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Material Behaviour

Role of intrinsic flaws upon flexural behaviour of a thermoplastic modified epoxy resin

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Abstract

A bisphenol A-based epoxy resin (DGEBA) was modified with 15 weight percent polysulphone (PSU) and thermally cured using 4-4′diaminodiphenylsulphone (DDS). Starting from a homogeneous DGEBA/DDS/PSU mixture, the system developed a two-phase morphology upon network formation. Dynamic mechanical analysis (DMA), transmission optical microscopy (TOM) and scanning electron microscopy (SEM) studies showed that the system developed a co-continuous morphology consisting of two distinct domains. One of the domains was an epoxy rich matrix containing PSU particles while the other consisted of a dispersion of epoxy particles within a PSU rich phase. Flexural strength distributions of unmodified and thermoplastic modified epoxy resin were obtained by testing the materials in three-point bending according to the ASTM D790 protocol. The flexural behaviour of the epoxy resin was not improved by the presence of thermoplastic. In addition, the thermoplastic modified epoxy resin displayed a higher data scatter compared with the neat resin. The fracture mechanism of unmodified and thermoplastic modified epoxy resins was demonstrated to be sensitive to the intrinsic flaw distribution. The two-parameter Weibull model, which was used to analyse the experimental data, gave a good representation of the fracture loads distribution with regression coefficients of 0.99.

Keywords: Epoxy resins; Thermoplastic modified epoxy resins; Polysulphone; Flexural strength; Weibull statistics

1. Introduction

Epoxy resins are one of the most important classes of thermosetting polymers. These networks have many desirable properties, which include high modulus, excellent chemical and corrosion resistance and good dimensional stability. Unfortunately, these highly crosslinked networks are inherently brittle and consequently have limited utility in applications requiring high fracture strength.

Although epoxy resins can be substantially toughened by the addition of a rubbery phase [1], the improvement in toughness is inevitably accompanied by a significant loss in elastic modulus and yield strength. Furthermore, rubber toughening of highly crosslinked epoxies is shown to be inefficient, owing to the limited ability of these epoxies to undergo shear deformation. Therefore, an alternative approach has emerged in which epoxies are toughened by the incorporation of rigid thermoplastic particles [2–10]. Generally, the thermoplastics used possess a high modulus and a high glass transition temperature. Thus, the aim is to achieve an enhancement in fracture toughness for the modified epoxies, while retaining other desirable properties.

This study describes a series of flexural tests performed to determine the flexural strength distribution of a thermoplastic modified epoxy resin. The unmodified resin was also tested for comparison. The Weibull model [11], which is widely used in characterization of brittle

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materials, was employed to fit the rupture load distributions. The influence of the addition of a thermoplastic upon the flexural strength distribution was evaluated. Statistical differences among the different materials were assessed by the non-parametric Mann–Whitney test.

2. Experimental

2.1. Materials and sample preparation

A diglycidyl ether of bisphenol-A (DGEBA) epoxy monomer (DER 332, Dow Chemicals, number-average molecular mass, Mn, equal to 349 g/mol and an hydroxyl/epoxy ratio of 0.015) and an aromatic amine curing agent 4,4′- di-aminodiphenyl sulphone (DDS, HT 976 Ciba-Geigy) were employed in order to generate a thermoset material. The selected thermoplastic was polysulphone (PSU, Udel P1700, Amoco Chemicals). The PSU-modified thermoset containing 15-wt % PSU was prepared in a two-step process. First, DGEBA and PSU were dissolved in methylene chloride. Most of the methylene chloride was evaporated at room temperature followed by heating at 80°C for 24 h in order to eliminate the residual amount of solvent. Then, the solution was heated at 135°C and the DDS monomer was added stirring for about 5 min. Air bubbles introduced during hand stirring were removed keeping the sample under vacuum at 150°C for 10 min. The mixture was immediately poured into moulds to prepare specimens for subsequent mechanical characterization.

Plates for flexure specimens were obtained by casting the mixture into moulds consisting of two rectangular glass plaques covered by a thin layer of Teflon, spaced by a rubber cord and held together with clamps. The mixture was poured into the mould, which had been preheated to 200°C, and then degassed under vacuum for 10 min to remove trapped air. The samples were cured using the following schedule: 2 h at 200°C and 1 h at 220°C. The cured materials were allowed to cool slowly to room temperature. Then, the plaques were removed from the mould and machined to produce bars for mechanical testing.

2.2. Dynamic mechanical properties

The dynamic mechanical behaviour of both unmodified and modified epoxy resins was studied in a Metravib viscoanalyser in the three-point bending mode using $60 \times 12 \times 5$ mm^3 samples. Each sample was scanned from 20°C to 250°C at a heating rate of 3°C/min. During heating, the samples were subjected to strain at a frequency of 10 Hz while the storage modulus (E') and the damping factor (tan δ) were recorded. The temperature corresponding to the maximum in tan δ versus temperature plots was recorded as a measurement of the glass transition temperature (Tg).

2.3. Optical and scanning electron microscopy

Thermoplastic-modified epoxy samples were fractured at ambient temperature and examined by transmission optical microscopy (TOM) using a Leica DM LB microscope. Fracture surfaces of specimens tested in flexure were examined by scanning electron microscopy (SEM) using a Jeol JSM 35 CF apparatus, after coating the broken surfaces with a thin gold layer.

2.4. Mechanical characterization

The unmodified and modified epoxy resins were tested under flexure. Flexural tests were carried out at room temperature (23 ± 2°C) in a Instron universal testing machine Model 4467 at a crosshead displacement rate of 5 mm/min. Flexural strength and flexural modulus were measured in three-point bending using specimen dimensions equal to 3.3 ± 0.1 mm $\times$ 10 ± 0.2 mm cross-section and 90 ± 5 mm in length. The length between supports was equal to 50 mm as recommended by the ASTM D790 protocol [12].

The bars were loaded to failure and the flexural strength (σ_f), the maximum strain in the outer fibre (ϵ) and the flexural modulus (E) were calculated from the following standard relations:

$$\sigma_f = \frac{3FL}{2bd^2} \tag{1}$$

$$\varepsilon = \frac{6\delta d}{L^2} \tag{2}$$

$$E = \frac{L^3 s}{4bd^3} \tag{3}$$

where F is the load at break, b and d are the width and the thickness of the specimen respectively, L is the length between supports, δ is the maximum deflection of the centre of the beam and s is the slope of the tangent to the initial straight-line portion of the load-deflection curve.

Strictly, the ASTM D790 standard states that results of flexural strength calculated from Eq. (1) are valid if the maximum outer-fibre strain, ϵ, is lower than 5%. If strains exceed 5% before fracture the following relationship is recommended:

$$\sigma_f = \frac{3FL}{2bd^2}\left[1 + 6\left(\frac{\delta}{L}\right)^2 - 4\left(\frac{\delta d}{L^2}\right)\right] \tag{4}$$

Eq. (4) was used in cases in which the strain at fracture, calculated from Eq. (2), was higher than 5%.

3. Results and discussion

3.1. Characterization

The DGEBA/PSU blend prepared as described was homogeneous at the early stage of reaction. As the polymerisation reaction proceeded, the system developed a two-phase morphology. The sample became opaque due to the phase-separated structure developed in the mixture. However, the material at the end of cure process was transparent. The continuous change in the refractive index of the epoxy component during curing rendered an accidental matching of its refractive index with that of PSU.

The obtained morphologies were observed by transmission optical microscopy (TOM). Some characteristic micrographs are shown in Fig. 1(a),(b). In Fig. 1(a) a two-phase structure with interconnected domains, typical of a co-continuous structure is clearly discernible. A secondary phase separation in both phases is revealed at a higher magnification (Fig. 1(b).

Spherical particles, corresponding to epoxy-amine dispersed in a thermoplastic rich phase are observed in the dark zones whereas small PSU particles are visible in the thermoset rich phase (bright zone). The described structure was confirmed by scanning electron microscopy (SEM) observations on samples etched with methylene chloride. The solvent attacked the thermoplastic phase leaving the epoxy-amine phase un-attacked.

Dynamic mechanical data for the unmodified resin and the material containing 15-wt % PSU are compared in Fig. 2. The unmodified resin displayed a single tan δ peak corresponding to its glass transition temperature. On the other hand, the tan δ traces of the modified resin exhibited two relaxation peaks, confirming the development of a phase-separated morphology. The higher temperature relaxation peak of the PSU modified resin is attributed to the *Tg* of the epoxy-rich domain, whereas the lower temperature relaxation is associated with the *Tg* of the thermoplastic-rich phase.

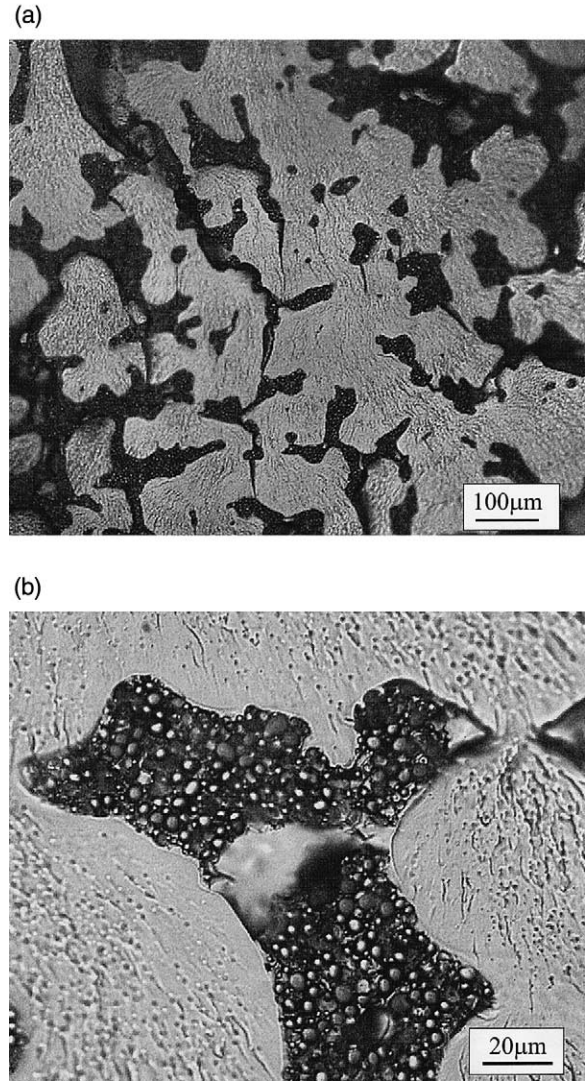

Fig. 1. (a) Optical microscopy for the PSU modified epoxy resin. (b) Optical microscopy for the PSU modified epoxy resin.

3.2. Flexural test

Of all the standard methods for measuring fracture resistance, tensile testing is the simplest. However, in the case of brittle materials, a slight misalignment of the axial load is sufficient to cause premature failure at the grips. For this reason, much of the work concerning the mechanical characterization of unmodified and thermoplastic modified epoxy resins has been performed by testing the materials under flexure [3–7]. Load-deflection curves were plotted to determine the flexural strength, the strain at break and the tangent modulus of elasticity. Fig. 3 shows typical plots of flexural strength versus strain calculated from Eqs. (1) and (4). All samples displayed maximum strain at break higher than 5%, therefore, the flexural strength was calculated from Eq. (4). Table 1 shows the mechanical properties measured for the unmodified and thermoplastic modified epoxy resin. It can be seen that the intrinsic modulus of the epoxy resin was slightly increased by the thermoplastic modification. Unfortunately, no significant flexural strength improvement was achieved by the incorporation of the thermoplastic modifier. This behaviour can be attributed to the relatively low elongation of the PSU at failure and the limited ability of the brittle matrix to undergo shear deformation.

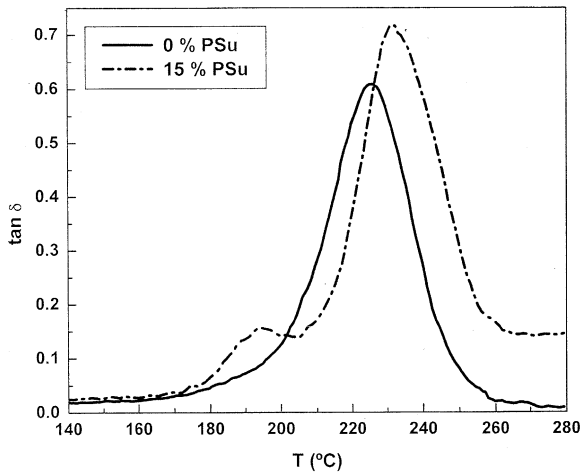

Fig. 2. DMA traces for the unmodified and PSU modified epoxy resin.

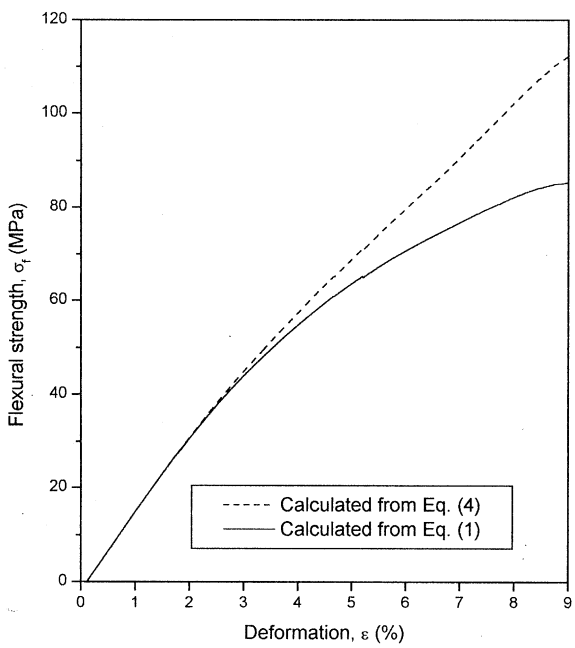

Fig. 3. Flexural strength versus strain in the outer fibre calculated from a load versus deflection register using Eqs. (1) and (4).

3.3. Microstructure

Visual examination of the fracture surfaces of the unmodified epoxy sample revealed that the crack showed flat propagation with a brittle aspect. SEM micrograph of the neat resin depicted in Fig. 4(a) a shows the presence of zones of different features with an abrupt transition between them. The zones are associated with different propagation crack modes. The very smooth "mirror-like" zone is associated with rapid crack propagation and the rougher zone with slow crack propagation. Fig. 4(b) shows the drastically different feature of the thermoplastic modified resin. The fracture surface is macroscopically very rough and three-dimensional which is indicative of considerable crack branching. The two different interconnected domains are more clearly differentiated in Fig. 4(c). Fig. 4(d) is a micrograph taken at a higher magnification. The initially dissolved epoxy resin precipitated as spherical particles, which were surrounded by the continuous thermoplastic domain. This micrograph shows a poor degree of adhesion between the epoxy particles and the thermoplastic. Debonding of the epoxy particles during the fracture process is clearly revealed by the presence of holes.

The flexural behaviour observed in the present work is in agreement with results reported by previous workers [2] who emphasized that good interfacial adhesion is extremely important in achieving a substantial enhancement in the toughness of thermoplastic-modified epoxies. The micrographs reveal that the PSU-modified epoxy develops a complex morphology during the cure process. The morphological features could account for the observed flexural behaviour.

Table 1
Flexural strength (σ_f), deformation at break (ϵ) and flexural modulus (E) for unmodified epoxy resin (UER) and 15-wt % thermoplastic modified epoxy resin (MER)

Material	σ_f (MPa)	ϵ (%)	E (GPa)
UER	137.5 (12.8)	7.65 (1.12)	2.63 (0.073)
MER	145.2 (19.4)	8.05 (1.66)	2.74 (0.123)

3.4. Analysis for the flexural strength data

From the results presented in Table 1, it emerges that the flexural strength values yielded an important data scatter, particularly for the thermoplastic modified resin. In order to analyse the flexural strength data distribution, a higher number of specimens than that recommended for the ASTM D790 protocol was tested. Table 2 shows the flexural strength results measured for the thermoplastic modified epoxy resin. The set of test results was ordered from lowest stress to rupture to highest and a cumulative probability of failure, P_f, to each specimen was assigned. The probability of failure was calculated by

$$P_f = \frac{i}{N+1} \tag{5}$$

where i is the rank number of the test specimen and N is the total number of specimens. The data presented in Table 2 were analysed according to the Gaussian distri-

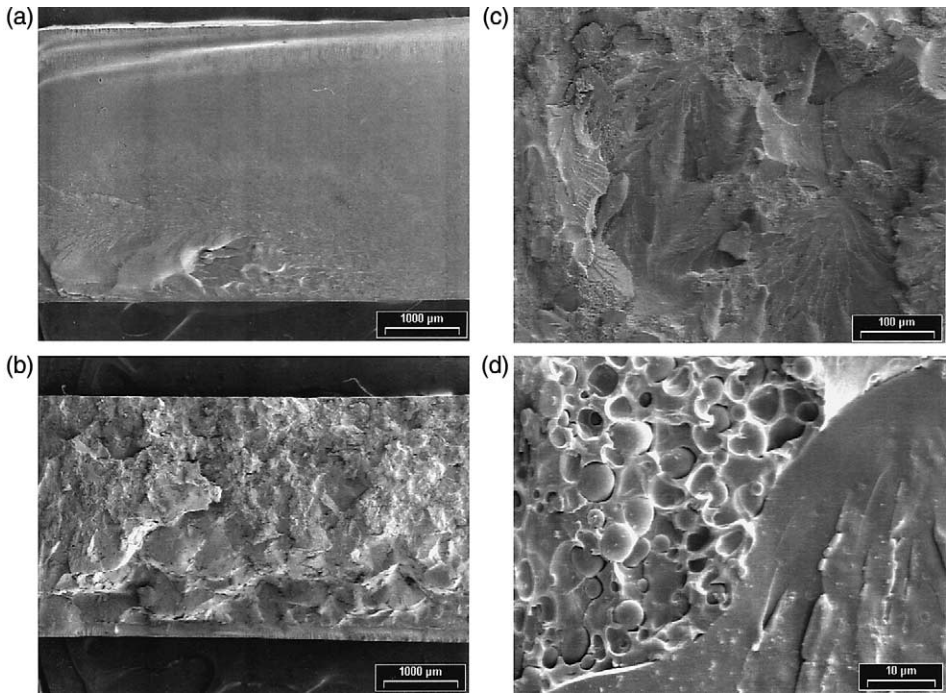

Fig. 4. (a): SEM micrograph of fracture surface of the neat epoxy resin. (b): SEM micrograph of fracture surface of the PSU modified resin. (c): SEM micrograph of fracture surface of the PSU modified resin taken at a higher magnification than in Fig. 4(b). (d): SEM micrograph of fracture surface of the PSU modified resin, showing the debonding of the epoxy particles.

Table 2
Flexural strength data for the thermoplastic modified epoxy resin (MER). i is the rank number of the test specimen, P_f is the failure probability calculated from Eq. (5) and σ_f is the measured flexural strength

i	P_f	σ_f (MPa)	i	P_f	σ_f (MPa)
1	0.023	96.13	22	0.512	148.69
2	0.047	109.45	23	0.535	149.16
3	0.070	116.98	24	0.558	149.46
4	0.093	118.40	25	0.581	150.19
5	0.116	121.62	26	0.605	151.16
6	0.140	122.63	27	0.628	153.89
7	0.163	127.27	28	0.651	154.10
8	0.186	129.60	29	0.674	155.65
9	0.209	130.41	30	0.698	155.85
10	0.233	130.64	31	0.721	155.90
11	0.256	130.86	32	0.744	159.13
12	0.279	132.49	33	0.767	159.59
13	0.302	132.53	34	0.791	159.83
14	0.326	135.98	35	0.814	164.04
15	0.349	136.55	36	0.837	164.22
16	0.372	137.26	37	0.860	164.72
17	0.395	141.28	38	0.884	166.60
18	0.419	144.66	39	0.907	173.93
19	0.442	147.05	40	0.930	177.20
20	0.465	147.78	41	0.953	179.36
21	0.488	148.60	42	0.977	185.53

bution function. In a convenient method for determining whether a sample frequency distribution approximates to a normal distribution, a cumulative frequency plot on normal probability paper is used. How well the data group around a straight line determines the degree of fit to the normal distribution by plotting the probability of failure for each specimen, P_f, vs σ_f. The cumulative frequency distribution presented in Table 2 was plotted in the described way and the results are depicted in Fig. 5. It is observed that for high rupture loads, about 60 percent of experimental points deviate from the linear curve. Hence, the flexural strength data do not obey the Gaussian distribution.

In light of the results obtained in Fig. 5, the Weibull [11] distribution function was analysed in order to assess its capacity to represent the rupture stress data presented in Table 2. The Weibull model is commonly used in characterization of brittle materials and is based in an empirical formula, which relates the probability of failure to the rupture stress. The two-parameter Weibull equation for the case of beams under flexure is given by [13]:

$$P_f = 1-\exp\left[-\left(\frac{\sigma_f}{\sigma_0}\right)^m Ve\right] \quad (6)$$

P_f is the fracture probability for the stress σ, Ve is the volume of material subjected to a uniaxial tension that would have the same probability of failure as the sample,

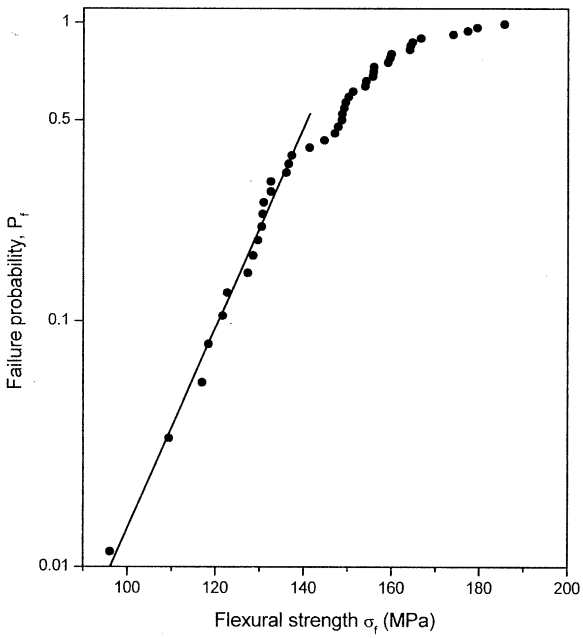

Fig. 5. Normal probability plot of data in Table 2.

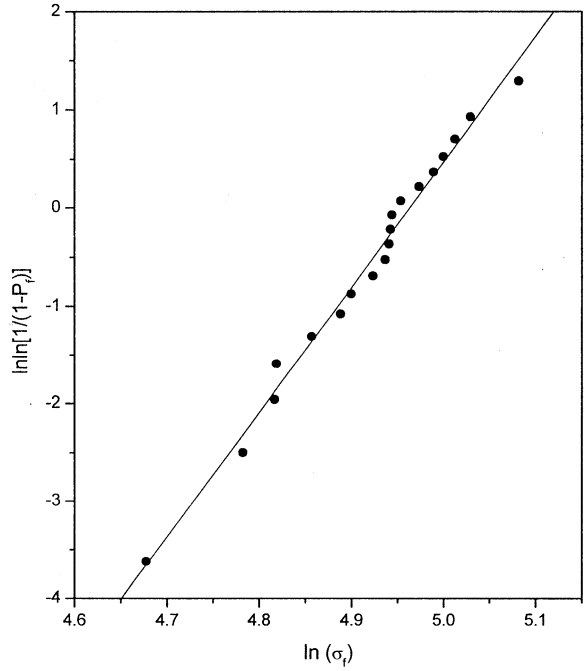

Fig. 6. Weibull plot for the neat resin.

m is the Weibull modulus and σ_0 is a scale parameter. The σ_0 value is related to the mean flexural strength of the distribution and the Weibull modulus is a reflection of the amount of data scatter. The higher the m value, the less the data scatter.

When strength testing of brittle materials is performed, a random sample is ideally taken from an infinite amount of specimens and the sample size has a large influence upon how well the mother population is described. This means that a minimum number of specimens should be tested in order to obtain a proper estimation of the parameters of the distribution. As a compromise between minimizing both the dispersion of the evaluation method and the experimental effort, the use of a minimum number of 20 specimens has been suggested [14–16]. The Weibull parameters, m and σ_0, were evaluated by the linear least squares method applied to the linearized form of Eq. (6):

$$\ln\ln\left[\frac{1}{1-P_f}\right] = m\ln\sigma_f - m\ln\frac{\sigma_0}{Ve^{1/m}} \tag{7}$$

The values of P_f for each σ_f were assigned by the following estimator [15–16]:

$$P_i = \frac{i-0.5}{N} \tag{8}$$

The data were plotted as $ln\ ln(1/1-P_f)$ versus $ln\ \sigma_f$ (Eq. (7)) and the results for the unmodified and thermoplastic modified epoxy resin are shown in Figs. 6 and 7, respectively. Close agreement is observed between the experi-

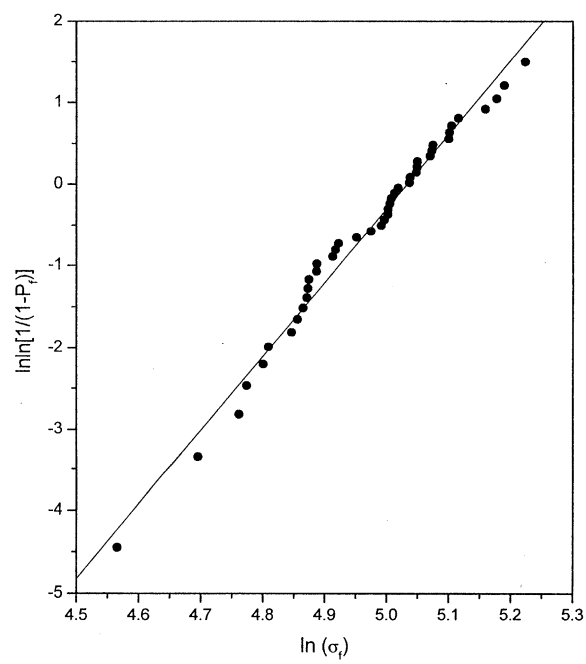

Fig. 7. Weibull plot for the PS modified epoxy resin.

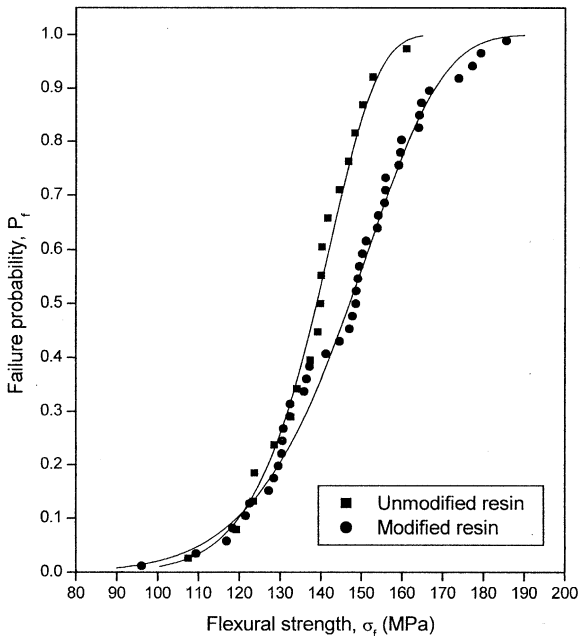

Fig. 8. Weibull cumulative strength distribution for the unmodified and PSU-modified epoxy resin.

mental results and the Weibull model. Cumulative distributions of failure probability, P_f versus σ_f calculated from Eq. (6) are also shown in Fig. 8.

The mean flexural strength of the Weibull distribution, σ_m, is given by:

$$\sigma_m = \frac{\sigma_0}{Ve^{1/m}}\Gamma\left(1 + \frac{1}{m}\right) \tag{9}$$

where $\Gamma\ (1 + 1/m)$ is the Gamma function and the values of $[\sigma_0 / Ve^{1/m}]$ were obtained from plots of Eq. (7). Values of the mean flexural strength (σ_m) calculated from Eq. (9), Weibull modulus (m) and regression coefficients for $ln\ ln(1/1-P_f)$ versus $ln\ \sigma_f$ are presented in Table 3.

Concerning statistical tests of hypothesises; one of the assumptions underlying the valid use of the Student *t*-test is that the population is normally distributed. When the form of the sample population is not normal, procedures that either are not concerned with population parameters or do not depend on knowledge of the sample population should be used. Hence, the Mann–Whitney nonparametric test was used for the comparison of the mean flexural strength of the studied resins. The Mann–Whitney test comparison of the mean flexural strength of the studied unmodified and thermoplastic modified epoxy resins indicates that, at the 99% confidence level, the means are not significantly different. Consequently, no improvement in the flexural strength by the incorporation of the PS was achieved. In addition, the modified epoxy resin displayed an increased data scatter compared with the unmodified resin, as emerges from the comparison of the Weibull modulus of each material.

Table 3
Mean flexural strength from Eq. (9), Weibull modulus and regression coefficient in Eq. (7) for the unmodified epoxy resin (UER) and the 15-wt % thermoplastic modified epoxy resin (MER)

Material	σ_m (MPa)	m	r
UER	138.8	9.1	0.994
MER	147.3	12.8	0.992

Brittle fracture occurs due to the propagation of flaws present in the material. Flaws not only include cracks but also inclusions, segregations or any centers which give rise to incompatible deformations. On the other hand, flaws of variable sizes, shapes and orientations with respect to the applied load are possible. It means that in one specimen the largest crack may be normal to the applied load while in another the largest crack may be at an angle to the applied stress. Obviously, the former has a lower strength than the latter. Hence, variable crack sizes and their orientations with respect to the applied load can account for the observed scatter of fracture strengths, when nominally identical specimens are tested under nominally identical loading conditions. It is worth noting that the comparison of fracture load distributions for materials having different morphology gives further insight concerning the role of the defects on the fracture behaviour. The morphological feature developed during the cure of the thermoplastic modified epoxy resin can be considered responsible for the observed flexural behaviour, particularly the data scatter.

The Weibull model makes it also possible to compare the effect of loading systems on the mean strength. For materials obeying the Weibull model, the ratio of mean strength measured in three-point bending to the mean strength in uniaxial tension is given by the following relationship [13,17]:

$$\frac{\sigma_{m\ 3PB}}{\sigma_{tensile}} = [(2(m + 1)^2]^{1/m} \tag{10}$$

Fig. 9 is a plot of the ratio of the mean flexural strength measured in three-point bending to the mean strength in uniaxial tension versus the Weibull modulus. For a material having a Weibull modulus of about 15, the Weibull model predicts a mean flexural strength about 50 percent higher than that measured under simple tension. This is in agreement with experimental results reported by previous workers on measurements of tensile and flexural properties of PSU modified epoxy resins [6]. In addition, Bucknall [18] pointed out that the values quoted in commercial data sheets for flexural strengths of polymers are usually much higher, sometimes by as

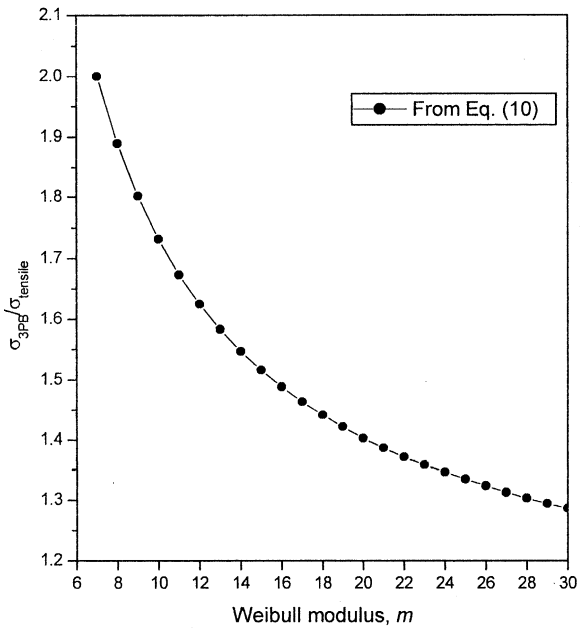

Fig. 9. Ratio between the flexural strength measured in 3PB to the tensile strength, from Eq. (10), versus the Weibull modulus.

much as 50%, than corresponding values obtained from tensile tests. These observations could be explained by the fact that these materials are flaw sensitive and consequently the fracture behaviour is governed by the flaw distribution.

4. Conclusions

Flexural strength distribution of both unmodified and thermoplastic modified epoxy resin was obtained by testing the materials in three-point bending. Fracture data were analysed according to Weibull statistics, which was proved to fit the flexural strength distribution of all the materials tested with regression coefficients equal to 0.99.

The flexural behavior of the epoxy matrix was not improved by the presence of thermoplastic. In addition, the thermoplastic modified epoxy resin displayed a higher data scatter compared with the unmodified resin. This behavior was explained in terms of the brittle nature of the epoxy resin and the resultant morphology of the thermoplastic modified material.

Acknowledgements

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