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Ductility potential of brittle epoxies: Thermomechanical behaviour of plastically-deformed fully-cured composite resins

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ABSTRACT

The thermoset matrices that are typically used in structural composites are generally well known for extreme brittleness, sensitivity to defects, and poor performance at complex strain states. These features impede a full material characterisation and an understanding of their behaviour. It is, however, of fundamental importance to separate the scale-dependent and defect-imposed failure from the bulk material performance of epoxies, to enable significant improvements in ductility to be realised. The current paper suggests a new experimental routine for investigating the ductility limits of brittle epoxies and accumulating the large macro-scale volumes of plastically deformed epoxies, necessary to study physical and mechanical properties of cured thermosets following yield. It has been shown that a fully cured, densely cross-linked epoxy can undergo at least 50% of the equivalent plastic strain without loss in stiffness and with no detectable degradation of internal architecture. It has also been shown that the deformed epoxies change their thermo-visco-elastic behaviour. A comparative study of plain and toughened epoxies has shown that the former have higher ductility potential than the systems heavily loaded with thermoplastics. This implies that in order to achieve improvements in thermoset ductility, a revised concept of epoxy modification may be required.

1. Introduction

The major problem associated with the mechanical performance of modern thermoset composites is brittleness which arises, to a large extent, from the behaviour of densely cross-linked polymers. Composites are known to experience the onset of matrix intra-ply cracking, which precedes fibre rupture, and typical values for the strain at the onset of failure are 0.6% for cross-ply laminate composites loaded in tension; 0.2–0.3% for textile composites [1–3]. Early cracking promotes development of critical failure modes such as inter-ply delamination, affects fatigue performance, compromises environmental resistance, and creates serious constraints for some applications such as pressure vessels. Above all, a damaged material will hardly be accepted for quality-critical components. Hence, the premature failure means that the potential of composite materials is far from being realised.

To fight the cracking in thermosets it is crucial to understand (1) the factors accelerating brittle failure and (2) the bulk behaviour of a flawless material. There are serious impediments to the separation of these two phenomena and thermosets are well known for exhibiting extreme sensitivity to the presence of defects [4]. The experiments of Asp et al. [5] have clearly highlighted the reason for this peculiarity, for by testing epoxies in hydrostatic tension they found a dramatic ten-fold drop of strain to failure compared to the values obtained in uniaxial tensile testing. The extreme sensitivity of the material to complex straining causes its intolerance to the presence of any inhomogeneity as it creates a complex stress-strain field around it.

While known for being very brittle, at certain conditions even fully-cured densely-cross-linked thermosets can be tremendously ductile. The largest deformations are seen in experiments undertaken in shear and compression where the thermosets reach characteristic values of 0.3–1.5 of true compressive strain and exceed 0.3–0.8 of shear strain [6–15]. Such ductility has been observed across a range of temperatures, strain rates and polymer systems (the above references include difunctional (diglycidyl ether of bisphenol A), trifunctional (TGAP), and tetrafunctional (TGGDM) epoxies, polyesters, vinyl esters, polystyrene, and polycarbonate resins). A characteristic ductility was also observed in

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bending response of cured epoxies [16,17]. The plastic flow has a characteristic pattern for many polymers: in general, they tend to show softening soon after the onset of yielding, then a large plastic plateau, before hardening prior to failure. It should be noted though that the shape of stress-strain curve may be strongly influenced by sample-press constraints [6,15], history of deformation [10], and sample shape [14]. At the hardening stage, the polymers may reach characteristic stress values of the order of 200 MPa, thus absorbing significant energy through deformation history.

The shear stress curves are similar, but normally do not exhibit the characteristic hardening stage. Even though this is much harder to achieve in practice, the high yielding of thermosets can be observed in tension as well. Odom and Adams [4] observed strong scale effect in toughness and tensile strength when testing epoxy samples. Hobbiebrunken et al. [18] produced fine epoxy fibres and tested them in uniaxial tension. Refining the fibre diameter helped to minimise the testing volume and hence, reducing the probability of obtaining a defect within. This precaution made possible the achievement of high plastic deformations for these fibres and even necking, while reaching a tensile strength of 166 MPa (for the HexFlow®RTM6 resin system). A similar concept of testing thin fibre-type samples was then utilised in the study of Misumi et al. [19] who also found exceptional ductility and energy absorption of micro samples.

Thus, while sensitivity to defects is determined by the type of loading, it can be suggested that the bulk material has high potential for plastic flow at various loadings. However, the premature brittle failure often does not allow a material's behaviour to be studied beyond the point at which sample disintegration occurs. This defect-induced failure should not be regarded as the material's strength, but instead it should be treated as a function of sample constraints, manufacturing methods, and quality of surface finish. Along with the study of these failure features, it is equally important to investigate the actual material response and, most importantly, the mechanisms driving these deformations.

The physical mechanisms behind softening, flow, and hardening are disputable. The softening may be related to volume relaxation occurring in the glassy state [10], however some experiments show volume reduction upon yielding onset [20]. The plastic flow at constant load level may be related to transition from the glassy to the rubbery state, where main chain reorientation becomes possible in the polymer. Mechanisms of epoxy flow can be related to the properties of the deformed polymer and need to be studied further.

This level of ductility and toughness observed in matrices is hardly seen in composites even when loaded perpendicular to fibres. The most important reason to account for this is multiaxial straining which matrices experience at the micro level. A high Poisson's contraction of the matrix is not allowed by stiff fibres. The constraints in the fibre direction create transverse and longitudinal stretching of the matrix even when the composite is exposed to pure transverse tension. Additionally, the stiff fibres act as stress concentrators and the interfaces promote failure initiation sites. On the other hand, shear-induced plasticity in epoxies is also well known from testing off-axis ±45° laminates, where unidirectional plies at the meso-level (and consequently the matrix at micro-scale level) are subjected to a combination of shear accompanied by longitudinal tension and slight transverse compression. Summarising these observations, it becomes evident that thermosets are intolerant to multi-axial strain states (typically values of around 0.6% volumetric strain are critical), moderately ductile in uniaxial tension (4–6% is commonly observed strain to failure), and extremely ductile in pure shear (with 40% shear angle to be expected).

The current paper suggests a new experimental programme aimed at understanding deformability of epoxies beyond their current limits imposed by composite architecture, thermal properties of fibres, and manufacturing methods. In the long run, this inform novel composite development strategies and define theoretical limits of composite behaviour. The specific aims are: (1) to explore the bulk material behaviour up to the limits of its performance; (2) to test stiffness degradation and the evolution of physical properties of plastically deformed epoxies (in addition to the previously reported effect such as yield stress evolution, softening behaviour change [10], and aging [21] resulting from plastic cycling); (3) to compare various grades of epoxies and study the implication of toughening on the ductility of as-manufactured and plastically deformed materials.

Two epoxies commonly used in aerospace and automotive industry have been selected for this study:

a) A difunctional epoxy intended for resin transfer moulding: displaying low viscosity, low exotherm, low curing temperature, transparent following cure, designed for efficient manufacture of large components. This resin will be referred as liquid moulding (LM) resin;
b) An epoxy blend used in prepregs for in-autoclave manufacturing: highly toughened with thermoplastic particles, very viscous, opaque following cure, designed for high energy impacts, hereafter referred to as autoclave toughened (AT) resin.

The characteristic properties of these resins are given in Table 1. The particular choice of these resins was dictated by the intention to probe the new experimental programme for most different materials and assess the implications of toughening on the ductility of these resin system.

The paper explores the behaviour of these resins in compression and studies the thermal (DSC), mechanical (shear loading) and thermo-mechanical (relaxation under thermal cycling) behaviour of the fully-cured and plastically-deformed samples.

2. Sample manufacturing

Manufacturing of AT samples followed the routine prescribed for composite prepreg manufacturing. Sheets of epoxy (10 plies of 0.6 mm thickness each) were laid on an aluminium tool, surrounded by the cork barriers to prevent leakage under pressure applied during curing, debulked, and then consolidated and cured in autoclave at 180 °C and 7 bars pressure.

LM samples were mixed with the extra-slow hardener in ratios as specified by the relevant data sheets, poured into a silicone mould, and degassed in vacuum at room temperature. No boiling could be seen at the end of degassing. The resin was then cured for 7.5 h at 65 °C as specified by the manufacturer's data sheets. The DSC analysis (discussed later) demonstrated that the resin had been completely cured (less than 1% of residual exotherm heat flow compared to the total heat generated by the complete cure of the resin).

The samples were then polished to eliminate surface porosity and defects using sand paper of grades 120, 800, and then 2500 sequentially. The cured samples of the non-toughened epoxy are transparent with no visible through-thickness or surface defects apart from the rare residuals of polished-off surface pores.

3. Experimental programme

3.1. Flat compaction testing

Being armed with an understanding that any tensile straining