Highly-interpenetrated and phase-separated UV-cured interpenetrating methacrylate-epoxide polymer networks

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Highly-interpenetrated and phase-separated UV-cured interpenetrating methacrylate–epoxide polymer networks: Influence of the composition on properties and microstructure

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ABSTRACT

Interpenetrating Polymer Networks (IPNs) based on a polybutadiene dimethacrylate and a dicyclohexylepoxy mixed at different ratios have been synthesized by photopolymerization. To obtain a complete overview of the formation and phase separation of these IPNs, and to predict the final morphology, miscibility before and after polymerization has been studied. By varying the methacrylate/epoxide ratio, it was possible to move from a miscible and highly-interpenetrated system to a totally immiscible and phase-separated one. Miscibility effects on the polymerization kinetics of both polymer networks, final properties and surface morphology were investigated by RT-FTIR, DMA, AFM and AFAM. This overall characterization gives a better understanding of the formation and phase separation process in this system, depending on the mixture composition.

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1. Introduction

Acrylates and methacrylates are widely used as monomers in UV-curing technology because of their high reactivity, commercial availability and moderate costs [1–3]. However, a drawback is a significant shrinkage up to 15% that may appear [4]. Furthermore, early vitrification of the network due to the high monomer reactivity can limit its conversion; combined with the density increase, this can lead to stress and cracks [5]. Furthermore, the free radical photopolymerization is known to be sensitive to oxygen inhibition leading to tacky surfaces [6–8]. Due to the ring opening polymerization, epoxides exhibit less shrinkage [4,9] and reactive species are able to polymerize in dark environment, leading to a full conversion [10,11]. However, the low polymerization rate of epoxides as well as their relative sensitivity to humidity and high brittleness turn out to be shortcomings for industrial applications [10,12,13].

In order to overcome the intrinsic limitations of both acrylate and epoxide polymerizations, Interpenetrating Polymer Networks

(IPNs) structure based on acrylate and epoxide can be synthesized. In this context, IPNs are defined as a blend of at least two crosslinked polymers which are permanently entangled [14–19]. The monomers polymerize according to different mechanisms [4,18,20] independently from each other [18,21], and the resulting IPNs combine properties of both acrylates and epoxides, which make them suitable for various applications [4,17,18]. They can be achieved in a one-or two-step process [18,21]. In the first case, the polymerization of the two networks occurs simultaneously according to independent and non-interfering reactions [11,12,14,15,18]. In a two-step approach, one polymer is firstly formed; then, it is swollen by a second monomer, which is further polymerized [14,15,18,22].

The formation of IPNs is generally governed by two processes which compete to give a large variety of final morphologies and degrees of mixing: the crosslinking reaction and the phase separation [14,18]. The first one may prevent the formation of domains depending on the reaction kinetics [23,24] whereas the second one is mainly governed by thermodynamics [23,25]. Thus, the final morphology results from the monomers or polymers miscibility and compatibility [20,23], polymerization method and sequence order of reactions [23], crosslinking density [18] and curing kinet-

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Table 1
Chemical structures and properties of the compounds used in this work.

Name	Structure	Viscosity (mPa s ⁻¹)	Refractive index at 19.3 °C	M _w /M _n
CN 301	Mixture of polybutadiene dimethacrylate ^a (80 wt.%) and 1,6 hexanediol diacrylate ^b (20 wt.%). Polybutadiene units are composed of 1,4- <i>cis</i> ; 1,4- <i>trans</i> and 1,2 conformations randomly distributed in the chain.	1000 at 60 °C	1.5013	2.33 ^a 1.02 ^b
UVR 6110		220–250 at 25 °C	1.4993	1.02
D 1173
TAS

M_w/M_n was determined by Size Exclusion Chromatography, using a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 μm MIXED-C columns and a refractive index detector (Shimadzu RID-10A). THF was used as an eluent at a flow rate of 1.0 mL min⁻¹.

ics [20,21,23]. In consequence, the morphology governs the final properties of the resulting IPN [15,26–28].

Homogeneous and highly-interpenetrated IPNs can be identified by a single intermediary glass transition temperature (*T_g*) and no discernible phase domains [29–31]. On the contrary, the presence of 2 *T_g*s is an indication of poor or absent miscibility. Increased interpenetration between the two networks results in *T_g*s that are moving toward each other [14]. The miscibility of the network components can be enhanced by matching the rates of the crosslinking reaction half-lives for formation of both networks (τ_i), and by minimizing the difference in solubility parameter ($|\Delta\delta|$) and *T_g*s of the linear chain components. The thermodynamic binary interaction parameter (χ) and the Gibbs free energy (ΔG) [30,31] may be decreased for enhanced miscibility.

UV-cured IPNs have been widely reported in the literature [4,19–21,32–36]. The kinetics of network formation, mechanical properties and surface morphology are usually the parameters that are investigated. The miscibility prediction of the final polymer was only described for conventional, thermally cured systems [14,15,18]. To the best of our knowledge, an overview combining a miscibility study, the relative kinetics of formation of both UV-cured networks and the corresponding effects on the final properties and morphology (and in particular the extent of phase separation) has still not been reported. Therefore, the purpose of the present paper is to synthesize UV-cured methacrylate–epoxide IPNs of different chemical compositions in order to get a better understanding of their formation and phase separation. A difunctional methacrylate and a cycloaliphatic diepoxide have been chosen for this study for different reasons: their structure and reactivity in the photocuring process can trigger a phase separation depending on their respective ratio. In addition, the two homopolymers present two different *T_g*s (low *T_g* for the methacrylate and high *T_g* for the epoxide) to afford mechanical resistance and hardness together with flexibility to the resulting UV-cured polymer. To get a complete overview of the formation and phase separation of these IPNs, the miscibility of the network components before and after the polymerization has been investigated. Real time (RT)-FTIR was used to follow the reaction kinetics. The mechanical properties and morphology of these UV-cured films have been characterized

by Dynamic Mechanical Analysis (DMA), Atomic Force Microscopy (AFM) and Atomic Force Acoustic Microscopy (AFAM).

2. Experimental

2.1. Materials

Monomers selected for this study are dimethacrylate from Sartomer (CN 301) composed of a mixture of polybutadiene dimethacrylate and 1,6 hexanediol diacrylate at a ratio of 80–20 wt.% respectively, chosen for its flexibility and low *T_g*, and (3,4-epoxycyclohexyl)methyl 3,4-epoxycyclohexylcarboxylate from Dow Chemical (UVR 6110) exhibiting high *T_g* and reactivity, as well as good mechanical properties. For improved readability, the names methacrylate or epoxide will refer to these difunctional monomers in the following sections. The radical photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) was obtained from BASF and the cationic photoinitiator, a triarylsulfonium hexafluoroantimonate salt (TAS), was purchased from Sigma–Aldrich. The latter is diluted in propylene carbonate (50 wt.%). All these compounds were used without any further purification. Their chemical structures and properties are shown in Table 1.

Photocurable formulations (Table 2) were prepared by mixing the epoxide and the acrylic resins at different weight ratios. Radical and cationic photoinitiators were added to the formulation at 1 and 2 wt.%, respectively. Since, TAS is diluted in propylene carbonate at 50 wt.%, the amount of active photoinitiator remains at 1 wt.% regarding the formulation. In the following, mixtures will be described as xAyE, A standing for the radical system (polybutadiene dimethacrylate + hexanediol diacrylate + D 1173) introduced at x wt.%, and E corresponding to the cationic polymer (diepoxide + TAS) introduced at y wt.%.

2.2. Methods

2.2.1. Miscibility study

For the monomers characterizations, the specific density was taken from the technical data sheet of the producers and M_n was

Table 2

Composition of the formulations investigated in this study.

Formulations ^a	Methacrylate (wt.%)	Epoxide (wt.%)
100A0E	97	0
95A5E	94	3
90A10E	89	8
80A20E	79	18
75A25E	74	23
70A30E	69	28
60A40E	59	38
50A50E	49	48
40A60E	39	58
30A70E	29	68
25A75E	24	73
20A80E	19	78
15A85E	14	83
10A90E	9	88
5A95E	4	93
0A100E	0	97

^a D 1173 and TAS were added at 1 and 2 wt.% based on total mixture, respectively.

determined with ^1H and ^{13}C NMR spectroscopy (Bruker Advance at 295 K, 400 MHz, CDCl_3). The solubility parameters were calculated by using the method of Hoftyzer and Van Krevelen [37]. Finally, the miscibility of the two selected monomers was assessed visually at 20 °C before and after the photopolymerization. Optical microscope pictures were taken with an Olympus BX51 microscope.

2.2.2. Fourier transform infrared spectroscopy

The photopolymerization kinetics of IPNs were followed by Real-Time FTIR using a Vertex 70 from Bruker Optics, at room temperature and under air, operating in a rapid scan mode and equipped with a MCT detector with a time resolution of 0.126 s. The spatial resolution was 4 cm^{-1} . A 60 μm thick film was deposited on a KBr pellet using a calibrated bar coater and exposed simultaneously to UV irradiation and IR beam for FTIR characterization. The polychromatic irradiation was provided by a mercury–xenon lamp (Hamamatsu L8252) equipped with a reflector at 365 nm and coupled with a flexible light-guide. Light intensity at the sample surface was set to 218 mW cm^{-2} and irradiation was performed for 600 s.

RT-FTIR spectroscopy allows studying separately the conversion of each monomer forming the IPN by following a typical vibration band. The C=C deformation vibration at 1410 cm^{-1} and the symmetrical stretching at 790 cm^{-1} were chosen for the methacrylate function and the epoxide ring, respectively [21,34]. All spectra were baseline-corrected prior to the integration with the software OPUS 6.0 and 7.0. The monomer conversion at time t is calculated from Eq. (1):

$$C(\%) = 100 \times \frac{(A_0 - A_t)}{A_0} \quad (1)$$

where A_0 is the initial absorption band area before exposure and A_t the absorption band area at time t . The maximum rates of polymerization (R_{pmax}) are calculated from the maximum of the first derivative of the conversion vs. time curves. To avoid any calculation errors, R_{pmax} are expressed in s^{-1} .

The viscosity of the various mixtures (except for 100A0E, see Table 4) was measured with a Brookfield Model DV-II+ viscometer at 25 °C and 20 rpm with a cone spindle CPA 52Z.

2.2.3. Final properties characterizations

Formulations were applied on a polypropylene substrate with a coating bar and photocured with a Fusion microwave Hg lamp (type H) at room temperature and under air, associated to a conveyor belt with an equivalent speed of 10 m min^{-1} . The total light intensity received by samples was measured by an UV-Power Puck II instrument resulting in UVA: 990 mJ/cm^2 , UVB: 720 mJ/cm^2 , UVC: 171 mJ/cm^2 and UVV: 1053 mJ/cm^2 . Tack-free films of about

Table 3

Thermodynamic solubility parameters of monomers [37].

	Polybutadiene dimethacrylate	1,6 Hexanediol diacrylate	Epoxide UVR 6110
Molecular weight $M_n \text{ g mol}^{-1}$	2052	226	252
Specific density	0.96	1.02	1.17
Dispersion contribution $\delta_d \text{ J}^{1/2} \text{ cm}^{-3/2}$	16.6	16.2	20.8
Polarity contribution $\delta_p \text{ J}^{1/2} \text{ cm}^{-3/2}$	0.3	3.1	3.5
Hydrogen-bond contribution $\delta_h \text{ J}^{1/2} \text{ cm}^{-3/2}$	2.5	7.9	7.8
Total solubility parameter $\delta_t \text{ J}^{1/2} \text{ cm}^{-3/2}$	16.7	18.4	22.5

 δ_t of the CN 301 mixture is 17.1 $\text{J}^{1/2} \text{ cm}^{-3/2}$.

50–70 μm thick were obtained. Conversion was evaluated at the end of the photopolymerization by FTIR. Differential scanning calorimetry (DSC Q200, TA instruments) was used to determine the glass transition temperature (T_g) of neat UV-cured diepoxide or dimethacrylate films under nitrogen atmosphere (50 mL min^{-1}), using about 6 mg of samples in aluminum hermetic pans heated at 10 °C min^{-1} . The second heating run was selected to determine T_{gs} . It should be mentioned that no T_g change was observed between the first and the second run for both polymers since they have reached almost full conversion as reported in Table 4.

Dynamic mechanical analysis (DMA Q800, TA instruments) was used to characterize the viscoelastic properties of UV-cured films in tensile mode at a frequency of 1 Hz. The storage modulus (E') representing the elastic behavior of the materials and the loss factor ($\tan \delta$) defined as the ratio between the loss modulus and the storage modulus were determined as a function of the temperature at a constant heating rate of 3 °C min^{-1} for samples of about 3 $\text{cm} \times 0.6 \text{ cm}$ wide with a thickness of 55–70 μm .

2.2.4. Morphology investigations

Morphology investigations were performed by atomic force microscopy (AFM) and atomic force acoustic microscopy (AFAM) on free surfaces of the UV-cured materials (Ntegra Spectra, NT-MDT). A NSG 01 tip (silicon, nominal resonance of 150 kHz, nominal spring constant of 5.1 N m^{-1}) was used for acquiring images in semi-contact mode. For the AFAM measurements in contact mode, a FMG 01 tip (silicon, nominal resonance of 60 kHz, nominal spring constant of 3 N m^{-1}) and an acoustic transducer (Olympus-Panametrics NDT) with a central frequency of 5 MHz were implemented.

AFAM is a non-destructive AFM technique which principle is to excite the cantilever into flexural vibrations when the tip is in contact with the sample surface [38]. A piezoelectric transducer placed below the sample generates acoustic waves which cause vibrations of the sample surface and of the cantilever close to its resonance frequency [38–41]. Out-of-plane vibrations of the surface sample and cantilever vibrations are measured [38,40–42]. The resulting acoustic CRF (Contact tip/sample Resonance Frequency) images, corresponding to the shift of the resonance frequency of the sample/tip system near the surface are recorded simultaneously to topography images [38,39]. These data deliver valuable information on the stiffness of the tip-sample contact interaction and allow a precise mapping of local variations in elasticity of the sample

[38,42]. In this study, the AFAM mode was found to be more suitable than phase imaging to investigate the morphology of the IPNs for these phase-separated systems and allow to get rid of topography effects.

For a more precise investigation of the different systems, the root mean square (RMS) roughness, defined as the RMS average of the height deviations from the mean value (Eq. (2)), was calculated [43–45]. It was obtained from AFM and AFAM topography images using the roughness analysis tool of Nova software from NT-MDT, applied on the whole scanning area.

$$R_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^n x_i^2} \quad (2)$$

where x is the height, phase or CRF difference between a given data point and the corresponding data point for the average plane, and n is the total of the measured points.

In the same manner, phase and CRF RMS values have been estimated from phase and CRF images. Scales of topography, phase and CRF images are expressed in nanometer (nm), degree (°) and kilohertz (kHz).

3. Results and discussion

3.1. Miscibility investigations

The solubility parameter, δ , defined as the square root of the cohesive energy density [37,46,47] (the energy of vaporization per unit volume) was determined in this study to predict the compatibility between the selected monomers. The Hoftyzer and Van Krevelen method based on the classical Flory–Huggins theory was chosen to evaluate δ [37,47]. The solubility parameter components were calculated from group contributions, while the total solubility parameter was determined from Eq. (3) [37,47].

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

Here δ_d , δ_p , δ_h are the dispersion, polar and hydrogen bonding contributions of the solubility parameter, respectively, and δ_t is the total solubility parameter. The molar volume (V) in $\text{cm}^3 \text{mol}^{-1}$ was calculated from the specific density and the molecular weight. The results are reported in Table 3.

The larger the differences between the δ_t s of the components of the mixture, the lower are the chances of solubility/miscibility between the monomers. Conventionally, immiscibility between two compounds starts when the difference of their solubility parameters reaches about $5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ [37]. In consequence, a value of $5.4 \text{ J}^{1/2} \text{ cm}^{-3/2}$ between the methacrylate and the epoxide selected for this study can account for phase separation [37]. A comprehensive study of the miscibility of the methacrylate monomer in the epoxide resin before UV-curing was carried out at 20 °C by gradually increasing the methacrylate ratio from 5 to 95 wt.% in the blend. The solubility limit of the monomer is reached between 20A and 25A (see SI—Fig. S1). Below this concentration, the mixtures showed haziness while above this limit, they were transparent. The partial miscibility between methacrylate and epoxide can be firstly explained by the presence of hexanediol diacrylate which has a δ_t of $18.4 \text{ J}^{1/2} \text{ cm}^{-3/2}$ and acts as compatibilizer of the system. In addition, the polybutadiene dimethacrylate resin (CN 301) was found to be quite polydisperse (Table 1) and the solubility parameters does not take into account polydispersity to predict compatibility between compounds.

Methacrylate/epoxide monomer blends were also investigated by optical microscopy. Good miscibility was found between the two resins for a 70A30E ratio whereas immiscible domains were highlighted for 20A80E system (see SI—Fig. S2). Further optical investigation of the UV-cured films (not presented here) points out

Fig. 1. Different cases of IPNs formation based on a phase diagram combining the observations for liquid state and UV-cured films, as a function of the weight ratio of the two monomers (A and E for radical and cationic system, respectively).

a miscibility limit between 30A and 40A. Below this concentration, UV-cured films were hazy. The difference of solubility limit found between liquid monomers and UV-cured films may be explained by shrinkage which appears during the polymerization and induces volume changes. As a consequence, the solubility parameters of both resulting polymers will be modified. This may account for immiscibility during polymerization, triggering hazy and heterogeneous UV-cured films.

Based on these observations and combining phase diagrams for liquid monomers and UV-cured films, three different cases of IPNs formation may be expected depending on the monomer ratios used (Fig. 1). For comprehension purpose, A stands for the radical system (polybutadiene dimethacrylate + hexanediol diacrylate + D 1173) and E corresponds to the cationic system (diepoxide + TAS).

Below 25A, monomers are immiscible and lead to a heterogeneous and phase-separated IPN. Between 25A and 40A, monomers are miscible but phase separation occurs during the polymerization, resulting in hazy UV-cured films. From 50A to 95A, both monomers are miscible and no phase separation takes place during the polymerization.

The next sections will focus on the polymerization kinetics and the characterization of the UV-cured samples by DMA, AFM and AFAM to corroborate the results compiled in this phase diagram (Fig. 1).

3.2. Kinetics and post curing

As indicated in the previous section, different kinetics profiles are expected, depending on the monomer ratios. The conversion curves for epoxide and methacrylate in the different mixtures are presented in Fig. 2a,b and the corresponding kinetics data and viscosities are reported in Table 4. Each experiment was repeated 3 times to check the reproducibility.

The photopolymerization of the neat epoxide (0A100E) is faster than for the neat methacrylate (100A0E) with R_{pmax} of 39.4 s^{-1} and 15.3 s^{-1} , respectively. This results from the high reactivity of the cycloaliphatic epoxide groups [48]. The fast vitrification of the epoxide network and its brittleness lead to a leveling of the conversion, which hardly reaches 68% after 600 s of irradiation. This thermomechanical behavior is well-known for polyether networks [9].

For 100A0E, the high viscosity and the lower reactivity of the methacrylate monomer account for a lower rate of polymerization and a longer time needed to reach R_{pmax} (1.7 s compared to 0.8 s for 0A100E). However, the low T_g (−73 °C measured by DSC) and the flexibility of the polybutadiene dimethacrylate network contribute

Table 4

Kinetics data and viscosities (measured at 25 °C and 20 rpm) for the neat resins and the various mixtures.

IPN systems		100A 0E	70A 30E	50E 50A	40A 60E	20A 80E	0A 100E
Epoxide	Viscosity (mPa s ⁻¹)	10380 ^a	4834	2682	1775	721	244
	R_{pmax} (s ⁻¹)	/	12.7	17.6	16.4	20.5	39.4
	Time needed to achieve R_{pmax} (s)	/	1.7	1.1	0.9	0.6	0.8
	Corresponding conversion (%)	/	9.2	8.4	6.0	5.7	11.7
	Final conversion after 600 s (%)	/	90	79	73	64	68
	Final conversion after 3 days of post-curing at RT (%)	/	96	94	95	92	93
Methacrylate	R_{pmax} (s ⁻¹)	15.3	27.5	34.6/37.8 ^b	34.6/39.3 ^b	65.6	/
	Time needed to achieve R_{pmax} (s)	1.7	1.1	0.5/1.2 ^b	0.5/1.4 ^b	0.8	/
	Corresponding conversion (%)	19.1	22.3	11.4/37.0 ^b	12.1/46.7 ^b	43.9	/
	Final conversion after 600 s (%)	97	98	98	98	98	/

^a Viscosity measured at 5 rpm for this highly viscous ratio.^b Presence of two maxima of the polymerization rate. **Fig. 2.** Conversion profiles of (a) methacrylates at 1410 cm⁻¹ (b) epoxides at 790 cm⁻¹ for different systems vs. irradiation time under polychromatic exposure (light intensity of 218 mW cm⁻²).

to reach a higher final conversion (97%). Finally, almost no effect of the oxygen inhibition on free radical polymerization is noticeable; the high viscosity of the formulation which slows down the diffusion of atmospheric oxygen into the sample [4] accounts for this results.

A gradual increase of the epoxide amount in the IPN mixture leads to a viscosity decrease (Table 4). As a consequence, the mobility of reactive species increases, methacrylate polymerization is enhanced [20,49] and an almost full methacrylate conversion is achieved for all ratios in a shorter time: R_{pmax} increases from 15.3 to 65.6 s⁻¹ and the time needed to reach R_{pmax} is shortened to 0.8 s. Concerning the epoxide polymerization, addition of the methacrylate monomer involves a viscosity increase compared to the 0A100E

Fig. 3. Comparison of (a) the kinetics in the neat resin and in 20A80E mixture (b) R_p curves vs. time for 20A80E. A and E stand for radical and cationic system, respectively.

system, inducing a limited diffusion of reactive species and a lower propagation rate constant [4,20]. R_{pmax} reflects a clear slowing down of the polymerization rate, from 39.4 s⁻¹ to 12.7 s⁻¹; the time needed to reach R_{pmax} raises from 0.8 s to 1.7 s. However, the higher flexibility of the methacrylate network triggers an increase in the epoxide final conversion from 68 to 90%. It should be noticed that epoxide never reaches full conversion after the irradiation and levels off at 90%. The post-curing effect resulting from the living character of the cationic polymerization [21] will be studied at the end of this section.

The 20A80E system is of particular interest: as described previously, the immiscibility of the monomers results in phase segregation before the light is switched on. Kinetic data show that the methacrylate polymerization is accelerated and R_{pmax} increases by a factor of 4 compared to 100A0E (Fig. 3). The formation of small methacrylate domains dispersed in a low viscous epoxide

Fig. 4. (a) Methacrylate R_p curves in the neat resin and for hybrid mixtures (b) epoxide and methacrylate R_p curves vs. time for 40A60E.

matrix may account for this faster polymerization kinetic. A thoroughly study of the domain size and surface morphology of the photocured films is reported in the following section. In contrast to 0A100E, the polymerization rate of epoxide drops by a factor of 2 for 20A80E. The viscosity increase (almost by a factor of 3) and the lower ability of radicals to be oxidized and to contribute to the cationic process explain this result. Therefore, these changes in kinetics compared to the neat monomers originate in concomitant radical and cationic polymerizations: R_p max is reached at almost the same time for both monomers (Fig. 3b). However, this simultaneous photopolymerization of the two networks does not contribute to the formation of a homogeneous system. In this case, the thermodynamic forces foster immiscibility between monomers that cannot be counterbalanced by the polymerization kinetics. They prevent the interpenetration of both networks, resulting in a phase-separated system as already reported in [26,50,51].

For the other 3 ratios (40A60E, 50A50E, 70A30E), different methacrylate R_p profiles are observed when compared to 100A0E. A shoulder and progressively a second maximum of polymerization rate appear when increasing the epoxide ratio (Fig. 4a). The 40A60E system is worthy of attention: it clearly emphasizes a first R_{pmax} at 0.5 s close to the time already mentioned for methacrylate polymerization in immiscible systems. Polymerization of methacrylate first starts and no epoxides are converted. The initial miscible liquid formulation probably turns to be immiscible because of the depletion of acrylate concentration in the medium and the decrease of the entropy of mixing during the polymerization. For irradiation time between 0.5 and 0.9 s, the slowing down in R_p can be directly linked to the epoxide polymerization (Fig. 4b). Finally, there is a second R_p increase after the rate of polymerization of epoxide has reached its maximum.

The 70A30E system shows only one R_{pmax} for the methacrylates. In addition, the maximal methacrylate and epoxide rates of polymerization exhibit the lowest difference compared to all other systems (Table 4). Reaction kinetics prevent phase separation and the mixture reaches a good polymer chain entanglement [26,50,51]. The 50A50E mixture is an intermediate system between heterogeneous and highly-interpenetrated IPNs. Two R_{pmax} values can be observed for methacrylate but the system still remains miscible during the photopolymerization.

Since epoxides do not reach 100% conversion even in the neat resin nor in IPN systems, post-curing process was investigated by FTIR after 3 days of dark storage at room temperature. As reported in Table 4, the conversion gradually increases with time and levels off to final values ranging from 93% for the neat epoxide to 96% for 70A30E. Interestingly, the post curing was faster for highly-interpenetrated IPNs (70A30E). The final conversion is reached only after 20 h storage whereas it requires 3 days for heterogeneous IPN (20A80E). The rigidity of the epoxide which is dominant in this system combined with the phase segregation that limits the plasticizing effect resulting from the acrylate moiety obviously account for a slower epoxide post-polymerization. All these results highlight how miscibility, phase separation during the irradiation and kinetics of curing strongly affect the final conversion of the systems and consequently the final properties of the films. They markedly outline that investigation of the polymerization rate profiles is the first milestone of a comprehensive understanding of IPN formation and possible phase separation under irradiation.

3.3. Mechanical properties and surface morphology characterizations

For DMA and AFM characterizations, relatively large samples are required and cured under a belt conveyor. Similar trend was observed for polymerization kinetics. Independently of the monomer ratio, methacrylate conversion is fast and reaches 100% in a short time. Epoxide polymerization is still limited to 80% just after irradiation. Therefore, DMA and surface morphology investigations were performed 3 days after the photopolymerization to allow epoxide to reach almost full conversion.

DMA characterization gives access to the storage modulus (E') representing the elastic behavior of the materials and the loss factor ($\tan \delta$). Table 5 summarizes the thermomechanical data corresponding to the different UV-cured films. The $\tan \delta$ and storage modulus curves are reported for only one ratio in each miscibility area, according to Fig. 1. In parallel to DMA experiments, a detailed surface characterization was carried out by AFM and AFAM. Phase and Contact tip/sample Resonance Frequency (CRF) distribution histograms were calculated to give insight on the surface topography or elasticity of these UV-cured films [44,52]. They express the ratio of points at a given phase or CRF relative to the total number of points [43] for an analyzed surface. The number and relative positions of the peaks in the histograms were used to qualitatively detect changes in homogeneity [43,45,52]. Indeed, CRF data represent a precise mapping of local variations in elasticity which can be related to the local distribution of methacrylate or epoxide monomer. The bearing ratio curve, calculated from the distribution histogram, represents the percentage of areas of differing stiffness (or phase or CRF values) [53] as the integral of the population repartition. AFAM was more suitable than AFM to investigate the morphology of the IPNs. By contrast, AFM was used for neat methacrylate or epoxide films. For comparison, 70A30E was the only IPN analyzed in terms of RMS roughness, phase or CRF values, distribution histograms and bearing ratio by AFM and AFAM. Table 6 reports the different RMS data.

Table 5

T_g , $\tan \delta$ and storage modulus values obtained from DMA characterization for different UV-cured samples. Storage modulus (E') values are measured in the middle of the transition. 0A100E and 100A0E are respectively too brittle or fragile to be characterized by DMA. Their T_g s were assessed by DSC and are 144.8 °C and –73.5 °C, respectively.

		10A 90E	20A 80E	30A 70E	40A 60E	50A 50E	60A 40E	70A 30E	80A 20E
Peak 1	T_g (°C)	–46.2	–58.2	–56.7	–55.4	–57.8	–59.2	–57.0	–54.4
methacrylate	$\tan \delta$	0.07	0.07	0.09	0.11	0.14	0.14	0.13	0.17
homopolymer	E' (MPa)	6643	3540	2754	2531	1607	1051	1605	927
Peak 2	T_g (°C)	/	/	84.3	82.0	83.1	81.3	84.0	83.3
interphases	$\tan \delta$	/	/	0.10	0.15	0.24	0.19	0.20	0.22
or IPN	E' (MPa)	/	/	826	292	74	44	51	24
Peak 3	T_g (°C)	169.3	174.5	165.2	161.6	160.9	150.2	170.7	172.7
epoxide	$\tan \delta$	0.49	0.51	0.47	0.37	0.30	0.22	0.08	0.12
homopolymer	E' (MPa)	nd ^a	197	45	26	9	8	8	7

^a Too fragile to be measured.

Table 6

RMS values of roughness, phase and CRF, calculated from $2 \times 2 \mu\text{m}^2$ surfaces characterized by AFM or AFAM.

		0A 100E	20A 80E	40A 60E	70A 30E	100A 0E
AFM tapping mode	RMS roughness (nm)	0.29	nd	nd	0.36	0.27
	Phase RMS value (°)	0.11	nd	nd	0.11	0.14
AFAM	RMS roughness (nm)	nd	6.63	3.11	1.10	nd
	CRF RMS value (Hz)	nd	1.78	1.32	0.87	nd

nd: not determined.

Fig. 5. $2 \times 2 \mu\text{m}^2$ AFM topography (left) and phase images (right) for 100A0E (up) and 0A100E (down) recorded in tapping mode for UV-cured films.

3.3.1. Neat methacrylate and epoxide polymers (100A0E and 0A100E)

For both systems topography images (Fig. 5) disclose very flat and homogeneous surfaces, with low RMS roughness of 0.27 nm and 0.29 nm for 100A0E and 0A100E, respectively. Phase contrast images do not reveal any apparent domains and phase RMS values are similar. The UV-cured films are too soft or brittle to be characterized by DMA in tensile mode. In order to assess their thermal properties, DSC experiments were carried out. T_g was determined to be –73.5 °C and 144.8 °C for 100A0E and 0A100E, respectively. The low T_g of the polybutadiene dimethacrylate network accounts

for its weak mechanical properties and the high brittleness of polyether networks is well-known from the literature [9].

3.3.2. Miscible monomers-homogeneous IPNs (50A50E up to 90A10E)

For these ratios, both monomers are miscible; the final UV-cured IPNs should be homogeneous and highly-interpenetrated. Only one peak in the $\tan \delta$ curve should be expected, as an evidence of a good interpenetration and compatibility between the two networks. It would confirm that the phase separation was either avoided or very limited [21].

Fig. 6. Tan δ and storage modulus curves for 70A30E UV-cured film as a function of temperature obtained by DMA 3 days after photopolymerization.

Fig. 6 represents the tan δ and the storage modulus curves for 70A30E UV-cured film, which exhibits three tan δ peaks at -57.0°C , 84.0°C and 170.7°C evidencing some heterogeneity in the system (Table 5). DMA was performed 3 days after the photopolymerization to allow epoxide to postcure and reach almost full conversion (Table 4). The first and the last peaks were assigned to the soft methacrylate and the hard epoxide phases. Indeed, the values are really close to the T_g obtained by DSC for 100A0E and 0A100E (-73.5°C and 144.8°C , respectively). It is known that a difference of around $20\text{--}30^\circ\text{C}$ could be observed in the T_g , depending on the characterization method used (DSC or DMA). The broad intermediate tan δ peak at 84.0°C was attributed to an IPN [14]. The Fox equation was used to estimate its composition according to Eq. (4) [28,54–56].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

where T_{g1} and T_{g2} (K) corresponds to T_g of 100A0E and 0A100E homopolymers, T_g (K) is the T_g of the network which is formed, and w_1 and w_2 represent the weight fraction of methacrylate and epoxide within the mixture.

The IPN corresponds to a 16A84E immiscible system that should result in a heterogeneous morphology. However, the shape of the tan δ that does not reach the zero value between the different peaks and the storage modulus curves indicate the occurrence of some interpenetration and entanglements between the different homopolymer and IPN networks, obviously resulting in a transparent UV-cured film. These results are strengthened by the polymerization kinetic parameters reported in Table 4. For 70A30E, the difference between the maximum rates of polymerization for methacrylate and epoxide was the lowest compared to the other systems. Consequently, homogeneity at the submicrometer scale was preserved as also observed by AFM: Fig. 7a exhibits a very flat and homogeneous surface and the phase image does not reveal any phase-separated domains (Fig. 7b). The RMS roughness or phase values are still really low and close or equal to those obtained for the homopolymers 100A0E and 0A100E (Table 6). AFAM study (SI—Fig. S3) shows a similar homogeneous height profile, as well as a narrow CRF distribution with low RMS values (Table 6). Finally, phase distribution histogram discloses only one sharp peak (Fig. 10a).

3.3.3. Miscible monomers-heterogeneous films (30A70E and 40A60E)

Fig. 8 represents the tan δ and the storage modulus curves for the 40A60E system. Two separated tan δ peaks with corresponding T_g s at -55.4°C and 161.6°C related to methacrylate and epoxide polymers can clearly be seen (Table 5). A shoulder between these two

Fig. 7. $2 \times 2 \mu\text{m}^2$ AFM topography (a) and phase (b) images recorded in tapping mode for 70A30E UV-cured films.

Fig. 8. Tan δ and storage modulus curves for 40A60E UV-cured film as a function of temperature obtained by DMA 3 days after photopolymerization.

peaks is seen at around 80°C . This thermogram suggests a phase-separated system composed of both 100A0E and 0A100E, and the presence of interphases formed with both networks at different compositions as already reported in [57,58]. This is also confirmed by the gradual decrease of the storage modulus. The homogeneous formulation turns to be immiscible after the fast consumption of methacrylate at the first stage of the irradiation as evidenced by the polymerization rate profile in Fig. 4b. Consequently, the UV-

Fig. 9. $2 \times 2 \mu\text{m}^2$ AFM topography (a) and phase (b) images recorded in tapping mode for 40A 60E UV-cured film.

cured film becomes heterogeneous and can be represented by an intermediate behavior between clear phase separation and homogeneity [59]. Topography, phase and CRF images strengthen this general picture (Fig. 9 and SI—Fig. S4). Some brighter and darker domains corresponding to methacrylate soft phase and epoxide hard phase could be identified in Fig. 9a. The intermediate color is probably related to interphases containing different proportions of both polymers. AFAM characterization reveals a RMS roughness of 3.11 nm that is 2.8 times higher than for 70A30E ratio (homogeneous IPN). The phase image (Fig. 9b) highlights a complex structure, with stiffer and softer domains corresponding to lower and higher phase values, and interphases with an intermediate phase value. CRF RMS value is 1.5 times higher than for 70A30E (Table 6). Since the two homopolymers have really different stiffness, an increase in the heterogeneity leads to higher differences in CRF values. As a result, the phase distribution histogram exemplifies a broader phase distribution confirming the phase separation for 40A60E film [60] (Fig. 10b).

3.3.4. Immiscible monomers-heterogeneous films (10A90E and 20A80E)

DMA characterization for the 20A80E UV-cured film is reported in Fig. 11. This system exhibits two well separated $\tan \delta$ peaks at -58.2°C and 174.5°C suggesting a totally phase-separated system (Table 5) [57]. Between these two peaks, the $\tan \delta$ values become very close to zero. The storage modulus curve confirms the two-

Fig. 10. Phase distribution histogram for 70A30E (a) and 40A60E (b) UV-cured films calculated from $2 \times 2 \mu\text{m}^2$ AFM phase images in tapping mode.

phase structure through the presence of two different and well-defined inflexions [58]. These observations are in good accordance with the miscibility experiments (Fig. 1), which showed that the immiscible monomers lead to heterogeneous films for 10A90E and 20A80E compositions.

Topography, CRF images and distribution histogram are reported in Figs. 12 and 13 and SI—Fig. S5. A bright matrix of epoxide with dark domains of methacrylate containing epoxide nodules can be seen. The RMS roughness reaches 6.63 nm, which is 6 and 2.1 times higher than for 70A30E and 40A60E, respectively (Table 6). CRF histograms plotted in Fig. 13 clearly confirm these results. 20A80E evidences two different populations centered at different CRF values, as already encountered in the case of inhomogeneous

Fig. 11. $\tan \delta$ and storage modulus curves for 20A80E UV-cured film as a function of temperature obtained by DMA 3 days after photopolymerization.

Fig. 12. $2 \times 2 \mu\text{m}^2$ topography (a) and CRF (b) images and $10 \times 10 \mu\text{m}^2$ CRF (c) images recorded in AFAM for 20A80E UV-cured film.

surface with domains of different stiffness [52]. The first one ranging between 314 and 320 Hz corresponds to the soft methacrylate domains. It is 3 times broader than the one corresponding to the hard epoxide domains centered at 321.5 Hz. It is possible to estimate the surface area corresponding to “soft” and “hard” parts with the bearing-ratio curve [43,53]. 50% of the surface corresponds to soft areas although the methacrylate amount is only 20 wt.% for 20A80E system. This unexpected value was attributed to the inclu-

Fig. 13. CRF distribution histogram of 40A60E (a), 20A80E (b), and bearing ratio (c) of 20A80E UV-cured films calculated from $10 \times 10 \mu\text{m}^2$ AFAM CRF images.

sion of epoxide nodules in methacrylate domains, resulting in a significant heterogeneity of this soft phase.

Surface characterization reveals without ambiguity the existence of phase separation and is fully consistent with the two clearly separated $\tan \delta$ peaks found with the DMA analysis. The thermodynamic forces are predominant and the immiscibility of monomers triggers the phase segregation. When polymerization proceeds, methacrylate and epoxide homopolymers are formed separately but concomitantly as demonstrated by the kinetic profiles in Fig. 3b.

4. Conclusions

In this paper, the formation and phase separation in polybutadiene dimethacrylate and cycloaliphatic diepoxide UV-cured Interpenetrating Polymer Networks have been investigated. Major parameters controlling the morphology and the phase separation,

namely monomer miscibility and synthesis parameters have been identified. By monitoring the stiffness changes on the film surface, atomic force acoustic microscopy (AFAM) gave precise and reliable results based on Contact tip/sample Resonance Frequency (CRF) images and distribution histograms. In conjunction with polymerization kinetic profiles and thermomechanical properties, they explained and corroborated the prediction made by miscibility investigations. Three cases of IPN formation were identified as a function of monomers ratio. Above 40 wt.% of methacrylate, monomers were miscible and the final UV-cured film exhibited homogeneity at the submicrometer scale. Below 20 wt.% of methacrylate, monomers were immiscible and the UV-cured layer exhibited a complete phase separation. Between these two domains, an intermediate behavior leading to partly interpenetrated systems was observed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mtcomm.2015.11.004>.

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