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Semi-interpenetrating polymer networks based on polyurethane and poly(2-hydroxyethyl methacrylate): Dielectric study of relaxation behavior

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ABSTRACT

The study of molecular dynamics by broadband dielectric spectroscopy (BDS) is presented for polyurethane (PU), poly(2-hydroxyethyl methacrylate) (PHEMA) and for semi-IPNs based on PU and PHEMA synthesized by photopolymerization. The dielectric properties were performed in wide range of frequencies and temperatures with the goal to establish the relation between the relaxations and the structure. Five relaxation phenomena were finally detected for PHEMA : γ-, βsw-, β-relaxations at low temperatures and α-relaxation at 150 °C at high frequencies plus ionic conductivity relaxation which starts at 0 °C. For semi-IPNs the overlapping of γ- and βsw-relaxations of PHEMA ($-125/-75$ °C), then with increasing the temperature α-relaxation in PU ($-75/0$ °C), next ionic conductivity relaxation which starts at 0 °C, and finally the α-relaxation of PHEMA (+125/+170 °C) were detected. The α-relaxation of PHEMA in semi-IPNs shifts to lower temperatures and became broader with increasing amount of PU due to incomplete phase separation in the system and formation of interphases. The dielectric relaxation phenomena were fitted with Havriliak–Negami equation. Activation energy, τ_o and α parameters were calculated. For α-relaxations corresponding dielectric characteristics have been determined from Vogel–Fulcher–Tammann equation. The relaxation map for investigated PU, PHEMA and semi-IPNs was built.

1. Introduction

Interpenetrating polymer networks (IPNs) are materials based on two or more polymers, each of them is chemically crosslinked and at least one network is synthesized in the presence of the other [1–4]. It is known [4,5] that synthesis of IPNs is usually carried out under thermodynamically unstable conditions. This process can start from one of three different, thermodynamically equilibrium states such as a mixture of monomers [6,7], a polymer network swollen with a second monomer [8,9], and a mixture of the starting linear polymers [10,11]. During polymerization and crosslinking processes, phase separation in the IPNs takes place as a consequence of a sharp decrease in the entropy of mixing in the system. The phase separation can lead to different phase morphologies in these materials. The process of the phase separation depends on characteristic parameters such as self- and inter-diffusion coefficients, and Flory interaction parameters. The rate of the phase separation is also connected with the rates of chemical reactions and can be controlled by the crosslinking density of polymers during a process of IPNs preparation [12–14].

The process of phase separation in the IPNs may be stopped at the different stages by the permanent entanglement of chains [15]. The curing rate of monomers is critical as it can prevent and/or limit the phase separation of the system [16]. By controlling the kinetics of both polymerization reaction and microphase separation, it is possible to prepare IPNs with dispersed phase domains ranging from a few tens of nanometers to a few micrometers [17–20]. Thus, from the same mixture of monomers or from polymer swelled with second monomer by controlling the kinetics of both polymerization reaction and microphase separation, materials with different degrees of polymer segregation can be obtained.

As found, this micro and/or nanoheterogeneous morphology of IPNs may result in the extraordinarily broad glass transitions domain in such systems [21–24]. The differences in local composition or packing density resulted in the different Tg's (i.e., in a dispersion of glass transitions), and the overall effect might be just a single, very broad glass transition. Detailed analysis of multiple segmental motions constituting anomalous glass transitions in complex,

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multicomponent polymer systems, such as IPNs and others, and the information obtained therefore are of special interest for predicting engineering performance of these materials.

This research was aimed at analysis of the molecular dynamics in the polyurethane-poly(2-hydroxyethyl methacrylate) semi-IPNs by dielectric relaxation spectroscopy with the goal to have a better insight on the dynamic of the chain and their relation with the structure having in view to develop improved materials for biomedical applications.

Poly(2-hydroxyethyl methacrylate) (PHEMA) is well known as a polymer with good biocompatibility but with unstable properties due to its high hygroscopicity. Semi-interpenetrating polymer networks (semi-IPNs) create an opportunity to synthesize PHEMA-based composites that retain PHEMA biocompatibility and acquire better stability, better mechanical properties and lower water uptake.

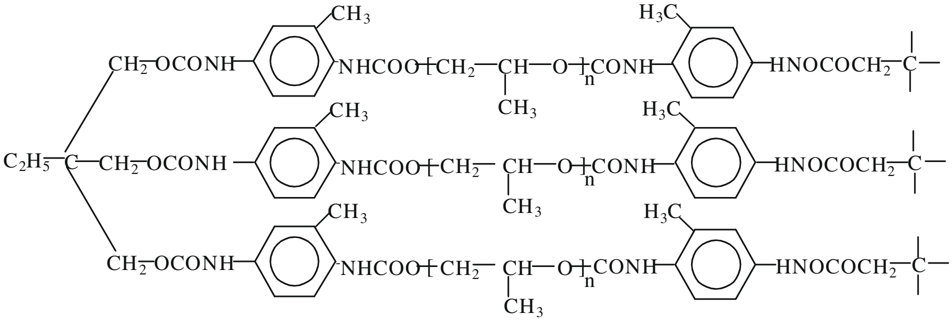
In our previous studies, semi-IPNs based on PU and PHEMA were synthesized [23] and their nanostructure [25,26] as well as the thermodynamic miscibility and dynamic mechanical behavior [23] have been investigated. During the process of polymerization, the entropy of mixing of PU and PHEMA, ΔS, sharply decreased [23], i.e., Gibbs energy of mixing $\Delta G = \Delta H - T\Delta S$ increased that must result in phase separation of the system. Actually, small-angle X-ray scattering (SAXS) study of PU–PHEMA semi-IPNs [25] showed their nanoheterogeneity, with characteristic quasi-periodicities of 6–9 and 26–28 nm, as a consequence of spinodal decomposition. These systems are considered as two-phase ones with incomplete phase separation. Dynamic mechanical analysis of these semi-IPNs [23] showed two broad mechanical loss, tanδ peaks related to glass transitions of constituent components. For PU network, the α-relaxation extended from −55 to 50 °C, with $T_{\max} \approx -30$ °C at 5–10 Hz. Besides, the temperature of the glass transition onset, as estimated by DSC, was practically unchangeable irrespective of IPN composition. For PHEMA, the extraordinarily broad tanδ peak, covering the temperature range between about 50 and 180–200 °C, was observed.

For better knowledge about relaxation phenomena in such complex system, dielectric investigations were performed on PHEMA, PU and semi-IPNs in wide range of frequencies and temperatures. The literature is quite rare on PHEMA dielectric investigations and deals with mainly low temperature domain [27,28]. PU dielectric studies are more common. It is rather difficult to evidence the dielectric behavior of semi-IPNs as it is a combination of the relaxations sensitive to the morphology as well.

2. Experimental

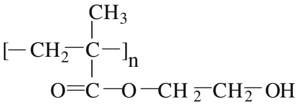
2.1. Materials

The semi-IPNs were prepared on the basis of polyurethane network (PU) and poly(2-hydroxyethyl methacrylate) (PHEMA). First the PU was synthesized by a two steps method, as described in Refs. [23,25]. The synthesized PU is depicted by the formula:



The semi-IPNs were obtained by a sequential method. For this purpose, the PU was swollen in freshly distilled under vacuum monomer 2-hydroxyethyl methacrylate which contains 2,2-Dimethoxy-1,2-diphenylethane-1-one (Irgacure 651) as photoinitiator. The swelling was carried out to the equilibrium state. Then the photopolymerization of the monomer at ambient temperature was carried out for two hours. The wavelength of UV light was 340 nm. The postcuring of the samples for 2 h at 100 °C was used to complete the polymerization of HEMA.

The obtained second polymer is poly(2-hydroxyethyl methacrylate):



$$[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle O{=}C-O-CH_2-CH_2-OH}{C}}-]_n$$

The prepared semi-IPNs prepared were then held in vacuum 10^{-5} Pa at 80 °C during 36 h to reach a constant weight. Different semi-IPNs samples with a range of compositions from 10% to 57% of PHEMA were obtained in form of films with a thickness of 0.7–0.9 mm.

2.2. Methods

2.2.1. Dielectric relaxation spectroscopy

DRS measurements were carried out in parallel plate geometry using circular electrodes having a diameter of 20 mm. The complex dielectric function:

$$\varepsilon^*(f) = \varepsilon'(f) - j\,\varepsilon''(f) \quad (1)$$

(f-frequency, ε'-real part, ε''-imaginary or loss part, $j = \sqrt{-1}$) was measured isothermally in the frequency range from 10^{-1} to 10^{6} Hz by a Novocontrol Concept 40 α-analyzer interfaced to the sample by a broadband dielectric converter (BDC, Novocontrol). The temperature of the sample was varied from −140 °C to 200 °C in steps of 3 °C and was controlled with a ΔT = 0.1 °C. To avoid the influence of water the measurements were carried out in two steps: first run from 20 °C to 150 °C, second run from −140 °C to 200 °C. The results of the second run were analyzed by fitting with the Havriliak–Negami [29,30] function to the isotherm curves data using the Novocontrol software WinFit. Thus the positions of the maximum of dielectric loss and the Havriliak Negami (HN) parameters like the dielectric relaxation strength $\Delta\varepsilon$ have been extracted for the relaxation process according to:

$$\varepsilon^*(\omega) = \varepsilon_u + \frac{\Delta\varepsilon}{[1+(i\omega\tau)^{\alpha_{HN}}]^{\beta_{HN}}}, \quad (2)$$

where ε_u is the unrelaxed dielectric permittivity, $\Delta\varepsilon$ is the dielectric increment or strength, τ is the relaxation time, ω is the angular