BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 15, pp. 2903–2913, 1995

0032-3861/95/$10.00+0.00

Processing of intractable polymers using reactive solvents: 3. Mechanical properties of poly(2,6-dimethyl-1,4-phenylene ether) processed by using various epoxy resin systems

R. W. Venderbosch, H.E.H. Meijer and P.J. Lemstra*
Centre for Polymers and Composites, Eindhoven University of Technology, PO Box 513, Den Dolech 2, 5600 MB Eindhoven, The Netherlands
(Received 15 September 1994)

The rather intractable polymer poly(2,6-dimethyl-1,4-phenylene ether) (PPE) can easily be processed by using epoxy resin as a reactive solvent. In this reactive solution processing technique, PPE is dissolved in epoxy resin at elevated temperatures and processed. After processing, the epoxy resin is polymerized and phase separation accompanied by phase inversion is initiated and the reactive solvent is subsequently integrated in the final material. In this paper, attention was focused on the possibility of tuning the properties of the *in situ* polymerized dispersed epoxy phase. A solvent system was studied which consisted of epoxy resins and diamine curing agents, based on bisphenol and poly(propylene oxide). Both resins could be used as a solvent for PPE and the resulting processable solutions exhibited upper critical solution temperature behaviour. Upon increasing the poly(propylene oxide) content in the reactive solvent system the properties of the dispersed phase could be varied gradually from non-ductile glassy to completely rubbery, and consequently the properties of the PPE/epoxy could be controlled over a broad range. The presence of a non-ductile glassy dispersed phase (with yield stress $\gg$ yield stress of PPE) resulted in an increase in the yield stress of the material and was shown to constrain yielding of the PPE matrix. Reduction of the yield stress of the dispersed phase facilitated ductile deformation of PPE in tensile loading but resulted additionally in a reduction in toughness. After changing the properties of the dispersed epoxy phase to completely rubbery a substantial increase in toughness was obtained. Interestingly, the rubber with the lowest level of adhesion proved to be the most efficient impact modifier for PPE.

(Keywords: intractable polymers; epoxy resins; reactive solvents)

INTRODUCTION

The successful application of engineering plastics does always depend on a proper balance between the final material properties and the materials processing characteristics. The development of high-temperature-resistant polymers, which are potentially of interest for structural applications, for instance, is often limited by the occurrence of degradation during processing at the high temperatures that are required and many high-T_g polymers, in fact, are intrinsically intractable. Additionally, the processability of polymers is governed by extrinsic parameters, such as flow length, mould geometry, etc., posed by the application which is aimed for and the subsequent choice of a specific processing technique. Consequently, for a successful and broad application of a polymer material, adaptability to specific processing requirements is essential.

In this series of papers[1,2], a novel technique is introduced for tuning the processing characteristics of thermoplastic materials. This technique is based on the use of reactive solvents, i.e. monomers, which during processing enable the control of certain properties, such as processing temperature and viscosity, and which after processing are polymerized and subsequently integrated into the final product (see *Figure 1*). This is in contrast to conventional solution processing techniques where the solvents have to be extracted after processing. This processing route was originally studied in order to introduce processability to poly(2,6-dimethyl-1,4-phenylene ether) (PPE). An epoxy resin system was used as a solvent to reduce the viscosity and the high processing temperatures that are normally required. Polymerization or curing of the epoxy monomer initiates phase separation and, even at relatively low PPE concentrations (>15 wt%), phase inversion. As a consequence, the epoxy resin system is converted into a dispersed phase. Interestingly, at processing temperatures as low as the T_g of neat PPE, this phase separation process was shown to be nearly complete[1]. Consequently, PPE is regained and dominates, as a result of the phase-inverted morphology, the properties of the final material.

In this paper the mechanical properties of PPE/epoxy

---

* To whom correspondence should be addressed.

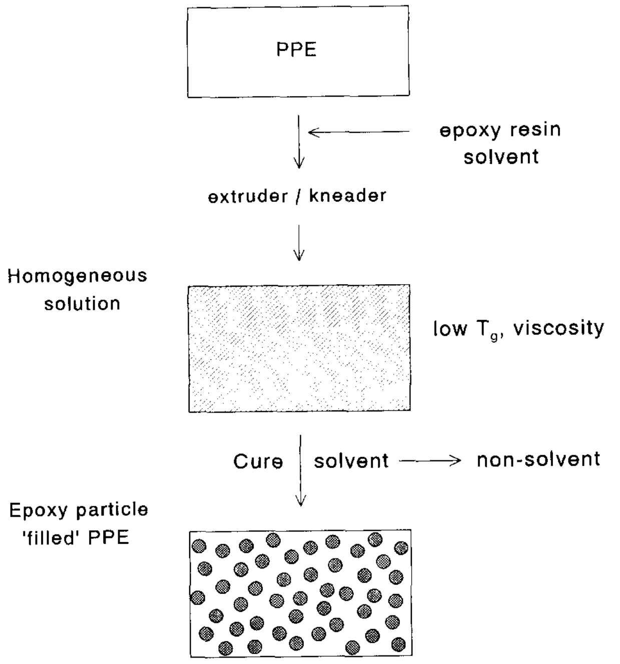


Figure 1 Schematic represenation of the concept of processing of intractable polymers by using reactive solvents

systems are investigated in more detail. The attention is mainly focused on the possibility of tuning the mechanical properties of the *in situ* polymerized dispersed phase. This will not only provide a route for adapting the properties of PPE, e.g. the dispersed epoxy phase may be exploited as a rubbery impact modifier, but additionally will give fundamental information concerning the effect of the dispersed epoxy phase on the macroscopic properties, in particular the ductility, of PPE.

In order to systematically vary the mechanical properties of the *in situ* polymerized dispersed phase, a suitable epoxy resin system had to be found. Starting from the bisphenol-A based epoxy resins, which are cured by using aromatic diamines, as used in parts 1 and 2 of this series, basically two routes are available for changing the mechanical properties, such as, for instance ductility: (i) by varying the crosslink density[3] and (ii) by varying the flexibility of the epoxy network[4].

The most straightforward method of varying the crosslink density is by using resins with a higher initial molecular weight. This will strongly reduce the solubility of PPE and, consequently, is not feasible in this study. Alternatively, an excess of curing agent or the incorporation of bifunctional curing agents could be used, thus yielding a more linear polymerization. These techniques, however, are sensitive to the stoichiometry, especially when low crosslink densities are required, and problems related to the reproducibility are to be expected. This is particularly a disadvantage when considering the final application in which all of the constituents of the epoxy resin system have to segregate from the originally homogeneous PPE/epoxy solution. In addition, a variation in the crosslink density only does not yield a broad enough range of mechanical properties, since the resulting materials will always exhibit a glassy nature. The lowest T_g achievable with bisphenol-A epoxy resins cured with aromatic diamines, even in the most extreme case of a linear polymer, will be in the range of 100°C. For these reasons, only the second route was explored in this investigation and a system was studied in which the overall flexibility of the epoxy resin network was gradually increased by introducing flexible poly(propylene oxide) chains. The components of the epoxy resin system that is investigated here are presented in *Figure 2*. The resins, as well as the curing agents, consist of 'rigid' bisphenol and 'flexible' poly(propylene oxide) monomer 'building blocks', all of which have a relatively low molecular weight of ~300–500 g mol^{-1}, thus facilitating the preparation of a large range of epoxy networks, while still maintaining the initial solubility.

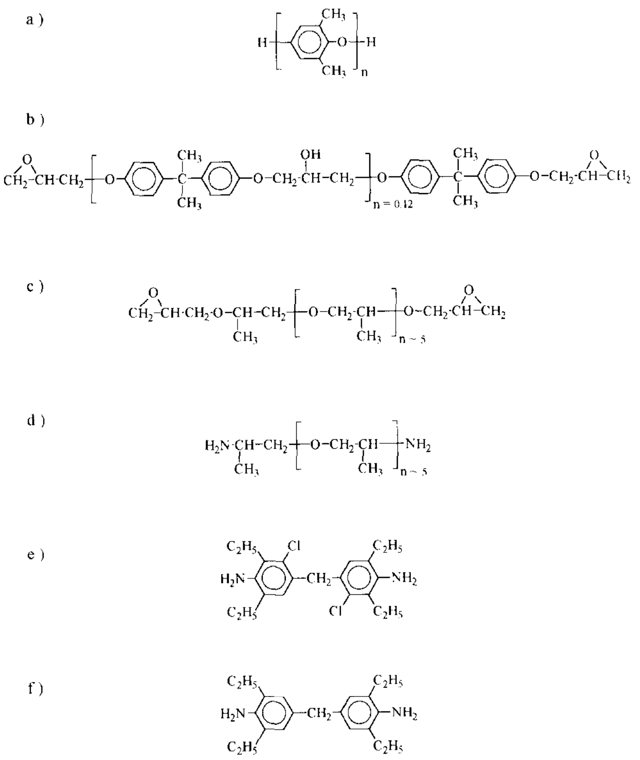


Figure 2 Structural formulae of PPE and the epoxy resin systems used in this work: (a) poly(2,6-dimethyl-1,4-phenylene ether) (PPE); (b) diglycidyl ether of bisphenol-A (DGEBA); (c) diglycidyl ether of poly(propylene oxide) (DGEPPO); (d) poly(propylene oxide) diamine (Jeffamine D-400); (e) 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (M-CDEA); (f) 4,4′-methylenebis(2,6-diethylaniline) (M-DEA)

In this paper, the mechanical and thermal properties of the epoxy resin system and its solubility towards PPE will first be discussed. Secondly, by using this epoxy system, the mechanical properties of the PPE/epoxy, such as tensile properties and mode-I fracture toughness, are discussed in terms of the mechanical properties of the dispersed phase. In view of the pronounced heterogeneity of most of the materials studied, the results are presented by taking into account the effects of morphology.

EXPERIMENTAL

Curing and preparation of the epoxy resin system

Two types of epoxy resin were used throughout this investigation, namely a diglycidyl ether of bisphenol-A (DGEBA, Epikote 828EL, 380 g mol^{-1}) supplied by Shell (Amsterdam, The Netherlands), and a diglycidyl ether of poly(propylene oxide) (DGEPPO, Epikote 877, 460 g mol^{-1}) supplied by Chemische Fabriek

Zaltbommel (CFZ, Zaltbommel, The Netherlands). The following curing agents were used: 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (M-CDEA, 379 g mol^{-1}) and 4,4′-methylenebis(2,6-diethylaniline) (M-DEA, 308 g mol^{-1}), both supplied by Lonza Ltd (Breda, The Netherlands), and poly(propylene oxide) diamine (Jeffamine D-400, 400 g mol^{-1}), supplied, by Texaco (Gent, Belgium).

Epoxy resin formulations were prepared using a DGEBA/DGEPPO ratio by weight of 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100, including M-CDEA or Jeffamine D-400 as a curing agent. These homogeneous mixtures were degassed for 1 h at a temperature of ~50°C under reduced pressure conditions (0.5 atm) and were subsequently cast into a simple mould consisting of a Teflon U-shaped spacer clamped between two plates which were coated with release agent (Frekote 44, Hysol Corporation). All of the mixtures were cured in an inert nitrogen atmosphere according to the curing cycles presented in *Table 1*.

The stoichiometric M-CDEA concentration for the DGEBA resin was determined by dynamic mechanic thermal analysis (d.m.t.a.). For this type of epoxy resin, the stoichiometric composition can be defined as the curing agent concentration which yields, after polymerization, the highest T_g. For DGEPPO type resins, the T_g depends not only on the crosslink density but, additionally, on the absolute content of aromatic building blocks. Therefore, the stoichiometric M-CDEA concentration for this resin was determined by swelling experiments. A series of cured samples of DGEPPO resin with various M-CDEA contents (initial weight = 0.25 g) were exposed to toluene. After swelling for 24 h, the relative increase in weight was measured. The stoichiometric concentration is subsequently defined as the concentration resulting in the lowest amount of solvent uptake. The stoichiometric concentrations found with M-CDEA for the DGEBA and DGEPPO epoxy resins (51 parts per hundred parts of resin by weight (phr) and 31 phr, respectively) were used to derive the required concentrations of Jeffamine D-400 (56 and 36 phr, respectively) and M-DEA (42 and 27 phr, respectively).

Phase diagram

In order to determine the miscibility of PPE with the DGEPPO resin, specimens with various PPE contents were placed between glass slides in a hot cell. Upon controlled slow cooling of the cell (at a rate of 1°C min^{-1}), the onset of phase separation, i.e. the cloud point temperature, was determined by using laser light scattering (He–Ne laser, 623.8 nm). For solutions which did not reveal phase separation (>70 wt% PPE), the glass transition temperature was determined by using d.m.t.a.

Curing and preparation of PPE/epoxy blends

A commercial grade poly(2,6-dimethyl-1,4-phenylene ether), (PPE 803, $M_w = 32\,\mathrm{kg\,mol^{-1}}$, $M_w/M_n = 2.3$) was supplied by General Electric Plastics (Bergen op Zoom, The Netherlands).

From the series of DGEBA/DGEPPO mixtures, four were selected as a reactive solvent, i.e. the formulations cured using M-CDEA and with a DGEBA/DGEPPO ratio by weight of 100/0, 60/40, 20/80 and 0/100. As illustrated by the curing cycles presented in *Table 1*, the reactivity of the DGEPPO resin is considerably lower than the reactivity of the DGEBA resin. To compensate for this lower reactivity, the formulations with a high DGEPPO resin content, i.e. the 20/80 and the 0/100 mixtures, were cured using M-DEA. This is a diamine curing agent with a structure similar to M-CDEA (see *Figure 2*) and a higher reactivity due to the absence of the chlorine substituents. Although in this way the overall reactivity of the solvent system is restored, the occurrence of copolymerization or grafting reactions with the phenolic end groups of PPE will be less likely, as a result of the lower reactivity of the DGEPPO resin. Therefore, with increasing DGEPPO content, particularly in the case of the system not containing any DGEBA, a weaker interface or lower level of adhesion is anticipated.

Solutions of PPE in the four solvent systems described above, with a total solvent content varying from 20 to 60 wt%, were prepared by using a Brabender Plasticorder kneader. Unfortunately, this mixing device gives a poor performance in these types of applications[5], and, consequently, at a temperature of 175°C a kneading time of ~1 h was required to obtain homogeneous transparent solutions. After the addition of curing agent (M-CDEA or M-DEA) mixing was continued for 10–15 min. The final compound was immediately moulded and cured in a hot press. All of the PPE/epoxy solutions were cured for 7 h at 200°C, with the exception of the solutions based on the solvent system with a DGEBA/DGEPPO ratio of 100/0, which were cured for 2 h at 225°C, followed by a post-curing treatment of 4 h at 200°C.

Thermal and mechanical analyses

The glass transition temperatures of the different systems were determined by dynamic mechanical thermal analysis (d.m.t.a) using a Polymer Laboratories MkII instrument in the tensile mode, employing a heating rate of 2°C min^{-1} and a frequency of 1 Hz.

Tensile experiments were conducted on a Frank tensile tester (81565 IV) equipped with an extensometer ($l_0 = 50$ mm) at an initial strain rate of $10^{-3}\,\mathrm{s^{-1}}$. Two

Table 1 Curing cycles used for the neat epoxy resin formulations

Epoxy formulation		Curing time (h)				
Resin	Curing agent	125°C	150°C	175°C	200°C	225°C
DGEBA	M-CDEA	4	—	4	—	4
DGEPPO	M-CDEA	24	48	24	—	—
DGEBA/DGEPPO mixtures	M-CDEA or D-400	—	48	24	12	—

dumb-bell-shaped geometries were used, depending on the glassy or rubbery nature of the sample. Glassy specimens, with dimensions according to ASTM D638 (2 mm thick, 13 mm wide in the narrow section, and 180 mm long) were machined and subsequently edge-polished, while rubbery specimens, with dimensions according to ASTM D412 (2 mm thick, 6 mm wide in the narrow section, and 150 mm long) were punched by using a sharp dumb-bell-shaped die. For samples that revealed pronounced necking, the elongation in the neck was estimated from the neck geometry, assuming incompressible behaviour. At least five specimens were tested for each composition.

The mode-I fracture toughness of the materials was determined by using the single-edge notched bend specimen geometry[6]. A sharp V-notch was machined and additionally sharpened with a fresh razor blade (total depth = 5 mm). The specimens ($50 \times 10 \times 4\,\mathrm{mm}^3$) were tested at room temperature using a span-to-depth ratio of 4. Low-speed experiments were conducted on a Frank tensile tester (81565 IV) at a crosshead speed of $10\,\mathrm{mm\,min}^{-1}$. High-speed experiments were conducted on a Zwick Rel servohydraulic tensile tester at a crosshead speed of $1\,\mathrm{m\,s}^{-1}$. Again, at least five specimens were tested for each composition.

Morphology

The morphology of the final materials was studied by using scanning electron microscopy (SEM) (Cambridge Stereoscan 200) on gold/palladium coated samples. Fracture surfaces obtained from the fracture toughness tests and prepared by cryogenic breaking were investigated. No additional staining techniques were used.

RESULTS AND DISCUSSION

Influence of chain flexibility on the mechanical and thermal properties of epoxy networks

Incorporation of flexible monomers will reduce the T_g of the cured epoxy networks. The glass transition temperatures of DGEBA/DGEPPO resin mixtures, cured with a stoichiometric amount of M-CDEA or Jeffamine D-400, are presented in *Figure 3a*. The markers represent the T_gs which were determined by using d.m.t.a., while the drawn line is calculated according to the equation of Fox[7], using the T_gs as found for the two extreme systems based on DGEBA and DGEPPO only. Clearly, a continuous range of epoxy networks is obtained with a T_g varying from 200 to −25°C. The materials are homogeneous over the entire composition range and, consequently, the T_g–composition relationship can be described simply by a rule-of-mixtures behaviour such as the Fox equation. Interestingly, the two curves obtained for both curing agents can be reduced to one general relationship if the composition of the epoxy network is expressed in terms of the total poly(propylene oxide) content (curing agent and epoxy resin) (see *Figure 3b*). Of course, the T_g of the final epoxy network is governed not only by the molecular nature of the building blocks but additionally by the crosslink density. However, assuming that the crosslink density is mainly controlled by the molecular weight of the starting monomers, a large variation in crosslink density is most unlikely.

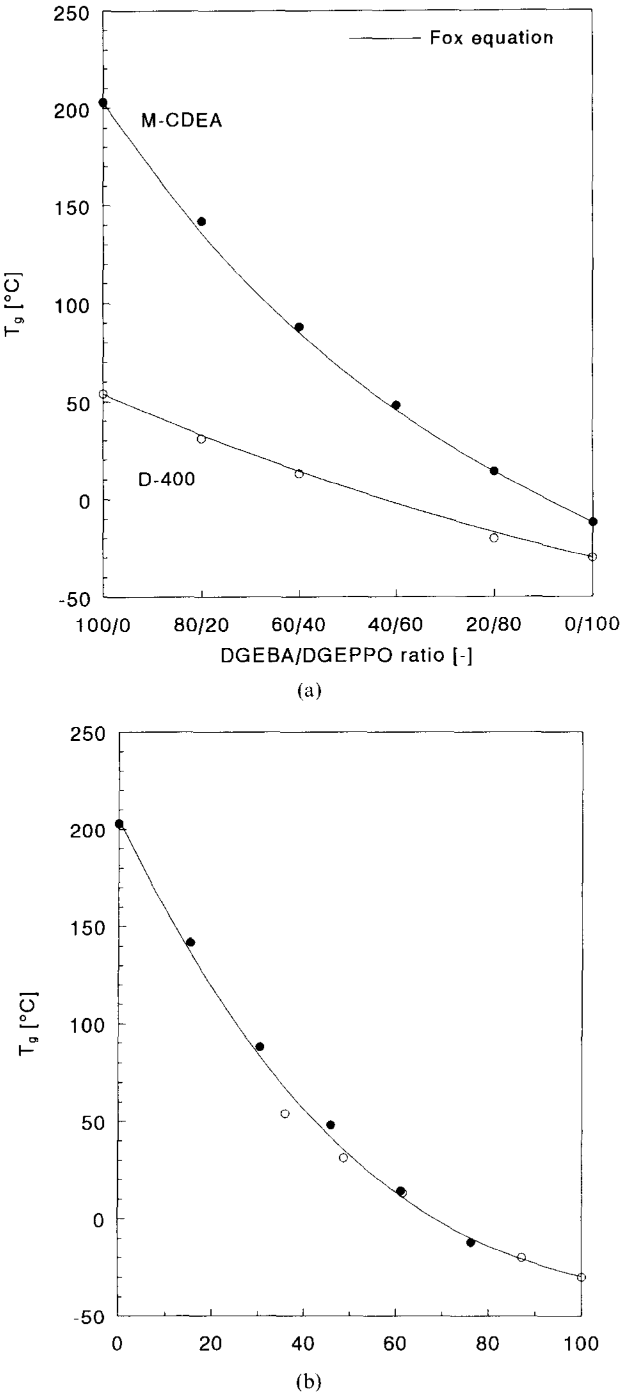


Figure 3 Glass transition temperatures, determined by using d.m.t.a. (2°C min^{-1}, 1 Hz), of mixtures of DGEBA and DGEPPO resins cured using M-CDEA (●) or Jeffamine D-400 (○) *versus*: (a) DGEBA/DGEPPO ratio (drawn lines are according to the equation of Fox[7]); (b) total poly(propylene oxide) (PPO) content

The tensile properties of the final epoxy networks are presented in *Figure 4*, where again the composition of the network is expressed in terms of the total poly(propylene oxide) content. As can be derived from the results obtained for the moduli (see *Figure 4a*) the influence of the introduction of flexible network chains is quite similar to increasing the testing temperature. Basically, only a minor influence on the modulus is measured until the T_g (see *Figure 3b*) is decreased to below room temperature, i.e. the testing temperature, at ~55 wt% poly(propylene oxide), and a sharp transition from a

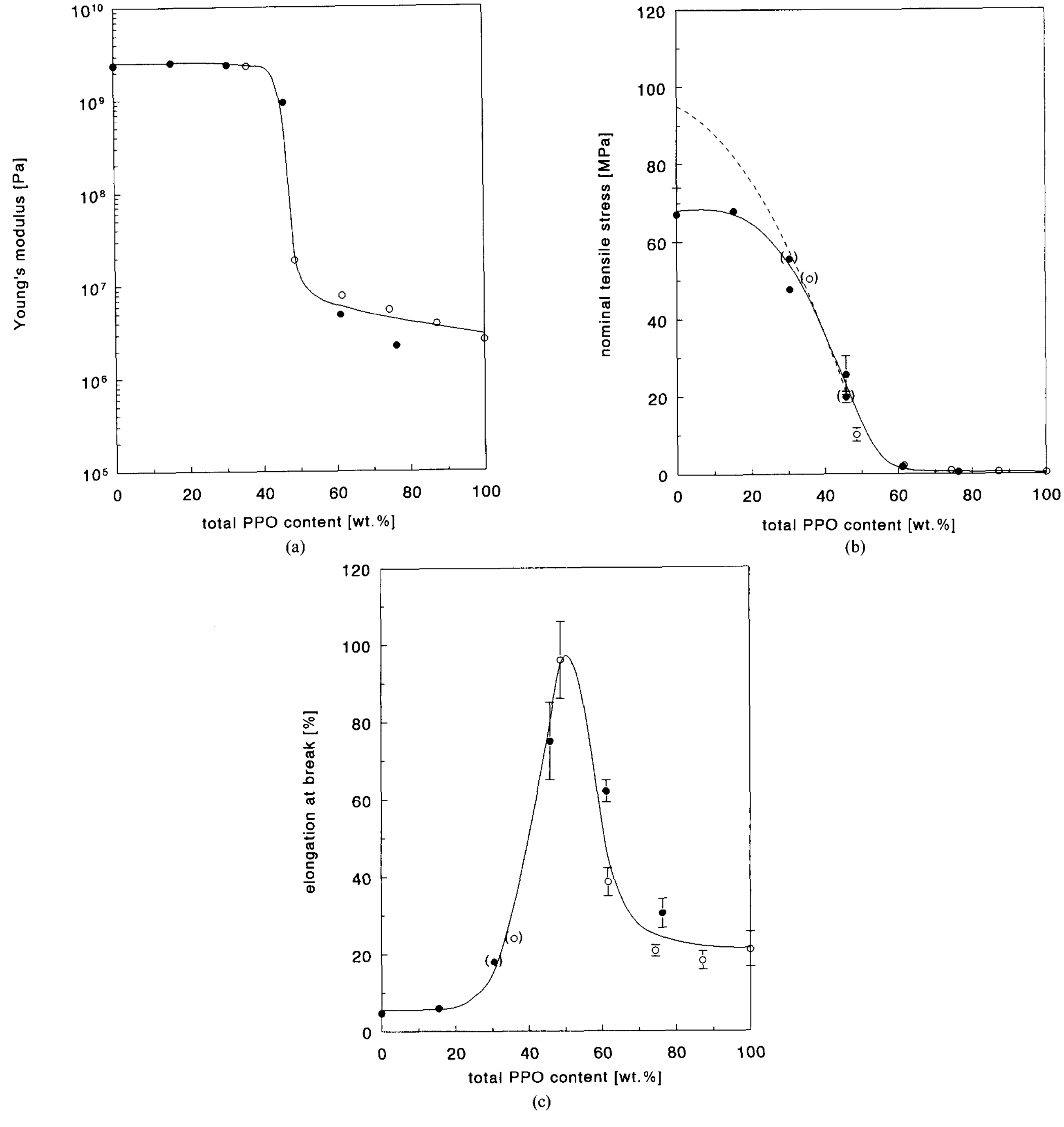


Figure 4 Tensile properties of the epoxy resin systems, cured with M-CDEA (●) or Jeffamine D-400 (○), *versus* the total PPO content: (a) Young's modulus; (b) stress at break (additionally, if observed, the yield stress is presented by markers in brackets); (c) elongation-at-break (values in brackets are estimated from the neck geometry)

glassy to a rubbery material is observed. The tensile strength at break and yield stress are presented together in *Figure 4b*. In the glassy region, the strength and yield stress decrease continuously with increasing poly(propylene oxide) content. However, as a result of the low fracture toughness of all of these relatively highly crosslinked materials, in the tensile tests a yield stress is observed only for the glassy specimens with a T_g close to the testing temperature. The reduction in yield stress with increasing network flexibility is presented schematically in *Figure 4b* (indicated by the dashed line). This line is constructed by assuming a tensile yield stress of 95 MPa for the material with a total PPO content of 0 wt%, which was estimated from a uniaxial compression test using a pressure-dependent Von Mises criterion[8,9]. The effect of T_g is clearly reflected in the corresponding elongation-at-break values presented in *Figure 4c*, which reveal a pronounced maximum. Increasing the flexibility of the network should yield a continuous increase in the elongation-at-break values. However, this behaviour is obscured by viscoelastic effects as a result of the additional continuous decrease in T_g. The influence of viscoelasticity on such properties was previously shown many years ago by Smith *et al.*[10-12], who studied the ultimate tensile properties for a number of elastomers as a function of strain rate and temperature. Close to the T_g the materials exhibit a more viscous behaviour and will be less sensitive to flaws in the sample. Consequently an optimum in elongation-at-break is found for those samples with a T_g close to room temperature. In fact, only the mechanical properties of these samples reveal the influence of network flexibility. The results obtained for the other materials are controlled merely by fracture mechanical features such as flaws, etc. To compensate for these viscoelastic effects, the mechanical performance of these materials should be evaluated at temperatures which are equidistant from T_g, i.e. at constant $T-T_g$.

Miscibility of PPE with DGEPPO and DGEBA epoxy resins

The solubilities of PPE in the DGEBA and DGEPPO resins are compared in *Figure 5*, which presents the phase diagrams obtained for both of these epoxy resins. Qualitatively, both phase diagrams correspond. The cloud point curves exhibit an upper critical solution temperature (*UCST*) behaviour and intersect the T_g–composition lines at high PPE contents (60–70 wt% PPE). As already discussed in part 1, as a result of these intersection points the phase diagrams can be divided into two regions: (i) one at lower PPE contents where phase separation will occur upon cooling, resulting in heterogeneous materials with a concentrated phase of constant composition, and consequently with a constant T_g, equal to that at the intersection point, and (ii) one at PPE contents higher than that of the intersection point where no phase separation will occur upon cooling, resulting in homogeneous glassy solutions with a T_g which is dependent on the composition. These types of phase diagrams are extensively described by Berghmans and coworkers[13-15] for various polymer–solvent systems.

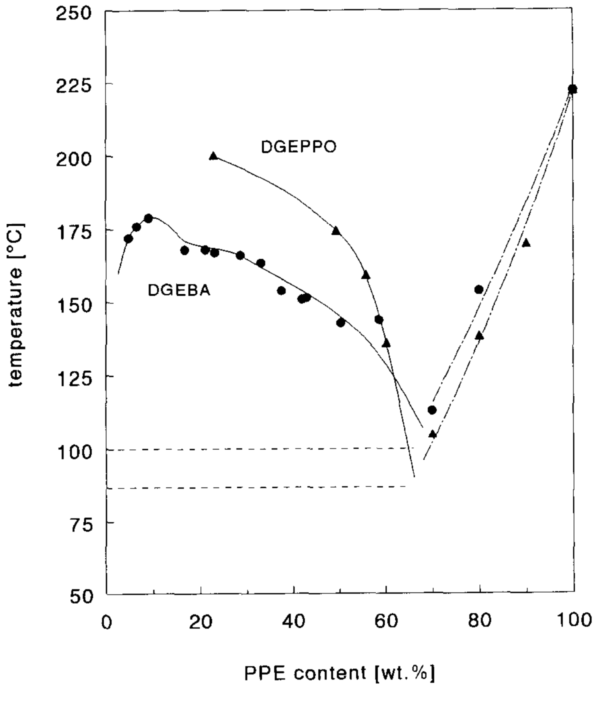


Figure 5 Phase diagrams of PPE in DGEBA (●) and DGEPPO (▲) epoxy resins: (——) cloud point curves; (– · –) T_g–composition lines in the homogeneous region; (- - - -) T_g–composition lines in the two-phase region

The DGEPPO resin yields, particularly at lower PPE contents, higher cloud point temperatures which illustrates its lower miscibility with PPE. Additionally, for DGEPPO a T_g–composition line is found at lower temperatures, due to the higher molecular flexibility of this resin. In the composition range of interest, i.e. for PPE contents higher than 50 wt%, the differences in solubility between both epoxy resins are relatively small. In particular, since in a large part of this range no phase separation will occur upon cooling. This may not be true in the case of curing. During curing at high temperatures in the homogeneous region, the monomer solvent system is slowly converted into dimeric species, etc., resulting in a gradual decrease in solubility and eventually resulting in phase separation. When we assume that the solubility of PPE in the bisphenol and polypropylene type monomers will not change drastically with the incorporation of curing agents, this process may be represented schematically by a broadening and shifting of the phase diagram to higher temperatures. Consequently, a lower miscibility of PPE with the DGEPPO resin, observed in *Figure 5* only for those samples with lower PPE contents, will probably also be true for samples with higher PPE contents during curing.

Morphology and mechanical properties of PPE/epoxy blends processed using various epoxy systems

From the large range of possible epoxy resin compositions, four formulations are investigated as a reactive solvent for PPE. In order to study to what extent the presence of a glassy dispersed phase interferes with the ductile deformation of PPE, two epoxy formulations are selected which result, after curing, in glassy materials, namely one with a yield stress which is higher and one with a yield stress which is lower than the yield stress of neat PPE, i.e. with DGEBA/DGEPPO ratios of 100/0 and 60/40, respectively. Additionally, two epoxy formulations with a DGEBA/DGEPPO ratio of 20/80 and 0/100 are selected which provide rubbery materials after curing, in order to evaluate their potential for rubber toughening. The mechanical properties of these solvent systems and that of pure PPE are presented in *Table 2*.

The morphologies of PPE processed using these four selected epoxy systems are shown in *Figure 6*. All of the fracture surfaces reveal the desired phase-inverted morphology of epoxy spheres in a continuous PPE matrix. Unfortunately, with increasing DGEPPO content a pronounced increase in the particle size of the dispersed epoxy phase is observed. The main reason for this phenomenon is found in the lower viscosities of the original homogeneous solutions, which promote more extensive coarsening after phase separation[1], and not in the lower solubility of PPE. In the most extreme situation of a solvent system consisting entirely of poly(propylene oxide) based constituents (DGEPPO/Jeffamine D-400), no stable morphologies could be generated and materials were obtained that were heterogeneous on a macroscopic scale.

Table 2 Mechanical properties of PPE and the cured epoxy resin solvent systems (sample standard deviations are denoted by the values in brackets)

Solvent system					
DGEBA/DGEPPO ratio	Curing agent	Tensil modulus (MPa)	Yield stress (MPa)	Tensile strength (MPa)	Elongation at break (%)
100/0	M-CDEA	2390(67)	(95)[a]	67.1(7.03)	5 (0.92)
60/40	M-CDEA	2412(124)	54.3(0.57)	—	18(2.5)[b]
20/80	M-DEA	4.1(0.07)	—	1.04(0.14)	29(4.5)
0/100	M-DEA	2.2(0.12)	—	0.53(0.06)	24(4.3)
PPE	—	2403(75)	70.1(0.64)	— —	89(17.3)

[a] See ref. 8

[b] Estimated from neck geometry

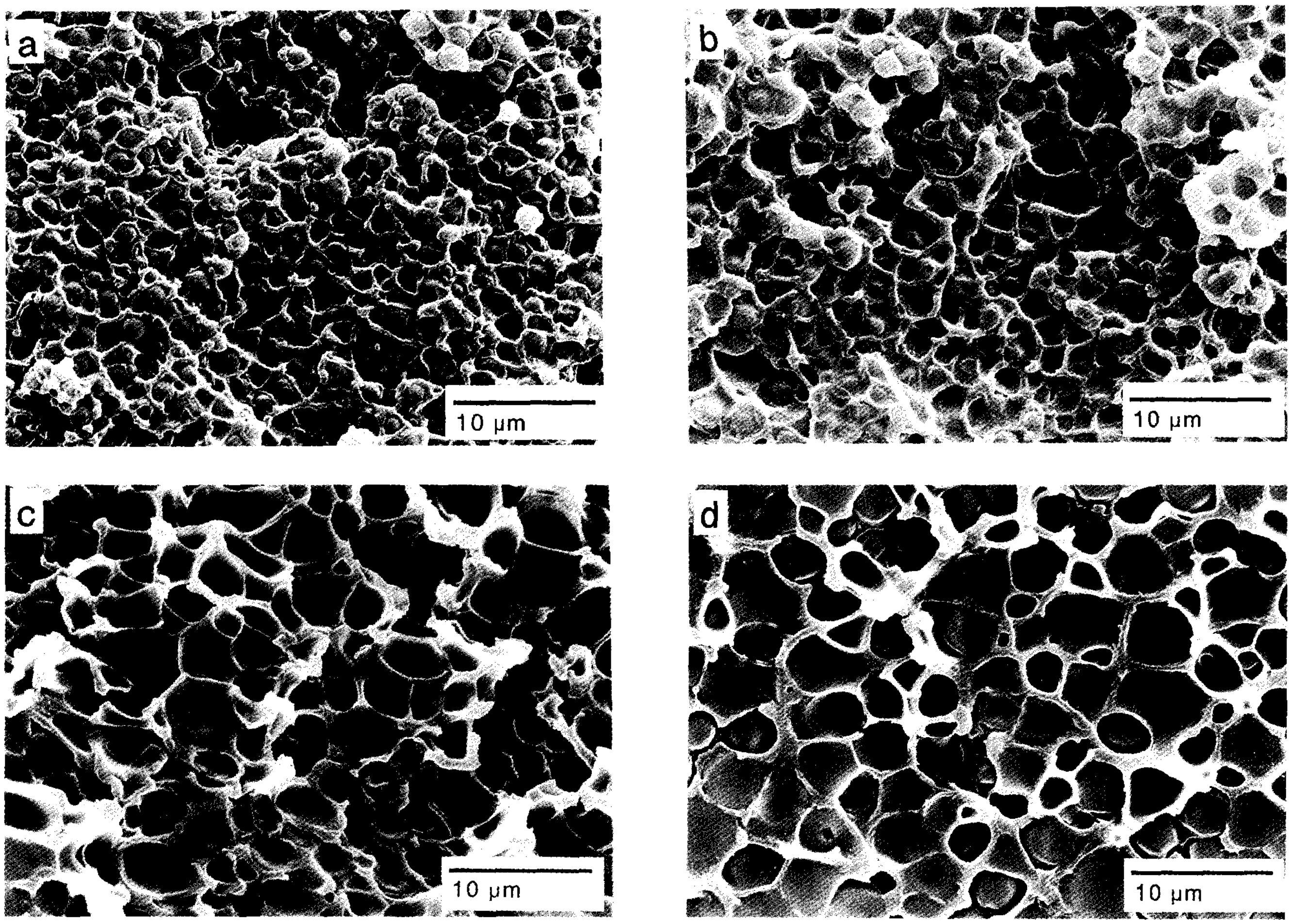
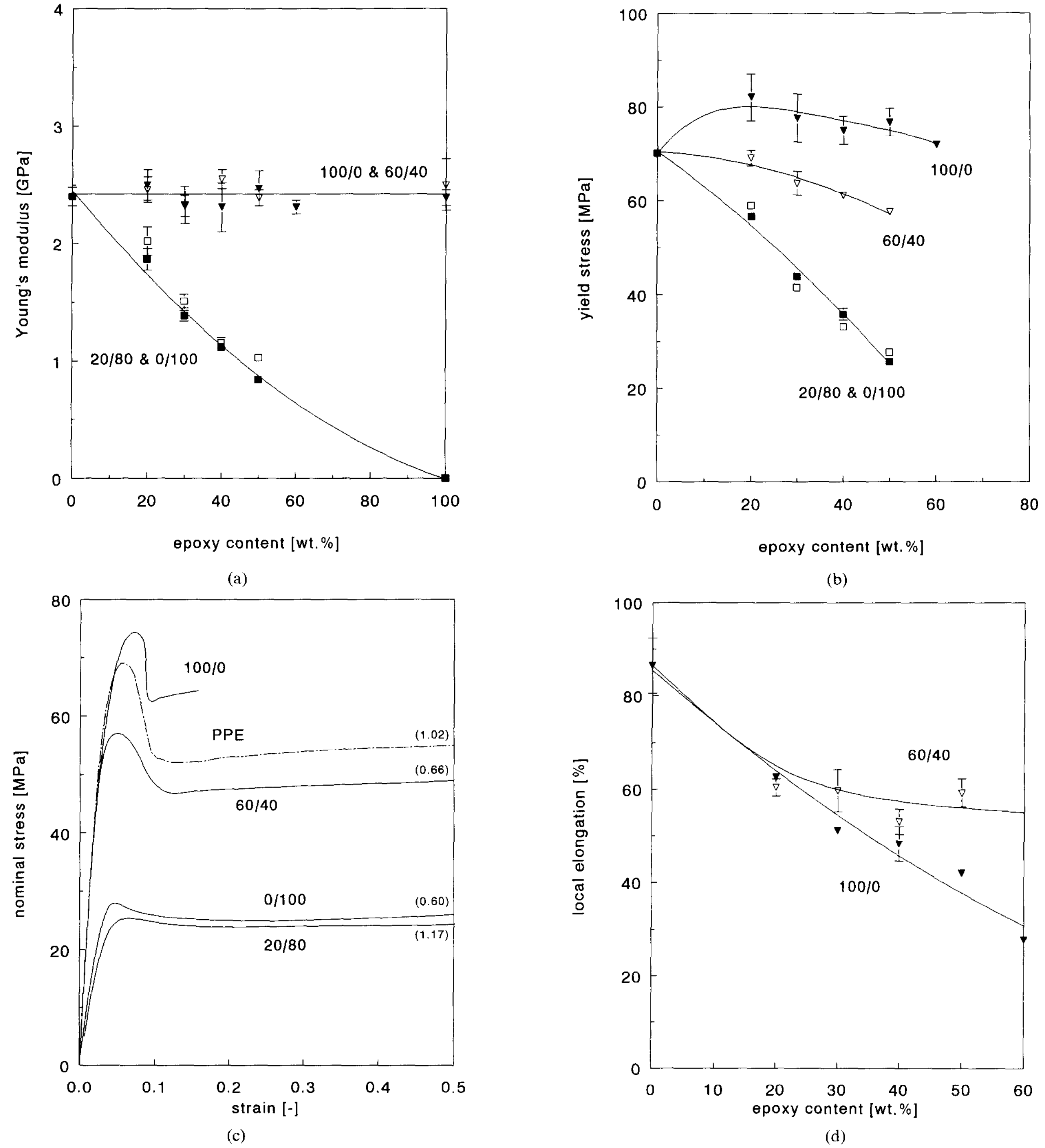


Figure 6 Scanning electron micrographs of the cryogenic fracture surfaces of PPE/epoxy (50 wt% epoxy) with: (a), (b) glassy dispersed phases with DGEBA/DGEPPO ratios of 100/0 and 60/40, respectively; (c), (d) rubbery dispersed phases with DGEBA/DGEPPO ratios of 20/80 and 0/100, respectively

In order to evaluate the extent of phase separation in the cured materials, the T_gs of the PPE matrices were determined using d.m.t.a. The results revealed that, in contrast to the solvent based on pure DGEBA, where almost complete phase separation is observed upon curing[1], in the case of the flexibilized epoxy systems the T_gs of the PPE are not fully regained after curing. Upon varying the DGEBA/DGEPPO ratio from 100/0 to 0/100, a reduction in T_g of the PPE-rich phase from ~220 to 200°C is found. This unwanted effect is the result of the chemical composition of the DGEPPO resin. Analyses of the stoichiometry revealed that the average functionality of this resin was ~1.7. Consequently, the resin will contain unepoxidized (or only partly epoxidized) poly(propylene oxide) which is not able to segregate completely from the PPE-rich phase. In order to estimate the efficiency of traces of DGEPPO in flexibilizing the PPE matrix, the tensile properties of PPE containing 10 wt% of dissolved DGEPPO resin were determined and compared with the properties of neat PPE. Probably because of the fact that this material has a relatively high T_g (175°C), no significant reduction in modulus and yield stress was found at room temperature, and flexibilization effects may therefore be neglected.

The tensile properties of the series of PPE/epoxy systems are presented in *Figure 7*. As can be derived from the Young's moduli of the materials (presented in *Figure 7a*), the values of the moduli of the *in situ* polymerized epoxy spheres correspond with those found for the pure epoxy resin formulations. Since the moduli of the glassy dispersed phases with a DGEBA/DGEPPO ratio of 100/0 and 80/20 coincide with the modulus of pure PPE, the moduli of the final materials are independent of composition. Consequently, during tensile loading both glassy dispersed phases will not induce stress concentrations and will act only as regions with a different yield behaviour. This is in contrast to the systems containing a rubbery dispersed phase, where an approximately linear reduction in modulus with epoxy resin content is observed. The yield stress values are presented in *Figure 7b*. For the blends containing the low modulus (and consequently relatively non-load bearing) rubbery epoxy particles, a continuous decrease in the macroscopic yield stress is observed with increasing epoxy content. In the case of a glassy dispersed phase a pronounced influence of the yield stress of the dispersed phase on the macroscopic mechanical properties is demonstrated. The glassy epoxy spheres with a yield



(a) (b) (c) (d)

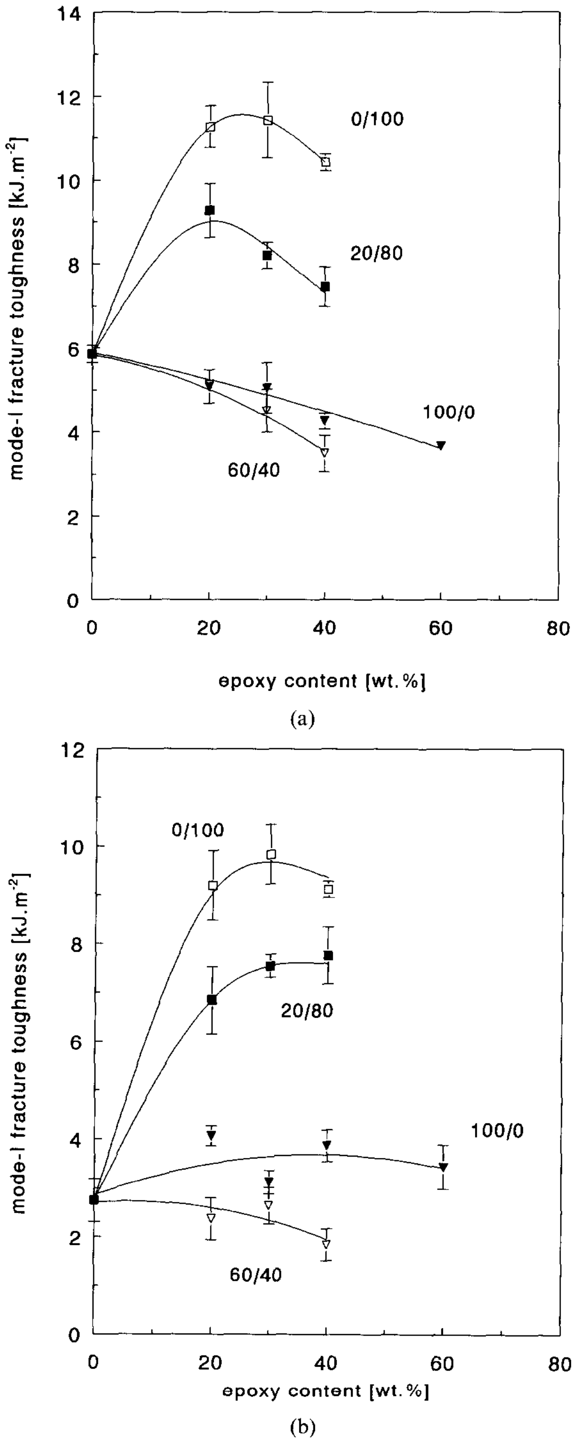
Figure 7 Tensile properties of PPE/epoxy *versus* the epoxy content, for DGEBA/DGEPPO ratios of 100/0 (▼), 60/40 (▽), 20/80 (■) and 0/100 (□): (a) Young's modulus; (b) yield stress; (c) stress–strain curves (strain at break is indicated by values in brackets); (d) local elongation stress higher than the yield stress of pure PPE, i.e. with a DGEBA/DGEPPO ratio of 100/0, clearly increase the yield stress of the system. In accordance with the results given in part 1 of this series, this is explained by considering that these relatively non-deformable epoxy spheres constrain the plastic deformation of the PPE matrix. It is remarkable that higher yield stress values are found for lower epoxy contents. This observation may be explained by the additional change in morphology. The particle size of the dispersed phase decreases continuously with increased PPE content[1]. For instance, in the case of this PPE/epoxy system, increasing the PPE content from 60 to 80 wt% yields a reduction in the particle size from 1.2 to 0.6 μm.

The effect of the epoxy inclusions on the deformation behaviour of PPE is demonstrated in the stress–strain curves given in *Figure 7c*. Besides the clear increase in yield stress found for the blends containing the relatively non-deformable epoxy spheres with a DGEBA/DGEPPO ratio of 100/0, in addition a sharp necking transition is observed which is indicative of a strongly localized yielding behaviour. As soon as the yield stress of the dispersed phase is reduced to below that of neat PPE, which is already the case for a DGEBA/DGEPPO ratio of 60/40, the epoxy resin inclusions no longer constrain the plastic deformation of the system. The yielding process is considerably less localized, i.e. a significantly less steep necking transition is observed, and stable necking accompanied by high maximum elongation is found.

Since most samples reveal pronounced heterogeneous deformation or necking the macroscopic elongations found in the tensile tests are not representative of the characteristic elongation of the materials. An attempt to define the maximum elongation more precisely is made by estimating the local elongation from the geometry of the neck. This was only possible for samples containing the glassy dispersed phases, since the rubber-modified materials revealed stress-whitening upon tensile loading, which is indicative of dilatation. As shown in *Figure 7d* for the systems containing the non-deformable glass (100/0), the local elongation decreases continuously with increasing epoxy content. This trend is less well defined for the blends containing the flexibilized glass with a DGEBA/DGEPPO ratio of 60/40, which is indicative of the additional deformation of the dispersed epoxy phase. The high local elongation values, when compared to the macroscopic strain at break, demonstrate that although the presence of the non-deformable epoxy spheres results in a more localized deformation of the PPE, they do not prevent yielding. However, the corresponding yielding process requires high stresses and will in practice often result in premature catastrophic failure due to the inevitable presence of flaws in the samples.

The toughness of this series of PPE/epoxy systems was analysed by using the mode-I fracture toughness test. As a result of the high intrinsic toughness of these materials it is difficult to comply with the requirements for fracture toughness testing, as proposed by the *European Group on Fracture*[6], using conventional specimen geometries. While the tests carried out on the specimens containing the glassy epoxy spheres can be considered valid, the tests on specimens which include rubbery epoxy systems were not valid with respect to both the linearity requirements and specimen geometry (thickness). Nevertheless, the mode-I fracture toughness tests are still useful for a mutual comparison of the materials that were prepared.

The results of the fracture toughness tests, which were conducted at a standard speed of 10 mm min^{-1} and at a high speed of 1 m s^{-1} are given in *Figure 8*. In general, the same trends upon changing the mechanical properties of the dispersed phase are found for both testing speeds. However, the high-speed experiments yield lower toughness values, probably



(a)

(b)

Figure 8 Fracture toughness (G_{Ic}) of PPE/epoxy *versus* the epoxy content, for DGEBA/DGEPPO ratios of 100/0 (▼), 60/40 (▽), 20/80 (■) and 0/100 (□), obtained at a testing speed of: (a) 10 mm min^{-1}; (b) 1 m s^{-1}.

as a result of the significantly higher deformation rate.

The rubbery epoxy systems are effective as impact modifiers for PPE, as is clearly illustrated in *Figure 8*. Because PPE is typically shear deforming, this toughening effect has to be related to the initiation of a multiple shear yielding mechanism. The micromechanics of this toughening mechanism have been extensively reported in the literature[16–25]. Although the exact mechanism, such as, e.g. the importance of adhesion, is still a matter of debate, it is recognized that it is not so much the rubber particle itself, but the resulting morphology or, to be more precise, the thickness of the material on the microscale, that plays a predominant role.

The low-and high-speed experiments prove that the rubbery epoxy formulation with the DGEBA/DGEPPO ratio of 0/100 yields significantly higher toughness values than the formulation with a ratio of 20/80. The reason for this observation is not clear, particularly since both rubbers differ only slightly in their mechanical properties. An explanation may be found in the slightly lower modulus (2.1 and 4.1 MPa) or, more likely, in a lower level of adhesion for the rubber with pure DGEPPO as a solvent, as was already anticipated based on the lower reactivity of DGEPPO compared to DGEBA. This assumption is supported by an examination of the fracture surfaces. In *Figure 9* scanning electron micrographs are given of the fracture surfaces of both rubber-toughened systems containing 20 wt% of rubber. Clearly, for the material with the more efficient rubber (in terms of toughening), an intensive dilated fracture surface topology is observed as a result of cavitation or debonding of the rubber particles. This is in contrast to the fracture surface of the sample containing the less efficient rubber, where no void formation is observed.

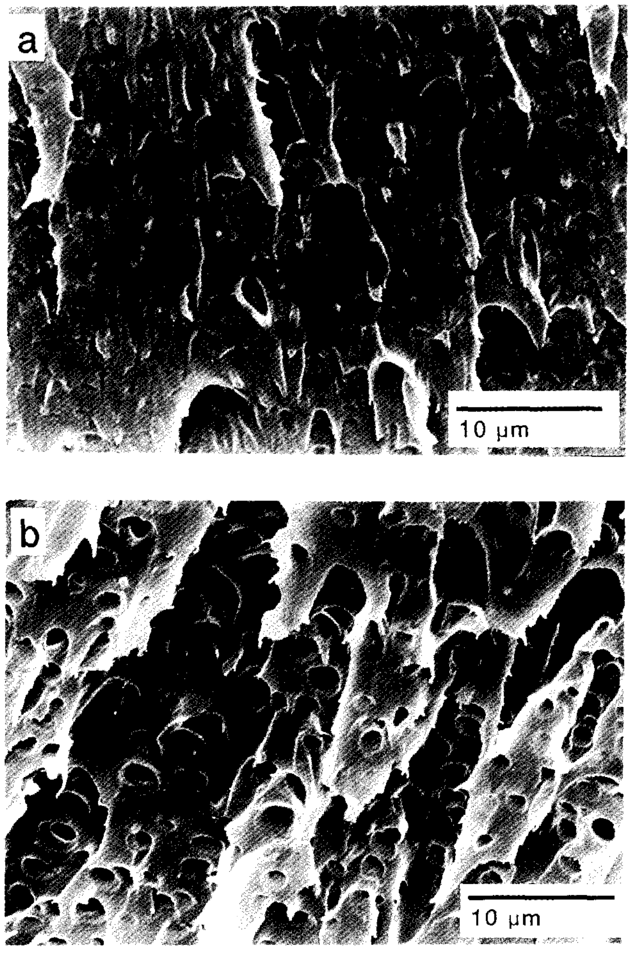


Figure 9 Scanning electron micrographs of the fracture surfaces generated in fracture toughness testing of PPE/epoxy specimens (20 wt% epoxy cured with 51 phr of M-CDEA) with a DGEBA/DGEPPO ratio of: (a) 20/80; (b) 0/100

As anticipated, in contrast to the rubbery systems, the introduction of a glassy dispersed phase does not enhance the toughness of PPE. The materials reveal a toughness on the same scale as pure PPE and, in general, a reduction in toughness is found with an increasing epoxy content. The results obtained for the system containing the non-deformable epoxy spheres, however, are contradictory. While for the low testing speed, in accordance with the previous results, a clear reduction in toughness is found, in the high-speed experiments an increase in toughness is observed when compared to pure PPE. This contradiction may be an artefact caused by the sample geometry, which may not provide sufficient plane strain testing conditions, resulting in an overestimation of the toughness, particularly for pure PPE, at low testing speeds. Although a moderate toughening effect by incorporating rigid particles is conceivable, more experiments are required to draw any definite conclusions. Interestingly, the results demonstrate that reducing the yield stress of the glassy dispersed phase consistently yields a lower level of toughness. This is in contrast to the tensile tests where the reduction of the yield stress was shown to be in favour of ductile deformation of the material.

CONCLUSIONS

It was demonstrated that epoxy resins based on bisphenol-A and poly(propylene oxide) can be applied as reactive solvents for PPE. The mixing of both types of monomer results in a continuous range of homogeneous epoxy resin networks with mechanical properties varying from non-ductile glassy to rubbery. Use of this epoxy resin system did not only introduce processability to PPE but, in addition, provided indirectly a route for tuning the mechanical performance of the final polymer blend. For example, the solvent system can be exploited to act, after phase separation, as an effective impact modifier for PPE. The rubbery impact modifier with the lowest level of adhesion proved to be most efficient in improving the toughness of the final blend. In addition, it was shown that the presence of non-ductile (high yield stress) epoxy spheres constrain the plastic deformation of the PPE matrix. A reduction of the yield stress of the dispersed phase, however, did not lead to an improvement in the mechanical performance, such as the fracture toughness of the material.

ACKNOWLEDGEMENTS

This research is supported financially by General Electric Plastics (Bergen op Zoom, The Netherlands). The authors would like to thank A. Landa (General Electric Plastics) for the gel permeation chromatography analyses. In addition, the authors are grateful to M. van de Sande for her assistance with a large part of the experiments and to T.A. Tervoort for valuable comments on the manuscript.

REFERENCES

1 Venderbosch, R.W., Meijer, H.E.H. and Lemstra, P.J. *Polymer* 1994, **35**, 4349

2 Venderbosch, R.W., Meijer, H.E.H. and Lemstra, P.J. *Polymer* 1995, **36**, 1167

3 Pearson, R.A. and Yee, A.F. *J. Mater. Sci.* 1989, **24**, 2571

4 Morgan, R.J., Kong, F.M. and Walkup, C.M. *Polymer* 1984, **25**, 375

5 Experiments conducted on a Werner and Pfleiderer ZSK 25 co-rotating twin screw extruder (closely intermeshing and self-wiping) revealed that the mixing time can be relatively easily reduced to ~5–10 min

6 Williams, J.G. and Cawood, M.J. *Polym. Test.* 1990, **9**, 15

7 Fox, T.G. *Bull. Am. Phys. Soc.* 1956, **2**, 123

8 The yield stress of Epikote 828EL, cured wtih 51 phr of M-CDEA, was determined in uniaxial compression using specimens with a geometry of $6 \times 6 \times 25\,\mathrm{mm}^3$, on a Frank tensile tester (81565 IV) with a strain rate of $10^{-3}\,\mathrm{s}^{-1}$. The yield stress of 107 MPa, which was found in this compression test, was subsequently used to estimate the yield stress in tensile conditions by assuming a modified Von Mises yield criterion with a coefficient of increase of yield stress with hydrostatic pressure equal to 0.1 (Peijs, T., Schellens, H., de Kok, J.M.M. and Govaert, L., unpublished results)

9 Ward, I.M. *J. Mater. Sci.* 1971, **6**, 1397

10 Smith, T.L. *J. Polym. Sci.* 1958, **32**, 99

11 Smith, T.L. and Stedry, P.J. *J. Appl. Phys.* 1960, **31**, 1892

12 Smith, T.L. in 'Rheology: Theory and Applications', Vol. 5 (Ed. F.R. Eirich), Academic Press, New York, 1969, p. 127

13 Arnauts, J. and Berghmans, H. *Polymer* 1987, **28**, 66

14 Vandeweert, P., Berghmans, H. and Tervoort, Y. *Macromolecules* 1991, **24**, 3547

15 Deberdt, F. and Berghmans, H. *Polymer* 1993, **34**, 2192

16 Wu, S. *Polymer* 1985, **26**, 1855

17 Wu, S. *J. Appl. Polym. Sci.* 1988, **35**, 549

18 Borggreve, R.J.M., Gaymans, R.J. and Schuijer, J. *Polymer* 1989, **30**, 71

19 Borggreve, R.J.M., Gaymans, R.J. and Eichenwald, H.M. *Polymer* 1989, **30**, 78

20 Yee, A.F., Li, D. and Li, X. *J. Mater. Sci.* 1993, **28**, 6392

21 Van der Sanden, M.C.M., Meijer, H.E.H. and Lemstra, P.J. *Polymer* 1993, **34**, 2148

22 Van der Sanden, M.C.M., Meijer, H.E.H. and Tervoort, T.A. *Polymer* 1993, **34**, 2961

23 Van der Sanden, M.C.M. and Meijer, H.E.H. *Polymer* 1993, **34**, 5063

24 Van der Sanden, M.C.M. and Meijer, H.E.H. *Polymer* 1994, **35**, 2774

25 Bagheri, R. and Pearson, R.A. in Proceedings of 9th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge, April 1994, p. 106