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



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### ABSTRACT

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.

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### 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 ( $\sim 1.5$  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(methacryloxy-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 ( $\text{Ph}_2\text{ISbF}_6$ ) (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%  $\text{Ph}_2\text{ISbF}_6$ , 1 wt% CQ and 1 wt% EDMAB.

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

### 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  $4500\text{--}7000 \text{ cm}^{-1}$  from 16 co-added scans at  $2 \text{ cm}^{-1}$  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  $6165 \text{ cm}^{-1}$  [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  $745 \text{ cm}^{-1}$  by attenuated total reflectance [13] using a diamond crystal ( $4 \text{ cm}^{-1}$ , 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  $1800 \text{ cm}^{-1}$  at a spectral resolution of  $4 \text{ cm}^{-1}$ . The irradiated spot on the sample surface was focused to a diameter of  $\sim 2 \mu\text{m}$ . 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  $300 \mu\text{m}$  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  $1640 \text{ cm}^{-1}$  [6] and is associated with the C=C stretching vibrations. The band representing the epoxide ring is located at  $1275 \text{ cm}^{-1}$  [6] and corresponds to the epoxide vibration. An internal reference band was selected at  $605 \text{ cm}^{-1}$  [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  $6165 \text{ cm}^{-1}$ . 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

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