulionis V, Svirskas Š, Banys J, Sánchez-Ferrer A, Jecg Chin S and McNally T 2013 *Phys. Status Solidi.* **A 210**, 2348-52

[6]   Macutkevic J, Kranauskaite I, Banys J, Moseenkov S, Kuznetsov V, and Shenderova O 2014 *J. Appl. Phys.* **115** 213702

[7]   Samulionis V, Macutkevic J, Banys J, Belovickis J, Shenderova O 2014 *IEEE IUS Proceedings* 1987-8

[8]   Valevicius V, Samulionis V, Banys J and Brilingas A 1996 *J. de Physique IV* **6** C8-405-9

[9]   Del Valle-Carrandi L, Alegria A, Colmenero 2010 *Eur. Phys. J. Special Topics* **189** 257-61

[10]   Fragiadakis D, Pissis P, Bokobza L 2005 *Polymer* **46** 6001-8

[11]   Fogel H 1921 *Z. Phys.* **22** 645-6, Vulcher G. S 1925 *J. Am. Ceram. Soc.* **8** 339-55

[12]   Liu Z Q, Leusink D P, Wang X, Lu W M, Gopinadhan K, Annadi A, Zhao Y L, Huang X H, Zeng S W, Huang Z, Srivastava A, Dhar S, Venkatesan T and Ariando 2011 *Phys. Rev. Letters* **107** 146802

[13]   Liu Z Q, Leusink D P, Lu W M, Wang X, Yang X P, Gopinadhan K, Lin Y T, Annadi A, Zhao Y L, Roy Barman A, Dhar S, Feng Y P, Su H B, Xiong G, Venkatesan T and Ariando 2011 *Phys. Rev. B* **84** 165106

[14]   Liu Z Q, Lu W, Zeng S W, Deng J W, Huang Z, Li C J, Motapothula M, Lu W M, Sun L, Han K, Zhong J Q, Yang P, Bao N N, Chen W, Chen J S, Feng Y P, Coey J M D, Venkatesan T and Ariando 2014 *Adv. Mater. Interfaces* **1** 1400155

[15]   Fuith A, Reinecker M, Sanchez-Ferrer A, Mezzenga R, Mrzel A, Knitte M, Aulika I, Dunce M, Schranz W 2011 *Sensors & Transducers* **12** 71-9

[16]   Starr F W, Schroder T B and Glotzer S C 2002 *Macromolecules* **35** 4481-92

[17]   Wei Ch, Srivastava D and Cho K 2002 *Nano Letters* **2** 647-50