Processing of intractable polymers using reactive solvents: 1. Poly(2,6-dimethyl-1,4-phenylene ether)/epoxy resin

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A new processing route for poly(2,6-dimethyl-1,4-phenylene ether) (PPE), an intractable polymer on account of its thermal and oxidative sensitivity, was explored. PPE can be dissolved at elevated temperatures in epoxy resin and these solutions can then be processed at temperatures as low as 175°C. For solutions of PPE with a molecular weight of 10, 20 and 30 kg mol^{-1}, the phase diagram and the flow curves in the homogeneous region were determined. The upper critical solution temperature (*UCST*) cloud point curves intersect the glass transition–composition lines at a PPE content of ~70 wt%. Below this composition, thermoreversible gelation is observed upon cooling which prevents complete phase separation. Curing of the homogeneous solutions, using diethyltoluene diamine, resulted in virtually complete phase separation. In the composition range that was studied (30–70 wt% PPE), the chemically induced phase separation is accompanied by phase inversion, yielding a final morphology of epoxy spheres dispersed in a PPE matrix. Thus, after processing, the (reactive) solvent is converted into a dispersed phase. The mechanical and thermal properties of the final materials, such as toughness and glass transition temperature, are dominated by the continuous PPE matrix.

(Keywords: intractable polymers; epoxy resin; reactive solvent))

INTRODUCTION

Synthetic polymeric materials are being increasingly used to substitute or to supplement more traditional materials. In order to be successfully applied as engineering plastics, the selected materials should possess properties such as high dimensional stability (i.e. a high glass transition temperature), toughness and strength. The development of high-temperature-resistant thermoplastic polymers is, however, often intrinsically limited by the occurrence of degradation during processing at the high temperatures that are required and many high-T_g polymers are, in fact, intractable.

A classical example of an intractable polymer is poly(2,6-dimethyl-1,4-phenylene ether) (PPE), an amorphous thermoplastic with a high T_g (220°C) and excellent mechanical properties, especially toughness. The high T_g, however, requires processing to be carried out in the 300–350°C temperature range. Due to the oxidative and thermal sensitivity of PPE, processing in this temperature range results in severe degradation, and therefore PPE could be classified as intractable. For this reason, PPE in practice is only applied in blends, notably the miscible system PPE/high-impact polystyrene (HIPS). This unique homogeneous polymer blend is available in various compositions that all exhibit a lower T_g than PPE itself and subsequently allows for considerably lower processing temperatures, thus avoiding degradation. Mixing with PS decreases the T_g of the final product and is, consequently, a compromise technique for introducing processability to PPE.

High processing temperatures can be avoided by using solution processing techniques. With these techniques, however, the solvents have to be extracted and recycled after processing and the application is strictly limited to products with a high surface-to-volume ratio, such as, e.g. coatings, fibres and prepregs for composite applications. A challenging solution to these problems can be found in the use of reactive solvents which, after processing, are polymerized into a constituent of the final material. Nelissen *et al.*[1], for example, presented a new route to prepare blends of polystyrene and PPE, which was based on the use of the styrene monomer as a reactive solvent. This chemical blending technique avoids the generally used extrusion blending step at high temperatures, thus avoiding degradation, and is successfully applied to prepare high-T_g foams.

Epoxy resins, such as the diglycidyl ethers of bisphenol-A, may also be classed as reactive solvents. In the literature[2–14], it is reported that epoxy resins are excellent solvents for most of the common high performance plastics, such as poly(ether sulfone), poly(ether ketone), poly(ether imide) and poly(phenylene ether). These studies are usually aimed at the improvement of the toughness of the epoxy resins. The general ideas behind these investigations are similar to the conventional liquid rubber toughening of epoxy resins and involve phase separation of the thermoplastic additive (nominally <30 wt%) during curing, which may result in a morphology of dispersed thermoplastic particles in an epoxy

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matrix. When compared to conventional rubber toughening, the dispersed thermoplastic particles are less capable of initiating yielding in the epoxy matrix. Therefore, this technique is mainly applied in highly crosslinked, high-T_g epoxy systems which are not capable of yielding, and consequently depend on secondary toughening mechanisms, such as particle tearing and crack bifurcation. One interesting phenomenon described in these investigations is that upon increasing the concentration of the thermoplastic modifier, the morphology will change via a co-continuous structure into a phase-inverted morphology of dispersed epoxy particles in a continuous thermoplastic matrix[3,6,8,9,12].

Both characteristic phenomena, i.e. *epoxy resin as a reactive solvent* and *phase inversion* during cure, have been adopted in order to explore a new processing route for a number of intractable thermoplastic polymers. This concept, in which a thermoset is used to tune the processing characteristics of the thermoplastics, is characterized by a number of sequential steps. First, the thermoset resin is applied as a solvent during processing, which reduces the viscosity and the required processing temperature, thus enhancing the processability. Secondly, upon curing, phase separation is initiated. At a sufficiently high thermoplastic concentration, this phase separation is accompanied by phase inversion and the thermoset resin is converted into a dispersed phase. Due to the final morphology, i.e. a thermoplastic which is filled with small thermoset particles, the resulting material characteristics are dominated by the continuous thermoplastic phase.

In this paper, the reactive processing route was studied for the case of PPE by using a standard bisphenol-A based epoxy resin as a reactive solvent. In order to gain information concerning the miscibility of PPE and epoxy resins, the PPE/epoxy system was first studied in the absence of curing agents. Secondly the curing agent was incorporated into the system, and some preliminary results concerning the curing, morphology and mechanical properties of the resulting materials are presented.

EXPERIMENTAL

Materials and blend preparation

Two types of poly(2,6-dimethyl-1,4-phenylene ether) (PPE), with a viscosity-average molecular weight of 30 and 18 kg mol^{-1}, and a molecular-weight distribution (M_w/M_n) of 2.5 and 2.2, respectively, were supplied by General Electric Plastics (Bergen op Zoom, The Netherlands). A further two types of PPE, with a viscosity-average molecular weight of 20 and 10 kg mol^{-1}, and a distribution of 3.1 and 2.0, respectively, were prepared in our laboratory by precipitation polymerization[15]. The reactive solvent selected was a standard diglycidyl ether of bisphenol-A (DGEBA, Epikote 828EL), supplied by Shell (Amsterdam, The Netherlands).

Solutions of PPE in epoxy resin, with a PPE content $\leqslant$20 wt%, were prepared by dissolving PPE in the resin by using a mechanical stirrer at temperatures $\leqslant$200°C. Epoxy/PPE solutions with a PPE content $>$20 wt% were prepared in a Brabender Plasticorder Kneader (with a volume of 60 cm^3). At a temperature of 175°C, a kneading time of approximately 1 h was required to obtain transparent homogeneous solutions. (This mixing time can be reduced to $\sim$5–10 min (residence time) by using a co-rotating twin screw extruder.)

The solutions were cured by using diethyltoluene diamine (DETDA, Ethacure 100, Ethyl Corporation). The curing agent was added to the homogeneous solution in the Brabender kneader, and after mixing for $\sim$2 min, the compound was compression moulded and cured. A curing cycle of 2 h at a variable temperature of 150, 175, 200 or 225°C was applied, followed by a post-cure treatment for 4 h at 200°C in an inert atmosphere.

Miscibility and rheology of epoxy/PPE solutions

In order to determine the miscibility of the epoxy resin and PPE, specimens with various PPE contents and molecular weights were placed into a hot cell between glass slides. Upon controlled cooling of the cell (1°C min^{-1}), the onset of phase separation, i.e. the cloud point temperature, was determined by using laser light scattering (at 488 nm). For solutions containing more than 70 wt% PPE, the glass transition temperature was determined by using dynamic mechanical thermal analysis (d.m.t.a.) (MkII, Polymer Laboratories). The samples were analysed in the tensile mode (1 Hz), using a heating rate of 3°C min^{-1}.

The dynamic rheological behaviour of the homogeneous solutions was studied by using a Rheometrics RDSII spectrometer. A parallel-plate test set up was applied in order to determine the dynamic viscosity in the frequency range 0.05–200 rad s^{-1} for several temperatures in the miscible temperature window up to 220°C. Depending on the absolute viscosity of the solution, a plate diameter of 25 or 50 mm, a gap distance of 0.5–2 mm, and a maximum strain of 3%, was applied. Finally, the complete flow curves were constructed by shifting the measured curves to a reference temperature of 170°C, according to the time–temperature superposition principle.

Morphology

The morphology of solutions that had been cooled from 200°C to room temperature (at a rate of 1°C min^{-1}) was determined by using scanning electron microscopy (SEM) (Cambridge Stereoscan 200). Depending on the molecular weight of the type of PPE applied, samples were prepared by either cryogenic cutting or breaking. The samples were etched for 10 min in an oxygen plasma and were finally coated with a gold/palladium alloy.

The morphology of the cured materials was studied at fracture surfaces that had been generated in the mode-I fracture toughness experiments (see below). The samples were coated with a gold/palladium alloy. No additional staining techniques were applied.

Mechanical analyses

The tensile modulus and strength of the cured materials were determined according to ASTM 638. Edge-polished specimens (180 × 13 × 2 mm^3) were tested on a Frank tensile tester (81565 IV), at a constant strain rate of 10^{-3} s^{-1} at room temperature.

The mode-I fracture toughness of the cured materials was determined by using the single-edge notched bend specimen geometry[16]. A sharp notch was machined and sharpened with a razor blade (total depth = 5 mm). The specimens (50 × 10 × 5 mm^3) were tested by using a span-to-depth ratio of 4 and a crosshead speed of 10 mm min^{-1} at room temperature.

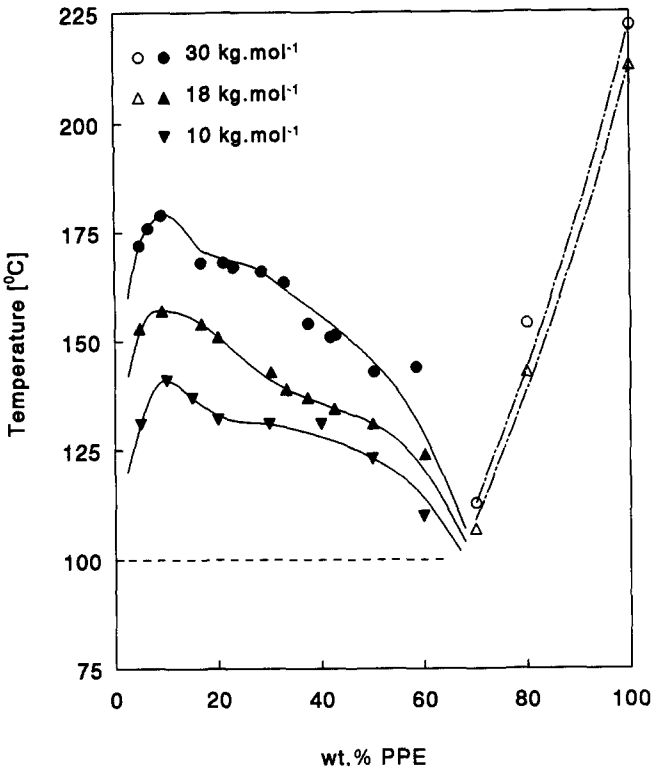

Figure 1 Phase diagram of PPE/Epikote 828EL solutions: (—) cloud point curves; (—·—) calculated T_g–composition lines; (----) T_g due to thermoreversible gelation

RESULTS AND DISCUSSION

As mentioned in the Introduction, prior to the curing experiments of the PPE/epoxy systems, the miscibility and solution characteristics of PPE in epoxy resin were investigated.

Miscibility and morphology of epoxy/PPE solutions

The results of the light scattering experiments are presented in *Figure 1*. It is observed that rather high temperatures are required to obtain homogeneous solutions of PPE in the epoxy resin. The cloud point curves exhibit a typical upper critical solution temperature (*UCST*) behaviour, commonly observed for polymer–solvent systems. As expected, a decrease in the PPE molecular weight enhances the miscibility of the system and results in a considerable shift of the cloud point curve to lower temperatures. Since PPE, as well as the epoxy resin, is polydisperse, the cloud point curves may not be regarded as binodal curves and do not give any information about the composition of the coexisting phases. The twist in the cloud point curves clearly reveals the influence of the molecular-weight distribution, i.e. the critical point is not situated at the top of the curves.

The T_g–composition lines of the system are also plotted in *Figure 1*. These lines were determined experimentally using d.m.t.a. (the markers represent the T_gs as found for solutions with a PPE content of 70 and 80 wt%) and were calculated according to the equation of Fox[17], using T_gs of 222 and 213°C for PPE with a molecular weight of 30 and 18 kg mol^{-1}, respectively, and a T_g of −18°C for the epoxy resin monomer. As demonstrated in *Figure 1*, these lines intersect the cloud point curves at a PPE content of ~70 wt%. This intersection point, described by Vandeweerdt *et al.* for the atactic poly(methyl methacrylate)/1-butanol system[18], has several important consequences. Solutions containing less than 70 wt% PPE will show phase separation upon cooling. However, complete phase separation cannot occur, due to the fact that the phase separation process will be arrested as soon as the PPE-rich phase vitrifies (at a PPE content of 70 wt%). As a result of this phenomenon, which physically can be regarded as a reversible gelation[18], all of the phase separated solutions will exhibit a T_g of ~100°C, schematically represented in *Figure 1* by the dashed horizontal line. Solutions with a PPE content exceeding 70 wt% will vitrify upon cooling before any phase separation can occur, and are homogeneous over the entire temperature range.

The morphology of solutions cooled from 200°C to room temperature (at a rate of 1°C min^{-1}), which differ in PPE content and molecular weight, is shown in *Figure 2*. In the scanning electron micrographs of samples containing ≥30 wt% PPE, a phase inverted morphology of epoxy resin droplets in a continuous PPE matrix is present. The concentration at which phase inversion occurs is in the range 15–25 wt%. This low concentration can be attributed to the fact that the occurrence of phase inversion is related to the volume ratio of the co-existing phases, and not to the absolute PPE content, as is normally assumed for immiscible polymer blends[19]. With increasing PPE content, a significant decrease in the diameter of the dispersed epoxy droplets is observed. This effect is related to the kinetic hindrance of the coarsening process of the spinodal demixed solution[20]. An increase in the viscosity of the solution, or an increase in the cooling rate, significantly retards the coarsening process and thus results in a less coarse morphology. The viscosity effect is enhanced by the additional decrease in cloud point temperature, or the decrease in temperature at the instant of phase separation. In accordance with the phase diagram presented in *Figure 1*, no phase separation can be distinguished in the scanning electron micrographs of solutions with a PPE content exceeding 70 wt%. Despite the pronounced influence of the PPE molecular weight on the miscibility, a significant influence of this molecular weight on the morphology of the phase separated solutions is not observed.

Rheology of epoxy/PPE solutions

The constructed master curves of epoxy/PPE solutions varying in PPE content and molecular weight are presented in *Figure 3*. These curves clearly exhibit the typical shear-thinning behaviour which is commonly observed for semi-dilute polymer solutions[21,22]. With an increasing epoxy content, or a decreasing PPE molecular weight, a strong decrease in the solution viscosity is observed. Additionally, the rheological characteristics assume a more pronounced Newtonian form as a result of the gradual decrease of the solution entanglement network density. This facilitates relaxation of the polymer chains and results in a shift of the onset of shear thinning to higher frequencies.

The results of the rheological measurements are summarized in *Figure 4*. In this plot, an overview of the zero-shear viscosities of the epoxy/PPE solutions is presented. For a high PPE content of, e.g. 70 wt%, the solutions based on a commercial grade PPE, with a molecular weight of 30 kg mol^{-1}, exhibit a rather high zero-shear viscosity. However, this viscosity, similar to that of standard polymer melts, is obtained at a low temperature, i.e. 200°C. Thus, the addition of the epoxy

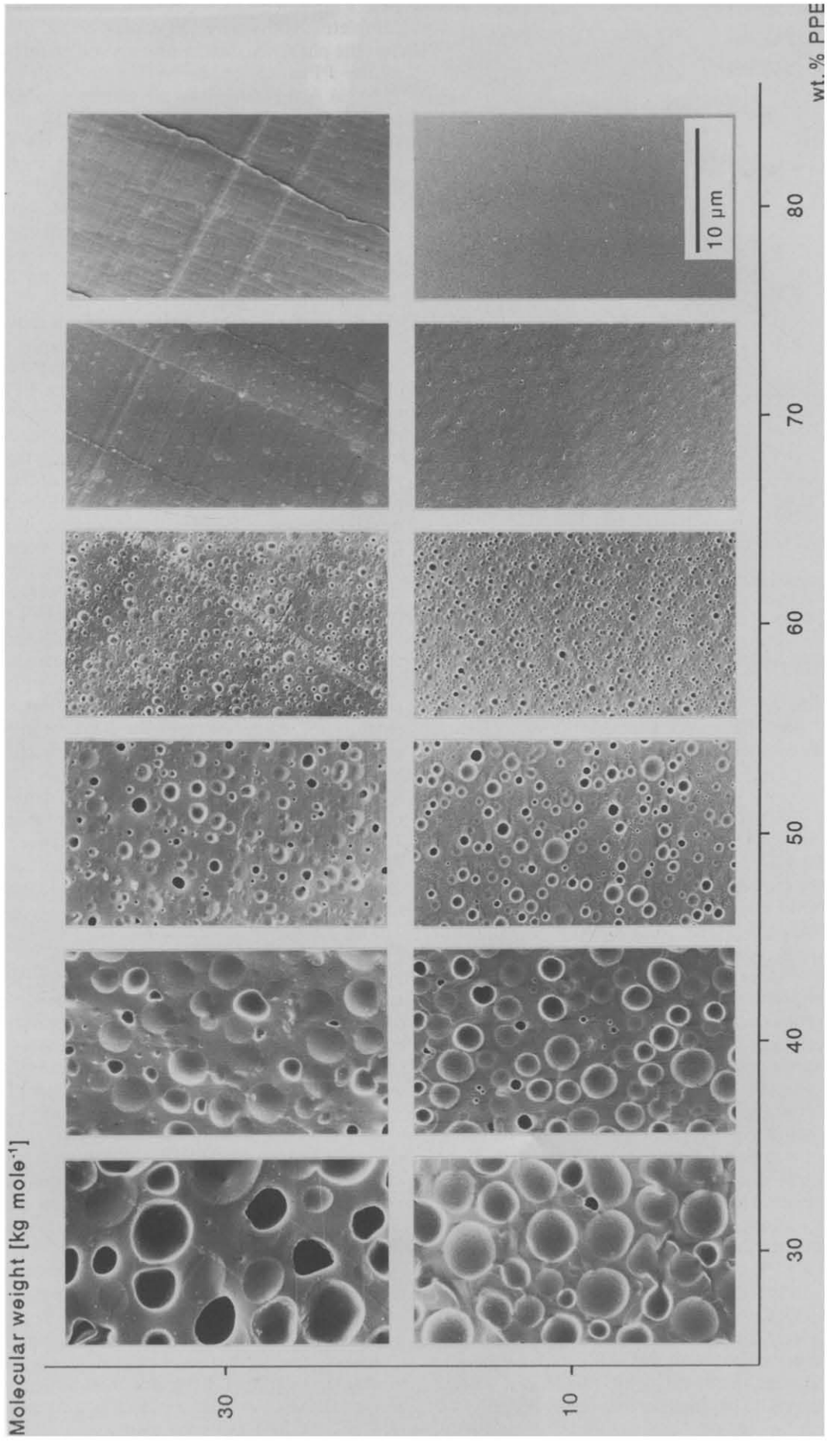

Figure 2 Scanning electron micrographs of epoxy/PPE solutions with a PPE molecular weight of 10 and 30 kg mol^{-1} and a PPE content of 30–80 wt%, after cooling from 200°C to room temperature at a rate of 1°C min^{-1}

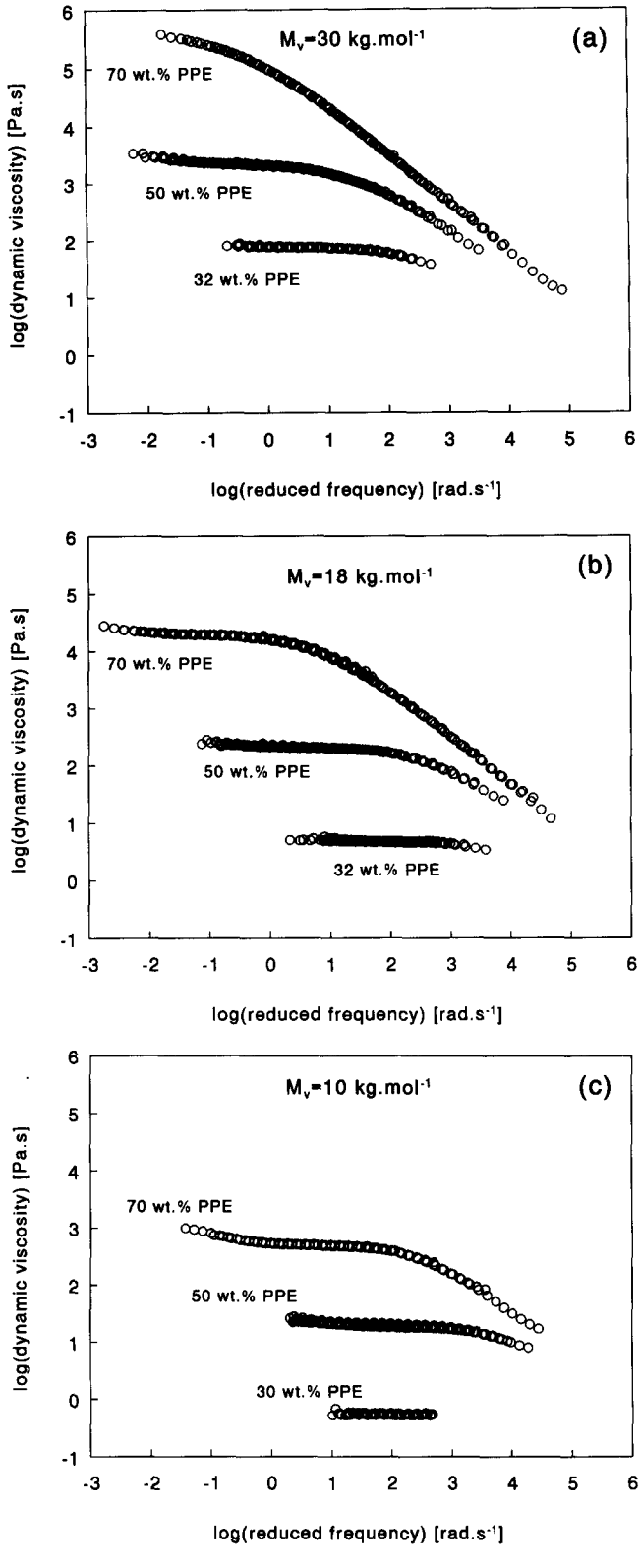

Figure 3 Flow curves of epoxy/PPE solutions varying in PPE content for PPE with different molecular weights: (a) 30 kg mol^{-1}; (b) 18 kg mol^{-1}; (c) 10 kg mol^{-1} (reference temperature is 170°C)

resin to a commercial grade PPE results particularly in a drop in the processing temperature required, from >300 to 200°C. This indicates that epoxy resin can be applied effectively to introduce processability, since the high processing temperatures required are the major threshold in the processing of pure PPE. However, a high PPE content combined with a low viscosity, which is desirable for, e.g. structural reactive injection moulding (SRIM), is only feasible if low-molecular-weight PPE is used.

Curing of epoxy/PPE solutions

Curing of homogeneous solutions of epoxy resin and PPE requires the incorporation of a curing agent which is compatible with the solution. Several curing agents were tested, including aromatic anhydrides and acids, catalytic curing agents, such as BF_3 amine complexes, and aromatic diamines. These experiments showed that aromatic diamines were particularly suitable as a result of their excellent compatibility with the epoxy/PPE solution. In order to gain some processing time, a relatively slow, sterically hindered diamine was selected, i.e. diethyltoluene diamine (DETDA). Due to the addition of the curing agent, which at least enhances the miscibility of the system, the phase diagram is not valid anymore. However, it still serves the purpose of indicating the minimal miscibility of the system. Visual examination of the ternary solutions still reveals an *UCST* behaviour and the absence of phase separation upon cooling at high PPE content. The region in the phase diagram in which no phase separation will occur upon cooling is of special interest for processing. The chemical activity at room temperature of the epoxy resin solvent in the resulting homogeneous glassy compounds will be very low, thus yielding a long shelf life.

Upon isothermal curing of the homogeneous solutions, the chemical transition of the epoxy monomer into the dimer, trimer, etc. gradually converts the solvent into a non-solvent. This process can schematically be represented as a shift of the cloud point curves to higher temperatures and will result, inevitably, in phase separation. Additionally, the chemical nature or polarity of the

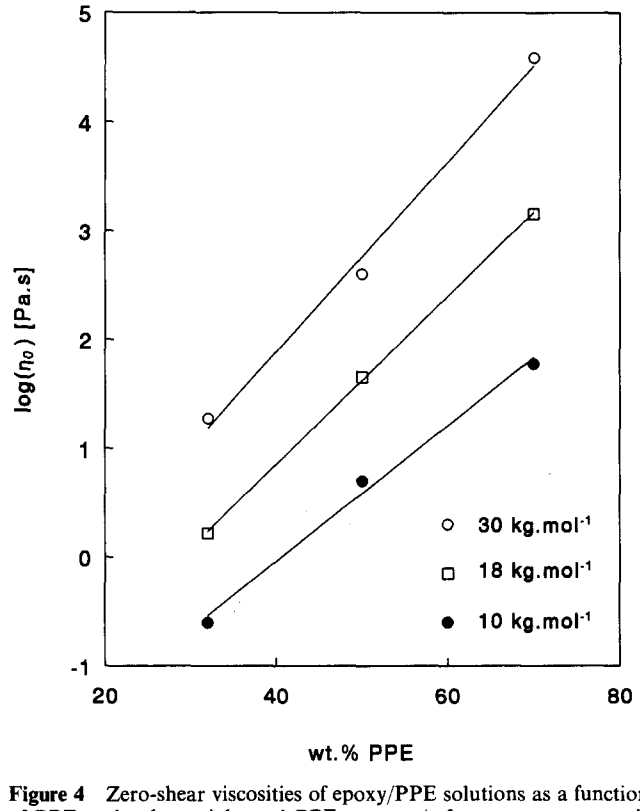

Figure 4 Zero-shear viscosities of epoxy/PPE solutions as a function of PPE molecular weight and PPE content (reference temperature is 200°C)

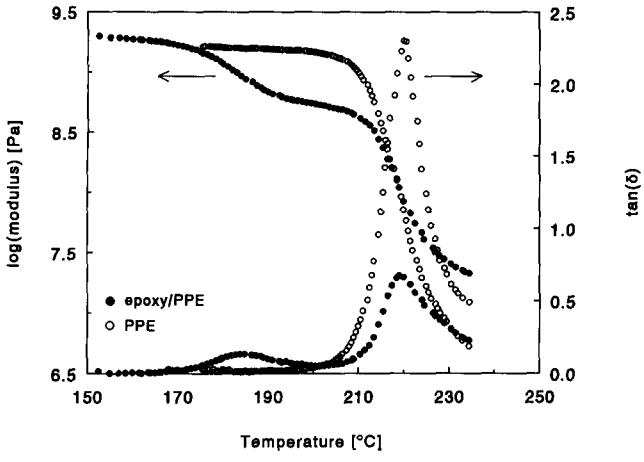

Figure 5 Dynamic mechanical data for PPE (30 kg mol^{-1}) and a cured epoxy/PPE blend containing 35 wt% PPE, using a heating rate of 3°C min^{-1}, and a frequency of 1 Hz

system will change, due to the conversion of the functional groups.

The dynamic mechanical data for neat PPE (30 kg mol^{-1}) and for a stoichiometrically cured blend containing 65 wt% epoxy resin are shown in *Figure 5*. For the blend, two distinct loss peaks are observed at temperatures of ~185 and 220°C, corresponding to the T_gs of the dispersed epoxy particles and the PPE matrix, respectively. From the T_g of the PPE matrix, which is approximately equal to the T_g of neat PPE, it can be concluded that, *in contrast to the results obtained via cooling*, virtually complete phase separation occurs during curing. The occurrence of complete phase separation, however, will theoretically be restricted by the curing temperature that is applied. Phase separation will be arrested as soon as the epoxy content in the PPE-rich phase is decreased to such an extent that the T_g of the PPE phase equals the curing temperature that is used. Unfortunately, these effects could not be studied because heating of the sample (which was necessary to determine the T_g) inevitably triggered the curing reaction, finally resulting in a shift of the T_g of the PPE phase towards 220°C. Therefore, thermal analysis was only possible for blends which were almost completely cured.

The required compatibility of the curing agent with the epoxy/PPE solutions makes it difficult to estimate for the appropriate concentration. For aromatic diamines, the concentration should be equal to the stoichiometric ratio, but an excess is likely to be required in order to compensate for any loss of curing agent due to dissolution in the PPE phase. For this reason, the optimum curing agent concentration, defined as the concentration which results in the highest T_g of the epoxy phase, was determined using dynamic mechanical analysis. The results of this study are shown in *Figure 6*, which presents the absolute values of the T_gs of the epoxy and PPE phase, which have been obtained for blends differing in curing agent concentration. A significant influence of the curing agent concentration on the T_g of the dispersed epoxy phase, as well as the PPE matrix, is observed. With an increasing curing agent concentration for the epoxy phase, a maximum in T_g, corresponding to the highest crosslink density, is obtained. This can be explained by the fact that a deficiency in curing agent concentration results in incomplete cure, while an excess in curing agent concentration results in linear polymerization, both of which lead to a substantial decrease in the crosslink density and subsequently the T_g. It is, however, remarkable that the optimum value for the curing agent concentration coincides with the stoichiometric concentration for the neat epoxy resin–DETDA system (24.5 parts per hundred parts of resin by weight (phr)). This implies that no curing agent remains in the PPE matrix after curing, despite its miscibility with PPE. This effect is of importance because significant traces of unreacted, toxic aromatic diamines would probably restrict future applications. An explanation for this phenomenon is likely to be found in the early stages of the curing process, in which the epoxy monomer solvent is converted into a non-solvent or epoxy oligomer/monomer mixture. When we assume that the first reaction step of the epoxy monomer with the curing agent will not result in phase separation, the major part of the curing agent is chemically bonded to the epoxy resin and will phase-separate upon further curing. If, however, too low a curing agent concentration is used, the epoxy monomer cannot be completely converted into non-solvent and some will remain in the PPE phase. This results in a flexibilization or decrease in T_g of the PPE matrix at low curing agent concentrations, as demonstrated in *Figure 6*.

Morphology of the cured materials

Scanning electron micrographs are presented in *Figure 7* of fracture surfaces of cured materials with variations in PPE content from 25 to 65 wt%. All of the samples studied clearly reveal a phase inverted morphology of dispersed epoxy particles in a continuous PPE matrix. In agreement with the results of the cooling experiments, phase inversion occurs at a very low PPE content of less

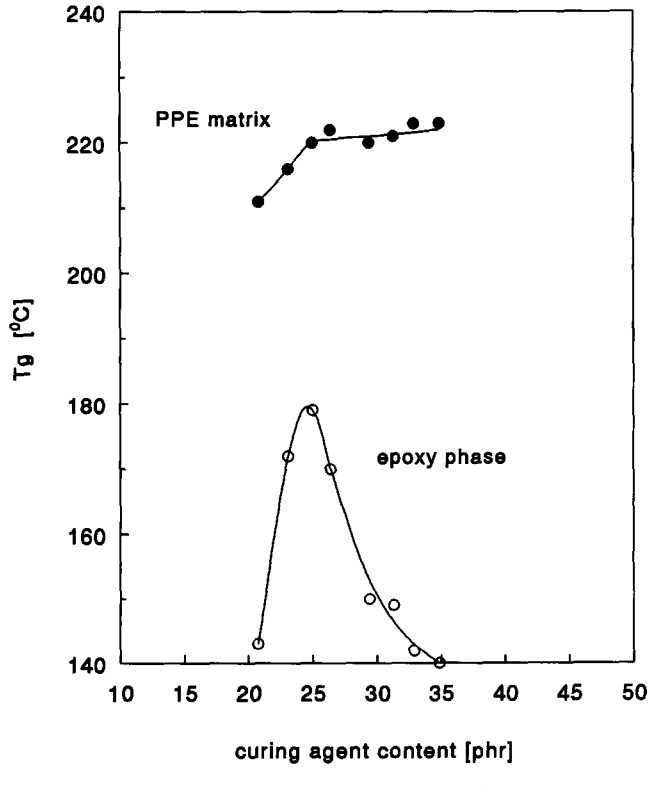

Figure 6 Glass transition temperature *versus* curing agent concentration of the epoxy and PPE phase, as determined using d.m.t.a. (heating rate = 3°C min^{-1}, frequency = 1 Hz) for cured blends containing 65 wt% PPE (30 kg mol^{-1})

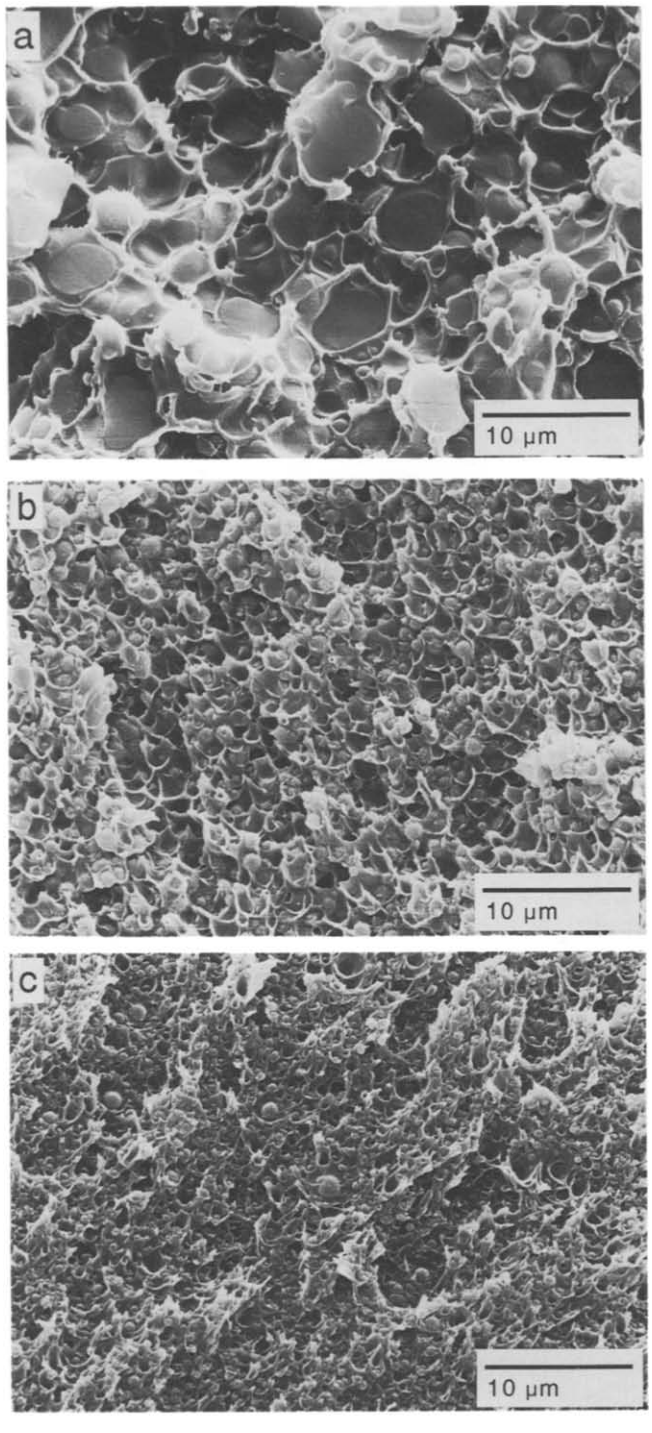

Figure 7 Scanning electron micrographs of mode-I fracture surfaces of epoxy/PPE (30 kg mol^{-1}) blends as a function of PPE content, cured at an initial temperature of 175°C: (a) 25 wt% PPE; (b) 45 wt% PPE; (c) 65 wt% PPE

than 25 wt%. This low concentration has also been reported in the literature for other systems, e.g. poly(ether imide)/epoxy resin[6] and poly(ether sulfone)/epoxy resin[8]. In *Figure 7*, the influence of blend composition on the coarseness of the morphology is again demonstrated. In accordance with the results obtained via cooling, an increase in PPE content results in a less coarse morphology.

In order to study the influence of the curing rate, the effect of a variation in the curing temperature from 150 to 225°C was examined. This gave, for the neat epoxy resin system, a reduction in the time to gelation from ~30 min to less than 5 min. The result of this experiment, for a blend containing 65 wt% PPE, is presented in *Figure 8*. Surprisingly, no significant influence on the particle size of the dispersed epoxy phase is observed. Although this experiment is not completely unambiguous, due to the additional change in viscosity, diffusion rates and conversion of epoxy resin at the instant of phase separation, the result indicates that the curing of epoxy resin (gelation) is not the major parameter controlling the morphology of the final material. Moreover, in this regime of curing rates and blend compositions, the development of the PPE-rich phase or the vitrification of the PPE matrix, in particular, plays an important role in the final morphology of the material. Therefore, a strong resemblance exists between the mechanisms determining the morphology of the solutions both after cooling and after curing.

Mechanical properties

The results of the mechanical tests are presented in *Figure 9*. *Figure 9a* reveals that all of the cured blends exhibit the same modulus of ~2.7 GPa, irrespective of cure temperature and composition. This is the result of the nearly matching moduli of the cured epoxy system and pure PPE. Consequently, the high volume percentage of dispersed epoxy spheres in PPE results in only minor stress concentrations in the material at relatively low strain levels. However, the tensile tests revealed that as a consequence of the high concentration of non-

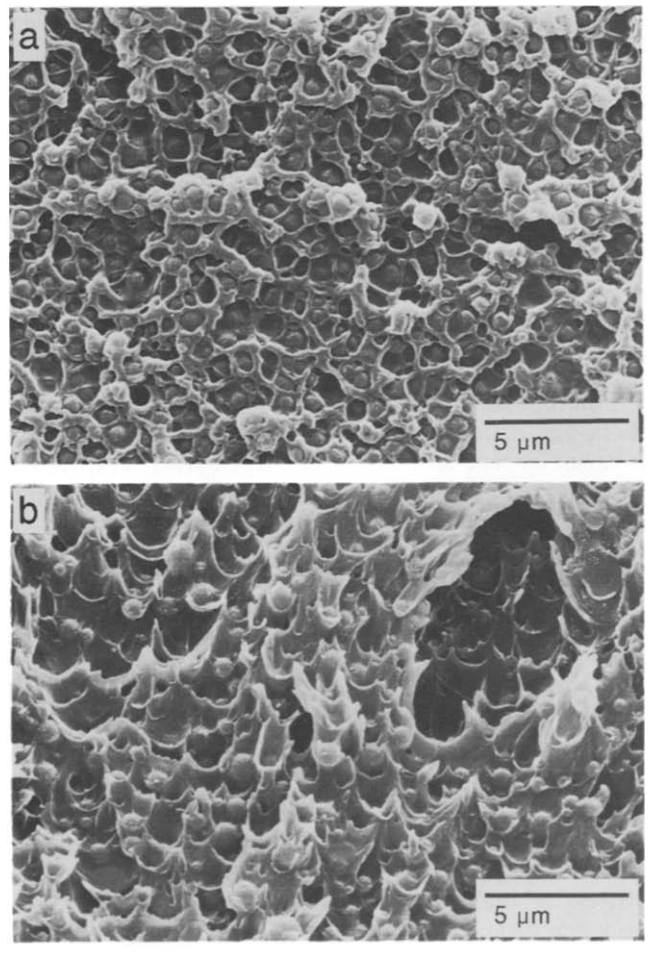

Figure 8 Scanning electron micrographs of mode-I fracture surfaces of cured epoxy/PPE blends containing 65 wt% PPE (30 kg mol^{-1}), as a function of initial curing temperature: (a) 150°C; (b) 225°C

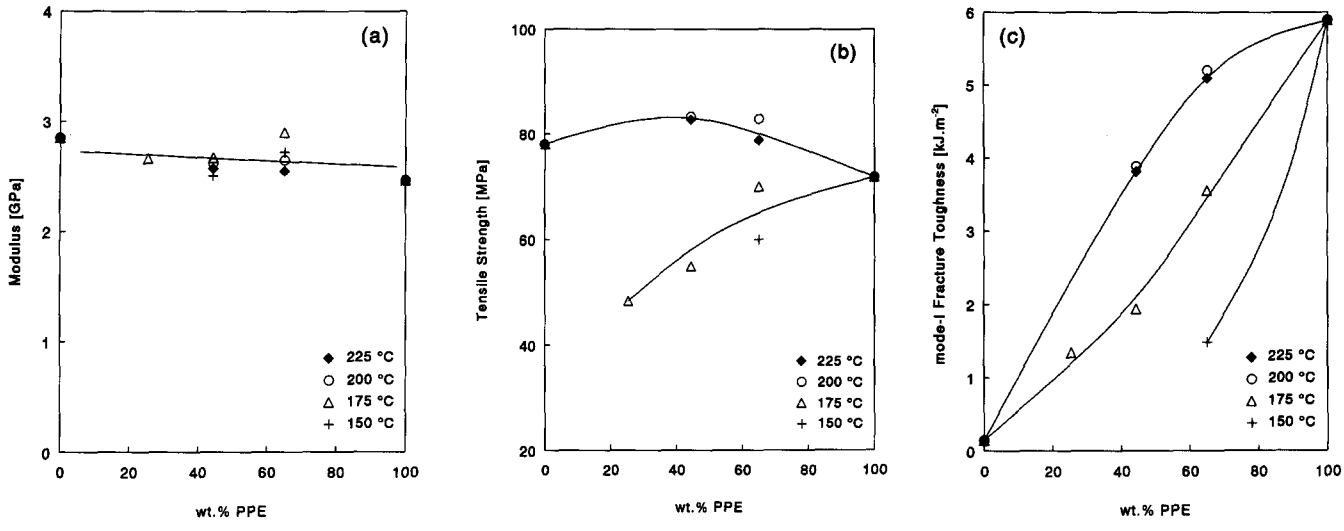

Figure 9 Mechanical properties of cured epoxy/PPE (30 kg mol^{-1}) blends as a function of PPE content and initial curing temperature: (a) tensile modulus; (b) tensile strength; (c) mode-I fracture toughness (G_{Ic})

deformable epoxy spheres, macroscopic yielding or a stable necking process was constrained. The samples cured at temperatures of 200 or 225°C revealed the initiation of a small yielding zone or shear band as soon as the yield stress was reached. However, this was immediately followed by catastrophic failure. Despite the relatively high local strain present in the yielding zone (>25%), this results, macroscopically, in a rather low strain to failure of ~8%.

As shown in *Figure 9b*, the tensile strength is strongly dependent on the initial curing temperature that is used. In contrast to the high tensile strength of ~80 MPa, which is found for samples cured at high temperatures (200 and 225°C), with the samples cured at low temperatures (150 and 175°C), a pronounced lower tensile strength is observed. This effect, which can also be observed in the scanning electron micrographs presented in *Figure 8* as a more ductile fracture surface for the blend cured at a temperature of 225°C, has to be attributed to a variation in adhesion. For this phenomenon, a chemical as well as a physical explanation can be found. At a low curing temperature, phase separation will result in the curing of epoxy droplets in a *vitrified* PPE matrix, thus enabling the epoxy spheres to detach from the matrix as a result of reaction shrinkage. At a curing temperature close to, or higher than the T_g of PPE, phase separation will result in the curing of epoxy droplets in a *rubbery* PPE matrix, thus preventing interfacial detachment due to reaction shrinkage. Moreover, at a high curing temperature, a grafting reaction of the PPE phenolic end-groups with the epoxy system is more likely to occur, which will also result in a higher level of adhesion. In order to differentiate between these different explanations for the distinct mechanical properties that are found in these studies, experiments with non-reactive or capped PPE need to be carried out.

The results of the mode-I fracture toughness experiments are presented in *Figure 9c*. Neat epoxy resin and PPE clearly exhibit brittle and tough fracture behaviour, respectively. As demonstrated in this figure, the fracture toughness values of the cured blends show an approximately linear variation with the blend composition. Consequently, the contribution of the epoxy phase to the toughness of the blend is negligible. Moreover, the deformation volume will be reduced due to the incorporation of the non-ductile epoxy spheres. Thus, the application of epoxy resin as a reactive solvent results in a reduction in fracture toughness, when compared to neat PPE. Corresponding with the results of the tensile tests, a significant influence of the initial curing temperature, or adhesion, is observed in *Figure 9c*. At the lower curing temperatures of 150 and 175°C (resulting in poor adhesion), crack initiation occurs at a lower stress, which results in a strong reduction of the mode-I fracture toughness value.

As demonstrated in the rheological measurements (see *Figure 4*), very low viscosities, as required for impregnation applications, reactive injection moulding (RIM) or structural RIM, can only be obtained when low-molecular-weight PPE is used. This, however, results in a deterioration of the final mechanical properties, as demonstrated in *Figure 10*, which shows the mode-I fracture toughness for blends based on PPE with a low molecular weight of 20 kg mol^{-1}. Qualitatively, the same trend is observed as that seen for the blends based on PPE with a molecular weight of 30 kg mol^{-1}. However, in this present case the absolute scale of toughness is decreased by one order of magnitude. This is the result of a decrease in the mechanical properties of the pure PPE that is used, due to the reduction in molecular weight affecting the entanglement structure[23,24].

This effect should be avoided if a grafting or coupling reaction of PPE with the epoxy system occurs, as shown by McGrath and coworkers[25] for blends of epoxy resin and poly(ether sulfone)s. In order to study this effect, the following, preliminary, experiment has been performed. A solution of low-molecular-weight PPE in epoxy resin was heated for 24 h at a temperature of 200°C under nitrogen, before the addition of curing agent and subsequent curing. Apart from all kind of unknown side-reactions, this heat treatment facilitates the (normally slow) reaction of the phenolic PPE end-groups with the epoxy resin, resulting in a solution containing large amounts of epoxy-capped PPE. After the heat treatment, the curing agent is added and the compound is cured for 6 h at 200°C. The mode-I fracture toughness value of this blend is also presented in *Figure 10*. Clearly, a pronounced increase in toughness is observed, i.e. from

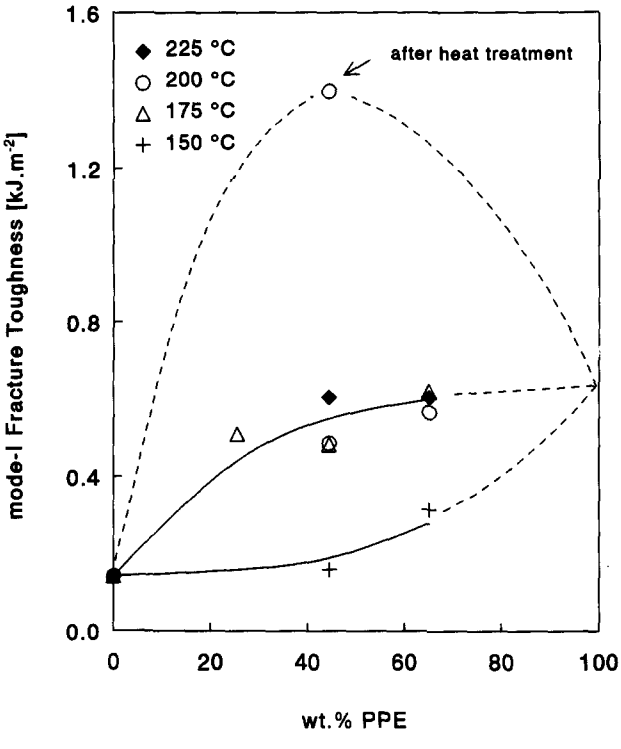

Figure 10 Mode-I fracture toughness (G_{Ic}) of cured epoxy/PPE blends as a function of PPE content and initial curing temperature for PPE with a molecular weight of 20 kg mol^{-1}. The fracture toughness value of a blend containing 45 wt% PPE, which has been heated for 24 h at 200°C before adding curing agent and curing, is also shown

~0.5 to 1.4 kJ m^{-2}, which has to be attributed to a copolymerization reaction.

Despite the crudeness of this last experiment, the result clearly indicates the necessity for copolymerization to occur. Low-molecular-weight PPE can only be used if a reaction of the PPE phenolic end-groups with the epoxy system occurs, resulting in chain extension or grafting of the PPE on to the epoxy network. Consequently, more research is needed in this area, aimed at the development of low-molecular-weight PPE which has been modified with reactive end-groups.

CONCLUSIONS

The use of epoxy resins as reactive solvents for PPE results in a significant decrease of the processing temperature required (> 300°C to 200°C), thus avoiding thermal degradation. For a commercial-type PPE (30 kg mol^{-1}), this results in solutions with viscosities in the range observed for normal polymer melts. Very low viscosities can only be obtained when low-molecular-weight PPE is used.

In contrast with the results obtained by vitrification of the solutions by cooling, curing with diethyltoluene diamine results in complete phase separation of both the epoxy resin and the curing agent. As a result of the complete phase separation and the phase inversion in the composition range being studied (30–70 wt% PPE), PPE is regained without any compromise in the final T_g of the product. PPE is the continuous phase and also dominates the final material properties. However, the presence of the glassy epoxy spheres inhibits macroscopic yielding, and results in some reduction of the toughness. The mechanical tests reveal the importance of adhesion, which is controlled by the curing temperature, and the necessity of the use of functionalized PPE, particularly if low-molecular-weight species are being used.

Our present research is aimed at a detailed investigation concerning the mechanical properties, morphology development and chemorheology of this system, and the synthesis and application of functionalized low-molecular-weight PPE. Additionally, this reactive processing technique is being studied as a new route to prepare rubber-toughened PPE and advanced carbon-fibre-reinforced thermoplastic composite materials. The results of these investigations will be reported in forthcoming papers.

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