Gradient Interphase between Reactive Epoxy and Glassy Thermoplastic from Dissolution Process, Reaction Kinetics, and Phase Separation Thermodynamics

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ABSTRACT: Planar interfaces have been prepared by assembling high-T_g thermoplastics such as poly(phenylene ether) (PPE) or poly(ether imide) (PEI) and epoxy−amine networks at different conversions of the epoxy groups, X_e, followed by a complete curing. Direct evidence of the structure of the interfacial regions was made by means of electron microscopies, SEM and TEM, and atomic force microscopy, after a complete curing of the epoxy−amine. The morphologies of the interfaces are explained from the competition between the dissolution process of a thermoplastic by nonreactive solvent and the thermodynamics and the kinetics of reactive epoxy−amine/thermoplastic system. If the phase diagram indicates that the epoxy−amine/thermoplastic system is nonmiscible, the interface remains very thin (<20 nm). In the opposite, a gap range of miscibility controlled by the polymerization rate allows a diffusion of the comonomers into the thermoplastic layer and its further dissolution. As a consequence, 100−400 μm thick interphases can be generated. A gradient morphology results from the gradient composition at phase separation. The gradient composition or concentration profile is shown to depend on the type of dissolution process that is mainly determined by the competition between the thermodynamic osmotic pressure and the swelling resistance of the thermoplastic.

Introduction

On the basis of the semi-IPN or IPN concept, it has been reported recently that a gradient interphase between a thermoset and a thermoplastic (TP) is a novel efficient technique for toughening brittle carbon fiber-based thermoset composites[1,2] or polysulfone (PSF)/epoxy structures.[3] Such morphologies were denoted nonproperly semi-IPN as a phase separation occurred, leading to a micrometer scale morphology. As a matter of fact, multilayered structures where a planar interface exists between a thermoset and a thermoplastic could be observed in many other cases where the reactive formulation can be used as coating or adhesive on or between thermoplastics, respectively. As a consequence, this morphology spectrum concept is very attractive for toughening.

The most efficient way for creating a gradient structure is to consider a miscible system. Mutual diffusion of the components can create a gradient concentration in the interfacial region. As a consequence, when reaction between comonomers proceeds, it will induce a phase separation leading to a gradient morphology in the interfacial zone, denoted as the “gradient” interphase. We have already reported the different types of resulting morphologies and the consequences on the interfacial toughness for thermoset/high-T_g thermoplastic.[4] Only few recent works have been dedicated to the study of interdiffusion between a reactive mixture of monomers, i.e., a thermoset formulation and a thermoplastic.[5,6] Unfortunately, the authors neither take into account the diffusion process as being coupled with dissolution of the thermoplastic nor inquired of the miscibility of the various components. Nevertheless, these parameters seem to be essential for a complete understanding and a further tailoring of thermoset/thermoplastic gradient interphases morphology and the related toughness of the interfaces.

In this paper, planar interfaces between high-T_g thermoplastics and epoxy−amine networks were prepared by assembling a glassy thermoplastic and an epoxy network at different epoxy conversions, X_e, of the reactive mixture. Epoxy−amine/thermoplastic systems were chosen according to the knowledge of their miscibility, i.e., phase diagram, phase separation mechanisms, morphologies of the blends, and reaction kinetics of epoxy−amine at a given amount of thermoplastic.[7−14] From a mechanistic point of view, mutual diffusion between an epoxy thermoset formulation and a thermoplastic that is glassy at the curing temperature should occur through the diffusion of the epoxy−amine low molar mass species into the thermoplastic and dissolution of the latter. This diffusion/dissolution process has been studied for nonreactive solvent/thermoplastic and is reported as a basis for understanding. The different morphologies created by varying the nature of the reactive epoxy and processing conditions were observed after a complete curing of the epoxy−amine by means of scanning and transmission electronic microscopy and atomic force microscopy. As reported, such types of morphologies can be explained from the knowledge of the competition between the dissolution process of a thermoplastic by nonreactive solvent and the thermodynamics combined with the kinetics of reaction of the epoxy−amine/thermoplastic systems.

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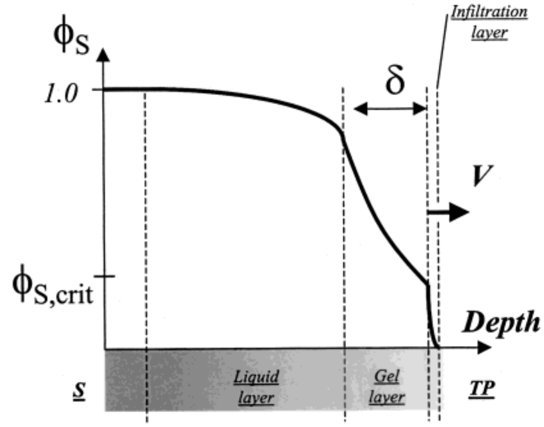
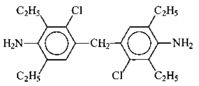
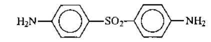
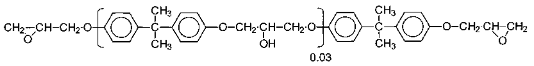
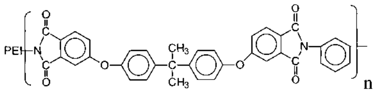
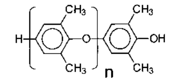


Figure 1. Solvent concentration profile for a case II diffusion with dissolution of the polymer at the interface between the gel layer of thickness δ and the liquid layer.

Table 1. Reactants Used To Synthesize Epoxy Networks and Thermoplastics

MCDEA, *380 g.mol^{-1},* *Lonza*	
DDS, *238 g.mol^{-1}, Aldrich*	
DGEBA, *348.5 g.mol^{-1}* *Dow Chem.*	
PEI *26 000 g.mol^{-1}, IP 2, Tg 215 °C,* *General Electric*	
PPE *12 000 g.mol^{-1}, IP 2, Tg 210 °C, General Electric.*	

Background: Swelling and Dissolution of a Glassy Polymer

Hereafter the subscript "S" will refer to the thermoset formulation while "TP" to the thermoplastic. Ueberrieter and co-workers[15] have thoroughly studied the dissolution process of glassy polymers and identified the following five regions in the diffusion zone according to the amount of decreasing polymer concentration: pure polymer, infiltration layer, gel layer, liquid layer, and pure solvent. The liquid layer is a typical diluted polymer solution with relatively free motions of entire macromolecules. The gel layer contains swollen polymeric material in a rubberlike state. In the infiltration layer, Fickian diffusion of the solvent molecules is observed. The solvent penetration front between the swollen region and the inner glassy polymer core is sharp and advances at a constant rate, V. This diffusion process is usually referred as case II diffusion. Because the mutual diffusion coefficient D varies by orders of magnitude even for low weight fraction variations, the typical concentration profile is very asymmetric (Figure 1). Swelling of a rubber polymeric network was early described by Flory.[16] Because the chains in between the network junctions are required to assume elongated configurations, an entropic elastic recovering force develops in opposition to the mixing force. For cross-linked rubber, the equilibrium swelling is obtained when the two forces are in balance, i.e., when lowering of the chemical potential due to mixing is balanced by an increase of the elastic reaction of the network. This one can be seen as an osmotic pressure, P_{os}. The Thomas and Windle case II diffusion model[17] considers a swelling of a glassy polymer as an osmotic-pressure-driven deformation. The difference in the chemical potential of the solvent from equilibrium value gives rise to an osmotic pressure, P_{os}, which is applied to the polymer network. The solvent equilibrium volume fraction, ϕ_{Seq}, is determined by the phase diagram of the system.[18,19] Time-dependent mechanical deformation of the polymer (chain relaxation) in response to this thermodynamic swelling osmotic stress could be approximated by a linear viscous relationship, and the swelling rate is

$$\frac{\mathrm{d}\phi_S}{\mathrm{d}t} = \frac{P_{os}(\phi_S)}{\eta(\phi_S)} \tag{1}$$

where $\eta(\phi_S)$ is the viscosity of the polymer/solvent mixture at a given composition, ϕ_S,. Case II diffusion process starts after an induction time where a critical surface volume fraction of penetrant, $\phi_{S,crit}$, is reached for which the swollen polymer yield stress, $\sigma_y(\phi_S)$, drops below the osmotic pressure.[20−23] Once formed, the case II front moves inward with a velocity, V, which follows Thomas and Windle's predictions:

$$V = \left[\left(\frac{D_{Sg}}{\phi_{S,crit}}\right)\frac{\mathrm{d}\phi}{\mathrm{d}t}\bigg|_{\phi_{S,crit}}\right]^{1/2} \tag{2}$$

where the swelling rate is considered at the swollen layer/glassy layer interface and D_{Sg} is the solvent-self-diffusion coefficient in the glassy polymer behind the front. Because the dissolution of a polymer involves chain disentanglement at the gel layer surface, models that couple the approach described above with reptation model were recently proposed.[24,25] Dissolution mechanism at the interface between gel and liquid layers can be disentanglement- or diffusion-controlled, and the thickness, δ, of the gel layer results from the balance between penetration velocity and dissolution rate. Increasing gel layer thickness with increasing polymer molecular weight has been observed for the polystyrene−toluene and polystyrene−methyl ethyl ketone systems.[15,25]

Experimental Section

Materials. The chemical structures and characteristics of the reactants are listed in Table 1. The epoxy networks were based on diglycidyl ether of bisphenol A prepolymer, DGEBA, and low reactivity aromatic diamines were used as curing agents: diaminodiphenyl sulfone, DDS, and 4,4′-methylenebis-(2,6-chlorodiethylaniline), MCDEA. The epoxy networks were synthesized considering a stoichiometric ratio of amino hydrogen to epoxy equal to 1. The cure schedule was 7 h at 135 °C followed by 2 h at 220 °C. The glass transition temperature, $T_{g\infty}$, of the fully cured DGEBA−DDS and DGEBA−MCDEA networks is 215 and 185 °C, respectively. The reactive epoxy−amine mixture was cured at different epoxy conversion before joining with the thermoplastic. This conversion was denoted X_e. Two amorphous thermoplastics were used: a poly(ether imide), PEI (ULTEM 1000, from General Electrics), and a poly(phenylene ether), PPE (BLENDEX 820, from General Electrics). Number-average molar masses, $\bar{M}_n$, are 26 000 and 12 000 g mol^{-1} for PEI and PPE, respectively, and $\bar{M}_w/\bar{M}_n = 2$. The glass transition temperature of the PPE and PEI is 210 and 215 °C, respectively.

Processing of Thermoplastic/Epoxy Interfaces. Processing of the thermoplastic involved three steps: (i) a 3 mm thick slab was prepared by compression molding between poly(tetrafluoroethylene) sheets at 270 °C for 20 min; (ii) after cooling to room temperature, the thermoplastic surface was scratched with wetted optical cleaning paper to eliminate the top layer contaminated with PTFE; (iii) the thermoplastic slab was heated again between (H_2SO_4/H_2O_2) cleaned float glass plate at 220 °C, i.e., just above T_g, for 1 h under low pressure and then slowly cooled at room temperature under compression, creating then waferlike surfaces.

The processing of the epoxy–amine/thermoplastic bilayers involved three steps: (i) the diamine was dissolved in the epoxy prepolymer at 90 °C for the MCDEA and 150 °C for the DDS, and the mixture was stirred under vacuum to eliminate trapped air; (ii) the unreacted system, i.e., $X_e = 0$, was poured onto the thermoplastic film, or epoxy–amine films at different epoxy conversions were prepared and poured, for $X_e < 0.40$, or pressed, for X_e from 0.40 to 1, onto the thermoplastic film; (iii) the assembly was then cured to reach a full conversion of the epoxy group, i.e., to reach $T_{g\infty}$ of the fully cross-linked epoxy network.

Measurements. The epoxy conversion was figured out from the measured glass transition temperature obtained by differential scanning calorimetry (DSC7 Perkin-Elmer; heating rate: 10 K min^{-1}) and Di Benedetto diagrams, i.e., plots of glass transition temperature, T_g, vs epoxy conversion. Cloud points were determined with a light transmission device that can detect a dispersed phase of average diameter larger than 0.1 μm.[9]

The morphology of the interfacial regions was analyzed after curing by means of scanning electron microscopy, SEM (Philips XL 20), combined with in-situ X-ray analysis, transmission electronic microscopy on 80 nm thick microtomed specimens, TEM (Philips CM 120; 80 kV accelerating voltage), and atomic force microscopy, AFM (Park Scientific Instrument), in the tapping mode. Staining was not necessary for TEM as a natural contrast existed between phases. For AFM, the difference in mechanical properties between phases during microtoming (at room temperature) created a topographic contrast. Exposure to vapors of selective solvent of one material was found to increase this contrast.[26] The concentration profile at the interface was computed from TEM or AFM micrographs with a homemade PCI3 image analysis software.[27] For blends of similar composition the mechanical relaxation peaks after full curing remain unchanged from the pure components and show the phases are practically pure.[28]

Results and Discussion

The DGEBA–DDS/PPE system is nonmiscible for the temperature and compositions range that will be studied. A very thin interface is observed after polymerization of the reactive DGEBA–DDS on the PPE film, consequently of this incompatibility. The thickness can be estimated in this case to be lower than 20 nm, which is the resolution of the technique (Figure 2). As expected, DGEBA–DDS/PPE interfaces obtained by joining at higher epoxy conversions followed by complete curing are also very thin since this system is nonmiscible whatever the epoxy conversion.

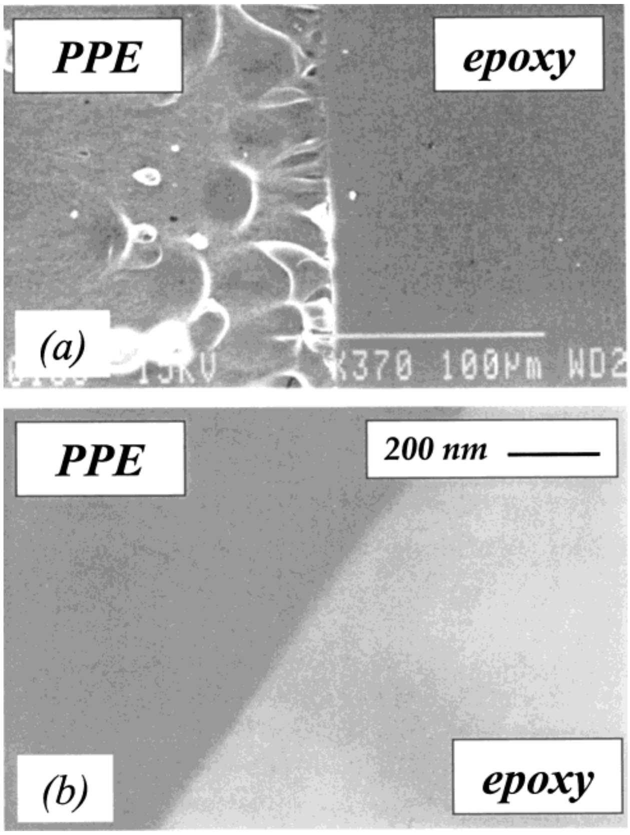


Figure 2. DGEBA–DDS/PPE interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C: (a) SEM and (b) TEM micrographs.

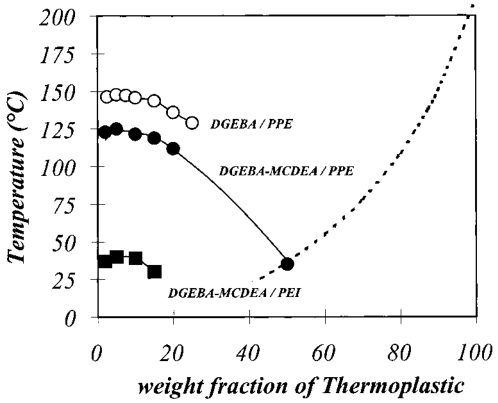


Figure 3. Initial phase diagram of the TP/epoxy blend, $X_e = 0$. Cloud point curves for (○) DGEBA/PPE, (●) DGEBA–MCDEA/PPE, and (■) DGEBA–MCDEA/PEI mixtures. Solid lines are a guide to the eye. The dashed line is the T_g–composition curve.

Phase diagrams for the reactive DGEBA–MCDEA/thermoplastic systems are given before reaction, i.e., at zero epoxy conversion, in Figure 3. Cloud point curve exhibits upper critical solution temperature, T_{max}, equal to 50 °C for PEI and 125 °C for PPE. At the curing temperature of 135 °C, both thermoplastics are soluble in the DGEBA–MCDEA reactive mixture, and diffusion of the epoxy–amine species in the thermoplastic films is therefore expected. The T_g–composition curve indicates for a curing temperature of 135 °C a PPE or a PEI layer is glassy until the weight fraction of the epoxy penetrant increases up to a $\phi_{S,crit}$ equal to 15 wt %. At this point, this mixed layer reaches a glass-to-rubber transition and eventually dissolves. However, this mutual diffusion should stop due to the molar mass increase of the reactive solvent as a liquid–liquid phase separation occurs at a given extent of reaction (Figure 4).

It can be observed in Figure 5 that for the DGEBA–MCDEA/PPE system a 210 μm thick gradient interphase is created from this mutual diffusion with dispersed PPE particles in the epoxy layer and the phase inverted morphology in the PPE one (Figure 5a–e). Nevertheless, a sharp interface is generated between the two biphasic regions (Figure 5f).[35] The thickness of these layers is 135 and 75 μm, respectively. Morphologies in epoxy–amine/thermoplastic blends depend on the thermoplastic concentration, ϕ_{TP}, with respect to the critical composition, $\phi_{TP,crit}$. They were found to be in the range of 10–15 wt % of thermoplastic.[7] Blends containing less than 10 wt % of TP exhibited morphologies of dispersed TP-rich particles in an epoxy-rich

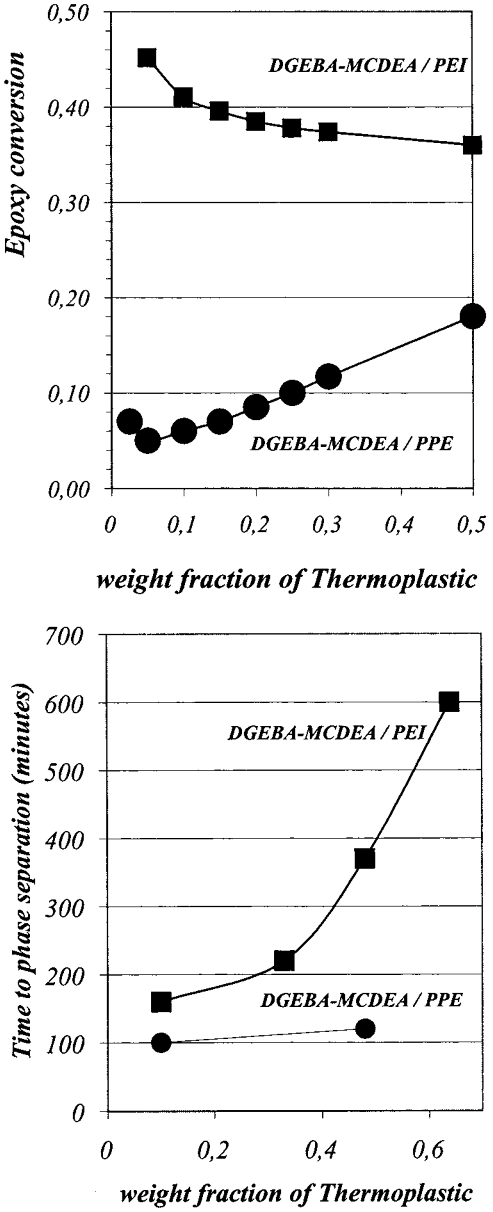


Figure 4. Cloud point conversions and time to phase separation during isothermal cure at 135 °C for (●) DGEBA–MCDEA/PPE and (■) DGEBA–MCDEA/PEI mixtures.

matrix. For 30 wt % and above, phase-inverted morphologies are generated. For these off-critical morphologies, sizes of the dispersed epoxy-rich particles decrease when the thermoplastic concentration, i.e., viscosity of the medium at phase separation, increases. As a matter of fact, the concentration profile shows that dispersed epoxy–amine-rich particles in a thermoplastic-rich matrix for TP concentration above 20% are observed, whereas the inverted morphology is observed for a concentration below 10% on the epoxy side. The diameter of the epoxy–amine dispersed particles increases from a few hundred nanometers near pure PPE to about 10 μm in the vicinity of the sharp interface, due to the changes of viscosity in the concentration gradient. The average diameter of the dispersed PPE particles remains constant along the 135 μm thick layer. A sharp interface can be observed between the two biphasic regions which is located at the critical composition (spinodal point) (Figure 5f).

Typical co-continuous structures usually result from spinodal decomposition at the critical composition. Such a morphology can be observed for a DGEBA–MCDEA/PEI fully cured blend with 15 wt % thermoplastic (Figure 6a). Because of the low viscosity at phase separation for the DGEBA–MCDEA/PPE blend, this co-continuous structure is changed to coexisting macroscopic domains with dispersion of PPE-rich particles in a DGEBA–MCDEA-rich matrix and inverted morphology[712] (Figure 6b). Although, whether phase separation mechanisms observed on homogeneous blends are affected by the gradient of composition is an exciting subject, it will not be developed here. Nevertheless, we can explain from the one-dimensional nature (*x*-direction) of the diffusion/dissolution and from the fact that the critical composition is encountered on only a few micrometers thick layer that a two-dimensional (*y*- and *z*-direction) phase separation occurred. This produced two coexisting macroscopic domains with dispersion of DGEBA–MCDEA-rich occlusions in a PPE-rich matrix and the inverted morphology separated by a straight thin interface (Figure 5f and Figure 7).

The underlying hypothesis for this analysis is that diffusion does not induce any deviation from stoichiometry. Faster diffusion of one of the two monomers due to a difference in size is not expected for the DGEBA–MCDEA system since their van der Waals volumes are very close, 290 and 310 Å^3, respectively. However, we could possibly imagine a selective diffusion of one of the two monomers based on their different chemical structure and affinity with the thermoplastic. In their study, Oyama et al.[6] measured composition profiles at the interface between poly(vinylpyrrolidone), PVP, and the DGEBA–DDS network after curing. They observed that the penetration front of the DDS monomer is 2 μm larger than for the DGEBA prepolymer at 40 °C below glass transition temperature of the PVP. Both molecular dynamics and compatibility with the thermoplastic of the two species could explain this slight difference in the location of the diffusion front. Rajagopalan et al.[5] studied the diffusion of each component of an epoxy reactive system into an amorphous polysulfone, PSF, at 80 °C. Their results suggest that molecular dynamics driven by the increased mobility has a large influence compared to the thermodynamics. Diffusivity into PSF of the low molecular weight aliphatic amine, bis(*p*-aminocyclohexyl)methane, PACM 20, is faster than for the more compatible DGEBA. When they diffuse alone, the ratio of self-diffusion coefficients is equal to 60. However, the latter decreases to 20 as the two monomers diffuse simultaneously. The DGEBA and DDS molar volumes, which are 290 and 195 Å^3, respectively, agree with the Oyama et al. results based on a molecular dynamics assumption. Fractionation between monomers and oligomers due to a difference in the size is likely to occur. Analyzing the DGEBA–MCDEA/PEI interphase will evidence this fact.

The shape of the concentration profile is notably asymmetric with the very broad thermoplastic zone into the epoxy and sharp epoxy–amine front into the thermoplastic one (Figure 8). The thickness of the interphase is determined by the distance that separates the ultimate penetration front of the reactive components from the dissolved thermoplastic chains that have diffused the deeper in the reactive solvent before the dissolution process stopped. The concentration profile is compared to viscosity at phase separation, computed

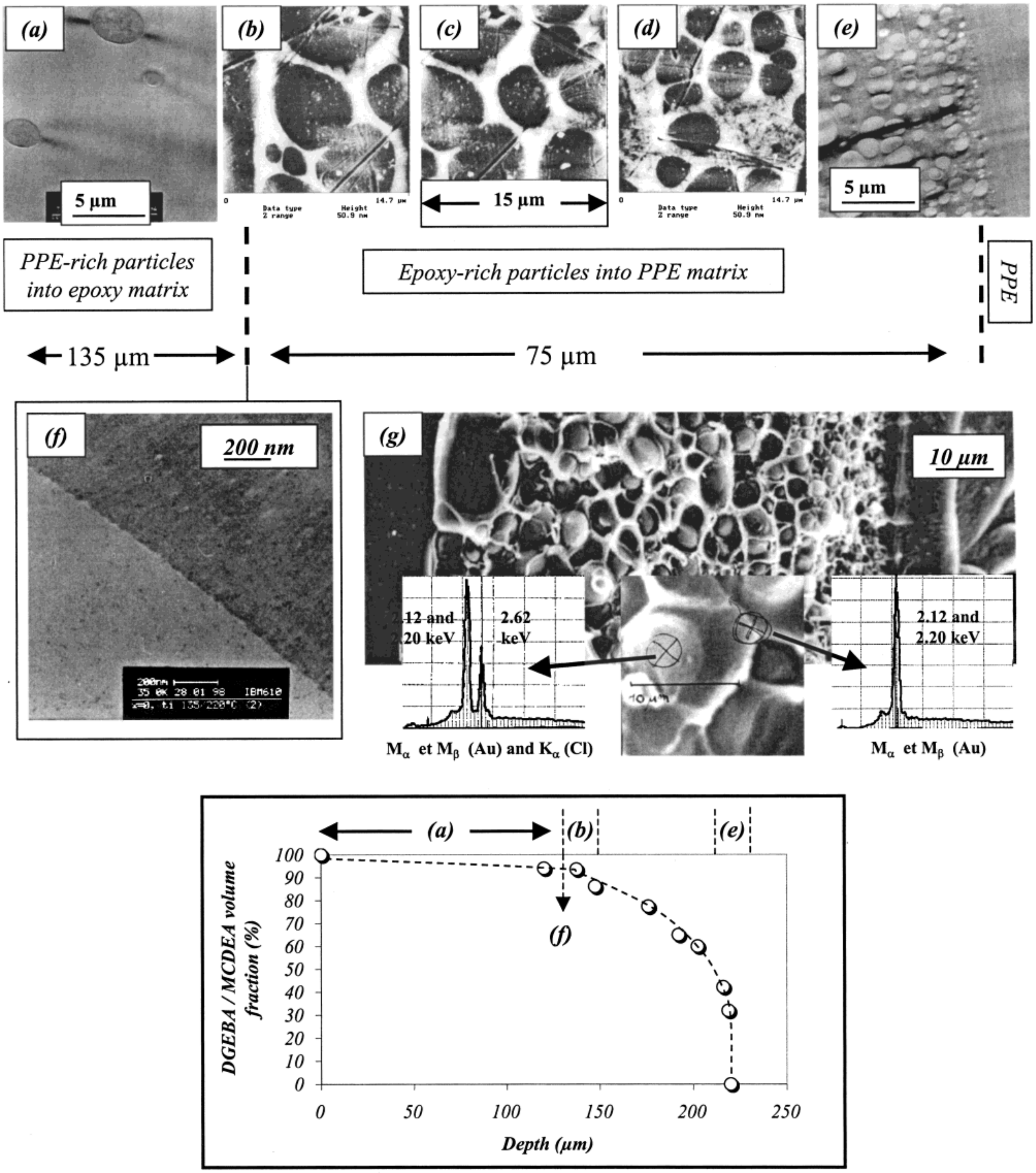


Figure 5. Micrographs of the DGEBA–MCDEA/PPE interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C: (a) dispersed PPE particles into the epoxy layer and (b–e) dispersed epoxy–amine particle into TP layer. (e) Ultimate penetration depth of the epoxy–amine species. (f) Sharp interface that delimits the two kind of morphologies. (g) SEM micrograph of the part of the interphase that corresponds to micrographs (b–e). X-ray analysis shows the matrix is TP-rich (no chlorine) while particles are epoxy–amine-rich (chlorine). Positions of the different micrographs are displayed on the concentration profile determined from image analysis.

from Venderbosch et al.'s data,[13] in Figure 8. It suggests when mutual diffusion stopped that there was a low-viscosity 170 μm thick liquid layer, a 30 μm thick boundary layer of much higher viscosity, and a few micrometers thick gel layer.

For the DGEBA–MCDEA/PEI assembly, an additional postcuring for 2 h at 240 °C was found to complete the phase separation process. In such a system a 330 μm thick mixed layer is created (Figure 9). As expected, a co-continuous morphology (Figure 9b) is observed at the critical composition. This one separates a 10 μm thick continuous thermoplastic phase with dispersed epoxy–amine particles (Figure 9a) from a 8 μm thick almost pure epoxy–amine layer (Figure 9c) followed by a 300 μm thick epoxy–amine continuous phase with dispersed PEI particles (Figure 9d).

The time-dependent formation of this gradient interphase could be schematized using the Bonnet et al.[10]

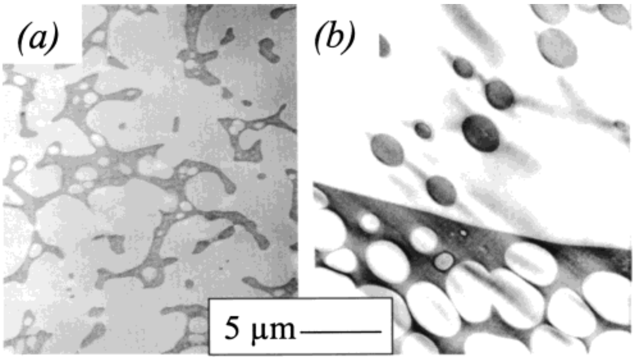


Figure 6. TEM micrographs of the fully cured blends near the critical composition: (a) PEI and (b) PPE. Composition for both is 15 wt % thermoplastic.

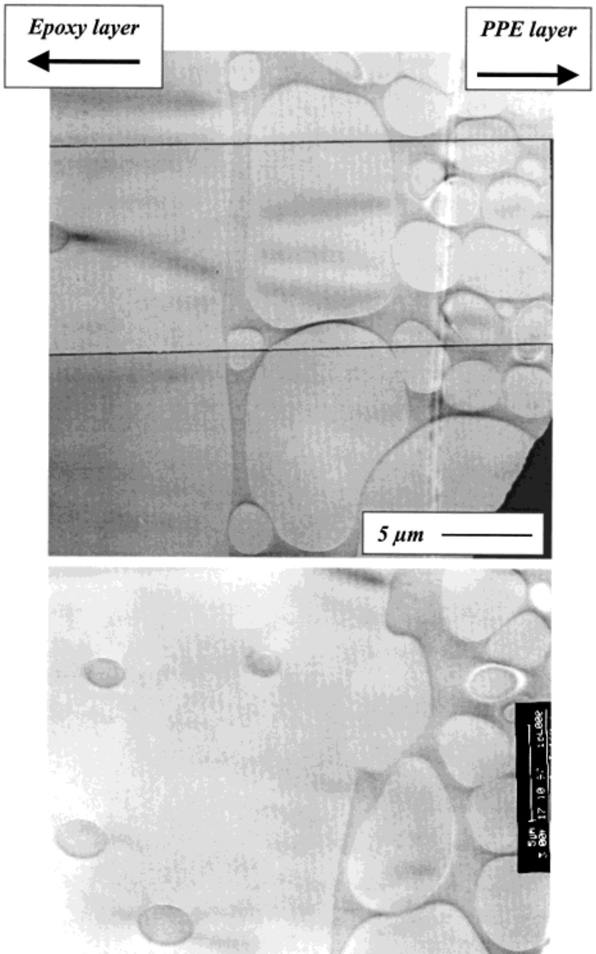


Figure 7. TEM micrographs of the cocontinuous morphology in the critical composition region of the DGEBA−MCDEA/PPE interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C.

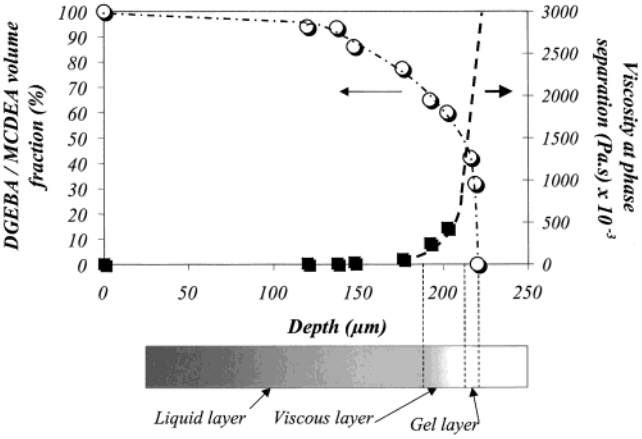


Figure 8. (○) Concentration profile and (■) viscosity at phase separation for the DGEBA−MCDEA/PPE interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C.

reaction kinetics data. Indeed, we consider that a gradient concentration has been established between the liquid DGEBA−MCDEA unreacted mixture and the thermoplastic and that this one is moving at a constant velocity into the thermoplastic (Figure 10). Neither shape nor depth of the concentration profile need to be considered here. After 100 min, a gradient of conversion among the epoxy−amine species has developed as a consequence of the gradient concentration: reaction rate decreases as thermoplastic content increases. Phase separation occurs first in the thermoset-rich zone. For the system considered here it will happen after 220 min at 135 °C. At this point, four different areas could be depicted in Figure 10: (i) pure epoxy−amine; (ii) demixed layer with mainly growing dispersed TP-rich particles in an epoxy−amine-rich matrix for ≤10 wt % of PEI and co-continuous phases for 10−20 wt % TP, (iii) homogeneous mixed layer for ≥20 wt % PEI ; and (iv) pure thermoplastic. Further diffusion deeper into the thermoplastic stops at this point: when DGEBA−MCDEA/PEI or PPE interfaces are joined at the epoxy conversion for which the system enters the two-phase region of the phase diagram, no diffusion occurred (this will be shown in Figure 15). After 420 min, gelation occurs in pure reactive epoxy−amine while phase separation is still to happen in the thermoplastic-rich layer. To check this hypothesis, a DGEBA−MCDEA/PEI interphase cured for 420 min at 135 °C followed by 120 min at 220 °C has been observed by TEM (Figure 11). One can recognize the 8 μm thick almost pure epoxy−amine layer followed by the 300 μm thick epoxy−amine continuous phase with dispersed PEI particles displayed in parts c and d of Figure 9, respectively. The 10 μm thick continuous thermoplastic phase with dispersed epoxy−amine particles and the co-continuous morphology displayed in Figure 9a,b have developed only during the supplementary postcure at 240 °C. Since it has already been postcured 2 h at 220 °C, the polymerization in the epoxy-rich phase observed in Figure 11 is definitely achieved. It means that further diffusion from the epoxy side into the PEI layer cannot occur at this point from a lack of available low molecular weight epoxy−amine species. Therefore, the morphologies evidenced in Figure 9a,b result from a phase separation during the supplementary postcure at 240 °C in an already swollen PEI layer by epoxy−amine species of low molar masses, mainly monomers. This situation is depicted in Figure 10 as a dashed line. The discrepancy between this experimental conversion−composition profile with the calculated profile gives evidence of a fractionation of reacted epoxy−amine species at the interface between the solution and the gel layer, leading to a thermoplastic swollen by monomers only. This is not surprising as in the glassy polymer, the diffusion coefficients of monomers are orders of magnitude higher than those of larger oligomers.[29] From this observation the diffusion/dissolution scheme proposed previously can

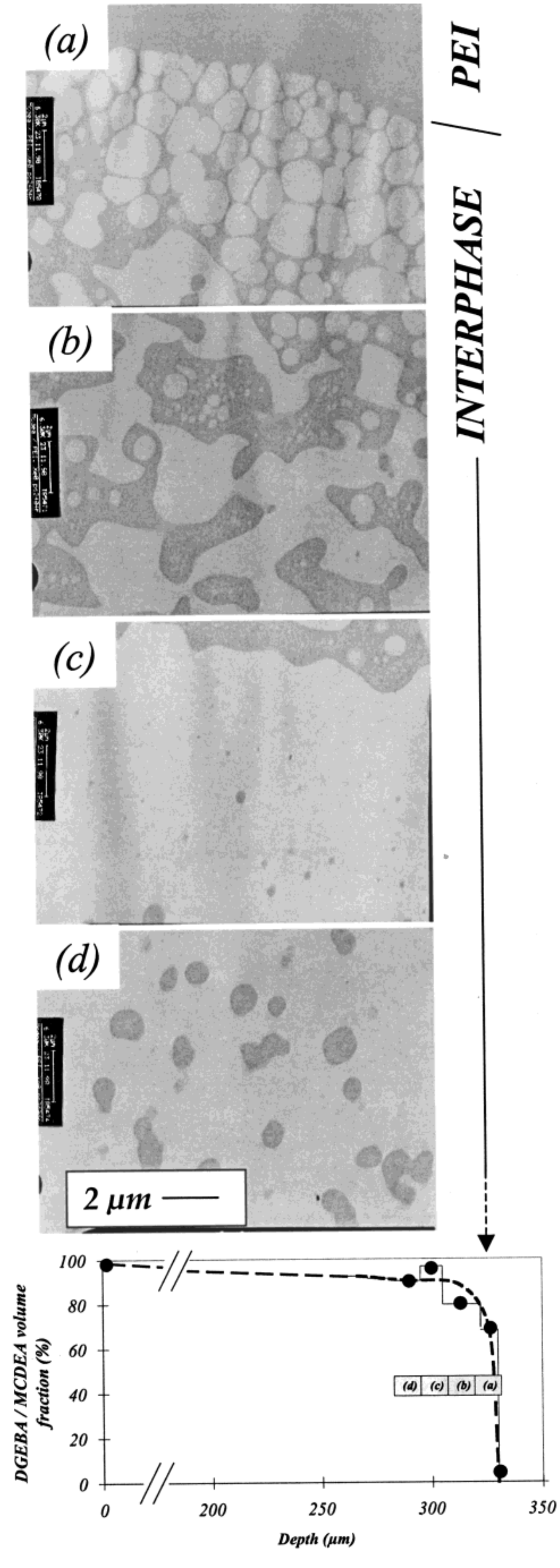


Figure 9. DGEBA–MCDEA/PEI interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C + 2 h at 240 °C: TEM micrographs (a–d) and concentration profile determined from image analysis.

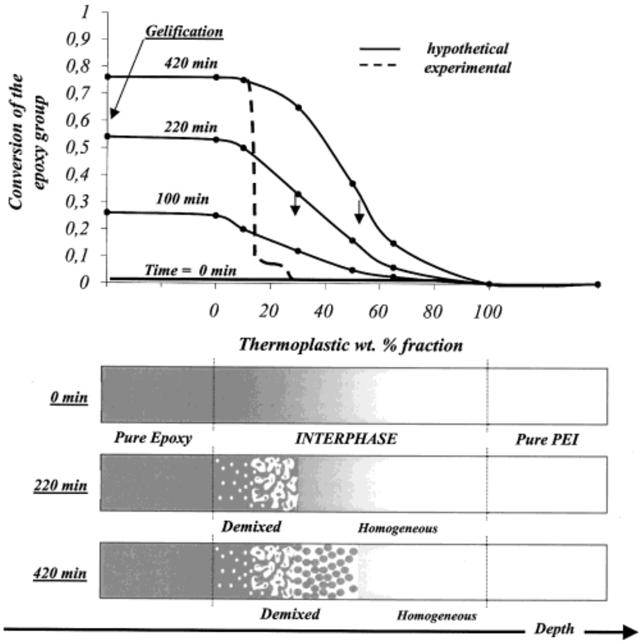


Figure 10. Time evolution of the conversion–composition profile for a model DGEBA–MCDEA/PEI interphase joined at $X_e = 0$ and cured at 135 °C. Arrows indicate phase separation has occurred for this TP % bw and below. T_{gel} in the pure epoxy–amine layer occurs at 300 min (7). Dashed line is the experimental profile at 420 min.

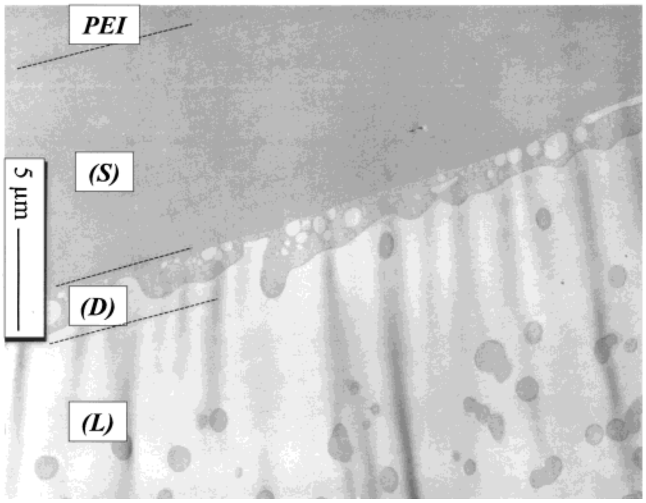


Figure 11. DGEBA–MCDEA/PEI interface joined at $X_e = 0$ and cured 7 h at 135 °C + 2 h at 220 °C. Before gelification, position of (L) liquid layer, (D) dissolution layer, (S) swollen or gel layer, and (P) pure PEI.

be specified. Before gelation of the reactive epoxy–amine system it exists: (i) a liquid layer (L) composed of PEI-rich particles dispersed in an epoxy–amine-rich (liquid) matrix; (ii) a gel layer of swollen PEI (S) with epoxy–amine species (mainly monomers); and in between, (iii) a dissolution layer (D) of irregular shape (Figure 11). The 8 μm thick almost pure epoxy–amine layer (Figures 9c and 11) is intriguing. We suspect it comes from the two-dimensional nature of the phase separation process. In the liquid layer for ≤10 wt % PEI it occurs by a nucleation and growth (NG) mechanism as for lends with the same compositions. For a tridimensional NG process, a distribution of PEI-rich particles homogeneously dispersed in an epoxy-rich matrix is produced.[9] The viscosity at phase separation

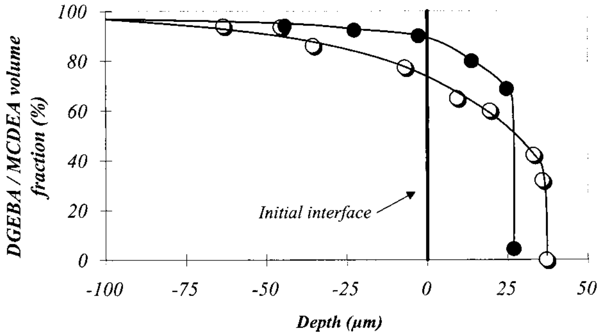


Figure 12. Concentration profile for DGEBA−MCDEA/PPE (○) and DGEBA−MCDEA/PEI (●) gradient interphase in relation with estimated position of the initial interface.

and the composition determine a mean interparticle distance. In the present case it is the distance between the epoxy particles and the interface.

We did not attempt to propose a time-dependent description of the DGEBA−MCDEA/PPE gradient interphase, but phase separation occurs at a much lower epoxy conversion and there is not a large change in the time to phase separation with reactive epoxy−amine content.

The shapes of the epoxy/PPE and epoxy/PEI concentration profiles are compared in Figure 12. By integrating the area below and above the curves, the position of the initial interface, i.e., before mutual diffusion, could be determined. The fact that the epoxy−amine penetration front position is further into the PPE than into the PEI although the time to phase separation is shorter is certainly a striking result (Figure 4). The penetration depth of the reactive mixture into the thermoplastics is limited by the relative penetration front velocity compared to the relative rate of polymerization which throw the system into the two-phase region of the phase diagram. The gap from thermodynamic equilibrium, $P_{os}(\phi_S)$, viscosity in the swollen polymer layer, $\eta(\phi_S)$, and diffusivity of the penetrant molecules into the glassy polymer, D_{Sg}, are the predicted parameters that likely govern the penetrant front velocity (eqs 2 and 3). In fact, the PEI is more miscible than PPE with DGEBA−MCDEA, and therefore $P_{os,PEI}$ is higher than $P_{os,PPE}$. The viscosity of the DGEBA−MCDEA/thermoplastic solutions are lower with the PPE than with the PEI. Steady-state viscosity at $X_e = 0$ was shown to follow the relation

$$\eta_{TP/S} = \eta_{TP} \exp[-m\phi_S] \tag{3}$$

where m is equal to 0.11 for PPE and PEI; η_{TP} is 3.2×10^8 and 1.2×10^{10} Pa·s for PPE and PEI, respectively.[11,14] In addition, as the density of PEI is much higher than that of the PPE, it could be assumed that the free volume is larger in the PPE leading to a faster diffusion of epoxy−amine species. As a consequence, for osmotic pressure large enough, i.e., far away from the binodal curve, the penetration front velocity is governed by the diffusivity into the glassy polymer and chain relaxations. However, the thickness of the interphase is higher for PEI because it is mostly determined by the maximum diffusion distance of the disentangled thermoplastic chains into the reactive solvent before it phase separates.

The interface obtained by casting the reactive DGEBA−MCDEA mixture with a mean conversion of 0.23 on a PEI film is showed in Figure 13. It has been created between pure thermoplastic and pure thermoset a 135 µm thick mixed layer of dispersed PEI-rich particles into a DGEBA−MCDEA matrix (Figure 13a). A sharp interface separates this region from the pure PEI (Figure 13b). No phase separation occurred into the PEI layer. This indicates that no gel layer was formed. It suggests that the ratio of the swelling rate to the dissolution rate decreases with increasing epoxy conversion and that the process changes from a dissolution with a gel layer at low conversion to a dissolution without a gel layer for higher conversions as depicted in Figure 14. A drop of the osmotic pressure could explain this swelling rate reduction as the system is approaching the binodal curve of the phase diagram.[33] Lipic et al. observed similarly on a mixture of poly(ethylene oxide)−poly-

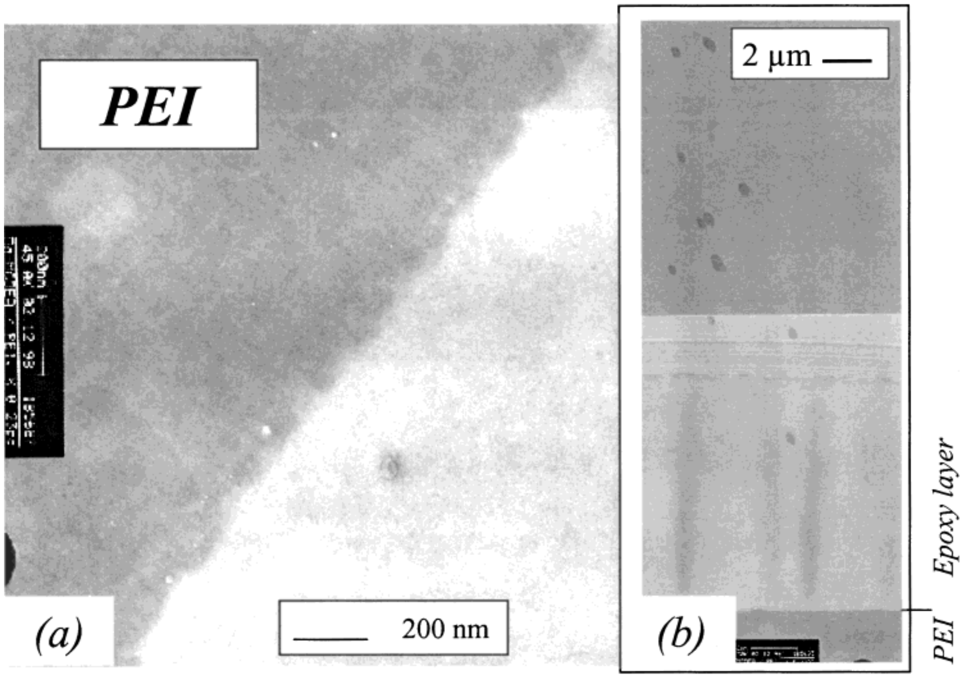


Figure 13. DGEBA−MCDEA/PEI interface joined at $X_e = 0.23$. The whole curing cycle is 7 h at 135 °C + 4 h at 220 °C.

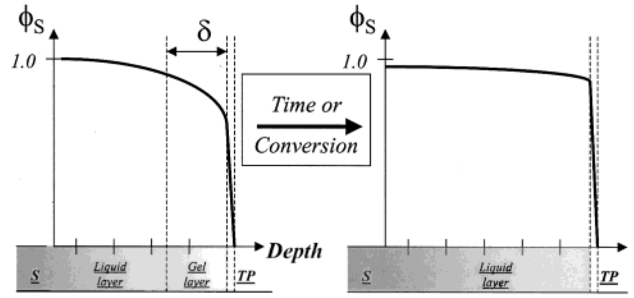


Figure 14. Evolution of the concentration profile resulting from variation in the dissolution process, from with a gel layer to without a gel layer, with increasing conversion.

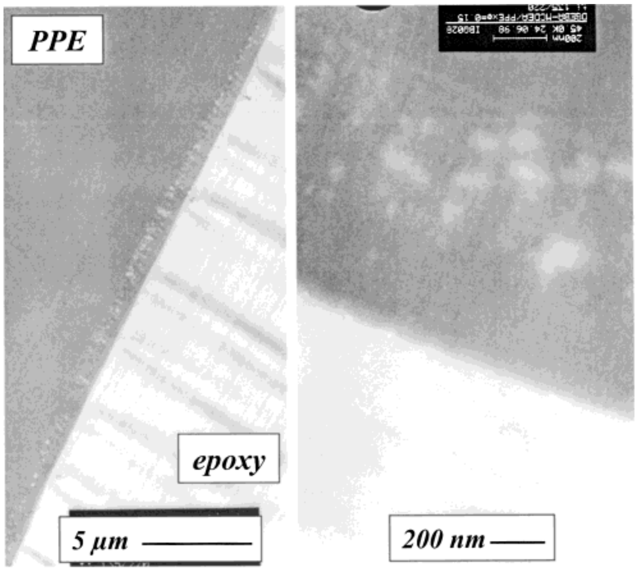


Figure 15. DGEBA−MCDEA/PPE interface joined at $X_e = 0.18$. The whole curing cycle is 7 h at 135 °C + 2 h at 220 °C.

(ethylene-*alt*-polypropylene) (PEO−PEP) diblock copolymer and an epoxy resin that selectively mixes with the PEO block that the degree of PEO swelling decreases as the epoxy cures.[34] The different types of dissolution processes, with or without a gel layer, have also been reported with nonreactive solvents.[35]

The interface obtained by casting the DGEBA−MCDEA reactive system with a mean conversion of 0.20 on a PPE film is shown after a complete curing in Figure 15. In fact, for these conditions the DGEBA−MCDEA/PPE blend enters in the two-phase region of the phase diagram (Figure 4). The diffusion of the epoxy−amine species has been very limited and extends only 1 μm deep into the PPE with a maximum ϕ_S below 10%. No dissolution of the thermoplastic is evidenced from the micrographs. This indicates that for this epoxy conversion where the system enters the two-phase region the osmotic driving force for diffusion is reduced below a critical value for which the swelling and dissolution rates are decreased to zero.

As the mean epoxy conversion at joining is increased to the cloud point conversion, i.e., $X_e \sim 0.35$, for the DGEBA−MCDEA/PEI interface, the dissolution of the thermoplastic does not occur, and a sharp interface identical to the DGEBA−DDS/PPE case is observed (Figure 2). This confirms the result obtained for the DGEBA−MCDEA/PPE system when joining is also done at the cloud point conversion.

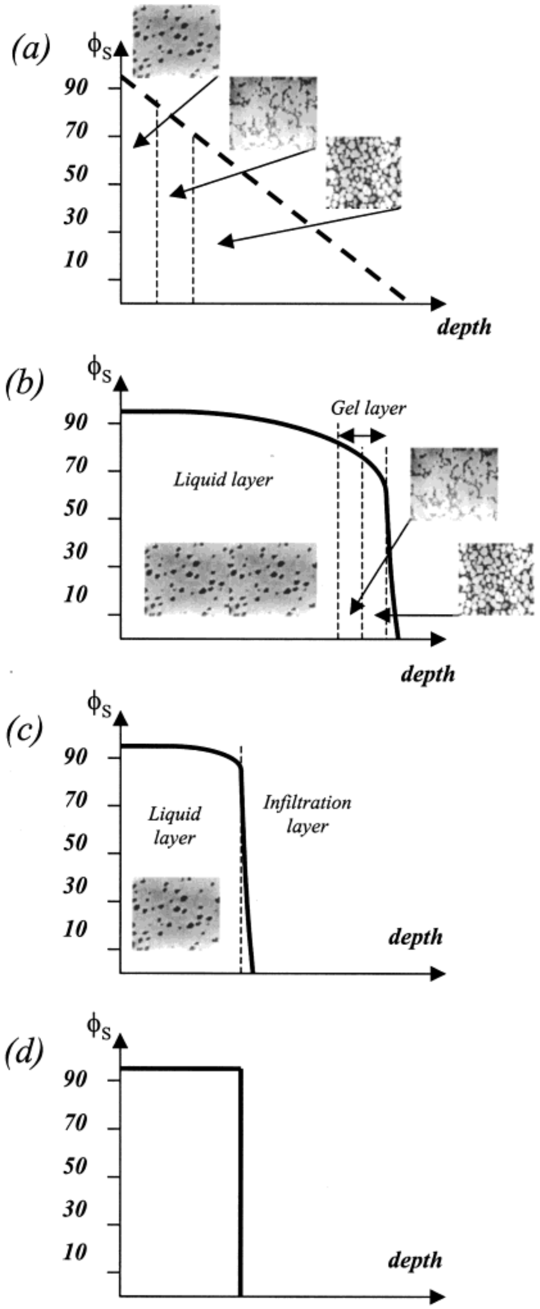


Figure 16. (a) Morphology spectrum achievable when interdiffusion between reactive DGEBA−MCDEA and PEI is envisaged at 135 °C. (b) Morphology spectrum displayed in the gradient interphase when diffusion/dissolution occurs with a swelled or gel layer for joining at $X_e = 0$, (c) when diffusion/dissolution occurs without a swelled or gel layer for joining at an intermediate $X_e = 0.23$, and (d) when no dissolution occurs for joining at the cloud point conversion $X_e = 0.35 = X_{CP}$.

Conclusions

Very different morphologies of the interfaces/interphases can be obtained from casting a reactive epoxy−amine system on a glassy thermoplastic by varying the chemical composition of the monomers or thermoplastic and processing conditions. If the phase diagram indicates that these ones are nonmiscible whatever the epoxy conversion, the interface remains very thin (<20 nm). In the opposite, a gap range of miscibility allows a diffusion of the comonomers in the thermoplastic layer. As a consequence, 100−400 μm thick interphases can be observed, and a gradient morphology results from the gradient composition at phase separation.

When the thermoplastic is glassy at the curing temperature of the reactive mixture, a mutual diffusion occurs through swelling of the thermoplastic layer by the low molecular weight species of the reactive solvent and dissolution of the disentangled TP chains into the epoxy−amine reactive solution. This diffusion/dissolution process stops as the thermodynamic driving force for mutual diffusion; the osmotic pressure drops below the swelling resistance of the pure glassy polymer. This phenomenon occurs for the systems studied in this paper, as the temperature is 80 K below the T_g of the thermoplastic, when they enter the two-phase region of their phase diagram. As a consequence, the time for mutual diffusion is controlled by the polymerization rate. In these conditions, it is observed that far enough from the binodal curve the swelling rate is limited by diffusivity into the glassy polymer and the chain relaxations. Approaching the binodal curve, the ratio of the swelling rate to the dissolution rate decreases, and the diffusion/dissolution process transforms from a dissolution with a swollen layer to a dissolution without a swollen layer and no further dissolution.

Figure 16 summaries these different processes involved for creating such interphases in the case of DGEBA−MCDEA joined to PEI.

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