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Fatigue behaviour of glass bead filled epoxy

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There is a relatively abundant literature on the mechanical properties of particle filled thermosets. Detailed experimental data are available on the effect of variables, such as the filler volume fraction, its surface treatment or shape factor, on the usual properties. In the case of epoxy matrix composites, data have been published on elastic properties. Kinetic studies on thermoplastics, as well as microscopic investigations clearly show that each particle acts as a crack initiation site. The present study deals with thermoset epoxy–glass bead composites. A noticeable advantage of the sphericity of the glass beads over the previously studied mineral fillers is that theoretical calculations, for instance of interparticle average distance, are easier. Some results are reported concerning the eventual role of the geometrical characteristics, including particle diameter, number of particles per volume unit, particle–matrix contact area, interparticle distance, on the fatigue characteristics of the composite as assessed from Paris or Wöhler plots. In addition, quasi-static crack propagation characteristics will be compared with dynamic ones. It is clearly shown that glass beads improved the fatigue crack propagation. Despite this fact, it is also shown that even a small amount of mineral filler, acting as crack initiator, can considerably reduce the fatigue life of epoxy composites.

1. Introduction

Much work has been done on the mechanical properties of particle filled thermoset composites, and a lot of experimental data have been collected on the effect of different parameters, such as the volume fraction, the surface treatment of particles and the shape factor [1–7].

Mainly elastic, plastic or fracture mechanics studies have been performed on epoxy thermosets, and only a few fatigue experiments have been developed [8–11]. In a previous study [12, 13] based on a ductile polypropylene thermoplastic matrix of mineral filled composite, it was shown that the most important parameter acting on the fatigue life was the number of particles per unit volume. Each particle can be a crack initiator under repeated loading. In this study some new data are presented about thermoset epoxy matrix filled with low concentration glass beads. In this case, in addition to the role of particle density, it is shown that the distinction between fatigue life, for an equivalent number of particles, can be discussed in terms of ductility of the matrix, through initial stress intensity, K_{Ic}, measurements. A comparative study between Paris and Wöhler tests results is proposed as a conclusion.

2. Experimental procedure

2.1. Materials

2.1.1. Matrix

The synthesis and properties of the epoxy matrix of composites have been described previously [14, 15]. This matrix was based on an epoxy prepolymer, diglylycidyl ether of bisphenol-A (DGEBA) $\bar{M}_n = 380\ g\ mol^{-1}$, and dicyandiamide (Dicy or DDA). Benzyldimethylamine (BDMA) was used as a catalyst and the molar ratio (amino hydrogen:epoxy) was equal to 0.6. With this chemical system, the cure schedule strongly influences the crosslink density [14], due to changes in the reaction pathway with curing temperature.

Thus, a single and well defined cure schedule was chosen: 1 h at 120 °C followed by 1 h at 180 °C in rotated, PTFE coated moulds to prevent Dicy or glass bead sedimentation. The glass transition temperature of the network in the pure matrix and in the composites was about 140 °C, measured by differential scanning calorimetry (DSC) at 10 K min^{-1}.

2.1.2. Filler

The glass beads, without special surface treatment, were provided under two mean diameters, D, 8 and 40 μm, as shown in Table I. Using the particle size distribution, the fraction of glass beads introduced was calculated (see Table II) in order to obtain composite materials with the same number or the same area of particles as the reference composite with 20% by volume of glass beads.

The interparticle distance, d_p, is calculated using the following formula

$$\frac{D}{d_p} = 3\phi_v/2(1 - \phi_v)$$

TABLE I Designation of filled composites

Materials	Basic composite	Same area	Same number
Material code	2040	2008 S	2008 N
Vol. fraction (%)	22.8	6.2	0.44
Mean diameter of glass beads (μm)	22.7	6.2	6.2
Nb of particles N	N	15.5N	N
Contact area S	S	S	0.06 S
d_p (μm)	61	65	1373

TABLE II Mechanical properties of the various glass beads composites at 25 °C

Materials	Pure matrix	2040	2008 S	2008 N
E (GPa)	2.8	5.5	3.6	2.8
ν	0.4	0.38	0.4	0.4
σ_y (MPa)	108	122	112	109
K_{Ic} (MPa m$^{-1/2}$)	0.7	1.47	1.19	0.79

proposed by Young and Beaumont [16], where ϕ_v is the glass volume fraction.

2.1.3. Processing

Table I presents composites studied. The basic composite is labelled 2040 for 20% range of 40 μm glass beads. Two other composites have been processed to have a constant polymer–glass contact surface (2008 S) and an equivalent number of particles (2008 N) with 8 μm glass beads. The samples for mechanical tests were machined from moulded plates.

2.2. Mechanical testing

2.2.1. Mechanical properties

The static properties were performed according to French standards (NFT 51 034 and 51 001). The flexural fatigue tests were run at 23 °C on laboratory made machines at 10 Hz under a complete reverse loading [17]. Elastic properties (Young's modulus E, Poisson's ratio ν), compressive yield stress, σ_y, and K_{Ic} values, obtained at 25 °C are summarized in Table II, according to already described experimental techniques [14, 15].

The Young's modulus and yield stress, σ_y, are increasing functions of the glass volume fraction. The change of yield stress versus D/d_p fits the relationship $\sigma_y = \sigma_{y0} + kD/d_p$ [18] with good agreement. In this case, $\sigma_{y0} = 108.7$ MPa and $k = 35.5$ MPa, Fig. 1.

This means that the yield stress increases when the interactions between the stress fields around the particles increase. These interactions are unfavourable to the propagation of plasticity defects.

The critical stress intensity factors, K_{Ic}, shown in Table II increase linearly with the volume fraction of glass beads [2, 3, 15].

2.2.2. Fatigue crack propagation (FCP)

Compact tension (CT) specimens were used with the specifications recommended by Williams and Cawood [18].

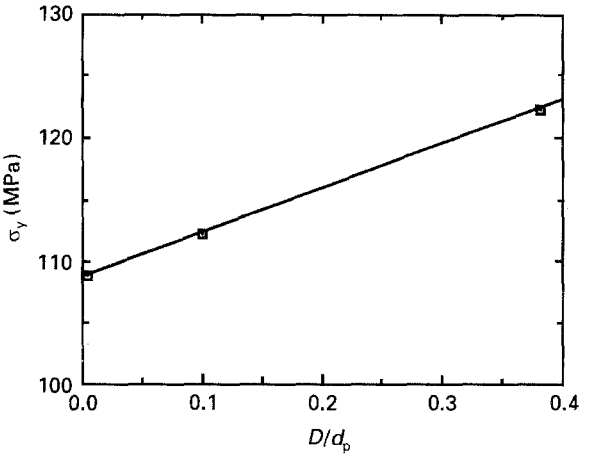

Figure 1 Evolution of the compressive yield stress, σ_y, at 25 °C versus D/d_p.

Cracks of varying length, a, were machined using a fine diamond saw and then finished with a razor blade at room temperature. A Zwick REL 1853 closed loop servohydraulic machine was used, at 25 °C with a frequency of 5 Hz. Cycling was performed under load control with a load ratio $F_{min}:F_{max}$ close to zero (tension mode). The maximum load, F_{max}, was chosen in order to start the test with $\Delta K = K_{max} - K_{min}$ close to $K_{Ic}/2$; the shape factor $f(a/w)$ was taken from reference [18]

$$\Delta K = \frac{\Delta F}{Bw^{1/2}} f\left(\frac{a}{w}\right)$$

where B is the sample thickness and w the width.

The crack growth was followed with a Vishay–Micromeasures CPA1 gauge stuck on one face of the CT specimen, perpendicular to the crack propagation direction. The gauge consists of 20 equidistant wires. These measurements (crack length, a, against number, N of fatigue cycles), allow the determination of the slopes da/dN from the graphs.

3. Results and discussion

The FCP experiments are plotted, according to Paris' law, $da/dN = A(\Delta K)^m$. Fig. 2 shows the good linear fits obtained in log–log diagrams, as was already found with other epoxy networks [8–10].

The increase of the glass volume fraction shifts the FCP curves towards high ΔK values without large changes in m values. The high values obtained for m, in the range 7–12 [8, 9, 10, 19], demonstrate the strong influence of a small increase of ΔK on FCP; the crack propagation being easier in filled thermosets than in

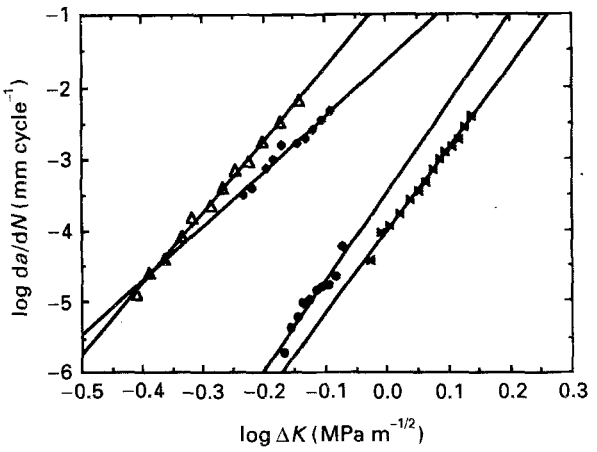

Figure 2 Fatigue crack propagation according to Paris' law for the various composite materials at $f = 5$ Hz, temperature = 25 °C: (●) 2008 S, (◆) 2008 N, (△) matrix, (*) 2040.

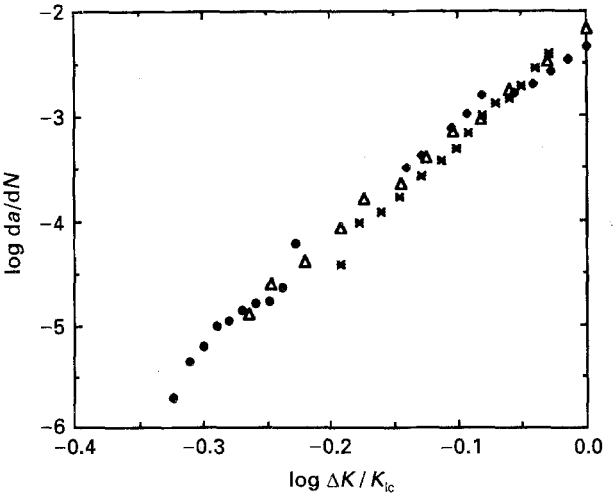

Figure 4 Fatigue crack propagation versus reduced value $\Delta K/K_{Ic}$ for: (●) 2008 S, (◆) 2008 N, (△) matrix, (*) 2040.

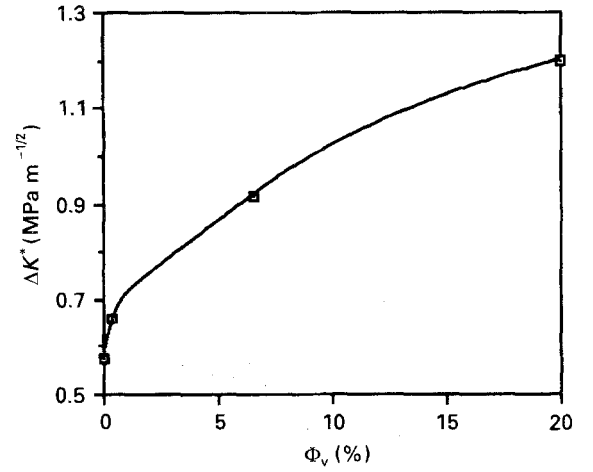

Figure 3 Evolution of ΔK^* versus glass volume fraction for the various composites ($da/dN = 10^{-3}$ mm cycle^{-1}).

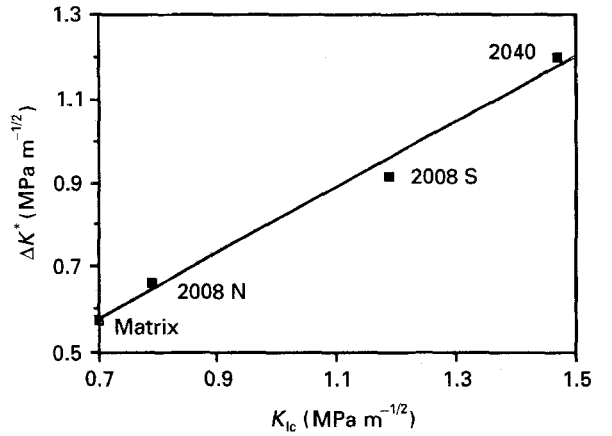

Figure 5 ΔK^* ($da/dN = 10^{-3}$ mm cycle^{-1}) versus K_{Ic} for each material.

thermoplastics. It is possible to compare these materials by using the ΔK^* value necessary to achieve a given crack propagation rate, chosen at $da/dN = 10^{-3}$ mm cycle^{-1} [10]. On Fig. 3, ΔK^* is plotted versus glass volume fraction. This improvement of the FCP resistance of thermosets filled with rigid particles is generally attributed to the crack front pinning mechanism [2, 3, 6, 9, 19, 20]. This mechanism is mainly governed by the interparticle distance, d_p. As shown in Table I, d_p is lower for the higher glass volume fraction. With the same number of particles (for samples 2040 and 2008 N) the FCP is higher for the smaller interparticle distance. This effect seems to be similar with static failure, where K_{Ic} increases with the volume fraction of glass beads [2, 14, 15]. To take into account the different static toughnesses of the materials, Fig. 4 is plotted showing da/dN versus the relative values $\Delta K/K_{Ic}$. A single master curve is obtained, which clearly demonstrates that the intrinsic toughness governs the FCP of these filled thermosets. Fig. 5 confirms this assumption by showing the linear relationship between ΔK^* and K_{Ic} as already mentioned [9, 10].

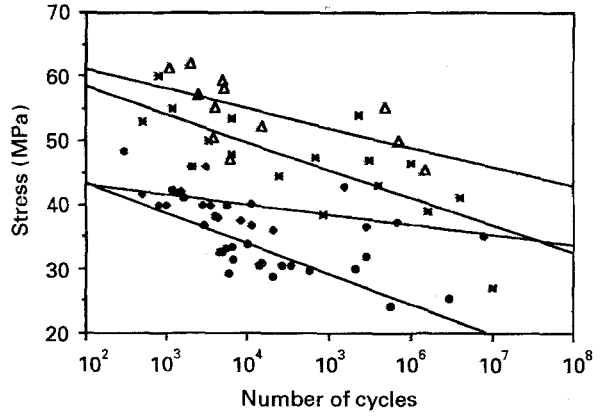

Figure 6 S:N curves for pure epoxy: (●) 2008 S, (◆) 2008 N, (△) matrix, (*) 2040.

The stress : cycles to failure ($S:N$) curves for the four materials studied is shown in Fig. 6. The first observation to note is that the fatigue results are very scattered, even for pure resin. This can be attributed to the non-homogeneous dispersion of the mineral in the

matrix due, on the one hand, to the low weight content of mineral and, on the other hand, to the difficulty in keeping the mineral in a good state of dispersion during the curing of the resin. The second observation is that the addition of any quantity of glass beads lowers the fatigue resistance. This is not in opposition with the observed improvement of the FCP, because the fatigue life of non-precracked samples is strongly influenced by the crack initiation step. As previously mentioned [12, 13] for thermoplastics, the mineral particle acts as a crack initiator. This is very important for thermosets, for which the main part of their fatigue resistance is devoted to the creation of crack(s). This point is confirmed by the difference, in terms of number of cycles for failure (N), between the 2008 S and N samples; 2008 S, with more than 15 times more particles, is the less resistant.

If one considers the 2040 and 2008 N samples, with an equivalent number of particles, one can make a correlation with the FCP results. For the same sensitivity to crack initiation, the same hierarchy is observed in fatigue life as the one measured with the FCP method, namely 2040 > 2008 N.

4. Conclusions

The fatigue resistance of any material is the combined resistance to crack initiation and crack propagation. It is shown that for a brittle thermoset, such as epoxy, glass beads reduce the fatigue life by acting as strong crack initiators. This crack initiation stage being the most important for filled brittle thermosets.

Fatigue crack propagation is improved by glass beads and this is attributed to a crack front pinning mechanism, which is mainly governed by interparticle distance. Thus, for a given number of particles, the fatigue life is in good correlation with the FCP data.

In conclusion, despite the fact that the FCP resistance is improved, it is shown that even a small amount of mineral fillers can reduce considerably the fatigue life of epoxy composites by several decades.

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