

COMPATIBILITY OF EPOXY/THERMOPLASTIC MODIFIER/NANOFIL

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Introduction

Despite the good properties of epoxy resins their brittleness is well known. Brittle thermoset materials can be toughened by the incorporation of thermoplastic additive, which can be dispersed within epoxy matrix. If curing agent is added to homogeneous solution of thermoplastic modifier in thermoset precursor, the molar mass of the latter increases, and liquid–liquid phase separation occurs at certain level of conversion of thermoset epoxy, at constant temperature. To predict morphologies and properties, one must begin with a study of the thermodynamic description of the phase separation of system, starting with thermoset precursor or epoxy monomer–thermoplastic modifier, to continue with the thermodynamic description of the final system of thermoplastic modifier within epoxy matrix or the description of system thermoplastic modifier + nanofil within epoxy matrix. Polymer–clay composites constitute new class of materials, where nanoscale clay particles are molecularly dispersed within polymer matrix, with superior improvements in properties. However, factors that control the formation of such hybrid mixtures are not well understood, especially with regard to the mixture of clay-sheets with mixtures of two polymers, and such formations must be well understood, because properties will depend on mixture thermodynamic stability, which can be analyzed *via* phase diagrams. Despite there are examples in the literature in which polymer blend–clay composites are more stable than the polymer blend precursor, our experience is opposite. Here, small amount of co-polymer poly(styrene-*b*-methyl methacrylate) [P(S-*b*-MMA)], mixed with thermoplastic polystyrene (PS), makes compatible its mixtures of with epoxy precursor monomer, with cured epoxy matrix and with epoxy matrix cured with 1% of nanofil, which initially was mixed with still non-cured system thermoplastic/epoxy precursor.

Experimental

Prepolymer epoxy resin (DER336) and thermoplastic PS1450N were previously described. Co-polymer was poly(styrene-*b*-methyl methacrylate) [P(S-*b*-MMA4)] (Polymer Source)

with M_n of: PS(172 000 g·mol⁻¹) PMMA(7 300 g·mol⁻¹), $M_w/M_n = 1.06$ with PMMA content of 4% (w/w). Density: 1.096 g·mL⁻¹, molar volume: 1.734×10⁵ mL·mol⁻¹. P(S-*b*-MMA22) (Polymer Source) shows M_n of: PS(123 000 g·mol⁻¹) PMMA(35 000 g·mol⁻¹), $M_w/M_n = 1.09$ with PMMA content of 22% (w/w). Density: 1.124 g·mL⁻¹, molar volume: 1.537×10⁵ mL·mol⁻¹. Initial temperatures and times of phase change T_{cpi} and t_{cpi} were obtained with previously described equipment. Dichloromethane (J. T. Baker) shows 84.93 g·mol⁻¹ and richness of 99.5%. Curing agent was 4,4'-methylenebis(2,6-diethylaniline) (MDEA, Lonzacore, Switzerland). Nanoparticles were organophilic montmorillonite (Nanofil® 919, N919, Süd Chemie). Filling interacting with polymers contains only one hydrocarbon chain.

Results and Discussion

Fig. 1 shows the comparison of signals of transmitted light intensity vs. initial temperature of phase change for systems epoxy monomer 336(A)/PS1450N(B) + P(S-*b*-MMA22)(C) in ratio 90:10 (w/w) of A/(A+B+C):(B+C)/(A+B+C), and the binary ratios 2:98, 3:97 and 4:96 (w/w) of C/(B+C).

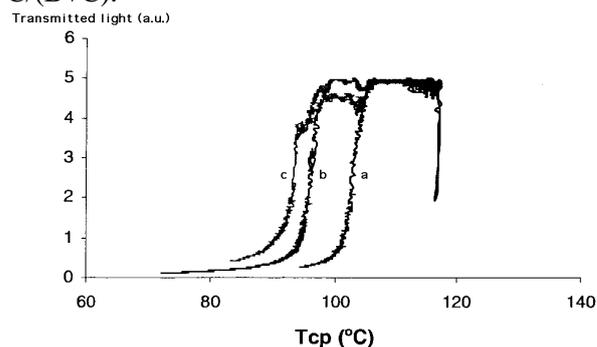


Fig. 1. Comparison of signals of transmitted light intensity (a.u.) vs. T_{cp} (°C) for systems epoxy336/PS1450N+P(S-*b*-MMA22) in the epoxy/thermoplastic mixture ratio of 90:10 (w/w). PS:P(S-*b*-MMA): a) 98%/2%, b) 97%/3% and c) 96%/4% (w/w).

Figure 2 reveals the phase diagrams of systems epoxy 336(A)/PS1450N(B) in the absence of co-polymer and 336(A)/PS1450N(B) + P(S-*b*-MMA4)(C) in the various ternary ratios of A/(A+B+C) to (B+C)/(A+B+C): 50:50, 60:40,

70:30, 75:25, 80:20, 85:15 and 90:10 (w/w). T_{cpi} is plotted vs. $B/(A+B)$ composition. Similar studies were performed for epoxy 336(A)/PS1450N(B) + P(S-*b*-MMA22)(C). Each diagram differs in binary weight fraction $C/(B+C)$: 2%, 3% and 4% (w/w). Increase in co-polymer in thermoplastic mixture raises system stability, augmenting miscible liquid phase and decreasing immiscible solid phase.

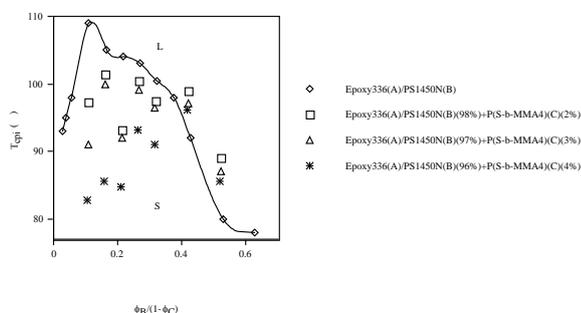


Fig. 2. Temperature of change of phase separation vs. $\phi_B/(1-\phi_C)$ in system epoxy336(A)/PS1450N(B)+P(S-*b*-MMA) (C) for volume fractions of C component in mixtures B+C with various wt.%: a) MMA4 and b) MMA22.

The signals of transmitted light intensity are compared vs. time that system takes in the changing of phase, as consequence of increase in the molar mass of thermoset in the presence of curing agent, and liquid-liquid phase separation occurs at certain level of conversion of thermoset epoxy, at constant temperature. The initial weight of each component is consigned. t_{cpi} are observed at 140°C in different weight ratios of thermoplastic, in that zone in which epoxy ratios are greatest, which is the most interesting one. t_{cpi} are examined vs. the percentage of thermoplastic in mixture. The inclusion of co-polymer in mixtures makes systems compatible with regard to reference, without co-polymer. To make polymers compatible with nanoparticles is difficult. Systems formed by epoxy monomer plus thermoplastic modifier, in the presence of nanospheres with/without the coating of epoxy groups, show opacity, being at present impossible to observe the effect of nanospheres on system compatibility to test theoretical results. Preliminary experiments show similar negative results, and only N919 incorporated in systems shows transparency at greater temperatures, undergoing phase change as temperature decreases. T_{cpi} changes with epoxy concentration in mixtures epoxy monomer/thermoplastic, at constant N919 concentration. However, T_{cpi} are greater than those in the absence of nanosheets, which indicates that system instability increases in the presence of nanosheets. The same was observed for epoxy cured in the absence of co-polymer, since N919 decreases t_{cpi} increasing system instability.

Although the stability of polymer-clay system depends on nanoparticle size, polymer and temperature, the penetration of extended chains between sheets causes large increase in entropy, which must be compensated by favourable polymer-sheet interactions. The inclusion of small amounts of co-polymer with proton-acceptor groups favours specific interactions with epoxy, facilitating system stability besides the increase in the amount of co-polymer in thermoplastic. The co-polymers improve the stability of systems cured epoxy/thermoplastic mixture/nanoparticle, with regard to these systems in the absence of nanofil. It was analyzed how the presence of co-polymer P(S-*b*-MMA4) can improve the stability of system epoxy matrix/thermoplastic without/with nanoparticles. Similar results were obtained in the presence of P(S-*b*-MMA22). Findings have great importance as with other nanosheets and PS co-polymers we find similar results [1,2] and with amounts of MMA in co-polymer greater than those used here or with different co-monomers in PS co-polymer, results are spectacular, making intensively compatible films with epoxy matrix plus thermoplastic mixture. The structure of N919 shows proton-donor groups, and co-polymer contains methacrylate. Compatibility between N919 and co-polymer may be due to order that causes N919 filling in polymers and co-polymers that are mixed with epoxy, penetrating into tunnels that form hydrocarbon chains. Detailed explanations can be found in the literature. Phase diagrams by the calculation of binodals in the systems produce the same conclusions.

Conclusion

Co-polymers stabilize the mixtures of epoxy monomer-thermoplastic modifier and the mixtures of epoxy monomer-thermoplastic modifier-N919. Co-polymers stabilize epoxy resin cured with thermoplastic modifier and epoxy resin cured with thermoplastic modifier in the presence of N919.

References

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2. Torrens, F., Castellano, G., Gómez, C. M., Monzó, I. S., Abad, C., and Campos, Modelling studies of the phase behaviour of monomer/disc composites. *Polym. Polym. Compos.*, submitted for publication.