European Polymer Journal 58 (2014) 125–134

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Influence of the molecular weight of a modifier on the phase separation in an epoxy thermoset modified with a thermoplastic

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ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form 19 May 2014
Accepted 23 June 2014
Available online 30 June 2014

Keywords:
Polymerization-induced phase separation
Thermodynamics
Morphology
Polymer blend

ABSTRACT

The effect of varying the molecular weight of a thermoplastic modifier on the phase separation in polystyrene (PS)-modified epoxy/amine blends was investigated by comparing blends with PS of different molecular weights. A thermodynamic analysis of polymerization-induced phase separation was performed using a model based on the Flory–Huggins theory, from which the phase diagram and species distribution in the separated phases were calculated. Morphologies developed by the blends were studied in terms of concentration and molecular weight of modifier. Trends in morphologies and thermodynamics of phase separation were exposed and discussed. An increase in the molecular weight of modifier caused a decrease in the miscibility of blend affecting phase diagram, molecular fractionation between the separated phases and morphologies developed showing that molecular weight is a tool to control the final materials.

1. Introduction

Thermoplastic–thermoset blends have gained importance in recent years. The reason for blending is mainly to improve some of the properties either of the thermoset, such as toughness and dimensional stability, or the thermoplastic, as facilitate processing or reinforce, among others specific needs [1]. In the case of epoxy networks, their inherent low toughness was improved by the incorporation of a thermoplastic phase dispersed into the epoxy matrix.

Thermoplastic–thermoset blends are often prepared via the mechanism of polymerization-induced phase separation (PIPS), in which the thermoplastic modifier is initially miscible in the thermoset precursors but is separated into phases in the course of polymerization [1,2]. PIPS mechanism may lead to different types of morphology, strongly affecting the final properties and applications of these materials [3–8].

Morphology developed depends largely on the thermodynamics of phase separation [9–11]. Perform a thermodynamic analysis of phase separation allows to know the phase behavior and obtain the phase diagrams of blends during polymerization, which is fundamental to explain and control the morphologies developed. The phase diagrams of polymer blends are qualitatively different from those of the other materials due to the inherent polydispersity of polymers [12,13].

Several experimental variables affect and determine the thermodynamic and/or kinetic aspects of the PIPS process directly influencing the morphologies developed. These variables include type and concentration of modifier [14], molecular weight of components, reactivity of the cure agent, polymerization conditions (especially temperature [14–17]), initial miscibility between thermoset and modifier, reaction rate, viscosity, among others.

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http://dx.doi.org/10.1016/j.eurpolymj.2014.06.017
0014-3057/

Establish correlations and apply theoretical models that relate the experimental variables (composition and cure conditions) with the thermodynamic properties and morphologies developed by materials is of great interest in order to control and get the appropriate morphology for a particular application.

We have recently studied the behavior and phase separation of blends based on epoxy–amine systems modified with a thermoplastic by investigating the influence of molecular structure and final crosslinking degree of epoxy–amine system, modifier concentration, and cure temperature [18–20].

The aim of this work is to continue and improve the study of those thermoplastic-modified epoxy–amine blends through the investigation of the effect of modifier molecular weight on phase separation and morphology developed by the materials.

Molecular weight of the components of a blend appears to be a critical factor in the miscibility of the blend. Thus, it is expected that an increase in the molecular mass of any component causes miscibility decreases so that phase separation begins at a lower conversion. Furthermore, it is expected that the molecular weight also vary the viscosity of the blend. Both conditions predictably affect morphology and hence final properties of the blends, displaying that the molecular weight of modifier can be a critical variable in the final materials.

This paper comprises firstly a study of the phase separation of blends during polymerization through a thermodynamic analysis of the PIPS process, from which the phase diagrams and a simulation of the species distributions in the separated phases could be obtained. A model based on Flory–Huggins theory [21,22] was used where the polydispersity of the components was taken into account and the dependence of the interaction parameter with composition was considered. In a second part of this paper, the morphologies developed by the materials were studied and morphological trends depending on concentration and molecular weight of modifier were established and discussed.

To study the effect of modifier molecular weight, blends based on an epoxy–amine system modified with a thermoplastic were studied and compared with other blends differentiated only in the average molecular weights of the thermoplastic that had been previously studied [18–20].

2. Experimental section

2.1. Materials

The epoxy–amine system was stoichiometric and consisted of the epoxy monomer diglycidylether of bisphenol A (DGEBA, Araldite GY260) characterized by a mass per mole of epoxy groups equal to 188 g mol^{-1} and a density of 1.2 g cm^{-3}. The diamine was 4,4′-methylenebis (2, 6-diethylaniline) (MDEA), supplied by Aldrich, with a molecular weight of 310.5 g mol^{-1} and a density of 1.35 g cm^{-3} [23]. The thermoplastic modifier was polystyrene (PS). Two PS with different average molecular masses and polydispersity were used, both were atactic with a density of 1.04 g cm^{-3} and supplied by Aldrich. The characteristics of both PS are listed in Table 1. All materials were commercial products and were used as received without purification.

DGEBA/MDEA + PS blends in the range of 0–30 wt.% PS were prepared as follows: first, PS was dissolved in epoxy prepolymer at room temperature using methylene chloride as solvent, which was later evaporated for a day at room temperature followed by several hours at 140 °C. In a second step, the PS/DGEBA blend was taken out of the oven at 120 °C and the corresponding amount of diamine was added at room temperature. Then the polymerization of the blend was carried out by placing the resulting solution in an oven at the temperature of 120 °C for 8 h. At the polymerization temperature all blends were initially homogeneous but become separated in phases in the course of polymerization.

2.2. Techniques

Cloud-points of the blends during polymerization were determined in two steps: first, the cloud-point time, t_{CP}, was determined in a transmitted light device with a He–Ne laser beam, as the onset of the decrease in the intensity of transmitted light. In a second step, the cloud-point conversion (p_{CP}) was calculated from measurements of residual heat after t_{CP} ($\Delta H_{RESIDUAL}$) and total heat (ΔH_{TOTAL}) of the epoxy–amine reaction by applying the following equation [23–25],

$$p_{CP} = 1 - \frac{\Delta H_{RESIDUAL}}{\Delta H_{TOTAL}} \quad (1)$$

$\Delta H_{RESIDUAL}$ and ΔH_{TOTAL} for each blend were determined in a differential scanning calorimeter, Perkin Elmer DSC7, by integration of the reaction peak obtained in dynamic temperature scans for the blends without polymerization and partially polymerized until t_{CP}.

Morphologies developed by the cured blends were investigated by scanning electron microscopy (SEM) using a JEOL JSM 6400 operated at 20 kN. Fractured samples of each blend were covered with a thin layer of gold and then were observed by SEM. Micrographs of the fracture surfaces were analyzed using an image analyzer program (Image Tools 3.00 from UTHSCSA).

3. Results and discussion

3.1. Thermodynamic study of phase separation

The thermodynamic study of the polymerization-induced phase separation (PIPS) was carried out on blends using a model based on the Flory–Huggins theory [21,22] extended with Staverman and Koningsveld approaches

Table 1
Characteristics of polystyrenes.

Polystyrene	Molecular mass (g mol^{-1})		Polydispersity index
	Mn	Mw	
PS$_L$	140,000	230,000	1.64
PS$_H$	170,000	350,000	2.06