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Dendritic hyperbranched polymers as tougheners for epoxy resins

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Abstract

Dendritic hyperbranched polymers (HBPs) show outstanding performance as tougheners in epoxy resins. The critical strain energy release rate, G_{Ic}, of a DGEBF resin is increased by a factor of 6 from 120 J/m^2 to 720 J/m^2 using only a 5% modifier weight content. This does not lead to a decrease in resin stiffness or glass transition temperature and the favourable processability of epoxy resins is fully maintained without requiring the use of solvents. Toughness properties are induced by a finely-dispersed particulate structure which is obtained by a controlled phase separation process during resin curing. A strong mechanical phase interaction is ensured by chemical bonding through reactive epoxy groups grafted onto the HBP. By tailoring the HBP's epoxy functionality and polarity to control reactivity, phase separation, final morphology and phase interactions, this toughening system is potentially applicable to a variety of thermoset resins. With this in view, the influence of the chemical architecture of the HBP modifiers on phase separation, processability, properties and toughening mechanisms is investigated.

Keywords: Toughness; Hyperbranched polymers; Thermoset resins

1. Introduction

Large amounts of epoxy resins are used world-wide in coatings, adhesives, moulding compounds and polymer composites. These resins have superior thermomechanical properties and excellent processability. However, the use of thermosetting materials is often limited by their toughness properties, which affect the durability of components and place strong constraints on design parameters. Impact resistance, fatigue behaviour and damage tolerance are some of the properties influenced. Therefore, over half of the epoxies used contain tougheners and a large majority of these are carboxy-terminated butadiene acrylonitrile (CTBN) rubber materials. Toughness properties of thermosetting materials have attracted widespread attention over the last decade and still remain a major topic in the development of these materials. The goal is to develop new tougheners which do not affect thermomechanical properties and the ease of processing. Finally, these toughener systems should be applicable to the wide variety of thermosetting materials presently used as composite matrices.

The processability of thermoset resins is critical to many applications. Low viscosity is for instance vital for moulding compounds and coatings. Modification of a resin system must not lead to phase segregation induced by phase instabilities which can be due to density differences between modifier and matrix or to unfavourable interfacial energy balances between the modifier, the epoxy resin and a substrate [1]. Furthermore, the modifier must not be filtered out, as can be observed with particulate tougheners during fibre bed impregnation in composite manufacturing [2]. The aim is therefore to obtain a sustainable toughening effect without affecting the viscosity of the uncured resins and without risking toughener segregation or filtering. This should be achieved with an initially homogeneous system and a low viscosity modifier.

Toughness implies energy absorption and can be achieved through various deformation mechanisms before failure occurs and during crack propagation [3]. On the one hand, toughening can be achieved by reduction of the cross-link density or use of plasticisers which lead to increased plastic deformation. This approach, however, may seriously affect modulus and thermal properties of the material for only a moderate increase in toughness. On the other hand, the most effective toughening mechanisms are induced by addition of a second phase in the form of particles. The toughening effect of particles, whatever their nature and properties, depends on their size, interparticle distance, particle/matrix interaction and volume fraction [4a,4b].

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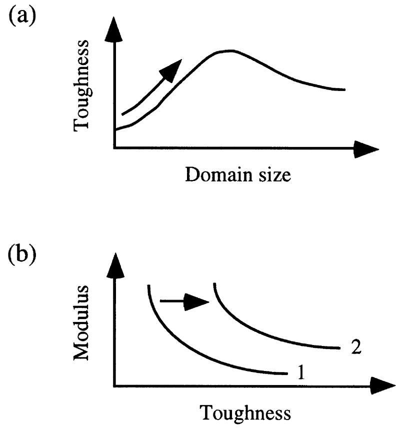

Fig. 1. General trends of (a) toughness properties as a function of the domain size of the dispersed phase and (b) the Young's modulus as a function of the toughness properties.

These parameters must be controlled and tailored for each thermosetting material.

The toughening system presented involves a phase separation process and by controlling the competing curing and phase-separating kinetics, the particle sizes and particle properties can be adjusted as discussed below. Fig. 1(a) schematically shows the toughness dependency on the secondary phase domain size which displays a maximum [5]. This maximum value will be shifted to other particle sizes for different resins. Therefore, a toughening system applicable to various thermosetting matrix materials must include a controllable phase separation process by which particle sizes can be adjusted. Most often, toughening of a matrix material is accompanied by a reduction in modulus, according to curve 1 in Fig. 1(b), due to a modification of the network structure. Thus, the objective is to increase the toughness of high performance thermoset materials without affecting their thermomechanical properties which would then shift curve 1 towards curve 2.

For processability purposes, a liquid toughening agent compatible with the uncured thermosetting resin should be used in order to have a homogeneous system during the initial stage of processing. Subsequently, the phase separation should only be induced upon curing. A relatively high molecular weight toughening agent will facilitate the control of the phase separation process and increase its effectiveness as a toughener. However, high molecular weight generally implies a high viscosity, which is to be avoided. In order to satisfy both requirements, low viscosity and a high molecular weight, a spherical molecular structure as opposed to a linear structure is more suitable. Dendritic polymers which possess a spherical structure have a lower viscosity than linear polymers for equivalent high molecular weights [6]. Similar properties are observed for some hyperbranched polymers characterised by a densely branched core/shell structure as shown in Fig. 2 [7,8]. The mechanical properties of these molecules are primarily defined by their core properties. On the other hand, the chemical structure of the shell controls the phase separation process. The chemical architecture of the shell can be adapted to various thermosetting resins without affecting the mechanical performances of the bulk. For all systems, reactive groups compatible with the thermosetting matrix should be grafted onto the shell to ensure an efficient stress transfer between the modifier and the resin.

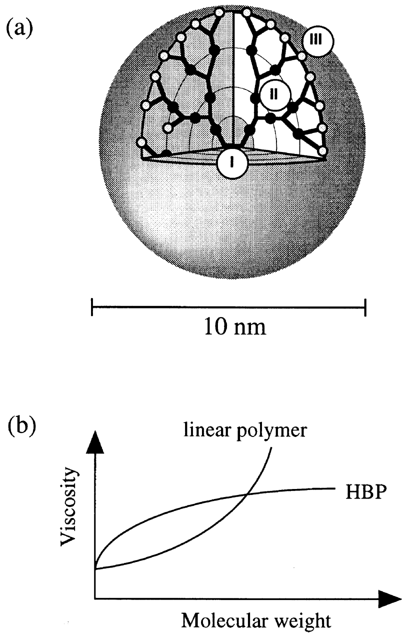

Fig. 2. (a) A dendritic hyperbranched polymer molecule with a structure composed of a multifunctional core (I), several layers of repeating units building up the bulk structure (II) and a multifunctional shell (III); (b) Viscosity behaviour as a function of molecular weight for linear polymers and hyperbranched polymers (HBPs).

Using a model system based on a commercial DGEBF epoxy resin, the influence of the processing conditions has been studied and a processing window established in the form of a time–temperature–transformation (TTT) diagram [9,10]. The phase separation process has been defined and the effect of the chemical architecture of the shell is also discussed. Finally, the modified resin deformation mechanisms are related to the structure and properties of the components.

2. Phase separation kinetics

A key issue when using HBP tougheners is the possibility to tailor phase separation, in order to ensure that it occurs after final resin flow. This also allows us to control the dispersed domain size, the particle distribution, the dispersed domain volume fraction, the phase interaction and the residual miscibility as will be discussed. All these parameters influence the resin toughness and thermomechanical properties. The phase separation process depends on the chemical nature of the components, and is kinetically controlled by the curing advancement [11]. Thus, the

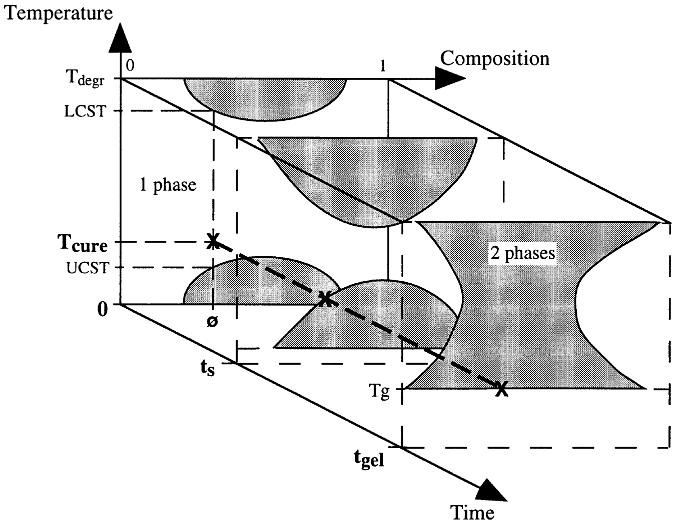

Fig. 3. Evolution of the phase diagram upon curing of the thermosetting material.

chemistry–process–structure–property relations are strongly influenced by the phase separation kinetics.

The effect of the chemical nature of the components is primarily seen at time = 0 in the static phase diagram schematised in Fig. 3. The diagram is determined by the balance of enthalpic forces and entropic related forces responsible for the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST) and describes the compatibility of the components [12]. The latter can be expressed in general terms by the Flory–Huggins equation for the total free energy of mixing [13]:

$$\Delta G_m = V_1(\delta_1 - \delta_2)^2\phi_1\phi_2 + RT(n_1 \ln \phi_1 + n_2 \ln \phi_2) \qquad (1)$$

where V is the molar volume, δ the solubility parameter, ϕ the volume fraction, and n the mole fraction. Subscripts 1 and 2 refer to the matrix and modifier, respectively. As the thermoset matrix cures, its molar volume increases which results in an increase of the first term in Eq. (1) and a decrease of the second term describing the configurational entropy which is negative [14]. Once a critical conversion is reached, the free energy of mixing becomes positive and phase separation occurs. It should also be noted that the solubility parameter of the matrix, δ, which can be expressed as:

$$\delta = (E_{vap}/V_1)^{\frac{1}{2}} \qquad (2)$$

with E_{vap} the energy of vaporisation, evolves as the extent of reaction increases [15]. Therefore, as curing proceeds, the phase diagram evolves with the change in both molar volume of the constituents and the interaction parameter, which can be expressed as the square of the difference in solubility parameters.

Isothermal processing at a temperature T_{cure} of a material with a volume fraction of modifier ϕ will induce a phase separation of the initially homogeneous mixture. The phase diagram evolution is shown in Fig. 3 at times 0, t_s and t_{gel}, the initial time at mixing, phase separation time and gel time, respectively. Phase separation will occur through a nucleation and growth process or a spinodal decomposition [12–16], depending on the initial composition and the ratio of the phase separation rate, ($\mathrm{d}s/\mathrm{d}t$), over the cure conversion rate, ($\mathrm{d}\alpha/\mathrm{d}t$), of the matrix material. If this ratio is small, spinodal decomposition occurs. This is often not desirable since it usually induces a considerable reduction of the thermomechanical properties of the cured modified matrix due to a higher residual miscibility of the modifier in the main phase. If the ($\mathrm{d}s/\mathrm{d}t$)/($\mathrm{d}\alpha/\mathrm{d}t$) ratio is large, phase separation occurs under equilibrium conditions and a minimum residual miscibility is obtained. In this case, the driving force for particle growth is small and growth is inhibited. However, nucleation is still active and a bimodal distribution of particle sizes will be obtained. In between these two extreme cases, the nucleation and growth process results in a limited amount of residual miscibility. To avoid a possible drop in thermomechanical properties the latter must be controlled. The nucleation and growth rates and hence the residual miscibility depend strongly on the diffusion constant, which may be expressed following the Stokes–Einstein relation [17]:

$$D_{AB} = kT/6\pi R_2\eta_1 \qquad (3)$$

where R_2 is the molecular radius of the dispersed phase and η_1 the viscosity of the matrix which is a function of the temperature and the extent of reaction. Thus, the size of the hyperbranched molecule will influence the phase separation process and modify the nucleation and growth rates, due to its effect on the diffusion coefficient. The viscosity at the cloud point, at which the phase separation initiates, is also very important for the final morphology. Processing conditions which modify the cure conversion and nucleation rates can also be used to control the phase separation behaviour and the obtained morphology.

3. Experimental

Various epoxy-functional hyperbranched dendritic molecules were synthesised following a procedure described by Pettersson et al. [18]. Polymerisation of the HBPs is performed by esterification in a batch process in which a predefined number of multifunctional repeating units are reacted onto a multifunctional core. The repeating units are arranged in layers around the core, each layer representing one generation of the HBP. Three and five generation HBPs built from a tetrafunctional core and trifunctional repeating units (Boltorn™-H30 and Boltorn™-H50, Perstorp) were used. These HBPs have 32 and 128 reactive sites on their shell respectively. Various shell chemistries subsequently added by esterification are evaluated for tailored phase separation and toughening properties as a function of molecular size, polarity and epoxy functionality. These functionalised HBPs all show a Newtonian behaviour. A three-generation HBP functionalised with hydroxyl groups and secondary aliphatic epoxy groups for which the epoxy ring was shielded (Boltorn™-E1, Perstorp) was chosen as the reference modifier. Specific characteristics of the other modifiers used are described in the following section. These materials were blended with a DGEBF commercially-available epoxy resin (LY5082, Ciba–Geigy). The modified resin was cured isothermally with an isophorondiamine hardener after having been degassed under vacuum for 5 min. The hardener was added in stoichiometric proportions. A blend with 5% of the reference modifier is generally used hereafter unless otherwise specified.

The phase separation process was characterised by turbidimetry. Surface tensions and interfacial energies were measured using the Whilhelmy plate method on a Sigma70 equipment (KSV Inc.). Rheological data and gelation and vitrification times were obtained using a parallel plate shear rheometer (Rheometrics RDA-II) at a frequency of 1 Hz under isothermal conditions. The gelation time is determined at the onset of the shear storage modulus (G') increase and the vitrification time is determined at tan $\delta = 1$ in accordance with [19]. Curing kinetics, i.e. the extent of reaction as a function of time, were analysed by differential scanning calorimetry (Perkin–Elmer DSC-7) under isothermal conditions. The degree of conversion is calculated as the ratio of the heat of reaction obtained divided by the total reaction enthalpy of a full isothermal cure measured at a temperature above the ultimate glass transition temperature of the resin system. Thermo-mechanical properties, modulus and glass transition temperatures T_g, were determined using a Rheometrics RSA-II equipment in a three point bending geometry at a frequency of 1 Hz and a heating rate of 5°C/min. Morphological analysis of the modified epoxy matrix was performed using optical microscopy (Olympus BH-2), transmission electron microscopy (TEM) (Phillips CM300) and scanning electron microscopy (SEM) (Cambridge S100) on thin sections, microtomed samples and fracture surfaces, respectively. Tensile, flexural and compact tension (CT) specimens were used to assess the mechanical properties of the cured materials. These samples were tested according to ASTM D3039M-93, D790M-93 and D5045-96 standards respectively at room temperature on a computer controlled conventional tensile testing equipment (UTS-100).

4. Results and discussion

4.1. Phase separation

Initial miscibility is controlled by the physical interactions between the modifier and the resin system. These interactions, which depend on the chemical nature of the HBP structure and on the architecture of its shell, modify the solubility parameter and therefore the free energy of mixing, as expressed by Eq. (1). The size, or generation, of the HBP does not affect the resin compatibility to a great extent when comparing the three and five generation HBPs. Phase interactions are mainly influenced by the chemistry and physical nature of the shell functional groups. In the systems studied, both a UCST and a LCST have been observed. Fig. 4 shows the static phase diagram of a 5% modified epoxy resin using a less polar HBP than the reference modifier. By increasing the modifier's polarity, the UCST is shifted to lower temperatures. When the UCST is shifted to temperatures below the uncured resin T_g, only a LCST is observed. Adding the hardener generally also results in a decrease of the UCST. For the system depicted in Fig. 4 at a HBP loading level of 5%, the UCST is reduced to 45°C upon addition of the hardener. With this low polarity HBP modifier, processing must be performed at a

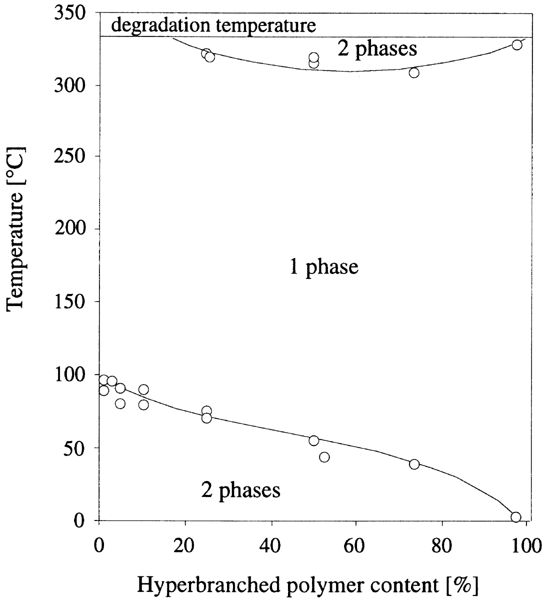

Fig. 4. Static phase diagram of a 5% HBP modified DGEBF epoxy resin without hardener.

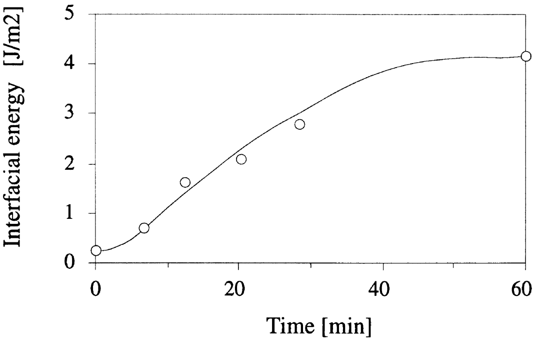

Fig. 5. Interfacial energy between HBP and epoxy resin as a function of cure time.

temperature above 45°C so as to obtain a homogeneous mixture and to avoid filtration effects as discussed earlier.

Phase separation is induced by a polarity change of the epoxy resin upon curing. The opening reaction of the epoxy ring forms a hydroxyl group, by which the polarity of this chemical unit undergoes a 3.9 fold increase. The polar component of the molar attraction function is 156 $(\mathrm{J \cdot cm^3})^{1/2}$/mol for the epoxy ring and 591 $(\mathrm{J \cdot cm^3})^{1/2}$/mol for the hydroxyl group [20]. Therefore, as curing proceeds, the interfacial energy of the HBP/epoxy resin increases as illustrated in Fig. 5. For phase separation to occur, the epoxy resin and the epoxy functional HBP must have different curing kinetics considering the HBP high functionality. Indeed, as the HBP cures, hardener and epoxy molecules are grafted onto the shell, which strongly compatibilises the HBP with the surrounding resin. Therefore, aliphatic epoxy has been used to functionalise the HBP. These epoxy groups cure at a lower rate than the DGEBF epoxy resin, which is confirmed by isothermal curing conversion measurements made on pure resin and HBPs with hardener.

Polar and reactive hyperbranched molecules with primary epoxy groups based on epichlorohydrane chemistry grafted onto the shell are initially miscible and do not phase separate. In this case, they act as plasticisers. The curing kinetics of these HBPs are similar to the curing kinetics of the resin. The absence of phase separation is due to the network formation linking the hyperbranched molecules already in the initial stages of cure. The toughening effect in this case remains moderate. With 25% of modifier, the stress intensity factor, K_{Ic}, increases from 0.63 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the neat resin to 0.83 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the modified resin system. However, the toughening effect is accompanied by a decrease in the final glass transition temperature from 104°C to 85°C, due to the modification of the epoxy network by this fully miscible modifier.

The reference hyperbranched modifier, which is less reactive, induces a phase separation resulting in a finely dispersed particulate structure, as shown in Fig. 6(a). This leads to a 2.5-fold increase in the K_{Ic} values, from 0.63 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the neat resin to 1.54 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the modified resin. This represents a 6-fold increase in the energy release rate G_{Ic} from 120 $\mathrm{J/m^2}$ for the neat resin to 720 $\mathrm{J/m^2}$ for the modified resin [21]. Using a 10% and 15% volume content of modifier, the K_{Ic} values are further increased to 1.75 and 2.03 $\mathrm{MPa}\sqrt{\mathrm{m}}$ respectively. However, at these amounts, as shown in Table 1, the modulus is reduced to 2.65 and 2.4 GPa for the 10% and 15% modified resins, respectively.

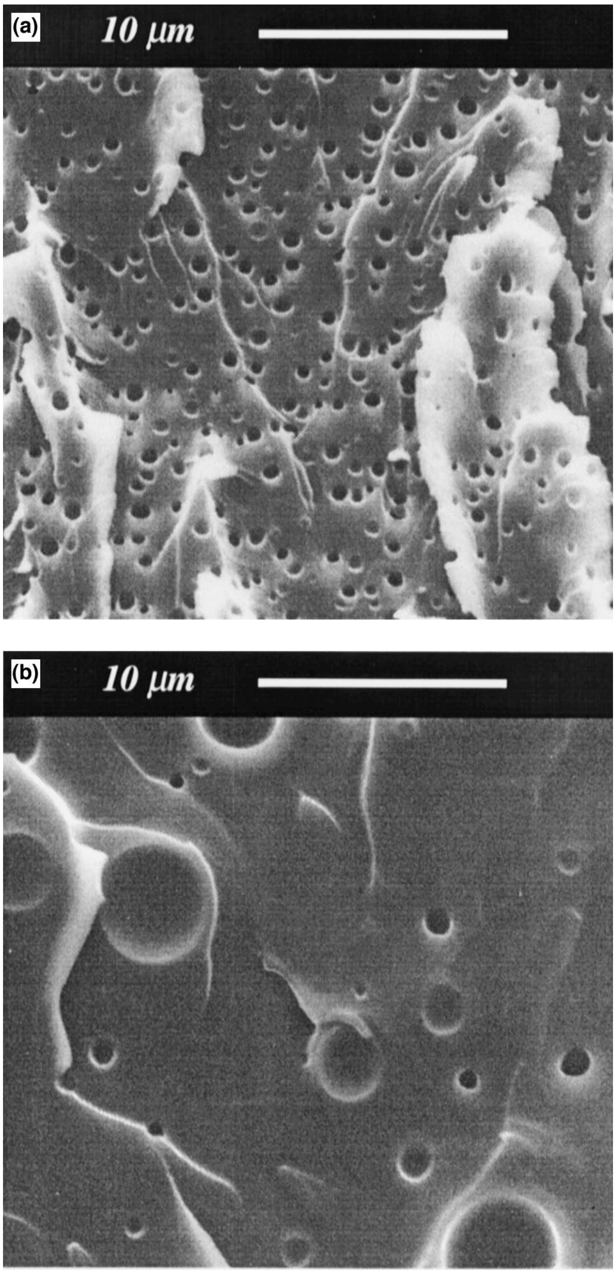

Fig. 6. SEM fracture surfaces of 5% modified DGEBF epoxy resin with (a) the Boltorn®-E1 reference modifier and (b) the low-polar epoxidised HBP, both cured at 80°C.

With 5% of an epoxidised but less-polar hyperbranched molecule, no homogeneous mixture can be obtained under 100°C, which is the maximum processing temperature for the epoxy resin used. After cure, a bimodal particle size distribution is obtained as shown in Fig. 6(b). The toughening effect is still significant, with K_{Ic} increased to

Table 1
Mechanical properties of a HBP modified DGEB-F epoxy resin

HBP modifier	Content	K_{Ic} [MPa$\sqrt{\mathrm{m}}$]	G_{Ic} [J/m^2]	E [GPa]
Unmodified DGEB-F epoxy		0.63	120	2.9
Most reactive HBP	25%	0.83	260	2.35
Boltorn-E1	5%	1.54	720	2.9
Boltorn-E1	10%	1.75	1010	2.65
Boltorn-E1	15%	2.03	1510	2.4
Less polar HBP	5%	1.34	540	2.9
Least reactive HBP	5%	1.24	470	2.9

1.34 MPa$\sqrt{\mathrm{m}}$. However, starting with an emulsion, composite processing may induce an unfavourable filtering effect, as discussed earlier. Storage of an unstable epoxy modifier blend in the uncured state without mixing could in some cases also result in segregation of the modifier, reducing the ease of handling and making it more difficult to control the particle size and distribution.

With 5% of a low-reactive hyperbranched molecule, functionalised with only a few secondary epoxy groups, toughening becomes less effective due to a limited capacity for stress transfer between the epoxy matrix and the dispersed modifier phase (Table 1).

Using 5% of the reference modifier in the epoxy resin cured at 80°C, the volume fraction of particles measured by TEM [22] is 4.4%. This shows that at least 0.6% of the HBP is dissolved in the epoxy resin. However, this residual miscibility is expected to be larger since the particles will include epoxy resin molecules due to the reactivity of the HBP, which traps these epoxy molecules as phase separation occurs. The residual miscibility can therefore not be neglected and will influence the toughening capacity of the modifier. The HBP molecules trapped within the continuous phase will enhance its capacity to deform plastically.

As shown above, it can be concluded that phase separation inducing a particulate structure enhances the toughening capacity of the HBP modifier. The phase separation process is strongly influenced by the relation of the reaction kinetics of the resin and the epoxidised HBP. The reaction kinetics also control the residual miscibility of the HBPs in the continuous phase which influences the toughening properties. The initial miscibility, which is important for processing and stability of the blend in the uncured state, is strongly dependent on the chemical design of the HBP shell.

4.2. Processing

Fig. 7 shows that the initial viscosity of the epoxy resin when toughened with 5% of the reference modifier remains under 100 mPas at room temperature. The processing temperatures recommended for this resin range from 20°C to 100°C. Within this range, the viscosity is almost unaffected by the presence of the modifier and processability is maintained because of the liquid nature of HBPs without requiring the use of solvents.

Fig. 8 represents the time–temperature–transformation (TTT) diagram of the modified epoxy resin. The successive events occurring during isothermal processing are determined following horizontal lines in the TTT diagram. The events represented are the phase separation behaviour as measured by turbidimetry, followed by the gelation and vitrification curves. The form of iso-conversion curves is also represented. These are of particular importance since the extent of conversion controls the phase separation. The iso-conversion curves allow us to monitor multistage processing if various temperature steps are required [23]. It is desired that the resin flow or mould filling should be completed before phase separation is initiated. If the resin flow is to be performed at 80°C and the entire process cannot be done within the time to phase separation at that temperature, mixing and degassing can be done at a lower temperature. The time available after increasing the temperature to 80°C can be estimated by following up to 80°C the iso-conversion curve attained after mixing. The process time remaining is then the difference between this conversion equivalent time and the time to phase separation at 80°C. In this way processability is easily defined. However, the fact that processing conditions influence phase separation, structure and thus also final properties must be considered.

After nucleation, phase separation proceeds until complete gelation, when diffusion of the modifier molecules within the continuous matrix phase is inhibited. From the onset of phase separation, the structure is evolving up to gelation at which particle dimensions and interparticle distances are fixed. As the processing temperature is increased, the times available for particle nucleation and growth become considerably shorter partly because the

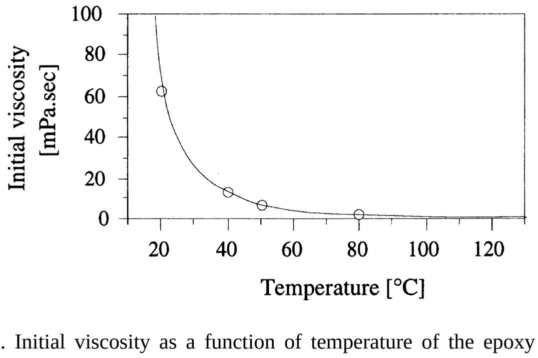

Fig. 7. Initial viscosity as a function of temperature of the epoxy resin containing 5% of the reference modifier.

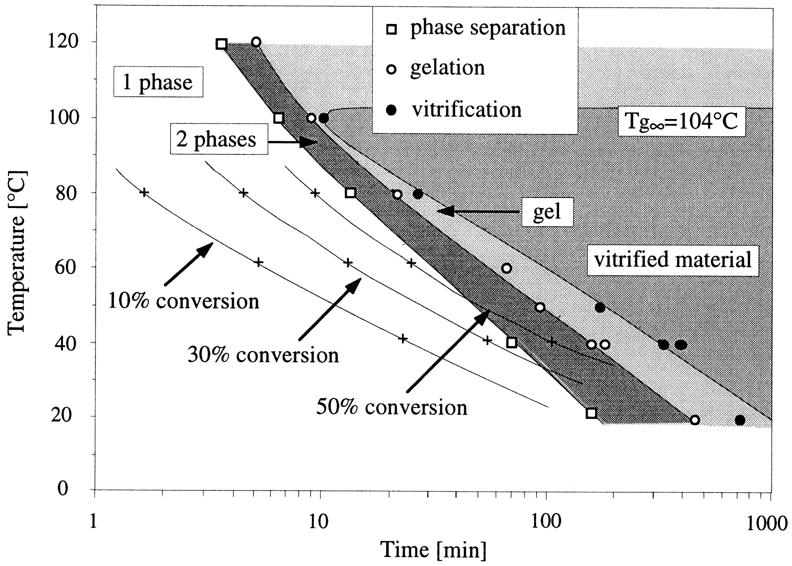

Fig. 8. Time–Temperature–Transformation (TTT) diagram of the epoxy resin with 5% of the reference modifier. Phase separation, iso-conversion, gelation and vitrification curves are defined under isothermal curing conditions.

compatibility is increased. At 80°C, phase separation is initiated at a conversion of 55%, as opposed to a conversion of 34% at 40°C. Thus, the epoxy groups on the modifier molecules have reacted to a large extent and their diffusion capability is decreased. However, the viscosity at which the phase separation takes place is reduced leading to a renewed increase of the diffusion coefficient of the modifier in the resin. These opposite trends attenuate the influence of processing temperature on obtained structures due to its influence on the modifier diffusion coefficient.

The structures obtained by curing at different temperatures vary due to the different nucleation and growth rates. When processing under the UCST as is the case with unpolar HBP modifiers at room temperature, a bimodal particle size distribution is obtained, as shown in Fig. 6(b). This is due to a large $(\mathrm{d}s/\mathrm{d}t)/(\mathrm{d}\alpha/\mathrm{d}t)$ ratio as discussed earlier. The largest particles observed have a diameter of approximately 4.5 μm. This remains small compared to other phase separating systems, since the large molecular weight of the modifier limits the diffusion rate. The smaller particles for the HBP modified resins showing a bimodal distribution (Fig. 6(b)), and the largest particles obtained by processing at higher temperatures (Fig. 6(a)), have diameters of less than 1.3 μm. Processing at higher temperatures also decreases the interparticle distances which is explained by the increased temperature dependent nucleation rate. Decreasing the interparticle distance has previously been shown to increase the toughening effect [21].

Residual miscibility of the modifier after curing seems to be small for all processing temperatures, at least small enough not to influence the glass transition temperatures and moduli of the cured materials, as depicted in Fig. 9. Upon curing at temperatures below 80°C, the resin does not reach the infinite T_g of 104°C. However, this value is approached by postcuring the material at 80°C. Postcuring does not affect the phase separated structure obtained at the initial curing temperature and can therefore be used to optimise the particle structure in a multistage process.

Fig. 10 shows a 2.5-fold increase of the K_{Ic} toughness values obtained for the epoxy resin with 5% of the reference modifier, compared to the unmodified epoxy resin.

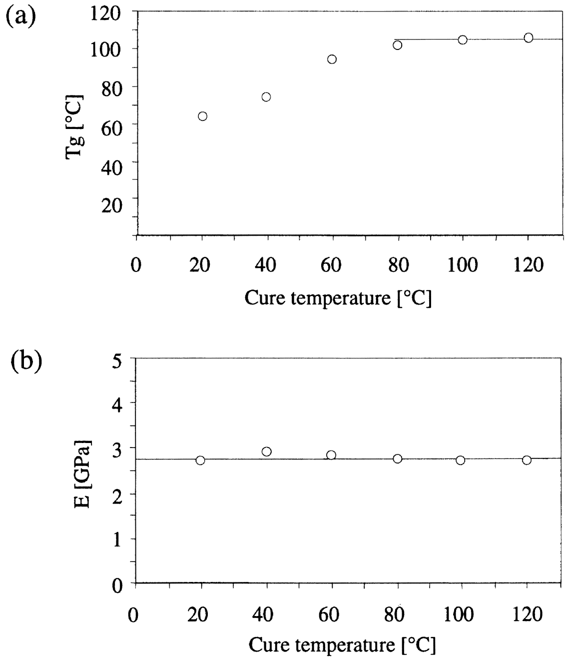

Fig. 9. Thermomechanical and toughness properties as a function of the isothermal cure temperature for the epoxy resin with 5% of the reference modifier; (a) The glass transition temperature, T_g (the solid line represents the infinite T_g of the neat resin); (b) The Young's modulus, E (the solid line represents the Young's modulus of the neat resin).

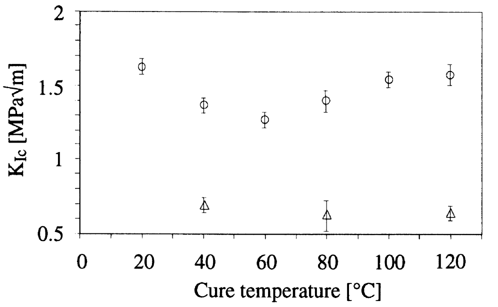

Fig. 10. Toughness properties expressed in terms of the stress intensity factor K_{Ic} as a function of the curing temperature for the modified (○) and the unmodified epoxy resin (△).

However, at 60°C, a minimum K_{Ic} value for the modified resin of 1.24 MPa$\sqrt{m}$ is obtained. This is due to a larger interparticle distance compared to the materials cured at higher temperatures. The higher values of toughness obtained for the materials cured at lower temperatures can partly be attributed to the fact that the resin is not fully cured which increases its capacity for plastic deformation. Upon postcuring these materials the toughness values drop. The dependence of the toughness on the respective ratio of the particle size over the interparticle distance has been reported earlier [24]. This relation, depicted in Fig. 11 for the HBP modified epoxy samples, is verified and proves the utility of taking into account the process–structure–property relationships.

It is thus useful to consider how processability can be optimised. As mentioned earlier, the time to phase separation determines the maximum processing time. Processing time can, however, be adapted by using a multistage isothermal cure, but can also be modified by tailoring the shell chemistry of the HBPs, which is unique to these tougheners. To illustrate this effect, the epoxy equivalent weight (EEW) has been varied by changing the number of epoxy groups per molecule. The effect on both the upper critical solution temperature (UCST) and the time to phase separation (t_s) is extremely pronounced, as shown in Fig. 12. The miscibility, illustrated by the UCST, is increased by the addition of epoxy groups which renders the HBP more polar and compatible with the epoxy resin. The same compatibilisation effect, combined with an increased interaction probability by the formation of chemical bonds as curing proceeds, increases the time to phase separation. The possibility to tailor the processability of the HBP modified resin is extremely interesting when considering the use of these materials in composite applications. Various processing techniques are used for composite materials each requiring specific processabilities of the matrix resin. Wet lay-up is a time-consuming process done at room temperature. For this application a HBP with a low EEW, having a low UCST and a long time to phase separation, can be used. Prepreg composite materials are generally processed at higher temperatures in short times. In this case, a HBP with a high EEW having a high UCST and a short time to phase separation can be used. Other composite processing techniques such as filament winding and RTM have intermediate requirements as far as processing times and temperatures. For these techniques a HBP with an intermediate EEW can be used. Thus, it is possible to obtain the appropriate structure for a maximised toughening effect and optimal processability. If required, the HBP core structure as well as its size can be adapted to control the phase separation rate.

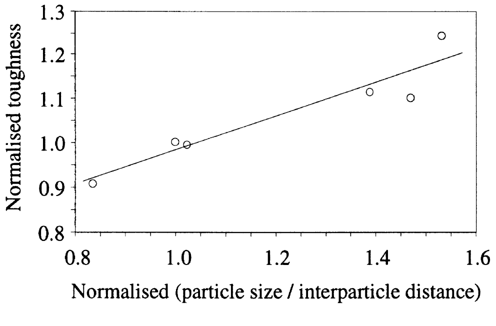

Fig. 11. The normalised toughness as a function of the normalised particle reinforcement morphology. Normalisation is relative to the epoxy resin with 5% of the reference modifier cured at 80°C.

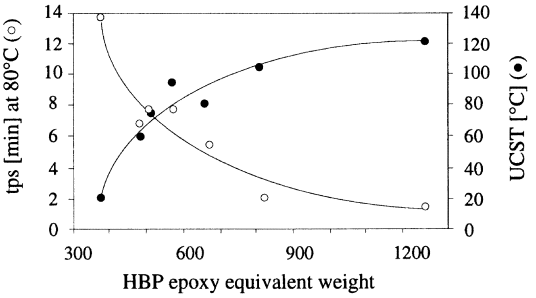

Fig. 12. The influence of the epoxy equivalent weight (EEW) on the phase separation behaviour expressed as the 'time to phase separation' (t_s) upon curing at 80°C and the 'upper critical solution temperature' (UCST) in the epoxy resin without hardener.

4.3. Toughening properties

In the previous sections it has been shown that as long as phase separation occurs and a particulate structure is formed, the shell chemical design of the HBP can induce a 20% increase in K_{Ic} for 5 wt% HBP modified resins (Table 1). In other resin systems, the effect of the shell chemistry on structure and properties should be more pronounced, in particular in more reactive epoxy systems. Processing conditions will influence the K_{Ic} values to a similar extent due to the influence on the morphologies obtained.

In Fig. 13, the normalised stiffness (E) and toughness (G_{Ic}) have been plotted for various commercially-used tougheners. The values have been normalised to the epoxy properties, to a value of 10 for E and a value of 1 for G_{Ic}. Normalisation is done because the epoxy resins used were not exactly the same in all cases. All unmodified resins,

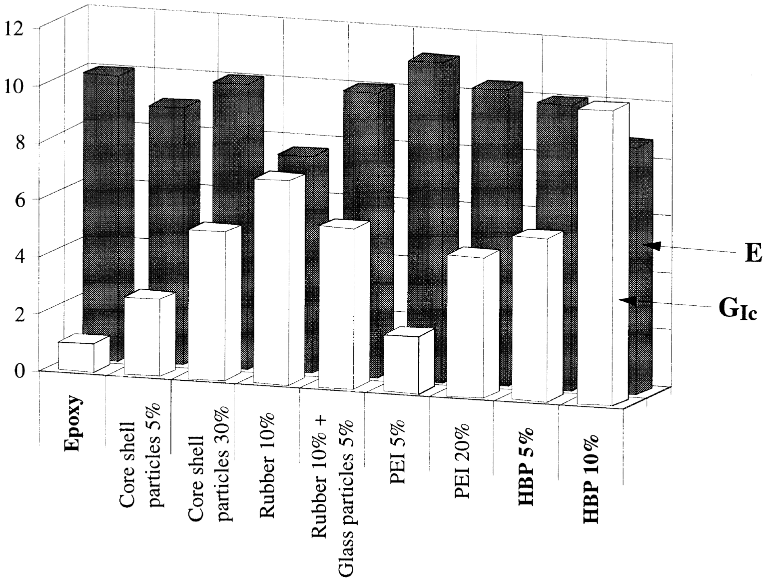

Fig. 13. The toughening effect of various commercially-available tougheners. Toughness, G_{Ic}, and modulus, E, are normalised to the unmodified epoxy resin properties.

however, had a K_{Ic} toughness in the range of 0.6 to 0.65 MPa$\sqrt{m}$ and a modulus ranging from 2.7 to 3.0 GPa. When using 5% of the HBP toughener, similar or better toughness properties are obtained in comparison with any of the other toughening systems and the thermomechanical properties are fully maintained. When using 10% of the HBP toughener, the largest toughening effect is observed with a 10-fold increase in G_{Ic}. This is, however, accompanied by a 10% drop for the modulus values.

With core–shell particles, it is necessary to use up to 30% of modifiers in order to obtain a comparable toughening effect to 5% of HBPs. Furthermore, core–shell particles can be filtered out during the fibre impregnation process in composite manufacturing or can agglomerate in an unstable dispersion, which in both cases induces defect zones within the material.

Rubber materials such as CTBN are by far the most widely-used tougheners. They induce a good toughening effect but lead also to a non-negligible decrease in thermomechanical properties, as can be seen in Fig. 13. The use of rubber tougheners also increases the viscosity of the uncured resins which limits their processability. They can generally not be used in processes such as RTM for which flow distances are long. To increase the modulus when using rubber tougheners, glass particles can be added. This does not, however, influence the reduction in glass transition temperature induced by the rubber. Furthermore, the processability will not only suffer from an increase in viscosity,

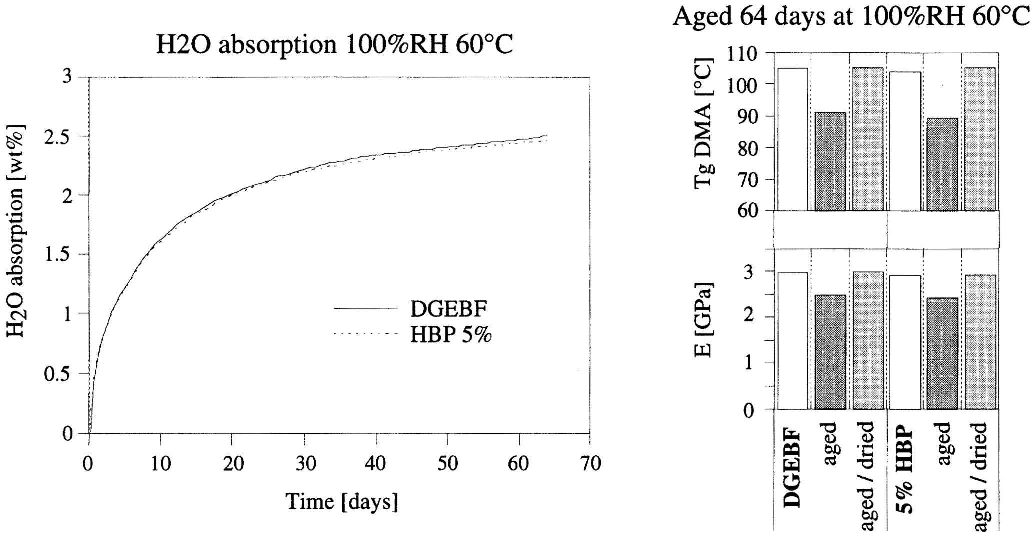

Fig. 14. Ageing properties of the unmodified and 5% HBP modified DGEBF epoxy resin. Ageing was performed in 100% relative humidity at 60°C during 64 days. Thermomechanical properties, glass transition temperatures (T_g) and moduli (E), were measured on the virgin, aged and subsequently dried samples.

but also from the risk of filtration of the glass particles. Compared to most rubber tougheners, HBP modifiers are not sensitive to humidity or to chemical ageing and do not require the use of solvents. Ageing tests have been performed in 100% relative humidity at 60°C during 64 days for the unmodified and 5% HBP modified DGEBF epoxy resin on 2.5 mm thick thermo-mechanical and tensile testing samples. The results presented in Fig. 14 show that the water absorption and thermomechanical properties of the aged samples are unaffected by the presence of the HBP modifier. Furthermore, upon subsequent drying of the samples after ageing, the thermomechanical properties are fully recovered for both the unmodified and 5% HBP modified resin.

Thermoplastic tougheners such as PEI have been developed and are promising as modifiers being able to induce good toughening without loss of thermomechanical properties. However, their chemistry can only to a very limited extent be adapted to different epoxy resins and they are as such not as versatile as HBP tougheners. Furthermore, for a similar effect to that obtained using 5% of HBP tougheners, 20% of PEI modifiers are required.

As mentioned, the advantages of HBP modifiers, in addition to the high K_{Ic} and G_{Ic} toughness values obtained, are the excellent processability of the modified resins, i.e. the processing conditions are hardly influenced compared to the unmodified resins, and the thermomechanical properties are maintained when using moderate modifier loading levels.

4.4. Toughening mechanisms

In the HBP-toughened resin, one of the toughening mechanisms observed is particle cavitation. The particles, especially after the cavitation process, induce large stress concentrations which lead to extensive shear deformation, a high energy-absorbing mechanism. Tests on thin films of HBP toughened epoxy resins clearly showed cavitated particles and extensive shear in the form of shear bands emanating from the cavitated particles.

These deformation mechanisms are also present in rubber particle-modified epoxies. However, as has been shown in Fig. 13, HBP toughening seems to be more effective. This can be explained by considering the phase interactions and the exact toughening mechanisms involved using HBP modifiers forming a particulate structure. Particulate toughening has been extensively studied in the literature using rubber, thermoplastic or glass particles. Depending on the nature of the particles and on their rigidity, different deformation and rupture mechanisms are initiated. It is therefore necessary to identify the properties obtained within the HBP particles. Epoxy functionalised HBPs cured with an amine hardener are characterised by a rubbery behaviour, as observed in tensile testing illustrated in Fig. 15.

During curing, even before phase separation is initiated, HBPs react with the epoxy material. It is thus expected that within the secondary phase particles formed by aggregation

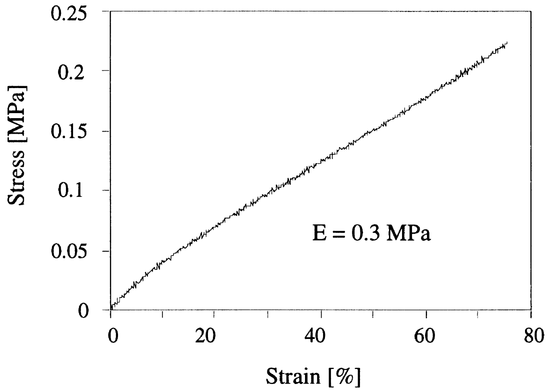

Fig. 15. Stress–strain curve of epoxy functionalised HBPs cured with an amine hardener.

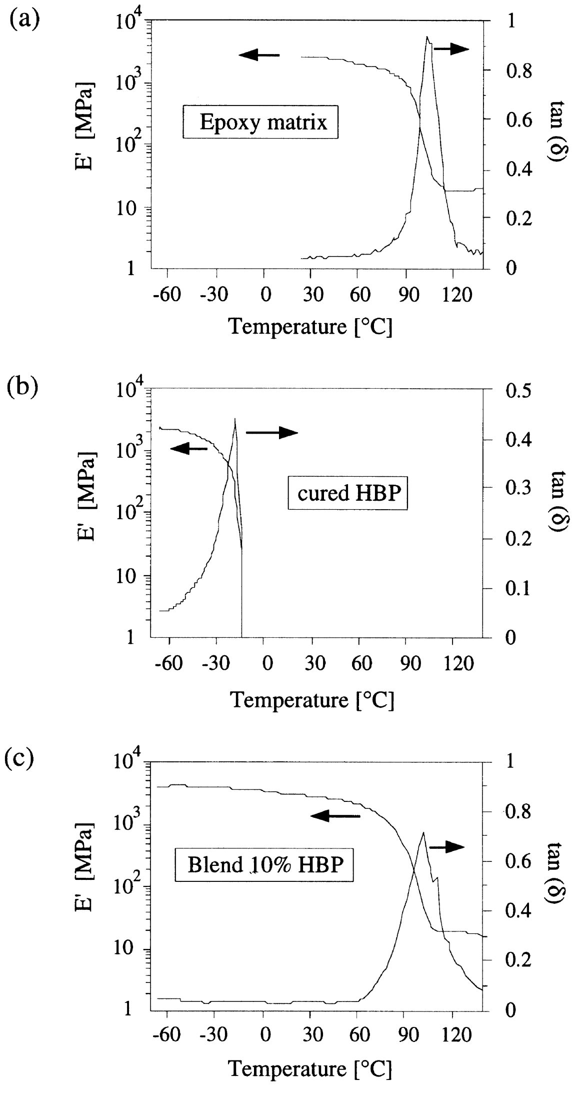

Fig. 16. Thermomechanical analysis in 3-point bending of (a) the cured epoxy resin; (b) the hardened HBP modifiers and (c) a cured blend of DGEBF resin toughened with 10% of HBPs.

of the HBP molecules, a large amount of epoxy is present. For the same reasons, it is expected that HBP molecules remain trapped within the epoxy matrix. As discussed in the phase separation section, the analysis of the particle volume fraction compared to the initial content of HBPs proves the existence of residual HBPs in the epoxy matrix. The thermomechanical analysis of the cured resin, HBP and blend shown in Fig. 16 confirm the existence of residual resin within the particles as well as residual HBP within the matrix. If the particles were entirely composed of cured HBP molecules, the tan δ curve of the blend would show a second peak at -25°C at the same position as the cured HBPs. The tan δ peak obtained for the blend has not shifted to a large extent compared to the epoxy resin, but is broader. Peak broadening is expected and found for a fully miscible HBP. The peak shown in Fig. 16(c) for a particulate structure is also wider than for the epoxy resin. The peak shape reflects the presence of HBPs trapped within the matrix but must also overlap the mechanical response of the particles. If this is the case, it would imply that the particles have similar properties to the resin and different from those of the pure hardened HBPs.

The HBP particle properties in the epoxy matrix were evaluated using the self-consistent model for particle reinforced composites, based on the Young's modulus and Poisson's ratio for the neat and modified resin:

$$G_p = \frac{G_{\text{eff}} G_m (3 - 5v_p) - 3G_{\text{eff}}^2}{G_{\text{eff}} (2 - 5v_p) - 2G_m} \text{ and } G = \frac{E}{2(1+v)} \tag{4}$$

where G and E are the shear and Young's modulus respectively, v the Poisson's ratio and V_p the particle volume fraction. Subscripts eff, p and m refer to the blend, particle and matrix respectively.

The calculated modulus for the HBP particles is 393 MPa. Even though the accuracy of this method is rather low, the order of magnitude for the calculated particle modulus is respected and can be compared to the measured modulus of 0.3 MPa for the cured neat HBPs and 2910 MPa for the cured epoxy resin. From these values, a rough estimation of the particle composition, based on the mechanical behaviour of purely miscible polymer blends, gives a HBP/epoxy volume ratio of 2/3. Taking into consideration the particle volume fraction and the composition of the modified epoxy, this particle composition ratio would suggest that about 2.5% of HBPs are dissolved within the matrix phase. This calculated residual solubility seems, however, rather high and should be verified. It does however indicate that dissolved HBPs contribute to the toughening effect of the secondary phase particles.

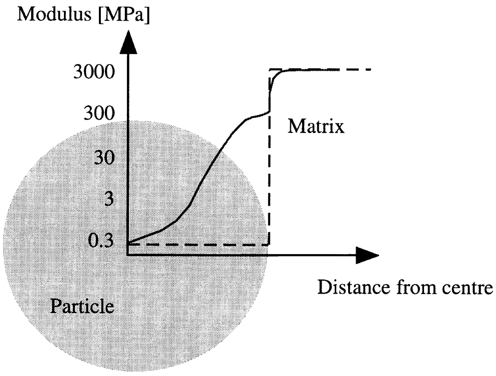

Fig. 17. A schematic of the Young's modulus as a function of the radial distance from the particle centre. The solid curve shows the gradient properties obtained in HBP phase separated particles. The dotted line shows a property singularity in the case of a homogeneous rubbery-like particle.

The particles thus have intermediate properties between those of the cured neat HBPs and the cured epoxy resin. It should be noted that the particle growth spans a certain time period. Therefore, the HBP molecules grafting onto the particles at the later stages of the growth process have reacted to a larger extent with the epoxy material. A property gradient over the radius of the secondary particle is thus expected. Compared to most conventional tougheners, any strong singularity of rigidity at the interface between the particle and the matrix is eliminated, as shown in Fig. 17. Instead of increasing stepwise from a modulus of 0.3 MPa in

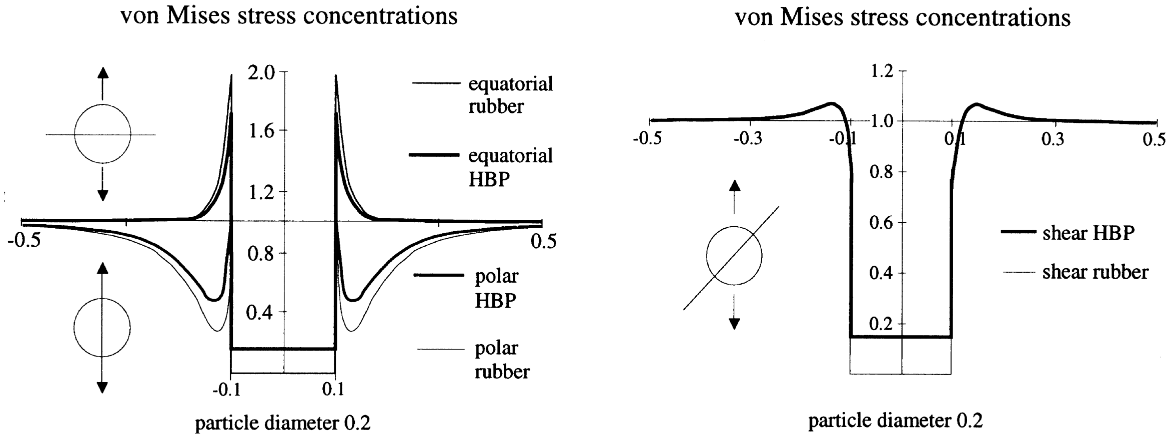

Fig. 18. Stress concentration in the epoxy resin as a function of radial distance from the centre of a HBP particle, compared to stress concentrations around a rubber particle. The overall stress level imposed on the structure is normalised to a value of 1.

the particle to 3000 MPa in the resin, the HBP particles will follow a gradual increase in modulus properties from their centre outwards.

The modulus values of the resin and the particles allow us to calculate stress concentrations around an uncavitated particle. This calculation is performed using an analytical model developed by Fond et al. based on Eshelby's model and a deformation energy field equilibrium within and around the particles [25]. Results are plotted in Fig. 18 and compared with stress concentrations around a rubber particle with a modulus of 0.3 MPa. Even though the HBP particle is considered as homogeneous, that is the property gradient along the particle radius is not taken into account, the stress singularity at the interface on the equatorial plane is about 25% lower than with rubber particles. The shear stresses generated, which will induce the shear deformation of the matrix, are the same. Since the stress concentration around an uncavitated HBP particle is lower and because the mechanical properties are higher compared to rubber particles, the particle cavitation process will be initiated at a later stage on the stress–strain curve, at higher stresses. The stress levels generated upon cavitation will in turn induce larger stresses in the matrix around a cavitated HBP particle. This should increase the potential shear deformation capacity of the matrix, which is further enhanced by the residual miscibility of the HBPs. Given these considerations, a higher toughening effect than with rubber particles is expected with epoxy functional HBP modifiers.

5. Conclusion

Dendritic hyperbranched polymers (HBPs) are very effective low viscosity liquid tougheners requiring no solvent during blending and processing. A 6-fold increase in G_{Ic} toughness values is obtained for a commercial DGEBF epoxy resin using only 5% by weight of a hyperbranched molecule modifier. This corresponds to a 2.5-fold increase of K_{Ic} values from 0.63 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the neat epoxy resin to 1.54 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the modified resin [21]. Toughening is reported to be more effective than with other presently-available tougheners without affecting the Young's modulus, the glass transition temperature or the processability of the resin system.

The multifunctional epoxidised hyperbranched polymers used for this study phase separate during the curing of the thermosetting resin. The chemical architecture of the shell, namely its polarity and reactivity, controls the initial miscibility and the kinetics of the phase separation process. It can be tailored to ensure a wide processing window while providing the desired structure for optimum toughness properties. The curing and phase separation kinetics influence both the processability of the toughened epoxy and the secondary phase structure. The structure obtained in turn determines the mechanical performance of the cured resins. The high toughening capacity of HBP modifiers is suggested to be induced by gradient properties obtained within the phase-separated particles. The particle properties and their load transfer capacity to the surrounding matrix result from the high interaction level generated by the large number of chemical bonds formed with each HBP molecule.

The processing window of the materials studied is suitable for most conventional processing techniques and even for those used in fibre-reinforced composite manufacturing. By adapting the shell chemistry, the HBP modifier system may be used in other epoxy resins than the one studied in this investigation. As a result, the HBP toughener has potential for use in all foreseen epoxy resin application areas. By changing the nature of the reactive groups grafted onto the HBP's shell, this modifier system may also be implemented in other polymeric resins.

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