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Phase separation in epoxy-copolyethersulphone blends: morphologies and local characterisation by micro-Raman spectroscopy

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Abstract

This study was aimed at using micro-Raman spectroscopy for the local characterisation of phase separated blends based on epoxy polymer and copolyethersulphone thermoplastic. The morphologies developed in the blends containing 25% by weight of thermoplastic were studied. The calibrations of the Raman data for the determination of the copolyethersulphone content and the epoxide conversion are presented in this paper and their applicability for spatially resolved Raman characterisation discussed. From spectra collected in both phases after increasing cure times, the evolution of the copolyethersulphone content in each phase was quantitatively determined, whilst a qualitative evolution of the epoxide conversion was obtained. To our knowledge, this study provided for the first time direct measurements of phase characteristics in thermoset-thermoplastic blends.

Keywords: Micro-Raman spectroscopy; Thermoset-thermoplastic blends; Phase characteristics

1. Introduction

The behaviour of thermoplastic-thermoplastic blends is reasonably well understood and a number of their properties can be predicted as a function of their composition and of the processing conditions. In thermoset-thermoplastic blends, challenging issues remain, however, to be addressed. These include developing an understanding of the complexity of the combined curing and phase separation phenomena and the resulting blend properties. Let us consider the case of epoxy-thermoplastic blends. Curing and phase separation phenomena can be influenced by the following parameters: the nature of the epoxy monomers; the nature and stoichiometry of the curing agent; the concentration and nature (backbone, molecular weight and chain-end reactivity) of the thermoplastic modifier; the presence of reinforcing fibres and the time-temperature profile of cure. Modifications of these parameters not only affect the blend morphology but also the phase properties and the adhesion between the phases. Ideally, all these features should be characterised in order to understand the resulting blend properties and to optimise the choice of the parameters described above so that the desired performances may be obtained.

The developed morphologies have already been studied in some detail using mainly techniques such as light scattering, transmission (TEM) and scanning (SEM) electron microscopies, etc. In some previous studies, the mechanical properties were also determined and compared to the various morphologies. Trends in the influence of the microstructure type on the toughness of the materials have been established. For example, on increasing the thermoplastic content in the blends, the toughness improvement became more pronounced as the morphology changed from particulate to co-continuous or phase-inverted [1–10].

The adhesion between the phases has also been studied by several authors, as discussed in a previous paper [11]. In these studies, reactions between the thermoplastic chain-ends and the growing epoxy network were indirectly evidenced and related to the adhesion properties.

However, fewer studies have been reported concerning the chemical characteristics of the phases, such as the thermoplastic content and the epoxide conversion. Up to

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now, only indirect measurements of these properties have been carried out on thermoplastic-modified epoxy networks. Phase composition and partial miscibility of the components have been qualitatively assessed in cured blends on the basis of the number and values of the glass transition temperatures (T_g). Macroscopic determinations of the T_gs were performed by differential scanning calorimetry (DSC) [1, 12–14], temperature modulated DSC [15,16] or dynamic mechanical analysis (DMA) [14,17–19]. In phase separated blends, most authors concluded that, at the end of cure, the epoxy-rich phase contained a low concentration of thermoplastic whilst a larger proportion of epoxy-curing agent species was dissolved in the thermoplastic-rich phase. Qualitative information about the extent of cure within each phase has also been deduced [14,19]. On the basis of measurements of T_gs [8,17] and of global conversion at gelation [20,21], hypotheses concerning preferential segregation of low molecular weight epoxy-curing agent species into the thermoplastic-rich phase have been proposed. Moreover, the appearance of stoichiometric imbalance in epoxy and curing agent components within each phase has also been discussed [14].

Thermodynamic analyses have been performed by a number of authors [17,22–26]. Equilibrium diagrams of global conversion versus composition have been obtained. These curves suggested that, for increasing conversions, content intervals between separated phases increased. Furthermore, models taking into account the polydispersity of the epoxy-curing agent species predicted the fractionation of low molar mass species into the modifier-rich phase [17,22,23]. Co-existence curves relating the points of conversion-composition of phases co-existing at increasing cure times have been simulated by Riccardi et al. [23] Finally, a stoichiometric imbalance has been predicted to occur in the phases [17,23].

In brief, the above mentioned experiments did not allow the quantitative determination of the chemical characteristics of the phases. Moreover, it seems that no method has been reported to provide direct local measurements of the phase features.

With the aim of filling this gap, this paper describes the use of micro-Raman spectroscopy as a direct method for characterising locally the phase chemical features in thermoplastic-modified epoxy systems. The targeted phase characteristics were the thermoplastic content and the conversion of epoxide groups.

In terms of spatial resolution, Raman microscopy is preferred to infrared. Lateral and in-depth resolutions of the order of a micron can be obtained with Raman systems [27–33] whilst those values are limited to 8–10 μm with infrared [30,31]. The combination of Raman spectroscopy and confocal microscopy is increasingly used for spatially resolved investigation of heterogeneous materials. In thermoplastic-thermoplastic blends, local qualitative or quantitative determination of phase composition has been performed [32–37]. However, micro-Raman spectroscopy has not yet been significantly used for the characterisation of epoxy-thermoplastic blends. For this latter type of blend, one qualitative study of rubber-modified epoxy has been reported by Garton et al. [37]

Drawbacks of the micro-Raman spectroscopy have, however, been mentioned by Markwort et al. [32] in which concerns about light-sensitive samples burning under the influence of the beam.

In this study, one type of blend was mainly examined, composed of methylene bis(2,6-diethylaniline), (MDEA)-based epoxy polymer and 25% by weight of amine-ended copolyethersulphone. The cure temperature (160 °C) was kept constant. It should be noted that the blend composition and the cure cycle studied here were chosen for experimental purposes and did not correspond to actual formulations of commercial blends.

Raman spectroscopy analysis was previously performed in non-phase separated MDEA-cured blends, containing amine-ended copolyethersulphone. Indeed, we have already developed calibrations for the determination of the copolyethersulphone content [38] from the Raman spectral intensities. Concerning the epoxide conversion, calibrations have previously been reported for epoxy mixtures based on 4,4′-diaminodiphenylsulphone (DDS) curing agent [39] but not for MDEA-based systems. Therefore, a calibration for determining the epoxide conversion in these latter systems is presented in the Experimental part of this paper. The calibrations used here have all been developed with the help of multivariate analysis. Their applicability to the spatially resolved characterisation of blends is also discussed.

In Section 3, the morphologies developed on curing are first presented for the selected blend, as observed by optical microscopy. The Raman local characterisation of phase separated blends is then reported. The blend samples were analysed by micro-Raman spectroscopy after increasing cure times and after quenching the reaction. The recorded Raman spectra contained information from a sample volume characterised by a lateral diameter of about 1–2 μm, but covering the whole thickness of the samples.

This paper represents the most relevant part of a broader work [40] involving the study of blends based on either MDEA or DDS curing agent and containing either amine- or chlorine-ended copolyethersulphone.

2. Experimental

2.1. Materials and sample preparation

The epoxy precursor mixture was composed of two epoxy monomers and of the diamine curing agent. The epoxy monomers were triglycidyl para-aminophenol (TGAP, EPON 1076 from Shell) and diglycidylether of bisphenol F (DGEBF, PY306 from Ciba-Geigy), mixed in a weight ratio close to 1:1. The diamine curing agent was methylene bis(2,6-diethylaniline) (MDEA from Lonza).

The epoxide-amine stoichiometry corresponded to an amino-hydrogen/epoxide ratio of about 0.7, i.e. to an excess of epoxide groups. This system was referred to as Epoxy-MDEA. The thermoplastic was an amine-ended copolyethersulphone supplied by Cytec Engineered Materials Ltd. Chemical structures are presented in Fig. 1.

The content of copolyethersulphone in the samples was 25% by weight of the total blend weight, which does not correspond to the values for commercial formulations. This value of initial copolyethersulphone level was expected to provide the largest possible phase sizes. Indeed as presented later, phase-inverted morphologies were observed at a content of 25% whilst co-continuous structures were obtained at 20%. In the literature, it has been shown that further increase in the thermoplastic content above the minimum required for phase inversion leads to decreasing nodule sizes [2,21,41,42]. According to the expected spatial resolution of Raman (see below), micro-spectroscopy studies would be facilitated by having as large a phase size as possible.

The blend components were mixed together by dissolving in dichloromethane. Samples were cast from this solution onto glass slides. The solvent was evaporated overnight under vacuum at room temperature. Preparation was such that about 5 mg (in practice, between 4.2 and 5.5 mg) of sample remained on the glass slide. A glass cover slip was placed on the sample. A sample thickness of about 8 μm was calculated for 5 mg of blend. The sample section was also observed by optical microscopy after transverse fracture and the thickness was estimated in the range of 10–15 μm. It is not impossible that studying such a small thickness could influence the type and size of the observed morphologies.

For each curing time, Raman measurements were obtained by studying two samples cast from two distinct solutions of the same formulation.

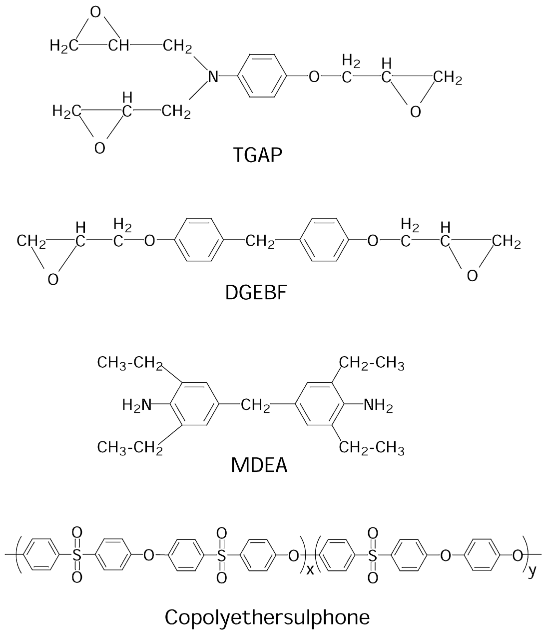

Fig. 1. Chemical structures of the blend components.

2.2. Techniques

Blend samples were cured at 160 °C using a hot stage (Mettler FP82HT). Morphology development was followed in situ by optical microscopy (Olympus AX70).

For Raman analysis, samples were taken from the hot stage after different cure times and the reaction was quenched by bringing the glass slide into contact with a heat conductive material. Raman spectra were recorded at room temperature. Local Raman observations were made within the area located at the same place in the hot stage, at the centre of the sample. In that area, spectra were recorded in different sample spots selected in dispersed points.

The confocal laser Raman spectrometer used was a Labram from Jobin Yvon S.A., equipped with a motorised XY-scanning stage. The excitation laser wavelength was 632.8 nm from a He–Ne laser source. The entrance slit of the spectrograph was set to 200 μm, which gave rise to a spectral resolution of about 3 cm^{-1}. A grating of 1800 grooves/mm was used and the spectra were collected on a CCD detector.

For all the measurements a high magnification objective (× 100) was used and the power applied to the sample was about 6 mW. For the assessment of calibration applicability, the confocal hole was set to 1000 or 500 μm and to 200 μm. For local Raman characterisation, the confocal hole was generally set to 200 μm.

On the basis of recent papers [43,44], it appears that the use of a glass cover slip is very detrimental to the depth resolution. As a consequence, it was expected here that the depth resolution would be determined by the sample thickness whatever the hole size. The whole thickness of the blends would be simultaneously analysed by micro-Raman. As mentioned above, the sample thickness was of the order of 10–15 μm. The effect of reducing the confocal hole would mainly be to reduce the intensity of the collected Raman signals. Furthermore, reducing the hole size would also slightly improve the lateral resolution, expected to be below 2 μm with a confocal hole of 200 μm.

Long accumulation times were chosen with the confocal hole of 200 μm, i.e. 8 or 10 min. Indeed, a very low signal to noise ratio was obtained in these conditions. The number of accumulations was 3. This small number was not only selected to limit the duration of analysis but also, mainly, to limit the time spent by the sample spot under the laser beam. Indeed, as mentioned in Section 2.3.2, exposure to the laser could cause modifications of the sample and of the spectra. Hence no time of fluorescence bleaching was scheduled before spectrum acquisition.

Spectra were recorded in the spectral region centred at 1200 cm^{-1} (from 685 to 1668 cm^{-1}). The fluorescence background had to be removed from the spectra. In this work, a polynomial baseline of the fifth order was subtracted, as described elsewhere [39]. Further spectral pre-treatments depended on the characteristic to be determined, thermoplastic content or epoxide conversion. It mainly involved a wavenumber selection followed by a spectrum normalisation. For all multivariate calibrations used in this study, a normalisation against unit area was performed.

The calibrations used in this paper for determining the thermoplastic content and the epoxide conversion are defined in Section 2.3.

2.3. Calibrations of the Raman data and applicability to blend characterisation

Calibrations were required in order to quantify the thermoplastic content and the epoxide conversion on the basis of the Raman spectral intensities. For this purpose, Raman data were collected with a large pinhole aperture (1000 or 500 μm) on non-phase separated samples. The calibrations were obtained by multivariate analysis, as reported in previous papers [38,39]. The applicability of the calibrations to spectra collected from small sample volumes (hole of 200 μm) was studied within non-phase separated blends and is also discussed here. The calibrations for the content and the conversion determination are considered separately below.

2.3.1. Copolyethersulphone content

The calibration for the determination of the copolyethersulphone content in MDEA-cured blends has been presented in a previous paper [38]. According to the reported study of applicability to spectra collected with a hole of 200 μm, the calibration named PLS-MDEA/C was used here. It is characterised by a root mean square error of prediction (RMSEP) of 3.0%.

2.3.2. Epoxide conversion

The study by Raman spectroscopy of the epoxide conversion has, as mentioned, already been reported in a previous paper for DDS-cured samples [39], but not for MDEA-cured samples. The calibration development is hence presented in this paper for these latter samples.

Calibration development. A similar strategy as the one previously described [39] in detail for DDS-cured samples was adopted. The determination of epoxide conversion from Raman spectra was calibrated with the use of DSC measurements.

The calibration was based on neat Epoxy-MDEA samples only. Indeed, reference measurements of conversion could be obtained by DSC for neat epoxy systems, but DSC conversions were not considered reliable in the presence of thermoplastic [39]. Spectra recorded on blends could thus not be included in the calibration. As a consequence, a strategy of wavenumber selection was adopted for treating the spectra of neat epoxy. This selection aimed at preventing contributions from the copolyethersulphone interfering with the determination of conversion, when applying the calibrations to blend samples. All wavenumber regions corresponding to copolyethersulphone peaks were suppressed from the useful set of spectral variables.

Two stoichiometric ratios were used. Amino-hydrogen to epoxide (A/E) ratio was either A/E = 0.7 (as for blend formulation) or A/E = 1.5. Samples were subjected to isothermal cure times at 180 °C after which the reaction was quenched. Equivalent samples were then submitted to DSC or Raman spectroscopy experiments.

Reference values of conversion in the partially cured samples were obtained by non-isothermal DSC experiments, using a temperature scan up to 300 °C. Maximum reaction enthalpy measured during heating of initially unreacted samples was −81.5 and −96.4 kJ/equivalent epoxide, respectively for A/E = 0.7 and 1.5. These values were assumed to correspond, in each case, to the total reaction enthalpy and each was used in the calculation of conversion in the corresponding samples. As discussed in the previous paper [39], the difference in complete heat of reaction with the stoichiometry could be explained by differences in the reaction enthalpies of epoxide reacting with either primary amine, secondary amine or hydroxyl groups, coupled with modified proportions of these reaction types, as a function of the A/E ratio.

Centred at 1200 cm^{-1}, spectra were collected on partially cured samples with a low magnification objective and a confocal aperture of 1000 μm. The wavenumber intervals actually used for the regression were 893–930 and 1225–1478 cm^{-1}. Remaining intensities were normalised against unit area. The calibration was performed by multivariate PLS regression. Spectra were divided into a calibration set (40 spectra) and a validation set (17 spectra). Because of the presence of MDEA crystalline peaks for unreacted samples, spectra corresponding to 0% conversion were not used. PLS with external validation was performed and the optimum number of latent variables (LV) was 3. Root mean square errors of calibration (RMSEC) and prediction (RMSEP) were respectively 4.6 and 5.7%. Calculated conversions are plotted against reference conversions in Fig. 2.

Calibration applicability. The applicability of this calibration to blends had to be assessed. For this purpose, blend samples were cured at 160 °C for 2 and 15 min, i.e. times shorter than required for phase separation. The epoxide conversion was determined for these samples and the results are presented in Table 1. For the blend cured for

Table 1
Epoxide conversion (%) determined from n spectra with the calibration Raman-DSC MDEA. The standard deviations and numbers n are given in parenthesis

2 min at 160 °C	15 min at 160 °C	
Hole 1000 μm	Hole 1000 μm	Hole 200 μm
42.8 (7.2, $n = 6$)	51.2 (2.4, $n = 3$)	64.1 (3.0, $n = 2$)

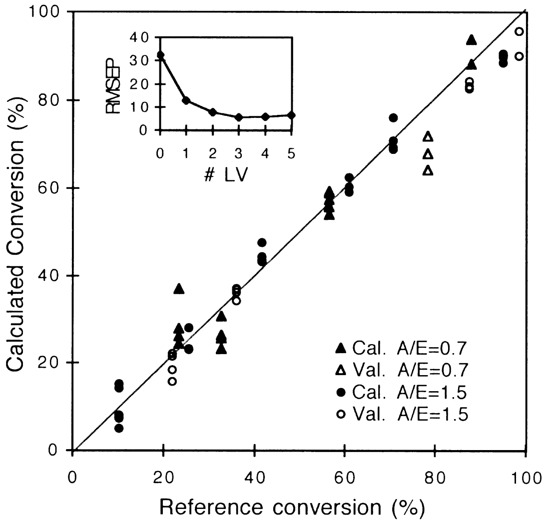

Fig. 2. Calculated versus reference conversion for the calibration Raman-DSC obtained for Epoxy-MDEA samples (PLS regression). For calibration and validation sets, spectra were recorded on Epoxy-MDEA with A/E = 0.7 or A/E = 1.5. Inside: RMSEP versus the number of LVs.

15 min, the results were obtained with hole values of 1000 or 200 μm.

The results given in Table 1 may be discussed as follows. Firstly, the range of the calculated conversion values can be criticised. In the framework of this study, no reliable reference measurement of conversion was available for the blends. The deviation amplitude of the Raman conversions could thus not be actually determined but only discussed in relation to the literature. Eloundou et al. [45] have studied the cure kinetics at 160 °C in neat DGEBA-MDEA at exact stoichiometry. They reported conversions of about 20% after 20 min and 60% (gelation) after 41 min. Epoxide conversions have also been recently measured by near infrared spectroscopy for Epoxy-MDEA A/E = 0.7 [46]. After 20 and 40 min at 160 °C, conversion values were respectively 13 and 39%. Furthermore, most reported studies have shown that the presence of thermoplastic slowed down the thermoset cure kinetics [13,16,20]. For equivalent cure times, the conversions obtained for neat epoxy should hence constitute upper limits in the presence of thermoplastic. However, the values given in Table 1 were much higher than the results reported for neat epoxy systems, hence large discrepancies could be suspected and assigned to a lack of robustness of the calibration towards the introduction of copolyethersulphone in Epoxy-MDEA. The adopted strategy of wavenumber selection was not sufficient to prevent a bias in the calculated conversions.

Secondly, the reduction of the Raman confocal aperture to 200 μm led to a significant increase in conversion (see Table 1). It must be noted that longer times of spectrum acquisition were required with a hole of 200 μm, for example 30 min, as compared to 7.5 min with the 1000 μm hole. In this study, it had to be assumed that the time of exposure to the Raman laser beam would have an important influence on the determined conversion. Extended time under the beam would induce higher calculated conversion. As a consequence, spectra should be acquired in similar conditions in order to allow a direct comparison of the results. The effects of the beam on the sample and spectra was more thoroughly discussed in a PhD thesis chapter [40]. In particular, a possible temperature rise was studied, in the case of blends containing chlorine-ended copolyethersulphone. It could however not account, by itself, for all the modifications in the results obtained with increasing exposure times.

In brief, results obtained from spectra collected with similar instrumental parameters and acquisition times could a priori be qualitatively compared with each other. However, the absolute values of conversion deduced from the calibration should not be considered as a reliable quantification of the extent of cure.

3. Results and discussion

3.1. Morphologies

The morphology development and kinetics of phase separation were followed at 160 °C by optical microscopy, as illustrated in Fig. 3. The observed starting time of phase separation was 16.5 ± 0.5 min. Small nodules became visible and grew rapidly at the beginning of the process. Coalescence was also observed. Domain sizes started to stabilise after about 25 min. At the same time, sub-inclusions appeared in both phases. Sizes of the sub-inclusions appearing in the continuous phase were around 1–2 μm, whilst they tended to be slightly smaller in the nodule phase.

Cured samples gave coarse phase-inverted morphologies with nodule sizes above 10 μm. The observation of phase-inverted morphologies with an initial thermoplastic content of 25% was in the range reported in the literature. Indeed, depending on the studied epoxy-thermoplastic blends, phase-inverted microstructures were obtained for modifier contents above 11% [47], 15%, [8] 20% [2,4,5], 25% [21, 41], 30% [42], or 35% [6].

3.2. Local characterisation by Raman

Chemical characterisation was obtained by micro-Raman spectroscopy after various cure times and quench of the reaction. As a reminder, for each cure time, several spectra corresponding to both phases were collected in two samples, but within regions with similar locations regarding the glass substrate geometry.

Dispersed point analysis is illustrated in Fig. 4 for a sample cured for 30 min and the corresponding results are reported in Table 2. As a first result, it was confirmed that the nodules corresponded to the epoxy-rich phase.

Results obtained in both phases as a function of cure time

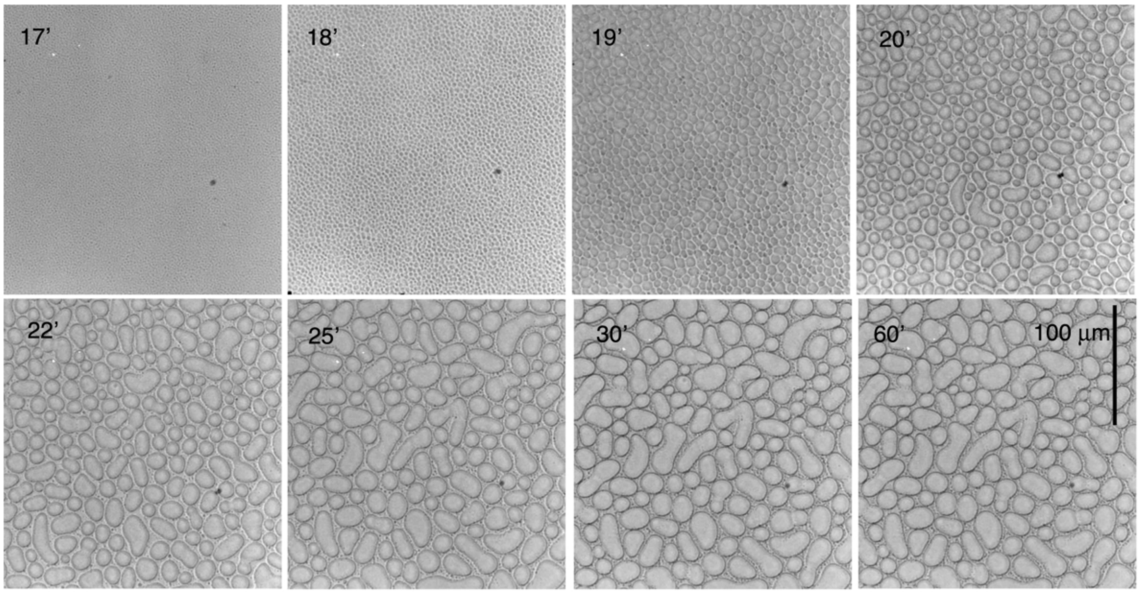

Fig. 3. Development of the morphology followed by optical microscopy as a function of cure time (in minutes).

are discussed successively in terms of copolyethersulphone content and epoxide conversion.

3.2.1. *Copolyethersulphone content*

Obtained by dispersed point experiments, the evolutions of the copolyethersulphone content in each phase are plotted in a time-content diagram (Fig. 5). For each cure time, results corresponding to equivalent phases within two samples showed moderate scattering. Indeed, the standard deviations associated with each point were smaller than the standard error of prediction (RMSEP) for the calibration used, except for the points at 30 and 60 min in the nodules. No particular trend in the error bar amplitudes was observed with cure time or by comparing the nodules and the continuous phase.

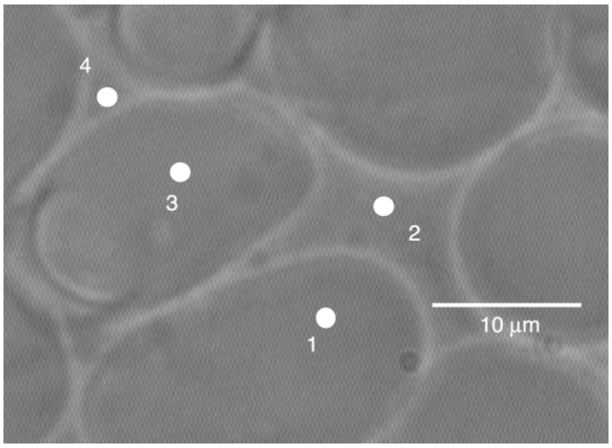

Fig. 4. Blend cured for 30 min at 160 °C and quenched. Image obtained with the optical microscope mounted on the Raman spectrometer and indicating the spot locations for dispersed point Raman analysis (see Table 2 for results).

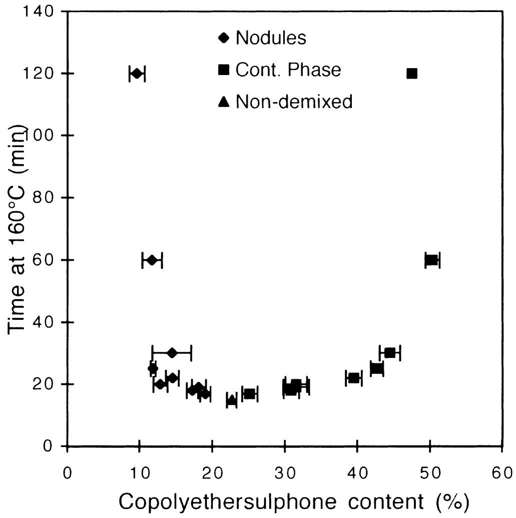

Fig. 5. Evolution of the copolyethersulphone content determined from Raman spectra collected in dispersed points corresponding to the nodules or the continuous phase. Error bars represent the standard error of the mean.

The calculated evolutions of phase composition tended to show that each phase was purifying itself during the curing process. However, for the longest cure times studied here, a large amount of epoxy-curing agent species remained in the thermoplastic-rich phase (about 50%) while some copolyethersulphone was kept in the epoxy-rich phase (about

Table 2
Copolyethersulphone contents and epoxide conversions calculated from the single spectrum collected in each point shown in Fig. 4

Point	Copolyethersulphone content (%)	Epoxide conversion (%)
1	16.0	75.8
2	41.7	57.4
3	18.2	67.4
4	46.0	62.5

10%). Surprisingly, in the copolyethersulphone-rich phase, the calculated copolyethersulphone content was observed to reach a maximum after 60 min of cure and to decrease from 60 to 120 min. However, the thermoplastic content kept decreasing slightly in the epoxy-rich phase.

The copolyethersulphone contents calculated in both phases after 60 min of cure appeared consistent with the qualitative results of phase composition deduced for various systems from T_g measurements [1,13,16,17,19]. Except the trend between 60 and 120 min, the results obtained as a function of the cure time coincided with the general predictions from thermodynamic models. Indeed, on the basis of the Flory–Huggins theory, several authors calculated equilibrium diagrams of conversion versus composition for various epoxy-modifier systems [23–26]. As shown schematically in Fig. 6, an asymmetric curve with a critical point at a modifier content well below 50% was typically obtained. Provided that equilibrium could be reached at each stage, phase compositions would follow the pseudo-binodal line. For increasing conversions, increasing content intervals between separated phases were thus predicted.

In particular, Riccardi et al. [23] predicted the evolution of modifier content upon curing and phase separation of epoxy-amine systems containing 15% by weight of rubber. They showed that, in the rubber-rich phase, the rubber content tended to a maximum value of about 67% in volume. Bonnet et al. [13] estimated the evolution of phase compositions after phase separation, on the basis of DSC measurements of T_g and ΔC_p at T_g. They obtained increasing and decreasing concentrations of epoxy-amine in, respectively, the thermoset-rich and the thermoplastic-rich phase. For a blend containing 48% by weight of PEI (polyetherimide), epoxy mass fractions calculated in the phases just before gelation of the epoxy-rich phase were 90 and 37% by weight. The copolyethersulphone contents calculated here in both phases after 60 min of cure appeared also consistent with both of these reported studies.

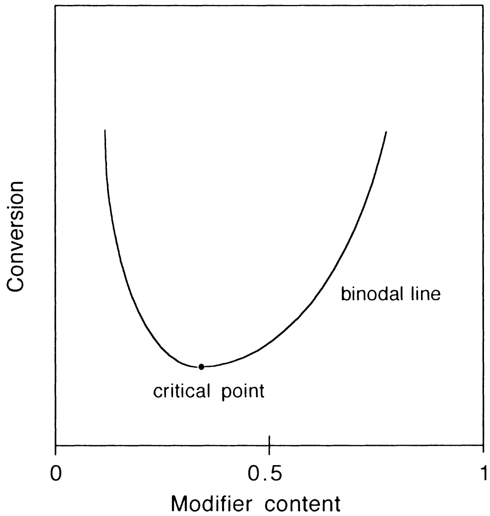

Fig. 6. Schematic conversion versus modifier content diagram deduced from thermodynamic models for epoxy-modifier systems.

In this paper, only small content differences were observed between both phases, at the beginning of phase separation. Although these results could correspond to the actual phase compositions, a measurement artefact could not be excluded. Indeed, at the early stages of de-mixing, the distance between two nodules was very small, of the order of one or a few microns. This distance could be smaller than the Raman lateral resolution, expected to be less than 2 μm, in the working conditions. The scattered beam could then contain information coming not only from the copolyethersulphone-rich continuous phase but also from the epoxy-rich nodules. The calculated thermoplastic contents in the continuous phase would hence be lower than the actual ones. In terms of lateral resolution, this possible artefact was considered negligible when the minimum lateral phase size had reached 3 μm and above. According to this criterion and according to the phase sizes observed in the analysed areas of Epoxy-MDEA containing copolyethersulphone, the results were considered reliable from 18 min in the nodules, and from 22 min in the continuous phase. This criterion based on the lateral dimensions did not ensure that only one phase was analysed in the depth dimension. However, it was assumed that the sample thickness was small enough to avoid the superposition of several phases or, at least, to limit the error. In fact, this hypothesis was partially confirmed by observing with the optical microscope the areas analysed by Raman. Indeed, for samples cured for times longer than the limit times given in this paragraph, different levels of phase boundaries could not be observed by changing the focus along the depth.

3.2.2. Epoxide conversion

Obtained by dispersed point experiments, the evolutions of the epoxide conversion in each phase are plotted against

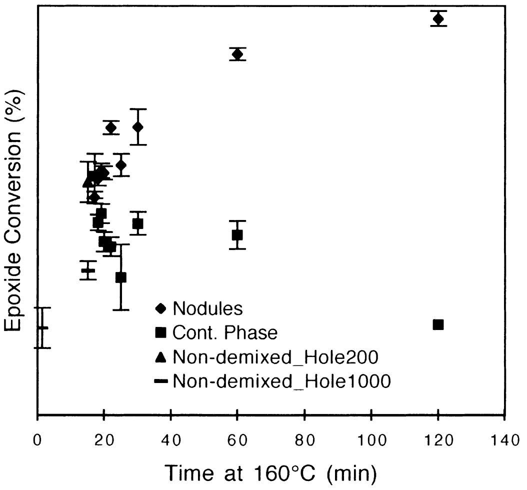

Fig. 7. Evolution of the epoxide conversion determined from Raman spectra collected in dispersed points corresponding to the nodules or the continuous phase. Error bars represent the standard error of the mean.

cure time, in Fig. 7. No quantitative scale was provided since it would not be significant.

Qualitatively, the calculated levels of conversion appeared lower in the thermoplastic-rich phase than in the epoxy-rich phase. Such behaviour has been suggested by several authors for epoxy-modifier systems, according to experimental studies [13,20,21] or to thermodynamic simulations [17,22,23]. Girard-Reydet et al. [20] attributed the decrease in conversion at gel point, observed in phase separated blends, to the segregation of species with low molar masses and low functionality into the thermoplastic-rich phase. In order to explain the overall decrease in the cure extent in the presence of modifier, Varley et al. [21] showed that the activation energy for the epoxy reaction was increasing with the level of conversion and with the content of thermoplastic. Less reaction would then occur in the modifier-rich phase. Thermodynamic models taking into account the polydispersity of the epoxy-curing agent species also predicted the fractionation of low molar mass species into the modifier-rich phase [17,22,23].

Conversions in the epoxy-rich phase (Fig. 7) followed the expected evolution, i.e. values increasing with cure times. In the copolyethersulphone-rich phase, conversion appeared to initially decrease, at the beginning of phase separation, and then to stabilise at higher cure times. Due to the limited Raman spatial resolution, the results in the early stages of de-mixing were likely overestimated in the continuous phase, because of the influence of the neighbouring epoxy-rich phase. From this point of view, actual conversions in the copolyethersulphone-rich phase would hence, at any time, be lower than before phase separation.

These results can be compared with relevant indicators provided in the literature. By thermodynamic simulations, Riccardi et al. [23] predicted that, in the modifier-rich phase at the beginning of phase separation, conversion would be slightly lower than the global level reached prior to de-mixing. However, Riccardi et al. and Bonnet et al., [13] predicted that conversions in the modifier-rich phase would continuously increase with cure time, although at a slower rate than in the epoxy-rich phase. This last trend was contradictory with the evolutions observed here with cure time. Nevertheless, Varley et al. [19] studied, by DMA, the isothermal cure of a TGAP-DDS system containing 30% of polysulphone. The T_g of the thermoplastic-rich phase was found to decrease in the first part of the curing process. Uncured epoxy precursors were assumed to keep on dissolving in the polysulphone phase, up to vitrification of the epoxy phase.

The results shown in Fig. 7 for the continuous phase could be explained by the combination of several phenomena. Firstly, as assumed by Varley et al., [19] a continued migration of low molar mass Epoxy-MDEA species to the copolyethersulphone-rich phase could take place. Secondly, at the same time, epoxy-MDEA oligomers could be expelled from the copolyethersulphone-rich phase, as soon as they reached a critical molecular weight, expected to be very low. Due to the plasticisation of the copolyethersulphone, by at least 50% weight of low molecular weight Epoxy-MDEA species, the transfer of these oligomers should remain possible either to the main epoxy-rich phase or at shorter distances, leading to the formation of sub-inclusions. Thirdly, a lack of affinity between MDEA and the copolyethersulphone could further decrease the MDEA content in the copolyethersulphone-rich phase at the beginning of phase separation. A slight stoichiometric imbalance could result and be further detrimental to the curing reactions.

3.2.3. Conversion versus copolyethersulphone content diagram

An alternative representation of the results is proposed. For each cure time, conversions in each phase were plotted against the corresponding copolyethersulphone contents (Fig. 8).

This graphical representation was further exploited. By extracting from Fig. 8 the trends in the results, the diagram relating conversion and copolyethersulphone content in co-existing phases is shown schematically in Fig. 9. This diagram corresponded to a cure temperature of 160 °C and an initial copolyethersulphone level of 25%. To our knowledge, it constituted the first experimental determination of co-existence curves describing the evolutions of phase characteristics along the curing and phase separation phenomena.

Such co-existence curves were proposed by Riccardi et al. [23] for epoxy-rubber systems, on the basis of thermodynamic simulations. In their model, they made the hypothesis of no mass transfer from the modifier-rich phase to the epoxy-phase. The appearance of sub-inclusions in the modifier-rich phase was hence predicted. The left branch of their diagram (epoxy-rich phase) has a shape similar to the curve shape shown in Fig. 9. The right branch of the co-existence curve was calculated for the rubber-rich phase, without taking into account the sub-inclusions present in

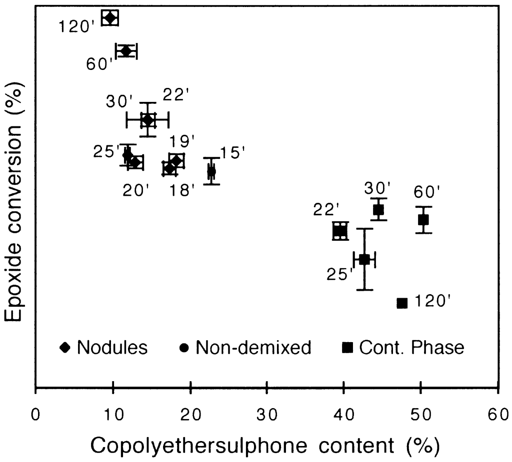

Fig. 8. Conversion versus copolyethersulphone content diagram for blends cured at 160 °C. The error bars correspond to the standard error of the mean.

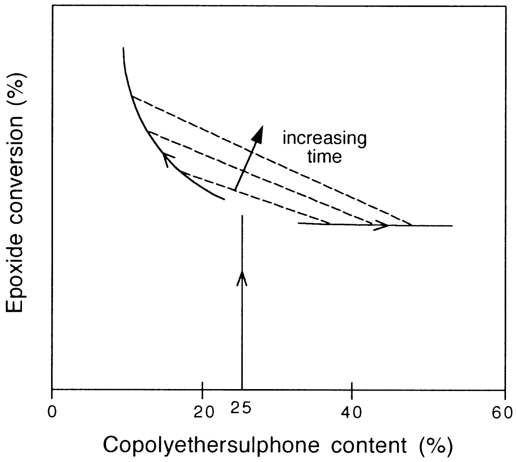

Fig. 9. Diagram relating the conversion and the copolyethersulphone content of phases co-existing along curing and phase separation processes, extrapolated from the experimental values given in Fig. 8. Broken lines relate, for each cure time, the points characterising the co-existing phases.

that phase. A curve corresponding to increasing conversion for increasing modifier content was then obtained.

In this work, without analysing the sub-inclusions, the right branch obtained for the copolyethersulphone-rich phase (Fig. 9), corresponded to stable or slightly decreasing conversions when the content in copolyethersulphone further increased. This trend differs from the simulations of Riccardi et al. The existence in our systems of mass transfer from the copolyethersulphone-rich to the epoxy-rich phase could contribute to explaining this difference.

4. Conclusions

Curing and phase separation phenomena taking place in epoxy-thermoplastic blends have been studied. The blends were based on MDEA diamine curing agent and 25% by weight of reactive amine-ended copolyethersulphone thermoplastic.

Morphologies developed upon curing at 160 °C were observed by optical microscopy. Phase inverted microstructures with nodule sizes of several tens of microns were obtained at the end of the curing.

Local characterisation of the thermoplastic content and the epoxide conversion was performed in the different phases by micro-Raman spectroscopy. Prior to carrying out these experiments, calibrations of the Raman data were developed. The quantitative aspects of these calibrations, when applied to blend characterisation, have been discussed in this paper. It appears that absolute quantification of the copolyethersulphone content can be obtained. However, the calibrations provide only qualitative estimations of the conversion. Furthermore, the samples and the spectra appear to be sensitive to the time of exposure to the laser beam. For this reason, results have only been deduced from spectra collected in similar conditions of confocal hole and acquisition time.

Despite the limitations related to the calibrations and to the time-dependence of collected spectra, the local characterisation of blend phase properties appears to give original and significant results. Among other things, the evolution of the copolyethersulphone content with cure time has been satisfactorily followed in both phases. For the first time, the experimental determination of co-existence curves, relating the epoxide conversion to the thermoplastic content in co-existing phases, appears possible in epoxy-thermoplastic blends.

From the results reported here, the potentials of the micro-Raman spectroscopy have been well illustrated. The technique could allow a broader understanding of the phase - and hence material - properties, as a function of the blend parameters, such as the curing agent nature or the thermoplastic chain-end reactivity. It should however be remembered that phase sizes have to be larger than the lateral resolution offered by the technique, i.e. at least larger than 1 μm. Furthermore, improvements of the calibrations would be required to provide full quantification of the phase features. In particular, the use of near-infrared (NIR) spectroscopy, instead of DSC, for developing the calibration for the epoxide conversion could improve the assessment of this feature within the blends. Moreover, as a further extension of the characterisation, calibrations could be developed to separately quantify the local concentrations of epoxy and curing agent species. Stoichiometric imbalance could then be studied in the phases. Finally, provided that the Raman spectrometer is equipped with an XY stage, the automatic recording of spectra along lines or within 2D-area could be easily performed.

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