Available online at www.sciencedirect.com

Polymer 47 (2006) 6048–6056

polymer

www.elsevier.com/locate/polymer

Polyisobutene/polycyclohexyl methacrylate interpenetrating polymer networks

Cédric Vancaeyzeele [a], Odile Fichet [a], Battatchona Amana [b],
Sylvie Boileau [c], Dominique Teyssié [a,*]

[a] Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise, 5, mail Gay-Lussac, Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France
[b] Département de Physique, Université de Cergy-Pontoise, 5, mail Gay-Lussac, Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France
[c] Laboratoire de Recherche sur les Polymères, UMR 7581 CNRS, 2, rue H.Dunant, 94320 Thiais, France

Received 17 January 2006; received in revised form 2 June 2006; accepted 14 June 2006
Available online 14 July 2006

Abstract

Interpenetrating polymer networks (IPNs) combining polyisobutene (PIB) and poly(cyclohexyl methacrylate) (PCHMA) networks were prepared using an in situ strategy. PIB networks were formed by alcohol–isocyanate addition between the hydroxyl end groups of telechelic dihydroxypolyisobutene and an isocyanate cross-linker, catalyzed by dibutyltindilaurate (DBTDL). PCHMA networks were obtained from free-radical copolymerization of cyclohexyl methacrylate (CHMA) with ethylene glycol bismethacrylate (EGDM) in the presence of dicyclohexyl peroxydicarbonate (DCPD) as the initiator. The network formations into the IPN architecture were followed by FTIR spectroscopy. In a large composition range, transparent IPNs exhibit two mechanical relaxation temperatures as determined by dynamic mechanical thermal analysis (DMTA), corresponding to those of a PIB enriched phase and of one interpenetrating phase containing the PCHMA network. This morphology was confirmed by IPN surface analysis by AFM. As expected, mechanical properties of PIB networks are improved by the presence of PCHMA network in such IPN architectures.

Keywords: α,ω-Dihydroxypolyisobutene; Polycyclohexyl methacrylate; Interpenetrating polymer networks

1. Introduction

Interpenetrating polymer networks (IPNs) are defined as the combination of two or more polymer networks synthesized in juxtaposition. The entanglement of two cross-linked polymers leads to forced "miscibility" compared with usual blends and the resulting materials exhibit good dimensional stability. The general aim for preparing such types of polymer associations is to obtain materials with improved mechanical properties, an increased resistance to degradation and a possible synergy of properties of homopolymers combined into the IPN architecture [1].

Ideally, in a "true" IPN, interpenetration occurs only through physical cross-links and the networks are entangled at the molecular level as long as no covalent bonds exist between the different polymers. Practically co-continuous phases are observed [1,2] and the interpenetrating degree of both networks into the IPN architecture can be analyzed by different techniques. For instance, by using dynamic mechanical thermal analysis (DMTA), the domain size is considered in the order of 5–50 nm if a single transition, corresponding to an interpenetrating phase, located at a temperature between those of the single networks, is observed in the loss factor (tan δ)–temperature curve [3]. Usually however, IPNs show two mechanical relaxations corresponding to two phases enriched in one of each polymer network, and only few IPNs are characterized by a single mechanical relaxation. For

---

[*] Corresponding author. Tel.: +33 1 34 25 70 50; fax: +33 1 34 25 70 70.
E-mail address: dominique.teyssie@chim.u-cergy.fr (D. Teyssié).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.06.047

example, polyurethane/poly(ethyl methacrylate) IPNs with weight compositions (30–70) and (20–80) show only one peak on the tan δ–temperature curves, indicating a high degree of interpenetration between both partner networks [4]. IPNs combining a polydimethylsiloxane (PDMS) network and a cellulose acetate butyrate one (CAB) exhibit only one mechanical relaxation temperature when the formation rate of the CAB network is correctly adjusted compared with that of the PDMS network [5]. This unique transition again witnesses a high level of interpenetration. Polyisobutene (PIB) is an elastomeric polymer, which flows at more or less high temperature [6]. In order to avoid this creeping and to improve the solvent resistance as well as the mechanical properties of the material, polyisobutene has been combined with an IPN architecture with a network synthesized from a thermoplastic polymer. This has been realized by using an in situ strategy, in which all components are first mixed together and the networks are then formed more or less simultaneously, according to different reaction mechanisms. Firstly, PIB networks have been combined with PMMA networks [7]. The precursors of both networks are not miscible and toluene must be used in order to obtain a homogeneous initial mixture. The highest interpenetration degree is obtained when the PIB network is formed prior to the PMMA one. The resulting IPNs are transparent but they show two distinct mechanical relaxations corresponding to rich PIB and rich PMMA phases, for all studied compositions and PMMA cross-linking densities. Secondly, the association of PIB and polystyrene (PS) networks in an IPN architecture has been studied [8]. In this case, the PS network precursor (styrene) plays the role of a solvent toward the PIB oligomer, thus those IPNs are synthesized without any additional solvent. The highest interpenetration degree is again obtained when the PIB network is first formed prior to the PS one. The final material properties depend on their composition. When the PIB network is the main component, it forms the matrix in which are dispersed PS rich domains and the resulting material presents reinforced elastomeric properties. The PIB and PS phase co-continuity is observed and the material is rigid when the IPN is mainly composed of PS. In all cases, the mechanical properties of the PIB network and the UV ageing resistance are again improved by the introduction of a thermoplastic network into the IPN architecture. Although interactions between both networks exist in those two associations, no "true" interpenetrating phase between both networks has been detected.

In this third study, the synthesis of IPNs combining PIB and poly(cyclohexyl methacrylate) (PCHMA) networks involves an in situ strategy. PCHMA has been chosen as the new partner of PIB because (i) cyclohexyl methacrylate monomer is more hydrophobic than methyl methacrylate or styrene [9] and can be used as a "reactive" solvent of PIB network precursors, (ii) the resulting polycyclohexyl methacrylate ($T_g = 128$ °C [10]) has a higher glass transition temperature than that of usual PMMA ($T_g = 108$ °C [11]) or polystyrene ($T_g = 100$ °C [11]), and (iii) PCHMA and PIB polymers have close solubility parameters (18.5 and 18.7 $\mathrm{MPa}^{1/2}$, respectively) which could lead to an improved interpenetration of both partner networks in the IPN architecture [12,13]. As in the case of PIB/PMMA and PIB/PS IPNs [7,8], the PIB network has been synthesized prior to the PCHMA one, according to different mechanisms, in order to obtain the highest degree of interpenetration. The conversion of reactive functions involved in the synthesis of each network during the IPN formation has been investigated as a function of time by near FTIR spectroscopy. In order to examine the extent of network interpenetration, thermomechanical properties of IPNs of all weight compositions have been studied by DMTA and morphology of final materials has been examined by AFM microscopy.

2. Experimental part

2.1. Material

α,ω-Dihydroxypolyisobutene ($\mathrm{Mn_{SEC}} = 4200\ \mathrm{g\,mol^{-1}}$, $\mathrm{Ip} = 1.2$ in THF, $M_{\mathrm{NMR}} = 4400\ \mathrm{g\,mol^{-1}}$ in C_6D_6, functionality = 1.9) was kindly provided by BASF. Dibutyltin dilaurate (DBTDL) (Aldrich), ethylene glycol dimethacrylate (EGDM) (Aldrich), dicyclohexyl peroxydicarbonate (DCPD, groupe Arnaud) and Desmodur®N3300 (Bayer) (NCO content by weight: 21.8 ± 0.3% according to the supplier) were used as received. This last compound is described as an isocyanurate mixture resulting from the condensation of three to several hexamethylene diisocyanate molecules and mainly composed of mono-, di- and tri-isocyanurates with a global functionality higher than 2. Thus mere "tri(6-isocyanatohexyl)isocyanurate" is not a proper description and the compound is referred to as isocyanate cross-linker or cross-linking agent [14]. Cyclohexyl methacrylate (CHMA, Aldrich) was distilled before use (69 °C/4 mm). Dichloromethane (CH_2Cl_2, Carlo Erba) was used as received.

2.2. Synthesis

The single PIB network was obtained as previously described [7]. The single PCHMA network was synthesized as follows: 1 g CHMA (5.9×10^{-3} mol) was mixed with 28 μL EGDM (1.5×10^{-4} mol, 3% by weight with respect to CHMA) and 10 mg free-radical initiator DCPD (3.5×10^{-5} mol, 1% by weight with respect to CHMA). The mixture was poured under argon into a mould made from two glass plates clamped together and sealed with a 0.5 mm thick Teflon® gasket. The mould was heated in an oven at 40 °C for 6 h and at 80 °C for 1 h. A rigid transparent film was obtained.

For the PIB/PCHMA (50/50) IPN, 1 g α,ω-dihydroxypolyisobutene (4.5×10^{-4} OH mol eq.) was mixed with 1 g CHMA (5.6×10^{-3} mol) and 28 μL EGDM (3% by weight with respect to CHMA, 1.5×10^{-4} mol) under argon. Then 10 mg DCPD (3.5×10^{-5} mol, 1% by weight with respect to CHMA), 3 μL DBTDL (5.9×10^{-6} mol, [DBTDL]/[OH] = 0.013) and 0.13 g isocyanate cross-linker ([NCO]/[OH] = 1.2) were added. The [NCO]/[OH] molar ratio is calculated from OH concentration deduced from SEC determination of the molecular weight of the α,ω-dihydroxypolyisobutene.

The mixture was degassed and then treated as the single PCHMA network.

IPNs with different PCHMA contents ranging from 40 to 80% by weight were synthesized keeping the same proportions between monomer, cross-linker and catalyst or initiator for each network. All investigated PIB/PCHMA compositions were reported in weight-by-weight ratio. Thus, an IPN obtained from a mixture of 0.70 g α,ω-dihydroxypolyisobutene and 0.30 g CHMA will be noted as PIB/PCHMA (70/30) IPN.

2.3. Analytical techniques

In order to estimate the amount of unreacted starting materials in the final product and thus the extent of network formation, single networks and IPNs were extracted in a Soxhlet with dichloromethane for 72 h. After extraction, the sample was dried under vacuum and then weighed. The extracted content (EC) was given as a weight percentage:

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

where W_0 and W_E are the weights of samples before and after extraction, respectively.

The rates of network formation were followed in the bulk, in real time, in the near and middle infrared (NIR and MIR) regions (7500–1800 cm^{-1}) using a Bruker spectrometer (Equinox 55). The PCHMA and PIB network formations were followed by monitoring the disappearance of the H–C=C overtone absorption bands at 6167 cm^{-1} [15] and of the isocyanate functions at 2270 cm^{-1} [16], respectively, as described previously [5]. Each peak area was directly proportional to the reagent concentration (the Beer–Lambert law has been verified), thus the conversion–time profile was derived easily from the spectra recorded as a function of time. The conversion of reactive bonds could be calculated as $p = 1 - (A_t/A_0)$ from the absorbance values where the symbols have the usual meaning and the subscripts 0 and t denote reaction times. IPNs were directly synthesized in the IR cell following the method described previously [7].

Dynamic mechanical thermal analysis (DMTA) measurements were carried out on film samples with a Q800 apparatus (TA Instruments) operating in tension mode. Experiments were performed at a 1 Hz frequency and a heating rate of 3 °C min^{-1} between −100 and 200 °C. Typical dimensions of the samples were $30 \times 10 \times 0.5\ \mathrm{mm}^3$. The set up provides the storage and loss moduli (E' and E'') and the damping parameter or loss factor (tan δ). All storage modulus values were normalized at 3 GPa at −100 °C in order to compare their relative evolution with increasing temperature.

The atomic force microscopy (AFM) apparatus is composed of a Dimension 3100 Scanning Probe Microscope and a NanoScope® IIIa from VEECO. The scanning window can vary from 100 μm down to a few nanometers. The probe tip frequency resonance is $f_0 = 250$ kHz.

3. Results and discussion

In the present work, PIB and PCHMA networks have been combined in an interpenetrating polymer network (IPN) architecture for the reasons explained in Section 1, which should lead to an IPN displaying a new interpenetrating phase.

3.1. Single networks

The PIB network is synthesized via an alcohol/isocyanate condensation reaction between the α,ω-dihydroxypolyisobutene and isocyanate cross-linker as described previously [7]. This reaction is catalyzed by dibutyltindilaurate (DBTDL). An insoluble transparent material, which contains a very low amount of extracted products (<1%) as found by a Soxhlet extraction with CH_2Cl_2 is obtained. In Fig. 1 are reported the storage modulus (E') and the loss tangent (tan δ) versus temperature curves of the single PIB network which are characterized by a quite broad α-relaxation composed of a peak centered at −30 °C and a shoulder located at −50 °C. Those two mechanical relaxation temperatures are associated with the PIB end local rotational chain motion ($T_\alpha = -50$ °C) and to the PIB cooperative backbone motion ($T_\alpha = -30$ °C) [17–19] and have been observed in other PIB based materials [20,21].

On the other hand, the PCHMA network is formed by free-radical copolymerization of CHMA with EGDM ([EGDM]/[CHMA] = 0.025, 3% by weight with respect to CHMA) as the cross-linker, initiated by DCPD ([DCPD]/[CHMA] = 0.006, 1% by weight with respect to CHMA). A rigid transparent material is obtained with a very low amount of extracted products (<1%) as shown by the Soxhlet extraction with CH_2Cl_2. Thermomechanical properties of this single PCHMA network are reported in Fig. 1B. Below 100 °C, the PCHMA network is in a glassy state. Above 100 °C, E' decreases rapidly down to a rubbery plateau value at 1 MPa. The sharp decrease of E' and the tan δ maximum value (tan $\delta = 1.9$) at 132 °C are associated with the mechanical relaxation temperature of PCHMA. A secondary relaxation peak at around −80 °C is observed. This γ relaxation can be associated with the boat–chair interconversion of the cyclohexyl

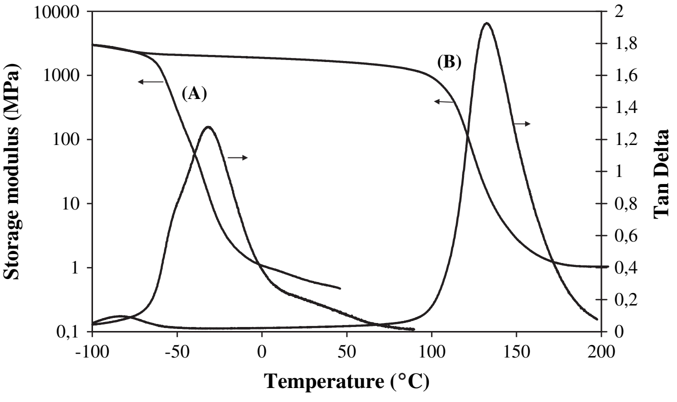

Fig. 1. (A) PIB and (B) PCHMA single network storage moduli and tan δ variations versus temperature.

side groups of the main chain [22,23,24]. This relaxation is accompanied by a slight decrease of the network modulus.

3.2. PIB/PCHMA IPNs

The study of PIB/PCHMA IPNs extends the conception of new resistant and damping materials [25]. As for all PIB based IPNs presented in the previous papers [7,8], the in situ synthesis pathway is chosen, i.e. all the reagents are mixed together: monomers, cross-linkers, initiator and catalyst forming a homogeneous solution.

An advantage of PCHMA is that the CHMA monomer is a fairly good solvent of telechelic PIB oligomer. Thus PIB/PCHMA IPNs with PCHMA content up to 40% have been synthesized (for lower contents the precursor mixture viscosity is too high and the reactive mixture is not homogeneous). According to PIB/PMMA and PIB/PS IPN syntheses, the best interpenetration degree is obtained when the PIB network is first formed. Indeed, under those synthesis conditions, the PIB network is swollen by the monomer of the second network. This state is thermodynamically stable and the phase separation between PIB and the other polymer (PS or PMMA) caused by the lack of compatibility between the two polymers is slowed down. When the second network is synthesized just after the PIB network, the interpenetration degree is improved. Thus, in this study, the initiator amount has been adjusted in order to obtain a network formation sequence similar to that of the PIB/PMMA IPN, i.e. PIB network is first formed and the PCHMA network is then polymerized and cross-linked inside the PIB network.

The PIB network synthesis is carried out according to optimized conditions; i.e. with [NCO]/[OH] = 1.2 and [DBTDL]/[OH] = 0.013. The PCHMA network is prepared by free-radical copolymerization of CHMA with ethylene glycol dimethacrylate (EGDM, 3% by weight with respect to CHMA) as the cross-linker and DCPD (1% by weight with respect to CHMA) as the initiator. The temperature is set at 40 °C. In order to check the network formation order, a PIB/CHMA (20/80) weight proportion is chosen for the FTIR monitoring of the network formations which are followed by the disappearance of the absorption bands of the methacrylate C=C–H bond at 6167 cm^{-1} [15] and of the isocyanate groups at 2270 cm^{-1} [26]. The conversion–time curves of the reactive function characteristic of each network formation are reported in Fig. 2.

The conversion of the PIB network reaches 40% at the time when the PCHMA network formation starts i.e. 30 min after the beginning of the reaction. This reproducible induction period corresponds probably to the destruction of a low DCPD radical amount by residual oxygen traces present in the reaction mixture. After 50 min at 40 °C the conversion of hydroxyl functions is around 55%. Between 50 and 80 min, it seems that a Trommsdorff effect self-acceleration is observed during the PCHMA network formation inducing an increase in the hydroxyl conversion rate. This assumption is supported by an increase of the slope of the hydroxyl function conversion curve as a function of time. Both conversion curves reach a plateau at around 90% after 100 min. A total conversion of the reactive functions is reached when the temperature is increased to 80 °C.

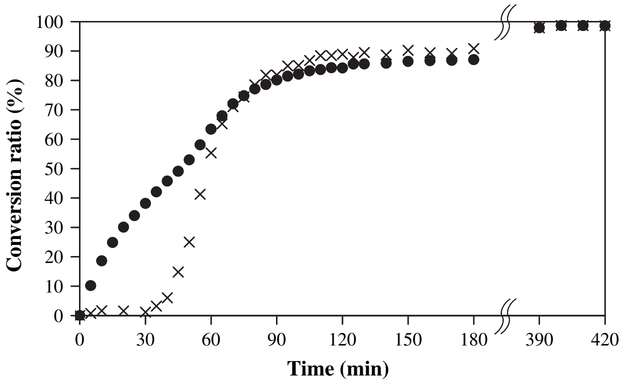

Fig. 2. Methacrylate (×) and hydroxyl (●) function conversion in PIB/PCHMA (20/80) IPN mixture – 1% DCPD and 3% EGDM by weight with respect to CHMA. [DBTDL]/[OH] = 0.013, [NCO]/[OH] = 1.2 – $T = 40$ °C.

As expected, those curves show that the PIB network is formed first, the PCHMA network formation starting after a 30 min induction period. After 6 h at 40 °C, the material is then annealed at 80 °C in order to reach the quantitative conversion of reactive functions. Thus all IPNs the properties of which are discussed below are synthesized under those experimental conditions with 1% DCPD (by weight with respect to CHMA). All transparent IPNs contain extracted amounts lower than 2%. Their analysis by ^{1}H NMR shows that they are mainly composed of linear PIB chains of higher molecular weight than the oligomer α,ω-dihydroxypolyisobutene used as PIB network precursor and they result from a extension reaction through isocyanate functions of the cross-linker. These extraction results are in agreement with the conversion–time curves (quantitative conversion of reactive functions) and show that both networks are well cross-linked.

The difference between the respective refractive indices of both polymers being extremely small (n_{D}^{20} $_{\mathrm{PCHMA}} = 1.506$ and n_{D}^{20} $_{\mathrm{PIB}} = 1.505$ [27] at 25 °C), the final material will be transparent whatever the interpenetration degree of both networks in the PIB/PCHMA IPNs and transparency cannot thus be regarded as a proof of a correct interpenetration between both networks.

An improvement in the poor mechanical properties of PIB and a high interpenetration degree of the networks were expected by combining PIB and PCHMA in an IPN architecture. Thus, thermomechanical properties of PIB/PCHMA IPNs are studied by DMTA, paying a special attention to the influence of IPN composition.

Fig. 3 shows the storage modulus E' versus temperature curves for different IPN compositions ranging from 40 to 80% PCHMA by weight every 10%. The PCHMA cross-linker weight proportion is set up at 3% by weight with respect to CHMA. All storage moduli are normalized at 3 GPa at −100 °C in order to analyze the modulus evolution as a function of PCHMA content.

All samples show a glassy phase below −70 °C, a temperature corresponding to the beginning of a PIB rich phase mechanical relaxation. When the temperature increases from

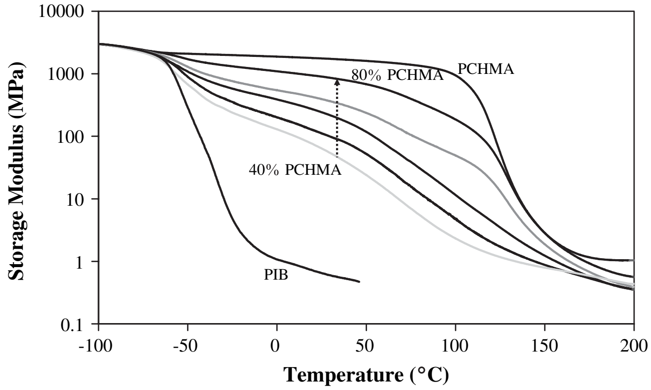

Fig. 3. Storage modulus of PIB/PCHMA (60/40, 50/50, 40/60, 30/70, 20/80) IPNs versus temperature. PIB and PCHMA single network values are reported for comparison.

−70 to 100 °C, the samples soften and the storage modulus decreases regularly for each composition when the PCHMA content decreases. In this temperature range, the storage modulus increases when the PCHMA weight proportion increases from 40 to 80%. Thus, the material is more and more rigid on increasing the PCHMA content. At around 120 °C, the storage modulus decreases again which corresponds to the beginning of the PCHMA phase mechanical relaxation.

Above 150 °C, which corresponds to the PCHMA mechanical relaxation temperature, the storage modulus hardly depends on the PCHMA content. Those materials do not flow at higher temperatures and a constant modulus value of around 1 MPa is observed up to 200 °C.

Several theories have been developed in order to correlate the modulus of a multiphase system with its composition and morphology. Most theories assume a perfect adhesion between the phases and samples being macroscopically isotropic. Kerner [28] described a theory for a matrix (noted 1) in which spherical inclusions (noted 2) are dispersed over the whole composition range. The material shear modulus G is then defined as:

$$\frac{G}{G_1}=\frac{(1-\Phi_2)G_1+(\alpha+\Phi_2)G_2}{(1+\alpha\Phi_2)G_1+\alpha(1-\Phi_2)G_2} \tag{1}$$

where G is the material shear modulus (the indices 1 and 2 correspond to the continuous phase and the inclusion spheres, respectively) and Φ_2 is the volume fraction of the inclusion spheres; α is a function of the matrix Poisson ratio according to:

$$\alpha=\frac{2(4-5\nu)}{(7-5\nu)} \tag{2}$$

where ν is Poisson's ratio. Generally, this model correctly predicts the polymer melt properties when the volume fraction of the dispersed phase (inclusion) is low, since it does not take into account the different interactions between the dispersed domains and the matrix.

Budiansky has developed a model, which predicts a phase inversion at middle-range compositions [29]. The material is composed of a continuous phase 1 in which the phase 2 is dispersed when the volume fraction Φ_2 is lower than 0.5. When Φ_2 is higher than 0.5, a phase inversion occurs and phase 2 becomes continuous, phase 1 being dispersed into phase 2. Then the shear modulus G obeys the expression:

$$\frac{\Phi_1}{1+\varepsilon(G_1/G-1)}+\frac{\Phi_2}{1+\varepsilon(G_2/G-1)}=1 \tag{3}$$

with

$$\varepsilon=\frac{2(4-5\nu)}{15(1-\nu)} \tag{4}$$

where ν is Poisson's ratio of the melt calculated using a linear combination of mixing, G the material shear modulus and Φ_i is the volume fraction of each component polymers. For a high content of one of the two components (Φ_2 close to 1 or 0), Kerner and Budiansky models give almost the same results.

Finally, Davies has developed a model [30], which takes into account different interactions between the phases and in which both phases are co-continuous over the whole material. Then the shear modulus G is expressed as:

$$G^{1/5}=\Phi_1G_1^{1/5}+\Phi_2G_2^{1/5} \tag{5}$$

where G is the whole material modulus, G_1 and G_2 are each phase moduli, and Φ_1 and Φ_2 the volume fraction of each polymer. This model and the two previous ones give the same results at extreme compositions.

Although these models have been established for the mechanical properties of polymer melts, numerous authors have found that they apply successfully to the description of IPN viscoelastic properties [4,31,32]. The "miscibility" between polymers is forced by permanent chemical cross-links formed during the synthesis. This "miscibility" determines the arrangement, the size and the interactions between both phases. Even if these models do not correspond to the material real morphology, they suggest an arrangement and interactions between phases, which could be confirmed by other analyses.

In order to compare the experimental data to the modulus values calculated from models, the authors report commonly the modulus variation of the materials versus their composition. Interestingly, Akay and Rollins [32] have noticed that, according to the polyurethane (PUR)/PMMA IPN synthesis pathway, the IPN modulus variation versus composition cannot be described by the same mechanical model. Indeed, when the in situ simultaneous synthesis is used, modulus can be correlated with Budiansky model (phase inversion). However, when the in situ sequential synthesis is used, the modulus can be described by Davies model (phase co-continuity). Hourston and Schäfer [4] have correlated the modulus values of PUR/poly(ethylmethacrylate) IPNs with the Budiansky model. The predicted phase inversion for intermediate compositions indeed occurs but is shifted to higher compositions of PUR (between 70 and 80% by weight according to the measurement temperature). The same shift has been observed on PUR/polystyrene (PS) IPNs [33], and the composition at which the phase inversion occurs also depends on the temperature at which the moduli are measured. Yeo et al. [34] have compared the poly(*n*-butyl acrylate)/PS IPNs modulus with those calculated according to the three models presented previously. None of the models correlates the experimental data over the whole composition range. Indeed, Davies model fits the experimental data for high PS contents whereas Budiansky model is in agreement with the experimental values for low PS contents. In this last case, PS domains are dispersed into a poly(*n*-butyl acrylate) matrix. When the PS content increases, the phase inversion predicted by Budiansky model corresponds to PS domain coalescence.

The shear moduli of PIB/PCHMA IPNs have been determined from the DMTA data (E' and $\tan\delta$) and compared with the values calculated with different mechanical models in order to estimate the phase morphology in the material. At 25 °C, the Poisson coefficients of PIB and PCHMA are equal to 0.5 [11] and 0.33, respectively (the PCHMA coefficient being supposed equal to that of PMMA [35]). The Poisson coefficient of IPNs is calculated as the weight average of those of both components. The shear moduli calculated according to each model and the experimental data deduced from DMTA analysis are reported versus PCHMA volume proportion in the IPN in Fig. 4. The phase co-continuity model (Davies model) correlates exactly with the IPN shear moduli in the studied composition range. This agreement suggests that the PIB/PCHMA IPNs could be described as two co-continuous phases identified by the $\tan\delta$ versus temperature curves (Fig. 5), for example.

The $\tan\delta$ values are associated with segmental chain move and also influenced greatly by the IPN weight composition. All IPNs show a complex phase morphology evidenced by two or three distinct mechanical relaxations: the $\tan\delta$ peaks centered at +134 and −50 °C correspond to the mechanical relaxations of rich PCHMA and PIB [20,21] phases. A third relaxation can be detected at +80 °C, a temperature located between those of the mechanical relaxations of PIB and PCHMA. This relaxation is characteristic of a new phase resulting from some kind of interpenetration between PIB and PCHMA networks.

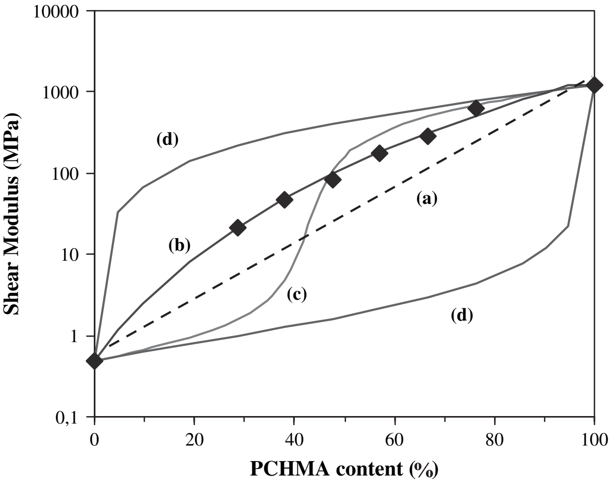

Fig. 4. Shear modulus of PIB/PCHMA IPNs versus PCHMA volume fraction compared with modulus–composition models (◆) shear modulus data (25 °C − 1 Hz) (a) logarithmic rule of mixing, (b) Davies equation, (c) Budiansky equation and (d) upper and lower limits of Kerner equation.

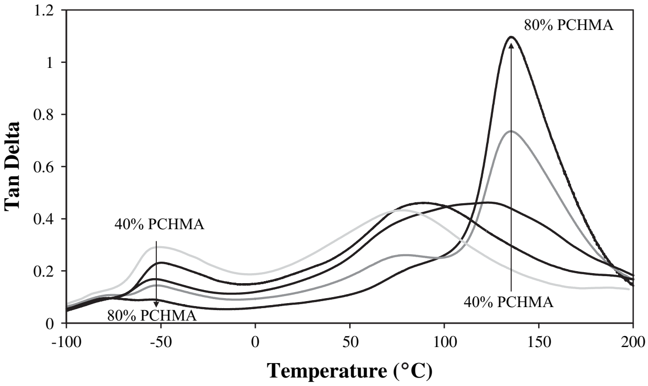

Fig. 5. Tan δ of PIB/PCHMA (60/40, 50/50, 40/60, 30/70, 20/80) IPNs versus temperature. PIB and PCHMA single network values are reported for comparison.

In the PIB/PCHMA (20/80) and (30/70) IPNs, $\tan\delta$ peak associated to the mechanical relaxation of a rich PCHMA phase is detected at 134 °C. The maximum value of the peak at −50 °C characteristic of the rich PIB phase is strongly affected by the PCHMA introduction to the point where it is not detected any more when the material contains more than 70% by weight PCHMA (and this cannot be assigned only to the dilution effect of the PIB in the IPN). Indeed it reveals that interactions develop between both networks into the IPN, i.e. the PIB chain segmental motions are hindered by the PCHMA network. The same phenomenon has been observed by Brachais et al. with poly(methylphenylsiloxane)(PMPS)/poly(methylmethacrylate) (PMMA) IPNs by solid state NMR analysis. The PMPS local chain motions are sensitive to the presence of the PMMA, which do not undergo any chain motion in the studied temperature range [36]. The same phenomenon is believed to occur here.

In the PIB/PCHMA (40/60) IPN the $\tan\delta$ peak characteristic of PCHMA phase disappears and the new peak characteristic of the interpenetrating phase appears at about +80 °C extending from 0 to 200 °C with a maximum $\tan\delta$ value equal to 0.46. This broad peak width highlights the presence of interpenetrating phases of different compositions.

In the PIB/PCHMA (40/60), (50/50) and (60/40) IPNs the position and the maximum $\tan\delta$ values of that peak characteristic of the interpenetrating phase do not vary significantly. Thus a large weight proportion of the PIB and PCHMA partners is included into the interpenetrating phase, a major component in the whole material. In the three IPNs the peak at −50 °C characteristic of the PIB rich phase, is also detected.

It would have been interesting to compare the experimental α-relaxation temperatures with those calculated starting from the Fox equation (assuming miscibility). However, the α-relaxation temperature of the new interpenetrating phase does not vary significantly with the IPN composition (its relaxation temperature remains more or less close to 80 °C for all

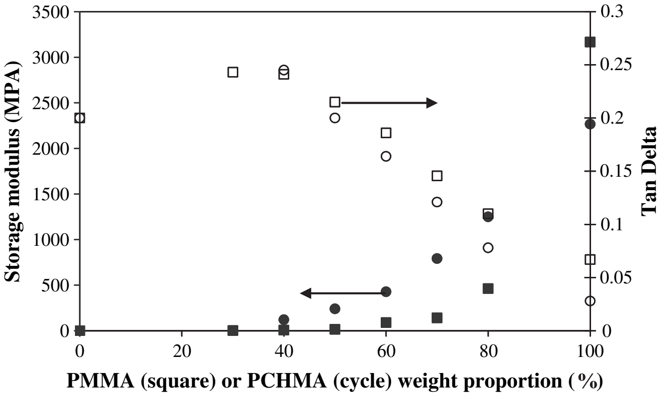

Fig. 6. Storage modulus (full) and tan δ (empty) measured at 25 °C for (●) PIB/PCHMA IPNs and (■) PIB/PMMA IPNs with different contents.

investigated compositions) and thus these temperatures are not in agreement with the Fox equation.

This interpenetrating phase has not been detected in the PIB/PMMA and PIB/PS IPNs studied previously [7,8]. Frisch et al. have noticed that it was easier to obtain IPNs with interpenetrating phases when the associated polymers have near solubility parameters [12,13]. The solubility parameters of PIB, PS, PMMA and PCHMA are equal to 18.50, 18.19, 19.65 and 18.7 MPa$^{1/2}$, respectively, at 25 °C [37]. According to those values, the compatibility between polymers increases for PIB/PMMA, PIB/PS and PIB/PCHMA combinations, in good agreement with those results.

In order to evaluate the effect of this new phase on the material properties, the thermomechanical properties of PIB/PCHMA IPNs at room temperature are compared with those measured of PIB/PMMA IPNs. Storage modulus and tan δ of each material at 25 °C are reported in Fig. 6. The IPN storage moduli increase from 120 to 1450 MPa when the PCHMA content increases from 40 to 80% by weight. Thus the material rigidity increases expectedly with the PCHMA content. Simultaneously, tan δ values decrease linearly from 0.24 to 0.03. At 25 °C, a part of the interpenetrating phase undergoes the mechanical relaxation, which ensures the material damping. The higher the PIB content, the better the damping properties of the material. This damping increase is of course associated with a rigidity decrease. These results are in good agreement with the macroscopic behavior of the final materials. Thus, the storage moduli and tan δ values depend on the methacrylate structure (methyl or cyclohexyl side group). Thus, for all IPNs in the studied composition range, the storage moduli of PIB/PMMA IPNs are lower than those of the corresponding PIB/PCHMA IPNs, for example, 500 and 1500 MPA, respectively, for a (30/70) composition. Simultaneously, tan δ values of PIB/PCHMA IPNs are slightly lower than those of PIB/PMMA IPNs (excepted for (60/40) compositions, which show identical values). For example, tan δ values of PIB/PMMA (30/70) and PIB/PCHMA (30/70) IPNs are equal to 0.15 and 0.12, respectively. In the studied composition range, the PIB/PCHMA IPNs are more rigid and show slightly lower damping properties at a given composition.

According to the comparison between experimental and calculated (from Davies model) shear moduli, each phase evidenced by DMTA might be continuous over the whole material. Such a morphology would correspond to the “dual phase continuity” as proposed by Sperling [38], i.e. the interpenetrating phase is composed of co-continuous PIB and PCHMA networks. Depending on the IPN composition, the interpenetrating phase is either associated with a PIB rich phase (in the PIB/PCHMA (60/40), (50/50) and (40/60) IPNs) or with a PCHMA rich phase (in the PIB/PCHMA (30/70) and (20/80) IPNs). This IPN morphology has been confirmed by AFM analysis of the IPN surfaces.

3.3. AFM image

AFM analyses in tapping mode are performed on the surface of three different PIB/PCHMA IPNs. The image contrast is given by the stiffness difference between a soft PIB very rich phase which appears pale and a hard PCHMA phase combined with undetermined (although depending on the IPN composition) amounts of PIB which appears dark on the images. The AFM images recorded on PIB/PCHMA (60/40), (40/60) and (20/80) IPNs are reported in Fig. 7.

The thermomechanical properties reported above clearly indicate the coexistence of two phases in these materials, one quite rich in PIB and another containing essentially of a closely interpenetrated PIB/PCHMA situation. Whatever the observation scale, the AFM images confirm that conclusion: a soft PIB rich phase appearing dark, and a hardest one apparently due to an increasingly interpenetrating PIB/PCHMA IPN appearing clear. In probable agreement with the fact that the PIB network is formed in a first stage of the synthesis and might remain morphologically dominant in the second stage, the variation in the imaging might be dependent on CHMA concentration and further diffusion and maybe repetition of the incipient PCHMA chains: hence the better dispersion or interpenetration of the two phases increases from (A) to (B). This observation comes somewhat closer to the idea of co-continuity suggested by the fitting the Davies model shown above. Unfortunately, for the (20/80) composition (C) the hardness contrast remains low whatever the strength applied on the AFM probe and for the moment no suitable image for a precise multiscaling image to corroborate a co-continuous situation.

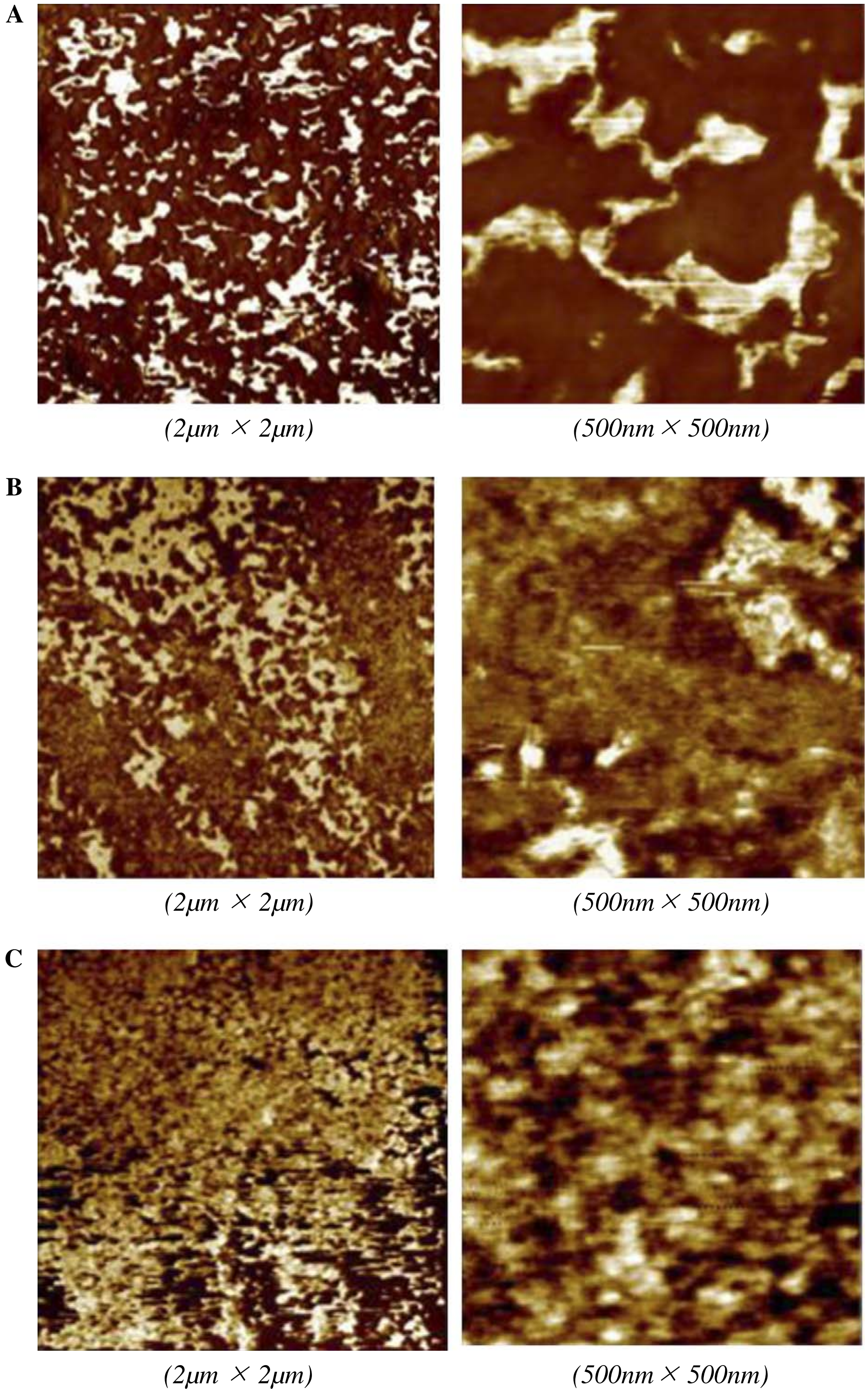

Fig. 7. AFM images of PIB/PCHMA 60/40 (A), 40/60 (B) and 20/80 (C) IPNs.

Co-continuous nanophase morphologies have been already observed in amphiphilic based-PIB co-networks in certain composition ranges by AFM microscopy. Poly(2-hydroxyethylmethacrylate)(PHEMA)/PIB co-networks show different morphologies according to their composition [39]. At low PIB content, spherical PIB domains of about 13 nm diameter are dispersed in the PHEMA matrix. At 50–70% PIB content, a co-continuous morphology is observed. PHEMA dispersed domains, of about 5 nm diameter, develop in the PIB matrix for PIB content higher than 70%. Particularly, in the PHEMA/PIB (36/64) co-network, both co-continuous phase morphology and dispersed PHEMA domains spaced of 17–22 nm are detected [40].

Thus, the different domain sizes are smaller in the based-PIB co-network (10 or so nanometers) than in the PIB/PCHMA IPN (about 100 nm). On the other hand, the co-continuous phase morphology is observed on a larger composition range in the IPN architecture than in co-network.

4. Conclusion

Association of a PIB network with a thermoplastic network in an interpenetrating polymer network (IPN) architecture has been described. Thus PIB/PCHMA IPNs in which PIB and PCHMA networks are independently cross-linked have been synthesized and characterized. The IPNs are synthesized through an in situ synthesis pathway in which the PIB network is formed prior to the PCHMA one. The obtained materials are transparent, soft and slightly elastic whatever the PIB/PCHMA weight proportion. As expected, the mechanical properties of the PIB network are improved by the introduction of the PCHMA network into the IPN architecture. The IPN shear moduli values are correlated to a phase co-continuity model, which supports the idea of two continuous phases in the material. The tan δ versus temperature curves show that the phase interpenetration, evidenced by the presence of a broad tan δ peak at intermediate temperatures, is the highest for intermediate weight proportion. This new tan δ peak is characteristic of phases in which the PIB and PCHMA networks are correctly interpenetrated. Simultaneously, the tan δ peaks corresponding to the PCHMA and PIB rich phases disappear or become weaker. The AFM images confirm a distribution at the IPN surface of co-continuous hard (PIB/PCHMA) and soft (rich in PIB) phases in the whole material.

Thus combining in an IPN PIB with PCHMA, polymers with very close solubility parameters, leads to the occurrence of an interpenetrating phase, although not unique throughout the material whereas in PIB/PMMA IPNs, a clearly PMMA and PIB biphasic material was systematically obtained instead. Moreover the PIB/PCHMA IPN moduli are close to those of PIB/PMMA IPNs, but the presence of the interpenetrating phase in the PIB/PCHMA IPN clearly improve their damping properties.

Acknowledgments

The authors thank BASF for financial support, and particularly Dr. H-P. Rath who very actively supported this research and also provided the α,ω-dihydroxy polyisobutene samples. They also thank Dr. R. Blackborow for many stimulating discussions.

References

[1] (a) Sperling LH. Interpenetrating polymer networks and related materials. New York: Plenum Press; 1981;
(b) Klempner D, Sperling LH, Utracki LA, editors. Interpenetrating polymer networks. Advances in chemistry series, vol. 239. Washington, DC: ACS; 1994.
[2] Sperling LH, Mishra V. Polym Adv Technol 1996;7(4):197–208.
[3] Sophiea D, Klempner D, Sendijarevic V, Suthar B, Frisch KC. Interpenetrating polymer networks. In: Klemper D, Sperling LH, Utracki LA, editors. Advances in chemistry series, vol. 239. Washington, DC: ACS; 1994. p. 39–76.
[4] Hourston DJ, Schäfer FU. Polymer 1996;37(16):3521–30.
[5] Fichet O, Vidal F, Laskar J, Teyssié D. Polymer 2005;46(1):37–47.
[6] Othmer K. Encyclopedia of chemical technology. New York: Wiley; 1998.
[7] Vancaeyzeele C, Fichet O, Boileau S, Teyssié D. Polymer 2005;46: 6888–96.
[8] Vancaeyzeele C, Fichet O, Boileau S, Teyssié D. Polymer 2006;46: 2046–60.
[9] Tanabe M, Sugimura T, Yasuda H. React Funct Polym 2002;52:135–41.
[10] Wu S. J Appl Polym Sci 1992;46(4):619–24.
[11] Brandrup J, Immergut EH, Grulke EA. Polymer handbook. 4th ed. New York: Wiley; 1999.
[12] Binder K, Frisch HL. J Chem Phys 1984;81(4):2126–36.
[13] Frisch HL. Prog Org Coat 1996;27:67–72.
[14] Nia H, Aaserudb DJ, Simonsick Jr WJ, Souceka MD. Polymer 2000;41:57–71.
[15] Stansbury JW, Dickens SH. Dent Mater 2001;17:71–9.
[16] Schapman F, Couvercelle JP, Bunel C. Polymer 1998;39(4):965–71.
[17] Plazek DJ, Chay IC, Ngai KL, Roland CM. Macromolecules 1995; 28(19):6432–6.
[18] Ngai KL, Plazek DJ. Macromolecules 2002;35(24):9136–41.
[19] Frick B, Richter D. Phys Rev B 1993;47(22):14795–804.
[20] Puskas JE, Antony P, El Fray M, Altstädt V. Eur Polym J 2003;39(10): 2041–9.
[21] Storey RF, Baugh DW. Polymer 2001;42(6):2321–30.
[22] Li X, Yee AF. Macromolecules 2003;36:9411–20.
[23] Heijboer J. Molecular basis of transitions and relaxations. In: Meier DJ, editor. Langhorne, PA: Gordon and Breach Science Publishers; 1978.
[24] Lauprêtre F, Virlet J, Bayle JP. Macromolecules 1985;18(10): 1846–50.
[25] Teyssié D, Vancaeyzeele C, Laskar J, Fichet O, Boileau S, Blackborow R, et al. Molding compound. Patent number WO 2005019285, 2005/03/03.
[26] Laskar J, Vidal F, Fichet O, Gauthier C, Teyssié D. Polymer 2004;45(15):5047–55.
[27] Seferis JC. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. Wiley, Inc.; 1999 [chapter 4].
[28] Kerner EH. Proc Phys Soc London B 1956;69:808–13.
[29] Budiansky B. J Mech Phys Solids 1965;13:223–32.
[30] Davies WEA. J Phys D Appl Phys 1971;4:1176–81.
[31] Kim SC, Klempner D, Frisch KC, Frisch LH. Macromolecules 1977;10(6):1187–91.
[32] Akay M, Rollins SN. Polymer 1993;34(9):1865–73.
[33] Hourston DJ, Schäfer FU, Gradwell MSH, Song M. Polymer 1998;39:5609–17.
[34] Yeo JK, Sperling LH, Thomas DA. Polym Eng Sci 1981;21:696–702.
[35] Leach RN, Stevens F, Seiler C, Langford SC, Dickinson JT. Langmuir 2003;19:10225–32.
[36] Brachais L, Lauprêtre F, Caille J-R, Teyssié D, Boileau S. Polymer 2002;43:1829–34.
[37] Ruzette AVG, Mayes AM. Macromolecules 2001;34:1894–907.
[38] Sperling LH. Interpenetrating polymer networks. In: Klemper D, Sperling LH, Utracki LA, editors. Advances in chemistry series, vol. 239. Washington, DC: ACS; 1994. p. 3–38.
[39] Iván B, Haraszti M, Erdodi G, Scherble J, Thomann R, Mülhaupt R. Macromol Symp 2005;227:265–73.
[40] Scherble J, Thomann R, Ivan B, Mulhaupi R. J Polym Sci Part B Polym Phys 2001;39:1429–36.