Chemically Induced Phase Separated Morphologies in Epoxy Resin-Hyperbranched Polymer Blends

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SUMMARY The morphology build-up in toughened epoxy blends using reactive hyperbranched dendritic polymers (HBP) and amine-cured epoxy resins has been investigated in the present work. By changing the processing conditions or the surface chemistry of the modifier, very different morphologies can be obtained, ranging from homogeneous blends to coarse two-phase systems. The morphology characterised by electron and optical microscopy has been interpreted combining constitutive equations for phase separation and thermodynamic modelling of phase interactions. The latter model, based on the Flory-Huggins lattice theory, was modified in order to take into account the addition reactivity of the HBP modifiers. This approach proved successful and can be used as a tool for final morphology prediction in any reactive blend formulation.

Introduction

Thermoset polymers and their composites are used in many applications due to their thermo-mechanical stability originating from their existence of cross-linked structure. However, this is also responsible for the brittleness of thermosets, which very often is a limitation to their use. In order to increase their toughness, several procedures have been developed during the past years. The most common approach is to blend into the thermoset a second polymer able to induce specific toughening mechanisms. So far, rubbers have been the most often used systems, and have been shown to be able to improve toughness of thermosets efficiently[1-3)]. However, using these modifiers, as well as other thermoplastic modifiers[4)], the increase in toughness is generally accompanied by a decrease in thermo-mechanical properties, such as Young's modulus or glass transition temperature, and by a decrease in processability. To avoid such drawbacks, hyperbranched polymers (HBP) have shown promising results, reaching toughening levels superior to rubber modification without affecting other thermo-mechanical properties and processability[5-7)]. These modifiers have a reactive thermoplastic nature with elastometric properties and a low viscosity characteristic of a dendritic structures. HBPs are subjected to chemically induced phase separation, which can be used to obtain a two phase morphology designed to improve the toughness. Phase separation occurs generally by nucleation and growth from an originally homogeneous

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mixture of resin and modifier which is desired to maintain full processability. For the moment, the mechanisms controlling the morphology build-up of these HBP modified resins and the properties obtained are not fully understood. The morphology build-up, which is considered to be a critical step to be able to fully exploit the potential of these modifiers, is addressed here. The theoretical thermodynamic development leading to a correct interpretation of the morphology is achieved by considering the controlling parameters, i.e. the temperature, the blend composition, the chemistry and the reactivity of both the resin and the HBP modifier.

Experimental

A Diglycidyl Ether Bisphenol A (DGEBA) Shell Epon 828 was used as the epoxy resin, which was cross-linked with Isophoron diamine (IPD) supplied by Fluka. Three experimental grades of 3-generation epoxidised hyperbranched dendritic polymers supplied by Perstorp AB, were used as reactive modifiers. The HBPs differed only in the epoxy equivalent weight (EEW) values and hence in their solubility parameters, having an EEW of 1050, 563 and 408 g/equivalent. They are referred in what follows as HBP40, HBP60, HBP95, respectively. Stoichiometric ratios of active amine hydrogen to epoxy groups were used in all cases. Cloud point experiments were performed on 30-50 mg of mixtures samples, cured on a temperature-controlled hot plate. Phase separation was assumed to start at the visual turbidity onset. The conversion at the onset of phase separation was obtained by cure kinetics studies performed on a DSC7 Perkin Elmer differential scanning calorimeter. A Rheometrics RDA 2 parallel plate rheometric analyzer was used at a frequency of 1 Hz to investigate viscosity evolution during curing. Samples for microscopy investigation of the final morphology were prepared using an 8 mm diameter glass pipe which was filled with the liquid mixture and put into an aluminium column inside a temperature gradient oven. Quantitative morphology characterisation was performed by scanning electron microscopy. In the cases where large particle were generated (diameter > 5 μm), optical microscopy coupled with a CCD camera, permitted recording of the morphology evolution during cure time.

Theory

Several authors have derived mathematical models, all based on the classical lattice theory of Flory-Huggins[8-9], in order to describe the main trends in chemically induced phase separation. According to this theory, the thermodynamic equilibrium of a system at constant pressure is described by the Gibbs free energy of mixing[10):

$$\Delta G_v = RT\left(\frac{\Phi_1}{V_1}\ln\Phi_1 + \frac{\Phi_2}{V_2}\ln\Phi_2 + \Phi_1\Phi_2\chi_{12}\right) \qquad (1)$$

where T is the temperature expressed in Kelvin, R is the perfect gas constant, Φ_1 and Φ_2 are the volume fractions of components 1 and 2 (polymer and solvent), and V_1 and V_2 are the molar volumes of the two components. The term χ_{12} is the ratio between the Flory-Huggins interaction parameter, and $(V_1)_0$ the molar volume of the lattice site, normally attributed in polymer-solvent blends to the monomer unit molar volume. Using a solubility parameter approach, χ_{12} can be expressed by the following expression(11):

$$\chi_{12} = 0.34/(V_1)_0 + [(\delta_{1h}-\delta_{2h})^2 + (\delta_{1p}-\delta_{2p})^2 + (\delta_{1d}-\delta_{2d})^2] / RT \qquad (2)$$

in which the subscripts designate the hydrogen (h), polar (p) and dispersive (d) components of the solubility parameters of component 1 and 2. In a thermoset modified system, the molar volume of the thermoset component is evolving during conversion of monomer into polymer. This problem has been treated by Vasquez et *al.* in rubber modified amine cured epoxy 8), for which the molar volume was assumed to evolve with conversion according to:

$$V_1(p_1) = \frac{1}{\rho_1}\frac{(M_A + 2M_{EP})}{(3-4p_1)} \qquad (3)$$

where p_1 is the conversion of the epoxy-amine component, M_A is the molecular weight of the amine, M_{EP} is the molecular weight of the epoxy and ρ_1 is the density of the amine-epoxy mixture. The enthalpy, which Vasquez et al. considered to be constant during the reaction, is in reality also evolving. Kiefer et *al.* recently modelled this evolution by assuming a linear dependence of solubility parameter with conversion. This assumption has been successively verified and is used here12). In our case, however, two new variables have to be included in the study due to the reactivity of the HBP. These are the evolution of the HBP solubility parameter, which has been shown to linearly evolve with the HBP-amine conversion, and the molar volume of the HBP. Its dependence on conversion, similarly to the epoxy resin, was assumed to be12):

$$V_2(p_2) = \frac{1}{\rho_2}\frac{(M_A + (4/f_{HBP}) * M_{HBP})}{(1 + 4/f_{HBP} - 4p_2)} \qquad (4)$$

where f is the functionality of the HBP, M_{HBP} is its molecular weight and p_2 the HBP-amine conversion, considered to be independent from the resin epoxy-amine reaction.

Results and Discussion

Once Eqs. 2 to 4 are implemented into Eq. 1 and the linear dependence of solubility parameters with conversion is considered, the binodal curves, i.e. the curve which express as the phase separation conditions are simply obtained by imposing equality of chemical potential at two distinct compositions of the blend. These conditions ensure coexistence in the mixture of two phases of different compositions in equilibrium. Fig. 1 shows the good agreement between the phase diagram expressing resin conversion at phase separation as calculated according to the new model, and the experimental cloud points.

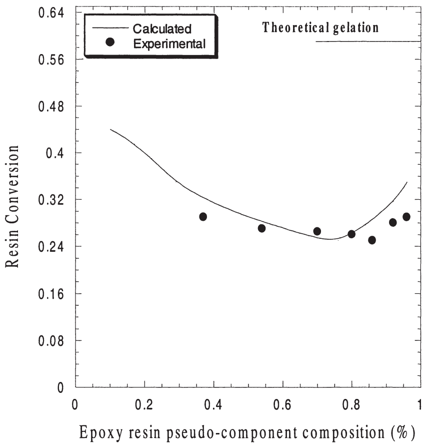

Fig. 1: Phase diagram for the HBP40 epoxy system cured at 80 °C with IPD. The epoxy resin pseudo-component composition is the volume percentage of epoxy resin-IPD in stoichiometric ratio.

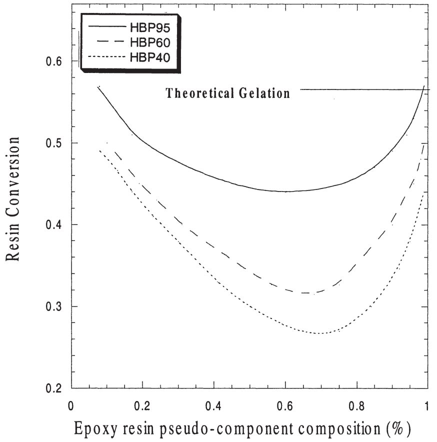

Fig. 2: Phase diagrams for the HBP40, HBP60 and HBP95 modifiers blended with epoxy and cured at 100 °C according to Eqs. 1 to 4

In Fig. 2 the phase diagrams are calculated for the epoxy resin blended with: HBP40, HBP60 and HBP95 at the curing temperature of 100 °C. As can be observed, increasing the compatibility of the modifier with the matrix results in phase separation occurring at later stages. The favourable theoretical window available for phase separation is limited between the cloud point and the theoretical gel point (0.577 for the epoxy resin according to Flory case theory of gelation[10)]).

The phase diagrams, calculated with the model described above, can be used to predict and interpret the final morphology of HBP-modified epoxies. In fact, due to the high number of variables involved, no other mathematical approach to model the morphology development has been shown to be directly applicable. On the other hand, an empirical approach was proposed by Verchère et al. for rubber modified epoxies which allows one to predict morphology distribution[13)]. The approach of Verchère expresses the linearity between the logarithm of the viscosity at the cloud point, $ln(\eta_{CP})$ and the average diameter of particles, and can be combined with the theoretical phase diagrams developed here. The linear dependence should be a direct consequence of the constitutive equations of nucleation and growth rates. Although several complex chemo-reological models for the evolution of viscosity with conversion and temperature, have been developed[14)], a simple exponential dependence of viscosity on conversion p can be used for constant temperatures, and for conversions reasonably lower than the gel point, i.e. within the phase separation range:

$$\eta(p) = B_1 * e^{-B_2 *(p_{GEL} - p)} \qquad (5)$$

where B_1 and B_2 are experimental constants, while p_{GEL} is the conversion at the gel point. In our case, Eq. 5 fits well the experimental value of complex viscosity evolution with conversion in the range where the cloud point appears. Once the parameters B_1 and B_2 have been determined by best fitting the viscosity-conversion curve with Eq. 5, the viscosity at the cloud point can be calculated using the cloud point conversion determined from the phase diagram. Fig. 3 shows the linear dependence obtained between the average diameter of the 10 phr HBP blends cured at 100°C for all the three HBPs, and the term p_{GEL}-p_{CP}, which according to Eq. 5, is proportional to $ln(\eta_{CP})$. Fig. 4 shows the linear dependence between p_{GEL}-p and the number average diameter of particles for HBP60 blends with different concentration cured at 80 °C. The phase separation window is modified as a consequence of the different amounts of HBP added to the epoxy, shifting the cloud point according to the binodal curve. It was, however, assumed that the limited quantity of HBP added to the epoxy resin did not affect its viscosity.

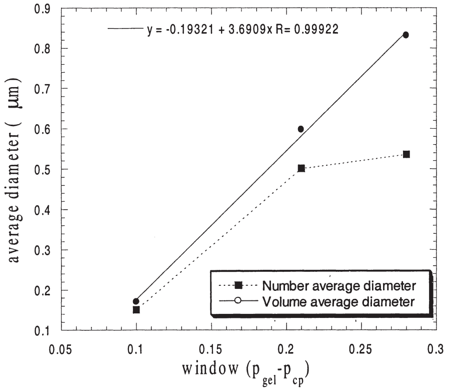

Fig. 3: Number average and volume average particle diameter for the HBP40, HBP60, HBP95 modifiers cured at 100°C. The number average diameter is affected by the limited capacity of detection of small particles by SEM.

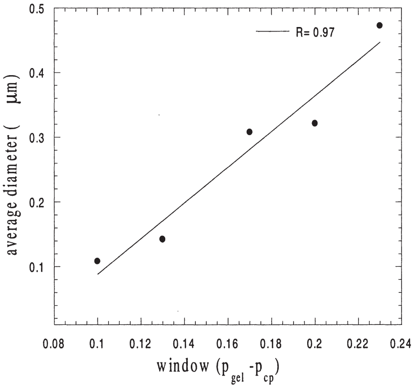

Fig. 4: Number average diameter for IPD cured epoxy with different concentrations of HBP60 cured at 80 °C.

Conclusions

A new thermodynamic model was developed considering both the evolution of entropy and enthalpy contributions of the resin and the reactive modifier. The entropy of mixing was modelled as a function of the molecular weight evolution of the two pseudo-components. The latter was considered a unique function of the conversion of the epoxy groups. The conversion of epoxy groups of the resin and that of the modifier were assumed to be distinct and their time evolution was considered equivalent to the corresponding pure pseudo-component. The enthalpic evolution of the reactive modifier was expressed using a linearly evolving solubility parameter as a function of the conversion. The model was shown to be in good agreement with cloud point experiments. The build-up of final morphologies in HBP-epoxy blends was characterised by image analysis and scanning electron microscopy. The morphologies were interpreted by combining an empirical law, which expresses linearity between the average particle diameter and the logarithm of cloud point viscosity, with the conversion at the cloud point obtained by the calculated phase diagrams. As a consequence, a linear dependence appeared between the average diameter of the particles and the resin conversion at the cloud point. The approach developed here can be applied as a tool for final morphology prediction in any reactive blend formulation.

Acknowledgements

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