

A depolarized light scattering study of the phase separation process in an epoxy-elastomer blend

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(Received 27 June 1996; revised 24 October 1996)

Phase separation between two or more isotropic polymers is usually studied by unpolarized or polarized light scattering (SALS). Depolarized SALS has never been used, but it is also able to bring useful information about the kinetics and mechanisms of the phase separation. Such a new technique is tested here by studying the evolution of a phase separation in a pseudo-binary mixture of bis-phenol A diglycidylether (epoxy monomer), a cycloaliphatic diamine (comonomer or cross-linking agent) and an epoxy terminated butadiene-acrylonitrile random copolymer (additive). The depolarized light scattering patterns during the phase separation have four lobes positioned at 45° of the position of the polarizers. The position of the lobes does not vary with time, suggesting that the mechanism of spinodal decomposition is responsible for the phase separation. The resulting periodic distance between composition fluctuations is calculated from the position of the lobes using two methods. It was found in agreement with the distance deduced from the position of the scattering ring observed in unpolarized light scattering. © 1997 Elsevier Science Ltd

(Keywords: phase separation; light-scattering; thermoset)

INTRODUCTION

One method of improving the mechanical properties of thermosetting polymers is to add a thermoplastic or elastomer to the epoxy monomer and cross-linking agent to create an initially miscible polymer blend¹⁻⁵. As the polymerization proceeds the decrease in the entropy of mixing drives a phase separation resulting in the formation of a heterogeneous composite. The mechanical properties of such materials are dictated by the morphology^{1,2,4,5,7}, which in turn depends upon the characteristics of the phase separation mechanism.

There are two possible mechanisms by which such a phase separation may occur, nucleation and growth (NG), and spinodal decomposition (SD)^{7,8}. Nucleation occurs through the random formation of isotropic nuclei which may either be eliminated as a consequence of the high surface energy of small nuclei, or continue to grow. This is generally a slow process in comparison to SD, which is initiated by small concentration fluctuations throughout the sample. The SD process has been classified into several stages⁹. In the early stage of SD the concentration fluctuations are approximately linear and are well described by the theory of Cahn¹⁰. During this stage the amplitude of the concentration fluctuations increases while the characteristic distance between fluctuations remains constant. During the later stages nonlinear behaviour dominates and this leads to a saturation of concentration fluctuations and an increase in the characteristic separation between them. In a latter stage, interfacial tension dominates, leading to the breaking of the structure into nodules.

The precise control of mechanical properties requires a detailed knowledge of the morphology at any time. The final morphologies arising from NG and SD are very similar. In the absence of cross-linking, both causes the morphology to evolve towards a spherical domain structure⁷. However the initial morphologies, which are often frozen by vitrification, are quite different. NG is initially manifested in the form of isotropic spheres in an isotropic matrix^{7,13,14} whereas SD originally gives rise to a co-continuous structure^{11,12}. It is therefore vital to obtain information during the entire course of the phase separation process. For many systems direct observation by optical or electron microscopy does not provide proof conclusive enough to identify either process as the dominant mechanism of the phase separation process⁷. In these cases additional information concerning either the time evolution of the phase diagram or more subtle probes of the morphology are needed. A variety of techniques have been employed to complement microscopy observations, including light scattering^{11,12,15}, d.s.c.¹⁵⁻¹⁹, FTi.r.^{19,20}, absorption^{19,20}, dielectric measurements²¹, and rheology^{6,18-22}.

Static light scattering is a classical tool for studying phase separation in general. In all cases involving polymers, unpolarized or linearly polarized scattering geometries have been used. Inoue has used light scattering to probe the evolution of the morphology^{11,12,15,16}. In two studies he could conclude that SD was responsible for the phase separation, partly on the basis of polarized light scattering studies which showed an increase in the characteristic repeat distance with time, a feature which is compatible with the later stages of SD.

The objective of this study is to show that depolarized light scattering can be a very interesting way of gaining

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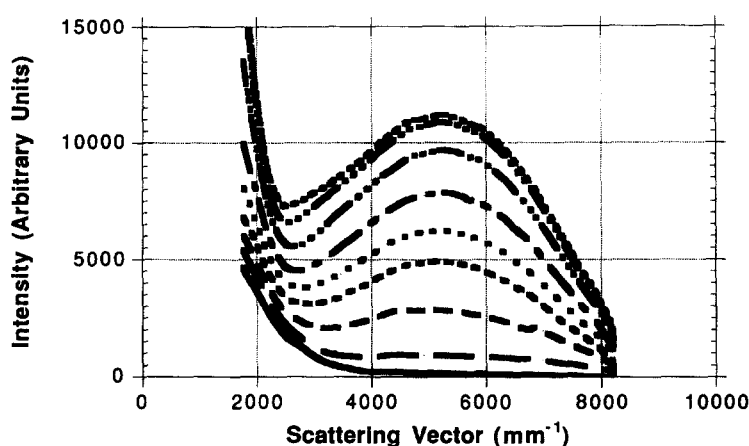


Figure 1 Scattered intensity functions $I(q)$ for a sample cured at 75°C. Profiles were recorded after times of (from the least to most intense), 1520, 1710, 1895, 2080, 2850, 3325, 3800, 4250 and 9500 s. For each case the initial scattered intensity function recorded at 20°C has been subtracted to reduce the effect of parasitic scattering

information on the phase separation. To our knowledge, no one has considered such a scattering geometry. Depolarized light scattering provides additional information about the morphology which enables the phase separation mechanism to be better determined, allowing unpolarized scattering data to be more reliably interpreted. We will test this concept by studying the evolution of a phase separation in a pseudo-binary mixture of bis-phenol A diglycidylether (epoxy monomer), a cycloaliphatic diamine (comonomer or cross-linking agent) and an epoxy terminated butadiene-acrylonitrile random copolymer (additive), using both unpolarized and depolarized light scattering and varying the curing temperature. Such a system has been extensively studied by the group of J. P. Pascault^{23,24}. The relevant features of this work for our purpose are that it is possible to see by SAXS that a phase separation proceeds through nucleation and growth much before anything can be detected by light scattering. Preliminary light scattering data shows the occurrence of a correlation peak which can be interpreted as the sign of a spinodal decomposition. There is thus an apparent discrepancy between the results of these two methods. We will discuss this point in the light of the unpolarized and depolarized experiments.

EXPERIMENTAL

Materials

The materials were kindly provided by Professor J. P. Pascault from Insa, France. They are the same as the ones studied in refs. 23 and 24. Epoxy used was a bis-phenol A diglycidylether (DGEBA), the cross-linking agent was a cycloaliphatic diamine (4,4'-diamino-3,3'-dimethyldicyclooxymethane, 3DCM) and the elastomer additive was an epoxy terminated butadiene-acrylonitrile random copolymer (ETBN). Details on the preparation of these compounds can be found in ref. 23.

The mixture was prepared by thoroughly mixing the three components in the following weight fractions at 20°C, 43.6% DGEBA, 21.5% 3DCM and 34.9% ETBN. These mass fractions means that we have 15 wt% of butadiene-acrylonitrile random copolymer. A small quantity of the mixture was then placed between two glass plates. Several samples were prepared from each batch and heated *in vacuo* at 50°C for 15 min to remove air bubbles.

The sample with the fewest air bubbles was selected for investigation at one of three curing temperatures, 60, 75 or 90°C, the others being discarded.

Light scattering measurements

Unpolarized light scattering. Freshly prepared samples were mounted in a Linkam THM600 sample stage, controlled by a Linkam TMS91 temperature controller. Samples were heated at a rate of 10°C min⁻¹ to 60, 75 or 90°C. It was assumed that no polymerization occurred during heating. The samples were illuminated by unpolarized HeNe laser light (wavelength 632.8 nm), through a small aperture in the sample stage (~1 mm in diameter). The scattering pattern generated by the sample was visualized using a white paper screen mounted 65 mm from the sample. A standard CCD video camera was used to record the light scattering pattern shown on the screen. Light scattering patterns were collected and analysed every 95 s using TRAMS (Time Resolved Analysis and Measurement of Scattering), an image acquisition and analysis software system developed at the Centre de Mise en Forme des Matériaux. The scattering intensity function $I(q)$ was extracted from each pattern, where q is the scattering vector, corrected for refraction at the air/sample interface, defined as

$$|q| = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (1)$$

where θ is the angle through which the radiation is scattering in the sample (angle between the incident and the scattering light) and λ is the wavelength of radiation in the sample. The units of q are mm⁻¹.

The samples were held at the required temperature for 90 min or until no further changes were noted in $I(q)$.

In order to reduce the effect of parasitic scattering arising from the cell and impurities in the sample, an initial profile obtained at 20°C was subtracted from all subsequently recorded profiles once the sample had been heated to the curing temperature. The scattered intensity data were not corrected for absorption in the sample, nor were profiles from different samples corrected to account for variable sample thicknesses. The corrected scattered intensity functions were then analysed to extract the angular position and intensity of any diffuse maxima.

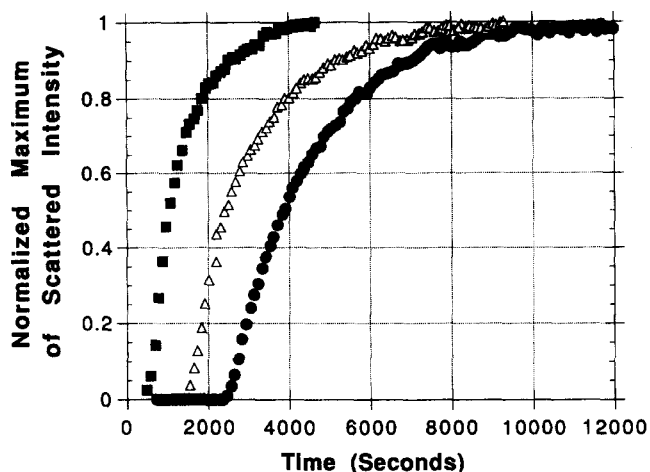


Figure 2 The normalized peak intensity as a function of curing time for samples cured at (●) 60°C, (Δ) 75°C and (■) 90°C

Depolarized light scattering

A second set of scattering investigations were conducted with crossed polarizer and analyser positioned above and below the sample, respectively. The depolarized scattering was considerably weaker than the polarized scattering. Polaroid film (film speed 50 ASA) was used to record the patterns since the video camera was not sensitive enough to detect the scattered radiation. In addition to this the introduction of an analyser between the heating stage and screen made it impossible to position the film close enough to record information over the range of angles of interest. Therefore a different approach was adopted. Freshly prepared samples were heated to 75°C in the Linkam sample mount and cured for times of 12, 24, 45, 50 and 80 min. The samples were then removed and mounted between the crossed polars and polaroid photographs of the resulting scattering patterns were taken. The exposure times were varied between 30 and 1.5 s.

RESULTS

The typical development of the unpolarized scattering intensity profiles for a sample cured at 75°C is shown in Figure 1. It can be seen that about 25 min after curing began a diffuse maxima developed between 4000 and 6000 mm^{-1} . The intensity of this peak was found to increase monotonically with time until a plateau value was attained. Figure 2 shows the peak intensity normalized to the maximum of the last profile as a function of time for each of the three curing temperatures studied. The angular positions of the maxima were found to remain constant throughout the course of each investigation.

Unpolarized light scattering patterns provide information about spatial correlations between regions of the same refractive index. A scattering maximum indicates periodic changes in the refractive index²⁵ and therefore periodic variations in the composition of the sample. This suggests that a phase separation is occurring. The position of the diffuse maxima can be used to estimate the characteristic repeat distance Λ between regions of the same composition, via the Bragg relationship

$$n\lambda = 2\Lambda \sin(\theta/2) \quad (2)$$

where n is the diffraction order and λ is the wavelength of the radiation in the sample.

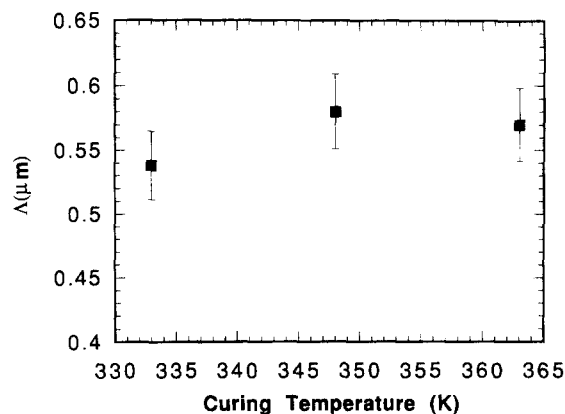


Figure 3 The mean characteristic repeat distance calculated from unpolarized light scattering data plotted as a function of the curing temperature. The error associated with each value is $\pm 5\%$

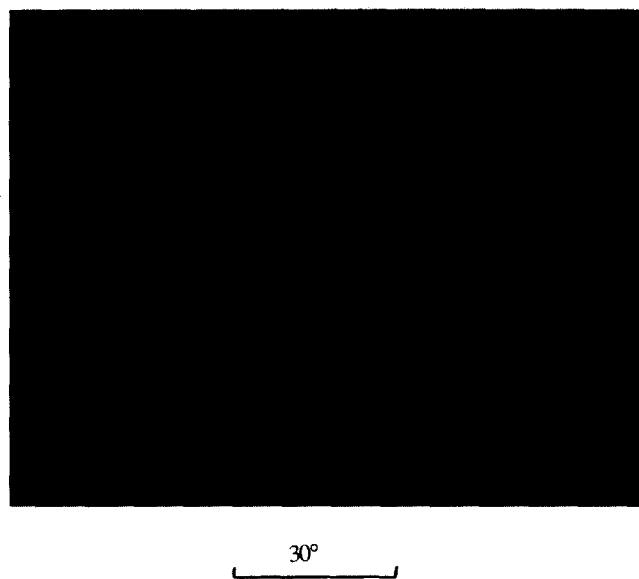


Figure 4 Depolarized scattering patterns obtained from samples cured at 75°C

Equation (2) yielded distances of between 1.1 and 1.2 μm for samples cured at 75°C in these investigations, in agreement with the results given in ref. 23. Figure 3 shows the mean characteristic repeat distance for all samples studied as a function of the curing temperature. It can be seen that there is no clearly defined trend in the relationship between these two parameters, however these data do not rule out the possibility that Λ slightly increases with increasing curing temperature.

Polaroid photographs of depolarized scattering patterns obtained from samples cured for various times at 75°C are shown in Figure 4. It can be seen that the patterns have four lobes, each at $\sim 45^\circ$ to the polarizer axis. The lobes began to appear at approximately the same time as the diffuse maxima in the polarized scattering patterns. Whilst it is not strictly valid to make quantitative comparisons between patterns obtained from different samples, two general points can be noted. Firstly the positions of the diffuse maxima were found to be approximately the same for all samples, independent of the curing time. Secondly the fact that shorter exposure times were required to record successive patterns

indicates that the scattered intensity increased with time.

There are two ways to analyse the data. The first is to consider again the Bragg law, at the maximum intensity. Applying equation (2) gives a characteristic repeat distance Λ of $1.1 \mu\text{m}$, which is in good agreement with the results obtained by unpolarized scattering.

Another way of considering the scattering pattern is to recall the structure of the mixture at that stage, shown to be mainly formed of spherical domains of about the same size. The appearance of four lobes at $\pm 45^\circ$ to the polarizer axis is thus reminiscent of the scattering by spherical entities, or at least by entities with an axis of revolution²⁶. If we are dealing with isotropic entities, we can use Mie theory. It predicts that the relationship between the scattering angle and entity radius can be expressed as²⁶

$$U = \frac{4\pi a}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (3)$$

U is a dimensionless parameter between 2.8 and 3 for the first order²⁶, a is the radius of the sphere, θ is the polar scattering angle in the sample and λ is the wavelength of the incident radiation in the sample.

After correction for refraction at the air/sample interface the experimental data gives values between 0.54 and $0.59 \mu\text{m}$ for the sphere radius. Similar values have been reported by Verchère *et al.* for the same system²⁷, based on direct observations of the samples by electron microscopy.

DISCUSSION

Light scattering and phase separation

The observations by unpolarized light scattering shows that we are dealing with a SD mechanism. This is not incompatible with the SAXS experiments, which show the occurrence of a NG phase separation before anything can be detected by SALS. One can easily imagine that, depending on the concentration and the viscosity of the material, the entrance into the phase separated region starts in the metastable region with kinetics fast enough to produce the beginning of a NG mechanism and then continues further into the unstable region where the SD mechanism is the quickest process. Such a scheme has been recently reported for another material²⁸. The fact that SD is the dominant mechanism for the phase separation is in conflict with most current theories^{13,14} and many authors' interpretations of the observed morphology^{13,27,29,30}, which assume a NG type phase separation. However it should be remembered that the system studied here is a relatively fast reacting system and that the composition studied here is close to the critical composition. Therefore it is quite possible that the mixture enters the spinodal region of the phase diagram even after some NG separation occurs.

The depolarized observations are new. They show that the interface between the two phases is depolarizing enough for the incident light to be recorded. This is not due to any anisotropy of each of the phases, but is an interfacial effect. It shows that the interface is sharp (strong segregation effect). As said before, there are two ways to see the data, either as due to the scattering by strongly spatially correlated interfaces or by the scattering of spheres. In fact it is not possible to discriminate between these two possibilities since they should give the

same result, if both are coming from a SD mechanism. This can be understood in the following way. If we have a SD typical morphology, Bragg law will apply and a characteristic length Λ will be obtained from the angular position from the maximum intensity. If the morphology is constituted by spheres coming from the SD morphology, they will have all the same diameter which is the characteristic length Λ . The predictions for the position of the maxima are $2\Lambda \sin(\theta_B/2) = \lambda$ for the Bragg law and $\lambda = (2\pi\Lambda/3) \sin(\theta_{HV}/2)$ for the spheres. This gives the relation

$$\sin(\theta_B/2) = \pi/3 \sin(\theta_{HV}/2) \quad (4)$$

This shows that the position of the scattering maximum for these two cases is located at the same scattering angle ($\theta_B = \theta_{HV}$). This arises because the parameter U in equation (3) is around 3 for isotropic objects.

Another reason for discounting NG arises from the observation that the intensity of the depolarized scattering increases whilst the angular position of the diffuse maxima remains constant. If NG were responsible for the phase separation then the size of the spheres would change and the scattering maxima should move towards lower angles. The fact that the intensity increases whilst the angular position of the depolarized lobes remains constant rules out NG, but is compatible with SD.

Phase separation kinetics

It is accepted that SD occurs in several stages⁹. However many authors have noted that only during the early stage of SD does the position of the diffuse maxima remain fixed³¹⁻³³. In this stage the decomposition may be described by the linear theory of Cahn¹⁰. This suggests that the phase separation studied here does not progress beyond the early stage of SD. The Cahn theory also leads to the prediction that during the early stage of SD the scattered intensity should increase exponentially with time. The development of the scattered intensity with time shown in *Figure 2* shows no evidence of an exponential increase, except perhaps in the first few minutes after the onset of the phase separation. However, the development of the curves shown in *Figure 2* is similar to the development of invariant¹⁵, transmittance^{6,12,19} and epoxy conversion^{14,15,18} curves reported for similar systems. The reason for this almost certainly lies in the complex kinetics of the system. The polymerization of the epoxy will increasingly inhibit the mobility of the component molecules and, in accordance with the diffusion equation¹⁰, reduce the rate at which concentration changes occur. This trend will be opposed by changes in the entropy of mixing, also driven by the polymerization of the epoxy, which will favour a more rapid phase separation. The curves shown in *Figure 2* mirror these factors and support theoretical predictions of the development of the structure factor using a Monte Carlo simulation³⁴. It was suggested that there was an initial increase followed by a decrease in the rate of development, passing a maximum as the reactivity between the epoxide group and cross-linking agent increased.

Our SALS observations can be classically explained in terms of the effect of the molar mass of the epoxy and cross-linking density on the diffusion rate. At low molar masses the epoxy has little effect and the phase separation proceeds ever more rapidly and the rate of increase of the scattered intensity rises. The increasing

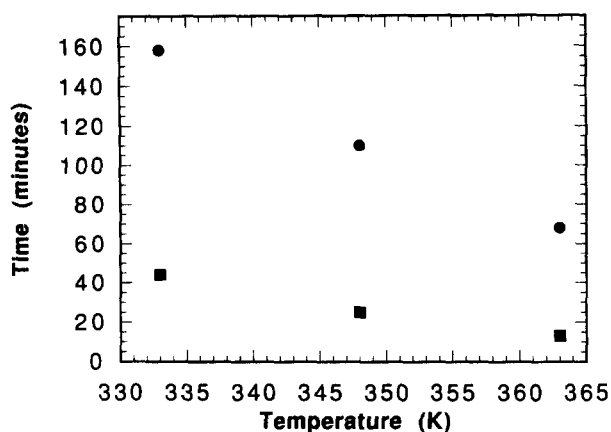


Figure 5 The time in minutes for the onset of the phase separation (■) and the vitrification of the epoxy (●) as a function of the curing temperature in Kelvin

molar mass of the epoxy has a greater and greater adverse effect on the diffusion rate and the rate of increase of the scattered intensity begins to fall until a plateau is reached. This indicates that no further phase separation is occurring due to the vitrification of the epoxy. Such an explanation has been proposed by several groups^{11,12,14,15,19,22,34}, and have formed the basis of preliminary attempts to control the morphology via the curing temperature^{11,12,22}. However there is some disagreement regarding the effectiveness of such methods. In some cases the temperature does seem to influence the morphology^{11,12}, whereas in at least one the temperature seems to have no effect²². Previous data for our system suggests that the average particle radius increases with increasing curing temperature²⁷. However no such definite trend was observed over the temperature range considered in this study (Figure 3), indicating that any influence of the temperature on the characteristic size is marginal.

Figure 5 shows the time required for the onset of the phase separation and the vitrification of the epoxy as evaluated by light scattering as a function of the curing temperature (these data being evaluated from Figure 2). It can be seen that there is a significant variation in these times over the temperature range studied caused by an increase in the rate of polymerization. Closer examination reveals that the total time during which phase separation can occur in a sample cured at 90°C is less than half of that available for a sample cured at 60°C.

CONCLUSIONS

Results obtained from unpolarized and unique depolarized light scattering studies of an elastomer modified epoxy resin during cure showed the occurrence of a phase separation. The additional information available from depolarized scattering studies confirms that the phase separation occurred via spinodal decomposition, and raises the possibility that this technique could be useful in other cases where the mechanism of the phase separation is uncertain. An interpretation of the depolarized data shows that it is difficult to distinguish between Bragg scattering and sphere scattering when the spheres come from the breaking of a spinodal morphology.

ACKNOWLEDGEMENTS

We would like to thank DRET for financial support (Contract 92/017), Prof. J. P. Pascault and his group for providing the samples and for many discussions, J. Maugey for his help during the preparation of this manuscript, the European Community Erasmus programme for an undergraduate grant to LB and the European Community for a research training grant to PK.

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