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Analysis method

Monitoring of visible light photopolymerization of an epoxy/dimethacrylate hybrid system by Raman and near-infrared spectroscopies

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Hybrid systems formulated with epoxy and methacrylate monomers at mass fraction either 50:50 or 75:25 were studied. The individual monomer conversions during photopolymerization with visible light were monitored by Raman and near-infrared spectroscopies. The rate of polymerization and final degree of conversion of the methacrylate groups were raised when the epoxy monomer was present. This is attributed to enhancement of the mobility of the reactive species caused by the presence of the epoxy monomer. Conversely, the earlier vitrification of the system due to the faster polymerizing methacrylate network resulted in reduced conversion of epoxy rings.

1. Introduction

Hybrid polymers are produced from a combination of co-monomers with different functional groups and curing mechanisms. Several hybrid systems based on mixtures of certain acrylates and either vinyl ethers [1,2] or epoxides [3–5] have been developed. One of the main advantages of those systems is that the oxygen inhibition of free radical polymerization is greatly reduced [6], and this allows obtaining higher photopolymerization rates and conversions, as well as reducing shrinkage during polymerization [7,8].

The most widely used techniques to monitor progress of the photopolymerization of hybrid systems have been differential scanning calorimetry (photo-DSC) and direct chemical analysis of conversion by infrared spectroscopy in the mid region (mid-IR). The photo-DSC technique provides a measure of monomer conversion based on the enthalpy of the exothermic polymerization process. However, for some hybrid systems in which two reactions occur simultaneously, the measured reaction enthalpy corresponds to the sum of polymerization enthalpies of the two monomers. It is then not possible to distinguish the contribution of each one to the global reaction. Concerning the widespread use of mid-IR spectroscopy to monitor the progress of polymerization reactions, this technique limits the samples to thin films, typically 5–30 mm thick, due to strong molar absorption coefficients in this spectral region. In the case of thicker specimens, only the surface regions can be analyzed with reflectance-based mid-IR techniques. In recent years, the Raman scattering technique has emerged as an alternative spectroscopic method for the characterization of polymers. The Raman scattering technique is based on changes in the wavelength of the incident light after interaction with the rotational and vibrational energy levels in molecules. Thus, it is particularly suited for direct measurement of monomer conversion [9] as well as to assess degradation of polymeric materials [10,11].

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The objective of the present study was to explore the possibility of using Raman spectroscopy as an alternative spectroscopic method to individually monitor the extent of reaction of epoxy and methacrylate monomers during polymerization. Epoxy resins are readily photopolymerized by a cationic mechanism while methacrylates polymerize by a free radical mechanism. The selected epoxy/methacrylate system was photoactivated with a camphorquinone/amine pair in combination with an iodonium salt. The extent of reaction of the individual monomers was followed by Raman spectroscopy and Fourier transform infrared in the near region (NIR). Conversion values at the surface of thick specimens (~ 1.5 mm) were evaluated by attenuated total reflectance (ATR).

2. Experimental

2.1. Materials

The methacrylate monomers used for this study were 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BISEMA, from Esstech, Essington, PA), and 1,6-bis (methacrylyloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane (UDMA, from Esstech, Essington, PA). The epoxy monomers were 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexane carboxylate (UVR) (UVR-6110, Dow Chemical Co., Midland Michigan, USA) and diglycidylether of bisphenol A (DGEBA DER 332 Dow Chem. Co.). The iodonium salt was *p*-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) (OMAN 071, Gelest Inc., Philadelphia, USA). Camphorquinone (CQ) and ethyl-4-dimethyl aminobenzoate (EDMAB) were from Sigma Aldrich, Buenos Aires, Argentina. All materials were used as received. All the resins were activated for visible light polymerization by the addition of 2 wt% Ph_2ISbF_6, 1 wt% CQ and 1 wt% EDMAB.

The radiation source was a LED unit (Valo, Ultradent, USA) with a wavelength range 410–530 nm and irradiance equal to 600 mW cm^{-2}.

2.2. Methods

Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific. Near-infrared (NIR) spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. The resins were sandwiched between two glass plates separated by a 1.5 mm rectangular rubber spacer and were tightly attached to the sample holder using small clamps. The moulds used for resins containing the epoxy monomer were previously treated with a release agent in order to avoid adhesion between the epoxy and the glass after polymerization. The background spectra were collected through an empty mould assembly fitted with only one glass slide to avoid internal reflectance patterns. With the assembly in a vertical position, the light source was placed in contact with the glass surface. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure interval. The conversion profiles of methacrylate monomers in thick specimens were calculated from the decay of the absorption band located at 6165 cm^{-1} [12]. The extent of reaction of epoxy monomer at the surface of 1.5 mm thick specimens was evaluated from the decay of the band at 745 cm^{-1} by attenuated total reflectance [13] using a diamond crystal (4 cm^{-1}, 64 scans).

Raman studies were performed with an Invia Reflex confocal Raman microprobe (Renishaw). A non-contact sampling objective (0.75 NA) with a 0.37 mm working distance was used and the excitation source was provided with the 785 nm emission line of a diode laser to the sample, thereby inducing the Raman scattering effect. The power of the laser was reduced to 10% to prevent damage by heating. At this power level, no thermal damage was observed. Raman spectra were taken averaging two acquisitions. The exposure time for each spectrum was 10 s. The spectra were collected in a Raman shift range between 400 and 1800 cm^{-1} at a spectral resolution of 4 cm^{-1}. The irradiated spot on the sample surface was focused to a diameter of ~2 μm. Samples were sandwiched between a slide and a coverslip separated by a 1.5 mm thick rubber spacer with a 10 mm diameter circular hole. The circular hole of the assembly was filled with the reactive mixture and held using small clamps. Then, the assembly was introduced into the compartment of the Raman spectrometer for spectra collection. All spectra were collected at 300 μm below the surface of the coverslip. Samples were irradiated at consecutive irradiation intervals of 4 s. After each exposure interval, the samples were transferred to the Raman sample compartment for the spectrum collection. The conversion profiles were calculated from the decay of the characteristic absorption band of each reactive group. The reactive band representing the methacrylate C═C double bond is located at 1640 cm^{-1} [6] and is associated with the C═C stretching vibrations. The band representing the epoxide ring is located at 1275 cm^{-1} [6] and corresponds to the epoxide vibration. An internal reference band was selected at 605 cm^{-1} [6], which represents the skeletal bending of the non-reactive methacrylate C–C═O group. The peak areas under each band were integrated and used to calculate the concentration of related functional groups. Three replicates of each of the resins were used in the measurement of conversion.

3. Results and discussion

This section is divided into two parts concerned first with photopolymerization studies of neat methacrylate and epoxy monomers followed by analogous studies of hybrid epoxy/ methacrylate systems. Methacrylate conversion of BisEMA and UDMA monomers was assessed by NIR spectroscopy. Samples were irradiated at consecutive irradiation intervals, and after each exposure interval NIR spectra were collected. Representative NIR spectra are displayed in Fig. 1. The extent of reaction was assessed from the decay of the absorption band located at 6165 cm^{-1}. Epoxy groups conversion of the neat cycloaliphatic epoxy (UVR) cannot be monitored by NIR or Raman spectroscopy because of the absence of characteristic absorption bands in the NIR region and a strong fluorescence exhibited during Raman experiments. Thus, the conversion of the neat UVR was evaluated at the surface of 1.5 mm thick samples

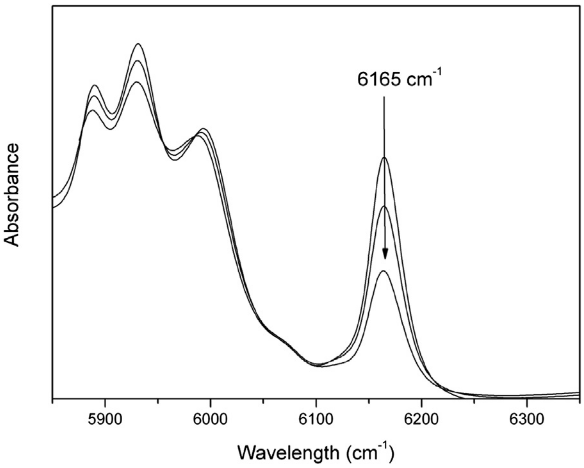


Fig. 1. Magnified methacrylate double bond region in the NIR spectra of BisEMA showing the decrease of the absorption at 6165 cm^{-1} at different collection times.

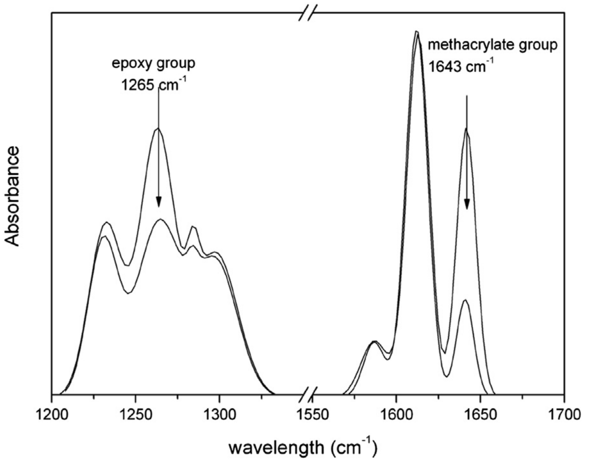


Fig. 3. Characteristic peaks in Raman spectra of an epoxy/methacrylate mixture. The band representing the methacrylate double bond is located at 1643 cm^{-1}. The band at 1265 cm^{-1} is assigned to the epoxy group.

by attenuated total reflectance. Fig. 2 are typical ATR spectra showing the decay of the band at 745 cm^{-1} associated with the conversion of epoxy rings. Unlike the neat epoxy monomer, the Raman spectra of epoxy-methacrylate mixtures were free from fluorescence. Fig. 3 shows representative spectra of a mixture epoxy-methacrylate 50:50 mass ratio. The band at 1265 cm^{-1} in Fig. 3 is assigned to vibrations of the epoxy group. In addition, the band located at 790 cm^{-1} (not shown in Fig. 3) is associated with the symmetric epoxide ring deformation [6]. The band at 605 cm^{-1}, which represents the skeletal bending of the non-reactive methacrylate C–C=O group, was selected as internal reference band. No significant differences between the conversion values of epoxy groups calculated by the decay of the band at 1265 cm^{-1} or that at 790 cm^{-1} were found. The conversion of methacrylate groups was calculated from the decay of the band located at 1640 cm^{-1} (Fig. 3), which is associated with the C=C stretching vibrations [6].

The conversion of methacrylate groups, measured by NIR and Raman spectroscopy, as a function of exposure time for BisEMA and UDMA is presented in Figs. 4,5 respectively. The impact of the photoinitiator nature on the extent of reaction was analyzed by studying the polymerization of resins photoactivated with the CQ/EDMAB pair in either the presence or the absence of iodonium salt. Fig. 4 shows that conversion values of methacrylate groups calculated by Raman are higher than those calculated by NIR. This is attributed to attenuation of the light along the irradiation path because of the presence of light absorbing

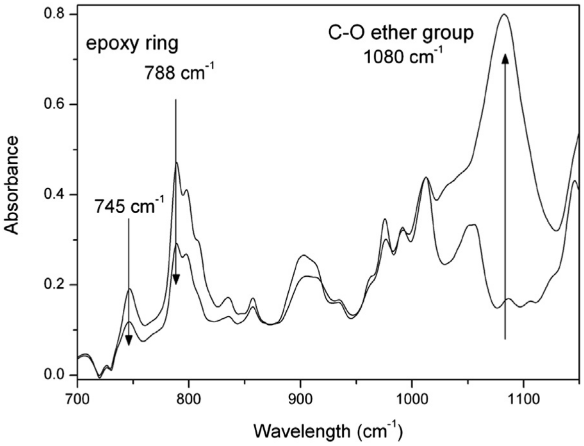


Fig. 2. Typical ATR spectra of the cycloaliphatic epoxy monomer showing the decay of the band at 745 cm^{-1} associated to the conversion of epoxy rings.

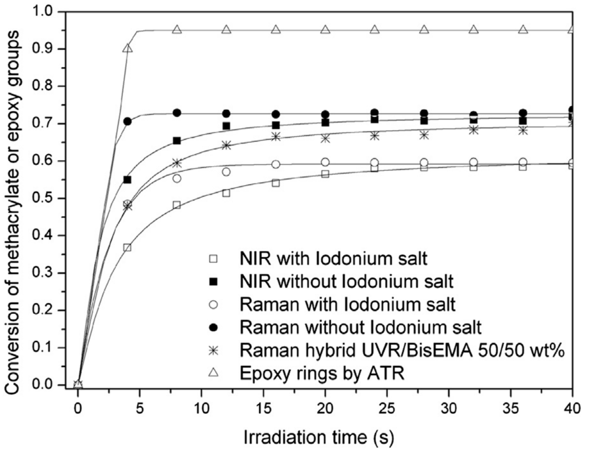


Fig. 4. Monomer conversion versus irradiation time measured by NIR (squares) and Raman (circles) for BisEMA containing 1 wt% of the CQ/EDMAB pair in either the absence of Ph_2ISbF_6 (filled symbols) or the presence of 2 wt% Ph_2ISbF_6 (hollow symbols). The conversion of methacrylate groups in the epoxy/methacrylate 50:50 wt%, containing 2 wt% Ph_2ISbF_6 in combination with 1 wt% of the CQ/EDMAB pair (stars) is also shown. The conversion of neat epoxy monomer (UVR) containing 2 wt% Ph_2ISbF_6 in combination with 1 wt% of the CQ/EDMAB pair (triangles) is shown for comparison. The thickness of the specimens was 1.5 mm.

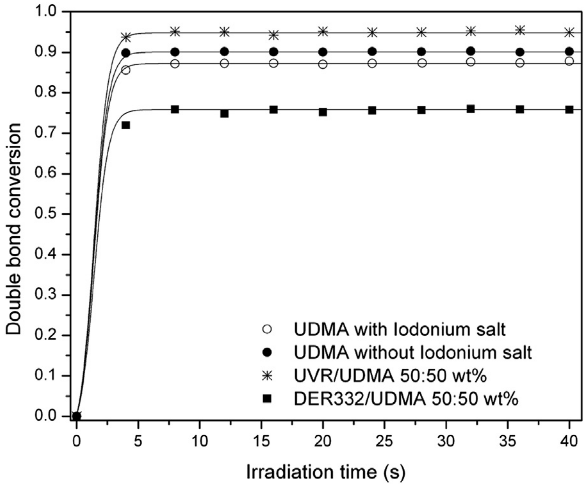


Fig. 5. Monomer conversion versus irradiation time measured by Raman spectroscopy for UDMA containing 1 wt% of the CQ/EDMAB pair in either the absence of Ph_2ISbF_6 or in the presence of 2 wt% Ph_2ISbF_6. The conversion of UDMA in mixtures epoxy/methacrylate UVR/UDMA and DER 332/UDMA 50:50 by mass, containing 2 wt% Ph_2ISbF_6 in combination with 1 wt% of the CQ/EDMAB pair is also shown. The thickness of the specimens was 1.5 mm. No polymerization of the epoxy monomer occurred in these systems.

compounds [14–16]. This effect occurs when the light fails to reach the deeper layers of a sample because the absorbing species near the irradiated surface absorb most of it. As a result of light attenuation in 1.5-mm-thick specimens, the value of conversion at the irradiated surface is higher than that at the non-irradiated surface [17]. In Raman spectroscopy experiments, the conversion is measured at the irradiated surface, while in NIR experiments the conversion is averaged along the irradiation path. Thus, conversions values from Raman are greater than those from NIR. As the polymerization proceeds, the differences in conversion by Raman and NIR are reduced (Fig. 4) as a result of the well-known "dark cure" or "post-polymerization" effect [7] which is accompanied by photobleaching of the CQ [14,15]. The conversion of epoxy rings in the neat UVR monomer calculated by ATR is also presented in Fig. 4 for comparison. Fig. 5 shows the conversion of UDMA monomer containing a photoinitiator system identical to that used in the BisEMA monomer (Fig. 4). Only values obtained by Raman spectroscopy are shown in Fig. 5 for clarity purposes. Figs. 4 and 5 show that the polymerization of BisEMA and UDMA leads to glassy resins in which only part of the available double bonds are reacted. The conversion of methacrylate groups experienced a rapid rise during the first 5–10 s irradiation, after which it exhibited a plateau as a result of a reduction in the rate of photopolymerization due to vitrification of the network [15]. With regards to the epoxy monomer, Fig. 4 shows that the three-component system efficiently photoinitiates the polymerization of UVR under irradiation with visible light. Moreover, almost complete conversion of UVR occurs in the absence of external heating. Results presented in Figs. 4 and 5 are explained on the basis of the mechanism of polymerization of each monomer.

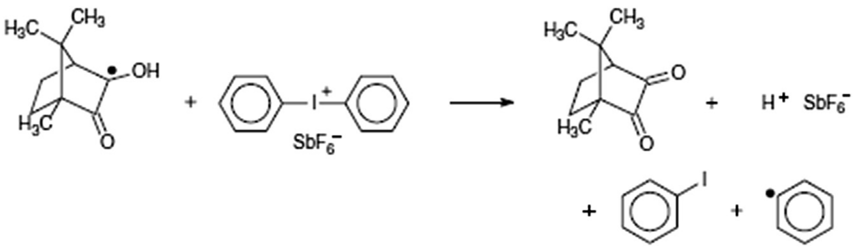
Under visible light irradiation, the CQ photoinitiator is excited to the excited singlet state which converts to the reactive triplet state (CQ*) via inter-system crossing. CQ* reacts with hydrogen donors, such as tertiary amines, to generate radicals by electron and proton transfer through a short lived charge-transfer intermediate complex to give pinicol and amine derived radicals. It is generally considered that the amine radical is responsible for initiating the polymerization and that the radical formed from the ketone is not an efficient initiator and dimerizes.

The cationic ring-opening polymerization of epoxy resins is photoinitiated by onium salts [3,18–23]. Although the major absorption bands of these initiators fall in the deep UV region, it is possible to extend the spectral sensitivity of diaryliodonium salts into the visible region of the spectrum by using dyes as photosensitizers. The use of camphorquinone (CQ) as a visible light photosensitizer in the iodonium-initiated cationic polymerization of epoxy has been reported in recent studies [3,12]. Oxman et al. [3] studied the free radical/cationic hybrid photopolymerizations of acrylates and epoxides using CQ as sensitizer in a three-component photoinitiator system. The possible initiating mechanism in systems containing a diaryliodonium salt in combination with CQ has been proposed by previous researchers [3,24] As described previously, irradiation of the CQ with visible light results in the formation of its singlet state, which is rapidly converted to its triplet state by intersystem crossing. The excited CQ molecule is initially reduced by a hydrogen donor (in our case the amine) to the ketyl radical which in turn is oxidized back to CQ by the iodonium salt (Scheme 1).

The resulting strong Brønsted acid derived from this process initiates the cationic ring-opening polymerization. In the case of the CQ/EDMAB pair, the initiating mechanism involves the generation of α-amino radicals by the abstraction of a hydrogen atom from the amine by the photoexcited dye (Scheme 2). The diaryliodonium salt oxidizes the α-amino radicals to the respective cations, which initiate the polymerization. Subsequently, these free radicals induce the chain decomposition of the diaryliodonium salt, producing a dramatic rate enhancement in the polymerization.

It is worth mentioning that the function of the aromatic amine in the cationic polymerization is dictated by its basicity and nucleophilicity toward the propagating cationic centre. If the amine has low basicity and the carbocation is less electrophilic, then the amine functions mainly as co-initiator. Otherwise, it will function as a terminator. Different from free radical photopolymerization, the only part of a photoinitiated cationic polymerization that is dependent on light is the photolysis of the photoinitiator. Once the active species are formed, the polymerization itself proceeds by a normal cationic process. This contrasts with most free radical photopolymerizations, which cease after the irradiation is extinguished because of rapid termination.

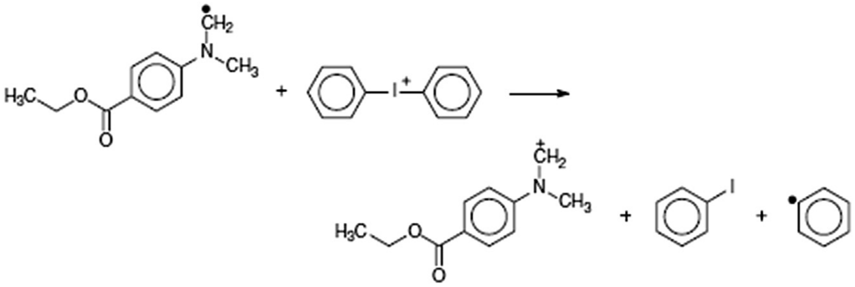
The decomposition mechanism of onium salts leads, in the presence of a hydrogen donor molecule, to the formation of a Brönsted acid responsible for the cationic initiation and also for the formation of radicals likely to initiate polymerization (Scheme 1) [18–24]. Thus, the addition of onium salts should involve higher concentration of free radicals and, therefore, an increase in conversion and polymerization rate. Scranton et al studied three-component radical



Scheme 1. Photosensitization of Ph_2ISbF_6 by CQ during irradiation with visible light.

photoinitiator systems based on a light-absorbing compound, an electron donor and an iodonium salt [25,26]. The author found that, under irradiation, the iodonium salt produced active radicals able to act as initiating radicals. In another study on the photopolymerization of hybrid methacrylate-silicone-epoxycyclohexane monomers, Acosta Ortiz found that radicals produced by irradiation of a diaryliodonium salt were efficient initiators of the methacrylate groups [5]. However, when the CQ/EDMAB pair is used in combination with the iodonium salt, it is surprising that a cumulative effect on the reaction evolution is not observed. Indeed, a comparatively slower polymerization occurs in the BisEMA resin containing the three-component photoinitiator system. This is in agreement with results reported by Lecamp et al. for the polymerization of methacrylate/epoxy systems photoactivated with salts of triarylsulfonium hexafluoroantimonate in combination with 2,2-dimethyl-2-hydroxy acetophenone [4]. The authors reported that, when the two photoinitiators were used, no effect on the reaction evolution was observed. Similarly, in a study of the polymerization of a methacrylate/vinyl ether system photoactivated by 2,2-dimethoxy-phenylacetophenone in combination with an iodonium salt, Stansbury et al. [1] found that presence of the iodonium salt had no effect on the free radical methacrylate polymerization profile. The reduced polymerization rate of BisEMA and UDMA photoactivated with the three-component photoinitiator system (Figs. 4 and 5) cannot be attributed to light attenuation effects arising from the presence of the iodonium salt because it does not absorb in the emission range of the irradiation source. The different factors that affect the photoinitiation efficiency include the rate constants for the formation and deactivation of the excited triplet state and its exciplex with the reducer, the fraction of excited states that leads to radicals, and the proportion of these radicals that add to the monomer. To explain the effect of the presence of the iodonium salt on the polymerization rate of BisEMA and UDMA shown in Figs. 4 and 5, we can assume that different interactions exist among the radicals produced by the three-component photoinitiator system. The reduced efficiency of the CQ/EDMAB pair as radical photoinitiator of methacrylate monomers in the presence of iodonium salt (Fig. 4) can be explained considering that either the higher amount of free radicals or a great affinity between each radical species of the three-component photoinitiator system can lead to higher recombination reactions. In addition, oxidation of the amino-derived radicals by the iodonium salt (Scheme 2) reduces the amount of free radicals available for the initiation step.

In this section, the photopolymerization of epoxy/methacrylate mixtures (UVR/BisEMA) at either 50:50 or 75:25 mass fractions is described. As mentioned before, NIR spectroscopy cannot be used because of the absence of characteristic bands of the cycloaliphatic epoxy. In addition, the decrease of the band at 745 cm^{-1} (Fig. 2) associated with the conversion of epoxy groups in epoxy/methacrylate mixtures by ATR is accompanied by the appearance of a new band. Fig. 6 show typical ATR spectra of each monomer showing the overlap of the bands during irradiation, which prevents calculation of conversion. On the other hand, as shown in Fig. 3, in the case of the selected epoxy/methacrylate systems, Raman spectroscopy provides high quality spectra. The intrinsic sharpness of most bands (Fig. 3) significantly improves the resolution, and hence the quantitative analysis. Thus, Raman spectroscopy was used to monitor the individual monomer polymerization in the hybrid epoxy/



Scheme 2. Proposed photosensitization of Ph_2ISbF_6 by CQ in the presence of EDMAB.

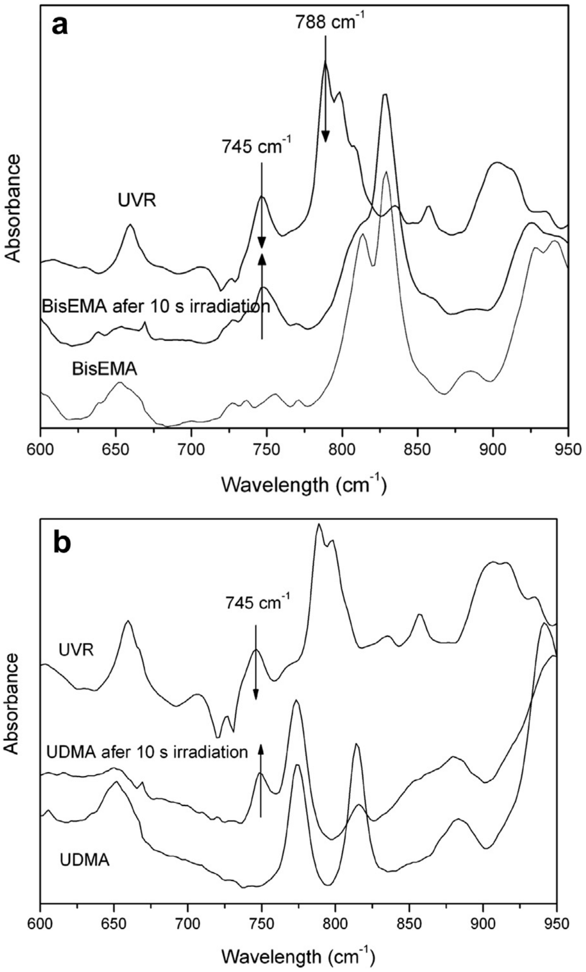


Fig. 6. ATR spectra of (a) UVR and BisEMA (b) UVR and UDMA. Irradiation of the BisEMA and UDMA monomers results in the appearance of a new band, which overlaps the band at 745 cm^{-1}, associated with the conversion of the epoxy rings. This prevents the calculus of conversion of epoxy groups in epoxy/methacrylate systems.

methacrylate systems. Again, epoxy group conversion was followed by the decrease of the band at 1265 cm^{-1} while methacrylate group conversion was monitored by the peak centred at 1643 cm^{-1} (see Fig. 3). The conversion curves of the individual monomers during exposure to visible irradiation in the presence of both cationic and radical type photoinitiators are presented in Fig. 7. It is seen that the rate of polymerization and final conversion degree of the methacrylate groups are raised when the dicycloepoxide monomer is present, as has been observed in other epoxy/methacrylate systems [4]. After 40 s of irradiation, the conversion of methacrylate groups is 0.58 and 0.72 in the neat BisEMA and the epoxy/methacrylate 75/25 by weight respectively. In contrast, the epoxy monomer exhibits a lower conversion in blends than in neat UVR. Fig. 7 shows that the methacrylate network delays the epoxy polymerization, and thus the formation of epoxy network within the final structure. While an almost complete epoxy conversion is reached after 8 s of irradiation of neat UVR, the conversion of epoxy groups in the blends 50/50 and 75/25 UVR/BisEMA was 0.35 and 0.26 respectively, and a high proportion of residual epoxy groups remains trapped into the glassy polymer network. Nevertheless, it should be mentioned that the remaining epoxy groups could continue to react slowly upon storage of the samples in the dark because of the living character of cationic polymerization. The decrease on epoxy group conversion in the hybrid mixture can be explained by the earlier vitrification of the system due to the faster polymerizing methacrylate network, which reduces the molecular mobility of the epoxy groups as the whole network vitrifies.

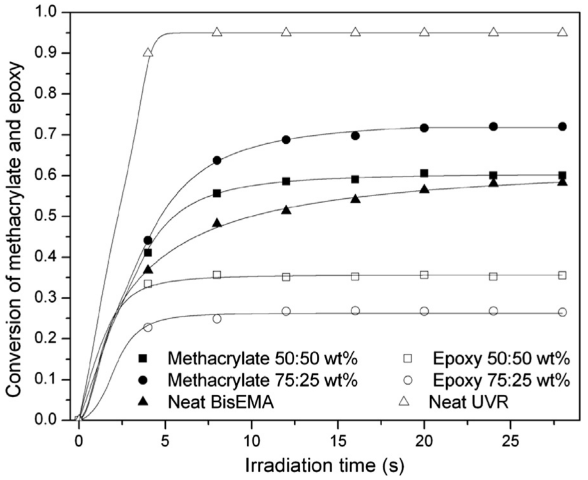


Fig. 7. Conversion of methacrylate groups (dark symbols) and epoxide groups (white symbols) versus irradiation time in hybrid systems.

Free radical chain photopolymerization of methacrylate monomers is a diffusion controlled process due to the almost instantaneous build-up of high molecular weight and cross-linked polymer [18]. During polymerization, the conversion of monomer to polymer results in an increase in viscosity. This increase, in turn, causes a decrease in both the translational diffusion of monomer and polymer and the segmental diffusion of the polymer. When the diffusional limitations become large enough to restrict the diffusion of growing polymer chains, the termination rate by combination or disproportionation will decrease, causing a buildup in radical concentration and, hence, autoacceleration. Eventually, at greater double bond conversion, the propagation mechanism also becomes diffusion controlled and autodeceleration is observed, as denoted by the rapid decrease in the polymerization rate. The presence of UVR in the mixtures has two antagonistic effects. The first is a decrease in the concentration of methacrylate groups in the mixture. In this case, a decay of reaction rate should be observed. The second effect is an enhancement of the mobility of the reactive species, UVR acting as a solvent and then as a plasticizer during polymerization of the BisEMA methacrylate monomer. According to experimental results (Fig. 7), solubilizing and plasticizing effects are more important than the concentration one.

In mixtures of epoxy methacrylate containing the UDMA monomer, no polymerization of the epoxy monomer was observed. It is well known that certain compounds such as water, alcohols and amines are inhibitors or retarders of cationic polymerization. The UDMA monomer, which includes a carbamate functional group, contains labile hydrogen atoms in its structure and, therefore, it acts as inhibitor of the propagation reaction. This is supported by the observation that CQ is photobleached in UDMA monomer even in the absence of added amine [15]. In the absence of any coinitiator, the hydrogen donor is the monomer itself, and so the consumption of CQ is attributed to the presence of labile hydrogen atoms in UDMA. Fig. 5 shows that, similar to the UVR/BisEMA systems, the rate of polymerization and final conversion degree of UDMA in the UVR/UDMA mixture were higher compared to those of the neat UDMA. Conversely, the values were markedly reduced when UDMA was mixed with the epoxy DER 332. This aromatic epoxy resin displays a much higher viscosity compared with the cycloaliphatic UVR. Thus, the reduced polymerization rate in the system containing DER 332 is attributed to the decrease of the mobility of the reactive species as a result of the increase in viscosity.

From results obtained in the present research, it emerges that the progress of the polymerization of both epoxy and methacrylate groups in hybrid systems can be accurately monitored by Raman spectroscopy. The intrinsic sharpness of the bands improves significantly the resolution and hence the quantitative analysis.

4. Conclusions

The individual extent of reaction within a selected hybrid epoxy/methacrylate system based on a cycloaliphatic epoxy and an aromatic dimethacrylate was assessed.

The hybrid systems were efficiently polymerized by the addition of a three-component photoinitiator system composed of the camphorquinone/amine pair in combination with an iodonium salt.

Epoxy groups conversion of the neat cycloaliphatic epoxy cannot be monitored by NIR or Raman spectroscopy because of the absence of characteristic absorption bands in the NIR region and a strong fluorescence exhibited during Raman experiments. Conversely, the Raman spectra of epoxy-methacrylate mixtures were free from fluorescence. Raman spectroscopy provides high quality Raman spectra of both epoxy and methacrylate in hybrid systems. The intrinsic sharpness of the bands significantly improves the resolution, and hence the quantitative analysis.

The rate of polymerization and final degree of conversion of the methacrylate groups were raised when the epoxide monomer was present. This is explained in terms of an enhancement of the mobility of the reactive species caused by the presence of the epoxy monomer. Conversely, the conversion of epoxy groups in the mixtures was markedly reduced in comparison with the final conversion of the neat resin. This is attributed to the earlier vitrification of the system due to the faster polymerizing methacrylate network.

Acknowledgements

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