NANOCOMPOSITES BASED ON MULTICOMPONENT POLYMER MATRIX AND ARTIFICIAL DIAMOND NANOFILLER

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Abstract
Nanocomposites based on Polyurethane/Poly(2-hydroxyethyl methacrylate) multicomponent polymer matrix and atrificial diamond nanofiller were created and the thermodynamic miscibility, dynamic mechanical, physico-mechanical properties and segmental motions have been investigated. The free energy of interaction values between the polymer components and nanofiller, calculated based on vapour sorption results, were negative and the thermodynamic affinity of PU network to the nanodiamonds is more powerful in compare with PHEMA. Dynamic mechanical analysis have demonstrated the essential changes in nanocomposites behaviour especially in the temperature range of PU glass transition. The creep rate spectroscopy have shown the suppression of segmental motion of PU and PHEMA in the nanocomposites, the maximal effect have been obtained for samples containing 0.25% of nanofiller. Introduction just of 0.25% of nanodiamond filler into the multicomponent polymer matrix resulted in the significant growth in stress at break and in Young's modulus.

1 Introduction
Polymer composites with small additives of nanofillers attracted great attention last decade, both in industry and academician studies, since a considerable enhancing mechanical, thermal and other properties may be attained in nanocomposites compared with those of virgin polymers. To date, the greatest number of studies have focused on polymer nanocomposites with two-dimensional (2-D) nanoscale silicate layers [1,2] and one-dimensional (1-D) carbon nanotubes (CNTs) [3,4]. The key to their enhanced efficiency is to achieve good dispersion, uniform spatial distribution and alignment (for CNTs) of nanoparticles, however, the critical role of two more points is also usually emphasized, viz.., (a) a high aspect (e.g., length-to-diameter for CNTs) ratio, typically of 10^3 or more, for a nanofiller, and (b) the necessity of chemical "functionalization" of nanofiller surface to provide its covalent coupling with a polymer matrix for improving interfacial properties and matrix performance. In addition, dispersion of nanoparticles may also be inproved due to functionalization. The points (a) and (b) are typically considered as the prerequisites for attaining the highest performance of a polymer nanocomposite, in particular a low "percolation rheological threshold" (distinct effect of improved rheological behavior) at nanofiller content of less than 1 wt % [5,6] .

Among different nanocarbon structures used as polymer nanofillers (CNTs, carbon nanorods, fullerenes, ultra-dispersed artificial diamond (nanodiamonds, NDs)), the latters have been available on a relatively large scale for last two decades and are also of interest. Synthesis and processing of 3-D NDs have been described in refs. [6-9]. There are the examples of their successful applications in polymer nanocomposites as electronics materials, materials with protonic conductivity or enhanced thermal conductivity, in selective membranes, sensors, catalytic systems, nonlinear optical materials, and as an active filler increasing strength, wear and heat-ageing resistance of elastomers [6,8,9-11].

In our previous works [12-14], dynamic-mechanical behaviour, segmental motions, elastic and phisico-mechanical properties have been studied in several polyurethane-poly(2-hydroxyethyl methacrylate) semi-interpenetrating polymer networks (PU-PHEMA semi-IPNs) over the temperature range –140 to 180^{0}C, by using combined DMA, laser-interferometric creep rate spectroscopy, differential scanning calorimetry analysis. These systems had basically two-phase, nanoheterogeneous structure with incomplete phase separation, and the pronounced dynamic heterogeneity within the extraordinarily broadened PHEMA and PU glass transitions, practically the united glass transition extending over the range from -60 to 160^{0}C, were observed in these semi-IPNs. Such dynamic behavior and, additionally, improved biocompatibility of PU-PHEMA semi-IPNs are of interest for developing improved biomedical, damping or membrane materials based thereon.

In the present research we investigated, using thermodynamic and physico-mechanical approaches, the properties and their relation to nanostructure in nanocomposites based on the PU-PHEMA semi-IPNs filled with artificial 3-D NDs.

2 Materials and testing methods

2.1 Materials

Neat PU and PHEMA, their semi-IPNs, and ND-containing nanocomposites based thereon were prepared as described elsewhere [12, 14]. First, PU network was obtained from the adduct of trimethylol propane, toluylene diisocyanate and poly(oxypropylene)glycol (PPG) with M_w = 2.000 g mol^{-1}. The semi-IPNs with 17, 37 and 57 wt. % PHEMA were obtained by swelling PU network with 2-hydroxyethyl methacrylate (HEMA) and its subsequent photo-polymerization (the wavelength of UV light 340 nm).

For preparing the nanocomposites with PU, PHEMA and semi-IPN matrices, the ultra-dispersed diamond powder (NDs) obtained by the shock-wave method (supplied by Alit Company, Ukraine), with the particle sizes of 2 to 100 nm and specific surface area of 220 m^{2}g^{-1}, was used. NDs were introduced in the amounts of 0.25 – 20.00 wt. % into a polymer system at the stage of PU synthesis, or into HEMA in the case of preparing the nanocomposite based on neat PHEMA. NDs were dried for 48 h at 200^{0}C before using.

The prepared films with 1 mm thickness were post-cured for 2 h at 100^{0}C and then were held for 36 h at 80^{0}C in vacuum 10^{-5} Pa.

2.2 Testing methods

2.2.1 Vapour sorption and thermodynamic calculations

The dichloromethane vapour sorption by semi-IPN samples and by nanocomposites samples was studied using a vacuum installation and a McBain balance [12]. The changes in partial free energy of dichloromethane by sorption (dissolution) were determined from the experimental data using equation 1

$$\Delta\mu_1 = (1/M)RT \ln (P/P_0), \tag{1}$$

where M is the molecular mass of dichloromethane and P/P$_o$ is the relative vapour pressure. The value $\Delta\mu_1$ changes with solution concentration from 0 to - ∞.

To calculate the free energy of mixing of the polymer components with solvent, the changes in partial free energy of the polymers (native polymers, semi-IPNs, nanocomposites) needs to be determined. The requires the calculation of the difference between the polymer chemical potential in the solution of a given concentration and in pure polymer under the same conditions ($\Delta\mu_2$). $\Delta\mu_2$ for the polymer components were calculated using the Gibbs-Duhem equation:

$$\omega_1 d(\Delta\mu_1)/d\omega_1 + \omega_2 d(\Delta\mu_2)/d\omega_1 = 0 \quad , \tag{2}$$

where ω_1 and ω_2 are the weight fractions of a solvent and of a polymer. This can be rearranged to give equation 3

$$\int d(\Delta\mu_2) = - \int (\omega_1/\omega_2) d(\Delta\mu_1) \tag{3}$$

Which allows the determination of $\Delta\mu_2$ for each polymer from the experimental data by integration over definite limits. The average free energy of mixing of solvent with the individual components, semi-IPNs of various compositions for the solutions of different concentration, was then estimated using equation 4 and using computational analysis.

$$\Delta g^m = \omega_1 \Delta\mu_1 + \omega_2 \Delta\mu_2 \tag{4}$$

2.2.2 Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) measurements were carried out using a Dynamic Mechanical Thermal Analyzer Type DMA 2980 from TA Instruments over the temperature range from -140 to +200° C and at fixed frequencies (5, 10, 15, 20, 30 Hz) with a heating rate of 3°C/min. The experiments were performed in the tension mode on rectangular specimens (35mm x 5 mm x 1 mm). As Poly(2-hydroxyethyl methacrylate) is a hydroscopic polymer, all samples were dried at 80°C for 48 hours under vacuum before measurements. The samples were subsequently subjected to the following thermal cycle during DMA measurements : a first run from 20 °C up to 100 °C, then second run from -140 up to +200° C. The second run was used for analysis of the results.

2.2.3 Creep rate spectroscopy

CRS, the high-resolution method of relaxation spectrometry and thermal analysis, developed at Ioffe Institute [15], was used here for analysis of the heterogeneity of segmental dynamics over the broad temperature regions of PU and PHEMA glass transitions in the studied semi-IPNs and nanocomposites based thereon. The CRS setups and the experimental technique have been described in detail elsewhere [15]. It consists in precisely measuring creep rates at a constant low stress as a function of temperature, using a laser interferometer based on the Doppler effect. The time evolution of deformation is registered as a sequence of low-frequency beats in an interferogram whose beat frequency v yields a creep rate

$$\dot{\varepsilon} = \frac{\lambda v}{2 I_0} \tag{5}$$

where $\lambda = 650$ nm is a laser wavelength, and I_0 is an initial length of the working part of a sample. The stress was chosen in the preliminary experiments as capable of inducing sufficient creep rates to be measured, while maintaining also a high spectral resolution,

without smoothing and distortion of a spectral contour, and preventing a premature rupture of a sample.

2.2.4 Mechanical testing

Mechanical properties of the neat PU and PHEMA, their semi-IPNs, and ND-containing nanocomposites were measured using a Series IX Automated Instron Materials Testing System. The samples were cut into micro dumb-bell shapes with gauge length of 20 mm, widths between 4-5 mm and sample thickness between 0.7-0.9 mm. Samples were processed at a continuous strain rate of 25 mm/min.

3 Results and Discussion

The vapour sorption of dichloromethane by filled individual networks and by filled semi-IPNs was studied and thermodynamic affinity of network components to the filler was estimated. The calculated free energy of interaction values between the polymer components and nanodiamonds were negative (Fig.1), and the thermodynamic affinity of PU network is more powerful in compare with PHEMA. This means that ultra-dispersed diamond filler could be reinforcing filler for investigated polymer systems.
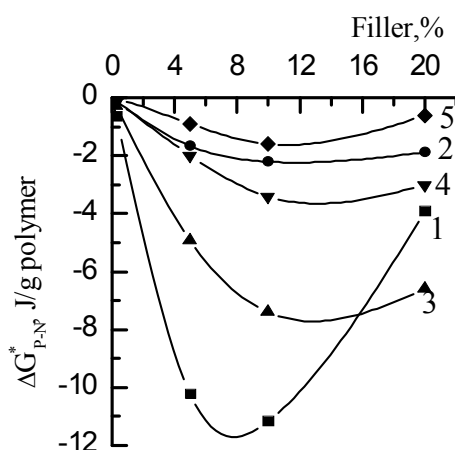

Figure 1. Free energies of mixing of individual networks and semi-IPNs with artificial diamond nanofiller: PU (1), PHEMA (2), semi-IPNs with 17% PHEMA (3), with 28% PHEMA (4), with 37% PHEMA (5).

Dynamic mechanical analysis data of unfilled semi-IPNs have revealed a pronounced change in the viscoelastic properties of semi-IPNs with different amounts of PHEMA in the samples. The semi-IPNs have two distinct maxima of tan δ related to the presence of two polymers in their glass transition temperature domains (Fig.2). The tan δ maximum of PHEMA is shifted towards higher temperature and its amplitude increases with the increasing fraction of PHEMA (Fig.2). These results confirm that the studied semi-IPNs are two-phase systems with incomplete phase separation and "frozen" non-equilibrium structure. The segregation degree α was calculated for semi-IPNs and it was shown the values are equal to 0.22-0.35. This means that phase separation in the semi-IPNs was "frozen" in the initial stage by permanent entanglements of the chains.

The introduction of ultra-dispersed diamond filler in the semi-IPN samples result in essential changes in dynamic mechanical behaviour of materials especially in the temperature range of PU glass transition (Fig.3). The introduction just 0.25% of filler into PU network lead to decreasing of amplitude of tan δ and broadening of glass transition domain of PU due to formation of boundary layers of polymer on the surface of filler particles and, as result, some restriction of polymer dynamics.
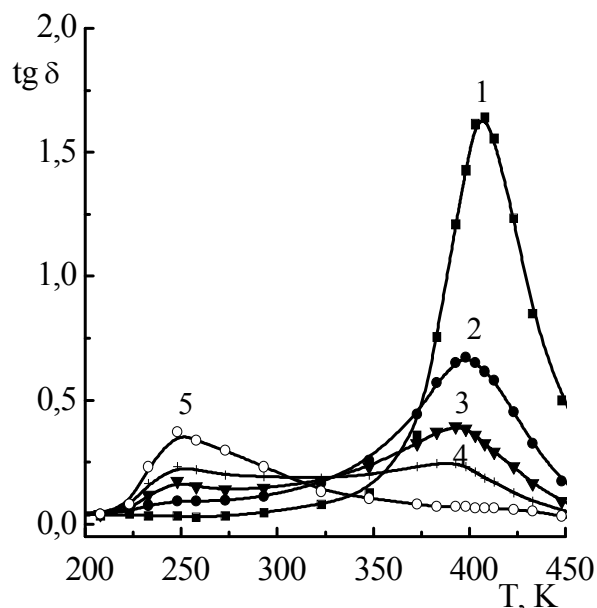
Figure 2. Dynamic mechanical measurements of tanδ versus temperature for unfilled semi-IPNs: PHEMA (1), semi-IPNs with 57% PHEMA (2), with 32% PHEMA (3), with 17% PHEMA (4), PU (5)

The formation of boundary layers of PU on the surface of filler particles could result also in separation of hard and soft segments of PU as the two maxima could be observed in glass transition temperature domains of filled polymer (Fig.3). For filled semi-IPNs the superposition of two glass transition temperature domains of PU and PHEMA for small content of PHEMA and full suppression of segmental motion of PU for large amount of PHEMA were observed (Fig.3).
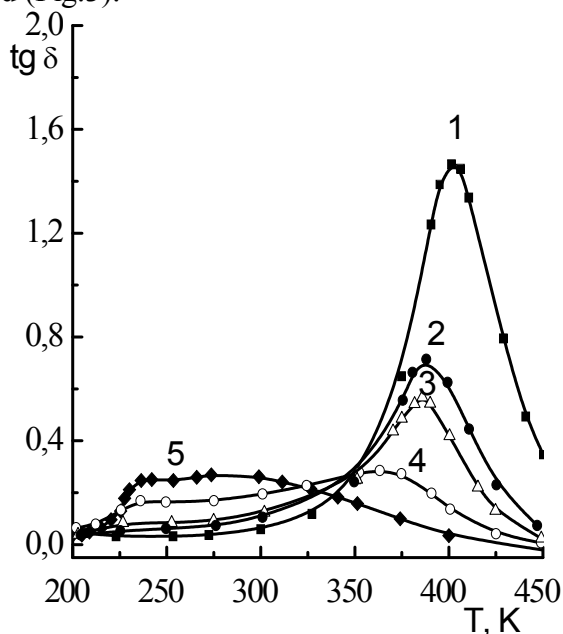

Figure 3. Dynamic mechanical measurements of tanδ versus temperature for semi-IPNs contained 0.25% of nanodiamonds: semi-IPNs with 57% PHEMA (2), with 37% PHEMA (3), with 17% PHEMA (4), PU (5)

The essential changes just for PU could be due to preferential adsorption of PU chains on the surface of filler particles during process of formation of boundary layers of polymers as have been shown by thermodynamic affinity of network components to the filler particles (Fig.1).

The creep rate spectroscopy investigation of nanocomposites gave the results which are in compliance with DMA results [5]. The maximal effect have been obtained for samples containing 0.25% of filler. The separation of hard and soft segments is clearly observed for filled PU.

Figure 4 shows the creep rate spectra obtained for neat PU network and ND-containing nanocomposites based thereon in the temperature region of PU glass transition. The pronounced dynamic heterogeneity in the glass transition of this PU network has already been displayed by CRS in the previous article [14]. As shown, its CR spectrum, located between –60 to 50^{0}C, consists of four overlapping peaks, with the maxima at about –30(I), –10(II), 10(III) and 40^{0}C (IV). Peaks I-III were tentatively assigned to step-like unfreezing of a few segmental dynamics modes within five-segment PPG crosslinks (M_w=2.000 g mol^{-1}), due to different positions of segments regarding PU network junctions and, respectively, different hindering dynamics. Peak IV was assigned to unfreezing of network-junction motion. Figure 4 shows that the introduction of ND particles results in some redistribution of the intensities of spectral peaks; nanofiller affects stronger lower-temperature peaks. Interestingly, below 0^{0}C the suppression effect was the largest at the minimal ND content in a nanocomposite.
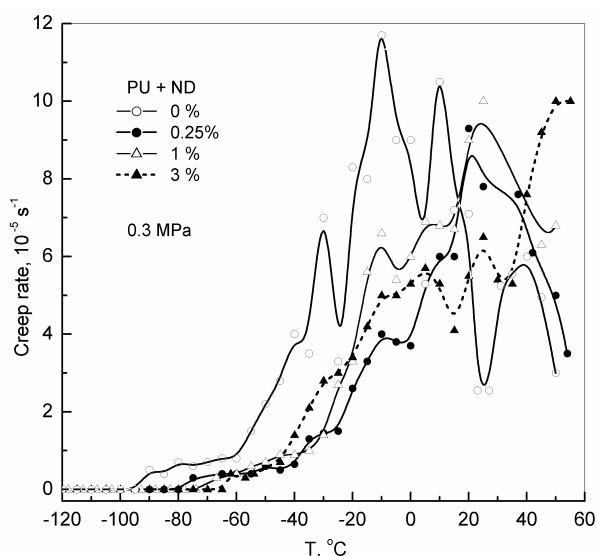

Figure 4. Creep rate spectra obtained for neat PU network and ND-containing nanocomposites based thereon at tensile stress of 0.3 MPa in the temperature region of glass transition. ND weight contents are indicated.

Figure 5 shows the CR spectra of the 83PU-17PHEMA-ND nanocomposites, obtained over the temperature range covering both PU and PHEMA glass transitions. The introduction of 17 wt. % PHEMA into PU network, with formation of hybrid semi-IPN, resulted in some suppression of segmental dynamics at low temperatures [15]. Therefore, the increased tensile stress of 3 MPa was used to register the distinct CR spectra of these compositions at –100 to 40^{0}C (Fig. 5, a). On the whole, the complicated influence of the added NDs on glass transition dynamics in the 83PU-17PHEMA network is observed. Fig. 5, a shows some suppression of dynamics by ND particles at the lowest temperatures of –80 to –40^{0}C but, contrarily, accelerated creep in nanocomposites with 1 or 3 % NDs starting from –30^{0}C. This effect of increased mobility (creep rates) in nanocomposites, compared to that in unfilled semi-IPN, is retained up to 50-80^{0}C (Fig. 5, b).

Further, a single, very intense glass transition peak with T_{max}= 90^{0}C, observed in the CR spectrum of neat PHEMA, changed only slightly in the PHEMA-ND nanocomposite [16].

At the same time, cardinal spectral changes in PHEMA glass transition were observed in the 83PU-17PHEMA-ND nanocomposites (Fig. 5, b): the introduction of ND particles strongly

changed the "relaxation picture" at elevated and high temperatures. The main effect here is a sharp suppression of PHEMA segmental dynamics (creep at low stress) over the range of 90 to 180^{0}C, that corresponds to disappearance of high-temperature heat capacity anomaly in the DSC curve. The highest creep resistance at 150-180^{0}C is observed at the minimal ND content of 0.25 wt.% in the nanocomposite whereas, contrarily, the least effect of suppression of dynamics by nanofiller is registered at 3 wt.% NDs (Fig. 5, b).

Again, the introduction of ND particles resulted also in the opposite effect of some accelerating segmental dynamics at 20-70^{0}C (Fig. 6, b), i.e., increasing creep rates in the temperature region between the β- and α- transitions of PHEMA.
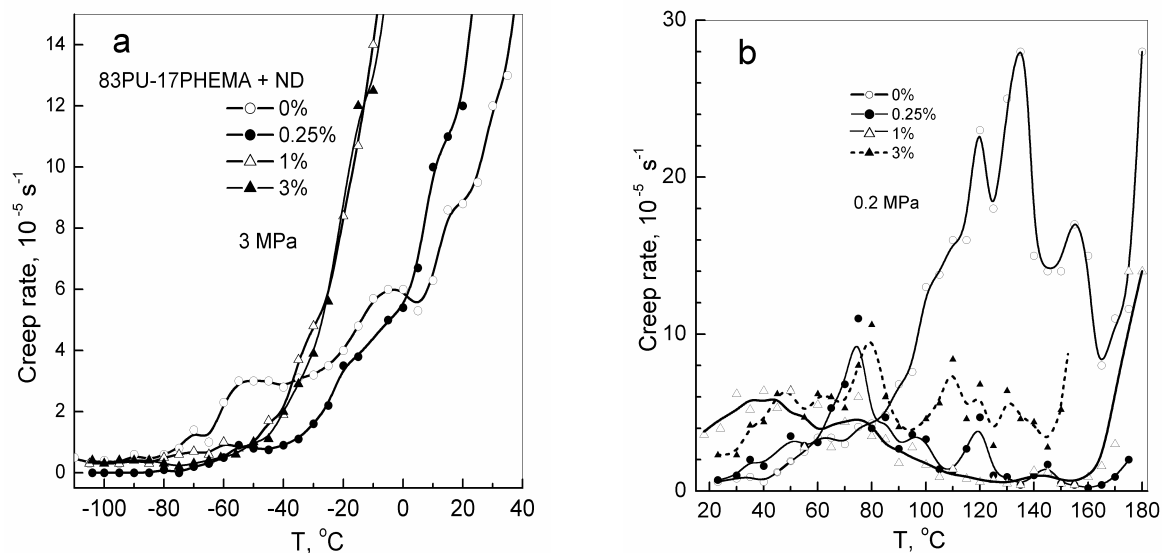

Figure 5 (a, b). Creep rate spectra obtained for the 83PU-17PHEMA network and ND-containing nanocomposites based thereon in the temperature regions of PU glass transition, at tensile stress of 3 MPa (a), and of PHEMA glass transition, at tensile stress of 0.2 MPa (b). ND weight contents are indicated.

The mechanical properties of semi-IPN samples reflect the changes in structure with increasing amount of PHEMA in the systems. The stress at break changes from 3.5 MPa to 24 MPa but strain at break has the extremum at 40% of this polymer. Young's modulus increases from 13 MPa up to 658 MPa with fraction of PHEMA. The introduction of ultra-dispersed diamond filler in the semi-IPN samples resulted in the significant growth in stress at break and in Young's modulus (Fig.6). The maximal effect have been obtained for samples with 0.25% of filler. The increasing amount of filler in the semi-IPN samples resulted in relative decreasing of reinforcing effect.

4 Conclusion

The ultra-dispersed diamond nanofiller could be reinforcing filler for multicomponent polymer systems such as IPNs and semi-IPNs. Just small amount of nanofiller (0.25% by weight) gave the maximal effect on the dynamic mechanical, physico-mechanical properties and segmental motions of materials.
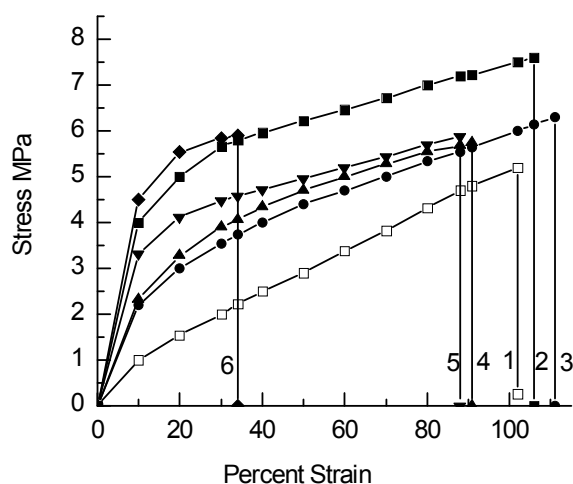
Figure 6. Stress-Strain curves for PU/PHEMA semi-IPN with 28% PHEMA and with different amount of diamond nanofiller: 0% (1), 0,25% (2), 1% (3), 5% (4), 10% (5), 20% (6).

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