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Poly(ethylene oxide)/polybutadiene based IPNs synthesis and characterization

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Abstract

Interpenetrating polymer networks (IPNs) were prepared from hydroxytelechelic polybutadiene (HTPB) and poly(ethylene oxide) (PEO) via an in situ process. The PEO network was obtained by free radical copolymerization of poly(ethylene glycol) methacrylate and dimethacrylate. Addition reactions between HTPB and a pluri-isocyanate cross-linker (Desmodur® N3300) led to the HTPB network. Polymerization kinetics were followed by Fourier transform spectroscopy in the near and middle infrared. Mechanical properties and the IPN morphology were investigated by dynamic mechanical analysis and transmission electron microscopy. The relation between the formation rates of the two networks and the IPN final morphology is discussed.

Keywords: Interpenetrating polymer networks; Hydroxytelechelic polybutadiene; Poly(ethylene oxide)

1. Introduction

Interpenetrating polymer networks (IPNs) are described as an intimate combination of two (or more) cross-linked polymers [1]. The tight entanglement of these networks ensures a good interpenetration of the two components and a good dimensional stability. Moreover, one can observe an improved combination of the properties of its components. In that prospect, poly(ethylene oxide) (PEO) based IPNs could represent an interesting medium as solid polymer electrolytes (SPEs) in practical electrochemical devices. For example SPEs as poly(methylmethacrylate)/PEO IPNs were developed by Siow and Hou [2,3], displaying conductivities as high as 10^{-3} S cm^{-1} at 25 °C. In our laboratory PEO/polycarbonate IPNs were prepared as the SPE matrix for actuator application based on a combination of electronic and ionic conducting polymers [4,5]. The PEO network is able to complex lithium salts and to behave as the SPE whereas the polycarbonate network should ensure good mechanical properties. However, for these actuators, the stress induced by bending deformations leads to crack formations at room temperature. In order to prevent cracks, polybutadiene elastomer was used instead of polycarbonate in the actuator design since this elastomer is able to absorb large deformations [6,7].

Polybutadiene (PB) based IPN studies have been already reported in the literature. Two main synthetic routes have been investigated. In the first one, PB was radically cross-linked through the pendent vinyl groups and alkene double bonds along the polymer chain [8–11], and/or chain transfer reactions as well [12], leading to a PB network. So various types of PB network and also the cross-linked PB latex particles have been swollen with methacrylic monomers which were subsequently polymerized in the networks leading to IPNs [13].

In a second route, in addition to the fact that polyurethane (PU) single networks based on isocyanate cross-linked α,ω-hydroxyl terminated polybutadiene (HTPB) have been widely

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used in composite, solid propellants, explosives, adhesives, sealants, pervaporation membranes and coating materials [14], HTPB has been also combined with other polymers in order to prepare IPNs. Glassy polymers have been combined with HTPB into IPNs in order to obtain reinforced elastomers or rubber reinforced high impact plastics. In addition PU-(HTPB)/poly(methylmethacrylate) [15–18] and PU-(HTPB)/polystyrene IPNs have been examined [19]. These studies have pointed out the role of the hard PU segments in the HTPB. These hard segments are more compatible with the poly(methylmethacrylate) matrix indicating that the interpenetration occurs through the rigid blocks of the PU. Depending on the composition, the domain sizes in the IPNs range from 10 nm to several microns. Furthermore they can show dual phase continuity. In general, the IPN mechanical properties are superior to those of blends.

IPNs can be prepared through different routes, for example in the one shot in situ process all reactants are mixed together and the reactions leading to the formation of the two networks are started at the same time, promoting a more or less simultaneous formation of the networks. In this case, noncompeting processes for both networks' synthesis are, generally but not necessarily, required, typically a step and a chain polymerization [20].

In this study, the one shot in situ method was chosen to synthesize PEO/HTPB IPNs. The PEO branched network is obtained by free radical copolymerization of poly(ethylene glycol) dimethacrylate and methoxy poly(ethylene glycol) methacrylate, thus containing low molecular weight dangling poly(ethylene oxide) chains. The presence of these dangling PEO chains should increase the proportion of volume available for the migration of ions [21–24]. The HTPB network is formed by the addition of the OH functions of HTPB with a NCO cross-linker (Desmodur® N3300). IPNs being quite complicated systems, it is important to understand how one network is formed in the presence of the other. Kinetic and mechanical investigations can be efficient techniques to understand the resulting morphology and the material properties. Accordingly, the kinetics of HTPB network, PEO network and IPN formations were investigated by middle and near FTIR spectroscopy while mechanical properties were studied by dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

Poly(ethylene glycol) dimethacrylate (PEGDM, Mn = 875 g mol^{-1}) (Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGM, Mn = 475 g mol^{-1}) (Aldrich), hydroxyl end-functionalized polybutadiene – (HTPB, Mn = 2800 g mol^{-1}, alcohol functionality $f_{OH} = 2.4$) (Cray Valley), dicyclohexylperoxydicarbonate (DCPD) initiator (Groupe Arnaud), Desmodur® N3300 (pluri-NCO cross-linker, 5.2×10^{-3} mol of NCO per gram of Desmodur®) (Bayer), lithium perchlorate (Aldrich) and dibutyltindilaurate (95%) (DBTDL) (Aldrich) were used without further purification. Toluene (VWR) was distilled before used.

2.2. Synthesis

2.2.1. Preparation of single networks

PEO single networks were prepared by the following procedure: 0.75 g PEGM, 0.25 g PEGDM, 22 mg DCPD (2.2 wt% with respect to the sum of methacrylate oligomers' weight) were stirred together under argon atmosphere for 30 min at room temperature. The mixture was then poured into a mould made from two glass plates clamped together and sealed with a 250 or 500 μm thick Teflon® gasket. The mould was then kept at 50 °C for 3 h. The sample was then cured for 1 h at 80 °C.

HTPB single networks were prepared by dissolving 1 g HTPB into 1 mL toluene. 0.18 g Desmodur® N3300 ([NCO]/[OH] = 1.1) and 32 μL DBTDL ([DBTDL]/[OH] = 0.06) (cross-linker and catalyst for the HTPB network formation, respectively) were added to this solution. The mixture was then poured into a mould made from two glass plates clamped together and sealed with a 250 or 500 μm thick Teflon® gasket. The mould was then kept at 50 °C for 3 h. The sample was finally cured for 1 h at 80 °C and dried for 8 h at 50 °C under vacuum.

2.2.2. IPN preparation

DCPD was used for methacrylate radical initiation of PEGDM and PEGM methacrylate functions, while Desmodur® N3300 was the cross-linker for HTPB and DBTDL was the catalyst for the reaction between NCO and OH functions. The given amounts of PEGDM, PEGM, HTPB were poured as such into a flask. In all IPN preparations reported in this study, PEGM and PEGDM were introduced in a 1:3 weight ratio corresponding to 75 wt% PEGM and 25 wt% PEGDM into the PEO network. Desmodur® was then added to the mixture ([NCO]/[OH] = 1.1) as well as the DCPD initiator (2.2 wt% with respect to the sum of methacrylate oligomers weight). The minimum volume of toluene (typically 1 mL for a total weight of 1 g of PEGDM, PEGM and HTPB) is then added to ensure the homogeneity of the mixture. The obtained solution was stirred under argon atmosphere for 30 min, and DBTDL catalyst was then added ([DBTDL]/[OH] = 0.06). The mixture was poured into a mould made from two glass plates clamped together and sealed with a 250 or 500 μm thick Teflon® gasket. This mould was then kept at 50 °C for 3 h. The sample was then post-cured for 1 h at 80 °C and dried for 8 h at 50 °C under vacuum.

In the following text, (X/(100 − X)) IPN stands for an IPN obtained from X wt% PEGM/PEGDM and (1 − X) wt% HTPB in the starting mixture.

2.3. Kinetic experiments

IPNs were directly synthesized in a single use small size IR cell assembled for each experiment. The mixture of all required reagents was injected into that cell which is formed by two selected plates separated by a Teflon® gasket. A glass window cell and 1 mm thick gasket were used to record the methacrylate group conversion versus time curves since the corresponding harmonic absorption band (6160 cm^{-1}) is located in the near infrared. On the other hand, fluorine windows (CaF_2) and a 250 μm thick gasket were used when the NCO conversion versus time curves were recorded in the middle infrared region (2270 cm^{-1}). The cell was inserted into an electrical heating jacket with an automatic temperature controller (Graseby Specac), the temperature of the block being constant within +/−1 °C of the set temperature. The infrared and near-infrared spectra were recorded with a Bruker spectrometer (Equinox 55) in the range 4000–1000 cm^{-1} (fluorine plates cell) and in the range 7000–4000 cm^{-1} (glassware plates cell), by averaging 10 consecutive scans with a resolution of 4 cm^{-1}. During kinetic studies, accumulation was repeated for every 5 min. Conversion was calculated from the change of the normalized absorbencies of the C–H stretching vibrations in C=C–H group (methacrylate functions) at 6160 cm^{-1} and the NCO vibrations (Desmodur® N3300) at 2270 cm^{-1}. The conversion–time profile was easily derived from the spectra. Indeed, the relative conversion of the reactive chemical functions can be evaluated from the absorbance values as $p = 1 - (A_t/A_0)$ where the A's subscripts 0 and t denote reaction times. No thickness correction was necessary, owing to the geometry of the sample holder that prevented thickness variation during the reaction. It was also checked that the temperature variations from 20 to 100 °C do not affect the molar extinction coefficients of these absorption bands.

2.4. IPN characterizations

2.4.1. Soxhlet® extraction

In order to estimate the amount of unreacted starting material in the final product (single network, IPN) and thus the efficiency of cross-linking reactions, a known weight of the product was extracted in a Soxhlet® with dichloromethane for 3 days. After extraction the sample was dried in a vacuum oven for 8 h at 50 °C. The extractible content (EC) is given as weight percentage:

$$\mathrm{EC}(\%) = \frac{(W_0 - W_\mathrm{e})}{W_0} \times 100$$

where W_0 and W_e are the sample weights, before and after extraction, respectively.

2.4.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measurements were carried out on single networks and IPN samples (typically $L \times w \times t = 15 \times 8 \times 0.5$ (mm)) with a Q800 model (TA Instruments) operating in tension mode (strain: between 0.05 and 0.07%, pre-tension: 10^{-2} N). Experiments were performed at 1 Hz frequency and with a heating rate of 2 °C/min from −100 to +50 °C. The set up provided the storage and loss moduli (E' and E'') and the damping parameter or loss factor (tan δ) was defined as $\tan\delta = E''/E'$.

2.4.3. Transmission electron microscopy (TEM)

TEM analysis was performed with a Jeol 200FX microscope. The ultrathin membrane samples were prepared at −90 °C with an ultramicrotome using a diamond knife, and then stained with OsO_4.

3. Results and discussion

3.1. Single network and IPN synthesis

The PEO single network is obtained by radical copolymerization of PEGM and PEGDM in the presence of DCPD as initiator (2.2 wt% with respect to PEGM and PEGDM). All the PEO single networks are composed of 25 wt% PEGDM and 75 wt% PEGM. Due to the high (25 wt%) proportion of difunctional monomer used as a cross-linker, it is clear that the PEO network should be considered rather as an AB-cross-linked copolymer. This particularly high PEGDM/PEGM ratio was selected in order to obtain a network containing the highest amount of dangling chains (PEGM) while presenting reasonably good mechanical properties, i.e., tear strength. This property is sought in particular for the subsequent actuator application where the material is subjected to repeated handling operations [7].

The HTPB single network is obtained through cross-linking reactions between HTPB and Desmodur® ([NCO]/[OH] = 1.1) in the presence of DBTDL as catalyst ([DBTDL]/[OH] = 0.06). Both PEO and HTPB network precursor mixtures are heated at 50 °C for 3 h, leading to the formation of the IPN and then post-cured for 1 h at 80 °C.

The PEO/HTPB IPNs are synthesized via the one shot in situ method where all reactants, initiators and catalysts (same molar proportions for each network as indicated for single network synthesis) are mixed together prior to initiation. The IPN synthesis requires the addition of a minimum of toluene since HTPB and PEGDM/PEGM are not miscible. The mixture is heated at 50 °C for 3 h, leading to the formation of the IPN, and then post-cured for 1 h at 80 °C.

A series of PEO/HTPB IPNs are prepared accordingly in order to examine the effect of varying the relative PEO weight proportions (80, 60, 50, 40 and 20 wt%). In order to estimate the amount of unreacted starting material in the final IPNs and thus the efficiency of cross-linking reactions, the samples are Soxhlet® extracted: the extracted material amounts to less than 1 wt% for all synthesis indicating that there are very few free polymer chains in the IPNs and that the formation of the networks is fully completed under those experimental conditions. The following part will establish whether there is a relationship between the kinetics of the formation of the two networks and the morphology of the final IPN material.

3.2. IPN formation kinetic studies

As already described elsewhere [25], the HTPB network formation kinetics can be monitored by the disappearance of the Desmodur® isocyanate group absorption band at 2270 cm^{-1}. In order to calculate the OH conversion of the

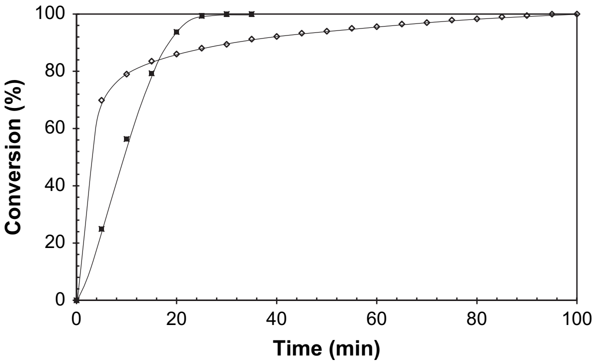

Fig. 1. Methacrylate (■) and NCO (◇) conversions versus time during PEO and HTPB single network synthesis. DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM; DBTDL catalyst content: [DBTDL]/[OH] = 0.06.

HTPB during the cross-linking, it is assumed that each NCO group which disappears has reacted with one HTPB alcohol group and that no side reactions occur. On the other hand, the radical copolymerization of methacrylate oligomers (PEGM and PEGDM) leading to the PEO network formation is followed by FTIR spectroscopy in the near-infrared region using the $CH_2{=}C(CH_3)-$ overtone peak at 6160 cm^{-1}.

Unfortunately it is not possible to study simultaneously and in a unique cell both time-conversion curves of methacrylate functions at 6160 cm^{-1} and NCO functions at 2270 cm^{-1}. Indeed the extinction coefficient of NCO functions at 2270 cm^{-1} is very large while the extinction coefficient of methacrylate functions at 6160 cm^{-1} is comparatively very low being in the harmonic frequency range. Thus the conversion kinetics must necessarily be monitored in two separate experiments using two cells with different thicknesses. A 250 μm thick cell is used for the conversion study of the NCO functions because they exhibit a saturating signal in a 1 mm cell. Conversely a 1 mm thick cell is used for the monitoring of methacrylate functions which exhibit a very weak signal in a 250 μm cell.

As indicated in the previous paragraph, the experimental conditions have been chosen such that the full conversion of the methacrylate and NCO functions in the single networks is reached within 2 h at 50 °C (Fig. 1).

The NCO conversion–time profile versus the HTPB weight proportion (20–80 wt%) in a series of IPNs is reported in Fig. 2a–d. Under the synthetic conditions near to 100% conversion is achieved after 100 min reaction for all cases. The initial reaction rate only slightly decreases upon increasing the PEO weight proportion.

In the same IPN series methacrylate function conversion–time profiles (Fig. 2a–d) display a noticeable initial reaction rate decrease with decreasing the methacrylate function concentration (PEO weight proportion). The final conversions are close to 100% for all compositions. The quite irregular double bond conversion–time profile for the (40/60) IPN could arise from the very weak methacrylate absorbance intensity. For the lowest weight proportion of methacrylate oligomers ((20/80) IPN), the situation is even worse and no accurate determination of methacrylate conversion can be performed.

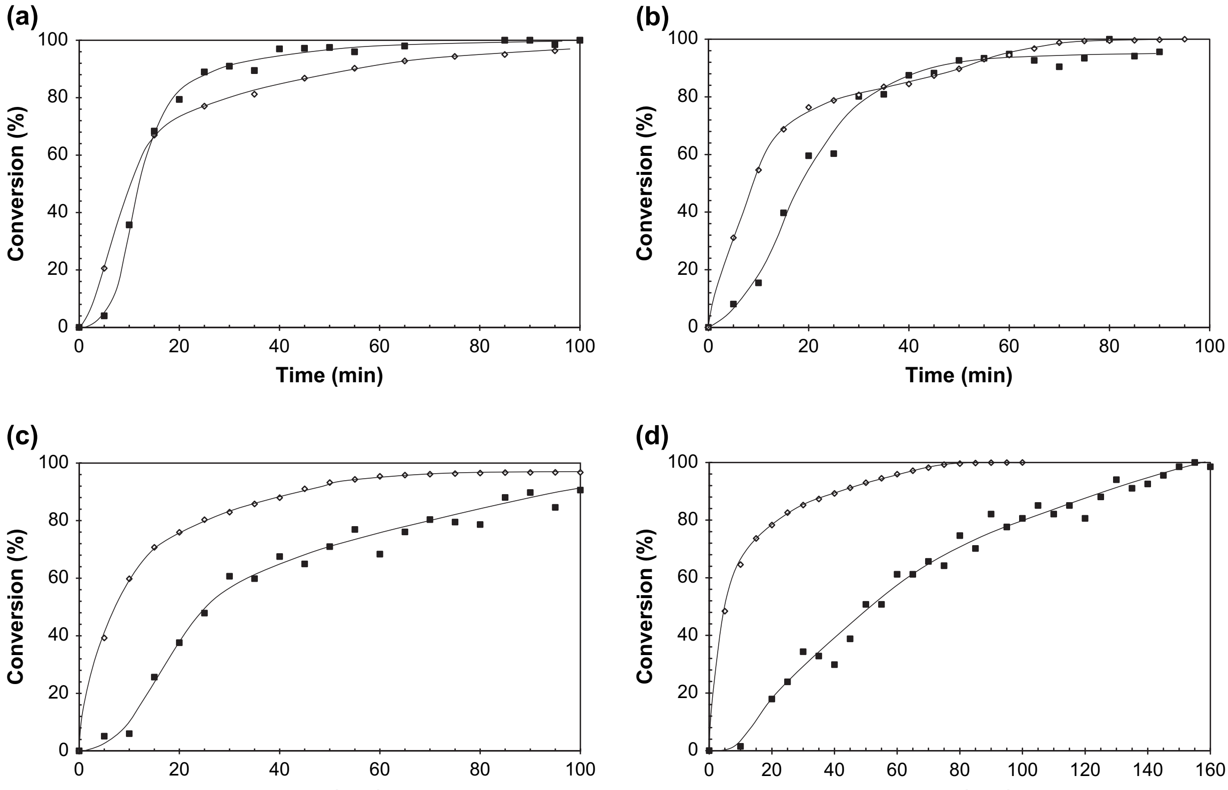

Fig. 2. Methacrylate (■) and NCO (◇) conversions versus time for PEO/HTPB (X/100 − X) IPNs. X = (a) 80 wt%, (b) 60 wt%, (c) 50 wt%, (d) 40 wt%. DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM; DBTDL catalyst content: [DBTDL]/[OH] = 0.06.

Fig. 2a–d too allows the comparison of NCO and methacrylate conversions versus time for IPNs containing 80, 60, 50 and 40 wt% PEO, respectively. For the 80 wt% PEO composition, the NCO and methacrylate group conversions are nearly simultaneous. For all other compositions, the conversion rate of NCO groups remains faster than those of methacrylate functions and expectedly, the difference between the rates of the two reactions increases with increasing HTPB content. In other words, the HTPB network always forms before the PEO network.

The refractive indices of HTPB and PEO are 1.5180 and 1.5063, respectively [26], a difference which is sufficient to obtain an opaque material if an extended phase separation occurs. Indeed, the material transparency is a meaningful indication of the interpenetration degree. All PEO/HTPB IPNs are transparent materials, except the IPN containing 80 wt% PEO which is translucent meaning that the interpenetration degree is less satisfactory. In this particular synthesis, i.e. (80/20) IPN, the two partner network formation rates are simultaneous and the resulting material is translucent. For all other IPN compositions, the HTPB network is formed first leading to transparent samples. This suggests that the interpenetration degree of both polymers is enhanced if the HTPB network conversion is significantly high before the PEO formation proceeds.

In other words it should be possible to prepare a transparent (80/20) IPN if the PEO formation network is significantly slowed down. In order to check this point, an IPN containing 80 wt% PEO was synthesized using an amount of DCPD radical initiator three times lower (0.7 wt% instead of 2.2 wt% with respect to methacrylate oligomers), in order to decrease the PEO network formation rate. Fig. 3 shows the NCO and methacrylate conversions versus time for this particular example. In this case the HTPB network forms before the PEO network and leads to a fully transparent IPN material.

Conversely, decreasing the ratio of DBTDL catalyst from [DBTDL]/[OH] = 0.06 to [DBTDL]/[OH] = 0.006 during the synthesis of a (50/50) IPN, leads to a decrease in the NCO conversion rate. Consequently the formation of the PEO network occurs somewhat before the formation of the HTPB network (Fig. 4), leading to a translucent final IPN as expected. From these kinetic studies, the conclusion can be drawn that a transparent IPN can be obtained when the HTPB network is formed before the PEO network.

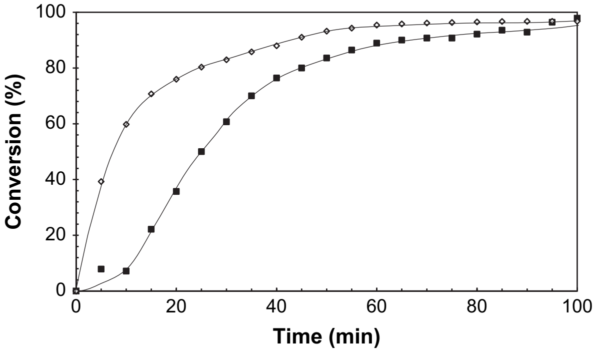

Fig. 3. Methacrylate (■) and NCO (◇) conversions versus time for PEO/HTPB (80/20) IPNs. DCPD initiator: 0.7 wt% with respect to PEGM/PEGDM; DBTDL catalyst content: [DBTDL]/[OH] = 0.06.

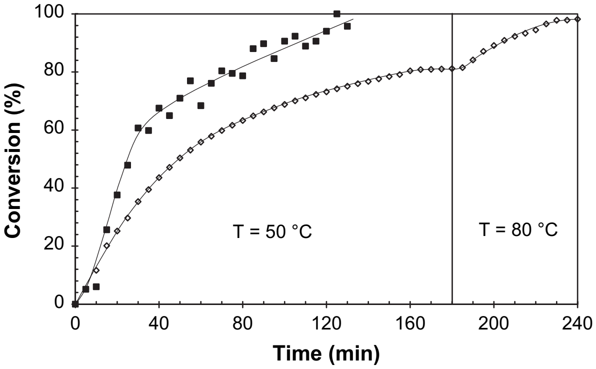

Fig. 4. Methacrylate (■) and NCO (◇) conversions versus time for PEO/HTPB (50/50) IPN. DBTDL catalyst content: [DBTDL]/[OH] = 0.006. DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM. The temperature is raised for 1 h at 80 °C after a 3 h curing at 50 °C.

Those two experiments show that for a given PEO/HTPB relative composition a transparent or a translucent IPN is obtained depending whether the HTPB or the PEO network is formed first. This demonstrates again the importance of the relative kinetics of the formation of the partner networks in the design of IPN materials.

As far as IPN synthesis is concerned, it is indeed well admitted that the relative kinetics of formation of the two networks affect the overall IPN morphology. In some cases it has been established that the following two parameters are likely to reduce the extent of phase separation: (i) increasing the rate of the two network formations and (ii) seeking for a simultaneous formation of the two networks [27]. However, in this study, the highest level of interpenetration was not obtained when the networks are formed simultaneously (Fig. 2a). Similarly, we have recently shown [28] that in a polyisobutylene/polystyrene IPN, the highest level of interpenetration is obtained when the polyisobutylene (PIB) network is synthesized before the polystyrene one. Thus in the PIB/polystyrene IPN synthesis as well as in the PEO/HTPB IPN synthesis transparent materials are obtained only under non-simultaneous synthesis conditions. A similar behaviour is observed in the case of polysiloxane/cellulose acetate butyrate IPN synthesis [29].

Different authors have reported that the first formed network induces and determines the morphology of the final IPN. The first network tends to be continuous in space and for high concentrations of the second polymer, dual phase continuity is likely to occur [1]. For IPNs containing 60, 50 and 40 wt% PEO, the HTPB network is formed first as shown in Fig. 2b–d and one might thus expect that HTPB phase should be the continuous one in the IPNs as will be discussed below.

3.3. Dynamic mechanical analysis

3.3.1. Single networks

The typical viscoelastic behaviour of single networks was studied at a frequency of 1 Hz, from −100 °C to +50 °C (heating rate: 2 °C/min). Fig. 5 shows the E' storage moduli and the loss factors (tan δ) of the HTPB and PEO single networks. Schematically, three temperature domains can be observed for both polymers. First at the lowest temperatures, the materials are in the glassy state, i.e., out of equilibrium, and the storage moduli E' are almost constant. At intermediate temperatures, a strong decay of E' is observed during the so-called main or α relaxation. At the same time, tan δ values display a maximum ($T_\alpha = -61$ °C and −44 °C for HTPB and PEO networks, respectively). Beyond this point, the behaviours of the two networks diverge. The HTPB network modulus does not reach a plateau but monotonously decreases as the temperature increases. This behaviour has been also observed for polyurethane based HTPB prepared in the presence of 1,4-butanediol chain extender [15,17,30]. In such a system, a microphase separated structure of hard and soft segment phases is reported which is due to the difference in polarity between the urethane and polybutadiene segments. The presence of urethane cross-linker aggregates linked to HTPB chains has been reported even for a PU based HTPB prepared without chain extender [31]. It is believed here that the nonhomogeneity of the HTPB network can explain the slow decay (from −61 to + 40 °C, i.e., ≈ 100 °C range) of the storage modulus before reaching the rubbery plateau.

On the other hand, the elastic part of the modulus E' of the PEO network reaches a plateau (rubbery state) at 3 MPa within a rather narrow temperature range (from −44 to −20 °C, i.e., $a \approx 25$ °C range). Now the question arises whether the microstructure of the PEO network will significantly be altered by the very high proportion of PEGDM (25 wt% compared to PEGM 75 wt%). In particular could the DMA behaviour of the PEO network indicate the presence of heterogeneities or clusters of the di-functional monomer such as it has been reported for similar systems by Kannurpatti et al. [32].

In these systems for example *n*-octyl methacrylate/diethylene glycol (or poly(ethylene glycol)) dimethacrylate, the effect on the DMA behaviour has been reported for a proportion of di-functional monomer up to 100%. Observing that the width of the tan δ curve is narrower when poly(ethylene glycol) dimethacrylate is used as the cross-linker, the authors conclude that the network is more homogeneous in this case. Indeed the width of the main relaxation is correlated to the structural heterogeneity of the network.

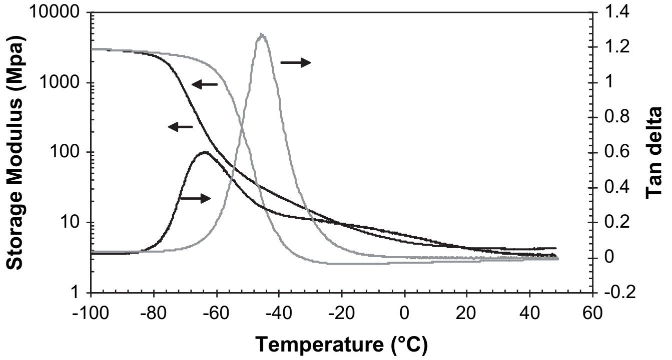

Fig. 5. Dynamic mechanical analysis. Storage modulus and tan δ as a function of temperature for single PEO (gray) and HTPB (black) networks.

As far as the DMA curves which are reported in Fig. 5 on the PEGDM (875 g mol^{-1})/PEGM (475 g mol^{-1}) single network are concerned, one can conclude that the PEO network is rather homogeneous, the maximum width of the tan δ peak being not more than 40 °C.

3.3.2. PEO/HTPB IPNs

The effects of interpenetrating PEO and HTPB networks into IPNs with various compositions can be derived from the tan δ versus temperature curves (Fig. 6). Single PEO and HTPB network tan δ curves are reported for comparison (Fig. 6 curves a and g, respectively). Two distinct transitions corresponding to the HTPB and PEO single networks, i.e., at −61 °C and at −44 °C, respectively, can be observed for compositions where the PEO weight proportion increases from 20 to 50 wt% in the IPNs (Fig. 6 curves d, e and f). These results indicate that in this composition range IPNs present dual phase morphology and are not interpenetrating on a molecular scale but on a larger scale.

The (80/20) and (60/40) IPN tan δ curves display a very similar appearance to that of the single PEO network (Fig. 6 curves b and c). It could thus be assumed that the PEO is the continuous phase not surprisingly since PEO is the major compound in those IPNs. However, the rather close α relaxation temperatures of the two networks and the small intensity and broadness of the HTPB α relaxation could explain why only one transition can be clearly observed. The HTPB α relaxation is probably hidden under the high PEO tan δ peak. Also, the fact that the α relaxation temperatures of the two networks are quite overlapping prevents the observation of an intermediate transition corresponding to an interpenetrating phase if any.

3.4. Microscopic investigation

Transmission electron microscopic (TEM) pictures were recorded on OsO_4 PEO/HTPB stained samples showing black

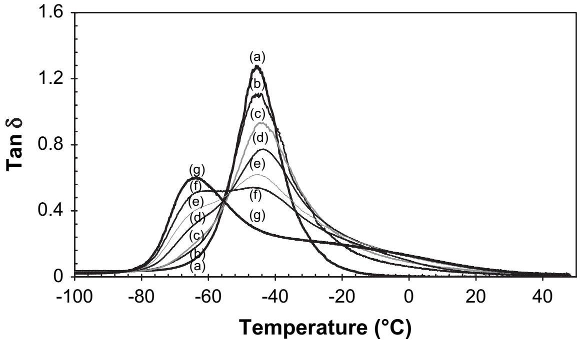

Fig. 6. Dynamic mechanical analysis. Tan δ as a function of the temperature for (a) single PEO network, (g) single HTPB network, and for PEO/HTPB (X/100 − X) IPNs. X = (b) 80 wt%, (c) 60 wt%, (d) 50 wt%, (e) 40 wt%, (f) 20 wt%. DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM; [DBTDL]/[OH] = 0.06.

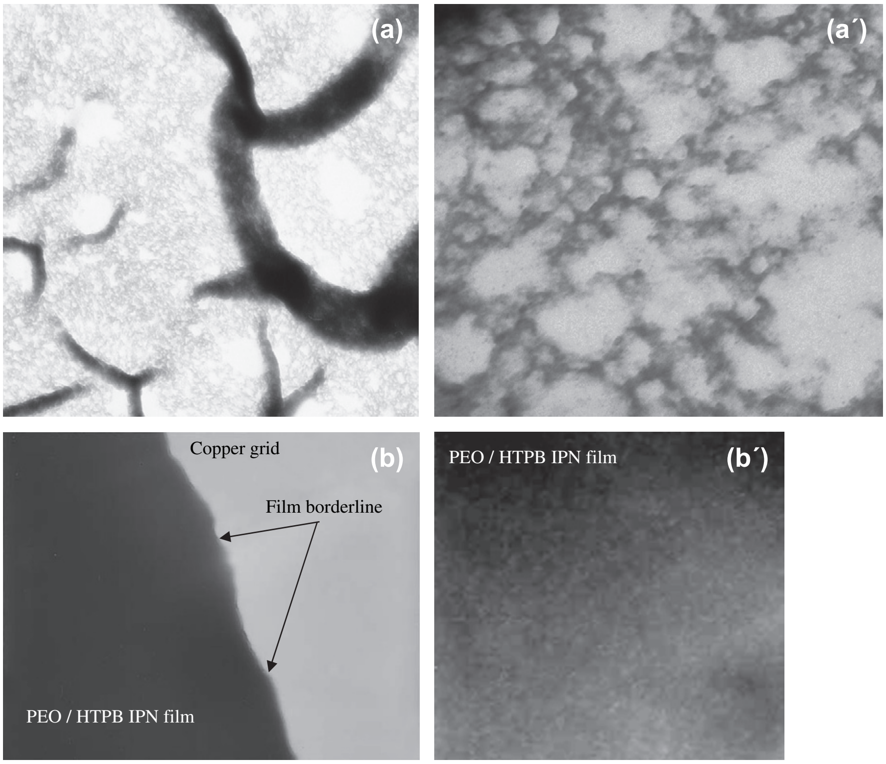

Fig. 7. TEM pictures of PEO/HTPB (*X*/100 − *X*) IPNs. (a, a′): $X = 80$ wt%; (b, b′): $X = 50$ wt%. For TEM pictures (a, b) magnification: ×10 000 (1 cm = 1 μm). For TEM pictures (a′, b′) magnification: ×50 000 (1 cm = 200 nm). DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM; [DBTDL]/[OH] = 0.06.

and white domains. Since only the HTPB polymer can be preferentially marked by OsO_4, the black domains can be interpreted as being rich polybutadiene phases and thus rich PEO phases appear as white domains.

For (80/20) IPN a macrophase separation takes place giving rise to a PEO dispersed phase in a continuous HTPB matrix. As shown in Fig. 7 (pictures a and a′) the PEO domain sizes are between 80 and 400 nm and aggregates have obviously formed. Furthermore the PEO domain threshold is obviously achieved in this IPN which leads to PEO phase continuity. This (80/20) IPN is a translucent material, which is consistent with the PEO large domain sizes.

Fig. 7 (pictures b and b′) also shows the TEM pictures of the (50/50) IPN. Although the TEM picture is mainly gray, very small white dots can be observed in the dark part, thus representing a very finely distributed PEO phase in a HTPB matrix. The PEO domain sizes are well below 100 nm which is consistent with the transparency of the sample.

For the (40/60) and (20/80) IPNs gray uniform phases all over the samples are observed which indicate that the HTPB is the continuous phase in the IPNs. Due to the low PEO weight proportion, PEO domains are not visible anymore most probably because they are dispersed in the HTPB matrix with domain sizes much lower than 100 nm.

As mentioned in the kinetic study, the (50/50) IPN is transparent if the synthesis is carried out with a ratio [DBTDL]/[OH] = 0.06 (HTPB network forms prior to PEO network) and translucent if the amount of DBTDL is decreased to [DBTDL]/[OH] = 0.006 (HTPB network forms after PEO network). The difference in those two synthetic pathways clearly

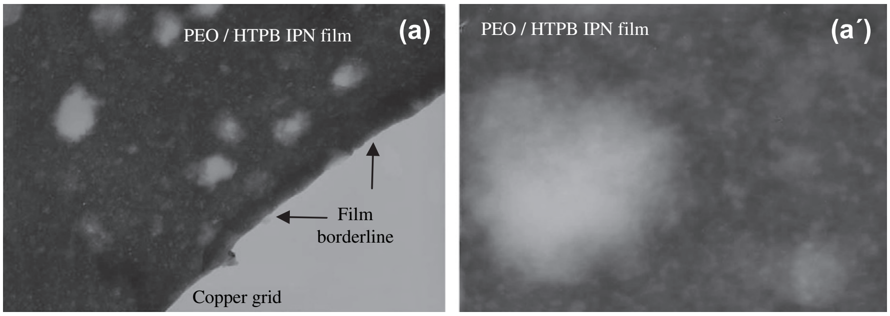

Fig. 8. TEM pictures of the PEO/HTPB (50/50) IPN (DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM; [DBTDL]/[OH] = 0.006). Magnification: (a) ×10 000 (1 cm = 1 μm), (a′) ×50 000 (1 cm = 200 nm).

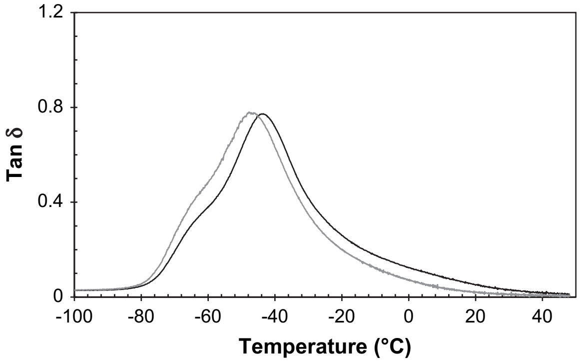

Fig. 9. Dynamic mechanical analysis. Tan δ as a function of the temperature for PEO/HTPB (50/50) IPN. Black: [DBTDL]/[OH] = 0.06. Gray: [DBTDL]/[OH] = 0.006. DCPD initiator: 2.2 wt% with respect to PEGM/PEGDM.

leads to different morphologies as shown in Fig. 7 (pictures b and b′) and in Fig. 8 (pictures a and a′), respectively, where the origin of the translucent character clearly origins in large PEO domain sizes higher than 500 nm. It should be pointed out that the DMA responses for those two samples with different morphologies are nearly identical (Fig. 9). Thus several techniques must be preferably combined in order to conclude precisely about IPN morphologies.

4. Conclusion

A series of PEO/HTPB interpenetrating polymer networks containing 80, 60, 50, 40 and 20 wt% PEO have been synthesized. The synthesis involves an in situ process in which all components are first mixed together and the networks are formed independently. The amounts of extracted material measured on these samples are lower than 1 wt%.

The kinetic studies have shown that HTPB network forms first for composition ranging from 60 to 20 wt% PEO (40–80 wt% HTPB). On the other hand, a quasi-simultaneous synthesis of the two networks occurs for the IPN containing 80 wt% PEO. Transparent materials are obtained only in the cases where the HTPB network forms first.

From DMA and TEM characterizations, it can be concluded that the HTPB phase is continuous in space for all compositions and that macrophase separation occurs. The PEO phase appears as nodules in the matrix and for the highest PEO content, i.e., 80 wt% PEO domains are in close contact and the material displays dual phase continuity.

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