DOI: 10.1002/masy.200850716

Morphology of Different Epoxy-Amine Systems Modified with a Thermoplastic: Influence of Temperature, Thermoplastic Concentration and Molecular Structure of Epoxy Systems

Carmen Ramírez, Maite Rico, Joaquín López, Belén Montero, Marcelino Ladra*

Summary: The morphologies generated by polymerization induced phase separaron (PIPS) in different epoxy-amine systems modified with a thermoplastic, polystyrene (PS), were studied by SEM. The amino groups of the epoxy-amine systems were provided by a monoamine and a diamine in different proportions, so that the resulting polymer would vary from a linear polymer (epoxy-MA) to a highly cross-linked polymer (epoxy-DA). The effects of reaction temperature, initial modifier concentration and degree of crosslinking of epoxy-amine system on the morphology were discussed and trends for the size, distribution and concentration of dispersed particles were deduced. Different types of morphologies were obtained depending on the initial PS content. Typical morphologies of compositions close to critical point were observed for the 9 and 12 wt. % of PS in all the studied systems.

Keywords: morphology; phase separation; degree of crosslinking; thermoplastics; epoxy-amine system

Introduction

Epoxy resins are generally used as advanced composite matrix materials due to their good properties. However these materials are brittle. The toughness of these materials may be improved by the incorporation of thermoplastic components which are initially miscible with the reactive monomers but are segregated in the course of polymerization. This mechanism is known as polymerization induced phase separation (PIPS).[1,2]

Different structures have been observed in thermoplastic/thermoset blends [3,4]: sea island, nodular, bicontinuous, dual phase, ribbonlike. The final properties of the modified epoxy resin depend on the morphology generated during the curing process. The developed morphology is influenced by the amount of modifier and cure conditions which determine the size, shape and relative proportions of the separated phases. Therefore, a control of the developed morphology is necessary to regulate the final properties of material.[5]

The aim of this work is to analyze the morphologies generated by PIPS in different epoxy-amine systems modified with a thermoplastic. The amino groups of the epoxy-amine systems were provided by a monoamine (MA) and a diamine (DA) in different proportions. This way, the molecular structure of the epoxy-amine systems was modified by means of the formulation from the linear polymer (epoxy-MA) to the highly crosslinked polymer (epoxy-DA). In addition, the effects of reaction temperature, initial modifier concentration and degree of crosslinking of epoxy-amine system on the morphology were discussed.

The crosslinking degree of the epoxy-amine system as well as the gelation absence can affect the developed morphology to a great extent. There are few papers that study this fact, as it is our intention.

Dpto de Física, Universidad de A Coruña. E. U. P.
Avda. 19 de Febrero s/n 15405 Ferrol, Spain
E-mail: labpolim@udc.es

Experimental Part

The themoplastic modifier was a polystyrene (PS) with a number and weight-average molecular weigh of Mn = 140000 and Mw = 23000 respectivelly. The epoxy-amine systems were constituted by stoichiometric amounts of epoxy groups and amine hydrogens. The epoxy precursor was a diglycidyl ether of bisphenol A (EB). The amine hydrogens were provided by a monoamine (MA, a-aminodiphenylmethane) and a diamine (DA, 4,4′-methylenebis (2,6-diethylaniline)) in different proportions: 100%MA, 75%MA-25%DA, 50%MA-50%DA, 25%MA-75%DA and 100%DA expresed as percentage of amino equivalents.

The blends were prepared of following way: First, the PS was dissolved in epoxy prepolymer using methylene chloride (CH_2Cl_2) as solvent which was later evaporated. Next, the corresponding amounts of mono and diamine were added. The resulting solutions were mixed and placed in an oven at the studied polimerization temperature. Three temperatures were considered for the systems 100%DA: 100, 120 and 140 °C whereas for the other systems only the temperature of 100 °C was studied.

The morphology of blends was studied by scanning electron microscopy (SEM) using a JEOL JSM 6400 apparatus. The fracture surfaces of samples without the postcure step were observed after coating with a fine gold layer. Micrographs were processed with the aid of a Image Analyser (UTHCSA Image Tool 3.00).

Results

Various morphologies were seen in the studied systems, which can be grouped in three different types: sea-island morphology, nodular morphology and dual phase morphology (Figure 1). The initial PS proportion was the factor controlling the type of morphology. [6]

In the case of low modifier composition, 3 and 6 wt. % of PS, all the systems showed a morphology consisting in spherical thermoplastic domains dispersed in epoxy-rich matrix known by sea-island morphology (Figure 1a). High thermoplastic composition, 15, 20 and 25 wt. % of PS, showed a nodular morphology with nodular epoxy particles dispersed in thermoplastic matrix (Figure 1c). Finally, all the systems with 9 and 12 wt. % of PS showed a complex morphology consisting of macroscopic domains of both, sea island and nodular sturctures. This morphology is known as dual phase morphology (Figure 1b) and it is typical for composition region close to the critical point.

Several morphologic parameters were analyzed for each morphology[7,8]: average diameter of particle, number of particles per unit area, volume fraction of dispersed phase, and particle size distribution. Subsequently, the effects of initial modifier

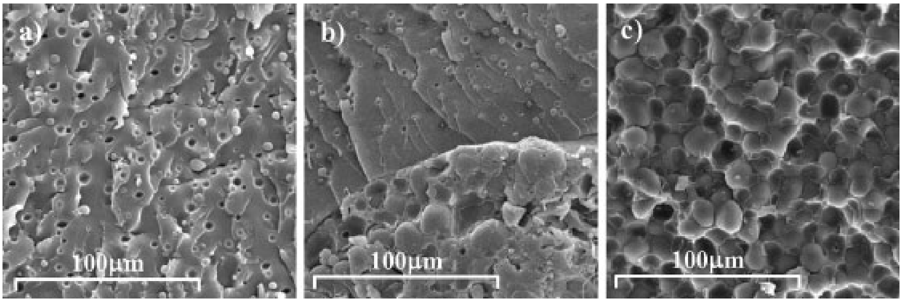

Figure 1.
Morphology of the PS + EB/100%DA (1:1) systems modified with various compositions of PS cured at 100 °C; PS = a) 6, b) 12 and c) 20 wt. % PS.

composition, temperature and structure MA/DA on these morphologic parameters were analyzed.

Effect of Initial Modifier Composition

For the blends showing sea-island morphology, the particle size, the number of particles and the volume fraction of the dispersed phase increased with the initial PS content. This is due to the increasing initial PS proportion and decreasing onset conversion of phase separation.

For the blends showing epoxy nodular morphology the increase in the PS proportion led to a decrease in the average size of disperse particle and an increase in the number of particles. This is caused by the smaller content of the component that forms the dispersed phase (epoxy system) as well as by the increase of viscosity produced by the PS.

The size distribution of dispersed particles was more dispersed and with a higher size when the initial PS content decreased for nodular morphology. It is observed in Figure 2.

For blends showing dual-phase morphology, the increase in PS content caused that the proportion of nodular structure increased and the one of sea-island decreased.

Effect of Temperature

The effect of temperature was only studied in the modified epoxy/100%DA systems. Temperature affected of opposite form both, nodular and sea-island morphologies.

Table 1 shows the average size and the concentration of dispersed particles of the morphologies obtained to different cure temperatures.

It is observed that the increase in temperature caused a major number of dispersed particles but with a minor size for sea-island morphologies, however, in nodular morphologies, temperature decreased the number of particles but they were higher size.

This opposite trend can be explained because in sea-island morphology the phase separation is controlled by the polymerization of the epoxy matrix whereas in the nodular morphology by the viscosity of the PS-matrix.

Effect of DA/MA Ratio on Structure

The systems with 100%MA showed different morphologic trends that the rest of MA/DA systems. It can be due to the absence of gelation leading to a greater rate of coalescence.

The increase of the DA/MA ratio led to an increase in the size of dispersed particles

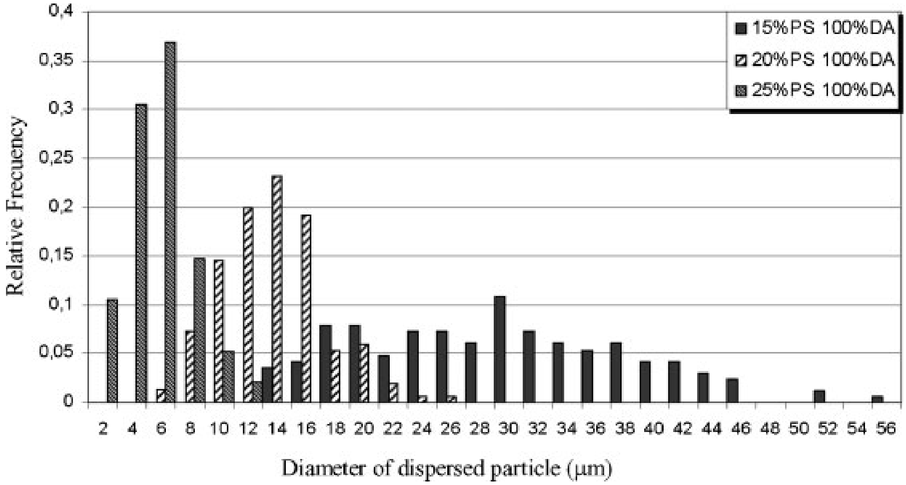

Figure 2.

Size distributions of dispersed particles obtained for the EB/100%DA systems modified with the 15, 20 and 25 wt. % PS cured at 100 °C.

Table 1.
Average diameter of particles, $\overline{D}$ and number of particles per unit area, N, for the morphologies of the epoxy/100%DA systems with various mass percentage of PS

T (°C)	$\overline{D}$ (μm)					N (part/μm^2)				
	3%	6%	15%	20%	25%	3%	6%	15%	20%	25%
100	2.1	3.5	30.1	14.7	6.6	0.00819	0.00938	0.00120	0.00630	0.01415
120	2.7	3.0	46.3	23.0	11.7	0.00833	0.01506	0.00066	0.00220	0.00602
140	2.0	2.6	90.1	29.2	15.5	0.00936	0.01776	0.00011	0.00163	0.00493

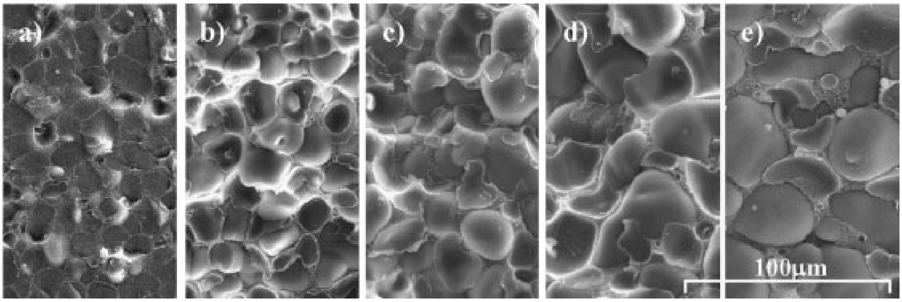

Figure 3.
Morphology of DGEBA/MA-DA systems modified with 15%wt. PS cured at 100 °C with different MA-DA proportions: a) 100%MA, b) 75%MA-25%MA, c) 50%MA-50%DA, d) 25%MA-75%DA y e) 100%DA.

and a decrease in the number of particles for both morphologies of very slight form (Figure 3). This trend is opposite to it expected since the particle size should decrease because viscosity of system increases with the crosslinking degree (DA/MA ratio). This trend can be due to that the miscibility of our systems resulted to decrease with the DA/MA ratio, leading to a decrease of both, the conversion and viscosity to the onset of phase separation.

To analyze the effect of the crosslinking degree of the epoxy-amine system on the structure of material, the samples were subjected to the action of a solvent (CH_2Cl_2) and the resulting surfaces before and after adding solvent were compared. An example is Figure 4.

The solvent removed the PS-rich phase and the thermoplastic part of the epoxy-amine system, leaving the thermoset part. Then, in the 100%MA systems, the total

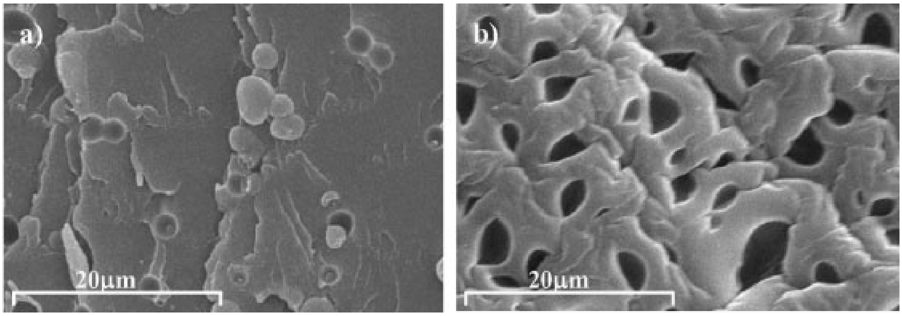

Figure 4.
Morphology of the 6%PS + EB/75%MA-25%DA system cured at 100 °C. a) without solvent, b) with solvent.

dissolution of the sample was produced indicating the absence of gelation. In the other systems: for nodular morphologies, the solvent removed the matrix leaving a dispersion of nodules. For sea-island morphologies, the amount eliminated by the solvent decreased when the DA/MA ratio increased due to the increase of the thermosetting part.

Conclusion

The morphologies of different epoxy-amine systems modified with PS were observed and analyzed as a function of reaction temperature, initial modifier composition and crosslinking degree of the epoxy-amine matrix. Three types of morphologies were obtained depending on the initial PS content: sea-island morphology for low %PS, nodular morphology, in which the separated phases were inversed, for high %PS and dual phase morphology for blends of 9 and 12wt. % PS indicating the location of the critical point, which did not vary greatly with temperature nor either with DA/MA structure.

The developed morphology by each system was analyzed measuring average size, number, distribution and volume fraction of dispersed particles. The following trends were deduced: the size of particles increased with increasing %PS, increasing DA/MA ratio or decreasing temperature for the sea-island morphology and with increasing temperature, increasing DA/MA ratio or decreasing %PS for nodular morphology. The number of particles increased with increasing %PS or decreasing DA/MA ratio. It also increased with temperature for sea-island morphology but decreased for nodular morphology.

[1] D. Verchère, H. Sautereau, J. P. Pascault, S. M. Moschiar, C. C. Riccardi, R. J. J. Williams, in: "*Toughened Plastic I: Science and Engineering*", C. K., Riew, A. J. Kinloch, Eds., American Chemical Society, Washington **1993**, p. 335.

[2] I. A. Zucchi, M. J. Galante, J. Borrajo, R. J. J. Williams, *Macromol. Symp.* **2003**, *198*, 295.

[3] J. W. Park, S. C. Kim, in:, "*IPNs Around the World*", S. C., Kim, L. H. Sperling, Eds., J. Wiley & Sons, Chichester **1997**, p. 27.

[4] M. L. Auad, J. Borrajo, M. I. Aranguren, *J. Appl. Polym. Sci.* **2003**, *89*, 274.

[5] M. L. Auad, M. Proia, J. Borrajo, M. I. Aranguren, *J. Materials Sci.* **2002**, *37*, 4117.

[6] C. E. Hope, M. J. Galante, P. A. Oyanguren, R. J. J. Williams, E. Girard-Reydet, J. P. Pascault, *Polymer Engineering and Science* **2002**, *42*, 2361.

[7] D. S. Kim, S. C. Kim, *Polymer Engineering and Science* **1994**, *34*, 1598.