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Polymer 48 (2007) 778–790

polymer

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Novel phosphorus-modified polysulfone as a combined flame retardant and toughness modifier for epoxy resins

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Received 26 September 2006; accepted 4 December 2006
Available online 8 January 2007

Abstract

A novel phosphorus-modified polysulfone (P-PSu) was employed as a combined toughness modifier and a source of flame retardancy for a DGEBA/DDS thermosetting system. In comparison to the results of a commercially available polysulfone (PSu), commonly used as a toughness modifier, the chemorheological changes during curing measured by means of temperature-modulated DSC revealed an earlier occurrence of mobility restrictions in the P-PSu-modified epoxy. A higher viscosity and secondary epoxy-modifier reactions induced a sooner vitrification of the reacting mixture; effects that effectively prevented any phase separation and morphology development in the resulting material during cure. Thus, only about a 20% increase in fracture toughness was observed in the epoxy modified with 20 wt.% of P-PSu, cured under standard conditions at 180 °C for 2 h. Blends of the phosphorus-modified and the standard polysulfone (PSu) were also prepared in various mixing ratios and were used to modify the same thermosetting system. Again, no evidence for phase separation of the P-PSu was found in the epoxy modified with the P-PSu/PSu blends cured under the selected experimental conditions. The particular microstructures formed upon curing these novel materials are attributed to a separation of PSu from a miscible P-PSu–epoxy mixture. Nevertheless, the blends of P-PSu/PSu were found to be effective toughness/flame retardancy enhancers owing to the simultaneous microstructure development and polymer interpenetration.

Keywords: Flame retardants; Phosphorus-modified polysulfone; Fracture toughness

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1. Introduction

Epoxy resins are widely used as high-performance matrices in fibre-reinforced composites for many modern engineering applications. As a result of the increasing usage of such polymers, varying qualification requirements as well as the current trend towards the sustainable conservation of resources, the flame resistance and thermal stability as well as the toxicological consequences of combustion of flame-retarded epoxies have recently become a subject of considerable attention [1]. Many approaches have been made to improve the fire–smoke-toxicity (FST) properties of epoxy resins using either non-reactive or reactive flame retardants [1–8]. However, as many cured epoxies are already rather brittle in nature due to their high crosslinking density, the addition of such flame retardants often induces a further severe degradation of the overall physical and mechanical properties of the resulting material [9–11]. Traditional concepts to overcome the problem of epoxy brittleness are: (i) the addition of liquid rubber copolymers with various functional end groups [12–16] and (ii) a modification based on thermoplastics [17–30]. Yet, a combined addition of both modern flame retardants and

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0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.12.011

established toughness modifiers in order to optimise the overall product performance has not been extensively studied so far.

Although the addition of liquid rubbers in general has been successfully proven to lead to a high fracture toughness of the epoxy, such liquid rubbers often induce a severe degradation of other key properties of the system such as the hot/wet behaviour, the elastic modulus, and the glass transition temperature [15,31,32]. In addition, owing to the low thermal stability of the rubber, the decreasing thermal stability of the final material also is a disadvantage. In contrast, thermoset-toughening using thermoplastics often provides an effective means to minimise or even avoid this pronounced loss in stiffness, glass transition temperature, and thermal stability of the thermosetting material.

Many studies have been devoted to the evaluation of high-temperature thermoplastics such as poly(ethersulfone)s (PES) [14,19,29,33–35], poly(sulfone)s (PSu) [17,20–22,26–28,30] or poly(etherimide)s (PEI) [36–39] as toughening modifiers. In the case of an epoxy–amine system for example, a homogeneous blend is initially obtained when using suitable thermoplastics. With the advancement of the curing reaction the molecular weight of the epoxy–amine network increases and, consequently, the solubility of the thermoplastic in the mixture decreases and two phases are formed as a result of a reduction in the entropic contribution to the free energy of mixing during polymerisation [40,41]. It is this phase separation that leads to the desired improvement in fracture toughness of the epoxy without the deterioration of other mechanical properties. However, the fracture toughness enhancement strongly correlates with the final morphology of the two-phase system; a co-continuous or phase-inverted morphology especially is necessary in order to achieve a significantly higher fracture toughness of the material [19,26,27,31,42–44]. As commonly used flame retardants often lead to a significantly altered curing behaviour of epoxies, the combined addition of such flame retardants and toughness modifiers might not lead to the required morphology evolution in a straight-forward manner.

Somewhat surprising, little attempts have been made so far to combine both desirable functions in a single compound – to increase the flame retardancy and at the same time to improve the mechanical properties of epoxy systems by the addition of phosphorus-modified thermoplastics. An initial study [45] showed the feasibility of introducing phosphorus-containing groups into the chemical backbone of suitable thermoplastics, leading to the successful synthesis of a novel halogen-free flame retardant poly(sulfone) (P-PSu) with a glass transition temperature (T_g) exceeding 200 °C and of a poly(ether ether ketone) (P-PEEK) with an improved thermal stability. The incorporation of these novel modifiers into an amine-cured DGEBA epoxy system showed some promising improvements in flame retardancy as determined by the limiting oxygen index (LOI) [45,46], although no significant enhancement of the fracture toughness could be detected in these preliminary studies.

In order to further evaluate the potential of such phosphorus-modified poly(sulfone) (P-PSu) as a flame retardant and toughness modifier, a detailed characterisation of the curing kinetics and solid-state properties of a difunctional bisphenol-A based epoxy resin cured with an aminic hardener as a function of the weight fraction of the modified thermoplastic was carried out. Experimental results regarding the curing behaviour and phase separation are compared to a reference system based on a commercial PSu toughness modifier. As demonstrated here, the morphology evolution of the modified epoxy under various processing conditions reflects the chemical structure of the additive, which, in turn, influences the resulting fracture mechanical properties as well as the fire behaviour and flammability of the system. Lastly, promising results regarding the combined addition of both the modified and the commercial reference thermoplastic are presented, an approach that effectively allows the tailoring of the final product performance.

2. Experimental

2.1. Materials

A difunctional epoxy resin (DGEBA, Ruetapox 0162) with an epoxy equivalent weight of 173 g/eq and free of hydroxyl groups was supplied by Bakelite and was used as received. The 4,4′-DDS hardener, with an amine equivalent weight of 62 g/eq (synthesis grade), was purchased from Merck and was also used as received. The thermoplastic modifiers were a novel phosphorus-containing polysulfone (P-PSu), designed and synthesised in our laboratory ($M_w = 32.900\ \mathrm{g\ mol^{-1}}$, $M_n = 9200\ \mathrm{g\ mol^{-1}}$, $T_g = 228\ ^\circ\mathrm{C}$) [45] and a commercial grade polysulfone (PSu, Ultrason-S2010, BASF AG; $M_w = 41.800\ \mathrm{g\ mol^{-1}}$, $M_n = 13.400\ \mathrm{g\ mol^{-1}}$, $T_g = 185\ ^\circ\mathrm{C}$). The chemical structures of the materials used in this study are summarised in Fig. 1.

2.2. Preparation and curing procedure of thermoplastic-modified epoxy

Initially, epoxy formulations containing 0, 5, 10, 15, and 20 wt.% of the commercial PSu reference and of the phosphorus-modified P-PSu were prepared. In the case of the P-PSu, the selected weight fractions of the thermoplastic correspond to phosphorus contents of 0.3, 0.6, 0.9, and 1.2 wt.%. All formulations were prepared according to the following identical experimental procedure. The DGEBA was placed in a glass flask and was heated to 130 °C in an oil bath connected to a temperature controller. The desired amount of either type of polysulfones as fine powder (particle size < 8 μm) was then added slowly to the epoxy resin at this temperature and was extensively mixed using a mechanical stirrer until it was completely dissolved and the mixture was again homogeneous. Blends of P-PSu and PSu at different ratios (25:75, 50:50 and 75:25) were also mixed with the DGEBA, keeping the total amount of modifier in the mixture constant at 20 wt.% in order to maximise the phosphorus content in the system. Maintaining the temperature at 130 °C, the DDS was then incorporated into the mixture keeping a DGEBA/DDS mixing

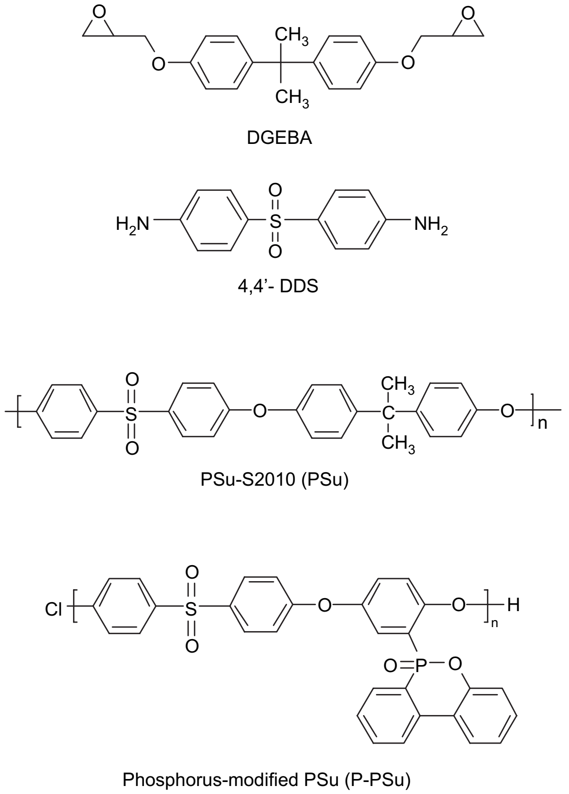

Fig. 1. Chemical structures of the materials employed in this study.

ratio of approximately 100:29 g g^{-1} (this ratio corresponds to an epoxy to amine equivalent of 1:0.8) using the mechanical stirrer. Stirring was continued for a further 30–40 min until the mixture was again homogeneous.

Following this intimate mixing, the hot mixtures were poured into preheated aluminium moulds at 130 °C and were then placed in a vacuum oven at the same temperature for 45–60 min for degassing. The modified epoxy resin was subsequently cured in a convection oven as follows: the curing cycle started by a 2 K/min ramp from room temperature to 180 °C. This temperature was held for 2 h and curing was completed with a −2 K/min ramp from 180 °C to room temperature. For easy release of the cured epoxy resin sheets, the mould surface was coated with a thin layer of Frekote-700NC.

Thus, a 110 × 110 × 3–4 mm^3 epoxy resin sheet was obtained and was subsequently machined to the desired specimen size for further testing. Control samples of DGEBA/DDS without modification were prepared following an identical procedure. An overview of the prepared systems is presented in Table 1.

Table 1
Overview of the epoxy-based systems prepared for this study

Material		Total modifier content [wt.%]	Phosphorus content [wt.%]
Neat resin (EP)		0	0
EP + PSu		5	0
		10	
		15	
		20	
EP + P-PSu		5	0.3
		10	0.6
		15	0.9
		20	1.2
Epoxy modified with P-PSu/PSu blends			
EP + P-PSu/PSu	25:75	20	0.3
	50:50		0.6
	75:25		0.9

2.3. Thermal and mechanical characterisations

Isothermal DSC measurements were performed using a TA Instruments Q1000 with a temperature-modulation option (TMDSC) in the temperature range between 150 and 240 °C. For these measurements, the calorimeter was preheated to the desired temperature before 6.0 ± 1.0 mg of unreacted sample was placed in the calorimeter cell. The heat flow was recorded immediately as a function of the time until a stable baseline was reached (end of the reaction). Following this isothermal curing, the samples were cooled to room temperature at 10 K/min and were then rescanned between 25 and 300 °C at 3 K/min. Crimped aluminium pans were used for all DSC measurements; nitrogen was employed as a purge gas (50 ml/min).

An amplitude of 1 °C and a period of 60 s were selected as conditions for the modulated experiments. TMDSC was employed in order to separate the two contributions to the overall heat flow signal: one originating from the heat capacity of the sample (reversible) and the other from the chemical reactions or enthalpic relaxations (non-reversible). The potential of TMDSC to measure both the advancement of the reaction and the effects of rheological changes in one single experiment with excellent temperature control has been highlighted recently in the literature [47,48]. More details about the benefits of using TMDSC can be found elsewhere [49–51]. As such, these experiments provide an efficient way to determine the glass transition temperature of the sample by isolating the change in heat capacity from other non-reversible thermal events.

Dynamic mechanical analysis (DMA) of the cured materials was performed using a RDAIII from Rheometric Scientific at a heating rate of 4 K/min between 25 and 250 °C. A rectangular specimen of 50 × 10 × 3 mm^3 cut out of the plates was used in the torsion rectangular geometry mode, at a frequency of 1 Hz and 0.1% of deformation. The glass transition temperature (T_g) was taken as the temperature at which tan δ showed a maximum.

The fracture toughness (K_{Ic}) and fracture mechanical modulus (E) of the cured materials were obtained from the opening mode test according to the ISO 13586, performed on compact tension specimens (CT). The size of the specimens used in this study was 41 × 40 × 3–4 mm^3. A sharp notch was machined into the specimens and then a sharp pre-crack was generated by tapping a razor blade into the notch. Tests were carried out using a universal testing machine model Zwick Z 2.5 at room temperature and at a cross-head speed of 10 mm/min. A minimum of four specimens of each epoxy formulation was tested.

Fracture surfaces from these K_{Ic} tests were subsequently coated with a fine gold layer and were analysed using a scanning electron microscope (Jeol-SEM848-IC) operating at 20 kV.

2.4. Pyrolysis and fire behaviour

The pyrolysis of the various epoxy systems was analysed by thermogravimetric (TG) experiments. The TG investigations were carried out using a TGA/SDTA 851 (Mettler Toledo, Germany), applying a nitrogen flow of 30 ml/min. The samples (about 5−10 mg) were heated in alumina pans from room temperature up to about 900 °C at a heating rate of 10 K/min. The flammability (response to a small flame) was characterised by the limiting oxygen index (LOI) test according to ISO 4589, using test specimens of $100 \times 6 \times 4\ \mathrm{mm}^3$. The flaming fire behaviour was investigated using a cone calorimeter (Fire Testing Technology, East Grinstead, UK); the tests were performed according to ISO 5660 using an external heat flux of $35\ \mathrm{kW\ m}^{-2}$. All samples (size: $100 \times 100 \times 2.8\ \mathrm{mm}^3$) were measured in the horizontal sample position using the retainer frame. The decreased sample area was taken into account for the calculations; all measurements were done in duplicate.

3. Results and discussion

At room temperature, uncured epoxy mixtures containing the phosphorus-modified polysulfone were opaque, with the final colour of the mixture depending on the weight fraction of the thermoplastic modifier (light brown). In contrast, uncured blends of the epoxy containing the commercial polysulfone remained transparent over the whole composition range. Following the standard curing protocol at 180 °C, all cured specimens were opaque, with a brown colour in case of the epoxy modified with P-PSu and a light yellow in case of the epoxy modified with the commercial PSu. Systems based on a blend of the two toughness modifiers at 20 wt.% of thermoplastic in total showed some intermediate colour following curing, the exact shade depending on the weight composition of the two thermoplastics. As expected for this temperature profile, no evidence for thermal degradation could be detected. However, the optical inspection of the specimens did not provide any further insight into the specimen morphology.

3.1. Fracture toughness and morphology of the cured materials

As an initial overview, the resulting fracture toughness (static K_{Ic} values) of all modified epoxy specimens containing either the commercial PSu or the phosphorus-modified PSu as a function of the thermoplastic additive content is summarised in Fig. 2. The representative SEM micrographs of the corresponding fracture surfaces highlight the correlation between toughness and specimen microstructure. As can be seen, the epoxy modified with the commercial PSu shows a pronounced maximum in fracture toughness at 15 wt.% of this particular modifier. The shown variations in specimen microstructure with increasing thermoplastic content are in good agreement with those reported in the literature for such PSu-modified systems [27]: at low additive concentrations, a particulate morphology (or sea-island) is formed, whereas higher additive contents lead to the evolution of a co-continuous morphology (at 15 wt.% of PSu) that correlates with the observed maximum in fracture toughness. A further increase in the thermoplastic concentration leads to a phase-inverted morphology (at 20 wt.% of modifier) and the fracture toughness decreases again, owing to the weak interface between the PSu and the epoxy matrix [18,33].

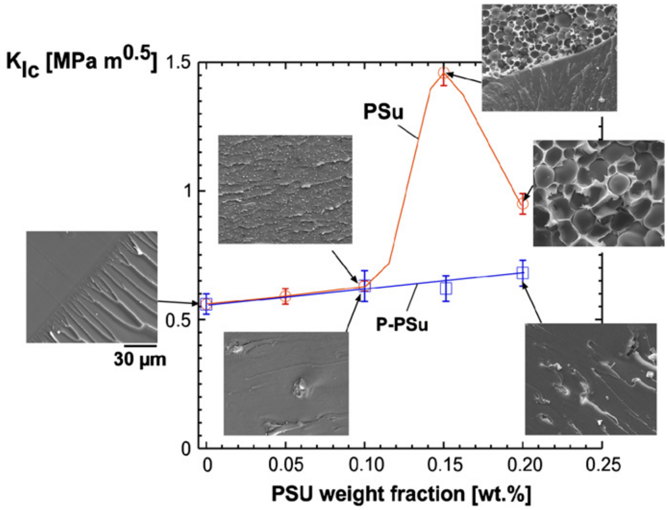

Fig. 2. Fracture toughness and representative scanning electron micrographs of the resulting epoxy morphology as a function of the polysulfone content.

In contrast, only a moderate linear improvement in the fracture toughness was observed for the epoxy modified with increasing contents of the P-PSu. This trend is mainly attributed to the absence of a phase-separated microstructure in this system modified with the P-PSu, as verified by the SEM micrographs. The fracture surfaces of the P-PSu-modified system show a particulate microstructure over the whole composition range, with the density of the particulate inclusions increasing with the P-PSu concentration. The overall improvement in the fracture toughness of the material is rather modest although tails and/or arrest lines behind the thermoplastic particles accompanied with plastic deformation of the epoxy matrix can be seen. Nevertheless, neither mechanism is sufficient to cause a significant increase in the fracture toughness.

The question remains as to why the epoxy modified with P-PSu did not develop a suitable morphology for improving the fracture toughness. In order to elucidate the morphology development during curing in more detail, a fundamental assessment of the curing behaviour of the epoxy modified with 20 wt.% of P-PSu is presented in the following sections, as this particular system with the highest phosphorus content should show the most pronounced improvement in flame retardancy.

3.2. Comparative evaluation of the isothermal curing behaviour of epoxy modified with 20 wt.% of P-PSu or PSu

Fig. 3(a) and (b) shows the recorded heat flow during the advancement of the reaction at various isothermal curing temperatures for the epoxy–amine systems modified with 20 wt.% of either polysulfones; for clarity, only the DSC curves at 150 and 165 °C are shown. Independent of temperature, there is an initial rate increase for the epoxy modified with the commercial PSu up to a maximum. This behaviour is characteristic for the epoxy–amine reaction [16], indicating an autocatalytic mechanism as also verified by the data for the neat epoxy system (not shown). For the epoxy modified with P-PSu, higher rates of reaction are seen at these curing temperatures and, as the curing temperature increases, the autocatalytic feature vanishes as seen in Fig. 3(b).

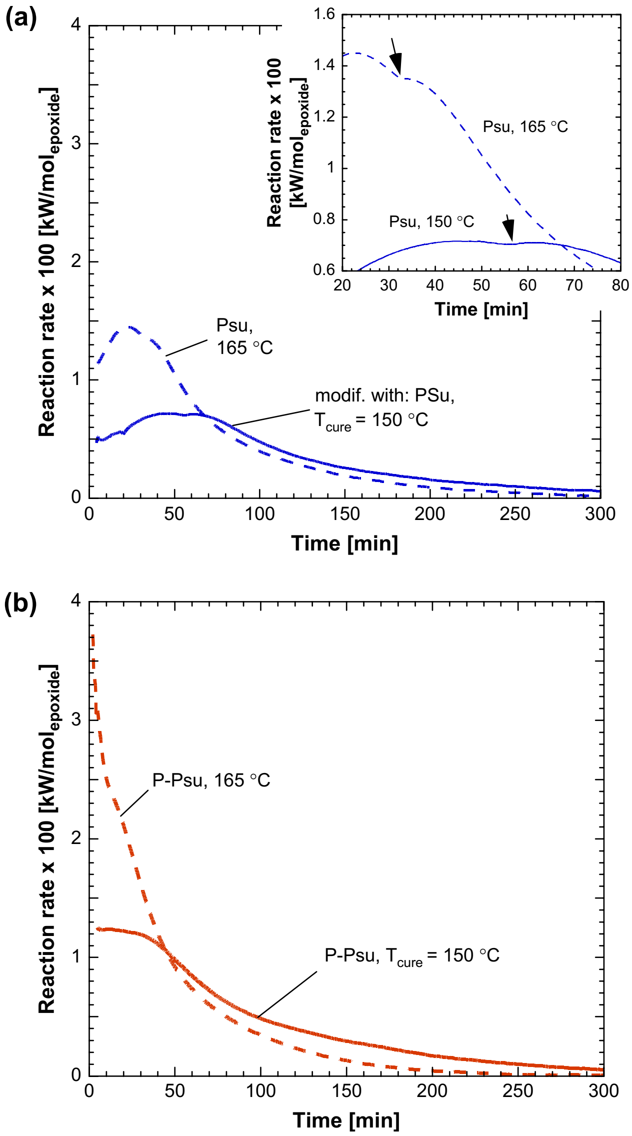

Fig. 3. Rate of reaction as a function of the time for the epoxy resin modified with 20 wt.% of (a) commercial PSu and (b) P-PSu; the curing temperatures are 150 and 165 °C.

The effect of addition of a thermoplastic on the kinetics of such epoxy–amine systems has been described in the literature [36,52–54]; yet, some controversy regarding the change in reaction rate remains. While the addition of poly(etherimide) (PEI) and polycarbonate (PC) to a tetrafunctional epoxy–amine system [36,52] was shown to enhance the rate of reaction (due to an enhanced mobility of the species), other studies showed that the addition of poly(ethersulfone) (PES) to a TGAP/DDS [53] or to a DGEBA/DDS [54] system can inhibit the epoxy–amine reaction (due to a simple dilution effect). More recently, it was reported that the addition of polysulfone has a modest effect on the rate of curing of such TGAP/DDS or DGEBA/DDM mixtures [55,56].

Here, both effects: (i) plasticization of the continuous epoxy phase by the presence of the thermoplastic (which enhances the mobility of the reactive groups) and (ii) dilution appear to influence the curing reaction of the epoxy modified with either P-PSu or PSu. In addition, owing to the higher polarity of the P-PSu, a stronger interaction with the epoxy is encouraged; an effect that might explain the enhanced reaction rate for this particular system. Another effect that can be seen in Fig. 3(a) (see also insert) is that the reactivity increases during the reaction-induced phase separation for the epoxy modified with the commercial PSu. This increase is evidenced for both curing temperatures as a shoulder in the heat flow rate and is consistent with previous reports where a sudden reactivity increase was found at phase separation at high thermoplastic contents [57–59]. It is worth noting that, in the present case, the acceleration of the reaction occurs at a lower content of modifier (20 wt.%) in comparison to those reported in the literature ($\gg$30 wt.%) for similar epoxy–thermoplastic blends [31,57].

The chemorheological changes in the system during the isothermal reaction can be monitored simultaneously by means of the heat capacity change and heat flow phase (phase angle between modulated heat flow and modulated heating rate) signals. These experimental results are shown in Fig. 4(a) and (b), highlighting the curing reaction of the epoxy modified with 20 wt.% of either PSu or P-PSu at curing temperatures between 150 and 240 °C. All data determined from these DSC measurements are further summarised in Table 2.

As can be seen in Fig. 4(a), the epoxy modified with the commercial PSu shows a step-like decrease in the heat capacity signal which shifts to lower times with increasing curing temperature. However, with increasing curing temperature the step in heat capacity becomes less pronounced as the mobility restrictions due to vitrification are reduced at these elevated temperatures. In comparison, the epoxy modified with the P-PSu shows a similar trend with increasing curing temperature, although the step-like change in heat capacity generally is more pronounced and shifted to even lower times. This behaviour indicates a higher extent of vitrification of the reacting blend ($T_{g\infty}$ of this epoxy–amine system is ca. 220 °C) as well as a sooner occurrence of mobility restrictions due to vitrification.

A more detailed analysis of the differences between the systems as a function of the curing temperature is possible

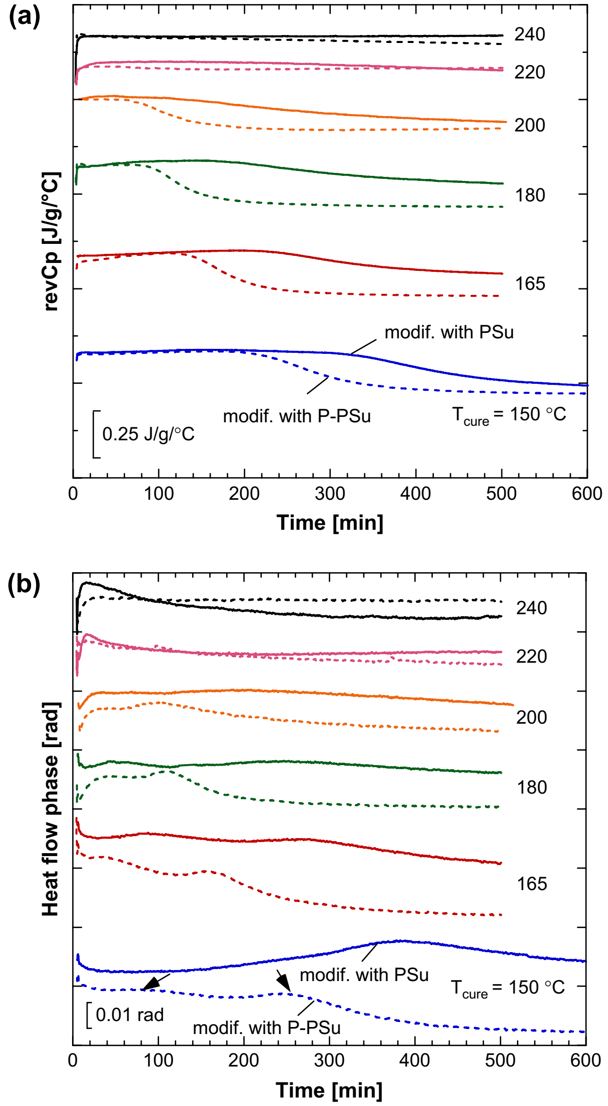

Fig. 4. Curing time-dependent (a) heat capacity change and (b) heat flow phase signals of the epoxy resin modified with 20 wt.% of either polysulfones at different curing temperatures.

by evaluating the heat flow phase signal as a function of the time, shown in Fig. 4(b). Indeed, the presence of two relaxation phenomena becomes apparent for curing temperatures up to 200 °C for both systems. The first peak appearing at a shorter time can be attributed to the relaxation of an incipient thermoplastic-rich phase with a T_g that eventually rises above the curing temperature and, consequently, vitrifies. The second relaxation peak at longer times coincides with the decrease in the heat capacity as discussed before and corresponds to the vitrification of the segregating epoxy-rich phase ($T_{g\infty} = 220\ °C$).

Table 2
Time to vitrification, heat capacity change, and glass transition temperatures of resulting phases after isothermal curing at the indicated temperatures

T_{cure} [°C]	T_g neat resin [°C]	PSu-modified resin				P-PSu-modified resin			
		t_{vit} [min]	ΔC_p [J/g/°C]	T_g α [°C]	T_g β [°C]	t_{vit} [min]	ΔC_p [J/g/°C]	T_g α [°C]	T_g β [°C]
150	155	375	0.18	164	148	274	0.22	174	–
165	171	289	0.11	178	156	174	0.24	191	–
180	184	235	0.11	188	163	126	0.21	204	–
200	198	200	0.14	211	174	119	0.16	203	222
220	216	–	–	215	178	–	–	189	219
240	220	–	–	220	183	–	–	204	–

The glass transition temperature of the unmodified system at the corresponding curing temperature is also listed for comparison.

The different times to vitrification as well as the change in magnitude of the step-like decrease in heat capacity for both systems can be related to the difference between the glass transition temperature of the modifiers and a particular curing temperature. As the glass transition temperature of the commercial PSu ($T_g = 185\ °C$) is lower than that of the modified P-PSu ($T_g = 228\ °C$), a fixed curing temperature up to 200 °C will always lead to a higher extend of vitrification of the system containing the P-PSu. The enhanced reactivity of this system might also contribute to this effect. At a curing temperature exceeding 200 °C, no relaxation events are seen for either systems in the heat flow phase signal, consistent with the absence of vitrification. The more pronounced change in heat capacity for the system modified with P-PSu may be ascribed to the vitrification of a homogeneous mixture with a higher glass transition temperature than that of the pure epoxy cured at the same temperature, as presented in Table 2.

It becomes evident that there exists an increasing mobility restriction during the advancement of the curing reaction and that it is related to the observed change in heat capacity upon vitrification when curing at $T \leq 180\ °C$. In order to further evaluate these results in a more quantitative manner, the mobility factor DF* based on the evolution of the heat capacity as a function of time and temperature ($C_p(t,T)$) can be calculated according to an approach proposed by Van Assche et al. [50]:

$$\mathrm{DF}^*(t,T) = \frac{C_p(t,T) - C_{pg}(T)}{C_{pl}(t,T) - C_{pg}(T)}, \tag{1}$$

where C_{pl} is the initial heat capacity in conditions where no mobility restrictions exist (start of the reaction), C_{pg} is the heat capacity corresponding to a state in which all movement has ceased (end of the reaction), and T is the curing temperature. The advantage of this approach, as pointed out by Van Assche et al. [50], is that there is no need of a model for the chemical kinetics. Fig. 5 shows DF* as a function of the curing time for the epoxy modified with either P-PSu or PSu at 180 °C as an example. Data for the neat epoxy system are included for comparison. At the initial stage of the reaction, the mobility factor is close or equal to one and decreases to zero towards the end of the reaction for all systems. In contrast to the system containing the PSu, the mobility factor of the P-PSu-modified epoxy decreases sharply, indicating a rapid freeze-in of the material.

The non-reversible and reversible heat capacity signals obtained after reheating the isothermally-cured systems are shown in Fig. 6(a) and (b), respectively. As can be seen, an endothermic relaxation peak is observed in the non-reversible heat capacity signal for the different systems cured at various

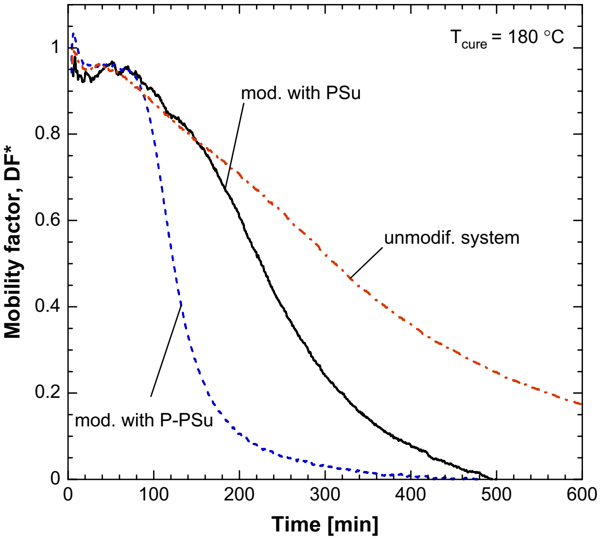

Fig. 5. Mobility factor as a function of the curing time of the epoxy resin modified with 20 wt.% of either polysulfones; the curing temperature is 180 °C.

temperatures, Fig. 6(a). For the PSu-modified epoxy, the height of the peak decreases and it becomes broader with increasing curing temperature, indicating a decreasing relaxation strength. Conversely, the height of the relaxation peak of the epoxy modified with P-PSu remains nearly unchanged with increasing curing temperature up to 180 °C, indicating a similar structural relaxation strength of the material. This observation is in agreement with the proximity of the curing temperature to the T_g of the pure components discussed above and it can also be related to the heat capacity changes summarised in Table 2. When curing the P-PSu-modified system at 200 or 220 °C, the strong relaxation event decreases significantly and two glass transition temperatures can be observed, Fig. 6(a) and (b). These phenomena indicate the existence of a heterogeneous system with glass transition temperatures corresponding to an epoxy- and a thermoplastic-rich phase. The glass transition temperature of the studied systems as obtained from the reversible heat capacity signal (Fig. 6(b)) is also presented in Table 2. In contrast to the behaviour of the PSu-modified system, increasing the curing temperature from 200 to 220 °C does not result in a phase-enrichment in the case of the P-PSu. Instead, the transition region becomes broader and the glass transition temperature of the epoxy-rich phase decreases by more than 10 °C.

When curing the P-PSu-modified system at 240 °C, the strong relaxation event virtually disappears due to the absence of vitrification. Only a single glass transition can be observed after curing isothermally at this temperature. Owing to the similarity of the glass transition temperature of both the fully cured thermoset ($T_{g\infty} = 220$ °C) and the P-PSu ($T_g = 228$ °C), a broader glass transition region at around 222 °C may be expected when curing at such a high temperature as vitrification is not expected to occur. While a broader glass transition indeed is obtained when curing at 240 °C, it nevertheless is about 20 °C lower than the expected value (thermal decomposition was ruled out by means of thermogravimetric analysis).

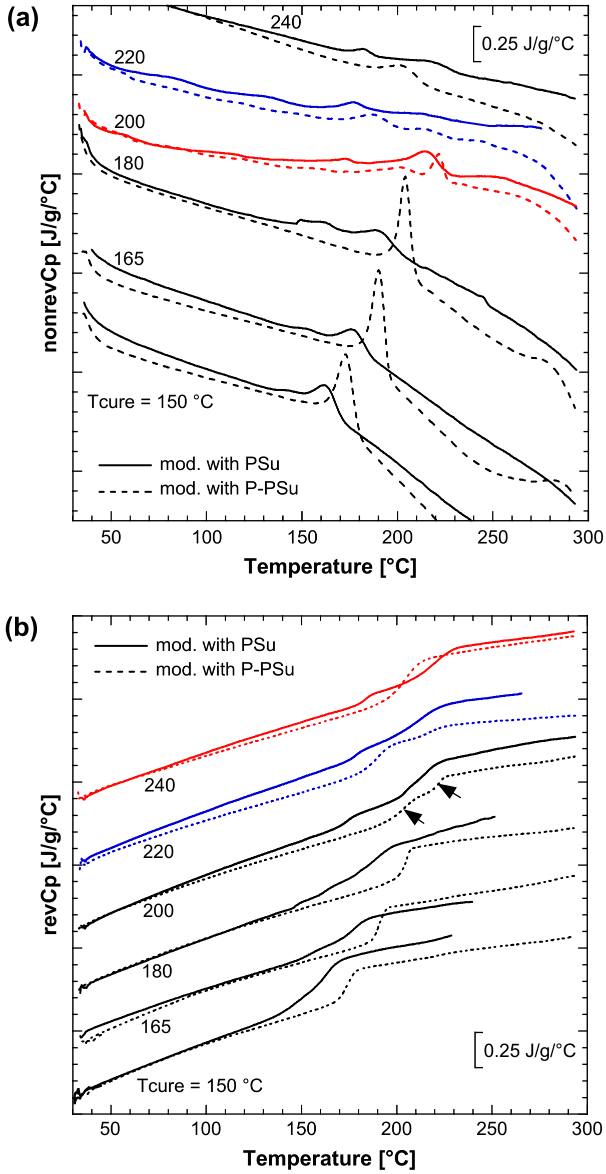

Fig. 6. Dynamic TMDSC thermograms following the isothermal curing of the epoxy resin modified with 20 wt.% of either polysulfones, (a) non-reversible and (b) reversible heat capacity signals.

The discrepancy may be explained by the occurrence of side reactions such as etherification of the epoxy with —OH groups generated from either the epoxy—amine reaction (greater flexibility of the ether linkage [60]) or terminal —OH groups of P-PSu (reduction in crosslinking density). Side reactions such as polyetherification and/or homopolymerisation have already been reported [26,27] for blends of a stoichiometric DGEBA/DDS system with OH-terminated polysulfone reacted at 180 °C. In these studies, the increase in the non-amine reactions was ascribed to a greater increase in resin viscosity due to the attachment of the large polysulfone molecules to the DGEBA.

In the present case, polyetherification is particularly favoured at high curing temperatures such as 240 °C. Yet, some polyetherification reaction might already occur at lower curing temperatures owing to the 20 wt.% excess of epoxy present in the mixture [26,27,61] and the decreased molecular mobility caused by the higher viscosity of the epoxy–thermoplastic blend. Such side reactions would explain the observed decrease in the glass transition temperature of the epoxy-rich phase after curing at 220 °C. In addition, the occurrence of polyetherification reactions has also been shown to be detrimental to the fracture toughness [17] and, as such, might contribute to the poor toughness improvement of the samples cured at 180 °C (Fig. 2).

When low molecular weight and OH-terminated PES is added to an epoxy–amine system, the curing reaction is accelerated at an early stage and then retarded due to the etherification of the thermoplastic with the epoxy [54]. Such a scenario would presumably lead to an increased average molecular weight between crosslinks and dangling chain ends; effects that can cause the depression observed in T_g. A similar decrease in T_g has been reported for OH-terminated PSu covalently incorporated into an epoxy network during curing [17,62].

In contrast, the PSu-modified epoxy shows a broad glass transition region indicative of two segregated phases, Fig. 6(b). The T_g of the epoxy-rich phase corresponds to the higher temperature feature of the transition while the small shoulder corresponds to the T_g of the PSu-rich phase. The T_g of the thermoplastic-rich phase is about 20 °C lower in the case of a curing temperature up to 180 °C, see Table 2. As the curing temperature is increased further, the glass transition of both phases also increases and approaches the glass transition temperature of the pure components, indicating an enrichment of the phases.

To summarise the results of the isothermal DSC experiments, the phase separation process in the P-PSu-modified system cured at the selected conditions is arrested most likely due to: (i) the higher reaction rate resulting in a faster increase in the molecular weight of the thermosetting system (effectively reducing the diffusion of components in the mixture [57]) and (ii) the faster and more pronounced vitrification of the homogeneous reactive blend.

3.3. Non-isothermal curing behaviour of epoxy modified with 20 wt.% of P-PSu or PSu

As shown by Swier and Van Mele [57], the diffusion rate is the rate-determining step during the reaction-induced phase separation of an epoxy–amine-PES system. In order to investigate the effect of an increased diffusion rate on the reaction-induced phase separation behaviour of the epoxy containing either type of PSus, non-isothermal curing experiments at 10 K/min were performed. The resulting thermal properties of the two systems after curing are shown in Fig. 7, the rescan of the isothermally-cured system at 180 °C is included for comparison. The broader transition observed for the P-PSu-modified epoxy cured non-isothermally as compared to the isothermally-cured sample indeed indicates the presence of two phases; however, a high degree of interpenetration of the two phases could also explain this thermal behaviour. In the case of the PSu-modified system, an equally broad transition region but shifted to higher temperatures is seen as a result of a continuous enrichment of the phases with increasing curing temperature. The width of this transition can be explained by the difference in T_g of both the epoxy-rich and the PSu-rich phase under this particular curing conditions.

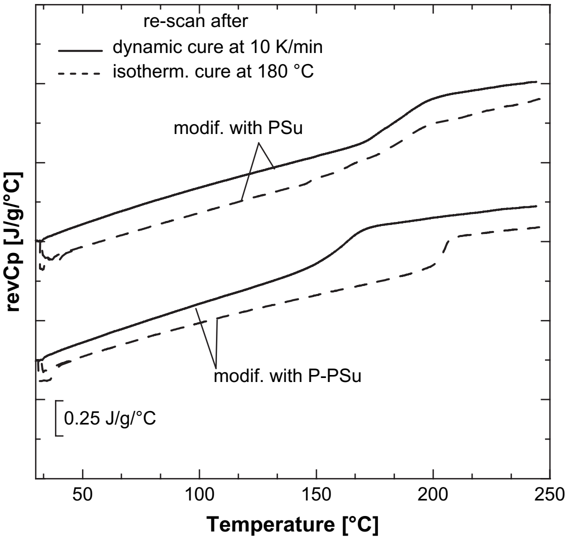

Fig. 7. Dynamic TMDSC thermograms showing the reversible heat capacity signal following the non-isothermal curing of the epoxy resin modified with 20 wt.% of either polysulfones. The dynamic rescan of the sample cured isothermally at 180 °C is included for comparison.

These initial experimental results are encouraging as they indicate that an optimisation of the chemical structure (e.g. increase in the molecular weight or altered thermoplastic chain termination) of the phosphorus-modified polysulfone might be a pathway to promote a suitable morphology development. However, this option would require a pronounced modification in the synthesis of the thermoplastic additive. In addition, decreasing the reactivity of the system by curing with a less reactive hardener also is an alternative. Decreasing the curing rate should provide the system with more time for phase separation to occur before gelation or vitrification of either phases takes place.

Furthermore, considering the results presented so far, the addition of blends of PSu and P-PSu to the epoxy resin appears attractive with regard to exploiting both the toughening and the flame retardancy effects provided by these modifiers. Experimental results of this approach are presented and discussed in the following sections.

3.4. Fracture toughness and modulus of the cured epoxy modified with 20 wt.% of the thermoplastic blends

In Fig. 8, the static K_{Ic} and the corresponding fracture mechanical Young's modulus of the modified epoxy as a function of the thermoplastic blend content are presented. As expected, the fracture toughness of the cured epoxy modified with the blend of P-PSu/PSu increases with an increasing content of the commercial PSu in the blend. This toughness enhancement can be achieved without a significant variation in the corresponding fracture mechanical modulus. Representative SEM

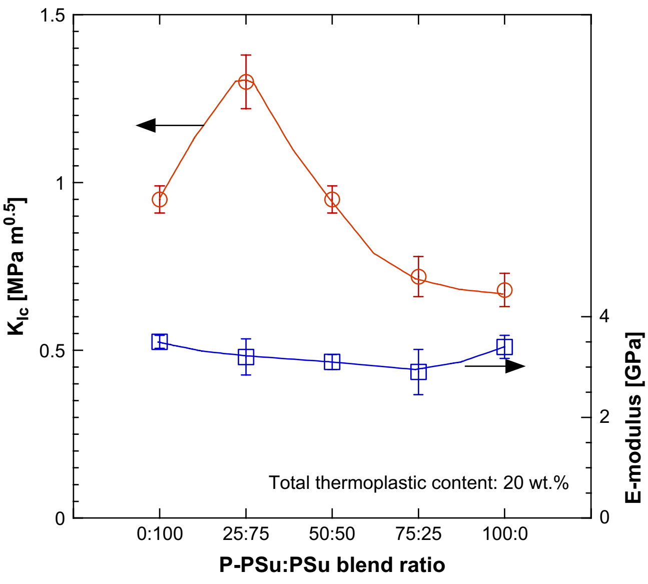

Fig. 8. Fracture toughness and fracture mechanical modulus of the modified epoxy as a function of the polysulfone blend composition.

micrographs highlighting the induced variation in the microstructure as a function of the blend composition are shown in Fig. 9.

As can be seen, a variety of morphologies were developed upon curing the modified epoxy samples depending on the composition of the thermoplastic modifier. The different resulting microstructures as a function of the blend composition are a combination of those observed for the modified system based on the neat thermoplastics; however, the increasing system viscosity with increasing P-PSu content clearly helps to lock in the morphology obtained by phase separation of the commercial PSu component. In turn, the increase in the K_{Ic} can be attributed to different fracture mechanisms such as: (i) an extensive plastic drawing of the thermoplastic-rich phase in the PSu-modified system, (ii) a significant amount of ductile tearing and/or plastic drawing of the thermoplastic-rich phase, combined with the plastic deformation of the surrounding epoxy matrix in the system based on a 25:75 P-PSu/PSu blend, (iii) a combination of ductile tearing of the thermoplastic-rich domains and deviation of the crack plane during crack propagation in the system based on either the 50:50 or the 75:25 P-PSu/PSu blend, and (iv) tails or arrest lines behind the thermoplastic particles in the P-PSu-modified system.

3.5. Dynamic mechanical and thermal analyses of the cured epoxy modified with 20 wt.% of the thermoplastic blends

In Fig. 10, the storage modulus (G') as well as the damping function (tan δ) of all epoxy samples cured at 180 °C containing a total amount of 20 wt.% of the P-PSu/PSu blend are plotted. For comparison, data for the neat epoxy reference are included (dashed line). As shown, the storage modulus of the systems is not significantly affected in the temperature range below the major transition. However, at higher temperatures, the rubbery modulus is observed to increase with an increasing content of P-PSu, eventually reaching a similar magnitude as that of the neat reference system. This observation can be explained by the two following effects arising simultaneously: (i) with a decreasing content of PSu, the crosslinking density increases as a result of the vanishing dilution effect, and (ii) with an increasing content of P-PSu, chain entanglement of the epoxy with the P-PSu is enhanced. Mimura et al. [29] reported a similar behaviour for the rubbery modulus of a PES-modified epoxy resin. Here, the increase in the rubbery modulus was attributed to the network interlock of the epoxy network and linear PES. In the present case, a similar interpenetration of polymer networks appears likely, although to a lesser extent owing to the possibility of occurrence of side reactions as discussed in the previous sections. As a result of these side reactions, the increase in the rubbery modulus with increasing P-PSu content is comparatively modest.

Up to three transitions can be seen in the tan δ spectra of these systems, depending on the relative composition of the modifier. The first transition, appearing at about 70 °C and with increasing magnitude as the content of P-PSu increases, presumably is related to the motion of looser sections in the epoxy network. Most likely, this transition is a result of the secondary epoxy-modifier reactions occurring during curing with the P-PSu as discussed before. In agreement with this interpretation, this transition is absent in the epoxy modified with the neat PSu.

At a higher temperature, two peaks related to the glass transition of a thermoplastic-rich phase and of an epoxy-rich phase at about 165 °C and 193 °C, respectively, can be observed for the epoxy modified with the pure PSu. The lower glass transition temperature of the thermoplastic-rich phase can be attributed to the remaining low molecular weight epoxy–amine species in this phase acting as a plasticizer. Additional free volume generated by blending the two materials can also lower the T_g of this phase [38].

As the content of the P-PSu increases, the peak observed at 165 °C turns into a shoulder which completely vanishes for the epoxy modified with the pure P-PSu. At the same time, the magnitude of the peak observed at 195 °C increases and shifts to slightly higher temperatures, eventually reaching a maximum temperature of about 205 °C. Moreover, the relaxation peak in case of the pure P-PSu is as narrow as that of the neat epoxy, indicating a narrow distribution of relaxation times and a high interpenetration of the epoxy network with the thermoplastic. These experimental results verify the change in the modified system from a two-phase to a single-phase morphology with a higher glass transition temperature with increasing P-PSu content, in good agreement with the results obtained by the TMDSC for the epoxy containing the P-PSu (Table 1). In addition, the DMA results correlate well with the observed changes in microstructure as shown in Fig. 9.

3.6. Pyrolysis and fire behaviour

It remains to be evaluated whether the interesting mechanical behaviour of the epoxy resin modified with the P-PSu/PSu

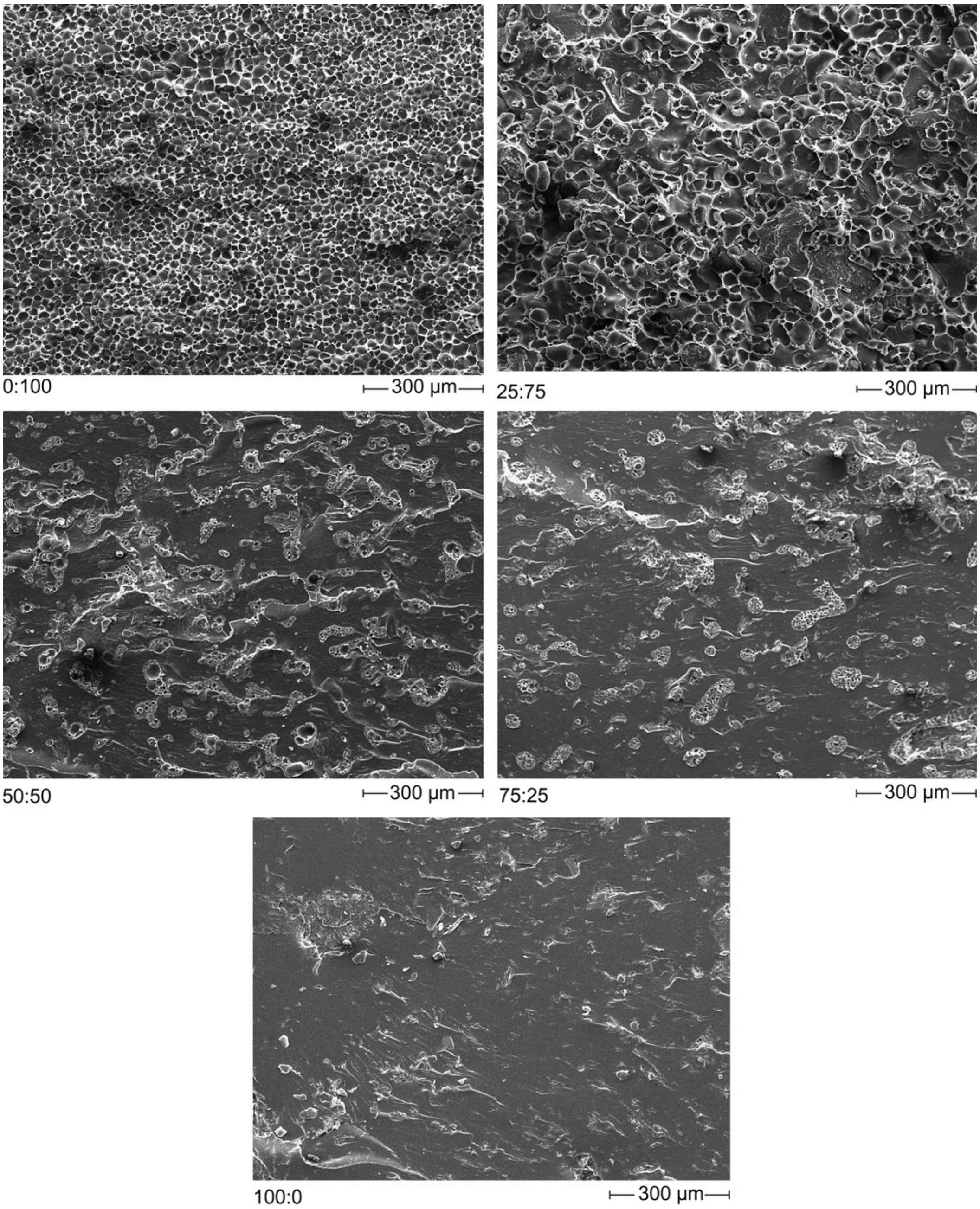

Fig. 9. Representative scanning electron micrographs of fracture surfaces of the epoxy modified with the various P-PSu/PSu blend compositions, crack growth direction is from left to right.

blends is accompanied by an improved fire behaviour, as intended. Some key investigations were performed in order to clarify this point. The pyrolysis and flammability were characterised for the most promising epoxy resin modified with the P-PSu/PSu 25:75 blend. The fire behaviour under flaming conditions was investigated for the epoxy resin modified with the P-PSu/PSu 50:50 blend. The experimental results were compared to the results of the epoxy resin modified with either 20 wt.% of P-PSu or PSu, which have been discussed previously in detail [46].

Whereas an independent decomposition of both components was observed for the PSu in the epoxy resin, a strong interaction between the P-PSu and the epoxy matrix was found [46]. This interaction was manifested in a reduction of the decomposition temperature, an increase of water, and a decreasing carbonyl release rate. It is postulated that the phosphorus catalyses the elimination of water from the epoxy matrix, a well established elimination reaction of secondary hydroxyl groups. The decomposition of the epoxy resin modified with the P-PSu/PSu 25:75 blend is characterised by an intermediate behaviour between those of the epoxy systems modified with neat P-PSu and PSu. The temperature of maximum weight loss occurred at 402 °C as compared to 419 °C for the PSu-modified epoxy and 385 °C for the P-PSu-modified epoxy.

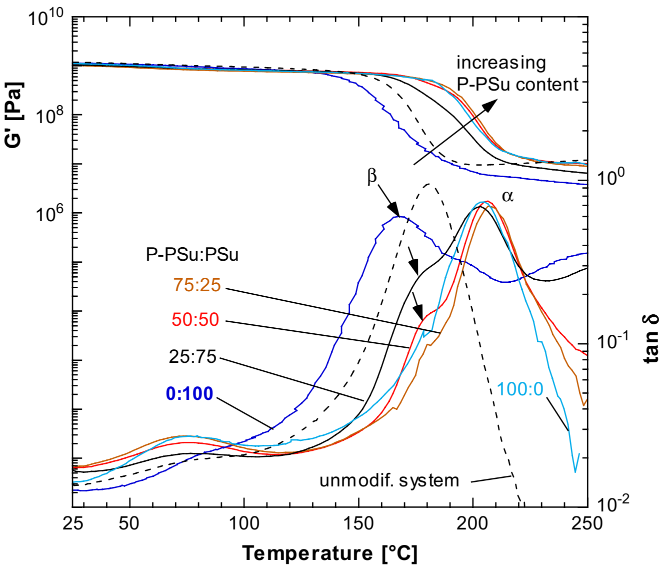

Fig. 10. Summary of the storage modulus and damping function of the cured epoxy formulations containing the various P-PSu/PSu blend compositions as a function of the temperature.

The pyrolysis indicates a lesser interaction with the epoxy matrix according to the lower phosphorus content in the sample. The LOI of 25.7% for the epoxy resin modified with the P-PSu/PSu 25:75 blend puts the performance of this particular system between that of the epoxy modified with PSu (21.3%) and that of modified with P-PSu (27.4%).

The fire behaviour in a flaming condition of the epoxy resin modified with PSu, P-PSu/PSu (50:50), and P-PSu is illustrated in Fig. 11. Some key results are summarised in Table 3.

Table 3
Cone calorimeter results for epoxy resin modified with PSu, P-PSu/PSu 50:50, and P-PSu

	THE [MJ m^{-2}]	Peak of HRR [kW m^{-2}]	Residue [%]	THE/TML [MJ m^{-2} g^{-1}]	TCO/TML [g g^{-1}]
Error	±3	±60	±3	±0.1	±0.01
Epoxy resin					
+PSu	63	698	26.9	2.3	0.05
+P-PSu/PSu 50:50	57	667	32.1	2.0	0.07
+P-PSu	46	472	41.0	1.9	0.08

THE = total heat evolved, peak of HRR = peak of heat release rate, THE/TML = THE/total mass loss, TCO/TML = total CO production/TML.

The fire risks such as total heat evolved (THE) and peak of heat release rate (peak of HRR) of the epoxy resin modified with the P-PSu/PSu 50:50 blend is, again, between the behaviour of the epoxy resin modified with either PSu or P-PSu. The residue clearly increased with an increasing phosphorus content, indicating an increasingly efficient charring mechanism. The THE/total mass loss (THE/TML) represents the effective heat of combustion multiplied with the combustion efficiency. The significant reduction in this value indicates an additional significant flame retardancy mechanism acting in the gas phase. The increase in the CO yield as an incomplete combustion product further confirms this interpretation. Again, the gas phase mechanism increased with increasing phosphorus content.

It can be concluded that both the char enhancement and the flame inhibition mechanisms due to the P-PSu are also active when using P-PSu/PSu blends. The final fire response properties of the epoxy resin modified with such P-PSu/PSu blends were found to lie between the behaviour of the epoxy resin

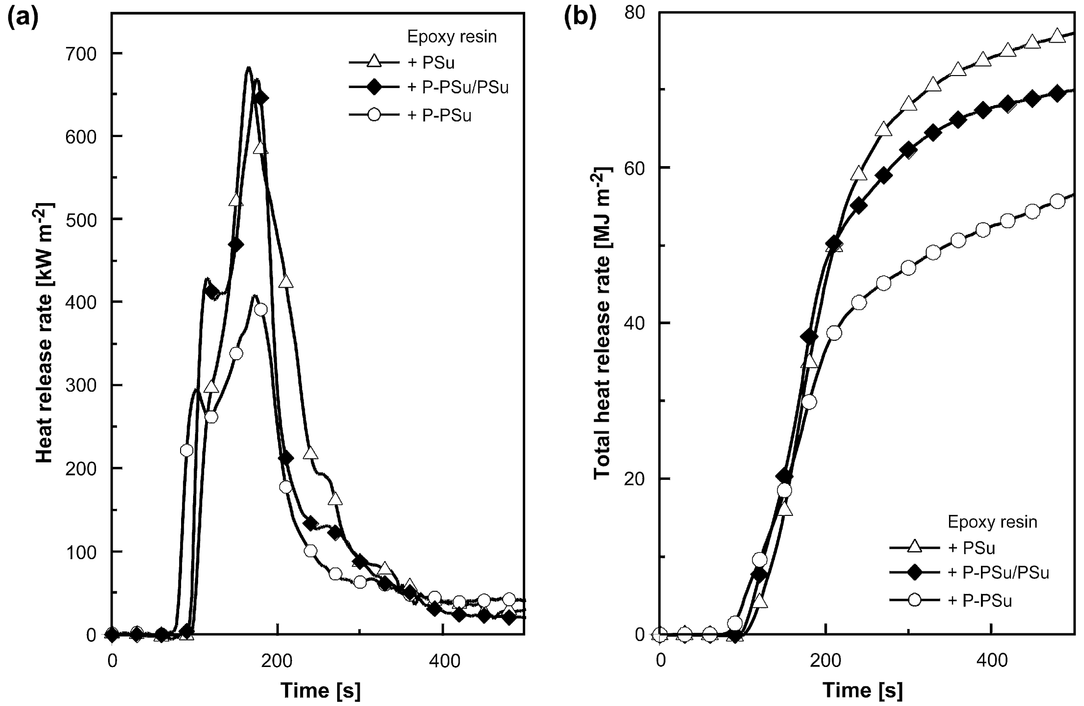

Fig. 11. (a) Heat release rates and (b) total heat release of epoxy resin modified with PSu, P-PSu/PSu 50:50, and P-PSu under flaming conditions (cone calorimeter with 35 kW m^{-2}).

modified with either P-PSu or PSu. This tendency was verified by the flammability tests as well as under flaming conditions. Most likely, the flame retardancy of such systems corresponds to the realised total phosphorus content present in the system.

4. Conclusions

The results presented in this study have shown that a cured bisphenol-A based epoxy resin can simultaneously be equipped with both an enhanced toughness and improved flame retardancy by adding a new type of polysulfone containing phosphorus in the backbone. These performance improvements were achieved without sacrificing the stiffness and the glass transition temperature of the resulting material. Furthermore, owing to the chemical structure of the phosphorus-modified polysulfone, an interlocked epoxy–thermoplastic network can be created under certain curing conditions, providing the cured epoxy resin with a higher glass transition temperature.

It was demonstrated by means of temperature-modulated DSC that the reaction-induced phase separation is suppressed when curing the material at temperatures equal or less than 180 °C and higher than 220 °C when using the phosphorus-modified PSu. An enhanced reaction rate, the occurrence of secondary reactions and an earlier vitrification of the reacting mixture were found to prevent any morphology development in the materials cured under these conditions. Hence, only about a 20% improvement in the fracture toughness was observed in samples cured at 180 °C. Nevertheless, the absence of phase separation contributed to a high interpenetration of the thermoplastic and thermoset networks, which significantly increased the glass transition temperature of the final material.

Modification of the epoxy with blends of a commercially available and the phosphorus-modified polysulfone indicated another interesting approach towards increasing the fracture toughness of the resulting material while maximising the total phosphorus content in the system. Such blends were found to be more effective to increase the toughness of the epoxy than the neat thermoplastics at a concentration of 20 wt.% owing to the particular resulting microstructures. By increasing the amount of the phosphorus-modified polysulfone in the blend, the viscosity of the reactive mixture also increased. This, in turn, contributed to "lock in" the observed morphologies. The microstructure change upon curing of the material was found to be crucial for the fracture toughness improvement, in agreement with the majority of the studies in the literature. However, a complete phase inversion or the formation of a co-continuous morphology will not necessarily result in the highest toughness. A combination of polymer interpenetration and phase separation appears to be an efficient way to simultaneously improve the toughness and glass transition temperature as well as the flame retardancy of thermosetting materials for modern-day applications.

Acknowledgements

Financial support of this work by the German Research Foundation (DFG) through the grants AL474/3-1, AL474/4-1/4-2; PO 575/5-1/8-1, SCHA 730/6-1 and DO 453/4-1/4-2 is gratefully acknowledged. Thanks are due to U. Knoll for her contribution to the fire tests.

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