

THERMAL AND REAL-TIME FTIR SPECTROSCOPIC ANALYSIS OF THE PHOTOPOLYMERIZATION OF DIEPOXIDE-VINYL ETHER MIXTURES

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Abstract

Both epoxides and vinyl ethers can be polymerized cationically albeit through different intermediates. However, in the case of epoxide-vinyl ether mixtures the exact mechanism of cationically initiated polymerization is unclear. Thus, although vinyl ethers can be used as reactive diluents for epoxides it is uncertain how they would affect their reactivity. Cationic photocuring of diepoxides has many industrial applications. Better understanding of the photopolymerization of epoxy-vinyl ether mixtures can lead to new applications of cationically photocured systems. In this work, photo-DSC and real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) were used to study cationic photopolymerization of diepoxides and vinyl ethers. In the case of mixtures of aromatic epoxides with tri(ethylene glycol) divinyl ether, TEGDVE, photo-DSC measurements revealed a greatly reduced reactivity in comparison to the homopolymerizations and suggested the lack of copolymerization between aromatic epoxides and TEGDVE. On the other hand, for mixtures of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, ECH, with TEGDVE the results indicated high reactivity of the blends. The polymerization mechanism might include copolymerization. To examine this mechanism, mixtures of the ECH with a tri(ethylene glycol) mono-vinyl ether, TEGMVE, were studied by both photo-DSC and RT-FTIR. Principal component analysis (PCA) proved to be an efficient tool in analyzing a large matrix of the spectral data from the polymerization system. PCA was able to provide insight into the reasons for the differences among replicated experiments with the same composition ratio and supported the hypothesis of copolymerization in the ECH/TEGMVE system. Thus, blends of cycloaliphatic epoxides and vinyl ethers seem to have a great potential for applications in high-productivity industrial photopolymerization processes.

Keywords: aromatic glycidyl ethers, cationic photopolymerization, cycloaliphatic epoxide, differential photocalorimetry, divinyl ether, mono vinyl ether, principal component analysis, real-time infrared spectroscopy

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Introduction

Epoxy resins and vinyl ethers can be polymerized by a cationic mechanism to yield products showing excellent adhesion to various substrates and good chemical resistance. Cationic photoinitiation can be extremely rapid and thus can lead to very high polymerization rates [1]. Moreover, this type of polymerization is not inhibited by oxygen, hence it does not require an inert atmosphere to carry out the process, which is typically necessary for free-radical polymerization [2, 3]. Photoinitiated cross-linking polymerization (photocuring) of epoxides has many industrial applications in the field of adhesives, encapsulants and coatings. Photocuring of epoxy composites is also being tested. Recently, photocurable epoxides have been used in the exciting field of computer-aided rapid prototyping [4] that is revolutionizing the process of developing new products (e.g., machine parts). Vinyl ether monomers are suggested as reactive diluents for photopolymerization of epoxides to reduce viscosity of the polymerizing system and enhance physical properties (especially toughness) of the resulting polymer. However, these two types of monomers polymerize cationically through different intermediates: oxonium ions for epoxides and carbocations (carbenium ions) for vinyl ethers and lead to different types of polymer backbones. In the case of epoxide-vinyl ether mixtures, the mechanism of cationically initiated polymerization is still unclear and it is not known to what extent vinyl ethers would affect the reactivity of different types of industrially important epoxides.

Photo-DSC can be used to measure the enthalpic effects during the photocure. In the case of homopolymerizations, the rate of heat release is directly proportional to the number of functional groups reacted but for polymerization of monomer blends the interpretation is more complex. However, we can compare the measured enthalpy of reaction for a blend with the enthalpy calculated by a linear combination of the values for homopolymerizations. If we repeat this for different compositions, we can prepare a diagram analogous to Raoult's diagrams used in physical chemistry and get an indication regarding interactions between the monomers during polymerization of monomer mixtures.

On the other hand, to get an insight into reaction mechanisms for cross-linking systems some spectroscopic techniques are necessary. Real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) is a powerful method for monitoring fast photopolymerization reactions [1, 2]. However, a full analysis of the results from RT-FTIR spectroscopy can be difficult since the RT-FTIR is able to produce thousands of raw spectra during a single experiment.

Principal component analysis (PCA) [5] has been applied to spectroscopic data in the chemometrics area. It provides a reliable way of extracting most of the information in a large data set using only a few principal components. Aries *et al.* [6] applied PCA to a curing reaction of epoxy resin and found that the epoxy curing process could be well summarized with three principal components.

The objective of this work was to elucidate the effect of vinyl ethers on the reactivity of industrially important epoxy resins and determine what types of epoxy-vinyl ether compositions have a potential to be used in high-productivity

photocuring processes. Thus, we investigated cationic photopolymerization of mixtures of different types of diepoxides with mono- and divinyl ethers using differential photocalorimetry as well as real-time FTIR spectroscopy with principle component analysis.

Experimental

Materials

Bisphenol-A diglycidyl ether, BADGE; epoxynovolac, EN (novolac glycidyl ether, $M_n=345$); 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate, ECH; triethyleneglycol divinyl ether, TEGDVE; triethyleneglycol methyl vinyl ether, TEGMVE; and triarylsulfonium hexafluoroantimonate, SA (50% solution of mixed salts in propylene carbonate) were purchased from the Aldrich Chemical Company. Diaryliodonium hexafluoroantimonate, IA (CD1012) is a product of the Sartomer Company. All these materials were used without further purification.

Photopolymerization and characterization

Polymerizations were carried out in bulk in a Photo-DSC (TA Instruments) at 30°C for mixtures containing 1 wt% IA as a photoinitiator. In selected cases, the temperature was ranging from 30 to 70°C. Samples were exposed for 12 min to the UV radiation of a medium-pressure mercury lamp and the sample size was about 3 mg. The light intensity was 40 mW cm⁻², which was measured by a radiometer (International Light IL-1400A). Photo-DSC was used to record polymerization heat evolution rate vs. time profiles. Then, by integrating the area under the curve, the heat of polymerization was determined.

FT-IR spectra for photopolymerizations were collected on a real-time FTIR spectrometer (ReactIR 1000). A diamond reflection ATR module was used and the probe was inserted into a Photo-DSC instrument. The spectrometer was equipped with a MCT detector and the spectra were recorded with a resolution of 8 cm⁻¹ at a time resolution of 3.5 s. Samples (0.36 mm thick) were put on the top of the probe at a room temperature (~25°C) and irradiated with the UV light in air atmosphere. Thus, the FTIR spectra were collected from the bottom of the sample while the UV irradiation was provided to the top of the sample. The UV light intensity used in these experiments was 3 mW cm⁻². A region of 2250~1850 cm⁻¹ for each spectrum was excluded due to a cutoff of the diamond probe. Thus, for our experiments no functional group absorbance peaks could be observed in this cutoff range. (Usually, in this region nitrile or sulphur containing groups can be detected.) Our FR-FTIR experiments consisted of polymerizations made up of repeat runs at five different composition ratios and corrected for the depth of infrared penetration in the ATR experiment. Within each run, FT-IR spectra were recorded at ca. 500 equal time intervals (observations). Digitized spectra were recorded at 882 wavenumbers (variables) over the range of 4000~600 cm⁻¹ for each observation.

Results and discussion

Photopolymerization of bisphenol-A diglycidyl ether/tri(ethylene glycol) divinyl ether mixtures

Diglycidyl ether of bisphenol-A and its oligomers are the main components of widely used epoxy adhesives, coatings and composites. Observing the photocuring process of bisphenol-A diglycidyl ether-tri(ethylene glycol) divinyl ether (BADGE-TEGDVE) blends allowed us to see a very intriguing behaviour of this epoxy-vinylether system. Figure 1 shows that the measured values of the heat of photocure (squares) for BADGE-TEGDVE blends at 30°C are clearly much lower than the values calculated by a linear combination of the values for BADGE and TEGDVE homopolymerizations, Curve (2). (These values should be anticipated if two simultaneous independent polymerizations proceeding through different intermediates took place.) In fact, for the blends the values of the heat of photocure are almost exactly equal to the contributions expected from the TEGDVE component only, Curve (3). A plausible explanation of the observed low values of reaction heat is that the presence of even small amounts of divinyl ether prevents cationic polymerization of the aromatic epoxy. This is evident even for the 9:1 ratio of epoxy to vinyl ether. Thus, contrary to the expected enhancement of epoxy reactivity, the addition of highly reactive vinyl ether is reducing the reactivity of bisphenol-A diglycidyl ether in cationic photopolymerization, at least in the investigated time scale (12 min) practical for photocuring. Therefore, this type of epoxy/vinyl ether blends is not expected to be useful for fast photocuring processes.

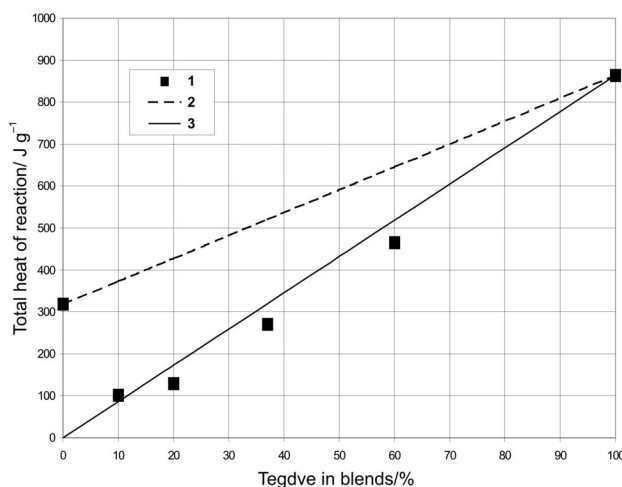


Fig. 1 Photopolymerizations of BADGE, TEGDVE and their blends. Total reaction heat for compositions with different TEGDVE contents: 1 – measured values, 2 – a trendline expected for a blend of the two independently polymerizing monomers, and 3 – contributions expected from independently polymerizing TEGDVE only

Photopolymerization of epoxynovolac/tri(ethylene glycol) divinyl ether mixtures

In order to verify whether this type of behaviour is common for aromatic epoxides, we investigated photocuring of a different aromatic glycidyl ether (epoxynovolac, EN) in mixtures with TEGDVE using a different photoinitiator (SA) at a concentration of 3 wt%. Epoxynovolacs are technologically important resins used in encapsulants for electronic parts.

Figure 2 shows that the measured values of heat of photocure (diamond symbols) for EN-TEGDVE blends are much lower than the values calculated by a linear combination of the values for the homopolymerizations, Curve (2). The heat of photocure for the blends is always almost exactly equal to the values that would be anticipated for the TEGDVE component only, Curve (3), even for the 9:1 epoxy to vinyl ether ratio.

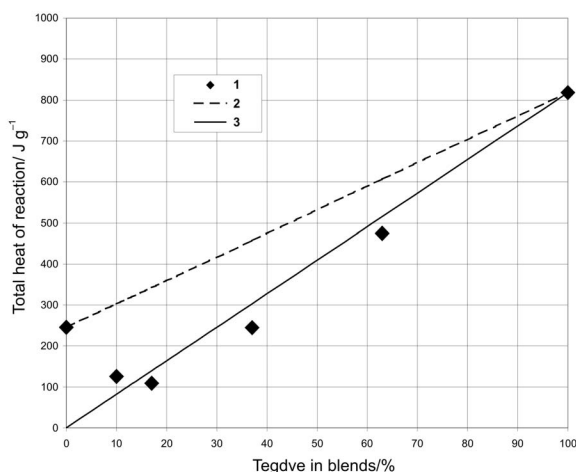


Fig. 2 Photopolymerizations of EN, TEGDVE and their blends. Total reaction heat for compositions with different TEGDVE contents: 1 – measured values, 2 – a trendline expected for a blend of the two independently polymerizing monomers and 3 – contributions expected from independently polymerizing TEGDVE only

Thus, photo-DSC measurements of the heat of photopolymerization for blends of two types of aromatic glycidyl ethers with aliphatic divinyl ether strongly suggest that there is no cationic copolymerization between these two classes of monomers. The results indicate that only homopolymerization of the divinyl ether is taking place under investigated conditions. Consequently, blends of these industrially important epoxy resins with vinyl ethers are not expected to be useful for fast photocuring processes.

Photopolymerization of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate/tri(ethylene glycol) divinyl ether mixtures

In our further studies of the reactivity of diepoxy/vinyl ether blends, we used again TEGDVE as the vinyl ether component but replaced aromatic epoxides with

3,4-epoxycyclohexylmethyl-3', 4'-epoxycyclohexane carboxylate (ECH) that is used extensively in coatings as well as in electrotechnology and rapid prototyping (stereolithography). Photo-DSC measurements in this case gave quite encouraging results. Figure 3 shows the heat of photocure for ECH-TEGDVE blends as a function of TEGDVE content at temperatures from 30 to 70°C. To the right of the graph there is a legend identifying different levels of the heat of reaction values in order to make analysis of the trends of the data in the three-dimensional (3-D) space easier.

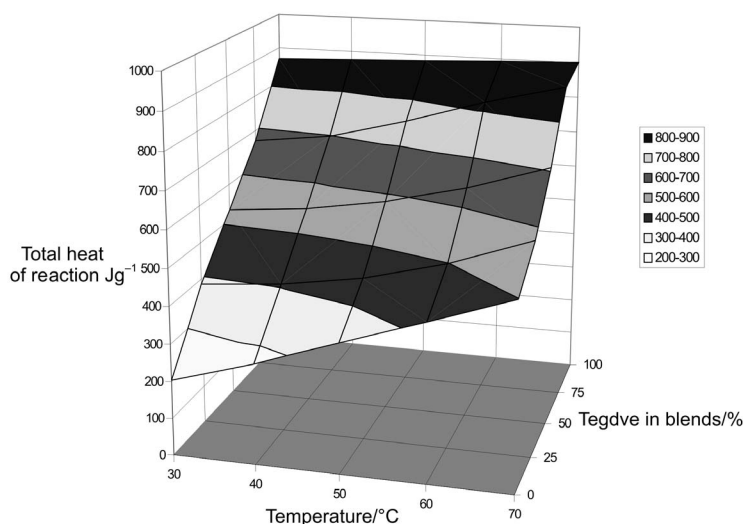


Fig. 3 Photopolymerizations of ECH, TEGDVE and their blends. Total reaction heat for different ECH/TEGDVE compositions at various temperatures

It can be noticed that for all temperature levels the heat of photocure for the blends shows values that lay between the values for two homopolymerizations. This is in contrast with a significant drop in the reaction heat values for aromatic epoxy-TEGDVE blends clearly visible in Figs 1 and 2. Moreover, analysis of the trends in Fig. 3 indicates that at higher temperatures and TEGDVE contents the reaction heat values are getting even higher than it might be anticipated for a combination of the homopolymerizations. Evidently, in this case the addition of TEGDVE does not reduce cationic polymerization reactivity of the epoxide and possibly enhances it. This indicates that cycloaliphatic diepoxides can effectively compete with vinyl ethers for active centres during cationic polymerization of the blends.

One good indicator of the reactivity of monomers in ionic photopolymerization is their ability to sustain the polymerization after removing the source of illumination ('dark' living polymerization). It is known that vinyl ethers show this effect [2], but there is no clear information in this respect in the literature regarding the cycloaliphatic epoxides. Our measurements performed on ECH using the irradiation for various periods of time and measuring the conversion during irradiation as well as

Table 1 Dark polymerization effect in cationic photopolymerization of ECH

Irradiation time/ min	Initial and Ultimate Conversion and the Contribution of Dark Polymerization		
	Conversion during irradiation/%	Ultimate conversion/%	Contribution of dark polymerization
0.03	0	8.51	1.00
0.05	0.03	20.30	0.999
0.10	1.10	25.50	0.961
0.25	9.4	31.00	0.967
0.30	12.1	31.10	0.611

the ultimate conversion (Table 1) confirms that this cycloaliphatic epoxide undergoes 'dark' living polymerization.

Photopolymerization of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate/tri(ethylene glycol) methyl vinyl ether mixtures

In order to scrutinize the reactivity of the ECH-vinylether systems, we replaced TEGDVE with its model monovinyl ether, i.e., triethyleneglycol methyl vinyl ether (TEGMVE). This compound should have the vinyl group reactivity very close to that of TEGDVE. On the other hand, TEGMVE should also ensure a better control of the highly exothermic reaction and thus enable us to obtain more information about reactivity of these highly reactive systems, especially in the initial stages of the photopolymerization.

In view of the results reported in the previous section, the question arises whether these two monomers polymerize independently or some more complex interactions are taking place. The results shown in Figs 4 and 5 for the initial stages of the photopolymerization of ECH, TEGMVE and their blends show that the mixtures clearly polymerize differently than it could be expected just for a combination of independent ECH and TEGMVE polymerizations. Thus, increasing the amount of ECH in the blends significantly decreased the reaction rate from that of pure TEGMVE at a polymerization temperature of 30°C (Fig. 4). During photopolymerization at 50°C (Fig. 5), the heat evolution rates for the monomer mixtures, Curves (3) to (5), increase significantly although they are still slow in comparison to the rate of homopolymerization of TEGMVE, Curve (2). This indicates again that the monomers do not react independently, as the heat evolution rates for the ECH/TEGMVE mixtures are much different from a combination of individual homopolymerizations. This might indicate that cross-propagation reactions (Fig. 6) take place and these reactions have activation energies different from homo-propagations. It should be pointed out that the polymerized blends are cross-linked (as we verified by attempting THF dissolution and extraction) and analytical techniques requiring sample dissolution are not applicable to this system.

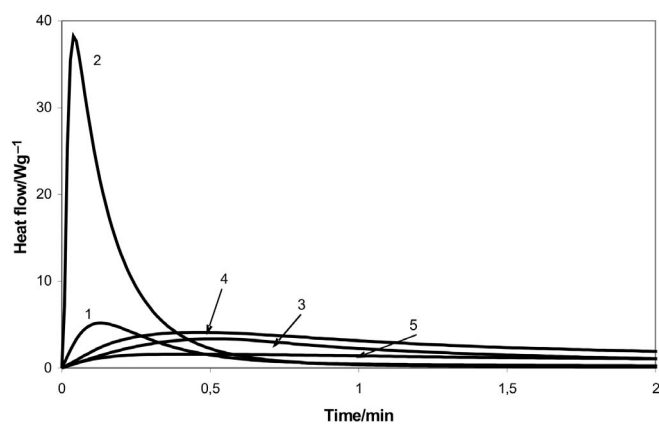


Fig. 4 Photopolymerizations of ECH, TEGMVE and their blends. Reaction heat evolution rates at 30°C for different compositions: 1 – ECH, 2 – TEGMVE, 3 – ECH/TEGMVE=80/20, 4 – ECH/TEGMVE=57/43 and 5 – ECH/TEGMVE=30/70 wt%

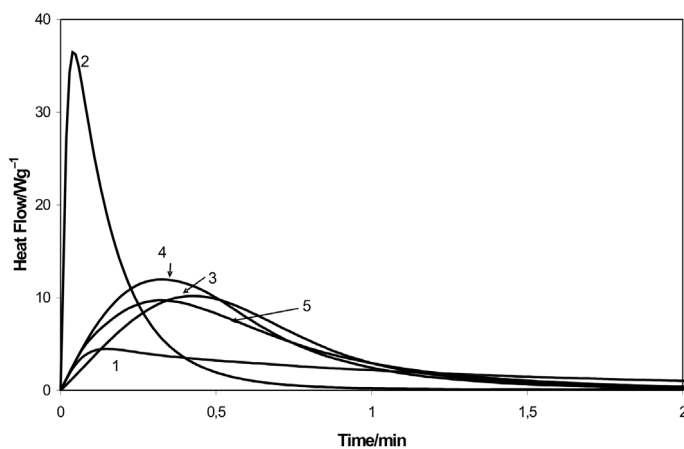


Fig. 5 Photopolymerizations of ECH, TEGMVE and their blends. Reaction heat evolution rates at 50°C for different compositions: 1 – ECH, 2 – TEGMVE, 3 – ECH/TEGMVE=80/20, 4 – ECH/TEGMVE=57/43 and 5 – ECH/TEGMVE=30/70 wt%

Photopolymerizations of ECH, TEGMVE and their blends were also followed by real-time Fourier Transform Infrared Spectroscopy (RT-FTIR). Figure 7 provides an example of overlapped entire IR spectra collected real-time for photopolymerization of ECH-TEGMVE mixtures. Typically, an analyst isolates just two or three IR bands for analysis ignoring the information contained in the rest of the spectrum. However, as it is demonstrated in Fig. 7, this approach in our case would lead to a significant loss of the information. It is obvious that – with the exception of

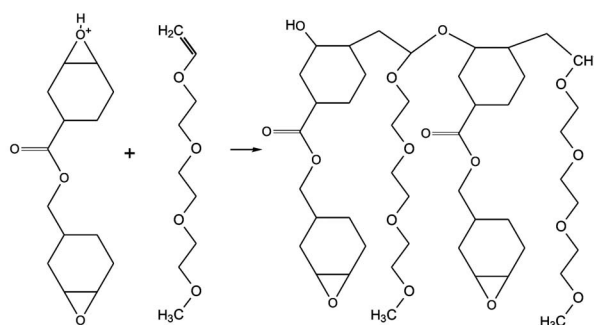


Fig. 6 Cross-propagation during cationic photopolymerization of ECH/TEGMVE blends

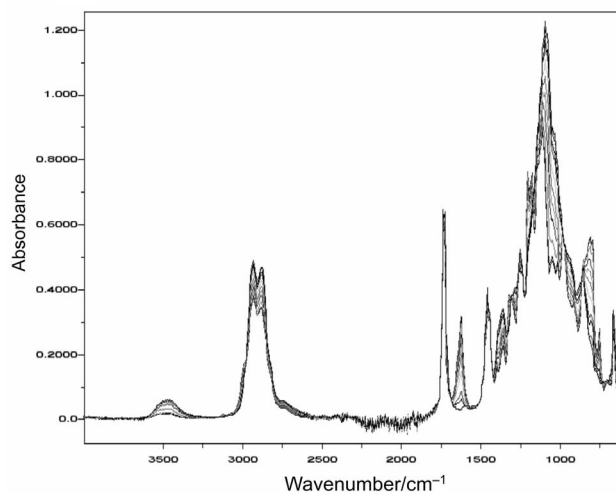


Fig. 7 Typical changes in FTIR spectra during photopolymerization of ECH/TEGMVE blends

the baseline between 3030 and 3300 cm^{-1} as well as 3600 and 4000 cm^{-1} – the entire IR spectrum undergoes changes during the photopolymerization. (Noisiness in the region 1850–2250 cm^{-1} results from a poor transparency of the diamond probe in this range.) Clearly, the absorbances at different wavenumbers are not independent of one another, but rather, are highly correlated as changes in molecular structures affect absorbances over a range of wavenumbers. Thus, it is also clear that in order to obtain maximum information about the reacting chemical system from the recorded spectral changes the analyst has to take into account entire spectra not – what is customary – just a few selected bands.

The data matrices from our FR-FTIR experiments were mean-centered (since we are interested in detecting the spectral changes) and analyzed using principle component analysis, PCA. PCA is a multivariate statistical projection method,

projecting the information contained in the data matrix into low dimensional spaces. (Details of the statistical analysis of the RT-FTIR results will be published elsewhere. Here for brevity we describe a sample treatment of the data.)

The data were arranged in a matrix (X) with rows consisting of the observed spectra at each of the 500 time intervals for all runs, and columns corresponding to the 882 wavenumbers for which the spectral values were recorded. The objective of this analysis was to utilize all the data in the X matrix but simplify the analysis using PCA. The variable dimension of the X matrix (882 in this case) is reduced down to a small number of orthogonal principal components (t_1, t_2, \dots, t_A) that summarize nearly all of the variance in the original data matrix.

The coordinate values of the observations on the new variables obtained from PCA are called scores. For example, score plots for ECH/TEGMVE=75/25 runs are shown in Fig. 8. Each point of the plot represents a full FT-IR spectrum recorded at one time during the polymerization reaction. A model extracted with 3 principle components (PCs) explained 98.9% (1st PC: 92.6%, 2nd PC: 5.1%) of the variation of the data for ECH/TEGMVE=75/25. The score plots for replicate runs for this blend can be separated into two groups. This is illustrated in Fig. 9 where t_1 and t_2 are plotted separately as a function of time. For polymerizations of ECH/TEGMVE=75/25 the t_1 score plot of one group of two runs is higher than that of the other group.

In order to understand which factors contribute most to the difference between the two groups, a contribution plot between the final point of run #2 (curve B in Fig. 9) and the final point of run #1 (curve A) in t_1 score space is computed. In this contribution plot (Fig. 10), all peaks having positive values are related to groups that are formed during the polymerization in the TEGMVE/ECH system, and negative peaks are related to groups whose concentrations decreased. Thus, negative peaks of the vinyl (1618.5 cm^{-1}) and epoxy groups (745.15 cm^{-1}) imply that both ECH and TEGMVE in the runs represented by upper curves in Fig. 9 are consumed more extensively. However, in Fig. 10 we can also notice a negative peak of the ester carbonyl group and a positive peak for a carbonyl group of carboxylic acid. Thus, the

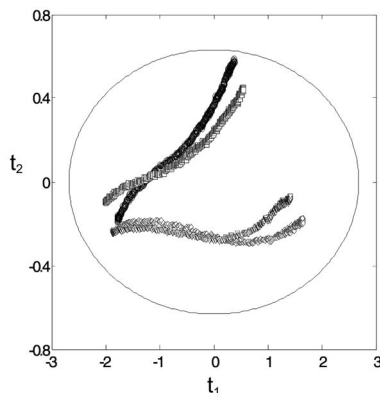


Fig. 8 The t_1 - t_2 score plots for FTIR spectra acquired during photopolymerization of ECH/TEGMVE=75/25 blend

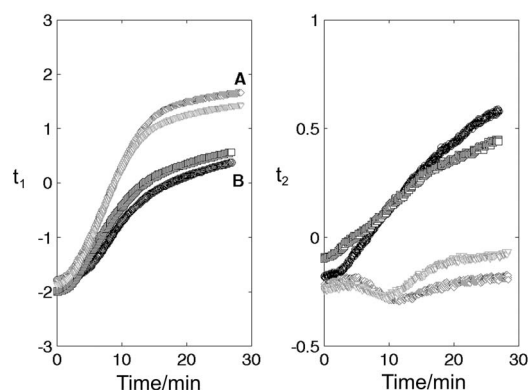


Fig. 9 The individual t_1 and t_2 vs. time score plots for FTIR spectra acquired during photopolymerization of ECH/TEGMVE=75/25 blend

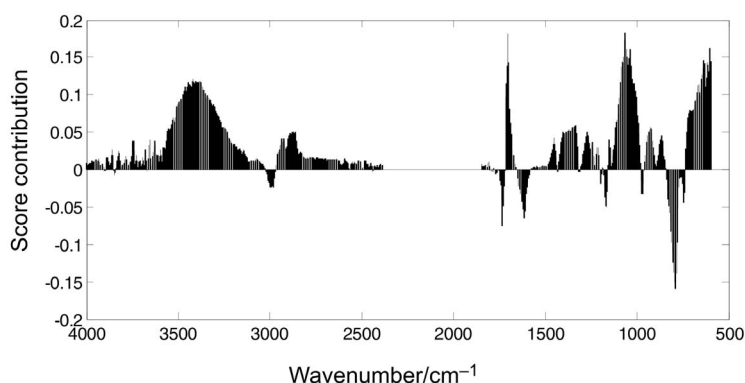


Fig. 10 Contribution plot between A and B in t_1 space for the photopolymerization of ECH/TEGMVE=75/25 blend

increase in the content of carboxylic groups is correlated with the increases of the conversion for both of the monomers. Hence, we hypothesize that the carboxylic acid resulting from adventitious hydrolysis of the ester group of ECH accelerates the polymerization reaction and causes the conversion differences between replicated runs represented by curves A and B in Fig. 9. Since conversion differences pertain to both epoxy and vinyl ether functional groups, it can be inferred that both of the monomers react at the same time, not in sequence, most probably by copolymerization. The PCA suggests that in addition to polymerization there are also some additional side reactions occurring in the polymerizing system which may enhance its reactivity. Thus, this study shows that for this fast photocrosslinking process RT-FTIR enhanced by the principle component analysis can give some insight into the mechanism of the complex process leading to insoluble products.

Conclusions

Better understanding of the photopolymerization of epoxy-vinyl ether blends can lead to new industrial applications for cationically photocured systems. In this work, photo-DSC and real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) were used to study cationic photopolymerization of different types of diepoxides with tri(ethylene glycol)-based vinyl ethers.

In the case of mixtures of aromatic epoxides with tri(ethylene glycol) divinyl ether, TEGDVE, photo-DSC measurements revealed a greatly reduced reactivity for the blends and suggested the lack of copolymerization between the epoxides and TEGDVE.

On the other hand, for mixtures of 3,4-epoxycyclohexylmethyl -3',4'-epoxycyclohexane carboxylate, ECH, with TEGDVE the results indicated high reactivity of the blends and the polymerization mechanism might include copolymerization. To examine this mechanism, mixtures of the ECH with a tri(ethylene glycol) mono-vinyl ether were studied by both photo-DSC and RT-FTIR. Principal component analysis (PCA) proved to be an efficient tool in analyzing a large matrix of the spectral data from the polymerization system. PCA was able to provide insight into the reasons for the differences among replicated experiments with the same composition ratio. PCA showed that in the case of cycloaliphatic diepoxide/vinyl ether mixtures both types of functional groups react simultaneously, most probably by copolymerization. These blends appear to have a great potential for application in high-productivity photocuring processes.

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