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Influence of curing conditions on the morphologies of a PMMA-modified epoxy matrix

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Abstract

The effect of curing conditions such as time and temperature on the morphology developed in a diglycidyl ether of bisphenol-A epoxy resin cured with diamino diphenyl methane, and modified with 15 wt% poly(methyl methacrylate), has been investigated. The reacting mixtures were precured at 80°C for a period of time ranging from 2 to 7 h, afterwards they were cured at 140°C and finally postcured at 200°C. The mixtures were opaque or transparent depending on the precuring time. Dynamic mechanical thermal analysis suggested that all mixtures were heterogeneous. However, phase separation occurred for all precuring times but to a lesser extent for samples precured for 5, 6 or 7 h than for those precured for shorter time intervals at 80°C. Two phases were clearly distinguished by atomic force microscopy, in all mixtures. The phase size was controlled, on one hand, by the time the phases had to grow, i.e. the interval between the cloud and gel points, and on the other hand, by the viscosity of the reacting mixture at the moment of phase separation.

Keywords: Poly(methyl methacrylate); Epoxy resin; Morphology

1. Introduction

Phase separation of binary polymer mixtures has been widely studied due to its importance from a scientific viewpoint as well as in the design and control of microstructures and properties. In thermoplastic-modified epoxy resins, phase separation usually takes place on curing because the conformational entropy of the system greatly decreases as a result of the increment of the molecular weight of the thermoset resin. In this way, the initially miscible uncured thermoplastic/thermoset resin mixture decomposes into a heterogeneous multiphase system via binodal or, more frequently, spinodal decomposition (SD). Many studies have been performed to analyse the effect of the nature and quantity of modifier or curative agent on the final morphology [1–10]. Usually, a single set of curing conditions is studied. However, some papers have dealt with the effect of changing the curing conditions [4–7]. Opaque, translucent or transparent phenoxy/epoxy blends have been obtained by kinetic control of the curing rate, obtained with different amounts of accelerator [4,5]. Butta et al [6] indicated for an amine-terminated butadiene–acrylonitrile/epoxy blend that, curing at low temperatures promoted formation of heterogeneous materials with poor fracture resistance, while at high temperatures, tough heterogeneous blends were obtained. Similarly, Jansen et al. [7], for similar mixtures, found that the final morphology can be tailored by controlling the polymerisation temperature with respect to the T_g of the original uncured solution.

In this paper, we further explore this possibility in order to obtain materials showing different levels of phase separation. The analysed mixture has been an epoxy resin, cured with diamino diphenyl methane (DDM), containing 15 wt% poly(methyl methacrylate) (PMMA), and submitted to different curing schedules. The obtained microstructures were observed by atomic force microscopy (AFM). They have been related to the particular conditions of the reacting mixture at the time of phase separation, especially to its viscosity and temperature.

This new approach is quite relevant because it offers to the final users the possibility of designing a full range of different materials with the same composition only by changing the processing conditions.

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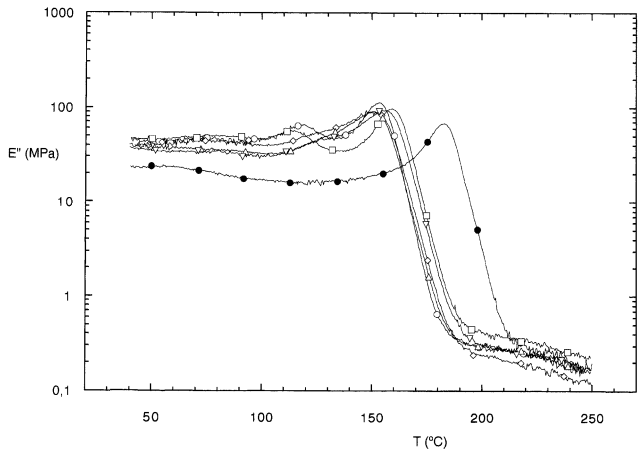

Fig. 1. Loss modulus vs. temperature for post-cured epoxy mixtures containing 15 wt% PMMA precured at 80°C for different times: ○ 2 h; □ 3 h; ◇ 5 h; △ 6 h and ▽ 7 h. ● Postcured neat epoxy matrix precured at 80°C for 3 h.

2. Experimental

2.1. Materials and sample preparation

The epoxy used was a diglycidyl ether of bisphenol-A, DGEBA, DER-332, kindly supplied by Dow Chemical. It has an epoxy equivalent weight of 175 and a hydroxyl/epoxy ratio of 0.03. The curing agent was DDM (HT-972), kindly supplied by Vantico. PMMA, Altuglas GR 9E from Elf-Atochem, was used as thermoplastic modifier. It has a M_n of 58,000 as measured by gel permeation chromatography in a Waters 150-C ALC/GPC instrument equipped with 3 columns PL Gel of 500, 10^4 and 10^6 Å, from Polymer Labs.

Epoxy mixtures containing 15 wt% PMMA were prepared in the following way: a weighed amount of PMMA was dissolved in methylene chloride (Panreac, PRS grade), and then, DGEBA was added to the solution and stirred until the dissolution of the resin was complete. Later, the solvent was removed by heating at 80°C. Afterwards, the mixture was kept overnight in a vacuum oven at 80°C to ensure complete removal of the solvent, no reaction between epoxy and PMMA was observed under these conditions. As hardener, a stoichiometric amount of DDM was added at 80°C.

The reacting mixtures were precured at 80°C for intervals ranging from 2 to 7 h. Afterwards, they were cured at 140°C for 1 h 30 min, and finally, post-cured at 200°C for 2 h in order to achieve the complete curing of the resin under optimal conditions.

2.2. Techniques

Differential scanning calorimetry (DSC) measurements were carried out in a Perkin–Elmer DSC-7 (in a dry nitrogen atmosphere and calibrated with an indium standard) working with 6–8 mg samples in aluminium pans. Two runs at a constant heating rate of 10°C/min were performed in a temperature range of 30–250°C. The glass transition temperature, T_g, was measured in the second scan as the middle point of the endothermic shift.

Dynamic mechanical behaviour of neat and modified mixtures was analysed in a dynamic mechanical thermal analysis (DMTA) equipment from Rheometric Scientific operating in the single cantilever mode. Temperature scans from 40 to 250°C at 3°C/min and 1 Hz were performed using $25 \times 12 \times 2$ mm^3 specimens.

The morphology of the fracture surfaces of specimens tested by bending was studied by AFM. The AFM scanning was performed with a scanning probe microscope (SPM) (Nanoscope IIIa, Multimode™ from Digital Instruments) operating in tapping mode. An extension of the tapping mode is phase imaging. The phase imaging measures the phase lag of the cantilever oscillations relative to the signal sent to the cantilever driver. The phase lag is very sensitive to variations in material properties, such as adhesion, viscoelasticity and stiffness. In this way, the tapping mode extension has been used as a contrast enhancement technique. Tapping mode measurements were performed using etched silicon probes with a cantilever configuration of single beam and 225 μm of length and with a tip of a nominal radius of curvature of 5–10 nm. Several specimens were scanned in different regions in order to analyse their morphologies. Similar images were obtained, thus demonstrating the reproducibility of the results. All images are shown without any image processing except in some cases where horizontal levelling and contrast enhancement were used.

3. Results and discussion

The PMMA-modified epoxy mixtures at the studied composition (15 wt% PMMA) were visually observed after each of the curing steps, i.e. precuring at 80°C, curing at 140°C and post-curing at 200°C. All samples were transparent after the different curing times at 80°C. Nevertheless, after the secondary curing at 140°C, samples precured for 2 or 3 h at 80°C appeared opaque, while samples cured for longer times at 80°C remained transparent even after post-curing at 200°C. This would indicate the existence of a two-phase structure in the mixtures precured for 2 or 3 h at 80°C. On the other side, the transparency observed for the mixtures precured for longer times at 80°C could indicate the existence of a single homogeneous phase. Other authors have also found that by using particular curing conditions, transparent thermoplastic-modified thermoset matrices may be obtained [7].

It must be stated that the gel and vitrification times were 198 and 263 min, respectively as measured at 80°C by a dynamic annular pumping test performed on the curing mixture.

In order to ascertain the phase behaviour, a calorimetric study of the mixtures was carried out. As we have previously reported [8], in accordance with the visual observations, the mixtures precured for 2 or 3 h showed two different T_gs changing with the precuring time. On the contrary, mixtures precured for 5, 6 and 7 h showed a single T_g independent of the curing time. The calorimetric data were corroborated by DMTA, a more sensitive technique than DSC, to investigate the microstructure of the mixtures. For comparison, the loss moduli for the neat epoxy matrix and the PMMA-modified mixtures are shown in Fig. 1. Two loss peaks are clearly distinguished in samples precured for 2 and 3 h at 80°C. The high temperature peak can be ascribed to an epoxy-rich phase, whereas the low temperature one is attributed to a PMMA-rich phase. Although both peaks have a rather similar height, that for the epoxy-rich phase peak is slightly higher than that for the PMMA-rich-phase, thus pointing a co-continuous morphology, even if the epoxy-rich phase seems to have a more pronounced tendency to be continuous. Besides, for mixtures containing PMMA, the epoxy-rich phase peak appears at around 25°C, below the neat epoxy matrix. This means that the epoxy phase in the mixtures contains a certain amount of PMMA. The more the PMMA it contains, the lower the peak temperature appears, though some stoichiometric imbalance cannot be discarded. This effect is more pronounced for the samples precured for 2 h. However, for samples precured for longer times, only a single peak is seen and a broad shoulder appears between the peak corresponding to the epoxy-rich phase and the region where the transition of PMMA should be observed. This fact suggests that in these samples, provided the phase separation occurs, it takes place at a lower extent than for samples precured for shorter times at 80°C.

Further, the characterisation of the mixtures was performed by AFM. For these samples, the tapping mode operation was used. Topographical and phase images were simultaneously obtained because of the high resolution of the phase contrast image, which highlighted the two-phase microstructure. In Fig. 2(a)–(e), the microstructures of the mixtures precured from 2 to 7 h at 80°C, and then submitted to the full cure procedure, are shown. As can be seen, all mixtures clearly exhibited two different phases, whose size is dependent on the precuring time. Both phases are continuous. Since the mixture contains only 15 wt% PMMA, the darkest phase could be attributed to the PMMA-rich phase and the other one to the epoxy-rich phase. It could be argued that the PMMA amount distinguished in the images is lower than 15 wt%. However, it has to be taken into account that, according to the DMTA data, not all PMMA is segregated from the epoxy rich-phase. In addition, it can be observed that the size of the epoxy-rich phase decreases with the precuring time from 2 to 5 h. Nevertheless, the samples precured for 5, 6 and 7 h, which were transparent, displayed similar phases sizes. Therefore, the transparency of the multiphase samples can be attributed to the size of their domains, which was smaller than the wavelength of the visible light (380–780 nm).

The observed morphologies are a result of the phase separation process from an initial homogeneous miscible mixture to a final heterogeneous state. The phase separation process is controlled by both thermodynamic and kinetic factors [9,10] and it takes place at conversions comprised between the cloud point conversion, X_{cp}, and the gel conversion, X_g, where the morphology is frozen. On one hand, the time available for phase separation depends on the polymerisation rate, which is also dependent on the curing temperature. On the other hand, the phase size is controlled by the time the phases have to grow and by the viscosity of the medium from where they are growing [11]. In Fig. 3, a hypothetical representation of conversion, X, versus time for a multi-step polymerisation of a 15 wt% PMMA modified epoxy mixture, is depicted. The horizontal straight lines represent the cloud point conversion and the gel conversion, respectively. At 80°C, the conversion-time curve would follow the path represented by line 'a'. At a higher temperature, such as 140°C, the polymerisation rate increases (line 'b'). If the mixture is precured at 80°C for 2 h and then the curing temperature is increased to 140°C, the conversion-time curve would separate from line a at point 1, and as the reacting mixture temperature progressively increases from 80 to 140°C, the followed path would progressively tend to be parallel to the curve b. This path is labelled in the figure as line 'c'.

However, when the initial sample is precured for 3 h at 80°C, the conversion-time curve would separate from line a at a higher conversion (point 2), closer to X_{cp}, following the path 'd'. As the temperature is increased from 80 to 140°C, when the X_{cp} conversion is reached, the real temperature of the mixture is lower than when the path c was followed. In this way, the slope of the curve is lower. This would suggest that more time for phase separation is available, as result giving bigger phase sizes. Nevertheless, it should be taken into account that the lower the temperature is, the higher the viscosity is, thus hindering the phase growing, as it was experimentally observed.

At longer precuring times, 5, 6 or 7 h, the X_g conversion has already been overcome. Thereby, all mixtures have the same time for phase separation and when the temperature is increased to 140°C, they are already gelated and consequently no size growing of the separated phases is possible. In this way, the phase size of the domains must be similar for the three mixtures. It should be noted that, even though the time for phase separation is longer for these precuring times than for the mixtures precured for only 2 or 3 h, the phase separation takes place at 80°C, and because of the high viscosity of the reacting mixture, the phase growing is highly hindered. As a result, smaller phase sizes than for shorter precuring times are observed.

The Flory–Huggins model applied to a binary blend consisting of a thermoset resin and a polydispersed thermoplastic allows one to calculate the critical composition for

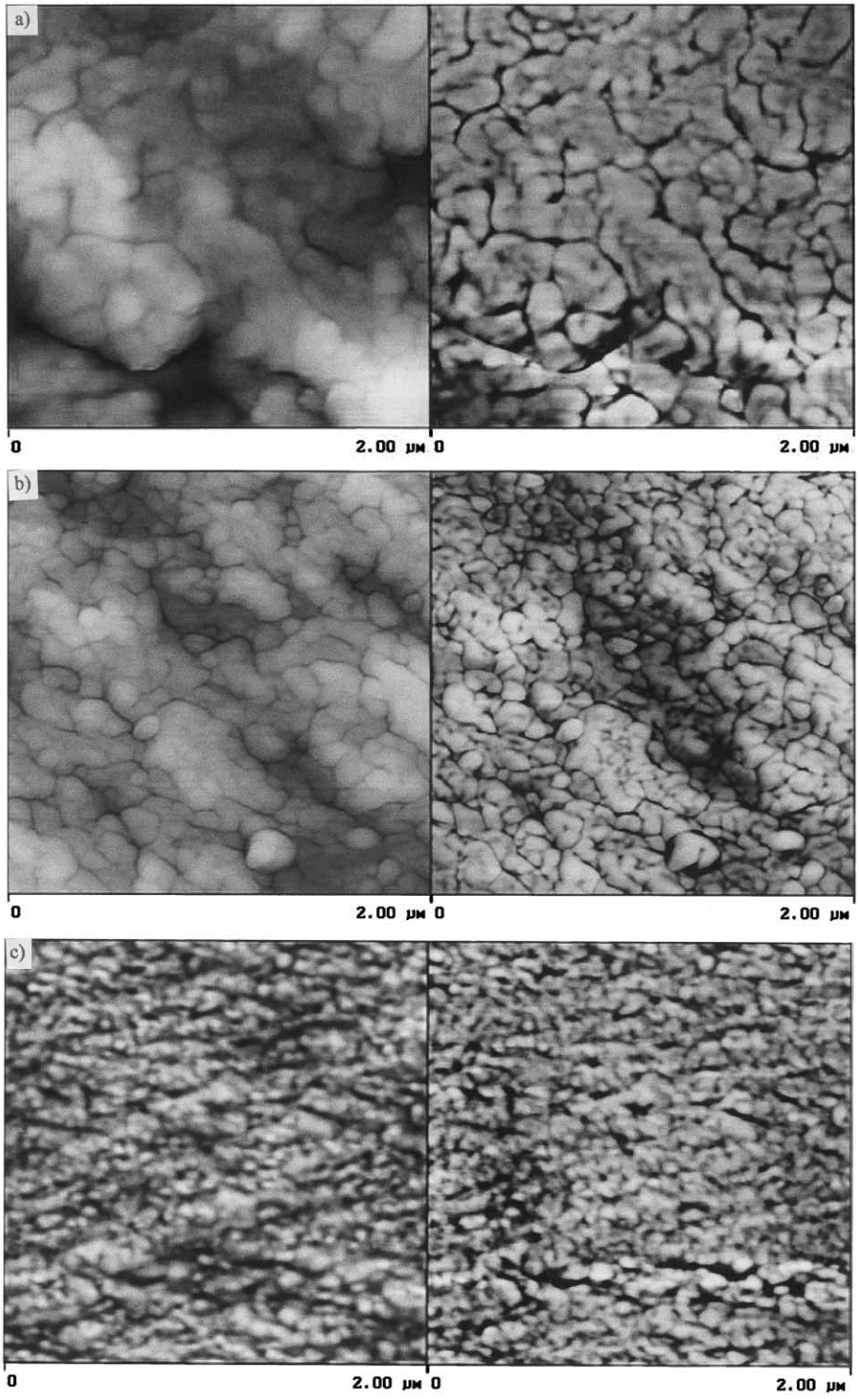

Fig. 2. Tapping mode AFM images of epoxy mixtures containing 15 wt% PMMA precured at 80°C for different times: (a) 2 h, (b) 3 h, (c) 5 h, (d) 6 h and (e) 7 h. Topographical (left) and phase images (right).

phase inversion. This model was applied to our system giving a value of roughly 5 wt% PMMA. Therefore, in the mixtures containing 15 wt% PMMA, phase inversion should have already taken place. However, no phase inversion was observed by microscopy but only a co-continuous morphology. The mechanism of decomposition for the reaction-induced phase separation in a reacting thermoset/thermoplastic blend has been revealed by light-scattering studies, which demonstrated that phase separation usually occurs via SD [10–15]. When the initial homogenous

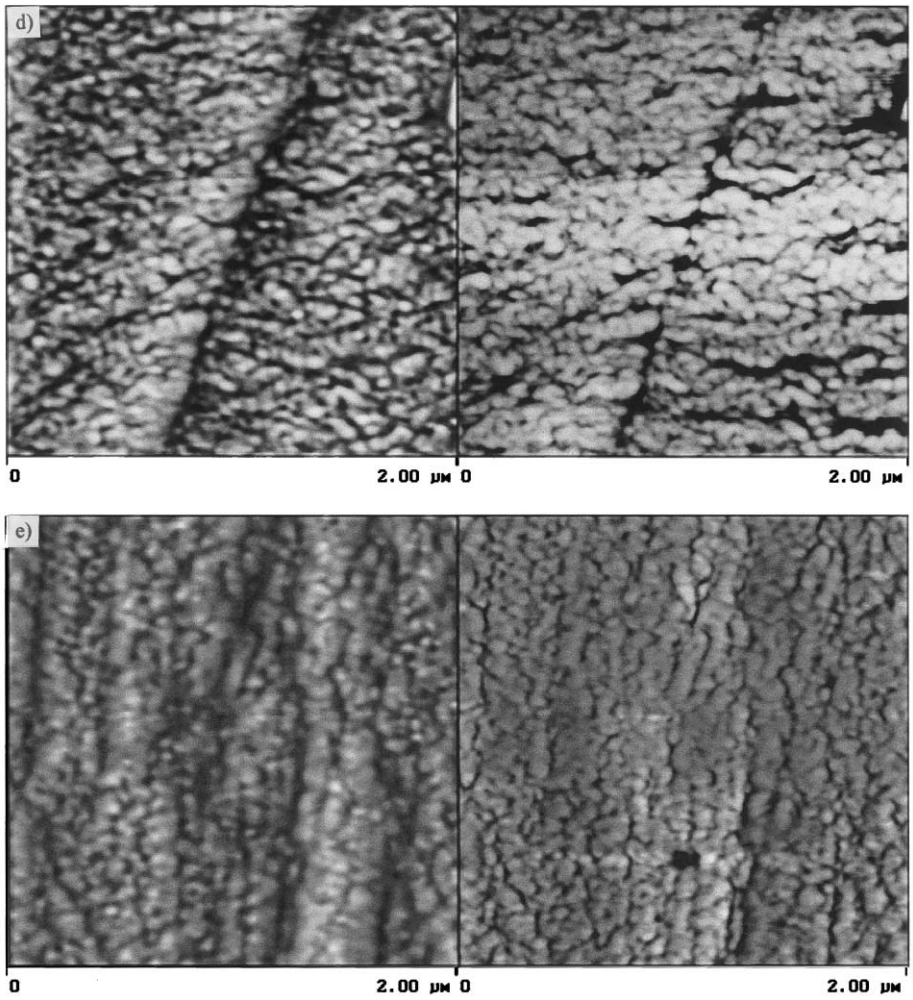

Fig. 2. (*continued*)

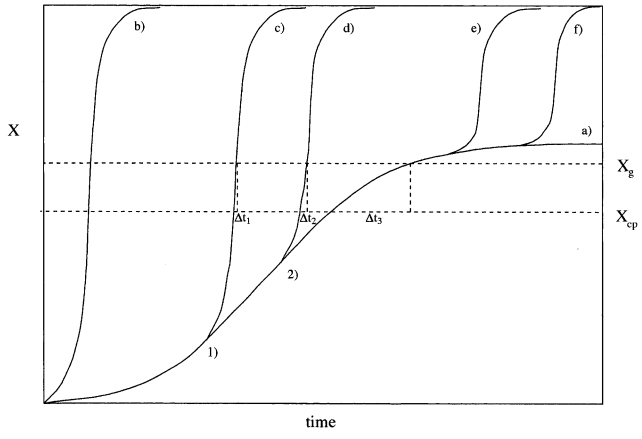

Fig. 3. Hypothetical conversion paths as a function of curing time for a multi-step polymerisation of a 15 wt% PMMA modified epoxy mixture. (a) Hypothetical curve for a curing temperature of 80°C, (b) idem for a curing temperature of 140°C, (c) idem for a curing temperature of 140°C after 2 h of precuring at 80°C, (d) same as (c), after 3 h of precuring at 80°C, (e) same as (c), after 5 h of precuring at 80°C, (f) same as (c), after 6 h of precuring at 80°C.

mixture begins to phase separate by SD, a co-continuous structure is developed. Later, when the phase separation proceeds, the periodic distance increases and, at the same time, phase connectivity may be interrupted by an increase in interfacial tension. However, if the epoxy-rich phase gels before phase-separation has ended, complete interruption can not be reached, resulting in a connected-globule structure, as the one observed in Fig. 2(c)–(e).

4. Conclusions

The research performed on phase separation and thermal behaviour for 15 wt% PMMA/epoxy mixtures precured at 80°C for different intervals of time reveals that the curing conditions have a great influence on the resultant final morphology.

Below a certain precuring temperature, no phase separation seems to have taken place and the obtained material is optically clear. However, when cured at 140°C, the transparent precured resin, opaque or transparent materials with several levels of miscibility can be obtained depending on

the precuring time. In this way, at short precuring times, opaque materials are obtained. On the contrary, when precured for longer times, the mixtures are fully transparent.

Independent of the opacity or transparency of the final product, it has been demonstrated by AFM that two different phases are always present. Even the visually transparent samples which gelate at 80°C, i.e. those precured for times equal or longer than 5 h, have two phases. Phase separation in these samples must have already occurred during the precuring at 80°C. The microstructure displays a co-continuous morphology where the epoxy-rich phase size decreases as the precuring time increases. Once the gelation has taken place, the phase size is no longer dependent on the precuring time. The observed final morphology is a result of the counter balance between the relative rates of polymerisation and phase separation. Besides, the phase size is governed by the time the phase has to grow and by the viscosity of the medium from where they are growing.

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