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New high-performance thermoplastic toughened epoxy thermosets

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Thermal, mechanical and morphological measurements of reactive thermoplastic modified epoxy resin are reported. Phase separation occurs during the curing. To a small decrease of the modulus of the final materials a large increase of the toughness of the thermoset is associated, as compared with the neat epoxy resin when cured with an usual curing agent. © 1997 Elsevier Science Ltd..

(**Keywords: epoxy resin; toughness; thermoplastic modifier; SEM**)

INTRODUCTION

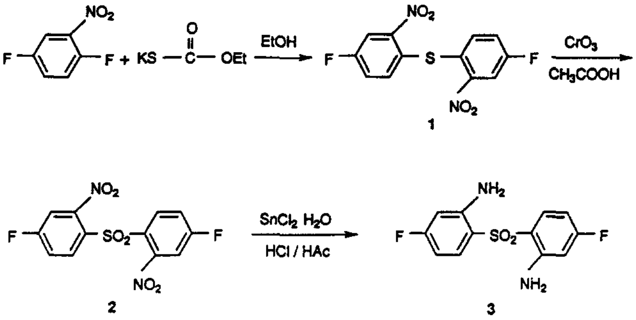
Thermosetting resins are used extensively in areas where their stiffness, temperature performance and solvent resistance are required. Their desirable properties stem from the high crosslink density which develops on cure; unfortunately, as a result of this crosslinking, the cured resin cannot yield and absorb energy under stress and, consequently, the fully cured resin is of a brittle nature. Although thermosetting resins may be toughened by the introduction of rubber[1] and by the reduction of crosslink density, both these routes generally lead to the loss of modulus, glass transition temperature (T_g) and solvent resistance, thus limiting the number of high-performance applications of these resins.

In the last few years much work has been directed to the use of functionalized polyaromatic thermoplastics as toughening agents for thermosetting resins, using the functionality to covalently bond the thermoplastic into the thermosetting resin[2–9].

One approach towards the incorporation of pendant functionalization involves the post-functionalization of polymers such as the modified poly(ethersulfone)s. However this approach sometimes requires quite severe chemical conditions which may lead to polymer degradation.

An alternative approach involves the preparation of pre-functionalized monomers and their subsequent polymerization.

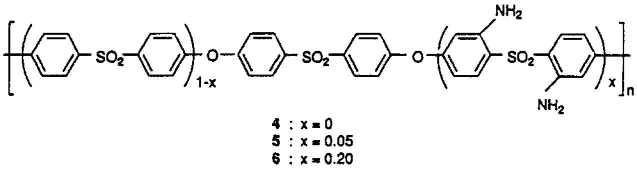
The polymers obtained have potential applications as either toughening agents in thermosetting resins or, with the incorporation of crosslinking moieties, as matrices in their own right[5].



Scheme 1

Recently[10], we have been able to report a new synthetic route to a functionalized monomer (3) compatible with poly(ethersulfone) type chemistry; this has been purified and fully characterized (*Scheme 1*).

The polymer synthesis was based on the reaction of 4,4′-difluoro-2,2′-diaminodiphenylsulfone (3) ($DFDDASO_2$) with bisphenol S (Bis S) and 4,4′-difluorodiphenylsulfone (DFDPS), with the aim of producing a copolymer comprising the repeat unit shown in *Scheme 2*.



Scheme 2

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The aim of the present work was to investigate the properties of a commercial epoxy resin (Epikote 828) when crosslinked in the presence of different percentages of the thermoplastic (**6**) which contains the amino groups as reactive curing sites.

Although the thermoplastic and thermoset used in this study were chosen to be thermodynamically compatible[11], during the curing process it is now recognized that the increasing molecular weight of the thermoset component initiates phase separation. This generates a heterogeneous cured material, which may exhibit different morphologies[12].

EXPERIMENTAL

Materials

The epoxy resin used in this work was a diglycidyl ether of bisphenol A (Epikote 828) supplied by Shell Chemical Co., UK. The synthesis of amine functionalized poly(arylene ether sulfone) (**6**) has been reported previously[10]. The polymer shows a reduced viscosity of $0.2\,\mathrm{dl\,g^{-1}}$ when measured in conc. H_2SO_4 at 30°C. The curing agent, used for the control system, was 4,4′-diaminodiphenyl sulfone (DDS, by Aldrich Chemical Co. Ltd, Italy).

The epoxy resin and DDS were used as supplied, whilst the thermoplastic was dried before use.

Cured samples were made by mixing the thermoplastic and the resin in different ratios (w/w%) and stirring the resulting mixture for 4h at 120°C and for 20min at 180°C. The blended resin mixture was then poured into a preheated silicone rubber mould and cured in an air conventional oven with a pre-optimized cure cycle: 3 h at 180°C, 5 h at 250°C and additional 4 h at 270°C, followed by slow cooling in the oven.

The prepared samples are presented in *Table 1*.

D.s.c. measurement

D.s.c. measurements were conducted using a Mettler TC 11 differential scanning calorimeter. In all cases a sample of approximately 10mg was used at a heating rate of $10°\mathrm{C\,min^{-1}}$ over a temperature range of 30–300°C. In these experiments, the sample was cured during the first temperature scan, allowing evaluation of the heat of reaction. The sample was then cooled slowly to room temperature and a second scan was run to determine the final T_g.

Mechanical testing

Flexural properties were assessed at 23°C by a three-point bend test using an Instron 4301 and according with the ASTM 790M-86 procedure. The sample size was 12 × 2.5 × 40mm and the specimens were tested with a crosshead speed of $1.0\,\mathrm{mm\,min^{-1}}$.

The Charpy Impact Strength of the unmodified and modified epoxy resin was measured by means of a Charpy Impact Test following the specifications ISO 179-1992E. The Charpy Impact Strength (a_{cu}) was calculated according to the equation

$$a_{cu} = \frac{W}{db} \times 10^3$$

as defined in the above mentioned specification for unnotched specimens. The dimensions of the specimens were approximately 80 × 10 × 4mm.

Table 1 Composition of blends used in this study

	Blends			
	A	**B**	**C**	**D**
Epikote 828	100	100	100	100
DDS (phr)	15	0	0	0
Polymer 6 (phr)	0	10	15	20

Table 2 Thermal and mechanical properties of the unmodified and thermoplastic modified epoxy systems

Blend	T_g (°C)	E (GPa)	σ_b (MPa)	ϵ_b (%)	a_{cu} ($\mathrm{kJ\,m^{-2}}$)
A	—	2.38	25.5	1.32	0.96
B	134	1.90	47	2.78	2.97
C	158	1.86	44.8	3.1	3.25
D	190	1.80	45.6	2.94	2.83

Morphological analysis

The specimens were fractured under cryogenic conditions using liquid nitrogen. The fractured surface was then coated with a thin layer of platinum and the observation was performed using a Cambridge 90 SEM.

RESULTS AND DISCUSSION

Thermal properties of the unmodified and thermoplastic modified systems were measured by means of d.s.c. In a first series of experiments the sample was cured during the first temperature scan to determine the magnitude of the curing exotherm, while a second scan was used to evaluate the final glass transition temperature of the cured material.

Variations of the glass transition temperature for the systems investigated are reported in *Table 2*.

A single T_g was observed in all blends due to the close proximity of the T_gs of the individual components. However the T_g depends significantly on the percentage of the thermoplastic in the blend, due to the reactions of the amino groups of the poly(ethersulfone), indicating an increase of the crosslinking density as the content of the reactive thermoplastic is increased.

The cured materials were also subjected to d.s.c. analysis. D.s.c. scans of the cured materials did not show any further exotherms indicating that the curing process is complete.

In order to investigate the effect of the reactive poly(ethersulfone) on the mechanical properties of the epoxy resin, flexural and impact tests have been performed on the cured samples. The results obtained for the thermoplastic modified and the control systems are reported in *Table 2*.

The data show that the presence of the thermoplastic modifies the mechanical behaviour of the epoxy matrix. An increase in the amount of modifier leads to a progressive small decrease in flexural modulus (E) of the blends with respect to the DDS cured resin, while the stress and strain at break (σ_b, ϵ_b), are greatly enhanced. From the results it appears that the flexural properties are essentially independent from the blend composition.

As expected the fracture toughness increases significantly with the incorporation of the thermoplastic modifier to the resin. The fracture energy value obtained for the modified samples is approximately triple that of the neat epoxy resin, as shown in *Table 2*. A slight decrease in the fracture energy value can be observed at 20 phr content of thermoplastic and this behaviour can be presumably accounted for by a different morphological feature developed upon cure, which will be discussed later.

Since the reactive thermoplastic polymer was obtained by laboratory synthesis limited amounts of material were available. Thin samples were used for testing so an investigation into the effect of sample thickness on fracture properties was not performed.

However the obtained values are self-consistent and show that the use of the amino functionalized poly(ethersulfone), even at low content (10 phr), is a useful means to improve the toughness of the epoxy resin.

It is widely recognized that in order to achieve good toughening in a thermoplastic modified epoxy system adequate interfacial adhesion is necessary[13].

The improved fracture toughness by poly(ethersulfone) modification of Epikote 828 epoxy resin is mainly attributed to the reactive amino groups along the thermoplastic chain, which provide chemical bonds between the thermoplastic and the thermoset resin.

SEM observation was carried out on the fracture surfaces of the modified epoxy systems to investigate the morphology which develops upon cure. From the electron micrographs all samples look similar and they all exhibit phase-separated morphology. In the case of blends **B** and **C** (10 and 15 phr content of thermoplastic modifier, *Figure 1*) the thermoplastic is homogeneously distributed in the resin matrix in the form of spheroidal particles whose size is around 0.8 μm. By increasing the content of thermoplastic (20 phr, *Figure 2*) a phase separation of the thermoplastic is still observed but, in this case, the particles of the modifier are smaller in size (0.4–0.7 μm) and unevenly distributed in the resin matrix. However in this blend, owing to the high concentration of thermoplastic, it is possible to find few droplets of much higher diameter. The non-uniform dispersion can be attributed to the low solubility of the thermoplastic in the epoxy resin which leads to aggregation of the particles to form greater domains. This morphological feature can be presumably considered responsible for the observed slight depression in fracture energy value for the blend containing the highest amount of thermoplastic (20 phr).

Moreover from the nature of the fracture surfaces it appears that, in all cases, the second phase is well anchored to the matrix, indicating good adhesion between the two phases, and the thermoplastic particles have acted as crack pinning points.

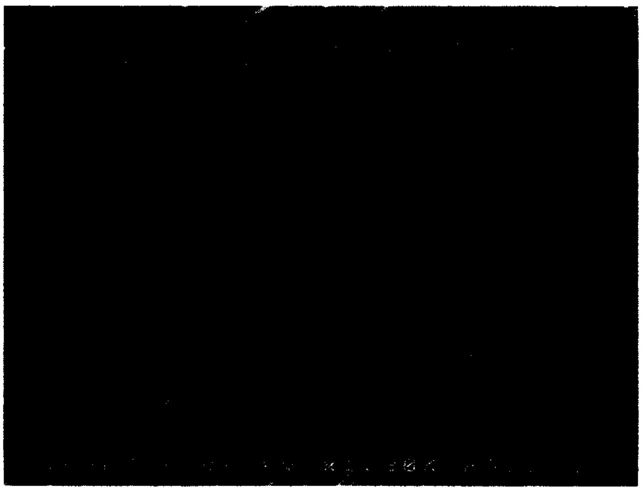

Figure 1 SEM micrograph of fracture surface of blend **C**

Figure 2 SEM micrograph of fracture surface of blend **D**

CONCLUSIONS

In this study the fracture toughness of an epoxy resin was found to increase when a reactive poly(ethersulfone) thermoplastic modifier was incorporated into the epoxy.

This remarkable toughening effect is associated with a small decrease in the flexural modulus as compared with the neat epoxy resin cured with a conventional curing agent.

The amino functionalization of the thermoplastic plays an important role in determining the properties of the cured resin. It enables the thermoplastic to behave as a curing agent for the epoxy resin and it also promotes interfacial bonding between the thermoplastic and the thermoset which is postulated to be a major factor in improving the fracture toughness. The toughness is also related to the reduced crosslink density of the cured resin, compared to DDS cured resin, due to the distance between amino groups on the thermoplastic and to the phase separation of the thermoplastic to give a particulate morphology

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