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Effect of compatibilizing compounds on the viscoelastic properties of interpenetrating polymer networks

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Abstract

The effect of various compatibilizing compounds on the viscoelastic behaviour of semi-interpenetrating polymer networks (IPNs) based on cross-linked polyurethane and poly(*n*-butyl methacrylate) was investigated. It was established that in many cases, because of the specific chemical structure of compatibilizing compounds, the modified system reveals only one maximum of mechanical losses instead of two for initial semi-IPNs. This effect may be called compatibilization throughout the whole volume of the initially phase separated system. The disappearance of two maxima, revealing only one shows that the segregation degree in the IPN diminishes and in some cases miscible systems are formed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Interpenetrating polymer networks; Compatibilization; Viscoelasticity

1. Introduction

During recent years much work has been published on the improving compatibility between two immiscible polymers in blends [1,2]. The interface formed between strongly immiscible polymers is fairly sharp and only a small extent of interpenetration of molecules is assumed based on highly unfavourable enthalpic interactions between two chemically different polymers. Therefore, reinforcement of phase separated blends becomes an important subject in designing polymer materials. This problem is usually solved by using compatibilizers of the di- and tri-block copolymer type. These compatibilizers, when added to the blend of two immiscible polymers, segregate to the interface where different blocks stretch into their respective homopolymer, forming entanglements with polymer chains of both phases. The theories of segregation of the di- and tri-block copolymers at the interface have been developed [3–9]. According to Kramer [3], the broadening of the interfacial region is due to the “roughening” of the equilibrium interface. The theories give good agreement between the measured and the calculated profile of the segment distribution near the interface. The effects of the reinforcement of the interface are also called compatibilization because compatibilizers improve the interaction between two phases. To improve the properties of the blends, various compatibilizers may be used [10]. It was established that after reaching the critical concentration for covering an interfacial area, the excess compatibilizer is present in the system in the form of a separate phase and is excluded from the compatibilization process. Some other polymers and additives may be used as compatibilizers. For example, the improving adhesion between polycarbonate and poly(vinylidene fluoride) [11] by adding poly(methyl methacrylate) was described.

Interpenetrating polymer networks (IPNs) are a specific class of blends of crosslinked polymers that are formed by simultaneous or sequential curing of two different polymers proceeding according to the independent mechanism [12]. In this way, only in IPN the interpenetration of different networks is observed without chemical interaction between them. Practically, most IPNs are phase-separated systems with incomplete microphase separation. The latter is the result of the simultaneous proceeding of both the chemical reaction and the phase separation by curing the system [13]. As a result of this, the problems of compatibilization in IPNs are of equally great importance. Up to now such compatibilization was observed only by the introduction of a filler [14]. The data on the viscoelastic properties of filled IPNs showed that introducing a filler leads to the disappearance of two maxima of mechanical losses, belonging to different phases, and to the appearance of only one broad maximum.

Till date the problem of compatibilization of IPNs using

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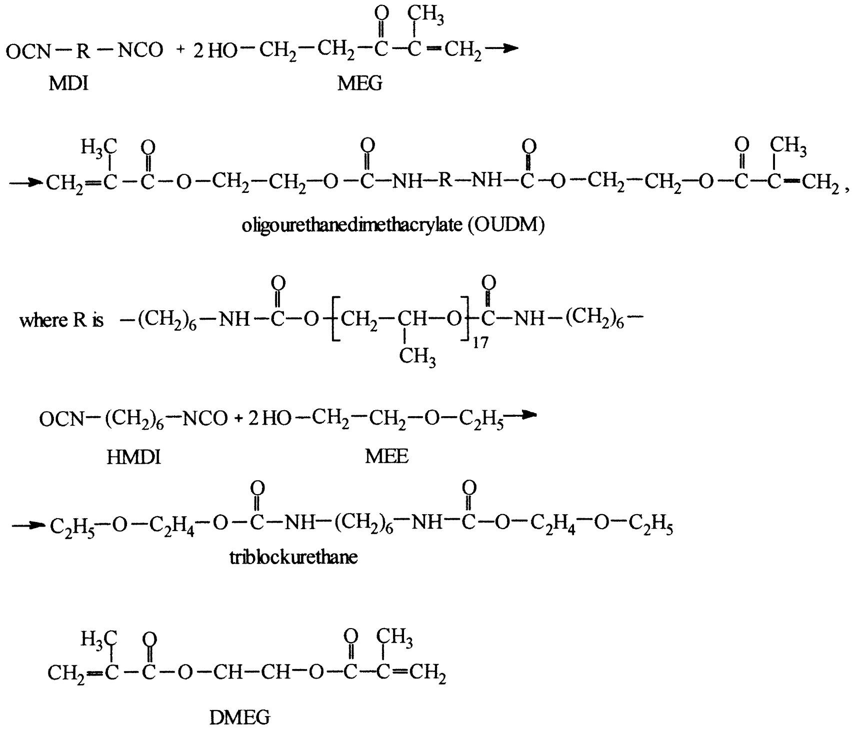

Scheme 1.

various compatibilizers has not been investigated. The aim of this article is to establish the effect of compatibilizing compounds on the viscoelastic properties, assuming that improving interfacial interaction will lead to the diminishing of the segregation degree in IPNs.

2. Experimental

Well described semi-IPN based on the cross-linked polyurethane (PU) and poly(*n*-butyl methacrylate) (PBMA) was chosen for the investigation with a component ratio of 75/25 and 50/50 by mass [15]. Semi-IPNs were obtained by the method of simultaneous formation of the cross-linked PU and the polymerization of butyl methacrylate. Cross-linked PU was synthesized from oligo(oxypropylene glycol) of molecular mass 2000 and adduct of trimethylol propane with 2,4-2,6-toluylene diisocyanate in the ratio 3:1. Dibutyltin dilaurate (1.4×10^{-4} mol/l) was used as a catalyst. Monomer was simultaneously introduced into the reaction mixture with the initiator of radical polymerization (2,2-azo-bis-iso-butironitryle) (2.96×10^{-2} mol/l).

As possible compatibilizers, the following compounds were tested:

1. Commercial product monomethacrylester of ethylene glycol (MEG) containing two functional groups—double bond and OH-group.
2. Oligourethane dimethacrylate (OUDM) with two end double bonds.
3. Triblockurethane containing urethane block and two CH_3CH_2–O–CH_2CH_2 groups.

OUDM was synthesized from macrodiisocyanate (MDI) based on oligopropylene glycol with a molecular mass of 1000, hexamethylene diisocyanate and MEG at the ratio of 1:2 at 40°C with the catalyst, dibutyl tin dilaurate (0.01 mass%) according to Scheme 1.

The reaction was performed till all the isocyanate groups were exhausted. The control under reaction was performed using reverse titration of NCO-groups by the Stagg method [16] and using IR-spectroscopy. The product was a viscous mass soluble in butyl acetate.

Triblockurethane was obtained from HMDI and monomethyl ether of ethylene glycol (MEE) (Scheme 1). Reaction was performed in bulk at the GMDI:MEE ratio of 1:2 in the presence of a catalyst (tin octoate) in dry argon at 60°C to full exhausting of isocyanate groups. The reaction control was as described earlier. By cooling, the crystallizable mass soluble in dichloroethane was formed. The product was extracted by precipitation with dry ether and had a melting point of 57–58°C and was soluble in toluene. Identification was done using thin-layer chromatography ($R_f = 0.82$, one spot (chloroform:dioxane:cyclohexanone:methanol in ratio 4:4:4:1)).

All the compatibilizing compounds were introduced into the reaction system before curing. Curing was done at 60°C with subsequent drying and evacuation in vacuum, of the unreacted butyl methacrylate to constant weight. Polymer films were studied by the method of dynamic mechanical

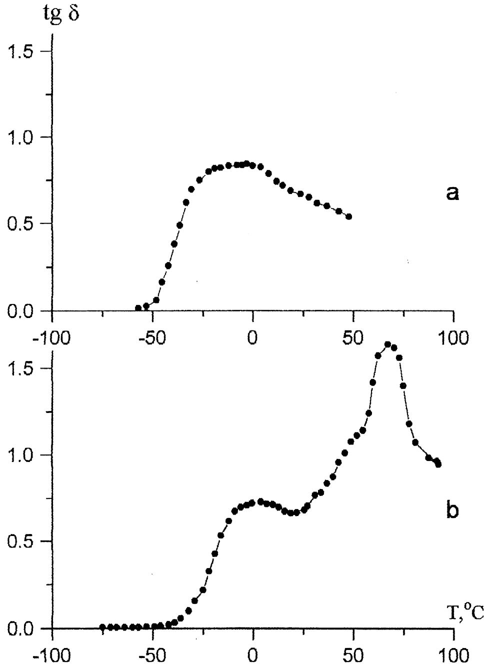

Fig. 1. Temperature dependence of mechanical losses for PU-network (a), and semi-IPN PU/PBMA 75/25 mass% (b).

spectroscopy using the frequency relaxometer [17] at the frequency of forced sinusoidal vibrations, 100 Hz.

3. Results and discussion

Fig. 1(a) and (b) shows the temperature dependencies of the tangent of mechanical loss angle, tan δ, for the initial PU network (as a component of IPN) and for the semi-IPN of the composition PU/ PBMA 75/25 mass%. Two distinct maxima are observed for semi-IPN being indicative of the two-phase structure of semi-IPN [15] with transition temperatures at −5°C for the PU-enriched phase and 70°C for the PBMA enriched phase.

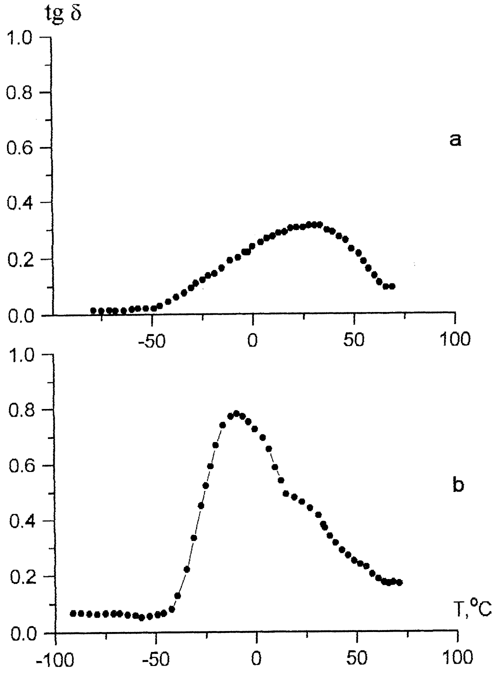

Fig. 2. Temperature dependence of tan δ for semi-IPN 75/25 mass% with 5 mass% MEG (a), and 5 mass% of triblockurethane (b).

Introduction of 5 mass % of MEG into the system, containing two functional groups may lead to the formation of grafted IPNs where chains are bonded via a double bond with PBMA and via a hydroxyl group with PU. Fig. 2(a) shows that in this case only one broad maximum of tan δ is observed in the region of 30°C (between the glass transition temperatures of PU and PBMA) and with a loss level of about 0.3. This result shows the formation of a one-phase compatible system due to possible chemical reaction between different chains.

Introduction of triblockurethane (5 mass%) with a long aliphatic chain (C_6) and two CH_3–CH_2–O–CH_2CH_2 groups again reveals only one peak of tan δ with a maximum near −10°C and small shoulder in the region 25–40°C. It is possible that triblockurethane segregates at the interface between two phases and interacts with them because of the identical block of PU and PBMA phases. This interaction diminishes microphase separation and reinforces the interface (increases compatibility). Here only a peak for the PU-phase that is continuous with discrete inclusions of PBMA-phase is observed.

Using DMEG as a cross-linking agent for butyl methacrylate diminishes, as it should be expected [14], the level of mechanical losses for both phases (Fig. 3(a)), the glass transition of PBMA enriched phase being shifted to higher temperatures, but two peaks are preserved. Introduction of OUDM, in spite of the fact that it may also serve as a cross-linking agent, gives another picture (Fig. 3(b)). OUDM contains a urethane block with a molecular mass of about 1500 identical to PU. In this case again only one maximum of mechanical losses is observed in the region 25°C and a shoulder at 40–55°C. The level of tan δ is 0.8. Such a behaviour of IPN may be explained by the fact that the OUDM interacts with PU like triblockurethane (Fig. 2(b)) and simultaneously serves as a cross-linking agent for butyl methacrylate. Such a combination prevents microphase separation during IPN formation, leading to the compatibilization and grafting, characterized by one high maximum of tan δ, its position being intermediate between the glass transition temperatures of PU and PBMA.

Now consider the effect of the compatibilizing compounds on the behaviour of the semi-IPN with a composition 50/50 by mass. Fig. 4(a) shows the temperature dependence of tan δ for initial semi-IPN. IPN also consists of two phases with two transitions at 0°C for the PU-enriched phase and 75°C for the PBMA-enriched phase. Introduction of DMEG leads to a sharp change in the viscoelastic behaviour. For the PBMA-enriched phase (Fig. 4(b)), the level of losses increases markedly as compared with

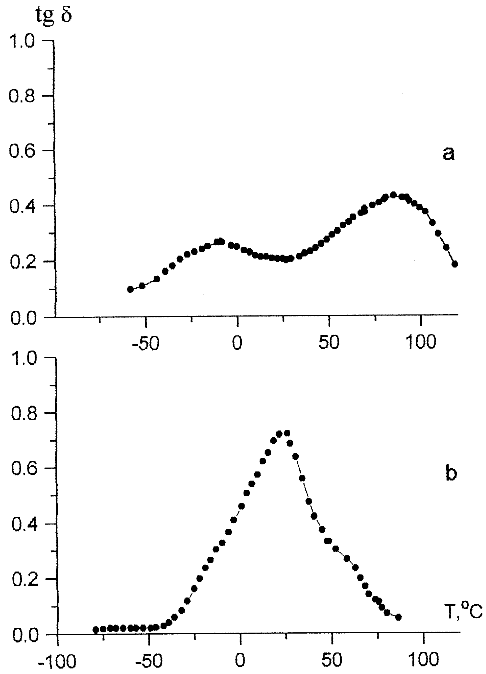

Fig. 3. Temperature dependence of tan δ for semi-IPNs 75/25 mass% with 10 mass% of DMEG (a), and 10 mass% OUDM (b).

pure IPN (Fig. 4(a)) and T_g increases by 10–15°C. For the PU-enriched phase, a slight transition may be detected in the region of glass transition temperature.

Introduction of 5 mass% OUDM leads to marked compatibilization (Fig. 4(c)). OUDM (5%) gives rise to the appearance of one sharp maximum at -2 to 0°C with high level of losses (1.0), and to a small additional transition at 30–35°C. It may be supposed that the introduction of OUDM enhances the formation of the structure where PU forms a continuous phase with the PBMA-phase discrete inclusions due to two types of interactions in the system: chemical interaction with butyl methacrylate and physical interaction with PU. The T_g of the discrete phase is 30–35°C lower as compared with the T_g of the PBMA-enriched phase in semi-IPN. Therefore, by adding OUDM, the level of microphase separation in the system is reduced. The difference between semi-IPN 50/50 and 75/25 is that in the first case, the T_g of constituent phases become closer, whereas in the second case only one maximum of losses is observed.

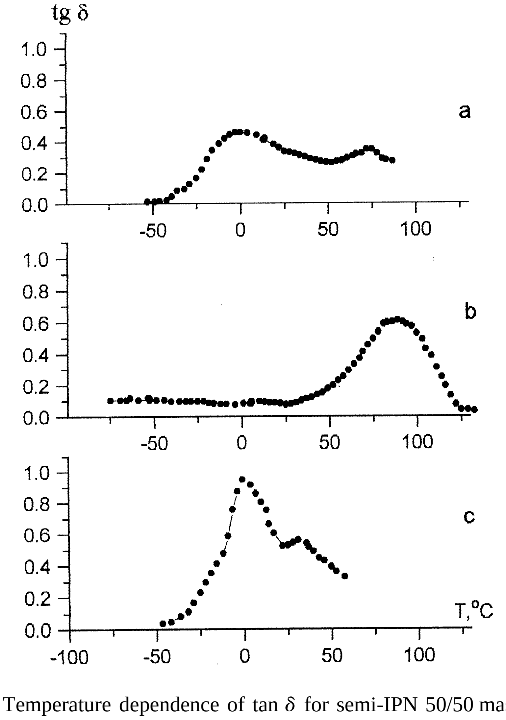

Fig. 4. Temperature dependence of tan δ for semi-IPN 50/50 mass% (a), and with 5 mass% DMEG (b), and 5 mass% OUDM (c).

4. Conclusion

Experimental data on the effect of various additives to semi-IPNs based on cross-linked PU and PBMA show that in many cases the temperature dependence of the mechanical loss tangent, tan δ, reveals only one maximum instead of two, typical of initial semi-IPN. This effect may be called compatibilization throughout the whole volume of the initially phase separated system. It is evident that in this case interfacial segregation of compatibilizer may proceed. In fact, if the compatibilizer molecules would segregate only at the interface between the two phases and improve the compatibility in the interfacial region, one should observe three relaxation maxima: two for initial phases and a third for compatible interfacial region, or two maxima, corresponding to initial phases, if the fraction of the interfacial region is small and cannot be detected by the method of mechanical dynamic spectroscopy.

The disappearance of two maxima and the presence of only one maximum shows that the segregation degree in the IPN [18] diminishes and that in some cases the miscible system is formed. For the explanation of these effects from the thermodynamic point of view, it is necessary to find the phase diagrams in the ternary systems: network-1:network-2:compatibilizer. Work on this is in progress.

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