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Influence of Actinic Wavelength on Properties of Light-Cured Interpenetrating Polymer Networks

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ABSTRACT: Interpenetrating polymer networks (IPNs) composed of different acrylate/epoxide ratios, were synthesized under UV and visible-LED curing conditions. The formation of the IPNs was explored in terms of phase separation, polymerization mechanisms, final mechanical properties and surface morphology. For these purpose, we uniquely combined results of miscibility investigations, confocal Raman microscopy, dynamical mechanical analysis and atomic force microscopy. Transparent films were obtained for all compositions and both irradiation sources. The thermo-mechanical properties of different IPNs were associated to the presence of acrylate- or epoxide-rich phases, as well as, mixed interphases, resulting from the high interpenetration between both networks. Although the final conversions were similar under UV and visible-LED irradiation, we have found evidence that the visible-cured samples provide higher IPN homogeneity and lower $T_g$ for a higher epoxide content. To explain this trend, the mechanisms and sequence of the acrylate or epoxide networks formation, under UV or LED irradiation, is discussed.

KEYWORDS: acrylate/epoxide polymerization; interpenetrating polymer networks; LED curing; morphology characterization; thermo-mechanical analysis

INTRODUCTION Interpenetrating polymer networks (IPNs) are a combination of two or more polymer networks forming permanent entanglements without being bonded to each other covalently.1 Overcoming the limitations of a standalone network and combining different properties have triggered the considerable attention paid to IPNs, which currently exhibit specific features such as high mechanical strength, good thermal stability and good chemical resistance.2–7 The use of interpenetrating polymers typically covers the area of damping materials, impact resistant materials, adhesives etc.1,8,9

IPNs with various polymer combinations have been synthesized simultaneously or sequentially by thermal processing combining radical or cationic polymerization and/or polycondensation.3–5,7,10–14 In this case IPNs are prepared by a process in which both components are polymerized concurrently according to non-interfering reactions.1,3,4,6 In contrast, in a sequential process, the second polymeric component is swollen and polymerized after the completion of the first network.1,5 The final IPN structures show a high interpenetration5 or various microdomain sizes4,7,13 due to the variable compatibility of the different networks. Factors affecting the extent of phase separation of IPNs are volume fractions,7 thermodynamic interaction between components,10 sequence order,12,15,16 kinetics of reaction and mobility of the polymer chains.4,10,11,17 Incompatible polymers do have a strong thermodynamic driving force so that phase separation occurs before gelation.10,13 Similar values of polymerization rates of the two networks are, in general, favorable for obtaining a high degree of homogeneity in the IPN.17 Eventually, the level of phase separation will affect the
mechanical and morphological properties. The compatibility of two different networks is indicated by a single glass transition temperature with no apparent phase domains in the morphology, whereas two clearly separated transitions are indicative for a phase separation with a coarse morphology. One broad transition is attributed to an intermediate degree of mixing.

An easy and efficient way to produce homogeneous IPNs is UV curing. While light induced polymerization has the advantage of being a room temperature reaction with a solvent free process, the fast crosslinking reaction reduces the phase separation and improves the final properties. Moreover, different polymerization mechanisms can be carried out independently from each other at the same time. Light induced polymerization can proceed either simultaneously with rapid network formation and limited phase separation which result in good mechanical properties, or sequentially with two-step irradiation which leads to phase-separated systems. Dual curing methods, such as UV/thermal and thermal/UV processes, can be also implemented and the final mechanical properties and phase domain sizes are controlled by changing the sequence order of curing. Among the different studies focusing on UV-cured IPNs, particular attention has been paid to acrylates or methacrylates and epoxide combinations. (Meth)acrylates are widely used monomers, due to their high reactivity, good adhesion, transparency properties and commercial availability. However, a significant shrinkage as well as early vitrification of the network may appear due to the high monomer reactivity leading to internal stress and cracks. These systems undergo free radical polymerization and are therefore sensitive to atmospheric oxygen during the polymerization process. Epoxide resins are well-known to exhibit excellent mechanical, thermal and electrical properties and a good dimensional stability and resistance to moisture, corrosion and chemicals. Due to the ring opening polymerization, epoxides exhibit less shrinkage. However, their high brittleness and relative sensitivity to humidity restrict their applications. IPNs consisting of acrylate and epoxide structures overcome the limitations of both networks and are therefore good candidates for rapid prototyping by stereolithography for which reduced shrinkage, improved impact resistance, limited brittleness and high flexibility are required.

Recently, due to the development of non-harmful light sources such as LED, efforts have been devoted to develop and optimize photoinitiating systems for the visible range (λ > 380 nm). Visible light LED sources are preferred due to their special characteristics, such as narrow bandwidth with stable irradiation, long life-time, low heat generation and more energy saving performance. However, by changing the irradiation conditions from UV to LED, new light absorbing systems are required. Numerous photoinitiating systems (PI) have been developed for free radical polymerization under visible light. In contrast, curing of cationic resins is much more limited. One of the attractive alternatives is to implement free radical promoted cationic polymerization (FRPCP) to produce a radical that can be oxidized by onium salts. The absorption of visible light and subsequent generation of the required radicals can be provided by using type I PIs such as benzoin and benzoin derivatives, acylphosphine oxides or bisacrylphosphine oxides, acyl germanes, etc. Moreover, the use of photosensitizers like titanocene, camphorquinone or thioxanthone/silane/iodonium salt systems improves the absorption properties of visible light absorbing systems and also reduces the oxygen sensitivity. Similarly, type II PIs with a combination of benzyl alcohol (BA) derivatives and iodonium salts could be another efficient system to apply the process. Many other systems have been reported in the literature.

Among all the studies published in this area, only a limited number of articles pertain to visible light-cured IPNs. They mainly focus on the efficiency of the photoinitiating systems, although there is a lack of information related to IPN formation and the resulting mechanical and morphological properties prepared under more environmentally friendly LED systems. Therefore, this paper describes a thorough investigation of IPN structures prepared under UV and LED irradiation. This study reports on the synthesis of light-cured epoxide/acylate IPNs and a comparison of their characteristics, after having selected the most suitable photoinitiating system. The degree of conversion (polymerization) has been determined by FTIR and confocal Raman microscopy (CRM), while the characterization of mechanical and morphological properties has been done by dynamical mechanical analysis (DMA), atomic force microscopy (AFM) and the scratch resistance.

**EXPERIMENTAL**

**Materials**

Polyethylene glycol 600 diacrylate (Sartomer SR 610, viscosity = 80 mPa·s at 25 °C) was chosen for its flexibility and low Tg (−30 °C). (3, 4-epoxycyclohexane) methyl 3, 4-epoxycyclohexylcarboxylate (Dow Chemical, UVR 6110, viscosity = 220–250 mPa·s at 25 °C) was selected for its high reactivity and good mechanical properties. The radical photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) was obtained from BASF and the cationic photoinitiator triarylsulphonium hexafluoroantimonate salt (TAS), diluted in propylene carbonate (50 wt %) was purchased from Sigma Aldrich. These two photoinitiators are used for the UV curing process. A combination of Isopropyl-9H-thioxanthan-9-one (ITX)/BA/(4-methylphenyl)[4-(2-methylpropyl)phenyl] iodonium hexafluoroantimonate, Irgacure 250) was used as LED-curing photoinitiating system. ITX and BA were obtained from Sigma-Aldrich and Irgacure 250, diluted in propylene carbonate (25 wt %) was obtained from BASF. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) and N-Vinylcarbazole (NVK) were obtained from Sigma Aldrich. All these compounds were used without any further purification.
Methods

Preparation of Photocurable Formulations

Photocurable formulations were prepared by mixing the acrylate and epoxide resins at different weight (%) ratios. Mixtures will be described as $xA_yE$, with $x$ standing for $x$ wt % acrylate and $y$E for $y$ wt % epoxide. Radical and cationic photoinitiators were further added to the formulation.

Table 1 provides the composition of the UV- and LED-cured systems.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>SR 610 (wt %)</th>
<th>UVR 6110 (wt %)</th>
<th>Darocur 1173/TAS$^a$ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100A0E</td>
<td>99</td>
<td>0</td>
<td>1/0</td>
</tr>
<tr>
<td>90A10E</td>
<td>89</td>
<td>8</td>
<td>1/2</td>
</tr>
<tr>
<td>80A20E</td>
<td>79</td>
<td>18</td>
<td>1/2</td>
</tr>
<tr>
<td>70A30E</td>
<td>69</td>
<td>28</td>
<td>1/2</td>
</tr>
<tr>
<td>60A40E</td>
<td>59</td>
<td>38</td>
<td>1/2</td>
</tr>
<tr>
<td>50A50E</td>
<td>49</td>
<td>48</td>
<td>1/2</td>
</tr>
<tr>
<td>40A60E</td>
<td>39</td>
<td>58</td>
<td>1/2</td>
</tr>
<tr>
<td>30A70E</td>
<td>29</td>
<td>68</td>
<td>1/2</td>
</tr>
<tr>
<td>20A80E</td>
<td>19</td>
<td>78</td>
<td>1/2</td>
</tr>
<tr>
<td>10A90E</td>
<td>9</td>
<td>88</td>
<td>1/2</td>
</tr>
<tr>
<td>0A100E</td>
<td>0</td>
<td>98</td>
<td>0/2</td>
</tr>
</tbody>
</table>

$^a$ Diluted in propylene carbonate at 50 wt %; the amount of active photoinitiator is thus 1 wt %.

Miscibility Investigations

Solubility parameters were calculated by using the method of Van Krevelen and Hoftyzer.$^{58}$ For the characterization of the monomers, the specific gravity was given in the technical data sheets while $M_n$ was determined using $^1$H and $^{13}$C NMR spectroscopy (Bruker Advance at 295 K, 400 MHz, CDCl$_3$). Furthermore, the miscibility of the two monomers was investigated experimentally at 20 °C, observing haziness before and after polymerization.

Curing Conditions for CRM, DMA, and AFM Characterizations

The various formulations were applied on polypropylene substrates. Photocuring was done at room temperature under air with a belt conveyor at an equivalent speed of 10 m-min$^{-1}$. For UV curing, a fusion microwave Hg lamp (type H) was used. The light dose received by samples for each pass (light exposure of 0.3 s) was measured by an UV-Power Puck II instrument and turned to be 978 mJ/cm$^2$ (UVA: 330 mJ/cm$^2$, UVB: 240 mJ/cm$^2$, UVC: 57 mJ/cm$^2$, UVV: 351 mJ/cm$^2$). Three passes were required to obtained tack-free films with a total irradiance of 3600 mW/cm$^2$. LED curing was performed by using a 395 nm Firejet FJ200 LED from Phos- eon (12 W/cm$^2$). The light dose received by samples for each pass (light exposure of 0.5s) was 310 mJ/cm$^2$ (UVA: 10 mJ/cm$^2$, UVV: 300 mJ/cm$^2$) with an irradiance of 550 mW/ cm$^2$ (after 10 passes). Tack-free and transparent films of about 50–70 μm thick were obtained.

Fourier Transform Infrared Spectroscopy (FTIR)

The neat acrylate and epoxide conversions were followed by FTIR (Vertex 70, Bruker Optics). A 50 μm thick film was deposited on a KBr pellet using a calibrated bar coater and cured under UV or LED. Conversions were calculated by following the C=C deformation band at 1640 cm$^{-1}$ and the symmetrical stretching at 790 cm$^{-1}$ for acrylate and epoxide, respectively.$^{21,22}$ The monomer conversion versus time was calculated using eq 1,

$$\text{Conv} (\%) = 100 \times \frac{(A_0 - A_t)}{A_0}$$

where $A_0$ is the initial absorption band area before exposure (at time $t_0$) and $A_t$ the absorption band area after various times of light irradiation (at time $t$). The maximum rates of polymerization ($R_p \text{ max}$) were calculated from the maximum of the first derivative of the conversion vs time curves.
Confocal Raman Microscopy

Measurements were performed on a Raman microscope (inVia Reflex, Renishaw) which couples a Raman spectrophotometer with a Leica DM2500 microscope. The excitation wavelength was provided by a Helium-Neon laser emitting at 632.6 nm. An accumulation time of 30 s was needed at each step to obtain signal-to-noise ratio values for deeper layers. Circular polarization of the laser beam was achieved by placing a λ/4 waveplate in the optical path of the incident light to get rid of polarization effects. A 600 l/mm grating optimized for the visible light and providing a spectral window on the CCD camera. The spectral resolution given by the spectrophotometer entrance slit opened to 20 μm in the back focal plane of the objective lens and a selection of 3 pixels perpendicular to the slit axis on the CCD camera. The spectral resolution given by the combination slit/CCD/grating was 8.7 cm⁻¹. The dry objective used was N PLAN 50x Leica with a numerical aperture of 0.75.

The UV and LED-cured samples were prepared as described. The decrease of functional bands has been followed by CRM. The C=O stretching band at 1636 cm⁻¹ (A(C=O)) and the oxirane ring deformation at 785 cm⁻¹ were followed as a function of depth for the acrylate and epoxide, respectively. In order to avoid misinterpretation due to the loss in intensity with increasing depth, fluctuations of the laser intensity or other external perturbations, the carbonyl band of acrylate and epoxide monomers (A(C=O)) at 1721 cm⁻¹—not affected by curing—was chosen to normalize the acrylate and epoxide functional bands for all formulations. The conversion was then calculated from eq 2.

\[ \text{Conv}_{\text{Raman}} (\%) = 100 \times \left( 1 - \frac{A_x}{A_m} \right) \]  

where \( A_x = (A(C=O)/A(C=O)_{\text{m}}) \) corresponds to the absorbance ratio of functional bands in the cured samples while \( A_m = (A(C=O)/A(C=O)_{\text{m}}) \) is the absorbance ratio determined from the liquid formulation. The conversion values of functional bands were calculated for several depths and positions in the film and the average of 10 of these values has been reported as the final conversion.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA Q800, TA instruments) was used to characterize the viscoelastic properties of IPN samples in tensile mode at a frequency of 1 Hz. DMA has been performed on UV and LED-cured films (~11 × 5.4 × 0.05-0.07 mm³ rectangular samples) to determine the storage modulus \( E' \), representing the elastic behavior of the materials, and the loss factor (tan δ), defined as the ratio between the loss modulus \( E'' \) and the storage modulus. Tan δ curves were obtained as a function of the temperature at a constant heating rate of 3 °C/min⁻¹. In the glass transition temperature region, a strong decrease of \( E' \) can be observed, whereas tan δ reaches a maximum that corresponds to the \( T_g \) of the photocured film. Furthermore, DMA provides information about the degree of heterogeneity of the polymer material. In order to give detailed explanations, a peak deconvolution process has been applied to the DMA curves by using the PeakFit 4.12 software.

Atomic Force Microscopy (AFM)

Morphology investigations were performed by AFM on the top air-interface of the cured materials (Ntegra Spectra from NT-MDT). A NSG 01 tip (silicon, nominal resonance of 267 kHz, nominal spring constant of 5.5-22.5 N m⁻¹) was used for acquiring images in semi-contact mode. For a more precise investigation of the different systems, the root mean square (RMS) roughness was calculated²⁵⁻⁶¹ from the AFM topography images using the roughness analysis tool of Nova software from NT-MDT, applied on the whole scanning area. In the same manner, the RMS values of phase have been estimated from phase images obtained in AFM. For both case we used eq 3.

\[ R_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} x_i^2} \]  

where \( x \) denotes either the height or phase difference between a given point and the average and \( n \) the total number of the measured points.

AFM experiments were also carried out on the cross-section of some samples by using a Solver type P47HT, NT-MDT device. A NSG 11 tip (silicon, nominal resonance of 267 kHz, nominal spring constant of 5.5-22.5 N m⁻¹) was used for acquiring images in semi-contact mode. The UV- and LED-cured films were embedded into an epoxy-based thermoset (Jeffamine D230 and Epikote 828 in 1:1 function ratio) and stored for 3-4 days at room temperature until complete polymerization was achieved. Microtoming was done (Leica Ultracut UCT Leica EM FCS) at 0 °C using a diamond blade (trim tool 45, Diatome) to obtain surfaces as flat as possible. The chamber of the microtome was cooled down by liquid nitrogen. After the process, the micromtomed samples were stored in a vacuum dryer overnight to eliminate the moisture introduced by condensation due to the liquid nitrogen temperature environment.

Scratch Resistance Tests

Scratch experiments of UV- and LED-cured samples coated onto a glass plate (thickness ~50 μm) were conducted at room temperature (Elcometer 3000 Motorised Clemen Unit). The tip was a 100 μm diameter diamond sphere and the sliding speed was kept constant at 1.925 cm s⁻¹ using loads between 0.5 and 2 N. The size and shape of the grooves on the coatings were evaluated by an optical profilometer (Altsurf 500 workstation) and optical microscopy.

RESULTS AND DISCUSSION

Miscibility Investigations

Miscibility of polymers is an important characteristic, which directly influences the phase separation behavior of IPNs.
The miscibility of the acrylate monomer in epoxide resin before UV curing was studied first, at 20 °C by gradually increasing the acrylate ratio from 5 to 95 wt % in the blend. No haziness has been observed (Supporting Information Fig. S1). Moreover, all the final films were transparent, indicating no visible phase separation during photopolymerization. This can be understood in terms of the solubility parameter \( \delta \), defined as the square root of the cohesive energy density. These parameters were calculated from group contributions using the Hoftyzer and Van Krevelen method, based on classical Flory–Huggins theory, as described in the literature. The results are reported in Table 2.

The total solubility parameters for epoxide (\( \delta_1 \)) and acrylate (\( \delta_2 \)) are 22.47 and 20.05 J\(^{1/2}\)/cm\(^{3/2}\), respectively. Conventionally, immiscibility between two compounds is expected when the difference of their solubility parameters reaches about 4-5 J\(^{1/2}\)/cm\(^{3/2}\). Therefore miscibility problems are not expected for the different liquid formulations, as confirmed by our experiments.

**Characterization of UV-Cured IPNs**

**Final Conversions**

The acrylate/epoxide combination used in this study was not suitable for FTIR characterization due to overlapping of epoxide and acrylate vibrational bands and corresponding integration problems. CRM was thus implemented to determine the final conversion of acrylate and epoxide for each IPN network (Table 3).

Acrylates were fully converted for all the ratios studied. Neat epoxide exhibits a limited conversion of 60% due to fast vitrification and brittleness of the network. However, it’s conversion rises up to 74% with increasing amount of acrylate acting as a plasticizer. The epoxide conversion for 90A10E could not be calculated due to the very low intensity of the corresponding functional band in the CRM spectrum. All the films have been stored in the dark and at room temperature for two days to investigate the effect of post-polymerization of the remaining epoxide functions. No significant change was observed except for 0A100E and 10A90E for which final conversions increases up to 72-76%. For these samples, the absence or limited amount of acrylate was not sufficient to act as plasticizer during the exposure and enable epoxide to reach its highest possible conversion level. In consequence, epoxide post-polymerization can be observed.

**Thermomechanical Properties**

DMA is an efficient technique to analyze the degree of interpenetration in IPN materials. The glass transition temperature (\( T_g \)) of crosslinked polymers can be obtained from the maximum of the tan \( \delta \) curves (Fig. 1). A narrow peak of tan \( \delta \) can be explained by a high degree of interpenetration between the two networks, while two clearly separated glass transition peaks are expected for each network.
transition peaks for each homopolymer indicate phase separation. An intermediate degree of mixing in IPNs is represented by a single broad transition. Damping properties of the sample can also be analyzed by observing the temperature range that the tan δ peak spans.

Sample 0A100E was too brittle to be characterized by DMA in tensile mode. However, a DSC experiment was carried out and the $T_g$ was found to be 145 °C. In general, DSC $T_g$ values are 20 to 30 °C lower than the ones determined by DMA. Therefore, one can expect a $T_g$ of 175 °C in DMA for 0A100E. Thermograms of the other samples are presented in the Figure 1 and the corresponding data are reported in Table 4. They show one to three distinct mechanical relaxations, due to complex phase morphology, as discussed later. From the deconvolution of the tan δ curves (presented in Supporting Information Fig. S2) and the determination of the acrylate/epoxide ratios for the attributed IPNs by applying the Fox equation (eq 4), one can highlight three different cases that deserve further comments.

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

For all the films prepared, co-continuous phases are observed since no separate epoxide or/and acrylate homopolymer peaks could be identified for any ratio. Both homopolymer networks are included in an IPN architecture of different compositions. However, peak broadening can be noticed upon increasing epoxide amount.

From 90A10E to 70A30E: A narrow single peak with a $T_g$ of $-28$ °C corresponds to the mechanical relaxations of an acrylate-rich phase ($T_g$ of $-30$ °C for the neat acrylate). With increasing epoxide amount, a shoulder and later a peak broadening reflect the presence of an epoxide/acrylate IPN, partly entangled in the dominating acrylate network. For 70A30E, two IPNs can be identified at 12 and 42 °C. The FWHM of 29 °C is still indicating a high homogeneity between the two networks, the first one being predominantly constituted by acrylate.
From 60A40E to 40A60E: The FWHM increased by more than a factor 3 for some ratios. Up to three relaxations can be detected after deconvolution. They are characteristic of a continuous phase of 2 or 3 IPNs with some kind of interpenetration, confirmed by the fact that the tan δ curve does not reach zero value. They result obviously in transparent UV-cured films.

For 30A70E to 10A90E: The tan δ characteristic of acrylate-rich phase disappears and a new broad peak appears. Its width highlights the presence of interpenetrating phases of different compositions. Deconvolution of the three tan δ curves suggests the presence of a neat epoxide network at about 175 °C together with IPNs rich in epoxide. The tan δ curves become narrower for 20A80E and 10A90E, in accordance with a higher amount epoxide in the samples.

Morphological Properties
Surface scan analysis (50 × 50 μm², 10 × 10 μm² or 1 × 1 μm²) was performed in AFM tapping mode for all acrylate/epoxide ratios. The most representative topography and phase contrast images (1 × 1μm²) are reported in Figure 2. In phase contrast, the harder component appears bright while the softer one is dark. RMS roughness and phase values have also been calculated from the topography and phase AFM images. Additionally, the bearing ratio curve has been determined and the corresponding curve represents the stiffness distribution of the analyzed area (phase image) calculated from the integration over the distribution histogram.

Very flat surfaces with height RMS values ranging between 0.10 and 0.14 nm were obtained for all systems (Table 5). These values are in the same order of magnitude as the homopolymer values (Table 5 and Supporting Information Fig. S3). AFM phase images do not reveal any apparent phase domains and the bearing ratio curve shows one population with a narrow phase distribution. Moreover, AFM of a cross-section of a 50A50E sample has been performed; whose thermogram exhibits three tan δ peaks (Fig. 3). No distinguishable domains could be detected, by also taking into account the possible smearing at the bulk surface, which might cause unclear image. Nevertheless, these observations

### Table 5: RMS roughness and phase values for UV-cured films, calculated from AFM tapping mode top surface topography and phase images

<table>
<thead>
<tr>
<th>Ratio</th>
<th>RMS roughness (nm)</th>
<th>RMS phase (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100A0E</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>70A30E</td>
<td>0.10</td>
<td>0.33</td>
</tr>
<tr>
<td>50A50E</td>
<td>0.12</td>
<td>0.37</td>
</tr>
<tr>
<td>30A70E</td>
<td>0.12</td>
<td>0.33</td>
</tr>
<tr>
<td>10A90E</td>
<td>0.14</td>
<td>0.56</td>
</tr>
<tr>
<td>0A100E</td>
<td>0.30</td>
<td>0.44</td>
</tr>
</tbody>
</table>
confirm a distribution at the sample top air-interface and also in the bulk of a co-continuous hard and soft phase resulting from a strong interpenetration of IPNs of different compositions.

It has been noticed in the literature that the domain size could be expected to be between 5 to 50 nm, if a single transition is located at a temperature between those of single networks. In the present case, there is no clear observation of the $T_g$'s of both homopolymers in any of the DMA thermograms. However, a $T_g$ peak of the homopolymers could be found after deconvolution, together with other transitions attributed to interphases. Therefore, the domain size can be assumed to be in the similar range than the one mentioned before. In addition, it was shown by TEM that the IPNs exhibit no clear phase separation or well-defined phase domains for samples where the thermomechanical relaxation is in between that of single networks, even when the mechanical relaxation of the IPN is close to one of the single networks.

In conclusion, the UV-cured films investigated in this study for the given acrylate/epoxide ratio are formed of several entangled IPNs of different composition. The phase contrast between these IPN structures remains low and the phase domains are probably too small to be clearly identified by AFM.

From UV to LED-Cured IPNs

Selection of Visible Light Photoinitiating System

When moving from UV to LED photopolymerization, a change in photoinitiating system is required for both acrylate and epoxide polymerization. FRPCP can be implemented to initiate the cationic ring opening. It involves long wavelength absorbing photoinitiators for radical generation which are able to be easily oxidized by onium salts (with high reduction potentials) to generate reactive cation species. In the case of IPNs, the photoinitiating system should also be able to initiate radical photopolymerization.

From the FRPCP systems reported in the literature two were chosen for the present study, taking into account easy applicability and commercial availability. The first combination was composed of BAPO, NVK and Irgacure 250. The radical photoinitiation mechanism is based on $\alpha$-cleavage of BAPO and direct initiation of acrylate polymerization. Moreover, by the addition of the generated radical to the double bond of NVK, a new carbon-centered radical that can be oxidized by iodonium salts is produced.

The second combination was composed of ITX, BA and Irgacure 250. The radical initiation is based on an excitation of ITX to the triplet state. Hydrogen abstraction from the H-donor results in the formation of ketyl and alkyl radicals. These latter are the only ones able to initiate the polymerization. In the present study, PEG-based monomers are efficient H-donors due to their ether bonds. For cationic photoinitiation, besides direct interaction of iodonium salts with the...
triplet state of ITX,\textsuperscript{69} BA leads to the generation of an aryl radical, which is oxidized by the iodonium salt to generate reactive cation species. Hydrogen abstraction from BA by ITX results in the formation of ketyl and alkyl radicals. The oxidation of both radicals by iodonium salts has been reported in the literature\textsuperscript{36,39,70} and the photochemical pathway is presented in Scheme 1.

The two photoinitiating systems were first compared for acrylate and epoxide homopolymers polymerization under LED irradiation (Fig. 4). For the BAPO/NVK/Irgacure 250 system, acrylate polymerization is faster than epoxide polymerization. The acrylate conversion reaches 100\% in less than 2 s, while epoxide conversion levels off at around 55\%, even for long exposure time. The fast vitrification of the epoxide network, its brittleness and the limited diffusion of reactive functions accounts for this result. For the ITX/BA/Irgacure 250 system, the opposite result is obtained and epoxide polymerization starts first. A greater efficiency of the ITX/Irgacure 250 system in generating reactive cations is evidenced through the combination with BA (Fig. 4b). The epoxide conversion is, however, still limited to 61\%, which is only slightly higher than for BAPO/NVK/Irgacure 250 system. The acrylate polymerization proceeds slower and reaches 90\% conversion after longer irradiation time.

A comparison of these photoinitiating systems in IPNs was made by CRM using 70A30E and 30A70E samples. For the other ratios, only the results corresponding to the most efficient PI system are reported in Table 6.

For 70A30E and 30A70E, the acrylate conversion is complete for BAPO/NVK/Irgacure 250; conversely, epoxide polymerization levels at 28\% and 45\%, respectively. This results from the very fast formation of the acrylic network and increase in viscosity which limits the mobility of the epoxide reactive groups. 30A70E was still sticky even after increasing the light dose up to 11 J/cm\(^2\), but became tack-free after a few hours waiting in the dark. The living character of the cationic polymerization that leads to further epoxide conversion accounts for this result.

As previously observed for the corresponding homopolymer (Fig. 4b), the ITX/BA/Irgacure 250 system leads to a higher epoxide conversion (78\% for 30A70E and 73\% for 70A30E).

### FIGURE 4
Radical and cationic polymerization kinetics for homopolymers under 395 nm LED in the presence of (a) BAPO/NVK/Irgacure 250 and (b) ITX/BA/Irgacure 250. ([BAPO]: 2 wt \%, [NVK]: 3 wt \%, [ITX]: 2 wt \%, [BA]: 4 wt \%, [Irgacure 250]: 3 wt \%; Light intensity: 550 mW/cm\(^2\)).

### TABLE 6
CRM conversion of IPN systems for the different PI systems. LED exposure at 395 nm (light intensity: 550 mW/cm\(^2\), light dose: 3-10 J/cm\(^2\) and total exposure time: 5 s). All films are tack-free

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Photoinitiating systems</th>
<th>Acrylate</th>
<th>Epoxide after exposure</th>
<th>Epoxide after 2 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>0A100E</td>
<td>ITX/BA/Irgacure 250</td>
<td>–</td>
<td>59</td>
<td>Not measured</td>
</tr>
<tr>
<td>10A90E</td>
<td>ITX/BA/Irgacure 250</td>
<td>86</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>30A70E</td>
<td>BAPO/NVK/Irgacure 250(^a)</td>
<td>100</td>
<td>28</td>
<td>Not measured</td>
</tr>
<tr>
<td></td>
<td>ITX/BA/Irgacure 250</td>
<td>95</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td>50A50E</td>
<td>ITX/BA/Irgacure 250</td>
<td>95</td>
<td>74</td>
<td>77</td>
</tr>
<tr>
<td>70A30E</td>
<td>BAPO/NVK/Irgacure 250</td>
<td>100</td>
<td>45</td>
<td>Not measured</td>
</tr>
<tr>
<td></td>
<td>ITX/BA/Irgacure 250</td>
<td>90</td>
<td>73</td>
<td>80</td>
</tr>
<tr>
<td>90A10E</td>
<td>ITX/BA/Irgacure 250</td>
<td>77</td>
<td>Not detectable</td>
<td>Not detectable</td>
</tr>
<tr>
<td>100A0E</td>
<td>ITX/BA/Irgacure 250</td>
<td>Not measured(^b)</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Cured under a light dose of 11 J/cm\(^2\).

\(^b\) This sample was tacky and has not been characterized by CRM.
in the IPNs. Besides the higher efficiency of this photoinitiating system, the plasticizing effect of acrylates may explain this result. In addition, tack-free systems could be achieved directly after irradiation. Interestingly, the acrylate conversion is higher for the IPN (90–95%) than for the homopolymer after the same exposure time. This result can be correlated to the fast increase in viscosity (epoxide polymerization starts before acrylate polymerization) and resulting limited oxygen diffusion.18,21 Nevertheless, the acrylate could not be fully converted.

Table 6 also reports acrylate and epoxide conversions for the other IPN ratios with ITX/BA/Irgacure 250 as photoinitiating system. As for 30A70E or 70A30E, the epoxide conversion is higher for the IPN than for the homopolymer. For acrylate, a lower conversion was observed for 10A90E (86%) and 90A10E (77%). For 10A90E the high amount of epoxide monomer and its high reactivity possibly trap some acrylate groups that remain unconverted. For 90A10E the lower efficiency of this PI system for radical polymerization and the limited amount of epoxide that cannot act as an efficient barrier to atmospheric oxygen contribute to this result. Since the neat acrylate homopolymer was not tack-free after exposure, CRM experiments were not performed.

Finally, acrylate and epoxide conversions reached under UV and LED illumination should be compared. When the BAPO/NVK/Irgacure 250 system is used, radical polymerization is favored and similar conversion ratios are observed under UV and LED illumination. However, the poor efficiency of this PI system to generate reactive species for cationic polymerization strongly limits the epoxide conversion at 395 nm. With the ITX/BA/Irgacure 250 system, cationic polymerization is more efficiently promoted and final conversions are slightly higher under LED illumination. Consequently, the acrylate polymerization is lowered to some extend when compared to UV-cured IPNs. For the further characterizations of LED-cured IPNs, the ITX/BA/Irgacure 250 combination was used as photoinitiating system.

**Thermomechanical and Morphological Properties**

DMA and AFM characterizations were performed to characterize LED-cured IPNs and establish a comparison with UV-cured samples. Two different behaviors can be distinguished:

### TABLE 7 DMA data concerning different ratios of acrylate/epoxide for LED-cured films

<table>
<thead>
<tr>
<th>Ratios</th>
<th>$T_g$ (°C)</th>
<th>FWHM (°C)</th>
<th>Number of peaks after deconvolution</th>
<th>$T_g$ after deconvolution (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70A30E</td>
<td>−10</td>
<td>34</td>
<td>2</td>
<td>−8</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50A50E</td>
<td>24</td>
<td>99</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>68</td>
<td></td>
<td></td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>30A70E</td>
<td>97</td>
<td>78</td>
<td>2</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99</td>
</tr>
<tr>
<td>10A90E</td>
<td>119</td>
<td>35</td>
<td>1</td>
<td>119</td>
</tr>
</tbody>
</table>

**TABLE 8 Conversion and maximum polymerization rate obtained by FTIR for neat acrylate and epoxide under UV (Darocur 1173): 1 wt %, [TAS]: 2 wt %) and LED ([ITX]: 2 wt %, [BA]: 4 wt %, [Irgacure 250]: 3 wt % for LED)**

<table>
<thead>
<tr>
<th></th>
<th>UV (3600 mW cm$^{-2}$)</th>
<th>LED 395 nm (550 mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylate</td>
<td>315</td>
<td>6</td>
</tr>
<tr>
<td>Epoxide</td>
<td>72</td>
<td>42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$R_p$ max (s$^{-1}$)</th>
<th>100</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final conversion (%)</td>
<td>90</td>
<td>61</td>
</tr>
</tbody>
</table>
up to 50 wt % of epoxide, the thermograms are very similar to the ones obtained under UV illumination (Fig. 5 and Table 7). When increasing the epoxide ratio from 50 to 90 wt %, the tan δ curves become narrower with a maximum at lower temperature. Since RT-FTIR is not suitable to follow the reaction kinetics in these systems, we first consider the homo-polymer polymerization under UV- and LED-irradiation to explain these results. As reported in Table 8, acrylate polymerization is more than 4 times faster than the epoxide polymerization under UV, whereas the opposite trend is observed in a more pronounced manner under LED irradiation. One can reasonably assume the same tendency in the IPNs. Therefore, at 395 nm, acrylate polymerization starts into a preformed epoxide network that promotes the entanglement between the two polymers and results in a narrow tan δ curve with one maximum. The lower Tg value can be attributed to the fact that BA may increase chain termination by chain transfer mechanism.71 Shorter chains and a less crosslinked network could be created, although the acrylate and epoxide conversion remains high and comparable to the value obtained under UV irradiation.

AFM characterizations of LED-cured IPNs do not provide evidence for structural inhomogeneity (Fig. 6). Cross-section measurements for 50A50E samples support this observation (Supporting Information Fig. S4). Interestingly, the phase RMS values for 50A50E, 30A70E and 10A90E are slightly lower than for the corresponding UV-cured ones (Table 9), indicating a better network interpenetration. This is also confirmed by the narrower tan δ curves observed in DMA.

Scratch Resistance Properties of UV And LED-Cured IPNs
The scratch resistance of UV- and LED-cured IPNs deposited onto glass plates has been assessed. The size and width of the grooves left on the surface by a moving scratching tip with increasing normal load has been analyzed by means of an optical microscope and a non-contact profilometer. As mentioned before, a different trend in terms of thermomechanical properties was observed depending on the actinic range: whatever the light source, similar Tg values and thermograms were found up to 50 wt % of epoxide. Lower Tg values with narrower curves were obtained under LED illumination for higher epoxy content. Therefore, 50A50E and 30A70E samples were selected for the scratch resistance investigation.

At 0.5 and 1 N, the deformation generated by the tip leads to a completely damaged surface for the 50A50E UV-cured film. These results can be correlated to the low Tg measured by DMA. When increasing the epoxy amount up to 70 wt %, the deformation becomes plastic and the scratches for the UV-cured coating become permanent and cracks appear in the film at 2 N. Besides a high Tg value and improved toughness, the UV-cured 30A70E sample exhibits a broad tan δ curve extending up to 250 °C, characteristic of the interpenetrating phases (Table 10). The LED-cured 50A50E sample show a similar behavior as the UV-cured sample, which is

![AFM height and phase images and the phase bearing ratio curve for LED-cured IPNs with different acrylate/epoxide ratios (1 × 1 μm2, Ntegra Spectra, NT-MDT).](https://www.wileyonlinelibrary.com)
reasonable considering the similar thermograms and comparable T_g. In contrast, the LED-cured 30A70E sample results in a poor scratch resistance, even at the lowest load (Table 10). The higher T_g of 97 °C and the narrower shape of the mechanical relaxation peak accounts for this results.

CONCLUSIONS

Photocuring of acrylate/epoxide IPNs was investigated under UV and visible LED irradiation at 395 nm. Characterization of the polymerization process by FTIR and CRM affords a precise understanding of the curing reactions and renders the selection of the most suitable photoinitiating system adapted to long range cationic photopolymerization possible. Highly converted tack-free, transparent IPNs were obtained for both types of irradiation. Mechanical and morphological characterization by DMA and AFM provide evidence for the formation of highly interpenetrated IPNs. Although the final conversions are similar under UV and LED irradiation, the thermograms for visible light-cured samples indicate a greater IPN homogeneity and a lower T_g for higher epoxide content. The sequence of acrylate or epoxide network formation under LED illumination accounts for this trend. Finally, the scratch resistance of the photocured samples is consistent with these thermomechanical results.

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REFERENCES AND NOTES


<table>
<thead>
<tr>
<th>Exposure</th>
<th>50A50E</th>
<th>30A70E</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_g (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Load</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 N</td>
<td>UV 13:81</td>
<td>LED 24:68</td>
</tr>
<tr>
<td></td>
<td>UV 132</td>
<td>LED 97</td>
</tr>
<tr>
<td>1 N</td>
<td>Not measured</td>
<td>Not measured</td>
</tr>
<tr>
<td>2 N</td>
<td>Not measured</td>
<td>Not measured</td>
</tr>
</tbody>
</table>
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