

Facile elaboration of polymethylmethacrylate / polyurethane interpenetrating networks using Diels-Alder reactions

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Abstract Thermo-reversible PMMA/PU interpenetrating polymer networks were successfully prepared by Diels-Alder (DA) reaction using a furan-functionalized polymethyl methacrylate, furan-functionalized polyurethane and a maleimide-based coupling agent. First, homo-networks were synthesized and characterized in order to predict the characteristics of the corresponding interpenetrating network. Polyurethane networks were confirmed to be reversible with a temperature of retro-Diels-Alder varying from 135 °C to 144 °C depending on the cross-linking density. PMMA/PU blends are completely immiscible as shown by the presence of two Tgs corresponding to the two phases in DSC results. Due to the presence of supramolecular interactions, no phase separation was observed in the simultaneously cross-linked PMMA/PU networks. Thermal behavior and de-cross-linking of the IPNs were studied by DSC, solubility tests and rheology. Swelling tests allowed the evaluation of the networks density.

Keywords Diels-Alder · Interpenetrating polymer network · Thermo-reversible · Rheology

Introduction

Polymer blends have received increasing attention because they represent an economic and efficient way to prepare new

materials with attractive and variable end-use properties. Multiphase blends are generally obtained when mixing immiscible polymers owing mostly to the large size of the polymer chains that decreases the mixing entropy. They have poor mechanical performance because of the low interfacial adhesion between the polymer phases.

Polymer blending of a brittle polymer like PMMA with a rubber modifier can be an effective way to improve its physical and mechanical properties. The PMMA-based blends with thermoplastic polyurethane (TPUs) as rubber modifier are of considerable interest principally for promoting the toughness of PMMA. The interest of TPU use is due to their excellent physical properties, chemical and abrasion resistance [1].

PMMA/TPUs blend were made either in bulk [1] or in solution [2–4] from linear polymers, or synthesized in situ from monomers [5–7].

Poomalai et al. [1] prepared different PMMA/TPU blends with different proportions of TPU and with major PMMA by extrusion of both polymers. Mechanical properties and abrasive wear of different blends were studied. A significant amelioration of elongation at break was observed. This improvement is accompanied by a decrease of the tensile strength and tensile modulus. However, neat PMMA showed better wear resistance compared to PMMA/TPU blends. The cracking and deep furrows in PMMA/TPU blends observed at the material surface can explain this property.

Film polymer blends prepared by casting lead to a better interaction between the two phases as shown by Machado et al. [2–4]. By FT-IR analysis, they observed the presence of hydrogen bonds between N-H of polyurethane and C=O of PMMA from the appearance of new bands in the spectrum. They affirmed that the blend became partially miscible due to this interaction.

An alternative way of creating polymer blends is the synthesis in situ from monomers as reported by Lipatov et al. [5, 6]. The PMMA/PU blends were prepared by simultaneous polymerization of the monomers. In this case, the conversion was

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limited by phase separation. The blends, composed mainly of PMMA, had a typical dispersion-droplet structure. The effect of the incorporation of additives (fumed silica or metals chelates) with blend components was studied. It was reported that, especially with fumed silica, the phase separation was delayed.

One of the known methods to reduce phase separation in polymer blends is the development of IPNs. An interpenetrating polymer network is a polymer comprising two or more networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other [8]. The entanglement of two cross-linked polymers leads to forced miscibility compared to usual blends and the resulting materials are expected to have a good dimensional stability [9]. Several types of IPNs can be found depending on the synthesis method: sequential IPNs, simultaneous IPNs, latex IPNs, concentration gradient IPNs, thermoplastic IPNs, semi-IPNs [10] and grafted IPNs [9].

Polyurethane/poly(methyl methacrylate) (PU/PMMA) simultaneous IPNs have been extensively studied [11–18]. One of the earliest works on PMMA/PU blend based IPN shows that the dispersion of PU particles in PMMA matrix is much thinner in an IPN than in a semi-IPN, and even more as compared to a blend of linear polymers [19].

Siddaramaiah et al. [20] reported the synthesis of PMMA/PU interpenetrating networks. The IPNs were obtained by simultaneous polymerization of castor oil, 4,4'-diphenyl methane diisocyanate, and methyl methacrylate, with benzoyl peroxide as an initiator and ethylene glycol dimethylacrylate as a cross-linker. The physico-mechanical properties, such as tensile strength, tear strength and surface hardness of PU/PMMA IPNs increased with the increase in PMMA content. This was explained again by hydrogen bond formation between the N-H group of PU and the C=O group of PMMA. More recently, Kong et al. [21, 22] have prepared similar IPNs composed of vegetable oil based polyurethane and polymethyl methacrylate. The morphological studies showed that the IPN presents five phases: sol phase, PU-rich phase, PU-rich interphase, PMMA-rich interphase, and PMMA rich phase. When PU presents the minor proportion in the system, the authors claim that the compatibilization is improved with higher NCO/OH molar ratio.

A higher compatibilization provides superior mechanical properties compared to the equivalent blends of immiscible linear polymers. However, and because of their cross-linked structure, they are not directly re-processable.

A convenient way for maintaining the possibility of re-processability is to use thermo-reversible networks. The Diels-Alder reaction between furan and maleimide moieties and its retro are particularly attractive to form and cut chemical

bonds under the effect of temperature. It is an approach that had been reported for different polymers [23–26] including PMMA [25] and PU [23–26] and for copolymers [27–33].

An organic–inorganic hybrid thermo-reversible IPN formation by means of DA reaction between maleimide and furan moieties was reported [34]. A mixture of two independent reactive systems was simultaneously cross-linked. Acid-catalyzed tetramethoxysilane was cross-linked while maleimide and furan-modified (poly(2-methyl-2-oxazoline)s) were cross-linked via Diels-Alder reactions. The thermo-reversibility of IPN was obtained when the cross-linked system constitutes the major phase, via retro DA reactions.

If immiscible initial furan-functionalized polymers are used, each of them is present principally in a different phase. In case a reaction with a multiimide occurs in each phase without any interaction with the other one, two different networks should be obtained: one in each phase.

Specific interactions between the two phases (supramolecular hydrogen bond) are in favor of entanglements between the different networks that can evolve under certain conditions to an IPN. In this study, the reactive system was chosen to maximize the interactions between the two phases and to obtain an IPN. The initially immiscible polymers are PMMA and polyurethane. These two polymers were chosen because of their specific interactions that should build the networks entanglement. This original and facile method for thermo-reversible IPN's elaboration will be evaluated in this study.

First homo-networks will be prepared. The characteristics, particularly thermal and thermo-mechanical properties of these networks will be used as reference for the characterization of the IPNs. Then IPNs will be prepared and characterized.

Experimental

Materials

4,4'-Methylenebis(cyclohexyl isocyanate) (H_{12} MDI, mixture of isomers, 90 %), furfuryl alcohol (FAL, 98 %), dibutyltin dilaurate and different solvents (THF, ethyl acetate, DMSO and DMF) were purchased from SIGMA ALDRICH. All reagents were used without further purification.

Hydroxyl telechelic polybutadiene (HTPB) Krasol[®] LBH-P 3000 ($M_n \sim 3,000 \text{ g.mol}^{-1}$, $f_{\text{alcohol}} = 1.9$) was offered by Cray Valley - Hydrocarbon Specialty Chemicals.

PMMA (from BIESTERFELD PLASTIC) with a molar mass of $100,000 \text{ g.mol}^{-1}$ and a glass transition of $95 \text{ }^\circ\text{C}$ was used.

Analysis

¹H-NMR analysis

¹H-NMR spectra were recorded in deuterated CDCl₃ and DMSO solutions at room temperature using a Bruker Avance II spectrometer operating at a frequency of 250 MHz. The chemical shift scales were calibrated on the basis of the TMS peak (0 ppm).

Size exclusion chromatography

Size exclusion chromatography (SEC) was conducted using a system (515 Waters) equipped with a triple detector consisting of a refractive index detector (Waters 2414), a Wyatt MiniDawn Treos low angle light scattering detector and a Wyatt Visco star viscosimeter. Two columns HR 0.5 and HR 3 from Waters were used. Molar masses were determined by DDL with index of refraction increment dn/dc values calculated for each sample using Wyatt Astra 5.3.4 software. The mobile phase THF flow rate was 1 mL.min⁻¹ and samples concentration was 3 mg.mL⁻¹. The injection volume was 100 μL.

DSC analysis

Differential scanning calorimetry (DSC) measurements were carried out with a Q10 instrument from TA Instruments. Samples were transferred to hermetic pans that were sealed. The samples were then analyzed during two sequences of heating/ cooling between -80 °C and 200 °C at a cooling and heating rate of 10 °C.min⁻¹. Transition temperatures (T_{gs}) were evaluated from the data recorded during heating by identifying the inflection points. The networks rDA temperature was determined from the first heating cycle. All the other data were collected from the second cycle.

Swelling characterization

For the swelling measurements, the gels were immersed in THF for 48 h at room temperature. Then they were removed from solvent and weighed at different times to determine the equilibrium swollen gel weight by extrapolation to the initial time. In order to obtain the weight of the dry gel, the samples were dried in a vacuum oven (2.10⁻¹ mbar) at 25 °C for 24 h.

Rheological analysis

Rheological studies were conducted in a ARES rheometer using parallel plate geometry (25 mm). The experiments were

performed within the linear viscoelastic regime under the dynamic oscillation mode using a 1 rad.s⁻¹ frequency. The gap between plates was maintained at 2 mm. Experiments were run from 160 °C to 70 °C at a constant cooling rate of 1 °C.min⁻¹.

Syntheses

PU networks synthesis

Furfuryl alcohol-HMM cyclo-adduct (FAL/HMM) synthesis
The used protocol of the N-hydroxymethylmaleimide (HMM) synthesis was described previously [26].

For the synthesis of FAL/HMM, 1.96 g (0.02 mol) of furfuryl alcohol and 2.54 g (0.02 mol) of HMM were refluxed for 24 h in a double necked flask under magnetic stirring. The white obtained precipitate was filtered under vacuum and washed several times with ethyl acetate. The powder was dried under vacuum for 24 h at 25 °C. The obtained yield was of 89 %.

Cross-linked polymer formation The synthesis of networks was conducted from HTPB, H₁₂MDI, FAL/HMM adduct and glycerol and with the dibutyltin dilaurate as catalyst. The catalyst/alcohol ratio was maintained at 10⁻². Four networks PUnet₁, PUnet₂, PUnet₃, PUnet₄, with various HTPB quantity were synthesized.

As an example, the synthesis of PUnet₁ was conducted as follows: 3.15 g (1.05*10⁻³ mol) of HTPB, 1.83 g (7*10⁻³ mol) H₁₂MDI, 1.01 g (4.5*10⁻³ mol) FAL/HMM adduct, 0.092 g (10⁻³ mol) glycerol and 0.041 g (6.55*10⁻⁵ mol) of the catalyst were mixed in DMF at 80 °C for 24 h. A swollen gel was obtained. It was then dried under vacuum at 35 °C for 24 h.

PU-PMMA networks synthesis

Furan-functionalized polyurethane (PU-F) synthesis Two PU-F, PU-F₁₁₀₀₀ and PU-F₄₆₀₀ with different chain lengths were synthesized from H₁₂MDI, FAL, glycerol and HTPB. The synthesis of PU-F₁₁₀₀₀ was carried out as follows. In a double necked flask with magnetic stirring, 0.588 g (6*10⁻³ mol) of furfuryl alcohol was mixed with 0.184 g (2*10⁻³ mol) of glycerol, 6.3 g (2.1*10⁻³ mol) of HTPB and 0.046 g (10.1*10⁻⁵ mol) of dibutyltin dilaurate at 80 °C until solubilization. Then 2.096 g (8*10⁻³ mol) of H₁₂MDI was added. The mixture was maintained at 80 °C for 3 h until complete reaction. Then the obtained solid was purified two times by dissolving in

chloroform and precipitating in water. The precipitate was dried under vacuum at 35 °C for 24 h.

Furan functionalized polymethyl methacrylate (PMMA-F) synthesis The furan-functionalized PMMA was synthesized by reactive extrusion between a commercially available PMMA and furfuryl alcohol and was described in a previous work [25].

Scheme 1 depicts the structure of obtained furan-functionalized PMMA.

Two polymers, PMMA-F₁₃ and PMMA-F₂₆ with furan functionalities of 13 and 26 respectively were synthesized. Their characteristics are given in Table 1.

Bis-maleimide (BMI) synthesis The bis-maleimide synthesis was performed according to a protocol described in a previous work [25]. The obtained bis-maleimide had an average molar mass $M_n=276 \text{ g.mol}^{-1}$, an average furan functionality $F_{\text{furan}}=1.9$ and a melting temperature $T_m=136 \text{ °C}$.

PMMA/PU IPN preparation Four 75/25 (by weight) PMMA/PU blends were prepared from the different furan-functional polymers. First, the two polymers were dissolved in chloroform and maintained under magnetic stirring at room temperature for 15 min. Then, the solvent was firstly evaporated at room temperature before removal in an oven under vacuum at 35 °C for 24 h. Thin films were obtained.

Networks were prepared by mixing the previous formed blends with BMI in chloroform at room temperature under magnetic stirring by keeping the molar stoichiometry between maleimide and furyl functions. When a homogeneous solution was obtained, the solvent was evaporated and the thin film

Table 1 Characteristics of the different PMMA-F prepared by reactive extrusion using two different catalysts

Sample	Catalyst	$M_n \text{ (g.mol}^{-1}\text{)}^a$	F_{furan}^b	$T_g^c \text{ (°C)}$
PMMA-F ₁₃	Sn(Oct) ₂	123,600	13	96
PMMA-F ₂₆	TBD	125,200	26	96

^a Determined by SEC

^b Determined by ¹H-NMR in CDCl₃

^c Determined by DSC

was heated in an oven at 170 °C for 15 min then cooled to room temperature at a 1 °C.min⁻¹ cooling rate. The cross-linked blends will be noted c-blend x (where x is the number relative to blend, i.e. c-blend 1 is the blend 1 after cross-linking)

Results and discussion

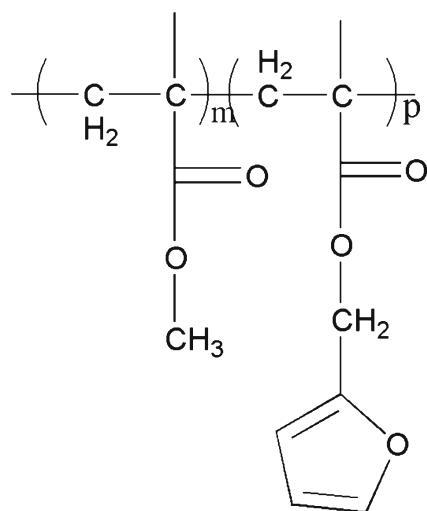
A correct evaluation of the co-cross-linked PMMA/PU material should be based on the properties of both PMMA and PU homo-networks prepared by Diels-Alder reaction. The characteristics, particularly thermal and thermo-mechanical of these networks will be used as reference for the characterization of the IPNs.

The synthesis and the properties of PMMA networks equivalent to those used in this study were previously reported [25]. A preliminary study concerning PU homo-networks was realized here.

Elaboration and characterization of PU homo-networks

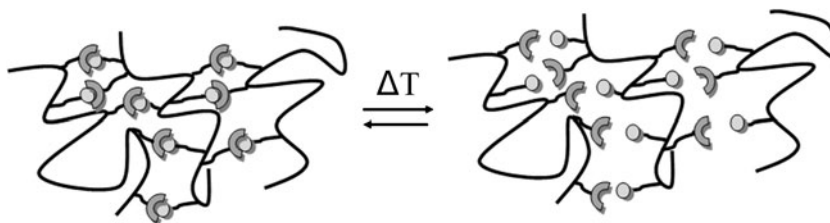
PU networks were obtained by Diels-Alder reaction in one step by reaction between a diisocyanate (H₁₂MDI) with glycerol (cross-linking agent), two diols HTPB (macro-dialcohol monomer) and a DA adduct (thermo-reversible link) (Scheme 2).

The different quantities of reactants were calculated by maintaining constant the glycerol and the adduct concentrations. H₁₂MDI and HTPB quantities were calculated using the Macosko-Miller equation [35] (Eq. 1) so that a cross-linking is obtained with the DA adduct formation. In this case the functionality of adduct is 2 and the p_{gel} value must be lower than 1 (before rDA at relatively low temperature the DA adduct is bi-functional). After rDA, the adduct is dissociated and becomes mono-functional (at relatively high temperature). In this case, the calculated p_{gel} must be higher than 1 to avoid a potential cross-linking.

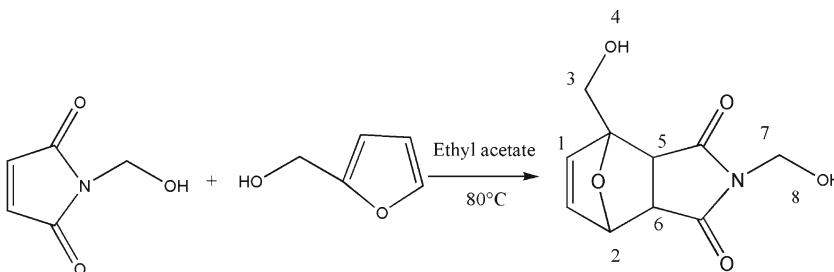


Scheme 1 Furan-functionalized PMMA structure

Scheme 2 Reaction of polyurethane networks dissociation



Scheme 3 The FAL/HMM cyclo-adduct formation reaction



$$P_{gel}^2 = \frac{1}{r(f_{al}-1)(f_{iso}-1)}$$

(1)

alcohol and isocyanate functionalities and f_i the functionality of each alcohol.

$$r = \frac{n_{iso} * f_{iso}}{\sum(n_i f_i)_{al}}$$

(2)

Furfuryl alcohol-HMM (FAL/HMM) adduct synthesis and characterization

$$f_{al} = \frac{\sum n_i f_i^2}{\sum n_i f_i}$$

(3)

The adduct used in the network elaboration was obtained by Diels-Alder reaction between furfuryl alcohol and N-hydroxymethyl maleimide as presented in Scheme 3.

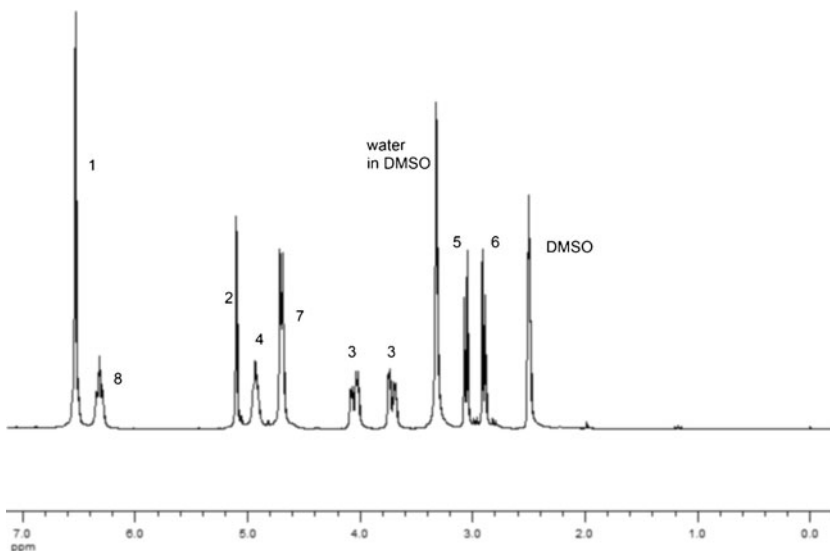
$$f_{iso} = 2$$

(4)

The obtained FAL/HMM adduct was first characterized by ¹H-NMR (Fig. 1) to verify its purity and the obtained forms (endo and exo). As expected, and since the reaction was done at relatively high temperature, only the exo form

With r is the alcohol/isocyanate molar ratio, n_i the molar quantity of each reactant, f_{al} and f_{iso} respectively the average

Fig. 1 ¹H-NMR spectrum of furfuryl alcohol-N-hydroxymethylmaleimide adduct in DMSO at 30 °C



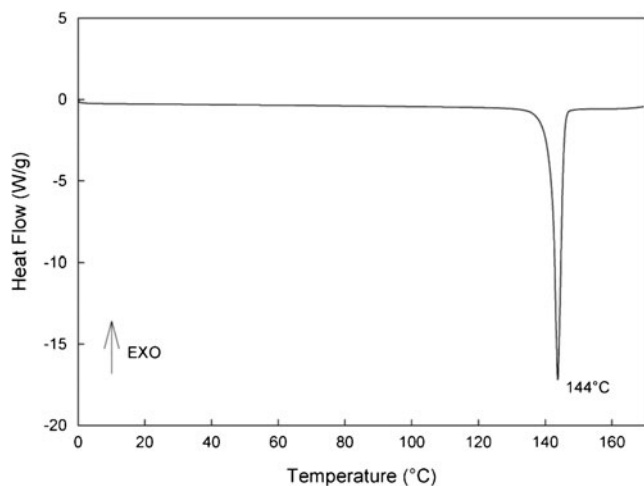


Fig. 2 DSC curve of furfuryl alcohol-N-hydroxymethylmaleimide adduct at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

was obtained [36]. All the peaks relative to different protons were attributed and the obtained product was pure.

The DSC was used to determine the retro-Diels-Alder temperature of the adduct. As seen in Fig. 2, the temperature associating to the rDA is about $144\text{ }^{\circ}\text{C}$.

a. Polyurethane networks characterization

The effect of the hydroxyl-telechelic polybutadiene chain extender quantity in the network is studied here.

Solubility and swelling tests First, solubility tests were conducted in DMSO. At room temperature, PUnet₄ remains insoluble in DMSO and an important swelling was observed. When the swollen sample was heated at $160\text{ }^{\circ}\text{C}$, it becomes soluble (Fig. 3) as a result of a de-cross-linking. This shows

Fig. 3 Solubility tests of PUnet₄ in DMSO: **a** specimen before immersion in DMSO, **b** specimen after immersion in DMSO at room temperature, **c** specimen in DMSO heated to $160\text{ }^{\circ}\text{C}$

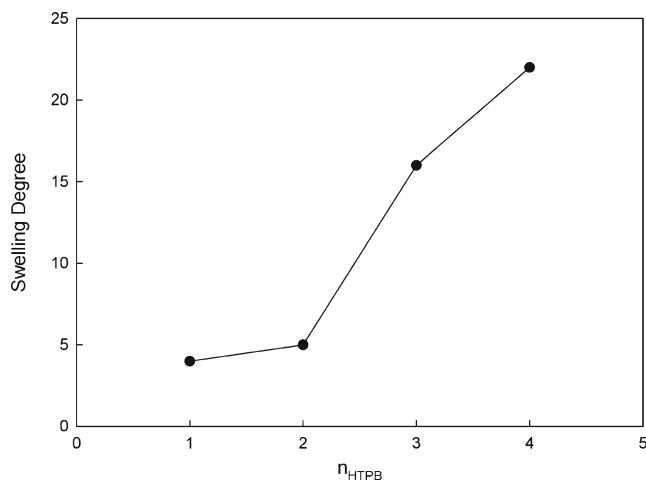
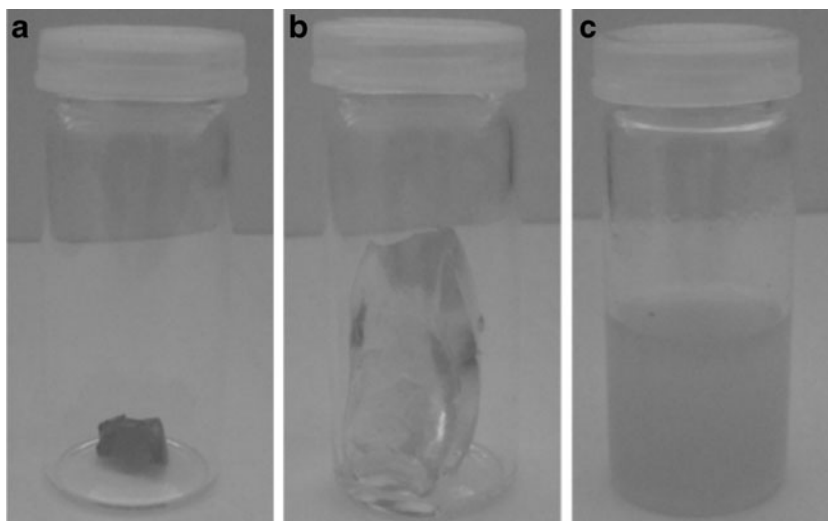


Fig. 4 Evolution of the swelling degree with the HTPB content

clearly a thermo-reversibility of the PUnet₄. Equivalent results were obtained for all the other PUnet.

Figure 4 presents the evolution of the swelling degree as a function of HTPB content. An increase of the swelling degree is observed when the HTPB content increases.

As expected, the network is denser with the minimum quantity of HTPB extender.

Thermal characterization The DSC curves of different networks are plotted in Fig. 5. It can be noticed that two Tg are observed. The first Tg (T_{g1}) represents the glass transition of the soft part composed mainly of HTPB and T_{g2} is that for the hard part composed mainly of H₁₂MDI, glycerol and DA-adduct. Also an endothermic peak is observed. It can be

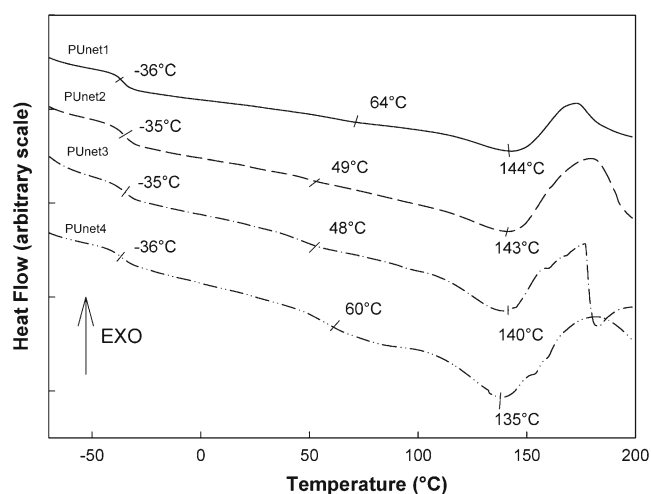


Fig. 5 DSC curves of the different polyurethane networks (from $-70\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$)

assimilated to the rDA phenomenon. After rDA, an exothermic peak was observed. This peak can be attributed to maleimide double bond polymerization that can lead to a secondary non-reversible cross-linking. This shows that for this system and to preserve the thermo-reversibility of cross-linking, the material should not be heated in bulk at temperatures higher than $150\text{ }^{\circ}\text{C}$.

The different thermal data are regrouped in Table 2. The glass transition T_{g1} is almost constant for the soft part of the different networks. For T_{rDA} , a decrease with the increase of HTPB content can be observed. Such result is expected, the network becomes looser when HTPB content increases. In this case the de-cross-linking is obtained earlier than for denser networks. The hard part T_{g2} evolution is more complex. A T_{g2} decrease is probably due to higher content of HTPB in this phase composed mainly of H_{12}MDI , glycerol and DA-adduct.

Table 2 Molar ratio of different reactants and thermal data collected by DSC of different polyurethane networks

Sample	Composition				T_{g1} ($^{\circ}\text{C}$)	T_{g2} ($^{\circ}\text{C}$)	T_{rDA} ($^{\circ}\text{C}$)
	H_{12}MDI	Glycerol	FAL/HMM adduct	HTPB			
PUnet ₁	7	1	4.5	1.05	-36	64	144
PUnet ₂	8	1	4.5	2.1	-35	49	143
PUnet ₃	9	1	4.5	3.15	-35	48	140
PUnet ₄	10	1	4.5	4.2	-36	60	135

Simultaneous cross-linking of PMMA/PU networks

PMMA/PU blends characterization

Obtaining a thermo-reversible cross-linked PMMA/PU blends is foreseeable by Diels-Alder reaction between furan-functionalized both PMMA and PU with bis-maleimide. As the synthesis and characterization of furan-functionalized PMMA were studied previously [25], only the synthesis and characterization of furan-functionalized PU will be studied here.

Furan-functionalized polyurethane synthesis and characterization

Furan-functionalized polyurethanes were obtained by addition reaction between a diisocyanate (H_{12}MDI) and several alcohols (furfuryl alcohol, glycerol and HTPB). Glycerol is used as ramification agent (in order to obtain different furan functionalities), HTPB is a macro-dialcohol monomer and furfuryl alcohol is a chain limiter. The used stoichiometries were calculated while maintaining $p_{\text{gel}} > 1$ using the Macosko-Miller equation to avoid a network formation.

Both prepared oligomers were analyzed by SEC (Fig. 6). The different obtained polymers present various chain lengths. The polymer PU-F₄₆₀₀ presents shorter chains. In fact, the presence of less quantity of HTPB allowed the obtaining of shorter chains. The average molar masses obtained by SEC are regrouped in Table 3.

Figure 7 depicts an example of ^1H NMR spectrum of PU-F. Its structure can be clearly identified by the presence of different characteristic peaks. Peaks relative to the furan group (1) and (2) were, respectively at 7.41 and 6.53 ppm.

The thermal properties of the two polyurethanes are given in Table 3. The T_g of the two polymers is almost the same as it is due to the presence of HTPB in the system.

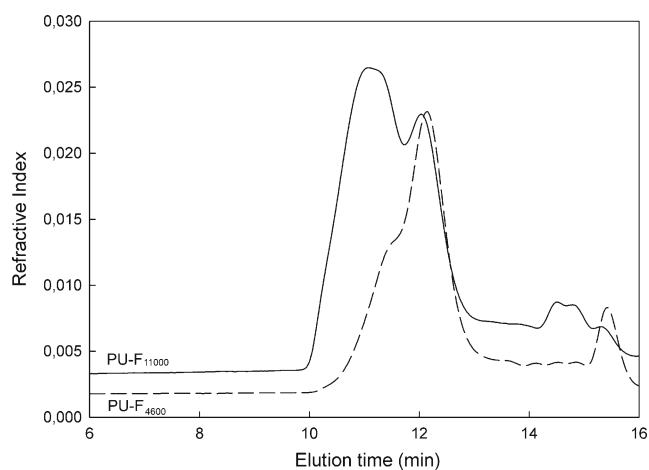


Fig. 6 SEC curves of different furan functionalized polyurethanes

Table 3 Molar ratio of different reactants and properties of the obtained PU prepolymers

Sample	Composition				Mn (g.mol ⁻¹) ^a	Mw (g.mol ⁻¹) ^a	Tg (°C) ^b
	H ₁₂ MDI	FAL	Glycerol	HTPB			
PU-F ₁₁₀₀₀	8	6	2	2.1	11,300	18,900	-38
PU-F ₄₆₀₀	6	5	1.7	1.05	4,600	9,060	-39

^a Determined by SEC^b Determined by DSC*Non reactive PMMA/PU blends elaboration and characterization*

In order to understand the properties and behavior of cross-linked PMMA/PU networks, a preliminary study of non reactive PMMA/PU blends is conducted.

First, thermal properties of the blends were obtained by DSC measurements. Figure 8 shows the DSC curves of the blend PMMA-F₂₆/PU-F₄₆₀₀. The blend presents two different Tgs: the first one at -40 °C corresponds to the PU phase, the second one at 98 °C is relative to the PMMA phase. These Tgs are identical to those of the two polymers taken separately. This shows that these initial polymers are not miscible.

Table 4 regroups the different Tgs. For all the blends, small evolutions of Tgs are obtained probably as a result of limited specific interaction. But evidently all these blends are immiscible.

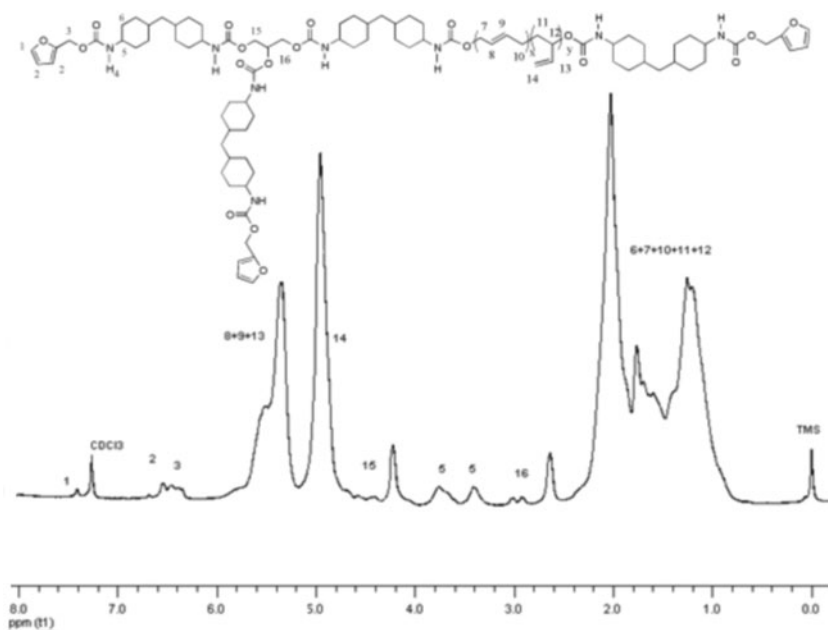
An example of rheological curves of PMMA/PU non reactive blends is given in Fig. 9. The obtained curve presents a typical of PMMA. Indeed, PMMA presents the majority phase in the blend. Two zones are identified: zone 1 which present the glass transition and zone 2 which present the rubbery zone. The rubbery zone finishes at about 160 °C

where the flow begins. At this temperature most of the entanglements and hydrogen bonds are broken.

As a conclusion, immiscible PMMA/PU blends were obtained by solution mixing and rheological data show an apparent behavior of PMMA matrix. Therefore, the compatibilization of these blends by means of IPN formation will be studied in the next paragraph.

Simultaneously cross-linked PMMA/PU characterization

Solubility tests were conducted in DMSO. The example of c-blend 4 is depicted in Fig. 10. A swelling at room temperature and a solubility at 160 °C were observed. This result shows that the cross-linking of the network was successful and that the thermo-reversibility was proved. In fact, when rDA temperature is reached, the chemical bonds are broken and the initial polymers are dissolved in the DMSO. However in the case of c-blend 1 and c-blend 2, a set of pieces of cross-linked chains is observed. Such result is expected as the majority phase is PMMA and it was proven in a previous work [25] that a very loose network was obtained with PMMA-F₁₃.

Fig. 7 ¹H-NMR spectrum of PU-F₁₁₀₀₀ in chloroform at 30 °C

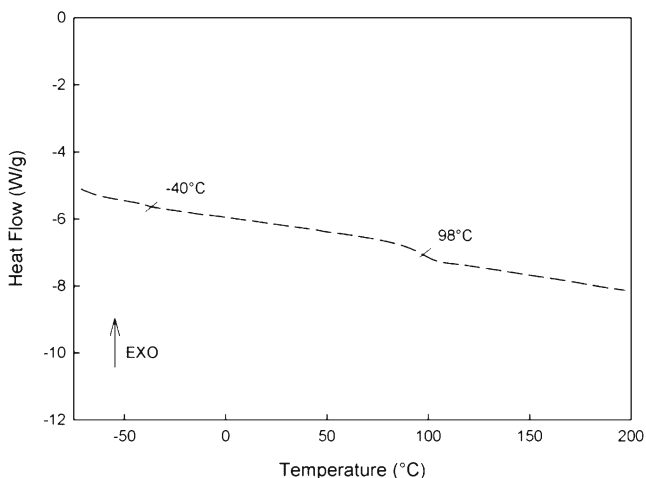


Fig. 8 DSC curves of blend 4 (PMMA-F₂₆/PU-F₄₆₀₀) at 10 °C.min⁻¹

Due to swelling measurements, average molar mass between cross-links at insoluble rates can be calculated. Flory-Rehner theory is used to calculate the values of M_c between crosslinks in the interpenetrating polymeric gel. According to this theory M_c values increase with the increase of swelling ratio of gels. Molar mass between cross-links is calculated by the following equation [37].

$$M_c = \frac{d_p v_1 (v_2^{1/3} - v_2/2)}{\ln(1-v_2) + v_2 + \chi v_2^2} \quad (5)$$

Volume fraction of the polymer (v_2) in the swollen gel is a measure of the amount of fluid that a gel can incorporate into its structure. It is calculated by the following equation [38]:

$$v_2 = \left[1 + \frac{d_p}{d_s} \left(\frac{M_a}{M_b} - 1 \right) \right]^{-1} \quad (6)$$

Where d_p and d_s are densities (g. mL⁻¹) of the gel and solvent respectively. M_a and M_b are the weights (g) of the swollen and dry gels respectively. v_2 (mL.mol⁻¹) is the volume

Table 4 Composition and thermal data of different PMMA/PU (75/25 weight ratio) non reactive blends obtained by DSC

Sample	Composition		T _{g1} (°C)	T _{g2} (°C)
	PMMA	PU		
Blend 1	PMMA-F ₁₃	PU-F ₁₁₀₀₀	-48	89
Blend 2	PMMA-F ₁₃	PU-F ₄₆₀₀	-50	95
Blend 3	PMMA-F ₂₆	PU-F ₄₆₀₀	-42	92
Blend 4	PMMA-F ₂₆	PU-F ₁₁₀₀₀	-40	98

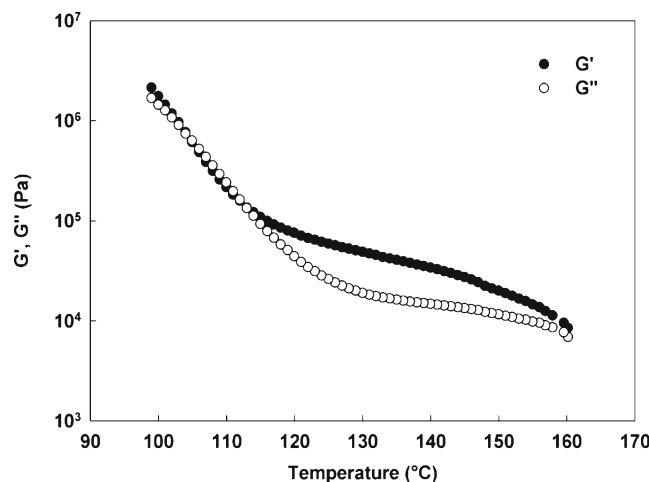


Fig. 9 Rheological curves of blend 4 (PMMA-F₁₃/PU-F₄₆₀₀) obtained by cooling from 160 °C to 95 °C at 1 °C.min⁻¹ at 1 rad.s⁻¹

fraction of the swollen gel in the equilibrium state and χ is the Flory-Huggins polymer solvent interaction parameter.

Solvent interaction parameter (χ) was calculated by Flory-Huggins theory. Equation used to calculate χ value is given below [39]:

$$\chi = -\frac{\ln(1-v_2) + v_2}{v_2^2} \quad (7)$$

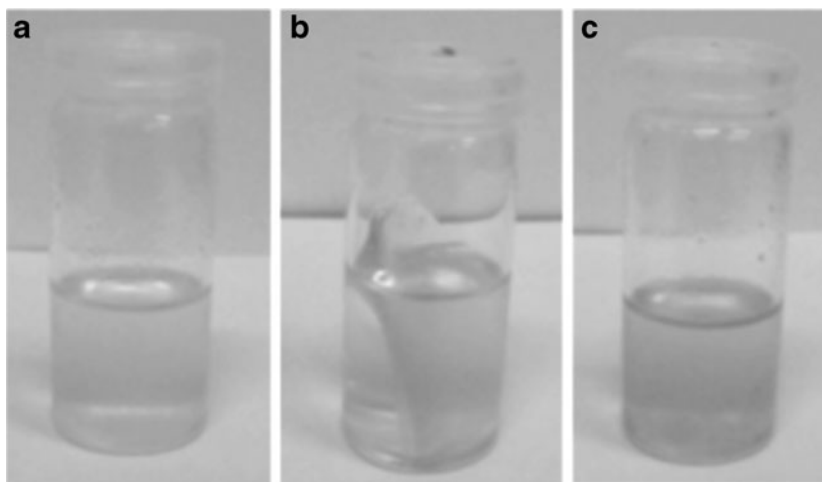
$\ln(1-v_2)$ can be replaced in Eq. (7) by: $\ln(1-v_2) = -v_2 - \frac{v_2^2}{2} - \frac{v_2^3}{3} - \frac{v_2^4}{4} - \dots$

when neglecting the last terms, Eq. (7) becomes:

$$\chi = \frac{1}{2} + \frac{v_2}{3} \quad (8)$$

The swelling measurements in THF are regrouped in Table 5. It can be noticed that the insoluble rate increases with the average furan functionality. But, it is more influenced by the PMMA functionality as it presents the majority phase. In fact, an important reaction rate is observed for c-blend 3 and c-blend 4. The swelling degree was only calculated for c-blend 3 and c-blend 4 as for c-blend 1 and c-blend 2 no consistent gel was obtained. A little decrease of the swelling degree was observed when PU-F₁₁₀₀₀ was used. Indeed, the polyurethane phase presents only 25 % in the network. So, it has not a big influence in the network properties. The molar mass between cross-links is relatively high as it exceeds the molar mass of a single chain of PMMA. Probably, in addition to its role as a cross-linker, BMI allowed the grafting of polymer chains and then extending the chain length.

Fig. 10 Solubility tests of cross-linked blend 4 (PMMA-F₂₆/PU-F₄₆₀₀) in DMSO: **a** blend 4 immersed in DMSO (soluble), **b** cross-linked blend 4 immersed in DMSO at room temperature (swollen), **c** specimen **(b)** heated to 160 °C



The DSC curves of the different networks are plotted in Fig. 11. From these curves, glass transition and retro-Diels-Alder temperatures can be determined. The different temperatures are given in Table 6. It can be noticed that only one Tg is observed varying from 51 °C to 58 °C. At first sight, no phase separation was obtained. This result can be confirmed by Fox empirical law.

$$\frac{1}{Tg(A+B)} = \frac{w_A}{Tg(A)} + \frac{w_B}{Tg(B)} \quad (9)$$

Where Tg(A+B), Tg(A) and Tg(B) are respectively the glass transition temperatures of A/B miscible blend, polymer A and polymer B.

w_A and w_B are the weight fractions of the polymers A and B with $w_A + w_B = 1$

According to the Fox law, in the case of miscible blend of PMMA/PU, a glass transition temperature of 50 °C is obtained. So, it can be affirmed that no phase separation in the network is obtained. The obtaining of one Tg can be due to either a cross-linked copolymer PMMA-PU or an interpenetrating PMMA/PU network.

Table 5 Data collected from swelling measurements of different simultaneously cross-linked PMMA/PU networks

Sample	Composition		Insoluble rate (%)	Swelling degree G	χ	Mc (kg.mol ⁻¹)
	PMMA	PU				
c-blend 1	PMMA-F ₁₃	PU-F ₁₁₀₀₀	42	—	—	—
c-blend 2	PMMA-F ₁₃	PU-F ₄₆₀₀	44	—	—	—
c-blend 3	PMMA-F ₂₆	PU-F ₄₆₀₀	67	11	0.53	707
c-blend 4	PMMA-F ₂₆	PU-F ₁₁₀₀₀	71	10	0.53	509

Since the two polymers present in the reactive system are initially non miscible, the cross-linking with the coupling agent begins in each phase. Then, with the favorable specific interactions, entanglements between the polymers of the two phases increase gradually leading finally to an IPN. The phase separation gradually disappeared and at the end only one Tg was obtained. It is also highly probable that coupling reactions with the bis-maleimide also occurs between PMMA and the PU. Nevertheless, it seems not realistic to consider a co-cross-linking leading to a single Tg by analogy with a random copolymer seen the high molar mass of the polymer constituents (100,000 for PMMA and for 10,000 PU).

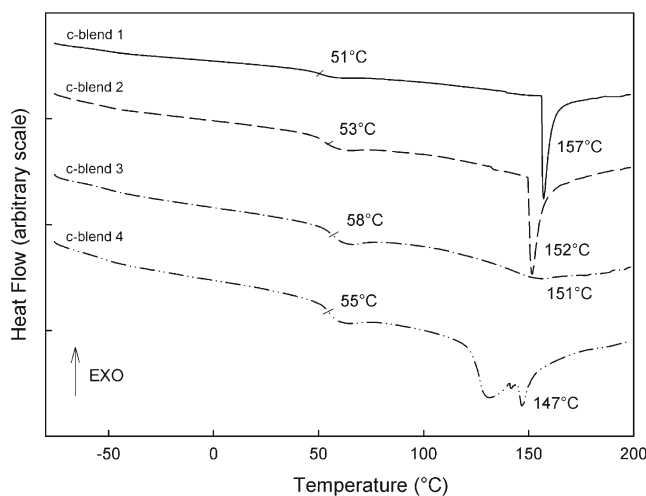


Fig. 11 DSC curves of the different simultaneously PMMA/PU cross-linked blends (heating from -70 °C to 200 °C at 10 °C.min⁻¹)

Table 6 Thermal data of different simultaneously cross-linked PMMA/PU networks collected from DSC

Sample	Composition		T _g (°C)	T _{rDA} (°C)
	PMMA	PU		
c-blend 1	PMMA-F ₁₃	PU-F ₁₁₀₀₀	51	157
c-blend 2	PMMA-F ₁₃	PU-F ₄₆₀₀	53	152
c-blend 3	PMMA-F ₂₆	PU-F ₄₆₀₀	58	151
c-blend 4	PMMA-F ₂₆	PU-F ₁₁₀₀₀	55	147

The rDA temperature is given by the top temperature of the endothermic peak. It lies between 147 °C and 157 °C. With the increase of the average furan functionality, a decrease of the rDA temperature is observed. It can be observed that two different rDA kinetics are obtained. In fact, for blends based on PMMA-F₁₃ a sharp peak is obtained with higher T_{rDA} values (rapid kinetic), while for the blends based on PMMA-F₂₆ a broad peak with lower rDA temperatures is observed (slower kinetic).

Figure 12 presents rheological curves of different networks. As the initial blend present physical interactions,

the general shape of the obtained curves is identical to that obtained with the same blend without cross-linking. However, the increase of G' before the rDA temperature and the increase of the temperature of the beginning of the flow zone show that a modification of the characteristics of the blend occurred. This modification is the result of the cross-linking. It can be also observed that the behavior of the network is almost dependent of PMMA. In fact, the glassy zone corresponds of that of PMMA. So, the PU particles act as filler in a PMMA matrix. This result confirms that an interpenetrating network was obtained where cross-linked polyurethane particles are dispersed in the polymethyl methacrylate matrix. It can be also noticed that G' is higher for the two first networks based on PMMA-F₁₃ than that for networks based on PMMA-F₂₆. Denser networks are obtained for c-blend 1 and c-blend 2. This is concordant with DSC results where T_{rDA} is higher for the two networks based on PMMA-F₁₃.

These results are confirmed by TEM photographs where no phase separation can be observed. Therefore it can be affirmed that thermo-reversible IPNs were obtained.

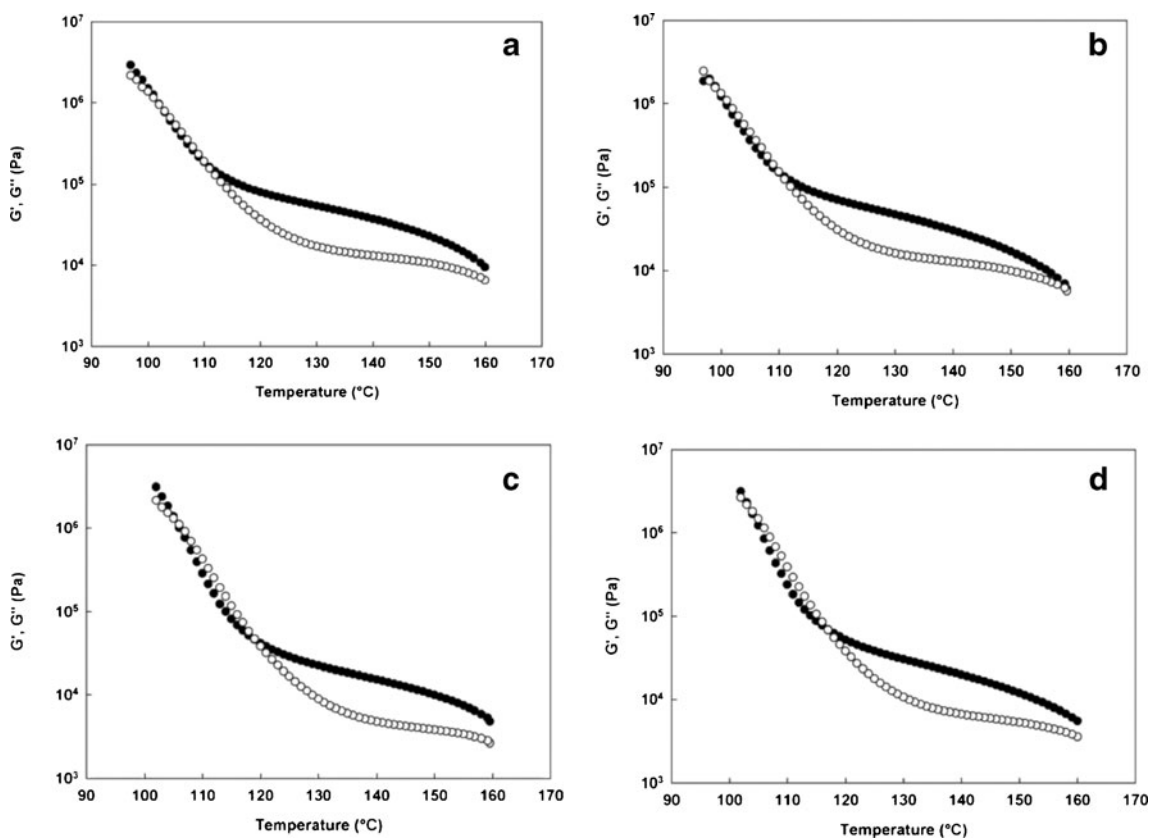


Fig. 12 Rheological curves of the different simultaneously cross-linked PMMA/PU networks: **a** cross-linked blend 1, **b** cross-linked blend 2, **c** cross-linked blend 3 and **d** cross-linked blend 4. (●) G', (○) G''

Conclusions

Thermally-reversible PMMA/PU IPNs were obtained by furan/maleimide Diels-Alder reaction.

Initially non-miscible reactants conducted to mono-phasic IPNs. The de-cross-linking of the IPNs occurred between 147 °C and 157 °C depending on the reactants functionalities and the supramolecular interactions between polyurethane and PMMA.

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