

Poly(phenylene Ether)/Epoxy Thermoset Blends Based on Anionic Polymerization of Epoxy Monomer

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ABSTRACT: Low molar mass poly (phenylene ether) (LMW-PPE) with phenol-reactive chain ends was used as modifier of epoxy thermoset. The epoxy monomer was diglycidylether of bisphenol A (DGEBA), and several imidazoles were used as initiators of anionic polymerization. The curing and phase separation processes were investigated by different techniques: Differential Scanning Calorimetry, Size Exclusion Chromatography, and Light Transmission measurements. The final morphology of blends was observed by Environmental Scanning Electron Microscopy and Transmission Electron Microscopy. The epoxy network is obtained by imidazole initiated DGEBA homopolymerization. Initial LMW-PPE/DGEBA mixtures show an UCST behavior with cloud point temperatures between 40 and 90°C. PPE

phenol end-groups can react with epoxy, leading to a better interaction between phases. The curing mechanism and phase separation process are not influenced by the chemical structure of initiators, except when reactive amine groups are present. The phase inversion is observed at 30 wt % of PPE. The mixtures with amine-substituted imidazole present important differences in the initial miscibility and curing process interpreted in terms of fast room temperature amine-epoxy reaction during blending. Final domain size is affected by this prereaction. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2678–2687, 2004

Key words: poly (phenylene ether); blends; imidazole; thermosets; phase separation.

INTRODUCTION

Thermoset (TS) /thermoplastic (TP) blends are materials resulting from the mixing of a TP polymer and TS precursors and the subsequent reaction of the precursors. Usually the initial mixture is homogeneous, but the molar mass increase of the TS precursors involves a decrease in the conformational entropy of mixing and a liquid-liquid phase separation occurs. One of the advantages of using the reaction-induced phase separation is the broad variety of morphologies that can be generated. One important factor controlling the phase separation process and the generated morphology is the initial composition of the blend, in terms of the mass fraction of TP, ϕ_{TP}^0 , according to the critical composition, $\phi_{TP, crit}^0$. If ϕ_{TP}^0 is lower than $\phi_{TP, crit}^0$ the final morphology will consist in a dispersion of TP-rich particles in a TS-rich continuous matrix. For off-critical compositions, TS-particles are segregated in a TP-rich continuous phase. But when the TP concentration is near to the critical point, various morphologies can be observed: bicontinuous structure, double

phase morphology, and ribbonlike structures. Besides the initial blend composition, the intrinsic miscibility of the TS precursors and TP polymers involved and the competition between reaction kinetics and phase separation rate may influence the phase separation process.

Diglycidyl ether of bisphenol A (DGEBA) is usually used as epoxy monomer in TS/TP blends, because it is a good solvent for many polymers. As curing agent, different hardeners can be employed; diamines are the most frequently used.^{1–6} There are several references^{1–3} in the literature about the influence of epoxy-amine reaction in phase separation process. Nevertheless, the influence of imidazoles or tertiary amines⁷ as initiators of chain-growth epoxy homopolymerization in TS/TP blends has not been studied in depth.

The imidazoles have been shown to be effective initiators for epoxy homopolymerization and network formation.^{8–10} The reaction mechanism is complex. It is known^{8,9} that the first step is the epoxy/imidazole adduct (1 : 1) formation. Then, several processes can occur: adduct (1 : 2) formation, O-etherification, OH-etherification, and imidazole regeneration by *N*-dealkylation or Hoffman elimination. Also, imidazoles are Lewis bases and can catalyze the epoxy-anhydride¹¹ and epoxy-phenol¹² reactions. The effect of different substituted imidazoles and their concentration in the

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reaction mechanisms have been analyzed.^{8–12} Several differences have been observed in adducts formation depending on the nature and position of the substituents. The chemical structure of the substituted imidazoles does not influence greatly the mechanism of epoxy homopolymerization,^{8,11} except when the *N*-hydrogen function is reacted⁹ (1-substitution).

The blending of epoxy TS with high-temperature-resistant TP, like polyetherimide (PEI)^{2,3,6,13,14} and poly(phenylene ether) (PPE),^{4,15–19} have been widely studied as a means to toughen epoxy network^{6,14,15} or to improve processing of the TP polymer.⁴ Most of the studies reported use nonreactive high molar mass TP, which significantly improve the fracture toughness only when bicontinuous or inverted structures are generated. But when the phase separation produces TP-rich particles dispersed in a continuous TS-rich matrix, little or no improvement of fracture properties is obtained, mainly due to the poor adhesion between phases. For this reason, several works have been developed for improving adhesion between phases, using a functionally terminated TP.^{17–19} The modifier reactivity can influence the blend behavior and must be used to control the phase separation process and the generated morphology.

The aim of this work is to investigate a new epoxy/PPE blend, using a low molar mass PPE with reactive-phenol chain ends. Different imidazoles have been used as initiators of epoxy homopolymerization but also as catalysts of epoxy-phenol reaction. The influence of imidazole chemical structure in the curing, phase separation, and, consequently, in the final blend morphology has been analyzed.

EXPERIMENTAL

Materials and sample preparation

The studied blend was composed of a classical epoxy monomer, diglycidyl ether of bisphenol A (DGEBA) and poly(phenylene ether) (PPE) of very low molar mass with phenol chain ends, as thermoplastic modifier. Four different imidazoles were used as initiators: 2-methylimidazole (2MI), 2-phenylimidazole (2PI), 2,4-diamine-6-(2'-methylimidazolyl-1'-ethyl)-*S*-triazine (2MZ), and 1-cyanoethyl-4-ethyl-2-methylimidazole (2E4). The chemical structures and properties of these compounds are shown in Figure 1 and Table I.

Homogeneous solutions of different amount of PPE (from 10 wt % to 60 wt %) in epoxy monomer were prepared using a mechanical stirrer at 185°C, during 45 min for solutions with less than 50 wt % PPE or 90 min for higher PPE contents. Phenol/epoxy equivalent ratio ranges from 0.017 to 0.228. Then, the imidazole was added in a 2 or 5 wt % with respect to total mass. The resultant mixture was stirred during 3 min

at different temperatures depending on PPE content, at 80°C for 10 and 20 wt % PPE, at 100°C for 30 and 40 wt %, and at 120°C for 50 and 60 wt %. Immediately after, the homogeneous reactive mixture was immersed into liquid nitrogen to stop any reaction.

Measurements

Cloud points were determined with a light transmission device,²⁰ a technique that begins to detect particles when its average diameter is of the order of 0.1 μm. Cloud point temperatures or times were determined as the onset temperature or time, respectively, when a decrease in the transmitted light intensity was recorded.

The total reaction enthalpy (ΔH) was measured using a differential scanning calorimeter (DSC, Mettler TA300; Columbus, OH) in the scanning mode. All measurements were made in a 30–200°C range with a heating rate of 10°C/min under argon atmosphere. This measure was followed by a rapid cooling, and a second scan was made on the same sample immediately after at the same heat rate. In this way, the glass transition temperature (*T_g*) of the network was obtained.

Size exclusion chromatography (SEC) was used to determine the epoxy conversion and the PPE soluble fraction in cured samples. A Waters 410 chromatograph with differential refractometry detector (Milford, MA) was employed. The eluent was tetrahydrofuran (THF) at a flow rate of 1 mL/min at 20°C.

The disappearance of epoxy monomer DGEBA is determined by the equation:²¹

$$X = 1 - \left(\frac{A_t}{A_0} \right) \quad (1)$$

where *X* is the conversion of DGEBA molecules *n* = 0, and *A*₀ and *A*_{*t*} are the height of the DGEBA peak at *t* = 0 and at a time *t*, respectively. Supposing that both epoxides have equal reactivity, the conversion of epoxy groups, *x*, is given by the equation:

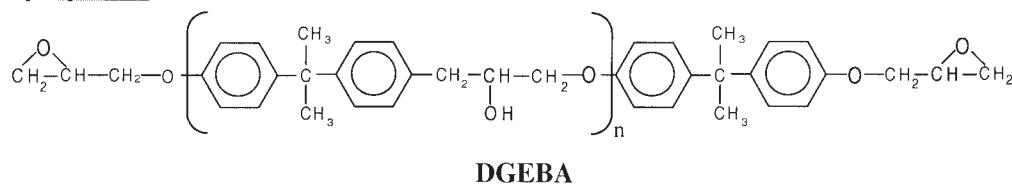
$$(1 - X) = (1 - x)^2 \quad (2)$$

Then the epoxy conversion can be calculated by the following equation:

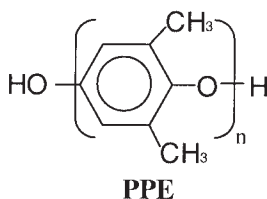
$$x = 1 - \left(\frac{A_t}{A_0} \right)^{1/2} \quad (3)$$

LMW-PPE is quite soluble in THF. The PPE soluble fraction can be easily measured by integration of its corresponding peak in the different blend solutions. These results were also checked by mass loss, with similar results.

Epoxy resin:



Thermoplastic:



Imidazoles:

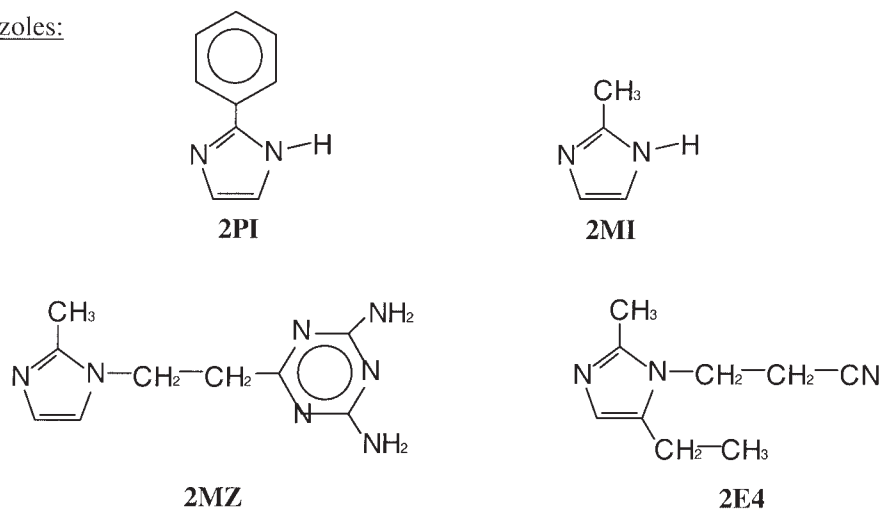


Figure 1 Chemical structures of epoxy monomer (DGEBA), poly(phenylene ether) (PPE), and the different imidazoles (2MI, 2PI, 2MZ, and 2E4).

Blend morphologies were examined by environmental scanning electron microscopy (ESEM, Phillips XL30; Eindhoven, The Netherlands) and transmission electron microscopy (TEM, JEM-200cX; Eindhoven, The Netherlands), over samples cured isothermally

(80°C during 1 hr followed by a postcuring at 150°C during 30 min). With this procedure, reached conversion is comparable to the one obtained by dynamic DSC scan. Samples were observed by ESEM without any coating at 0.7–1.0 torr of vapor pressure (approx-

TABLE I
Main Characteristics of Different Compounds Used

| Compound | Supplier | Molar mass (g/mol) | State |
|----------|-------------------------------------------------|-------------------------------------------------|---------------------------------------|
| DGEBA | Vantico, USA (LY556) | 382.6 ($\bar{n} = 0.15$) (191.3g/eq.epoxy) | Liquid (T _g = -25°C) |
| PPE | General Electric Plastics, USA (PPO857) | 2520 ($\bar{n} \approx 21$) (1260g/eq.OH) | Amorphous (T _g = 163°C) |
| 2MI | Aldrich, USA | 82 | Solid |
| 2PI | Aldrich | 144 | Solid |
| 2MZ | Anchor Chemical, India (CUREZOL 2MZ-AZINE-S) | 219 | Liquid |
| 2E4 | Anchor Chemical (CUREZOL 2E4-CN) | 151 | Liquid |

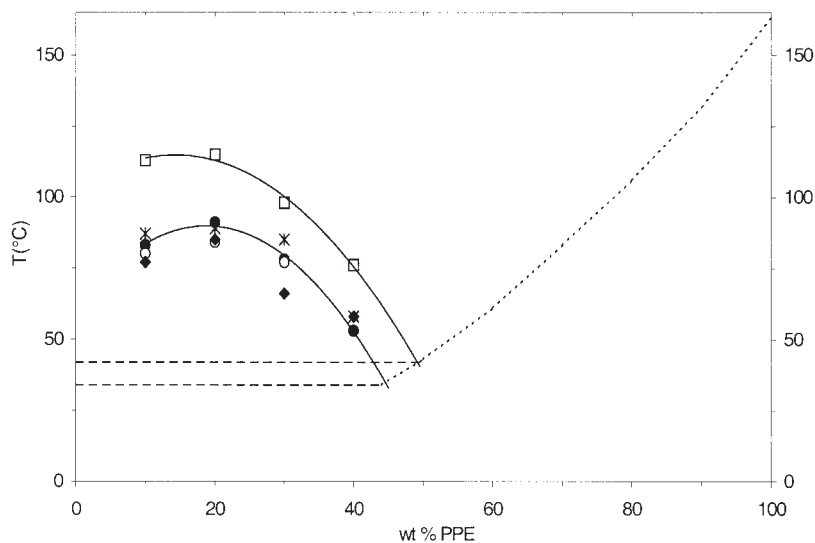


Figure 2 Initial phase diagram of LMW-PPE/DGEBA solution (\bullet) and with 5 wt % of different imidazoles: 2MI (\circ), 2PI (\blacklozenge), 2E4 (\times), and 2MZ (\square). Cloud point curves (—) and calculated vitrification curve (---).

mately 5% relative humidity). Phase inverted blends were immersed in THF before observation to expose the embedded spherical epoxy particles. Ultrathin sections of samples for TEM observation were prepared at room temperature. A contrast existed between phases when a 80kV accelerating voltage was used. The measurements of particles' diameter were carried out using an image analyzer (Image Pro-Plus version 3.0; Media Cybernetics, Silver Spring, MD).

RESULTS AND DISCUSSION

Initial phase diagram

The miscibility of PPE/DGEBA with and without imidazole prior to reaction is shown in Figure 2. The

cloud points were determined by light transmission, and the vitrification curve was calculated by Fox relationship.²² The cloud point curves exhibit an upper critical solution temperature (UCST) behavior, commonly observed for polymer-solvent system. Relative low temperatures, between 80 and 120°C, are required to obtain homogeneous solutions. The cloud point temperatures reported in the literature^{4,15} for high molar mass PPE/epoxy blends are in the range of 160°C. As expected, the decrease in the PPE molar mass enhances the miscibility of the system, resulting in a considerable shift of the cloud point curve to lower temperatures. The phenol end functionality of PPE also helps to increase the compatibility with DGEBA. When 2PI, 2MI, and 2E4 imidazole initiators

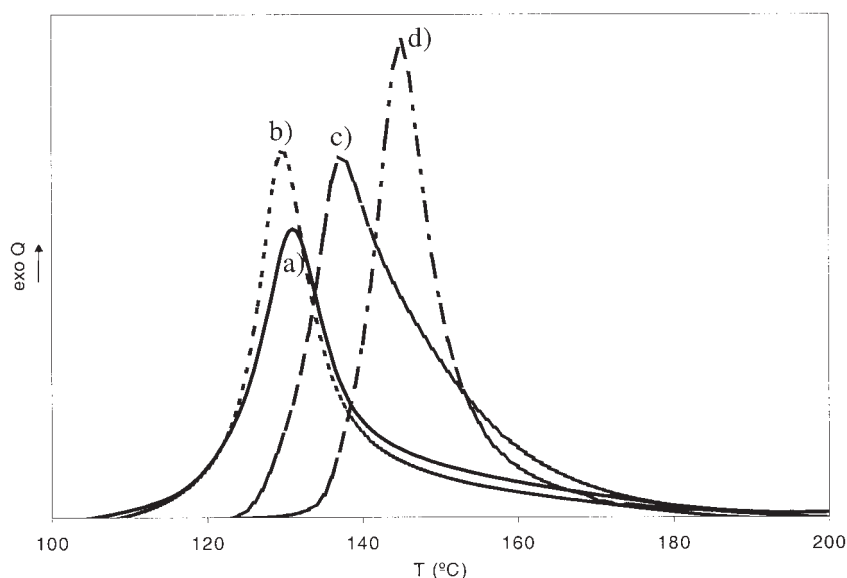


Figure 3 Thermograms of DGEBA with 5 wt % of imidazole: a) 2MI, b) 2PI, c) 2E4, and d) 2MZ.

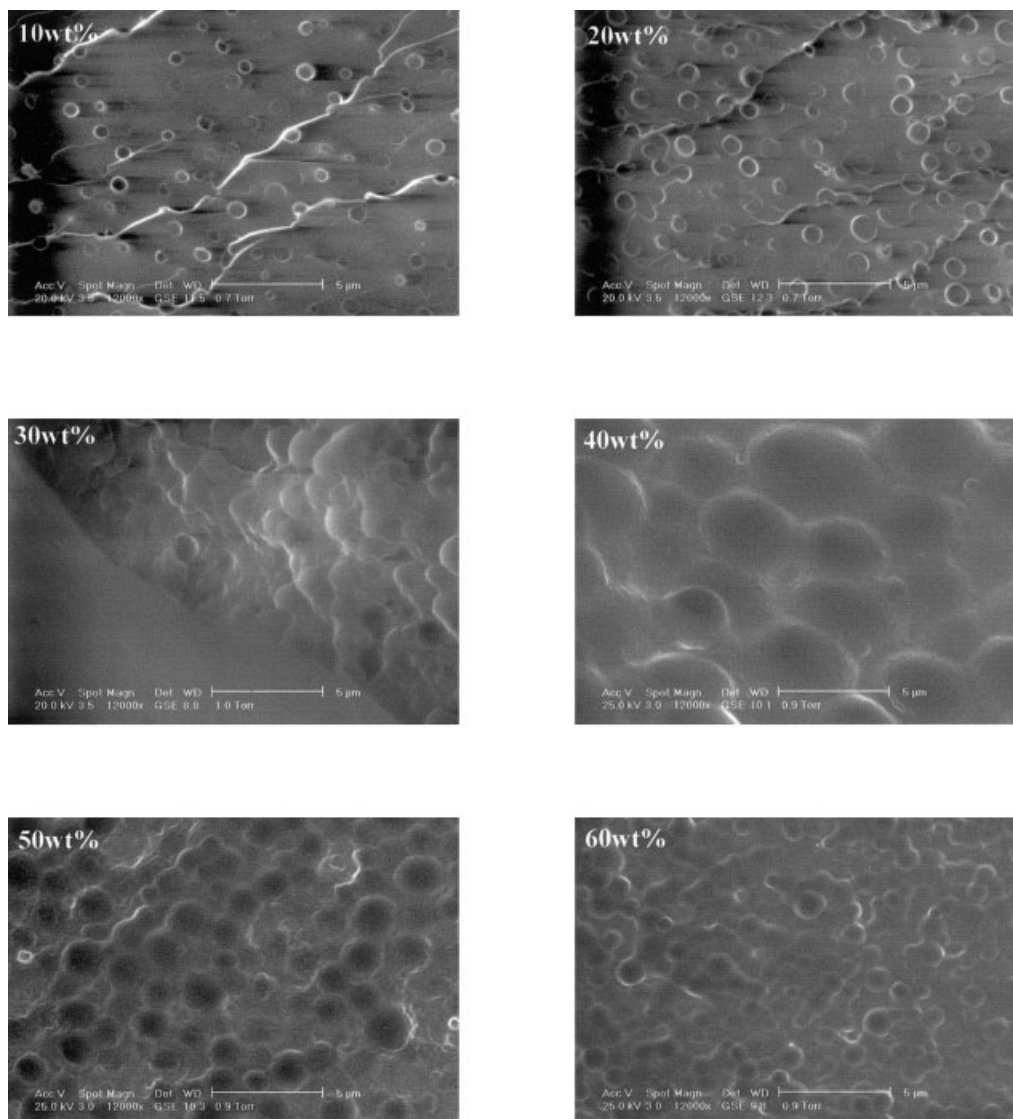


Figure 4 SEM micrographs of DGEBA/PPE/5 wt % 2E4 with different PPE contents (10–60 wt %).

are added, the obtained cloud point curves are similar to the DGEBA/LMW-PPE solution itself. Therefore, the initial blend miscibility is not affected by the presence of a low quantity of initiators. However, for samples with 2MZ, the cloud point curve shifts to higher temperatures. This imidazole has amino groups, which are able to react rapidly with epoxy, raising the average molar mass of the precursors and decreasing the PPE miscibility. The intersection of the cloud point and vitrification curves is called Berghmans point²³ and corresponds to a PPE percentage of approximately 50 wt %. This value is again lower than that reported¹⁷ for HMW-PPE/DGEBA blends due to the shift of the cloud point curve to lower temperatures and the decrease of the thermoplastic T_g . As a result of this intersection point, the phase diagram can be divided into two regions. At lower PPE content, phase separation process is achieved. The obtained

materials are heterogeneous with two phases (epoxy-rich and PPE-rich). The T_g and composition of PPE-rich phase should be defined by the Berghmans point. The second region is at higher PPE content. In this case, the PPE-rich phase vitrification will occur before phase separation, and solutions obtained out of equilibrium are homogeneous over the entire temperature range, which T_g s depend on the composition.

Kinetic measurements

The curing of neat DGEBA with 2 and 5 wt % of the different imidazoles was analyzed. Figure 3 compares the thermograms obtained for the same (%wt) initiator composition. Only one exothermic peak, corresponding to epoxy homopolymerization, was observed. With 2MI and 2PI, the reaction takes place at similar temperature, and the peak temperature is about

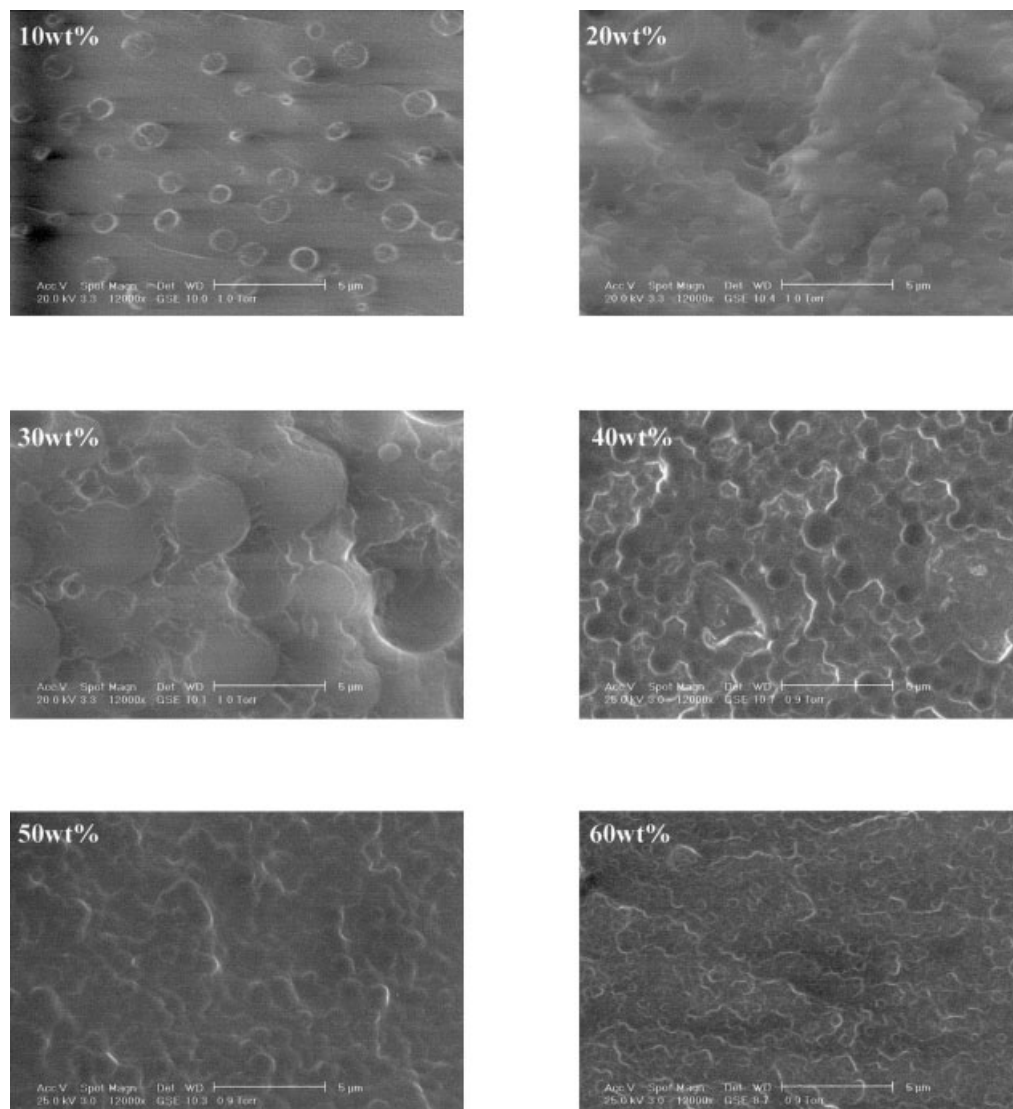


Figure 5 SEM micrographs of DGEBA/PPE/5 wt % 2MZ with different PPE contents (10–60 wt %).

130°C. For 2E4 and 2MZ, the peak shifts to higher temperature. This observation can be explained by the presence of cyano group in 2E4 molecule¹¹ and the triazine group in 2MZ. The inductive effect, present in both substituents, probably influences the reactivity of the pyridine-type nitrogen.

The exothermal peak shifts to lower temperatures with increasing imidazole concentration for all the initiators analyzed, showing the enhanced reaction rate with increasing initiator concentration.

In all cases, the obtained reaction enthalpy is lower than 100kJ/eq.epoxy, attributed value for complete epoxy cure, which is only obtained with 1-methylimidazole. This effect has been observed by other authors^{8,9} and is attributed to the fact that the network exhibits a lower reaction degree when 2MI and 2PI are used as initiators. With 2E4 and 2MZ, the reaction enthalpy is even lower, involving a lower conversion

and therefore, less effectiveness as initiator of *N*-alkyl imidazoles. This fact is reflected in the reached T_g s. When 2MI and 2PI are used as initiators, the T_g of the cured sample is about 135°C, and this value falls to 110 and 102°C when 2E4 and 2MZ are employed, respectively. In DGEBA/2MZ mixture, the reaction enthalpy is even lower due to the presence of amine groups. During this sample preparation, epoxy-amine reaction can occur, preventing the imidazole regeneration. Therefore, the measurements only correspond on the homopolymerization of residual epoxies.

Isothermal cloud point measurements at 120°C were obtained for samples of DGEBA with different PPE amounts and 5 wt % of initiator. After phase separation, samples were immediately immersed into liquid nitrogen to stop the reaction, and conversion at the cloud point was measured by SEC. The epoxy conversion is in any case about 0.25–0.30; except for samples

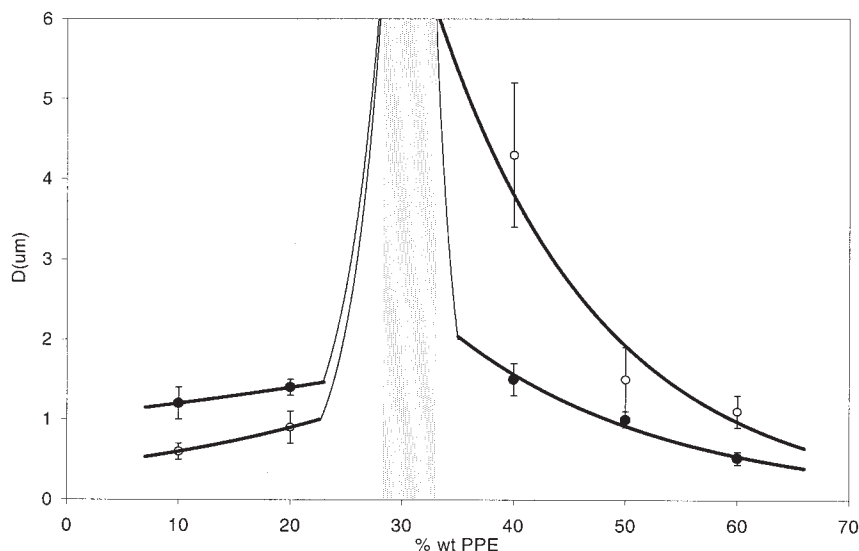


Figure 6 Average particle diameter and dispersion (in μm) as a function of the blend composition for samples DGEBA/PPE with 2E4 (\circ) and 2MZ (\bullet) as initiators.

with 2MZ, for which the phase separation occurs at lower epoxy conversion. This behavior can be related to the formation of bonds between the imidazole amine and epoxy groups, which prevent initiators' regeneration.

Cured samples

Figures 4 and 5 show scanning electron micrographs for DGEBA/LMW-PPE blends, cured with 5 wt % of 2E4 and 2MZ, respectively. The average particle diameter is presented in Figure 6 as a function of PPE content. The morphology observed is similar in both systems. At low PPE content (< 30 wt %), there are PPE-rich particles segregated in an epoxy continuous matrix. Nevertheless, some differences are observed on the fracture surface. The surface brittleness seems to be reduced when 2MZ is used compared to the sample cured with 2E4. As it was pointed out before in the neat epoxy/imidazole systems, the 2MZ initiator chemically links to the epoxy precursor, leading to the lowest final epoxy conversion. Then, its network has to be more flexible and with higher toughness than the one obtained with 2E4.

As expected,^{1,2} the particle size of the segregated phase increases with the PPE amount (Fig. 6) and tends to infinity at the PPE critical composition, where a bi-continuous morphology should be obtained. Above 30 wt % PPE content, the phase inversion occurs and the blends are constituted by PPE-rich matrix with segregated epoxy-rich particles. This change is emphasized by the different surface topology observed. As long as the PPE content moves away from the critical composition, a decrease on the diameter of the epoxy-rich particles is observed.

Using a thermodynamic model¹ based on the Flory–Huggins–Staverman approach, the critical composition of the blend (before reaction), $\phi_{TP, crit}$ can be calculated with the molar mass of the polymeric components. The obtained value for our DGEBA/PPE blend, expressed as a thermoplastic mass fraction, is 30 wt %. Therefore, good agreement is found with the experimental results.

Transmission electron micrographs for DGEBA/PPE/5 wt % 2E4 system are shown in Figure 7. According to theoretical predictions and SEM images, the inversion phase appears at 30 wt % PPE. At this PPE percentage, a complex structure can be seen with small epoxy nodules in a PPE-rich matrix and some large epoxy domains of the order to $30\mu\text{m}$ containing PPE subinclusions. This morphology is typical of a blend composition close to the critical composition.^{24,25}

The segregated PPE particles observed below the critical composition present quite different aspect if they are compared with HMW-PPE/DGEBA-diamine blends morphology.^{4,16} PPE-rich phases clearly show substructures inside, meaning the phenol chain ends of the thermoplastic can react with unreacted epoxy groups, enhancing the chemical linkage between phases. In comparison with reported nonreactive PPE/epoxy systems, the phenol-epoxy reaction gives rise to an improved interfacial bonding. The formation of this “copolymer” will most probably also work as a compatibilizer and, therefore, will somewhat reduce the final epoxy particle size in the blend.

Analysis by SEC of soluble fraction in cured samples will give information about nonreacted DGEBA and also about PPE soluble fraction. The idea was to confirm the reaction between LMW-PPE and epoxy

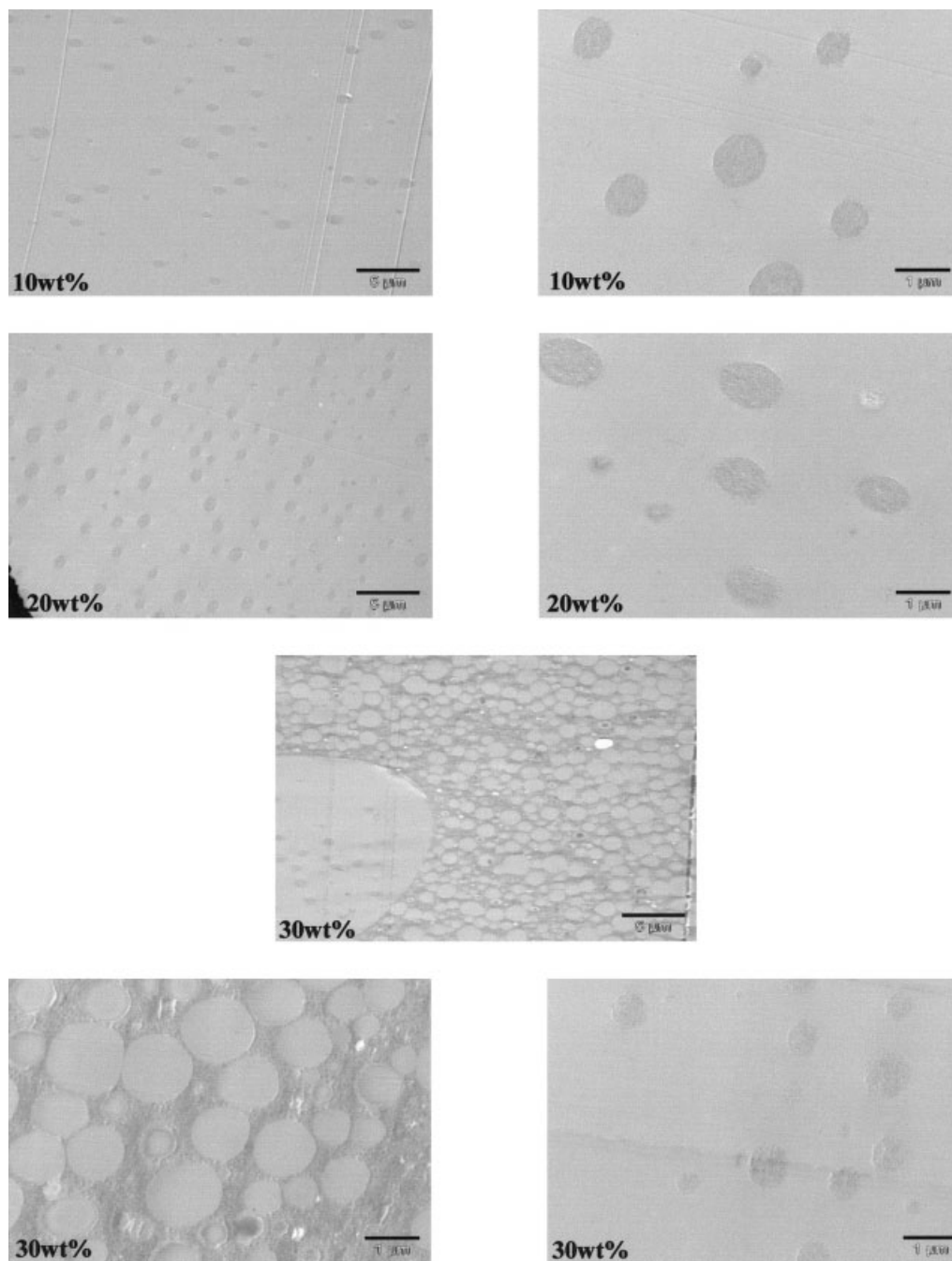


Figure 7 TEM micrographs of DGEBA/PPE/5 wt % 2E4 with different PPE content (10–30 wt %).

network. Figure 8 shows the obtained results for DGEBA/PPE/5 wt % imidazole blends. Both PPE soluble fraction and epoxy conversion are presented as functions of thermoplastic content. PPE soluble fraction increases continuously. Below the critical composition, PPE soluble fraction is very low, but the behavior changes at and above 30 wt %, where it increases very rapidly. This behavior does not seem to be affected by the imidazole structure. The nonsoluble PPE fraction can be caused only by the reaction between phenol groups and epoxy, attaching at the network.

These results agree with the observed morphology of blends, where the segregated PPE-rich phase presented substructures inside. The PPE percentage reacted with epoxy network is compiled in Table II. At low PPE content, more than 95% of PPE molecules react with epoxy matrix. When phase inversion occurs, part of PPE reacts with epoxy groups, but there are thermoplastic chains not attached to the network. In Figure 9, T_g of PPE-rich phase is shown for the different blends. No great differences are observed, after and before critical composition. The T_g for the

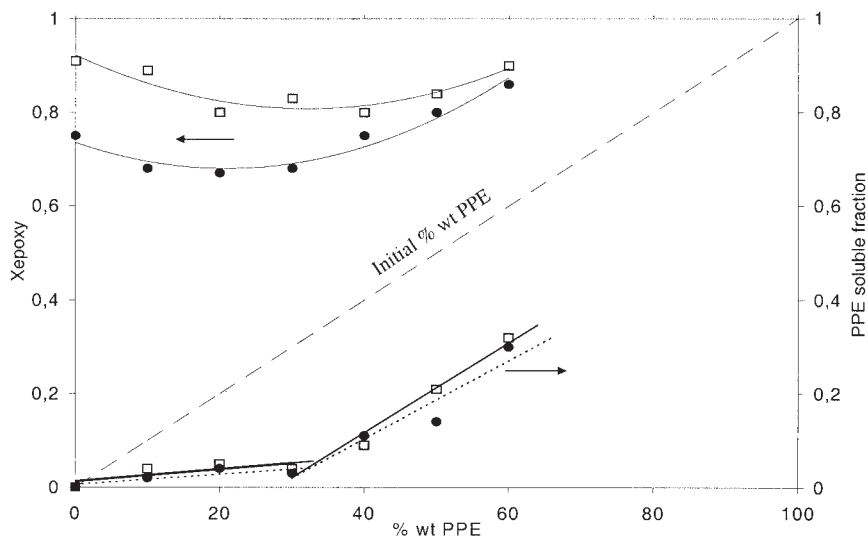


Figure 8 PPE soluble fraction and reached epoxy conversion in function of PPE content for cured samples with 5 wt % 2E4 (\square) and 2MZ (\bullet).

blend obtained by epoxy homopolymerization initiated by 2E4 is at all times higher than that observed for samples where 2MZ was used as initiator. Since no significant changes were observed on the PPE amount attached to the epoxy (Table II), this fact means that the thermoplastic-rich phase is plasticized by unreacted monomers when 2MZ is used as initiator.

Figure 8 also shows the reached epoxy conversion versus composition, taken from the soluble DGEBA fraction by SEC. Samples with 2E4 initiator always reach higher conversion than samples with 2MZ, in agreement with DSC results over neat epoxy/imidazole systems. The observation of the reached conversion joined with the T_g of the PPE-rich phase permits explanation of the different domain sizes observed in Figure 6. Lower conversion implies a lower viscosity and a lower crosslinking density, allowing better diffusion of DGEBA nonreacted species, which is the case of 2MZ compared to 2E4 initiator. Below the critical composition, PPE segregates in higher domain sizes

for 2MZ because the fraction of residual monomer on the PPE-rich phase is higher, according to the plasticizing effect observed on the measured T_g . Above the critical composition, the higher solubility of DGEBA in the PPE-rich phase leads to lower domain size of epoxy-rich phase when 2MZ is used as initiator.

CONCLUSION

Blend of low molar mass PPE and DGEBA were studied, exhibiting a typical upper critical solution temperature (UCST) behavior. The low molar mass and phenol chain ends of PPE enhance the miscibility, leading to critical temperatures far below those reported for PPE/DGEBA blends. The initial phase diagram is not affected by the addition of a low imidazole concentration, except when amine groups are present. They produce an increase of cloud point temperatures, due to the reaction with epoxy precursor.

The 1-substituted alkyl-imidazoles, 2MI and 2MZ, if used as epoxy homopolymerization initiators, are less effective than 1-unsubstituted imidazoles. If amine reactive groups are present on the substituent, the reaction with DGEBA prevents catalyst regeneration leading to even lower conversions.

In DGEBA/PPE blends crosslinked by imidazole anionic polymerization, phase separation occurs at about 30% conversion. Imidazoles are also able to catalyze the reaction between phenol chain-ends of the PPE with the epoxy groups, allowing the formation of chemical links between the thermoplastic and the epoxy network only when the thermoplastic concentration is below the critical composition. Above the critical composition the fraction of nonreacted PPE chains increases rapidly.

TABLE II
PPE Percentage Attached to Epoxy Network with Respect to the Total Mass (X_{PPE}) and with Respect to Added PPE Amount (x_{PPE}), for DGEBA/PPE with 5 wt % of 2E4 and 2MZ

| %PPE | 2E4 | | 2MZ | |
|------|-----------|-----------|-----------|-----------|
| | X_{PPE} | x_{PPE} | X_{PPE} | x_{PPE} |
| 10 | 9.6 | 96 | 9.8 | 98 |
| 20 | 19.0 | 95 | 19.2 | 96 |
| 30 | 28.8 | 96 | 29.1 | 97 |
| 40 | 36.4 | 91 | 35.6 | 89 |
| 50 | 39.5 | 79 | 43.0 | 86 |
| 60 | 40.8 | 68 | 42.0 | 70 |

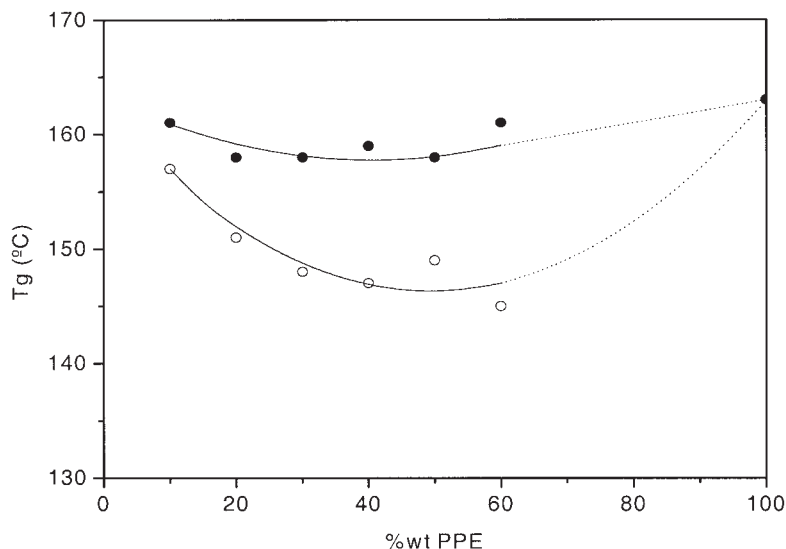


Figure 9 Tg of thermoplastic rich phase as a function of PPE content for blends DGEBA/PPE with 5 wt % 2MZ (○) and 2E4 (●).

The analysis of the final blend morphology reveals domains of about $1\mu\text{m}$ diameter dispersed in a continuous matrix. Phase inversion appears at thermoplastic concentrations about 30 wt %, independent of catalyst employed. Above critical composition epoxy nodules are dispersed into the continuous PPE-rich phase. Below critical composition the phase dispersed is mainly PPE. Analysis by TEM microscopy along with the study of the PPE soluble fraction reveals the chemical link between the thermoplastic and the network. The epoxy conversion at the cloud point is affected by the reactivity of the initiator used, and strongly influences the domain size of phase separated blends. Lower conversion at phase separation leads to higher PPE-rich and lower epoxy-rich particles below and above the critical composition, respectively.

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References

- Pascualt, J. P.; Williams, R. J. J. In *Polymer Blends, Volume 1: Formulation*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 1999; pp 380–412.
- Bonnet, A.; Pascualt, J. P.; Sautereau, H.; Taha, M.; Camberlin, Y. *Macromolecules* 1999, 32, 8517, 8524.
- Bonnaud, L.; Pascualt, J. P.; Sautereau, H. *Eur Polym Mater* 2000, 36, 1313.
- Venderbosch, R. W.; Meijer, H. E. H.; Lemstra, P. J. *Polymer* 1994, 35(20), 4349; 1995, 36(6), 1167; 1995, 36, 2903.
- Merfeld, G. D.; Yeager, G. W.; Chao, H. S.; Singh, N. *Polymer* 2003, 44, 4981.
- Girard-Reydet, E.; Vicard, V.; Pascualt, J. P.; Sautereau, H. *J Appl Polym Sci* 1997, 65, 2433.
- Hoppe, C. E.; Galante, M. J.; Oyanguren, P. A.; Girard-Reydet, E.; Pascualt, J. P. *Polym Eng Sci* 2002, 42, 12.
- Ooi, S. K.; Cook, W. D.; Simon, G. P.; Such, C. H. *Polymer* 2000, 41, 3639.
- Heise, M. S.; Martin, G. C. *Macromolecules* 1989, 22, 99.
- Baron, J. M.; Harmerton, I.; Howlin, B. J.; Jones, J. R.; Liu, S. *Polymer* 1998, 39, 1929.
- Bouillon, N.; Pascualt, J. P.; Tighzert, L. *J Appl Polym Sci* 1989, 38, 2103.
- Chen, Y. C.; Chiu, W. Y. *Polymer* 2001, 42, 5439.
- Girard-Reydet, E.; Riccardi, C. C.; Sautereau, H.; Pascualt, J. P. *Macromolecules* 1995, 28, 7599, 7608.
- Girard-Reydet, E.; Sautereau, H.; Pascualt, J. P.; Keates, P.; Navard, P.; Thollet, G.; Vigier, G. *Polymer* 1998, 39, 2269.
- Jansen, B. J. P.; Rastogi, S.; Meijer, H. E. H.; Lemstra, P. *Macromolecules* 1999, 32, 6290.
- Poncet, S.; Boiteux, G.; Pascualt, J. P.; Sautereau, H.; Seytre, G.; Rogozinski, J.; Kranbuehl, D. *Polymer* 1999, 40, 6811.
- Jansen, B. J. P.; Meijer, H. E. H.; Lemstra, P. J. *Polymer* 1999, 40, 2917.
- Jana, S. C.; Patel, N.; Dharaia, D. *Polymer* 2001, 42, 8681.
- Hedrick, J. C.; Patel, N. M.; McGrath, J. E. In *Toughened Plastics I*; American Chem Society: Washington, 1993.
- Verchere, D.; Sautereau, H.; Pascualt, J. P.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. *Polymer* 1989, 30, 107.
- Verchere, D.; Sautereau, H.; Pascualt, J. P.; Riccardi, C. C.; Moschiar, S. M.; Williams, R. J. J. *Macromolecules* 1990, 23, 725.
- Fox, T. G. *Bull Am Phys. Soc.* 1956, 1, 123.
- Vanderweerd, P.; Berghmans, H.; Tervoot, Y. *Macromolecules* 1991, 24, 3547.
- Ritzenthaler, S.; Girard-Reydet, E.; Pascualt, J. P. *Polymer* 2000, 41, 6375.
- Varley, R. J.; Hodgkin, J. H.; Hawthorne, D. G.; Simon, G. P.; McCulloch, D. *Polymer* 2000, 41, 3425.