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Experimental Studies for Modelling the Phase Behaviour of Monomer/Polymer/Disc Composites

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Summary: Nanoparticles do not stabilize the mixtures of epoxy monomer (prepolymer)/thermoplastic modifier (PS) and the ones of thermoplastic modifier dispersed within cured epoxy matrix. A small amount of thermoplastic co-polymer poly(styrene-*b*-methyl methacrylate) [P(S-*b*-MMA)] of MMA 4–22 wt.%, mixed with PS, makes compatible the mixtures with monomer epoxy precursor and cured epoxy matrix. The mixtures of cured epoxy matrix with thermoplastic consisting of PS and P(S-*b*-MMA), with nanofil 1%, are stable: the instability produced by the nanofil is overcome by the stability provided by the co-polymer. A model by Balazs' group to explain the phase behaviour of polymer/clay composites is extended.

Keywords: blends; nanocomposites; nanolayers; orientation; phase diagrams

Introduction

There was significant interest in the effect of nanoparticles on the behaviour of polymer systems, because nanoparticles addition dramatically changed the properties of polymers/polymer blends or their use as potential nanocompatibilizers for mixtures of immiscible polymers.[1–8] Simulations by Ginzburg *et al.*,[1–3] Laradji and MacNevin,[4,9] *etc.*[10] showed that nanoparticles slow the phase separation between the two polymers. Lipatov *et al.* studied the effect of SiO_2 nanoparticles on the cloud point of polymer mixtures, showing that the addition of nanoparticles shifted the location of the critical point and made the two polymers more compatible,[5,6] and formulated a semiphenomenological theory.[11] However the model did not take into account particle size, geometry or polymer size. Balazs *et al.* formulated a combined self-consistent field/density functional theory (DFT) general approach to describing the thermodynamics of block copolymer/nanoparticle mixtures.[7,12,13] Ginzburg developed an analytical theory, which indicates how spherical nanoparticles would influence a polymer blend behaviour.[14] The thermodynamic stability of polymer blend/clay composites was analyzed *via* phase diagrams, where stable/unstable mixture zones are well consigned.

Lyatskaya and Balazs proposed a model for the equilibrium phase behaviour of polymer/clay mixtures,[15] which served as a first approximation to polymer melt intercalation[16] depending on silicate functionalization and interactions.[17] They focused on interactions between two surfactant-coated surfaces and the surrounding polymer melt, and concluded the equilibrium behaviour of the overall mixture.[18] To generate a phase diagram, they developed an Onsager-type theory for a homopolymer/rigid disc mixture.[19] They expanded a model based on perturbation-type DFT to describe the complete phase diagram of an incompressible polymer–disc mixture[20] and a thermodynamic, multiscale approach to study the phase behaviour of model polymer–clay mixtures,[21] and investigated the phase behaviour of a mixture containing organically modified

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clay, non-functionalized polymers and a small volume fraction of end-functionalized chains.[22] Loring's[23,24] and Farmer's[25,26] groups reported structural details, dynamics and related fluctuations in model systems. Surve *et al.* analyzed a similar problem with nanotubes.[27]

In an earlier publication, the model by Balazs *et al.* of phase behaviour of polymer/clay[7,12,13,15] was extended to monomer/polymer/clay composites, obtaining an expression for free energy.[28] Minimizing free energy and calculating the chemical potentials of the three system components, phase diagrams for monomer/disc and monomer/polymer/disc mixtures were biult. *Via* diagram evolution the effects of nanodisc size, polymer molar mass and interaction parameters on mixture stability/morphology were studied. Diagrams were calculated *vs.* polymer length, disc diameter and thickness and molecular mass of polymer, for monomer/disc mixtures at monomer fixed compositions or for polymer at disc fixed compositions. Mixture morphology was discussed and conclusions, obtained from experiments on mixtures of clays and epoxy monomer or disc/styrene polymer of high molecular mass, were compared showing qualitative agreement with our theory. The present report shows how a small amount of co-polymer P(S-*b*-MMA), mixed with thermoplastic PS, makes compatible its mixtures with epoxy precursor monomer, cured epoxy matrix and epoxy matrix cured with 1% of nanofil, which initially was mixed with non-cured system thermoplastic/epoxy precursor.

Theory

The polymer is modelled as flexible chains of length N; the monomer diameter a is the length unit $a{\cdot}x = N$ where x is the polymerization degree. Since we assume the mixture system to be incompressible, the polymer volume fraction is given by $\phi_p = 1 - \phi_d$, where ϕ_d is the volume fraction of disc in the mixture system, which is an approximation since for soft matter there is plenty of pore space. The composite morphology in polymer/clay mixtures is important.[15] One must consider that in mixed state discs, by their orientation in the mixture, can cause two miscible regions in equilibrium: discs can be either randomly oriented with regard to each other and form the former isotropic phase (small ϕ_d), or relatively aligned and form the latter nematic phase (greater ϕ_d). To analyze the miscibility of one polymer/disc mixtures and examine the configuration of formed structural phases,[29–31] Onsager model was adopted,[32] which assumes that disc and chains move freely to equilibrate the system well, which requires a free volume. The model was used to describe liquid crystal-like ordering, and Ginzburg formalism to explain polymer/polymer interactions. The deduction of Onsager model follows,[32] beginning with its development for one polymer/disc by Lyatskaya and Balazs.[15] The mixture free energy is:

$$\Delta G = \Delta G_{\text{conf}} + \Delta G_{\text{ster}} + \Delta G_{\text{int}} + \Delta G_{\text{transl}} \tag{1}$$

where ΔG_{conf} describes the conformational losses because of the alignment of the discs:

$$\Delta G_{\text{conf}} = n_d \int f(\mathbf{u}|)\ln[4\pi f(\mathbf{u})]d\Omega_u = n_d(\delta + \text{const}) \tag{2}$$

where n_d is the number of discs in a unit volume and $f(\mathbf{u})$ is the orientational distribution function. Onsager used the variational method with a trial function for $f(\mathbf{u})$:

$$f(\mathbf{u}) = \frac{\alpha}{4\pi}\exp\left(-\frac{\alpha\theta^2}{2}\right) \tag{3}$$

where α is a variational parameter and θ an angle between director and test discs. Parameter δ distinguishes isotropic–nematic phases: in isotropic $\delta = 0$ while in nematic:

$$\delta_n = 2\ln\left[-\frac{2}{\pi^{1/2}}\frac{b}{v_d}\ln(1-\phi_d)\right]-1 \tag{4}$$

where $b = \pi^2 D^3/16$ is half of the excluded volume between two rigid discs (randomly oriented), $v_d = \pi D^2 L/4$ the volume of an individual disc and D and L the disc diameter and length. The ΔG_{ster} accounts for the steric interactions between the discs,[33–35] which represent the nonideal entropic free energy of discs; bearing in mind Equations (2) and (3):

$$\begin{aligned}\Delta G_{\text{ster}} &= n_d J(\phi_d) \iint f(\mathbf{u}_1) f(\mathbf{u}_2) B(\gamma)\, d\Omega_1 d\Omega_2 \\ &= \frac{n_d}{v_d}\ln(1-\phi_d) \iint \frac{\alpha^2}{16\pi^2}\exp^2\left(-\frac{\alpha\theta^2}{2}\right) b\frac{4}{\pi}|\sin\gamma|\, d\Omega_1 d\Omega_2 = -\frac{n_d}{v_d}\ln(1-\phi_d)\, b\rho\end{aligned} \tag{5}$$

where $J(\phi_d) = -(1/v_d)\ln(1-\phi_d)$ is a correction function to extend the model beyond the limit of low concentrations of discs, $B(\gamma) = b(4/\pi)|\sin\gamma|$ the second virial coefficient, γ the angle between two discs and $\rho = (4/\pi) < |\sin\gamma| >$. The phase equilibria of a polydisperse hard-disc system were investigated by Monte Carlo simulations, in the semigrand canonical ensemble.[36] The component ΔG_{int} describes the influence of nonspecific attractive forces between the discs; to a first approximation:

$$\Delta G_{\text{int}} = -\phi_d b (n_d/v_d)(\Theta/T) \tag{6}$$

where Θ denotes theta temperature for the system and T, temperature. For $T=\Theta$ the second virial coefficient is null for any N. For polymer/disc mixtures Θ depends on the enthalpic contribution, χ, and on terms describing entropic losses for polymers of length N since Θ is related to χ and N.[32,37] The ΔG_{transl} considers translational entropy of discs:

$$\Delta G_{\text{transl}} = n_d \ln \phi_d \tag{7}$$

Mixture of Disc and Only One Polymer. Taking into account Equations (1), (2), (5)–(7) ΔG, in the units of kT where k is the Boltzmann constant, can be written:

$$\begin{aligned}\Delta G &= n_d\delta - \frac{n_d}{v_d}\ln(1-\phi_d) b\rho - \phi_d b \frac{n_d}{v_d}\frac{\Theta}{T} + n_d \ln\phi_d + \text{const}\cdot n_d \\ &= n_d\left[\text{const} + \ln\phi_d + \delta - \ln(1-\phi_d)\frac{b}{v_d}\rho - \phi_d \frac{b}{v_d}\frac{\Theta}{T}\right]\end{aligned} \tag{8}$$

To ascertain the value of const one can express Θ/T in terms of the Flory-Huggins interaction parameter, χ, by equating Expression (8) for the free energy in the isotropic case ($\delta=0$, $\rho=1$) to the Gibbs free energy expression of an isotropic mixture:[38]

$$\Delta G = n_d \ln\phi_d + n_p \ln\phi_p + \chi n_d v_d \phi_p \tag{9}$$

where n_p is the number of polymer molecules in a unit volume. On equating Expression (8) with (9), it is considered that the isotropic phase is stable for low concentrations of discs, and this low concentration is taken into account to expand the logarithmic terms. From equating Expression (8) with (9) it follows that:

$$\frac{\Theta}{T} = 1 + \left(\chi - \frac{N}{2}\right)\frac{v_d^2}{b} \tag{10}$$

with $\chi = 1/2$ for $T = \Theta$ if $N = 1$. Equation (10) is obtained if in Equation (8):

$$\begin{aligned}\text{const} &= \chi v_d - \frac{n_p}{n_d}\phi_d - \frac{N}{2} v_d \phi_d \\ &= \chi v_d - \frac{v_d}{v_p}\phi_p - \frac{v_p}{2} v_d \phi_d\end{aligned} \tag{11}$$

which is reduced to $\text{const} = \chi v_d$ for low concentrations of discs. The substitution of Equation (10) in (8) produces:

$$\begin{aligned}\Delta G = n_d\Bigg[&\text{const} + \ln\phi_d + \delta \\ &- \ln(1-\phi_d)\frac{b}{v_d}\rho - \phi_d\frac{b}{v_d} \\ &- \chi v_d \phi_d + v_d \phi_d \frac{N}{2}\Bigg]\end{aligned} \tag{12}$$

In addition if one refers to the general case in which ϕ_d could have any value, *i.e.*, by substituting Equation (11) in (12), taking into account that $-n_p\ \phi_d \approx n_p \ln \phi_p$ and $N = v_p$ (the volume of a polymer molecule), the free energy has the form:[15]

$$\Delta G = n_d \left[\text{const} + \ln \phi_d + \delta - \ln(1-\phi_d) \frac{b}{v_d}(\rho - 1) + \chi v_d \phi_p \right] + n_p \ln \phi_p \tag{13}$$

To build cloud points in the equilibrium phase diagram, one must equate the chemical potentials of system components polymer with disc, in the isotropic and nematic phases:

$$\mu_p^i = \mu_p^n \tag{14}$$

$$\mu_d^i = \mu_d^n \tag{15}$$

where:[15]

$$\mu_p = \left(\frac{\partial \Delta G}{\partial n_p}\right)_{\text{pressure},T,n_d} = -\frac{N}{v_d}\left[\phi_d + \frac{\phi_d^2}{1-\phi_d}\frac{b}{v_d}\rho - \phi_d^2 \frac{b}{v_d}\frac{\Theta}{T}\right] \tag{16}$$

To obtain Equation (16) we use $\ln \phi_p + 1 - \phi_p \approx -\phi_d^2/2$, $\phi_i \approx n_i\ v_i/(n_d\ v_d + n_p\ v_p)$ $(i = d,p)$ and $v_p = N$:

$$\mu_d = \left(\frac{\partial \Delta G}{\partial n_d}\right)_{\text{pr},T,n_d} = \text{const} + \ln \phi_d + \delta + \frac{b}{v_d}\rho[\phi_d - \ln(1-\phi_d)] - \phi_d - 2\phi_d \frac{b}{v_d}\frac{\Theta}{T} + \phi_d^2 \frac{b}{v_d}\frac{\Theta}{T} \tag{17}$$

where const $\approx v_d\ \chi + 1$. The results of the disc/one monomer systems are analyzed *via* phase diagrams, which will allow establishing the basis of the behaviour of the disc/polymer systems *via* phase behaviour. Let us assume a clay formed by agglomerated sheets, which are piles or stacks of closely spaced parallel sheets. If a polymer is added it must penetrate the galleries that there are between the sheets. The properties and morphology of the obtained mixture will depend on the manner in which this is attained. Between two large sheets the produced tunnel is penetrated by the macromolecular chain. If there are polymer/disc repulsive interactions (large positive χ), the chain separates the discs (initially parallel, become randomly oriented, *i.e.*, isotropic), because the chain tends to retain its coil conformation and gain entropy (stability). If there are polymer/disc attractive interactions (either small positive or negative χ), the chain will slide like a worm across the gallery between parallel sheets, so the *flat* polymer losses conformational entropy (instability), which is compensated by the enthalpic gains of polymer/disc contacts. For large positive χ, the discs remain totally separated and randomly oriented in the polymer matrix, which is connected with an isotropic phase and with the final exfoliated structure. For either small positive or negative χ, the discs interpenetrated by polymer chains remain parallel between them, which is linked up with the nematic phase and the final intercalated structure. The discs are arranged in the same orientation. The concept of gallery may not be applicable when the discs are misoriented. The effect of chains on mixtures are not present in monomers ($N = 1$); however polymer molecular mass takes part in all these considerations, *e.g.*, a stable exfoliated structure with the discs forming isotropic phase requires not only large and positive χ but also intermediate or small molecular mass ($N \leq 100$).[15] On the other hand, stable intercalated morphologies with formation of a nematic phase require not only small or negative χ, but also high molecular mass ($N > 100$). In other possible cases of polymer/disc mixture, the material presents completely separated phases with rather wide instability zones in the corresponding phase diagram. In order to obtain polymer/disc phase diagrams, one must solve Equations (16) and (17) taking into account Equations (14) and (15):

$$\phi_d^i + \frac{(\phi_d^i)^2}{1-\phi_d^i}\frac{b}{v_d}\rho^i - (\phi_d^i)^2 \frac{b}{v_d}\frac{\Theta}{T} = \phi_d^n + \frac{(\phi_d^n)^2}{1-\phi_d^n}\frac{b}{v_d}\rho^n - (\phi_d^n)^2 \frac{b}{v_d}\frac{\Theta}{T} \tag{18}$$

$$\ln\phi_d^i + \delta^i + \frac{b}{v_d}\rho^i[\phi_d^i - \ln(1-\phi_d^i)] - \phi_d^i - 2\phi_d^i\frac{b}{v_d}\frac{\Theta}{T} = \ln\phi_d^n + \delta^n + \frac{b}{v_d}\rho^n\Big[\phi_d^n - \ln(1-\phi_d^n)\Big] - \phi_d^n - 2\phi_d^n\frac{b}{v_d}\frac{\Theta}{T} \tag{19}$$

For a set of N, v_d and b values, Θ/T and χ are proportional [Equation (10)] so, in the treatment of Equations (18) and (19), χ is considered identical in the two phases and chemical potentials, which is equivalent to assuming that the interaction parameter does not vary with concentration, which is not always true.[39–42] However it is adequate with a view to solving the algebraic mean-field equations. Such a crude mean field approximation is known for neglecting fluctuations, especially when examining the phase boundaries and phase transitions. To solve Equations (18) and (19) we take $\delta^i = 0$, $\rho^i = 1$, $\delta^n = 2\ \ln\,[-2/\pi^{1/2}(b/v_d)\ \ln\,(1-\phi_d^n)] - 1$ and $\rho^n = -2(v_d/b)/[\ln(1-\phi_d)]$. Taking into account that $\phi_d^i + \phi_p^i = 1$ and $\phi_d^n + \phi_p^n = 1$ the unknown quantities are ϕ_d^i, ϕ_d^n and Θ/T. If some values are given to Θ/T, both unknown quantities ϕ_d^i and ϕ_d^n can be calculated *via* Equations (18) and (19), and Θ/T *vs.* ϕ_d can be plotted, locating the isotropic and nematic boundaries *via* cloud points ϕ_d^i and ϕ_d^n, calculated for each Θ/T. To present disc/polymer 1/polymer 2 systems, we have chosen to add polymer 2 with various N_2 to the already explained disc/polymer 1 ($N_1 = 1$) systems. The examples were solved with equations from the approximation surface of disc with the same chemical nature as polymer 1 (sd = 1):[28]

$$-\left\{\phi_d^i + \frac{(\phi_d^i)^2}{1-\phi_d^i}\frac{b}{v_d}\rho^i - \left(\phi_d^i\right)^2\frac{b}{v_d} - \frac{v_d}{N_1}\left[\ln\phi_1^i + 1 - \phi_1^i - \frac{v_1}{v_2}\phi_2^i + \left(\phi_2^i\right)^2 v_1\chi\right]\right\} = -\left\{\phi_d^n + \frac{(\phi_d^n)^2}{1-\phi_d^n}\frac{b}{v_d}\rho^n - \left(\phi_d^n\right)^2\frac{b}{v_d} - \frac{v_d}{N_1}\left[\ln\phi_1^n + 1 - \phi_1^n - \frac{v_1}{v_2}\phi_2^n + \left(\phi_2^n\right)^2 v_1\chi\right]\right\} \tag{20}$$

$$-\left\{\phi_d^i + \frac{(\phi_d^i)^2}{1-\phi_d^i}\frac{b}{v_d}\rho^i - \left(\phi_d^i\right)^2\frac{b}{v_d} - \frac{v_d}{N_2}\left[\ln\phi_2^i + 1 - \phi_2^i - \frac{v_2}{v_1}\phi_1^i + \left(1-\phi_2^i\right)^2\frac{v_2}{v_1}\chi\right]\right\} = -\left\{\phi_d^n + \frac{(\phi_d^n)^2}{1-\phi_d^n}\frac{b}{v_d}\rho^n - \left(\phi_d^n\right)^2\frac{b}{v_d} - \frac{v_d}{N_2}\left[\ln\phi_2^n + 1 - \phi_2^n - \frac{v_2}{v_1}\phi_1^n + \left(1-\phi_2^n\right)^2\frac{v_2}{v_1}\chi\right]\right\} \tag{21}$$

$$\ln\phi_d^i + \delta^i + \frac{b}{v_d}\rho^i[\phi_d^i - \ln(1-\phi_d^i)] - \phi_d^i - 2\phi_d^i\frac{b}{v_d}\frac{\Theta}{T} + (\phi_d^i)^2\frac{b}{v_d}\frac{\Theta}{T} + v_d\chi\phi_2^i(\phi_d^i - \phi_1^i) + \phi_1^i\left(1 - \frac{v_d}{v_1}\right) + \phi_2^i\left(1 - \frac{v_d}{v_2}\right) + \phi_d^i(1 - v_d\phi_2^i) = \ln\phi_d^n + \delta^n + \frac{b}{v_d}\rho^n[\phi_d^n - \ln(1-\phi_d^n)] - \phi_d^n - 2\phi_d^n\frac{b}{v_d}\frac{\Theta}{T} + (\phi_d^n)^2\frac{b}{v_d}\frac{\Theta}{T} + v_d\chi\phi_2^n(\phi_d^n = \phi_1^n) + \phi_1^n\left(1 - \frac{v_d}{v_1}\right) + \phi_2^n\left(1 - \frac{v_d}{v_2}\right) + \phi_d^n(1 - v_d\phi_2^n) \tag{22}$$

where ϕ_1^i and ϕ_2^i are ϕ_1 and ϕ_2 in the isotropic phase, ϕ_1^n and ϕ_2^n, likewise in the nematic phase, and $\Theta/T = 1 + (vd2/b)(\chi–N_2/2)$ with $\chi = \chi_{2d}$. If in Equations (20)–(22) Θ/T is substituted with χ, five unknown quantities remain: ϕ_d^i, ϕ_d^n, ϕ_2^i, ϕ_2^n and χ, taking into account that $\phi_d^i + \phi_1^i + \phi_2^i = 1$ and $\phi_d^n + \phi_1^n + \phi_2^n = 1$. Values are given to χ for a given ϕ_2^i, and the unknown quantities ϕ_d^i, ϕ_d^n and ϕ_2^n are calculated *via* Equations (20)–(22), *i.e.*, for each χ, ϕ_d^i, ϕ_d^n, ϕ_1^i and ϕ_1^n will be known and phase diagrams can be represented as χ vs. binary compositions: $u_d^i = \phi_d^i/(1-\phi_2^i)$, $u_d^n = \phi_d^n/(1-\phi_2^n)$, $u_1^i = \phi_1^i/(1-\phi_2^i)$ and $u_1^n = \phi_1^n/(1-\phi_2^n)$ with $u_d^i + u_1^i = 1$ and $u_d^n + u_1^n = 1$. Calculations are possible assuming that χ is concentration independent and the approximation sd = 1 on constructing Equations (20)–(22). If in Equations (20) and (21) one makes $\phi_d = 0$ ($\phi_d^n = 0$,

$\phi_d^i = 0$):

$$\ln\phi_1^\alpha + 1-\phi_1^\alpha - \frac{v_1}{v_2}\phi_2^\alpha + (\phi_2^\alpha)^2 v_1\chi = \ln\phi_1^\beta + 1-\phi_1^\beta - \frac{v_1}{v_2}\phi_2^\beta + (\phi_2^\beta)^2 v_1\chi \quad (23)$$

$$\ln\phi_2^\alpha + 1-\phi_2^\alpha - \frac{v_2}{v_1}\phi_1^\alpha + (\phi_1^\alpha)^2 \frac{v_2}{v_1}\chi = \ln\phi_2^\beta + 1-\phi_2^\beta - \frac{v_2}{v_1}\phi_1^\beta + (\phi_1^\beta)^2 \frac{v_2}{v_1}\chi \quad (24)$$

Equations (23) and (24) were applied to component-1 monomer ($N_1 = 1$) and component-2 polymer.[39] However in Equations (23) and (24) we assume that ϕ is concentration independent, which is not always true and phase diagrams from solving Equations (23) and (24) are not quantitatively correct but valid with a view to comparing to the solution of Equations (20)–(22) to simulate the effect of ϕ_d on the stability of polymer mixture 1/2.

Experimental Part

The prepolymer epoxy resin (DER336) and thermoplastic PS1450N were previously described.[39,43] The co-polymer was poly(styrene-*b*-methyl methacrylate) [P(S-*b*-MMA4)] provided by Polymer Source, Inc., with M_n values of: PS(172 000 g·mol^{-1}) PMMA(7 300 g·mol^{-1}), $M_w/M_n = 1.06$ with a PMMA content of 4% (w/w). Density: 1.096 g·mL^{-1}, molar volume: 1.734×10^5 mL·mol^{-1}. The P(S-*b*-MMA22) was also provided by Polymer Source, with M_n values of: PS(123 000 g·mol^{-1}) PMMA(35 000 g·mol^{-1}), $M_w/M_n = 1.09$ with a PMMA content of 22% (w/w). Density: 1.124 g·mL^{-1}, molar volume: 1.537×10^5 mL·mol^{-1}. The initial temperatures and times of phase change T_{cpi} (°C) and t_{cpi} (s), respectively, were obtained with a previously described equipment.[39] The dichloromethane used to prepare mixtures was provided by J. T. Baker with 84.93 g·mol^{-1} and richness of 99.5%. The curing agent was the aromatic diamine 4,4'-methylenebis(2,6-diethylaniline) (MDEA) provided by Lonzacore (Lonza Ltd., Basel, Switzerland). Nanosheets were organophilic montmorillonite (nanoclay, Nanofil® 919, N919, provided by Süd Chemie), which contains only one hydrocarbon chain. Descriptions of the procedure of preparing mixtures and light-transmission device were reported in the literature,[39] and further details will be given in a future publication.[40]

Results and Discussion

Figure 1 shows the comparison of signals of transmitted light intensity (arbitrary units, a.u.) *vs.* initial temperature of phase change

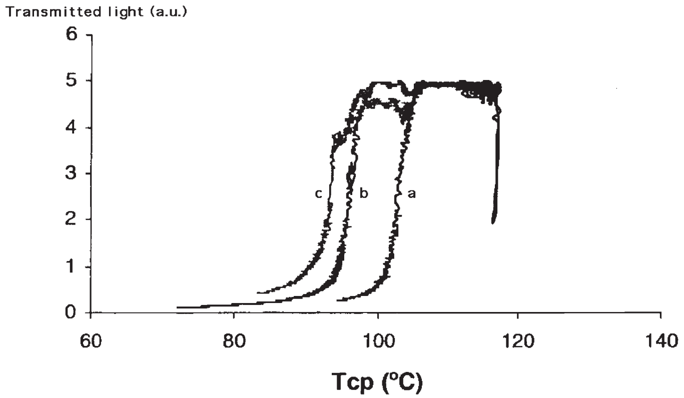

Figure 1.
Comparison of signals of transmitted light intensity (a.u.) *vs.* T_{cp} (°C) for systems epoxy336/PS1450N + P(S-*b*-MMA22) in the epoxy/thermoplastic mixture ratio of 90:10 (w/w). PS:P(S-*b*-MMA): a) 98%/2%, b) 97%/3% and c) 96%/4% (w/w).

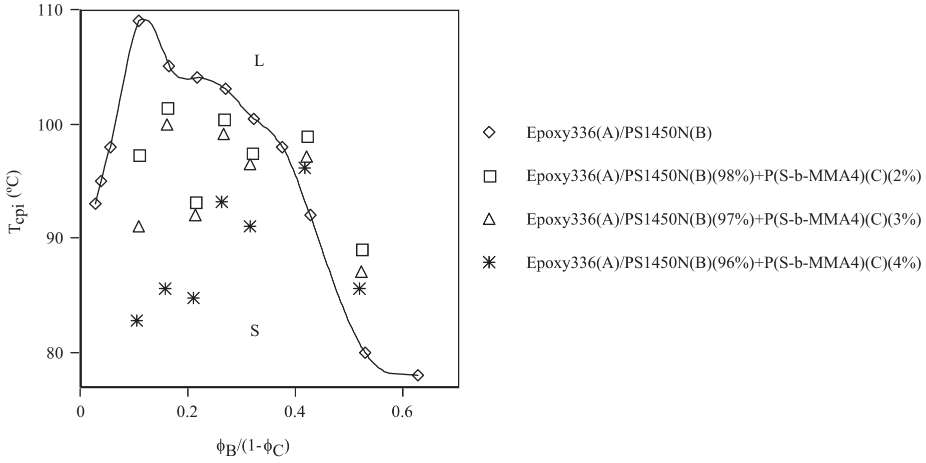

Figure 2.
Temperature of change of phase separation *vs.* $\phi_B/(1-\phi_C)$ in system epoxy336(A)/PS1450N(B) + P(S-*b*-MMA4) (C) for volume fractions of C component in mixtures B + C with various wt.%.

(T_{cpi}, °C) for the systems epoxy monomer 336(A)/PS1450N(B) + P(S-*b*-MMA22)(C) in the 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).

Figure 2 reveals the phase diagrams of the 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) each diagram: 50:50, 60:40, 70:30, 75:25, 80:20, 85:15 and 90:10 (w/w). In each diagram, T_{cpi} (°C) of each ternary mixture is represented *vs.* the B/(A + B) composition, expressed in the form of binary volume fractions, in such a way that $\phi_B/(1-\phi_C) + \phi_A/(1-\phi_C) = 1$. Each diagram differs in the binary weight fraction C/(B + C): 2%, 3% and 4% (w/w). The increase in co-polymer in the thermoplastic mixture raises system stability, augmenting the miscible liquid phase and decaying the immiscible solid phase.

As another example, Figure 3 exhibits, as primary information, the signal of transmitted light intensity *vs.* the time (in seconds) that the system takes in the changing of phase, as a consequence of the increase in the molar mass of the thermoset in the presence of curing agent, and a liquid–liquid phase separation occurs at a certain level of conversion of thermoset epoxy, at constant temperature. The initial weight of each component is: E(336) 90% (2.7000 g); PS(1450N) 10% (0.3000 g); MDEA (1.1448 g) 1.0000 g_E → 0.4240 g_{MDEA} (stoichiometric ratio). The t_{cpi} is 745 s.

Figure 4 reveals t_{cpi} *vs.* percentage of thermoplastic in the mixture. Inclusion of co-polymer in the mixtures makes systems compatible with regard to the one without co-polymer.

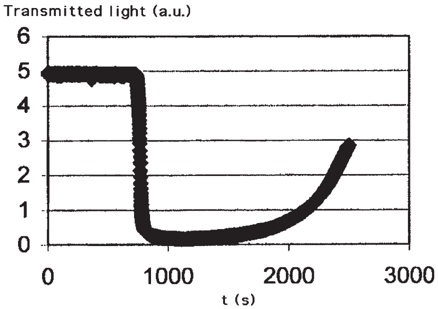

Figure 3.
Transmitted light intensity (a.u.) *vs.* *t* (s) at 140°C for E(336)–PS(1450N)–MDEA systems with initial weight ratios: E(336) 90% (2.7000 g); PS(1450N) 10% (0.3000 g); MDEA (1.1448 g) 1.0000 g_E → 0.4240 g_{MDEA} (stoichiometric ratio); $t_{cpi} = 745$ s.

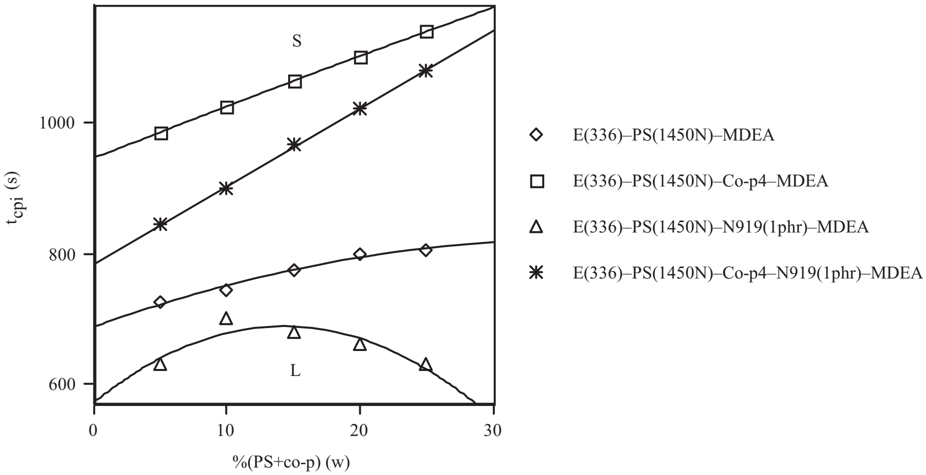

Figure 4.
Variation of t_{cpi} (s) *vs.* wt.% of thermoplastic mixture in total mixture at 140°C for studied systems.

Conclusion

From the present results and discussion the following conclusions can be drawn.

1. The main conclusion consists in that co-polymers stabilize the mixtures of epoxy monomer–thermoplastic modifier (provided data), and the mixtures of epoxy monomer–thermoplastic modifier–Nanofil 919 (indicated results). Moreover, it is shown how co-polymers stabilize epoxy resin cured with thermoplastic modifier and in the presence or not of Nanofil 919.
2. Expressions for phase diagrams were deduced in polymer/disc systems, examining the effects of disc size and temperature. The performed predictions between monomers and discs give criteria that advance the mixture properties. The used analysis is a good start for in-depth nanoindentation studies.

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