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Polydimethylsiloxane–cellulose acetate butyrate interpenetrating polymer networks synthesis and kinetic study. Part I

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Abstract

The synthesis of an interpenetrating polymer network (IPN) combining a polydimethylsiloxane (PDMS) network and a cellulose acetate butyrate (CAB) network is reported. The silicone network is formed through a thiol-ene addition between α,ω-divinyl-poly(dimethylsiloxane) and trimethylolpropane tris(3-mercaptopropionate) as a cross-linking agent. The CAB network is synthesized by pluri-isocyanate cross-linking through dibutyltindilaurate (DBTDL) catalysis. The IPN is prepared through a *one pot-one shot* process. Kinetic studies of the IPN synthesis showed that some thiol cross-linking functions react with DBTDL which slows down the CAB network formation by decreasing the available quantity of DBTDL catalyst. Thus, in order to obtain a transparent material withstanding the presence of thiol groups, the DBTDL content must be increased and the resulting IPN exhibits then only one transition temperature as measured by dynamic thermomechanical analysis witnessing a high level of interpenetration.

Keywords: Silicone; Cellulose acetate butyrate; Interpenetrating polymer network

1. Introduction

Siloxanes are relatively expensive materials and exhibit poor mechanical properties because of weak intermolecular interactions between polymer chains. Nevertheless, these polymers have a set of extremely interesting properties, i.e. very low surface energy, excellent gas and moisture permeability, good heat stability, low temperature flexibility and biocompatibility [1]. The high cost and low strength resistance of silicone rubbers limit their use to specialty applications where high thermal stability or extreme low temperature use are desirable [2]. Furthermore, a severe limitation of silicone rubbers for biomedical applications is their poor mechanical properties especially low failure stress and low tear resistance [3,4]. In order to reinforce silicone elastomers, they are often combined with other compounds exhibiting better mechanical properties. These combinations must be stable over time and can be designed as copolymers, blends or interpenetrating polymer networks (IPNs).

IPNs are defined as combination 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 aim of these types of polymer associations in general is to obtain materials with better mechanical properties, increased resistance to degradation and a possibly improved combination of the properties of their components. Semi-IPNs differ from IPNs in that they are composed of one linear polymer entrapped in a polymer network of identical or different nature. IPNs can be prepared through different synthetic routes. In the so called *one pot-one shot* IPN formation process—or in situ synthesis—all reactants are mixed together and the reactions leading to the formation of the two networks are started at the same time leading to the more or less simultaneous formation of the two networks. Hence in this *one pot-one shot* process the reaction mechanisms leading to

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the two network partners must be of different nature, otherwise a single copolymer network instead of a true IPN is formed through crossed reactions.

Combining silicones with any organic polymer into a new material brings about some unique challenges. Polymer science knows only few polymer pairs which can be considered thermodynamically compatible. Silicones, particularly PDMS, are known for their 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 increase the PDMS mechanical properties are reported in the literature [5]. For example, polydimethylsiloxanes have been combined with PMAA [6], polyurethane [7], PMMA [8,9], polystyrene [10] or polycarbonate [11]. These IPNs are reported to exhibit superior mechanical properties compared to single PDMS networks. However, they are consistently phase separated as shown by DSC, TEM, ^{1}H NMR, laser scanning confocal microscopy, AFM or dynamic thermomechanical analysis. This identified phase separation does not allow these materials to be classified as true IPNs.

Environment friendly polymer materials based on renewable polymers meet requirements for ecological safety of environment and show interesting economic aspects for manufacturing advanced materials. Among cellulose derivatives, ester modified celluloses (i.e. cellulose acetate butyrate) are very good highly transparent film-forming materials with higher scratch resistance than most thermoplastics, and are commercially available in different grades at a reasonable price.

Most described semi-IPN type materials based on cellulose derivatives are hydrogels [12–15]. In a completely different type of application, IPNs made from 'PAMAMOS' dendrimer networks and cellulose acetate butyrate network have been prepared in order to 'dilute' the PAMAMOS compound and to improve the mechanical properties of the dendrimer network and thus to decrease the price of a PAMAMOS-based material [16]. These IPNs are transparent exhibit a single glass transition temperature and their complexing properties are maintained.

The use of cellulosic ester semi-IPNs for the design of electronic conducting materials has been also investigated. The synthesis of polyaniline/cellulose acetate [17] and PEDOT/cellulose acetate butyrate [18] have been reported. In the last case, due to the fractal structure of the conducting polymer inside the cellulosic matrix, the electronic conducting polymer percolation threshold is as low as 3.6% (w/w).

Recently, a series of IPNs based on an aliphatic polycarbonate and CAB was prepared through simultaneous polymerization techniques [19]. In the reported composition range, the damping properties of the polycarbonate as measured by DMA are increased by the CAB introduction and the IPNs are transparent.

In the present study, the synthetic pathway of IPNs composed of cellulose acetate butyrate and a telechelic α,ω-divinyl-poly(dimethylsiloxane) are presented. The synthesis involves a *one pot-one shot* process in which all components are first mixed together and the networks are then formed through independent reaction mechanisms and more or less simultaneously according to the experimental conditions. The kinetics of the formation of the single PDMS network as well as the IPNs have been investigated by middle- and near-FTIR spectroscopy. In order to qualify the network interpenetration level, thermomechanical properties of the resulting materials have been studied by DMA. In this study, all the experiments were carried out with the same material composition in which the CAB and PDMS weight proportions are identical, i.e. 1:1.

2. Experimental part

2.1. Materials

α,ω-Divinyl-poly(dimethylsiloxane) (di-vinyl-PDMS in the text) $M_n = 650$ and $1150\ \mathrm{g \cdot mol^{-1}}$ (for one kinetic experiment) determined by ^{1}H NMR (ABCR), dibutyltindilaurate (DBTDL, Aldrich), Desmodur® N3300 (Bayer), trimethylolpropane tris(3-mercaptopropionate) (Trithiol in the text, Aldrich) and cellulose acetate butyrate (CAB in the text—4% acetate–50% butyrate–46% OH, Mn = 16000 g mol^{-1} Acros Organics) are used as received. 2,2-Azobis isobutyronitrile (AIBN, Acros Organics) is recrystallized in methanol before use. Chloroform (Carlo Erba, puro grade) is distilled before use.

2.2. Preparation of single networks

A PDMS single network is prepared as following: 1 g di-vinyl-PDMS ($M_n = 650\ \mathrm{g \cdot mol^{-1}}$), 0.46 g trithiol ([HS]/[C=C] = 1.1), 29 mg AIBN ([AIBN]/[C=C] = 0.05) and 2 ml chloroform are stirred together under argon atmosphere for 30 min at room temperature. The mixture is then poured into a mould made from two glass 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 uncasted and kept for 1 h at room temperature and then dried for 2 h at 50 °C under vacuum. After complete solvent evaporation, the sample is cured for 2 h at 110 °C.

A cellulosic single network is prepared by dissolving 1 g cellulose acetate butyrate (CAB) into 3 ml $CHCl_3$. Desmodur® N3300 (0.55 g) ([NCO]/[OH] = 0.60) and DBTDL (28 μl) ([DBTDL]/[OH] = 0.01) (cross-linker and catalyst for the CAB network formation, respectively) are added to this solution which is then poured in a Petri dish. The solvent is allowed to evaporate at room temperature for 12 h after which the mixture is cured at 60 °C for 2 h.

2.3. Preparation of IPNs and semi-IPNs

PDMS–CAB (1:1 by weight) IPN is prepared as following: 1 g CAB is dissolved in 5 ml chloroform, then 1 g di-vinyl-PDMS ($M_n = 650\ \mathrm{g \cdot mol^{-1}}$), 0.46 g trithiol ([HS]/[C=C] = 1.1), 0.55 g Desmodur® N3300 ([NCO]/[OH] = 0.60) and 29 mg AIBN ([AIBN]/[C=C] = 0.05) are stirred together under nitrogen atmosphere for 30 min. DBTDL (140 μl) ([DBTDL]/[OH] = 0.05, although this molar ratio has been later varied, see Section 4) is added as last component just before the mixture is poured into a mould. The mould is then kept at 50 °C for 16 h. After 16 h, the sample is dried and post-cured as described for the PDMS single network.

The synthesis of a semi-IPN in which CAB is the non-cross-linked compound entrapped in a PDMS network is similar to the IPN synthesis described above with the following modifications: Desmodur® N3300 and DBTDL are not introduced in the reaction medium. On the other hand, the synthesis of a semi-IPN in which di-vinyl-PDMS is the non-cross-linked component embedded in a CAB network, trithiol and AIBN are not introduced in the initial mixture and the molar ratio [NCO]/[OH] and [DBTDL]/[OH] are set at 0.60 and 0.01, respectively.

In all semi-IPN and IPN preparations reported in this study, CAB and di-vinyl-PDMS are introduced in one to one weight proportions.

2.4. Kinetic experiments

The cross-linking reaction kinetics of the components in the single networks, IPNs and semi-IPNs can be followed in bulk and in real time in the near and middle infrared (NIR and MIR) wavelength regions (7500–1800 $\mathrm{cm^{-1}}$). Indeed the PDMS network formation can be monitored both by the disappearance of the C=C terminal bonds and cross-linker H–S groups. These two chemical bonds show isolated absorption bands at 6136 and 2256 $\mathrm{cm^{-1}}$, respectively, and are chosen as witnessing the PDMS network formation kinetic. The cellulose network formation kinetics can be followed either by the disappearance of the vibration bands of the cross-linkable free hydroxyl groups of the CAB and/or the isocyanate groups of the Desmodur® N3300 cross-linker or alternatively by the appearance of the vibration band of the urethane N–H group which results from the reaction of the CAB OH-free groups with the NCO Desmodur® N 3300 groups. The vibration bands of alcohol (free CAB OH) and amine (urethane link formation) functions are located in the 3500 $\mathrm{cm^{-1}}$ IR region and not well separated. Moreover, the CAB IR spectrum does not exhibit well separated bands which could be used in order to follow CAB cross-linking. The most precise possibility is to follow the cellulosic network formation by the disappearance of the isocyanate group absorption band of the Desmodur® N 3300 cross-linker. The isocyanate function shows a characteristic absorption band in the middle-IR region at 2270 $\mathrm{cm^{-1}}$ [20] which will be used here. In order to determine the CAB hydroxyl group conversion during the cross-linking, it is assumed here that each NCO group which disappears reacts with one and only cellulosic OH group. Although some uncertainty remains whether a NCO group can be destroyed by contaminating water for instance.

A given peak area (A) being directly proportional to the given function concentration through its molar extinction coefficient ε, the conversion–time profile can be easily 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 $p = 1 - A_t/A_0$, where p is the symbol for the conversion ratio varying from 0 to 1 and the A subscripts *0* and *t* denote reaction times. No thickness correction is necessary, owing to the geometry of the sample holder that prevents thickness variation during the reaction.

PDMS single network and IPNs are directly synthesized in the IR cell which is made for each kinetic study from two plates separated by a Teflon® gasket. Glass windows and 1 mm thick gaskets are used to record the vinyl conversion because the corresponding absorption band is located in the near infrared. On the other hand, $\mathrm{CaF_2}$ calcium fluorine windows and 250 μm thick gaskets are used when the NCO and HS conversions are recorded in the middle infrared region. The cell is inserted in an electrical heating jacket with an automatic temperature controller (Graseby Specac). The temperature of 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 $\mathrm{cm^{-1}}$ by averaging of 10 consecutive scans with a resolution of 4 $\mathrm{cm^{-1}}$. During kinetic studies, accumulations are repeated every 5 min.

3. Characterization techniques

The amount of unreacted starting material is determined by a $\mathrm{CH_2Cl_2}$ Soxhlet extraction (48 h) of a known weight of each single network or (semi-)IPN sample. After extraction, the sample is dried in a vacuum oven at 50 °C for 8 h and then weighed. The extracted 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 weights of samples before and after extraction, respectively.

Dynamic thermomechanical analysis (DMA) measurements are carried out on single network, IPN or semi-IPN samples (typically 6 mm × 30 mm × 1 mm) with a Q800 model (TA Instruments) operating in tension mode. Experiments are performed at a 1 Hz frequency and a heating rate of 2 °C $\mathrm{min^{-1}}$ from −140 to 150 °C. The set up provides the storage and loss moduli (E' and E'') and the damping parameter or loss factor (tan δ) defined as the ratio tan $\delta = E''/E'$.

4. Results and discussion

In order to improve the mechanical properties of a silicone network, it was decided to associate it to a thermoplastic cellulose acetate butyrate (CAB) network into interpenetrating polymer network (IPN) architecture. As mentioned in Section 1, the *one pot-one shot* process in which all components are mixed together from the start is the most efficient way to prepare an IPN. However, in such a process the chemical reactions leading to the formation of the two networks must proceed according to non-interfering mechanisms. One the easiest way to cross-link di-vinyl-PDMS is to process through a Pt compound catalysed hydrosilylation. However, Pt catalysts are known to be strongly complexed both by tin compounds and urethane bonds. Thus, this possibility was discarded and a thiol-ene addition cross-linking considered instead. The PDMS network is obtained from di-vinyl-PDMS and trimethylolpropane tris(3-mercaptopropionate) (trithiol) as cross-linker through a thiol-ene radical process initiated with AIBN. The CAB network is cross-linked through its free OH groups with a Desmodur® N3300 pluri-isocyanate. The alcohol/isocyanate reaction is catalysed by DBTDL leading to urethane cross-links.

The IPN final material morphology results from a complex interplay between the relative cross-linking rates of the two networks and the rate of phase separation. In this work, we tried to avoid the CAB and di-vinyl-PDMS macrophase separation by controlling the relative formation rates of silicone and CAB networks.

4.1. Individual networks

Single CAB and PDMS networks and several semi-IPNs therefore have been synthesized separately in order to establish at least part of the experimental conditions for further IPN synthesis study.

A single CAB network is prepared by dissolving 1 g CAB into 3 ml chloroform. Then, 0.55 g cross-linker (Desmodur® N3300) and 28 μl catalyst (DBTDL) are added to the solution which is then poured into a Petri dish. If the mixture is directly cured at 60 °C, the resulting network is extremely brittle and further characterizations are not possible. A better result is obtained if the solvent is slowly evaporated at room temperature for 12 h. The mixture is then cured at 60 °C for 2 h. The sample can then be handled for further analysis (DMA for instance).

The PDMS network synthesis is carried out from 1 g di-vinyl-PDMS ($M_n = 650\ \mathrm{g \cdot mol^{-1}}$) and 0.46 g trithiol by thiol-ene addition initiated by AIBN. The thiol-ene reaction exhibits several unique advantages such as being generally uninhibited by oxygen [21] and proceeding rapidly with a reasonable amount of initiator typically 3% by weight [22].

The radical thiol-ene addition reaction proceeds through three steps: the formation of a thiyl radical promoted by AIBN initiation, addition of the thiyl radical to a vinyl group, followed by radical transfer from the ensuing carbon radical to a thiol functional group. These successive initiation/chain transfer reactions serve as the basis for the thiol-ene polymerization/cross-linking reaction [23]. It was therefore important to check that vinyl and thiol groups disappear simultaneously under our experimental conditions and thus be able to discard the possibility of disulfide link formation.

As far as the single PDMS network synthesis is concerned, the PDMS vinyl and cross-linker thiol function conversions at 50 °C as a function of time are shown in Fig. 1(a). Thiol conversion is monitored using the S–H absorption band variation at $2570\ \mathrm{cm^{-1}}$ [22]. The $CH_2{=}CH{-}$ overtone band at $6136\ \mathrm{cm^{-1}}$ is chosen to determine the time dependence of the terminal PDMS double bond conversion [24,25].

The vinyl and thiol function disappearance is clearly simultaneous and the conversion curve reaches a plateau corresponding to about 90% molar conversion for both functions after 30 min. An extra 5% conversion then slowly proceeds during the next hours. This kinetic study thus shows that vinyl and thiol groups react together and form a PDMS network where the S–S bond formation seems to be avoided. In these experimental conditions, the achievement of the synthesis of the PDMS network can be considered to proceed within 1 h at 50 °C.

Desmodur® N3300 cross-linked CAB is a rigid transparent material containing less than 3% unreacted material as estimated from Soxhlet extraction. In the case of the PDMS network which is also a transparent material, the amount of extracted material is lower than 5% and was identified as di-vinyl-PDMS by ^{1}H NMR.

Fig. 2 shows the storage modulus E' and the tangent loss (tan δ) of the single PDMS (a) and CAB (b) networks, respectively. Schematically, three temperature domains can be observed. Below −100 °C for single PDMS network and below +90 °C for CAB network, respectively, the materials are in the glassy state, i.e. out of equilibrium and the storage modulus E' is almost constant at 3 GPa. The response of the networks is mainly elastic. Between −100 and −50 °C for the PDMS network and between +90 and 130 °C for the CAB one, a strong decay of E' is observed during the so-called main or α relaxation. At the same time, tan δ display a maximum (tan δ (PDMS) = 1.4 at $T\alpha_{\mathrm{PDMS}} = -70$ °C and tan δ (CAB) = 0.85 at $T\alpha_{\mathrm{CAB}} = +113$ °C). This relaxation phenomenon is associated with an energy dissipation involving cooperative motions of chain sequences, in relation with the glass transition phenomenon. Then the elastic part of the storage modulus E' reaches a plateau (rubbery modulus) at 1 and 20 MPa for single PDMS and CAB networks, respectively. Thus, the α relaxation

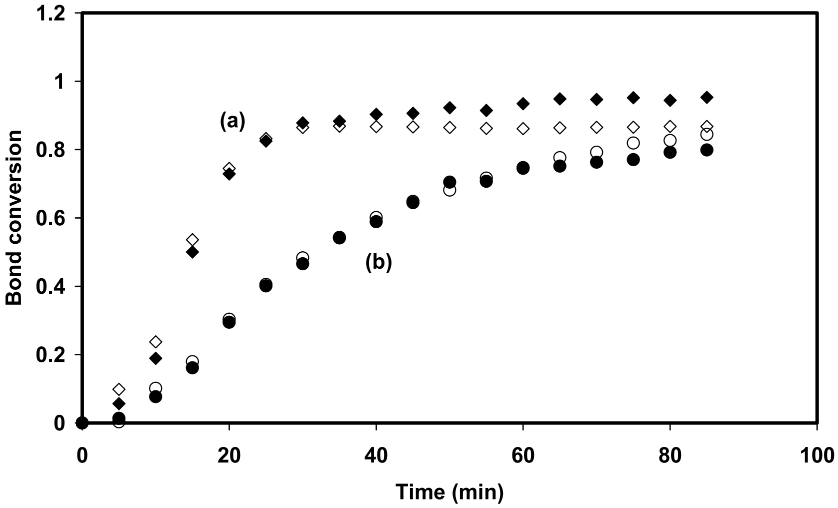

Fig. 1. FTIR conversion of (a) vinyl (♦) and thiol (◇) in a single PDMS network mixture and of vinyl (●) and thiol (○) in a PDMS/CAB (1:1) IPN mixture. [AIBN]/[C=C] = 0.05 and [HS]/[C=C] = 1.1. $T = 50$ °C.

approximately separates two different mechanical behaviours as classically observed.

4.2. Semi-IPNs: linear CAB in cross-linked PDMS

The PDMS–CAB (1:1 by weight) semi-IPN in which CAB is not cross-linked is translucent to opaque material. The amount of unreacted material as measured from Soxhlet extraction is about 43 wt% and is identified as linear CAB by ^{1}H NMR. Thus, almost all CAB material can be extracted from the PDMS network. This result shows that there is no or very weak interaction between the two polymers as expected and that the PDMS network forms with a similar cross-linking density in the presence of linear CAB as when it is synthesized alone (5% extractible material).

The mechanical behaviour of the PDMS–CAB (1:1) semi-IPN in which PDMS is cross-linked is displayed in Fig. 3. As expected the semi-IPN displays two main relaxations at −67 and +115 °C corresponding to the α relaxations of PDMS and CAB, respectively, indicating that macrophase separation occurs during the semi-IPN synthesis. The strong decay of E' from −70 °C followed by a second decay of E' +100 °C allows to assume that the continuous phase is the silicone phase with CAB macrodomains dispersed in the continuous phase. This result is in agreement with the general assumption that the continuous phase in a semi-IPN is usually the cross-linked phase which is formed first and that the non-cross-linked polymer is the dispersed phase [26,27]. These results are also in agreement with the macroscopic translucent aspect of the semi-IPN.

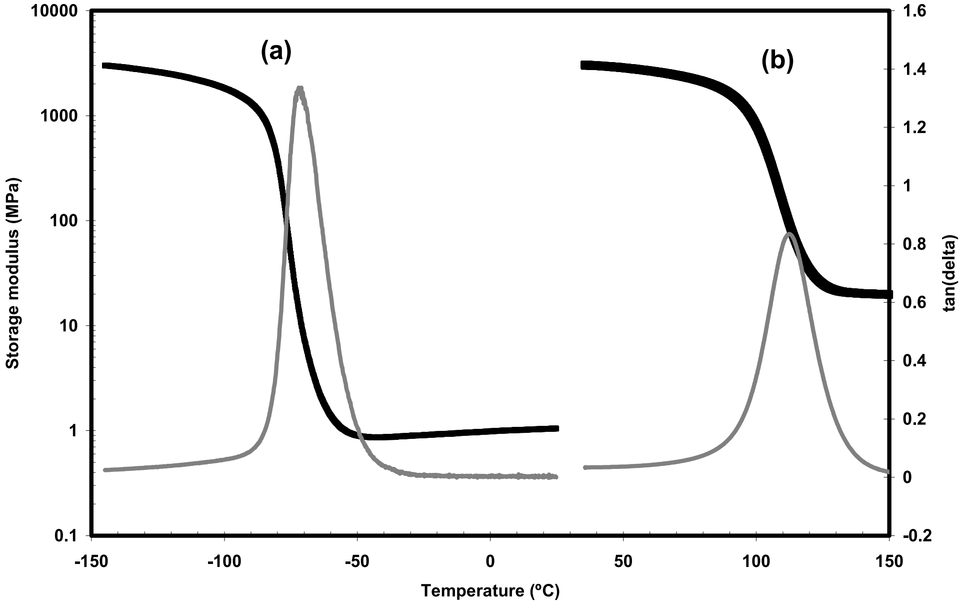

Fig. 2. (a) PDMS and (b) CAB single network storage modulus (black) and tan δ (grey) as function of temperature.

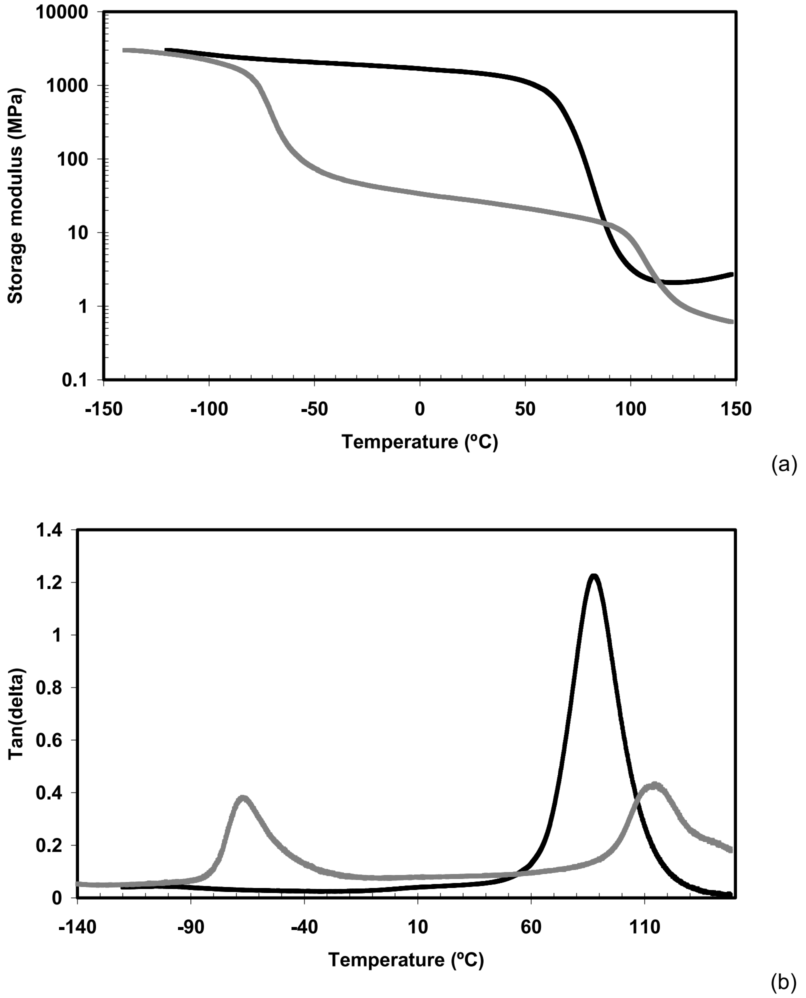

Fig. 3. (a) Storage modulus and (b) tan δ as function of temperature of semi-IPN in which (grey) PDMS is cross-linked and (black) CAB is cross-linked.

4.3. Semi-IPNs: linear PDMS and cross-linked CAB

The PDMS–CAB (1:1 by weight) semi-IPN in which CAB is cross-linked is white opaque material. The amount of Soxhlet extracted material is equal to 44% and identified as di-vinyl-PDMS oligomers by ^{1}H NMR. Similarly as for the other semi-IPN, this result shows that the CAB network formation is not impaired by the presence of the other polymer.

The effects of the presence of linear di-vinyl-PDMS oligomers in the CAB network can be discussed in the light of the DMA measurements (Fig. 3). Curiously this semi-IPN exhibits only one α relaxation close to 90 °C which can be assigned to the CAB phase. Since the PDMS used in this work is a very low molecular weight species ($M_n = 650\ \mathrm{g\ mol^{-1}}$) the α relaxation of this uncross-linked oligomer cannot be detected under our DMA experimental set up. The position of the $T\alpha_{\mathrm{CAB}}$ peak ($T\alpha_{\mathrm{CAB}} = 90$ °C) is shifted towards lower temperatures compared to its value measured on the CAB single network ($T\alpha_{\mathrm{CAB}} = 113$ °C). This decrease can clearly be assigned to the plasticizing effect of di-vinyl-PDMS oligomers embedded in the CAB network. Thus, it can be concluded that the mechanical properties of semi-IPN are close to those of a plasticized CAB network. On the other hand, the optical characteristics agree with macrophase separation, the material being opaque.

4.4. IPNs

PDMS–CAB (1:1) IPN is synthesized through a *one pot-one shot* process, i.e. all reactants are mixed together and the cross-linking reactions for both networks are started at the same zero time. Thus 1 g di-vinyl-PDMS ($M_n = 650\ \mathrm{g\ mol^{-1}}$), a thiol amount corresponding to a 1.1 molar ratio and 5% molar ratio AIBN with respect to C=C are mixed together. Then 1 g CAB network with Desmodur® N3300 ([NCO]/[OH] = 0.6) are added, the formation of the CAB network being catalysed by dibutyltindilaurate. The IPN is then formed at 50 °C. The molar ratio [NCO]/[OH] is set at 0.60 on purpose in this study. Indeed, this does not lead to complete cross-linking of all the free OH groups of CAB but this limitation in the cross-linking density was chosen in order to keep the final

IPNs as relatively flexible materials. The CAB cross-linking density effects on the final material mechanical properties will be described in a further paper.

Considering the nature of all components present in the starting medium it turns out to be necessary to examine in more detail *all* possible reactions which can occur in the medium and which are listed below schematically in each case for one function. The first two reactions are expected to lead to the formation of the desired IPN.

$$R_1\text{–CH=CH}_2 + \text{HS–}R_2 \rightarrow R_1\text{–CH}_2\text{–CH}_2\text{–S–}R_2 \text{ leading to the PDMS network formation} \quad (1)$$

$$R_3\text{–OH} + R_4\text{–NCO} \rightarrow R_3\text{–O–CO–NH–}R_4 \text{ leading to the CAB network formation} \quad (2)$$

The three following reactions may also occur to various extents and they will clearly interfere with reactions (1) and (2), i.e. with the regular formation of the IPN.

$$\text{HS–}R_2 + R_4\text{–NCO} \rightarrow \text{R–S–CO–NH–}R_4 \text{ leading to a grafted IPN [28]} \quad (3)$$

$$\text{HS–}R_2 + \text{HS–}R_2 \rightarrow R_2\text{–S–S–}R_2 \text{ leading to defects in the PDMS network structure} \quad (4)$$

$$\text{HS–}R_2 + \text{DBTDL} \rightarrow R_2\text{–SH–DBTDL leading to a DBTDL concentration decrease in the medium which will slow down reaction (2) [29]} \quad (5)$$

First of all, it is observed through FTIR kinetic monitoring that the disappearance of thiol and vinyl groups is simultaneous in the IPN synthetic medium as it is in the single network (Fig. 1(b)). However, it must be mentioned that this kinetic is significantly slowed down compared to what is observed in the formation of a single PDMS network and this decrease in the cross-linking rate clearly arises from the much higher viscosity due to the addition and further dissolution of solid CAB. Now we checked separately that these vinyl groups do not react when only AIBN is present in the medium, i.e. without the trithiol compound, which means that they are not reactive enough to undergo self-cross-linking. Thus it can be concluded that reaction (1) is to say the least preponderant in the starting IPN mixture.

As a second point in the study of possible side-reactions, it can be observed in that the thiol and vinyl group reactions

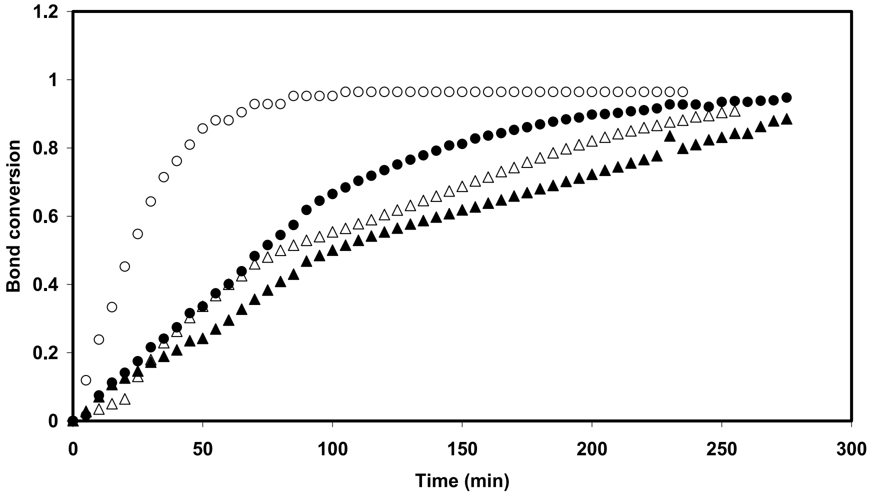

Fig. 4. FTIR conversion of thiol groups (○ and ●) and NCO groups (△ and ▲) in PDMS–CAB (1:1) IPNs with PDMS ($M_n = 650\ \text{g·mol}^{-1}$) and PDMS ($M_n = 1150\ \text{g·mol}^{-1}$), respectively; [DBTDL]/[OH] = 0.05, [NCO]/[OH] = 0.60, [AIBN]/[C=C] = 0.05, [HS]/[C=C] = 1.1, T = 50 °C.

remain simultaneous whether NCO groups are present (Fig. 1(b)) or not (Fig. 1(a)). From this observation it can be concluded that reaction (3) occurs to a very little extent if any otherwise the thiol disappearance kinetics would be enhanced compared to that of the vinyl one.

This is furthermore supported by the results (Fig. 4) of a similar kinetic study carried out with a di-vinyl-PDMS with $M_n = 1150$ g instead of $M_n = 650\ \text{g}\cdot\text{mol}^{-1}$, where half the thiol function amount of course is required in order to perform the cross-linking. In this case of course the rate of the disappearance of the thiol groups is divided by about two; however, it is observed that the kinetics of the disappearance of the NCO functions is almost not affected. Thus the possibility of grafting between the two networks can be reasonably discarded.

Reaction (4), however, cannot be excluded completely. Indeed after two-hour reaction (Fig. 5(a)) the thiol conversion reaches 100% although the HS molar amount is introduced with a 10% molar excess with respect to vinyl groups.

However, the excess thiol groups could also react with DBTDL according to reaction (5). Taking into account the fact that the equilibrium constant of this last reaction is equal to 1 [29], the reaction should be easily shifted towards the left by thioether (reaction (1)) and disulfide bridge (reaction (4)) formation. The only measurable effect of the occurrence of reaction (5) would be a slowing down effect on the CAB network formation.

Thus the main point we focused on next was to study the effect of DBTDL concentration in the medium keeping all other compound concentrations constant and the results are reported on Fig. 5. The [DBTDL]/[OH] molar ratio was varied from 0.1 to 0.01 in the initial PDMS–CAB (1:1) mixture. As depicted on Fig. 5(a), the PDMS formation kinetics is slightly affected by the DBTDL content. Indeed, the reaction (5) between thiol and DBTDL is shifted towards the right when the DBTDL amount is increased leading to a decrease in the free thiol group concentration: the thiol conversion initial rate is thus slightly decreased. However, the DBTDL amount has no effect on the thiol final conversion. Thus the PDMS network formation is not significantly affected (Fig. 5(a)).

In the same experiments, the NCO conversion versus time was examined next. This initial rate slightly increases when DBTDL content increases from 1 to 2.5% and remains unchanged up to 10% DBTDL content as shown in Fig. 5(b). The NCO conversion at 350 min increases from 60 to 100% when the DBTDL content increases from 1 to 10%. However, a pseudo-plateau is reached after about 100 min indicating that the CAB cross-linking reaction rate slows down. The pseudo-plateau conversion values increase from 15 to 60% when the [DBTDL]/[OH] ratio increases from 1 to 5%. This pseudo-plateau could arise from a significant increase in the viscosity of the medium which would decrease the mobility of the reacting species. Indeed the gel point of the PDMS network formation has been calculated as equal to 91% ($p = 2/f$ thiol-ene reaction is considered as a polycondensation) and occurs in time exactly where the pseudo-plateau appears in the CAB network formation kinetic curve. When the [DBTDL]/[OH] ratio is equal to 10%, the pseudo-plateau is not detected because the CAB has reached its own gel point before the PDMS does in these conditions. The CAB gel point cannot be calculated because the molar mass of Desmodur® N3300 is unknown.

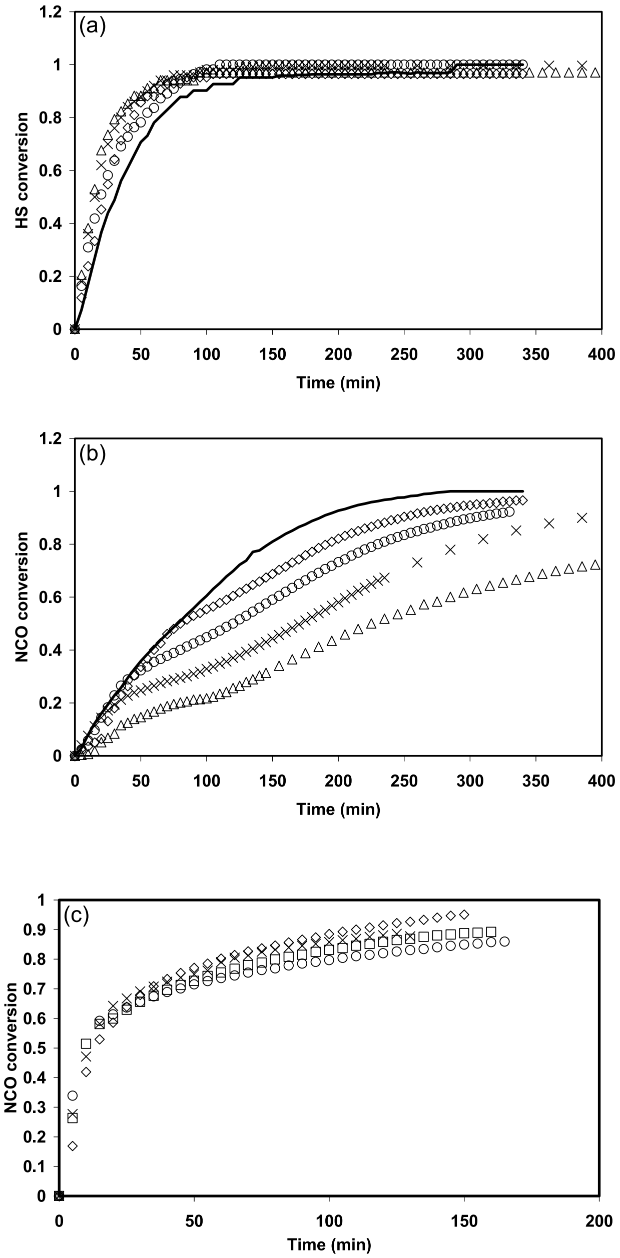

Fig. 5. (a) Thiol, (b) isocyanate conversions in IPN for different [DBTDL]/[OH] molar ratio (—) 10, (◇) 5, (○) 2.5, (×) 1.75 and (△) 1%—[NCO]/[OH] = 0.60, [AIBN]/[C=C] = 0.05, [HS]/[C=C] = 1.1, (c) isocyanate conversion in PDMS linear/CAB semi-IPN (1:1) for different [DBTDL]/[OH] molar ratio (□) 10, (○) 7.5, (◇) 5 and (×) 1%—[NCO]/[OH] = 0.60, T = 50 °C.

In order to better understand the effect of the presence of

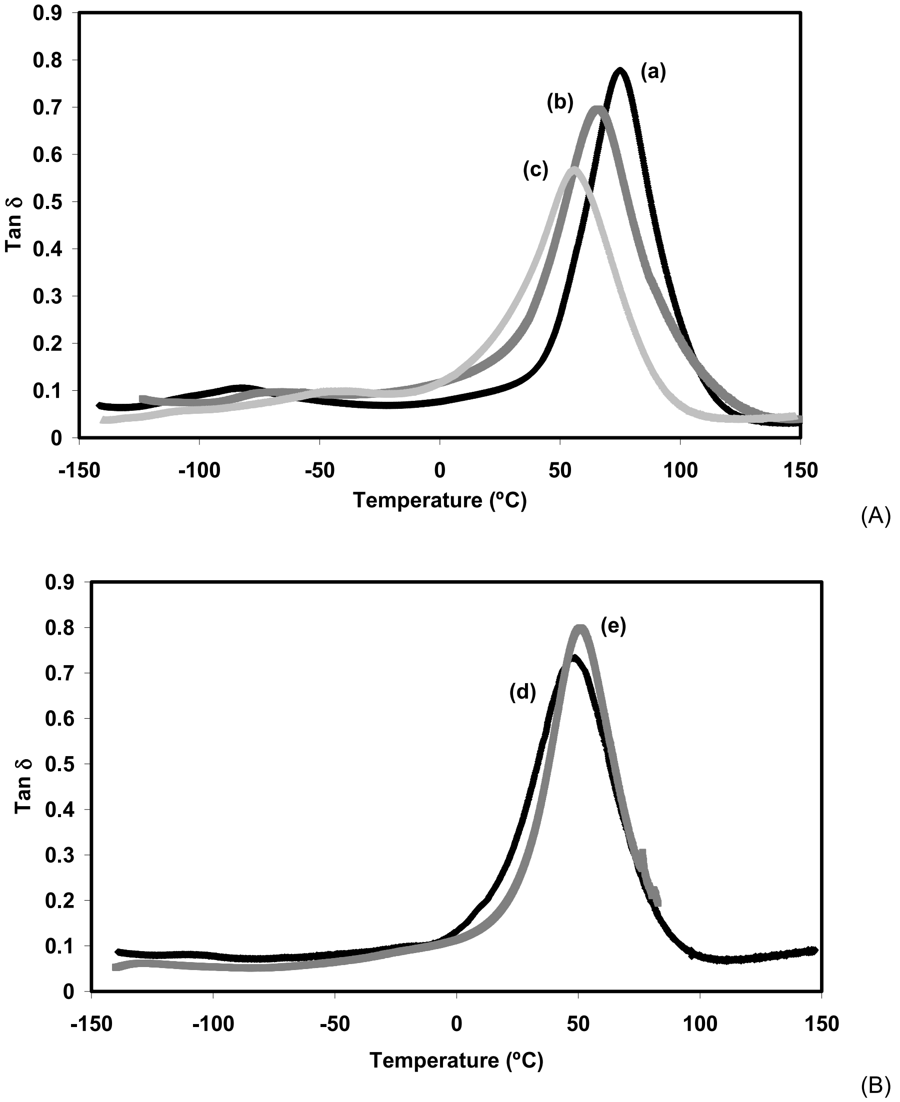

Fig. 6. DBTDL effects on thermomechanical properties of PDMS/CAB (1:1) IPNs (a) 1, (b) 1.75, (c) 2.5, (d) 5 and (e) 10% [DBTDL]/[OH] molar ratio—[NCO]/[OH] = 0.60, [HS]/[C=C] = 1.1, [AIBN]/[C=C] = 0.05.

thiol functions, kinetic studies were carried out on a semi-IPN mixture without thiol compound and AIBN leading to PDMS trapped in a CAB network (Fig. 5(c)). In this case too, the initial conversion is hardly affected by the DBTDL content (from 1 to 10%) but a huge difference is observed in the initial NCO conversion rate between the semi-IPNs and the IPNs. Indeed, after 10 min, the NCO conversion reaches 40–50% in the semi-IPN instead 7% in the similar IPN mixture. Thus the CAB network formation rate is drastically slowed down in the first 20 min when the thiol compound is present in the medium. This can only arise from the occurrence of reaction (5) between thiol and DBTDL. Furthermore, the conversion–time profiles in the semi-IPNs are quite similar for all experiments whatever the DBTDL amount from 1 to 10% which was not the case in the IPNs. A pseudo-plateau is reached after 60 min for NCO conversions between 70 and 80% according the proportion of DBTDL. Those results mean again that the thiol presence is really responsible for the differences observed in the NCO conversion.

When [DBTDL]/[OH] ratio is below or equal to 1.75%, the resulting IPNs are translucent. On the other hand, when this molar ratio is equal to or above 2.5% the IPNs are transparent which is characteristic of a better interpenetration of the two networks. It seems that 40% of the NCO groups must react before the PDMS network formation ends in order to obtain a transparent IPN. The material transparency is probably tightly linked to a competition between the CAB network formation kinetics and the thermodynamic phase separation. In order to obtain a transparent material the DBTDL content must be higher than 2.5%. Indeed, the NCO conversion must be significant before the complete PDMS network formation in order to avoid phase separation process.

In conclusion, these kinetic studies have shown that thiol functions do not seem to react with isocyanate groups such that the obtained IPN is not grafted. However, the thiol groups react with DBTDL leading to an inactive species which has the effect of slowing the CAB network formation. Furthermore, the thiol groups certainly react leading to disulfide bridges (according to reaction (4)) since they are introduced in a 10% molar excess over C=C groups and since they have totally disappeared at the end of the IPN formation. This last reaction would only introduce some defects in the PDMS network structure and do not seem to impair the properties, namely mechanical properties of the material. On the other hand, these possible defects are preferred to a lower quality of PDMS network cross-linking which is obtained when no excess thiol is introduced.

The extraction of PDMS–CAB (1:1) IPNs leads to less than 10% unreacted material which is composed of di-vinyl-PDMS (70 mol%) and CAB (30 mol%) as checked by ^{1}H NMR and that for all studied DBTDL contents. This result confirms that CAB and PDMS polymers are cross-linked and only few linear chains are still present after the IPN synthesis.

The PDMS–CAB (1:1) IPN properties were investigated by DMA measurements. The viscoelastic behaviour was studied at a frequency of 1 Hz over a −140 to 150 °C temperature range. The DMA analysis of PDMS–CAB (1:1) IPNs as a function of DBTDL proportion are shown on Fig. 6(A) and (B). From Fig. 6(A), it can be seen that IPNs prepared with 1% of DBTDL proportion exhibit two main transitions at −84 and 60 °C. The position of the first transition ($T\alpha_1 = -84$ °C), which can be assigned to the rich PDMS domains, are shifted towards higher temperatures with increasing DBTDL catalyst content from 1 to 2.5%. Simultaneously, the second transition which can be assigned to the rich CAB domains are shifted from +79 to +55 °C when [DBTDL]/[OH] molar ratio increases from 1 to 2.5%. Furthermore, these peaks decrease in height from 0.78 to 0.58 and become broader. These results suggest that macrophase separation decreases with increasing DBTDL catalyst.

The IPN transparency can be taken as one further evidence of the degree of material interpenetration. As mentioned before, IPNs prepared with 1 and 1.75% of DBTDL are translucent, whereas in the presence of 2.5% DBTDL catalyst, the IPN is a transparent material. These results are consistent with DMA measurements. IPNs synthesized with a [DBTDL]/[OH] molar ratio equal to 5 and 10% have also been analysed by DMA and the tan δ are displayed on Fig. 6(B). Only one main transition can be observed around 50 °C. The transitions which should correspond to the PDMS rich domains appear as a very small shoulder ([DBTDL]/[OH] = 5%) or are either not visible ([DBTDL]/[OH] = 10%). It can be assumed that the interpenetration between the two networks is better compared to those described on Fig. 6(A). Thus, the phase separation decreases with increasing the [DBTDL]/[OH] molar ratio from 5 to 10%.

These results (kinetic studies and DMA measurements) show that the phase morphology of the *one pot-one shot* IPNs was changed by changing the polymerization/cross-linking reaction kinetics of each network. When the rate of CAB cross-linking reaction is increased, materials are transparent and exhibit only one main transition.

5. Conclusion

Interpenetrating polymer networks combining cellulose acetate butyrate and di-vinyl-PDMS in one to one weight proportions have been synthesized. The synthesis involves a *one pot-one shot* process in which all components are first mixed together and the networks are then formed independently and quasi-simultaneously. The amounts of extracted material measured on these samples are always lower than 10%.

The kinetic studies have shown that thiol functions from the di-vinyl-PDMS cross-linker do not react with the isocyanate groups from the CAB cross-linker and that the obtained IPNs are not grafted. However, thiol groups form stable species with the DBTDL catalyst which have the effect of decreasing the actual available quantity of catalyst in the medium thus slowing down the CAB network formation. Consequently, in order to obtain a transparent material withstanding the presence of thiol functions the DBTDL proportion must be increased. Indeed, it was shown that the NCO conversion level must be at least 40% before the complete PDMS network formation in order to avoid phase separation.

When the DBTDL content is correctly adjusted, the synthesized IPNs are transparent and just one glass transition temperature lying between those of the single CAB and PDMS networks is observed by DMA analysis. This result shows that the two polymers are correctly interpenetrated and no phase separation is observed at the DMA scale. Moreover, this IPN exhibits some characteristics, which would allow it to be defined as a true IPN. This study has been pursued for different PDMS/CAB compositions and the results will be reported in a second paper together with the very peculiar stress–strain behaviour of the materials. Moreover, now that the feasibility of IPNs from CAB and a low molecular weight PDMS has been shown, the effect of increasing the PDMS molecular weight on the properties of the IPNs will be investigated.

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