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Biocompatible nanocomposites based on semi-interpenetrating polymer networks and nanosilica modified by bioactive amino acid tryptophan: Morphology, dynamics and properties

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ABSTRACT

The nanocomposites based on polyurethane and poly(2-hydroxyethyl methacrylate) (PU-PHEMA) semi-IPN matrices with 17 or 37 wt.% PHEMA, containing from 3 to 15 wt.% nanosilica (NS), were synthesized aiming at the biomedical applications. NS surface was modified using the mechanosorptive method, with formation of basically monomolecular layer of biologically active substance – amino acid tryptophan. The AFM analysis of morphology of the nanocomposites and the complex DSC-TSDC-DMA-CRS analysis of their thermal, relaxation and elastic properties over the broad temperature range, from −150 to 200 °C, were performed. Satisfactory nanofiller dispersion and the pronounced changes in matrix morphology were observed at 17 wt.% PHEMA in the matrix, whereas nanofiller submicro- and microaggregates prevailed in the nanocomposites with 37 wt.% PHEMA. As a result, just in the first case the most substantial "constrained dynamics" effect (e.g., increasing T_g by 20–30 °C) was observed in the nanocomposites.

1. Introduction

Polymer nanocomposites have attracted significant attention for last decades from both the academic and industrial points of view [1–6]. The main reason for that is the enhancement of mechanical, thermal and other properties of the nanocomposites compared with those of their unfilled matrices [1,3,6] and those of conventional composites [7]. Due to high specific surface of the nanofiller particles and formation of the interfacial polymer layers, manifesting "constrained dynamics" behavior, nanoparticles can influence on the majority of nanovolumes of polymer matrix; that results in enhancing properties of the nanocomposites [3,6]. For preparing nanocomposites most often individual polymers have been used as polymer matrices [3–6,8–11]. Meantime, of essential interest for this purpose could be multicomponent polymer matrices obtained by the method of interpenetrating polymer networks (IPNs) [12,13]. The existence of several levels of chemical and structural heterogeneities in such matrices could provide additional opportunities for regulation of nanocomposites' properties. It is known that the structure and properties of the IPNs are controlled in particular by kinetics of polymer networks formation and by the thermodynamics of polymer components mixing [12]. Introduction of fillers into such systems can lead to increasing the compatibility of polymer components [14,15]. There are a few successful

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attempts of introducing nanofillers into interpenetrating polymer networks [15–17]. Thus, the nanocomposites based on epoxy-polyurethane IPNs, containing nanosilica, demonstrated an increase in the compatibility of polymers and increasing damping properties, as compared with those of the unfilled matrix [16]. Polyurethane–poly(methyl methacrylate) semi-IPNs, reinforced by organomodified montmorillonite exhibited an increase in modulus and mechanical strength as well as increased thermal stability compared to the native matrix [17].

Of special interest is the creation of nanostructured IPN matrices containing the biocompatible components. The flexibility and capabilities peculiar to the methods of synthesis of IPNs or semi-IPNs allow to create advanced biomaterials [18–20]. The introduction into such polymer matrices of special nanofillers with surface modified by biologically active substances could provide specific pharmacological properties of the composites [21]. Adsorptive modification of the surface of fumed nanosilica allows to reverse the biologically active substances into the high dispersion condition with formation of mono- or multimolecular layers of the biologically active substances on the surface of nanoparticles [22].

In our previous works, the semi-IPNs based on polyurethane (PU) network and poly(2-hydroxyethyl methacrylate) (PHEMA) were synthesized and investigated [18,23,24], as well as the 3D nanodiamond-containing [25], oxide-containing [26,27], or carbon nanotube-containing [28] nanocomposites based thereon (as the biocompatible materials for medical applications or damping materials) were studied. It was shown that these systems had basically two-phase, nanoheterogeneous structure with incomplete phase separation and pronounced dynamic heterogeneity within the extraordinarily broadened PHEMA and PU glass transitions.

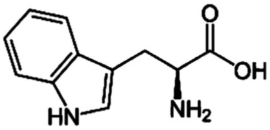
In the present study we use the abovementioned new approach to the nanocomposites for biomedical application. As nanofiller for the polymer matrix – PU-PHEMA semi-IPNs – we use nanosilica with surface modified by biologically active substance – amino acid tryptophan (TPh). The modification of nanosilica particles was performed by mechanosorbtive method [22]. It is known [29,30] that TPh is the key ingredient in making serotonin - one of the brain chemicals involved in regulating of mood. Since the body can't produce its own TPh, it must be taken from outside. There are attempts to create the carrier for TPh [31,32], among them lipid-polymer membrane [30]. It is supposed that the nanocomposites created in this study may be destined for the treatment of diseases that need systemic TPh concentration [33–35]. At the first stage, synthesis and studying morphology, dynamics and properties of the above nanocomposites have been performed in this work.

2. Experimental

2.1. Materials

Nanocomposite samples were prepared from PU-PHEMA semi-IPNs as the matrices. As nanofiller, nanosilica particles (NS) with surface modified by biologically active substance – amino acid tryptophan (TPh) – was used.

The synthesis of PU-PHEMA semi-IPNs, used as polymer matrices, was described earlier [18,25]. Fumed silica A–300 nanoparticles (99.87% purity, specific surface area $S_{\mathrm{BET}} = 342\ \mathrm{m}^2/\mathrm{g}$, of 9 nm in average diameter, pilot plant of the Institute of Surface Chemistry, Kalush, Ukraine) were used. The nanoparticles' surface was modified with TPh



by the mechanosorptive method [22] using a ball mill in a wet atmosphere. Humidity was created by adding water to the drum in amount of 500 mg per 1 g NS. The NS surface contained 0.8 mmol of free silanol groups as active sorption centers per 1 g nanoparticles; these groups manifested themselves as the narrow intense band at 3750 cm^{-1} in the IR spectrum in the absence of water. Therefore, NS and TPh were downloaded in a ceramic drum with an amount of 0.8 mmol of TPh per 1 g NS. The time of mechanical activation was 5 h. Then, TPh interacted with free silanol groups with formation of hydrogen bonds. It was located as monomolecular layer at silica surface since the 3750 cm^{-1} band totally disappeared in the IR spectrum of dehydrated modified NS particles, with displacement by ~400 cm^{-1} towards lower wavenumbers.

For creation of the nanocomposites, the TPh-modified NS (below *t*-NS) was introduced into the matrix at the stage of PU synthesis in the amounts of 3, 5, 10 or 15 wt.%. With the aim of their uniform distribution in the matrix, sonication of the mixture was performed with UZDN-A equipment during the process of synthesis. The filled PU network samples were subjected to swelling in 2-hydroxyethyl methacrylate (HEMA) monomer, containing the initiator of photopolymerization (Irgacure 819), to the degrees of 17 wt.% or 37 wt.% HEMA. Then, a subsequent photo-polymerization of HEMA monomer in the filled PU was carried out, i.e., the second polymer constituent of the matrix, PHEMA, was generated. Samples of nanocomposites were kept in vacuum (10^{-5} Pa) at 80 °C for 36 h before reaching a constant weight. Thus, the compositions of the polymer matrices used were PU: PHEMA (83:17), wt.% or PU: PHEMA (63:37), wt.%, and these matrices are designated throughout the text as semi–IPN17 and semi–IPN37, respectively. In turn, the nanocomposites under study are designated herein as semi-IPN17/*t*-NS3, semi-IPN17/*t*-NS5, semi-IPN17/*t*-NS10, semi-IPN17/*t*-NS15, and semi-IPN37/*t*-NS3, semi-IPN37/*t*-NS5, semi-IPN37/*t*-NS10, semi-IPN37/*t*-NS15, respectively. In all cases, composite films of about 0.5 mm in thickness were prepared.