Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 47 (2006) 3747–3753

polymer

www.elsevier.com/locate/polymer

Polysiloxane–Cellulose acetate butyrate cellulose interpenetrating polymers networks close to true IPNs on a large composition range. Part II

Frédéric Vidal, Odile Fichet, Judith Laskar, Dominique Teyssié *

Laboratoire de Physico-chimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay-Lussac, Neuville-sur-Oise,
95031 Cergy-Pontoise Cedex, France

Received 15 December 2005; received in revised form 21 February 2006; accepted 8 March 2006

Abstract

Interpenetrating polymer networks combining cellulose acetate butyrate (CAB) and α,ω-divinyl-polydimethylsiloxane (PDMS) in different weight proportions have been synthesized. The synthesis involves a one pot–one shot process in which all components are first mixed together. For each composition, the relative CAB and PDMS network formation rates are adjusted through the concentration of DBTDL used as CAB network formation catalyst. Thus, the chemically independent networks are formed quasi-simultaneously in order to avoid phase separation. The CAB cross-linking density effect on the PDMS/CAB IPN mechanical properties has also been particularly studied. All synthesized IPNs are transparent and only one mechanical relaxation temperature lying between those of the single CAB and PDMS networks is observed by DMTA analysis. These results show that the networks are correctly interpenetrated and no phase separation is observed at the DMTA level. Some mechanical properties of the PDMS network are significantly improved in this IPN combination and their stress–strain behavior has highlighted a synergistic effect arising from the IPN architecture. Thus, these IPNs exhibit many characteristics, which would allow defining them as close to ‘true’ IPNs.

Keywords: Silicone; Cellulose acetate butyrate; Interpenetrating polymer network

1. Introduction

Interpenetrating polymer networks (IPNs) are defined as combinations of two or more polymer networks synthesized in juxtaposition. The entanglement of two cross-linked polymers leads to forced ‘miscibility’ compared to usual blends and the resulting materials exhibit good dimensional stability. The general aim of these types of polymer associations is to obtain materials with better mechanical properties, increased resistance to degradation and a possibly improved combination of the properties of their components.

The first information about the extent of phase separation in the IPN can be derived straight after the synthesis from the relative transparency of the material. Indeed, the more transparent the material, the smaller the phase separation since any light wavelength will be diffracted by any phase domain the size of which is of the same order of magnitude, making the material appear translucent to opaque [1].

Dynamic mechanical thermal analysis (DMTA) should be an adequate tool in order to corroborate the interpenetrating degree of both networks inside the IPN architecture. Ideally, interpenetration should occur only through physical interactions and mixing should be homogeneous on a molecular scale without covalent bonding between the different networks. In this case, the DMTA analysis detects one phase only, witnessed by just one mechanical relaxation the corresponding domain size being estimated at about 5–50 nm depending on the width of the relaxation signal [2]. Thus, this ‘single’ phase is characterized in the loss factor (tan δ)–temperature curve by only one peak located at a temperature between those of the mechanical relaxation of the single networks combined inside the IPN architecture. In fact, many 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 example, polyurethane/poly(ethyl methacrylate) IPNs with weight compositions (30–70) and (20–80) show only one peak in the tan δ–temperature curves,

---

* 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.2006.03.030

indicating a high degree of interpenetration between both partner networks [3].

Polydimethylsiloxanes (PDMS) are known for their high level of incompatibility with other polymers. Their extraordinary flexibility makes it difficult to trap them into the non-equilibrium architectures of IPNs. Some IPNs associating PDMS with a rigid thermoplastic polymer expected to improve PDMS mechanical properties are reported in the literature [4–10]. As expected, these IPNs exhibit superior mechanical properties compared to single PDMS networks, however they are consistently phase separated. This identified phase separation does not allow these materials to be classified as 'true' IPNs [1].

In a first paper [11], the synthesis of polydimethylsiloxane (PDMS)/cellulose acetate butyrate (CAB) interpenetrating polymer networks (IPNs) have been reported. The silicone network is formed through a thiol–ene addition reaction between α,ω-divinyl-poly(dimethylsiloxane) and trimethylolpropane tris(3-mercaptopropionate) as a cross-linking agent. The CAB network is synthesized using a pluri-isocyanate cross-linking agent through dibutyltindilaurate (DBTDL) catalysis. The IPN is prepared through a one pot–one shot process. Particular attention was brought to tuning the formation rates of both networks into the IPN architecture. All studies were carried out on starting mixtures in which the polymers were in the same weight proportion (50/50). Since the success in obtaining a satisfactory interpenetrating degree is tightly linked to the competition between the individual network formation rates and the phase separation one (thermodynamic phenomenon) the respective network formation kinetics are crucial in this IPN synthesis. Indeed, when the CAB network formation is not sufficiently advanced (less than 40% conversion of the NCO functions of the pluri-isocyanate agent used as CAB cross-linker) before the PDMS gel point is reached (87% conversion of the PDMS end chain vinyl groups), translucent or opaque materials are obtained and two mechanical relaxations are detected. However, by adjusting the dibutyltindilaurate (DBTDL) catalyst concentration, i.e. the CAB network formation rate, a transparent material can be obtained and the two polymer networks are well interpenetrated since just one mechanical relaxation is detected by DMTA. Thus, by adjusting the relative rates of the network formations, a 'true' IPN as defined by Sperling, i.e. showing only one mechanical relaxation [2], can be synthesized.

In this second paper, the syntheses of PDMS–CAB IPNs containing different CAB weight proportion relative to PDMS are described. The relative network formation rates into the IPN have been particularly studied for each composition and the corresponding DBTDL concentration has been determined which leads to a transparent IPN. Some mechanical properties such as mechanical relaxation temperatures and stress–strain behaviour of these transparent PDMS–CAB IPNs are detailed. On the other hand, the CAB cross-linking density effect on the PDMS/CAB IPN thermomechanical properties was studied for a given IPN composition.

2. Experimental part

2.1. Materials

α,ω-Divinyl poly(dimethylsiloxane) (di-vinyl-PDMS in the text, $M_n = 650$ g mol^{-1} determined by ^{1}H NMR, ABCR), dibutyltindilaurate (DBTDL, Aldrich), Desmodur® N3300 (pluri-isocyanate cross-linker or agent in the text, Bayer), trimethylolpropane tris(3-mercaptopropionate) (Trithiol in the text, Aldrich) and cellulose acetate butyrate (CAB in the text, 4% acetate–50% butyrate–46% OH, Acros Organics) are used as received. 2,2′-Azobisisobutyronitrile (AIBN, Acros Organics) is recristallized in methanol and chloroform (Carlo Erba, puro grade) is distilled before use.

2.2. Synthesis of single networks and IPNs

The synthesis of PDMS and CAB single networks and PDMS/CAB (50/50) IPNs has been previously described [11]. The CAB cross-linking density in the PDMS/CAB (50/50) IPN has been varied by varying the molar ratio [NCO]/[OH] from 0.30 to 0.60. Only Desmodur® N3000 and DBTDL contents are changed the synthesis conditions being kept identical. Thus, in order to obtain a [NCO]/[OH] molar ratio set at 0.30, 0.45 and 0.60 quantities equal to 0.27, 0.41 and 0.55 g Desmodur® N3300 as well as 169, 190 and 140 μL DBTDL are added, respectively.

PDMS/CAB (25/75) IPN is prepared as follows: 0.75 g CAB is dissolved in 3 mL chloroform, then 0.25 g di-vinyl-PDMS, 0.12 g trithiol ([HS]/[C=C] = 1.1), 0.41 g Desmodur® N3300 ([NCO]/[OH] = 0.60) and 7 mg AIBN ([AIBN]/[C=C] = 0.05) are stirred together under argon atmosphere for 30 min. 52 μL DBTDL ([DBTDL]/[OH] = 0.025) are added as last component just before the mixture is poured into a mould made from two fluorine plates clamped together and sealed with a 1 mm thick Teflon gasket. The mould is then kept at 50 °C for 16 h. After 16 h, the sample is kept for 1 h at room temperature and then dried for 2 h at 50 °C under vacuum. After complete solvent evaporation, it is cured for 2 h at 110 °C.

PDMS/CAB (75/25) IPN is prepared as follows: 0.25 g CAB is dissolved in 3 mL chloroform, then 0.75 g di-vinyl-PDMS, 0.34 g trithiol ([HS]/[C=C] = 1.1), 0.14 g Desmodur® N3300 ([NCO]/[OH] = 0.60) and 22 mg AIBN ([AIBN]/[C=C] = 0.05) are stirred together under nitrogen atmosphere for 30 min. 52 μL DBTDL ([DBTDL]/[OH] = 0.075) are added as last component, the same procedure as described for the previous IPNs is then followed.

All investigated PDMS/CAB compositions are reported as weight by weight ratios. Thus, an IPN obtained from a mixture of 0.25 g di-vinyl-PDMS and 0.75 g CAB will be noted PDMS/CAB (25/75) IPN, PDMS ratio being always reported first.

2.3. Kinetic experiments

The formation rates of the PDMS and CAB networks into IPNs are followed in bulk and in real time in the near and middle infrared (NIR and MIR) wavelength regions (7500–1800 cm^{-1}). The PDMS network formation is monitored by the disappearance of the cross-linker H–S groups characterized by absorption bands at 2256 cm^{-1}. The CAB network formation is followed by the disappearance of the isocyanate groups of the pluri-isocyanate cross-linker showing a characteristic absorption band at 2270 cm^{-1} [12].

A given peak area (A) being directly proportional to the given function concentration, the conversion—time profiles are derived from the recording of successive spectra as a function of time. Indeed, the relative conversion of any one of the desired chemical function can be determined from the absorbance values as $(1-(A_t/A_0))$ where the A subscripts 0 and t denote reaction times.

IPNs are directly synthesized in the IR cell as previously described [11]. The cell is inserted in an electrical heating jacket with an automatic temperature controller (Graseby Specac). Heating within the cell holder is constant to 50±1 °C. The near-infrared spectra are recorded with a Bruker spectrometer (Equinox 55) in the range 7000–1800 cm^{-1} by averaging of 10 consecutive scans with a resolution of 4 cm^{-1}. Accumulations are repeated every 5 min.

2.4. Characterization

In order to estimate the amount of unreacted starting material contained in the IPN, a known weight of IPN is extracted in a Soxhlet with dichloromethane for 48 h. After extraction, the sample is dried under vacuum at 50 °C and then weighted. The extracted content (EC) is 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.

Dynamic mechanical thermal analysis (DMTA) measurements are carried out on film samples with a Q800 model (TA Instruments) operating in tension mode, experiments being performed at a 1 Hz frequency and a heating rate of 2 °C min^{-1} from −140 to 150 °C. Typical dimensions of the samples are 6 mm×30 mm×1 mm. The set up provides the storage and loss moduli (E' and E'') and the damping parameter or loss factor (tan δ). The stress–strain experiments are performed with a deformation rate of 1 mm min^{-1} at 35 °C. At least four measurements for each sample are carried out.

Glass transition temperature (T_g) values were taken as the onset point from the second heating curves recorded at 20 K/min heating rate between −90 and 170 °C on a DSC Q100 model (TA Instruments).

3. Results and discussion

The morphology of interpenetrating polymer networks (IPNs) is controlled by a complex interplay between the polymerization/cross-linking reaction rates and the occurrence of the phase separation. For the PDMS/CAB (50–50) IPN synthesis, macrophase separation can be avoided by controlling the formation rate of silicone and CAB networks. Indeed, the cross-linking of the CAB network must be sufficiently advanced (at least 40% conversion of the NCO functions before the PDMS gel point) in order to obtain a transparent material showing only one mechanical relaxation by DMTA analysis. However, when PDMS versus CAB weight proportions are modified, the reactive group concentrations in the reactive mixture are changed and the network formation rates do vary compared to what is observed in the 50/50 one. Thus, for each composition, it is necessary that the relative network formation rates remain unchanged compared with those of the PDMS/CAB (50/50) IPN synthesis in order to obtain a homogenous transparent material.

The PDMS network is synthesized from di-vinyl-PDMS ($M_n = 650$ g mol^{-1}) and trimethylolpropane tris(3-mercaptopropionate) (trithiol) as cross-linker through a radical thiol–ene addition reaction initiated with AIBN. The kinetics of the thiol–ene reaction is first and zero orders with respect to the thiol and vinyl group concentrations, respectively [13,14]. Thus the PDMS network formation rate is not dependent on the vinyl end-chain group concentration, hence of the PDMS concentration. In other words, the cross-linking reaction rate is only a function of the concentrations of thiol functional groups and AIBN. Accordingly, a decrease in the PDMS network proportion in the IPN composition leads to a decrease in the thiol concentration and thus to a slow down of the PDMS network formation rate.

CAB ($M_n = 16{,}000$ g mol^{-1}) networks are synthesized in presence of a pluri-isocyanate cross-linker via an alcohol/isocyanate reaction catalysed by DBTDL. The rate of this reaction is often described as first order with respect to both alcohol and isocyanate concentrations [12]. Although these partial orders depend on the medium viscosity and the compound molar weight [15,16], the CAB network formation rate still depends on the OH and NCO function concentrations. In addition, the apparent rate constant k of the isocyanate–alcohol addition reaction leading to the CAB network formation varies linearly with the catalyst concentration according to $k = k_0 + k_\mathrm{cat}$ [DBTDL] where k_0 and k_cat are spontaneous and catalysed rate constants, respectively [12]. Thus, when DBTDL concentration is increased in the reactive mixture, the apparent rate constant k is increased as well as the CAB network formation rate. So, the CAB network formation rate can be adjusted by the DBTDL concentration in the initial mixture.

In this study, the CAB cross-linker content is first set at 60% molar with respect to hydroxyl function, i.e. [NCO]/[OH] = 0.60, and we have chosen to control the formation rates of both networks playing only with the DBTDL catalyst concentration. As already discussed in part I [11], the DBTDL concentration is adjusted in order to obtain at least 40% of the NCO group conversion before the PDMS gel point is reached in order to avoid macrophase separation. For example, for the PDMS/CAB (75–25) IPN synthesis, the CAB content is lower than that in PDMS/CAB (50–50) IPN one, in which the [DBTDL]/[OH] molar ratio was chosen equal to 0.05. If this ratio is kept constant, then the CAB network formation rate will be slowed down due to the decrease in NCO and OH concentrations. In order to avoid the phase separation between PDMS and CAB networks, the CAB network formation rate must be accelerated by increasing the DBTDL concentration. Thus, the [DBTDL]/[OH] ratio should be higher than 0.05 in the PDMS/CAB (75–25) IPN synthesis in order to obtain a transparent IPN with only one mechanical relaxation temperature.

The PDMS–CAB (75–25), (50–50) and (25–75) IPN synthesis have been particularly studied. For each synthesis, the amount of chloroform used for the solubilisation of the initial compounds is adjusted in order to obtain a transparent initial mixture. Transparent PDMS–CAB (75–25), (50–50) and (25–75) IPNs are obtained when the molar ratio [DBTDL]/[OH] is set at 0.075, 0.050 and 0.025, respectively. In order to check that, in each case, the NCO conversion reaches at least 40% before the PDMS gel point is reached, the NCO and thiol group conversions have been recorded versus time (Fig. 1). As shown on these conversion-time curves, the isocyanate conversions reach 0.40, 0.43 and 0.61 in the PDMS–CAB (75–25), (50–50) and (25–75) mixture when the PDMS gel point is reached, i.e. when the thiol group conversion is equal to 0.87. So, by adjusting the DBTDL concentration for each composition, the NCO conversion can reach at least 40% before the quasi-quantitative PDMS network formation. All PDMS/CAB IPNs synthesized with the reported molar ratio [DBTDL]/[OH] are transparent, which means that macrophase separation is prevented, considering the very important difference between the respective refractive indices of both polymers ($n^{20}_{\text{D PDMS}} = 1.43$ and $n^{20}_{\text{D CAB}} = 1.47$ [17]).

The amount of extracted materials is below than 7% in all synthesized IPNs. Analysis of the extracted material by ^{1}H NMR shows that they are mainly composed of linear PDMS chains. These low amounts of extracted material are an indication of the satisfactory yield of the cross-linking reaction.

An improvement in the poor mechanical properties of PDMS is expected upon combining PDMS and CAB into an IPN architecture, prompting a study of the thermomechanical properties of PDMS/CAB IPNs by DMTA analysis and paying special attention to the influence of IPN composition and CAB cross-linking density.

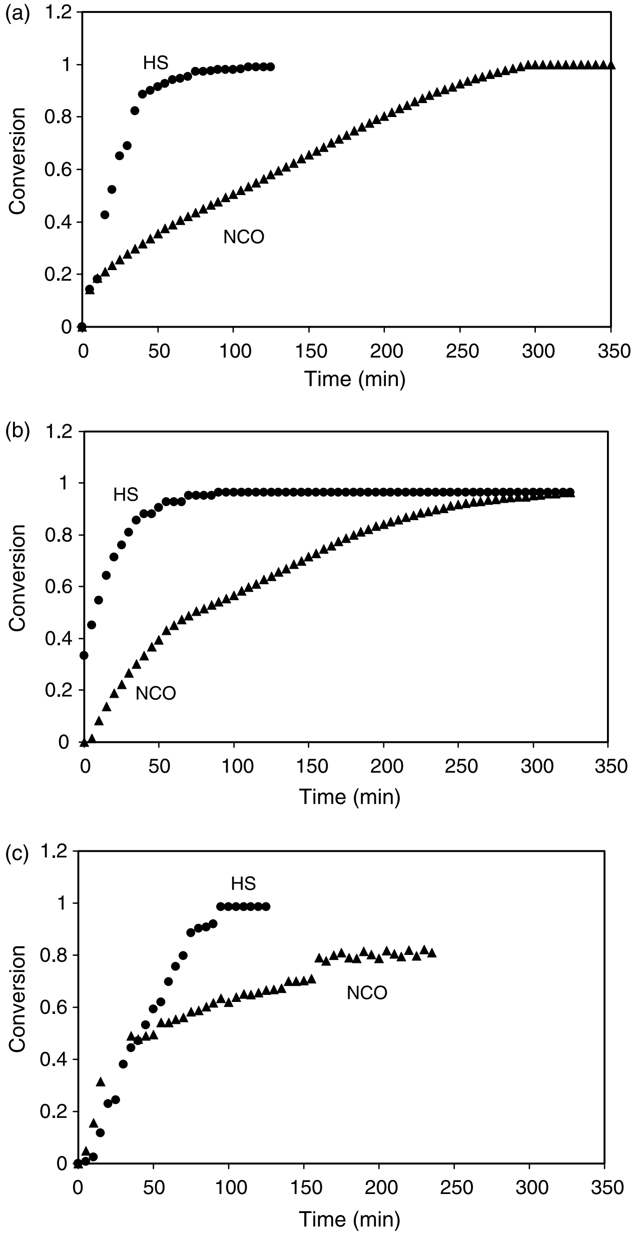

Fig. 1. Thiol (●) and NCO (▲) group conversions during the synthesis of (a) PDMS/CAB (75–25) IPN with [DBTDL]/[OH] = 0.075; (b) PDMS/CAB (50–50) IPN with [DBTDL]/[OH] = 0.050 and (c) PDMS/CAB (25–75) IPN with [DBTDL]/[OH] = 0.025, [NCO]/[OH] = 0.60, [AIBN]/[C=C] = 0.05, [HS]/[C=C] = 1.1, $T = 50$ °C.

The tan δ values are associated with segmental chain motion and are also greatly influenced by the IPN weight composition. As previously described [11], PDMS and CAB single networks show a mechanical relaxation characterized by a maximum tan δ value located at a given temperature (tan δ(PDMS) = 1.40 at $T\alpha_{\text{PDMS}} = -70$ °C and tan δ(CAB) = 0.85 at $T\alpha_{\text{CAB}} = +113$ °C) (Fig. 2(a) and (e)). The quality of the interpenetration of both networks inside the IPN architecture can be to a certain extent inferred from the tan δ–temperature curves. Indeed, the DMTA measurements detect just one phase, i.e. only one mechanical relaxation when the networks are correctly interpenetrated.

Fig. 2 shows the tan δ–temperature curves of PDMS/CAB IPNs for various compositions. PDMS/CAB (75/25) IPN shows a complex morphology highlighted by a very broad relaxation ranging over more than 130 °C between −80 and 50 °C, which displays two maximum at −50 and −5 °C. These two relaxations might be assigned to interpenetrated polymer domains with various composition as a rich PDMS phase containing CAB ($T\alpha = -50$ °C) and to a rich CAB one containing PDMS ($T\alpha = -5$ °C extending up to 50 °C). The

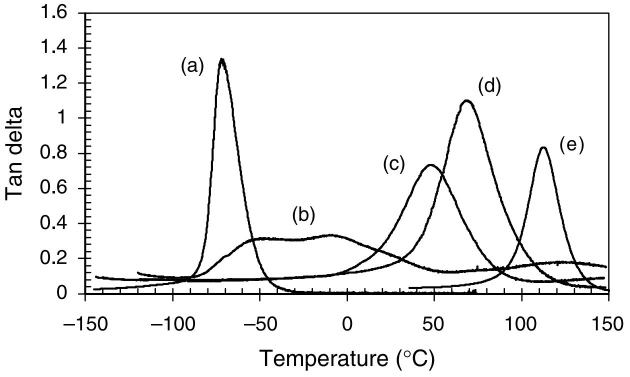

Fig. 2. tan δ versus temperature of PDMS/CAB IPNs with different weight compositions (b) 75/25, (c) 50/50 and (d) 25/75. PDMS (a) and CAB (e) single network curves are reported for comparison.

mechanical relaxation of the single PDMS network is not present anymore, however a mechanical relaxation with a weak intensity centred at 110 °C is still observed which might be assigned to a pure CAB phase. Thus, the PDMS/CAB (75/25) IPN is composed of interpenetrating domains with various compositions and also of CAB domains which means that the phase separation could not be avoided perfectly during the synthesis.

On the other hand, only one α mechanical relaxation located at +49 and +70 °C for PDMS/CAB (50–50) and (25–75) IPN, respectively is detected. In each case, the single peak is located at a temperature between those of the mechanical relaxation of the PDMS and CAB single networks. These results prove that the phase separation does not take place during the IPN synthesis or at least is considerably limited. Furthermore, these peaks (tan $\delta_{\max}$) are rather broad (for example the half-height width of tan δ peak is equal to 40 °C for the PDMS/CAB (50–50) IPN) compared to those of the single networks (the half-height widths of tan δ peaks are equal to about 20 °C for the PDMS and CAB single networks) indicating that the new interpenetrated phase has a rather constant composition. Indeed, the broader the tan δ peak, the less homogeneous the composition of the material. It should be noted that DSC measurements have also been carried out on all samples but no exploitable transition has been detected. Thus, these IPNs exhibit some characteristics that would allow them to be classified as true IPNs [1].

Besides the variation of the CAB amount, the effect of decreasing the CAB cross-linking density on the mechanical properties of the IPN has been studied. First of all, the necessary synthesis conditions in order to obtain transparent IPN have been determined. From here, the DBTDL concentration is expressed with respect to the exact amount of OH groups, which are chosen to react and thus correspond to the introduced NCO group amount, i.e. NCO concentration. For this reason, in this discussion part, the DBTDL concentration is expressed as the [DBTDL]/[NCO] molar ratio. The series of PDMS/CAB (50/50) IPNs in which the CAB cross-linking density, i.e. the [NCO]/[OH] molar ratio, varies from 0.30 to 0.60 has been synthesized. As already described above, at least 40% of the NCO functions must have reacted before the PDMS gel point is reached in order to obtain a transparent material showing only one mechanical relaxation by DMTA analysis. Therefore, when the CAB cross-linking density, i.e. the NCO function concentration decreases the DBTDL amount must be increased in order to increase the CAB network formation rate. This assumption was confirmed since the PDMS–CAB (50–50) IPNs in which the [NCO]/[OH] molar ratio decreases from 0.60 to 0.30 are transparent when the [DBTDL]/[NCO] molar ratio is increased from 0.08 (corresponding to the previous ratio [DBTDL]/[OH] = 0.05) up to 0.17. On the other hand, no transparent IPN is obtained when the [NCO]/[OH] ratio is below 0.20 even if the [DBTDL]/[NCO] ratio varies from 0.15 to 0.50. Indeed whatever this [DBTDL]/[NCO] ratio, the final IPN is consistently translucent which is characteristic of a phase separation. Thus, a low cross-linking density of the CAB in this type of IPN, i.e. the low cross-linker agent concentration, promotes intra-molecular cross-linking which in turn leads to phase separation.

In order to check that the CAB cross-linking density is affected by the variation of the [NCO]/[OH] values from 0.3 to 0.6 even in off-stoichiometric conditions, swelling experiments were carried out on PDMS/CAB (50/50) IPNs in which the [NCO]/[OH] ratios are set at 0.60 and 0.30, respectively. The samples are immersed in dichloromethane until constant weight at room temperature. The swelling ratios are equal to 5.1 and 3.4 when the [NCO]/[OH] ratios are equal to 0.30 and 0.60, respectively. These results confirm thus that the CAB cross-linking density is affected by the [NCO]/[OH] ratio values are in off-stoichiometric conditions.

The thermomechanical properties of transparent PDMS/CAB (50/50) IPNs with different cross-linking densities corresponding to [NCO]/[OH] molar ratio varying from 0.60 to 0.30 are reported in Fig. 3. Only one mechanical relaxation is detected on the tan δ–temperature curves whatever the chosen CAB cross-linking density. The decrease in the cross-linker proportion does not induce a phase separation when the network formation rates remain correctly ordered in time. The main relaxation temperature $T\alpha$ is hardly affected by the cross-linking density and is always located at about +49 °C. On the

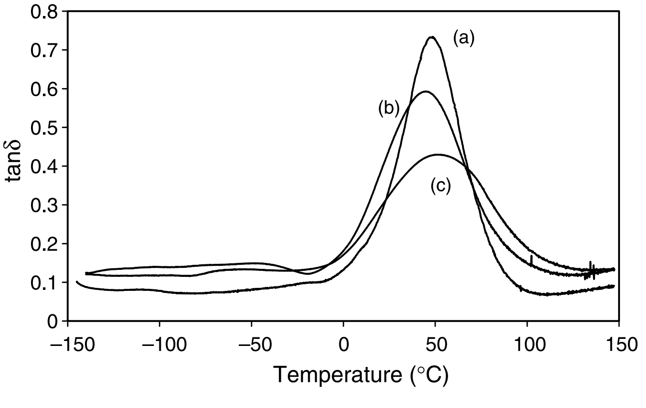

Fig. 3. PDMS/CAB (50/50) IPN tan δ versus temperature. IPNs are synthesized with different pluri-isocyanate cross-linker amounts (a) [NCO]/[OH] = 0.60 and [DBTDL]/[NCO] = 0.08, (b) [NCO]/[OH] = 0.45 and [DBTDL]/[NCO] = 0.15 and (c) [NCO]/[OH] = 0.30 and [DBTDL]/[NCO] = 0.17, [AIBN]/[C=C] = 0.05, [HS]/[C=C] = 1.1.

other hand, the tan δ maximum value decreases and the width at half height increases when the [NCO]/[OH] molar ratio decreases. For instance, the half height width increases from about 38 to 70 °C and the tan δ maximum value decreases from 0.75 to 0.40 when the [NCO]/[OH] molar ratio decreases from 0.60 to 0.30. Knowing that the broader the tan δ peak, the less homogeneous the composition of the material, the phase separation between PDMS and CAB networks is slightly amplified when the cross-linking density of CAB network decreases. Since tan δ maximum values decrease, the damping properties of the IPN decrease when the CAB cross-linking density decreases. However, in this composition range, a correct interpenetration of both networks is preserved since the mechanical relaxations of the individual single networks do not appear anymore. This behaviour should be attributed to a poorer compatibility between the two networks when the [NCO]/[OH] decreases. Indeed, the number of remaining free –OH groups on the CAB network increases when the [NCO]/[OH] molar ratio, i.e. the CAB cross-linking density, decreases and consequently leads to a more polar CAB network having a lower compatibility towards the PDMS network with which it is combined inside the IPN architecture.

Another consequence of the CAB cross-linking density decrease is that the number of intra or intermolecular hydrogen bonds in the CAB network increases since the number of remaining free –OH groups on the CAB increases, and the mechanical properties of the final material should be improved. Indeed, the pluri-isocyanate used as CAB cross-linker in the IPN synthesis should be considered as a 'soft' cross-linker when introduced in the IPN: a network synthesized from this pluri-isocyanate and butanediol shows a mechanical relaxation temperature around 60 °C, which is relatively low with respect to such a high cross-linking density. Thus, when the CAB cross-linking density decreases the chemical cross-linker is substituted by intermolecular physical cross-linking H-bonding. In order to check this assumption, firstly, the DSC curves of CAB polymer and CAB network ([NCO]/[OH] = 0.60) have been compared. The DSC curve of CAB polymer exhibits the typical behavior of an amorphous polymer with a single T_g at 104 °C whereas the CAB network shows a T_g at 82 °C. Thus, the CAB cross-linking by the Desmodur® N3300 causes a significant decrease in the T_g value the origin of which could hypothetically be assigned to a decrease in the extent of hydrogen bonding.

Secondly, the stress–strain curves of PDMS/CAB (50/50) IPNs in which the CAB cross-linking density decreases from 0.60 to 0.30 have been recorded and are shown in Fig. 4. The elongation at break increases from 60 to 110% when the [NCO]/[OH] molar ratio increases from 0.30 to 0.45. When the [NCO]/[OH] molar ratio is equal to 0.60, the elongation at break is over 150% and can even reach a 190% value. On the other hand, an order of magnitude of the Young's moduli E, can be estimated from the initial slope in the stress–strain curves. As expected, the Young's modulus, i.e. the initial slope, decreases when the CAB cross-linking density, i.e. the [NCO]/[OH] molar ratio, increases. This behaviour is in agreement with the increase in the remaining free –OH groups on the CAB leading to an increase in hydrogen bonding into the CAB network.

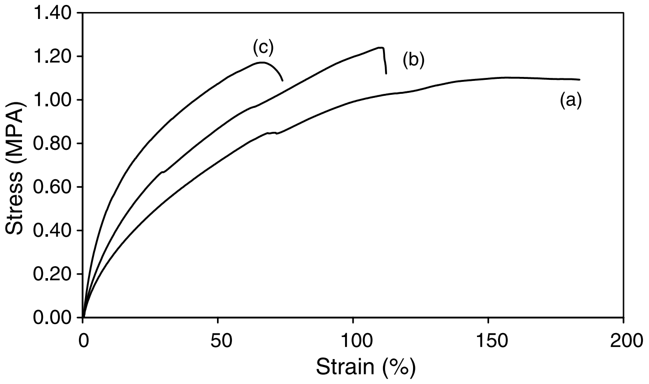

Fig. 4. Stress–strain curves of PDMS/CAB (50/50) IPNs. IPNs are synthesized with different pluri-isocyanate cross-linker amounts (a) [NCO]/[OH] = 0.60 and [DBTDL]/[NCO] = 0.08, (b) [NCO]/[OH] = 0.45 and [DBTDL]/[NCO] = 0.15 and (c) [NCO]/[OH] = 0.30 and [DBTDL]/[NCO] = 0.17, [AIBN]/[C=C] = 0.05, [HS]/[C=C] = 1.1, deformation rate: 1 mm min^{-1}, $T = 35$ °C.

So, this study on the CAB cross-linking effect shows that the PDMS/CAB IPN strain resistance can be definitely improved by increasing the CAB cross-linking density.

It is often reported in the literature that the IPN architecture can lead to a synergistic effect: however, this synergy is not often observed. In order to check whether the mechanical properties of the PDMS network are really improved by the CAB network introduction in a final IPN material, the stress–strain curves of single PDMS and CAB networks and PDMS–CAB IPNs with different compositions are shown in Fig. 5. The slopes of these curves are about equal to 0.02 and 16 MPa for the single PDMS and CAB networks, respectively and about 7 MPa for the PDMS–CAB (50/50) IPN, for example. The PDMS and CAB single networks break when less than 10 and 5% strains are applied, respectively, these strains corresponding to a stress of 0.08 and 20 MPa, respectively. On the other hand, the elongation at break is over 150% for the PDMS–CAB (50/50) IPN and the material stands a stress of about 1 MPa. Thus, the poor mechanical properties of the PDMS network (expected for a network made from very short oligomers, $M_n = 650$ g mol^{-1}) may be reinforced significantly by combining it

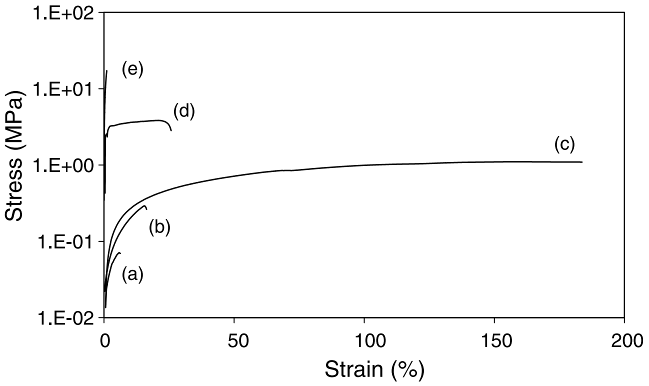

Fig. 5. Stress–strain curves of PDMS (a) and CAB (e) single networks and of PDMS/CAB IPNs with different compositions (b) 75/25, (c) 50/50 and (d) 25/75. Deformation rate: 1 mm min^{-1}, $T = 35$ °C.

into an IPN with 50 wt% rigid CAB. In the same way, the material stands a higher strain than the single CAB network. Thus, this stress–strain behaviour is indicative of a synergistic effect on the elongation at break arising from the IPN architecture. For the other IPN compositions, the extent of this synergetic effect is more limited but still exists. For example the elongation at break of the PDMS/CAB (75/25) IPN and PDMS/CAB (25/75) IPN are around 15–25%. If one considers that the synergistic effect is correlated with the extent of the interface between both networks, the PDMS/CAB (50/50) IPN must have a morphology allowing qualify it of true IPN.

4. Conclusion

Interpenetrating polymer networks combining cellulose acetate butyrate and di-vinyl-PDMS in different weight proportions have been synthesized. The synthesis involves a one pot–one shot process. For each composition, the relative network formation rates are adjusted by the DBTDL concentration introduced in the reactive mixture. Thus, the networks are formed independently and when the CAB network formation reaches at least 40% before the PDMS gel point is reached, the phase separation of both network is avoided.

When this DBTDL content is correctly adjusted, the synthesized IPNs are transparent and only one mechanical relaxation temperature lying between those of the single CAB and PDMS networks is observed by DMTA analysis. The amounts of extracted material measured on these samples are always lower than 7%. These results show that both polymers are correctly interpenetrated and no phase separation is observed at the DMTA level.

On the other hand, the study of the increased CAB cross-linking effect on the PDMS/CAB (50/50) IPN has shown that increasing the [NCO]/[OH] molar ratio from 0.30 to 0.60 leads to an interpenetrating phase with a better interpenetration degree and a better strain resistance. The stress–strain behaviour of these PDMS/CAB IPNs has highlighted a synergistic effect arising from the IPN architecture.

References

[1] Sperling LH, Mishra V. IPNs around the world: science and engineering. New York: Wiley; 1997 p. 1–25.
[2] Sophiea D, Klempner D, Sendijarevic V, Suthar B, Frisch KC. In: Klemper D, Sperling LH, Utracki LA, editors. Interpenetrating polymer networks. Advances in chemistry series, vol. 239. Washington, DC: American Chemical Society; 1994. p. 39–76.
[3] Hourston DJ, Schäfer FU. Polymer 1996;37(16):3521–30.
[4] Mazurek M. In: Jones RG, Ando W, Chojnowski J, editors. Silicon-containing polymers. Dordrecht, Boston, London: Kluwer Academic Publishers; 2000. p. 113–39.
[5] Turner JS, Cheng YL. Macromolecules 2003;36:1962–6.
[6] Vlad S, Vlad A, Oprea S. Eur Polym J 2002;38:829–35.
[7] Huang GS, Li Q, Jiang LX. J Appl Polym Sci 2002;85:545–51.
[8] He XW, Widmaier JM, Herz JE, Meyer GC. In: Klempner D, Frisch KC, editors. Advances in interpenetrating polymer networks, vol. 4. Lancaster: Technomic Publishing Co.; 1994. p. 321–56.
[9] Hamurcu EE, Baysal BM. Macromol Chem Phys 1995;196:1261–76.
[10] Boileau S, Bouteiller L, Ben Khalifa R, Liang Y, Teyssié D. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, editors. Silicones and silicone-modified materials. American Chemical Society Symposium, Washington DC, vol. 729; 2000, 2000. p. 383–94.
[11] Fichet O, Vidal F, Laskar J, Teyssié D. Polymer 2005;46(1):37–47.
[12] Schapman F, Couvercelle JP, Bunel C. Polymer 1998;39:965–71.
[13] Cramer NB, Reddy SK, O'Brien AK, Bowman CN. Macromolecules 2003;36:7964–9.
[14] Cramer NB, Davies T, O'Brien AK, Bowman CN. Macromolecules 2003; 36:4631–6.
[15] Tabka MT, Chenal JM, Widmaier JM. Polym Prepr (ACS Div Polym Chem) 2001;42(2):664–5.
[16] Krol P, Wojturska J. J Appl Polym Sci 2003;88(2):327–36.
[17] Seferis JC. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook. 4th ed. New York: Wiley; 1999 [chapter 4].