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Preparation and study of aramid/epoxy prepregs

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Solid epoxy resin compounds were studied for their suitability as matrices for the preparation and curing of prepregs containing aramid fibres. Acid anhydrides were shown to be incompatible to the epoxy resin, producing a dispersed crystalline phase upon drying, whereas *o*-phenylenediamine is a miscible cross-linking agent. Also, diamine is safer because it reacts with the epoxy at temperatures considerably higher than the anhydrides. Composite specimens prepared by these prepregs display similar tensile strength and lower modulus than those derived from the one-step process, by the use of conventional liquid epoxy systems.

1. Introduction

Aramid fibres are characterized by exceptional physical and technical characteristics and display an increased potential as reinforcement for advanced technology applications. Many researchers have, therefore, studied and reported their properties and performance when incorporated into thermoset or thermoplastic matrices [1–3].

A recognized drawback is the poor interfacial adhesion to the most resin matrices which can lead to compressive breakdown. This is further enhanced by the microfibrillar structure of aramid, as a result of the complete orientation of the liquid crystalline structure. To utilize fully the exceptional reinforcing properties of aramid fibres, obvious improvements must be made in the area of interlaminar adhesion. Thus, many attempts have already been made to modify the aramid fibre surface and promote adhesion, including commercial coupling agents [4, 5], boiling in water [6], chemical modification [7, 8] or treatment with bromine [9], unsaturated chloride [10, 11] and isocyanates [12]. Also, complete wetting of the fibre is an additional factor that contributes to improved design of composites. This is critical, especially in cases where the viscosity of the resin is high and air bubbles or voids are likely to be formed.

The technique of preparation of prepregs, i.e. systems of reinforcement impregnated with a liquid resin, appears to be attractive with respect to productivity, fibre wetting and properties of the final products. Thus, much attention has been paid to the preparation and study of prepregs, which are considered basic in advanced composites technology [13]. Production lines for manufacture, resin systems, gelling tunnels and control devices have been the subject of intense research [14].

Thermoplastic matrices have been extensively used as they are suitable for fast production rates of composites [15]. Resin deposition on the reinforcement can be carried out by solution, emulsion or melting technique depending on the inherent viscosity of the polymer. More recently, techniques based on electrostatic coating in a fluidized bed of powdered resin were also described [16]. Regarding the thermoplastics used in prepreg manufacture, poly(ether ketone), poly(ether ether ketone), polyamides, polyetherimide and polyimides have been reported [17]. Similarly, thermoset matrices and especially epoxies were used for the impregnation of reinforcements. In the case of reactive matrices, a tight control of curing characteristics is necessary in order to prevent premature setting during storage [18]. Thus, low-temperature moulding prepregs were designed and said to display dimensional accuracy and good performance characteristics with the additional advantages of simple cure [19]. Also, systems cured by ultraviolet radiation that provides safe processing, have been proposed [20].

In this work, prepregs of aramid fibres with an epoxy matrix were studied. Emphasis was placed on the characteristics of the resin system and the possibility of obtaining samples with acceptable mechanical properties by a two-stage process that displays many advantages in terms of the design of final products.

2. Experimental procedure

The epoxy resins used were Epikote 1001 and 828 (Shell) with the following characteristics: Epoxy group content (mmol kg^{-1}), 200–2200; viscosity at 25 °C, 0.12–0.17 Pa s; colour Gardner (max), 2; density, 1.19 g ml^{-1}. Twaron fibres (Akzo Fibers) were used as reinforcement. Typical properties of these fibres are given in Table I.

The following curing agents were added to the resin at stoichiometric ratio: maleic anhydride (Merck), tetrachlorophthalic anhydride (Fluka), phthalic anhydride (Merck), and *o*-phenylenediamine (Merck). The mixture was dissolved in acetone and microphotographs

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TABLE I Typical properties of Twaron fibres

Density ($g\,ml^{-1}$)	1.44
Filament diameter (μm)	12
Filaments, N	250
Tensile strength (GPa)	2.75
Elongation at break (%)	3.2
Modulus of elasticity (GPa)	80

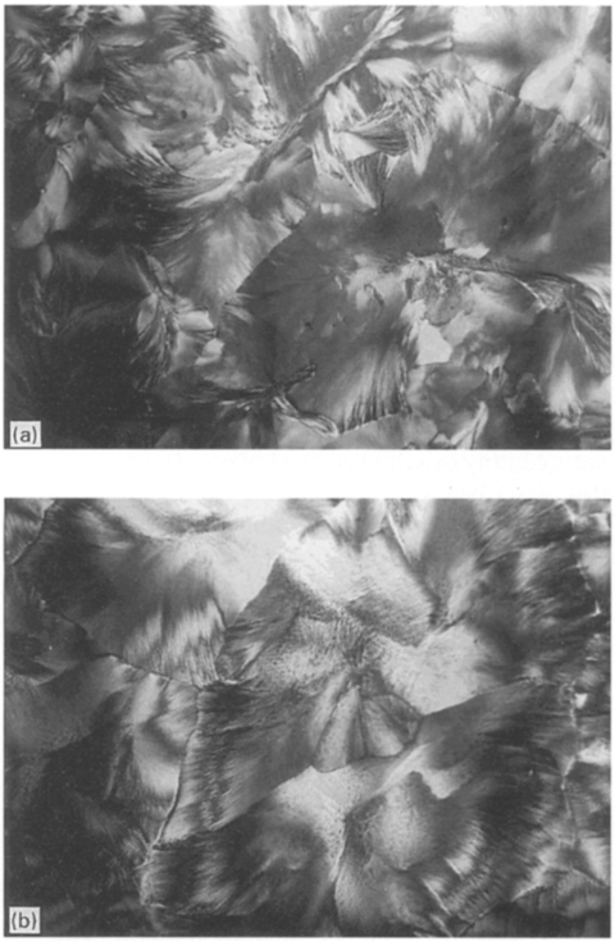

Figure 1 (a, b) Micrographs of Epikote 1001/phthalic anhydride system obtained from acetone solution after drying at room temperature.

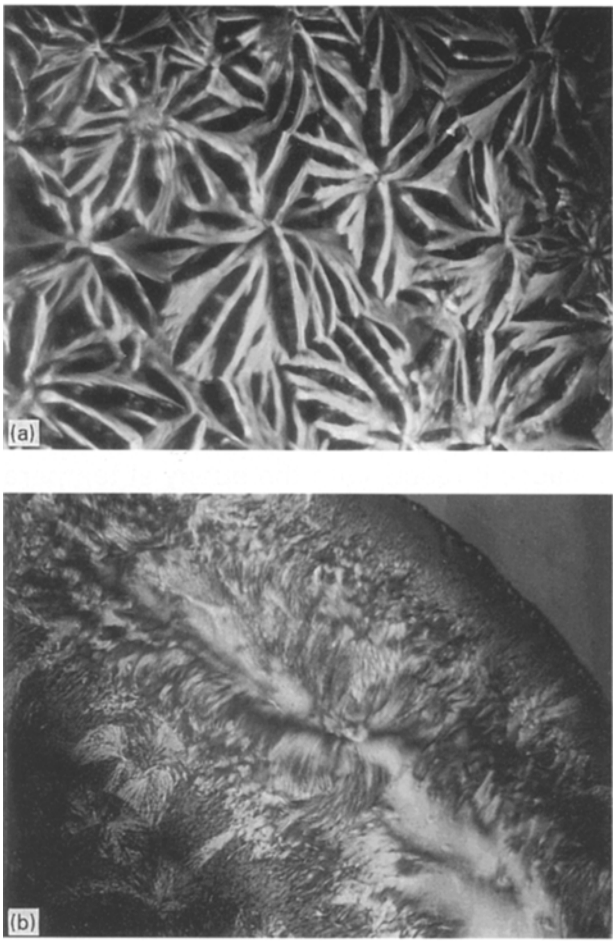

Figure 3 (a, b) Micrographs of Epikote 1001/phthalic anhydride system obtained from acetone solution after drying at 80 °C.

were taken after evaporation of the solvent, in order to examine the miscibility of the components. An Amplival (Jenoptik Jena GmbH) was used equipped with a camera to record microscopic images. In all cases a magnification of X 78 was used.

The curing characteristics, in terms of setting time, were studied in an oven, at temperatures of 100–150 °C. Also, thermographs were taken in a Perkin–Elmer DSC-4 (Switzerland), working at a heating rate of 10 °C min^{-1}.

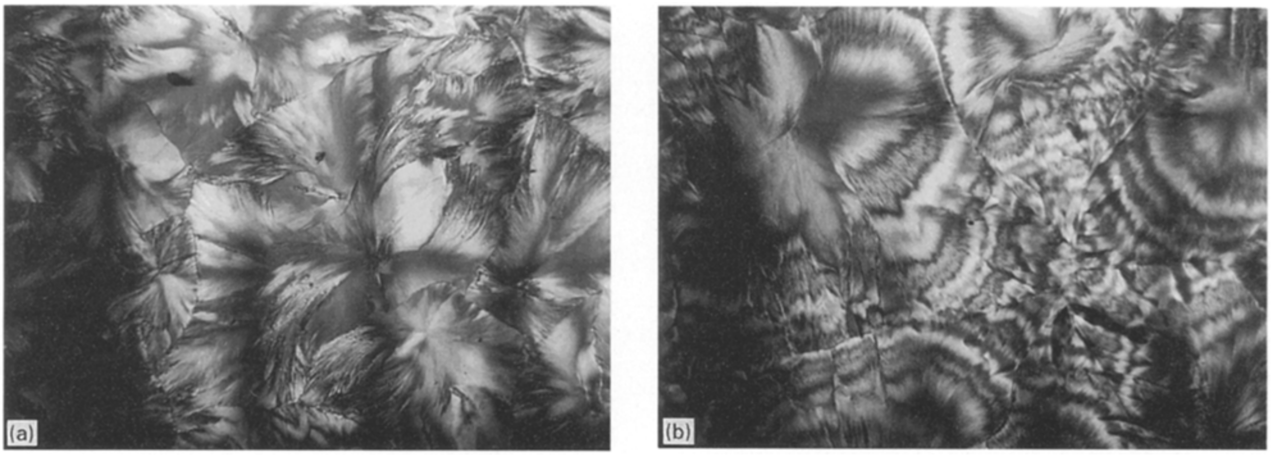

Figure 2 (a, b) Micrographs of Epikote 1001/phthalic anhydride system obtained from acetone solution after drying at 45 °C.

Test specimens, for the determination of mechanical properties, were prepared by impregnation of continuous aramid filaments in the epoxy/o-phenylenediamine solution. After drying, the prepregs were moulded in a heated plates hydraulic press, at 110 °C. As a reference, additional specimens based on Epikote 828/Epilink 147 mixtures were prepared, at the same filler volume fractions. An Instron TT-CM (England) tensile testing machine was used for the measurement of tensile strength, with a grip separation speed of 5 mm min^{-1}.

3. Results and discussion

All types of anhydride used in this work were found to be immiscible with the epoxy resin, unlike o-phenylenediamine that produces clear, homogeneous mixtures. Phase separation upon drying is a major problem for the epoxy systems used in prepregs, because it can lead to overcured or undercured areas. Thus, finely divided crystals of the anhydride are necessary in order to give mixtures with the highest possible homogeneity that can be cured safely to uniform products. Micrographs of the epoxy/phthalic anhydride systems (Figs 1–3) show different crystal size according to the temperature. Thus, drying at room temperature gives large anhydride crystals (Fig. 1a, b) as compared to those obtained at 45 and 80 °C, shown in Figs 2 and 3, respectively. It is clear that increased temperatures result in a fast formation of crystals which corresponds to small crystal size and gives more uniform consistency of the resin mixture.

The differential scanning calorimetry (DSC) scans, of various epoxy resin systems are presented in Figs 4–6. For maleic anhydride, a smooth thermograph is obtained (Fig. 4a) with an exotherm in the area of 140 °C, which suggests that cross-linking reaction reaches a maximum rate at that temperature. Similarly, the curves for phthalic and chlorophthalic anhydrides shown in Figs 5 and 6 respectively, display exotherms at 170 °C, indicating that thermosetting in these systems takes place at higher temperatures as compared to curing with maleic anhydride. The above exotherms of the systems based on phthalic and chlorophthalic anhydrides are accompanied by large endotherm peaks at 181 and 185 °C respectively, that are likely to correspond to sublimation of the anhydride. On the other hand, o-phenylenediamine gives a smooth thermograph (Fig. 4b), similar to that of maleic anhydride, but the exotherm emerges around 190 °C, suggesting that the amine is the safest cross-linking agent for the design of a prepreg free of the hazards of premature cross-linking.

The mechanical characteristics of specimens prepared with the prepreg (Epikote 1001/o-phenylenediamine) compound and the reference mixture (Epikote/Epilink), are presented in Figs 7–9. A linear

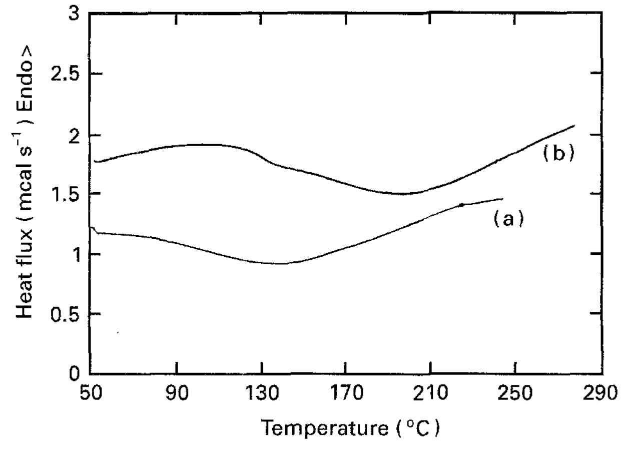

Figure 4 Thermographs of Epikote 1001 with (a) maleic anhydride, (b) o-phenylenediamine.

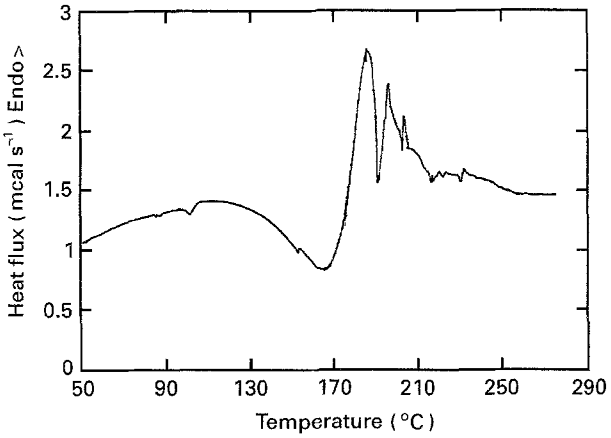

Figure 5 Thermograph of Epikote 1001 with phthalic anhydride.

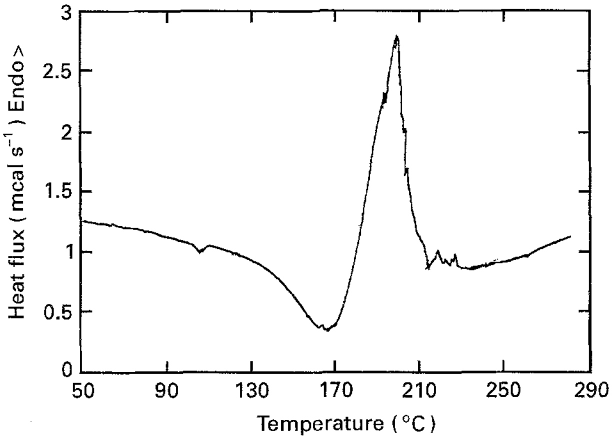

Figure 6 Thermograph of Epikote 1001 with chlorophthalic anhydride.

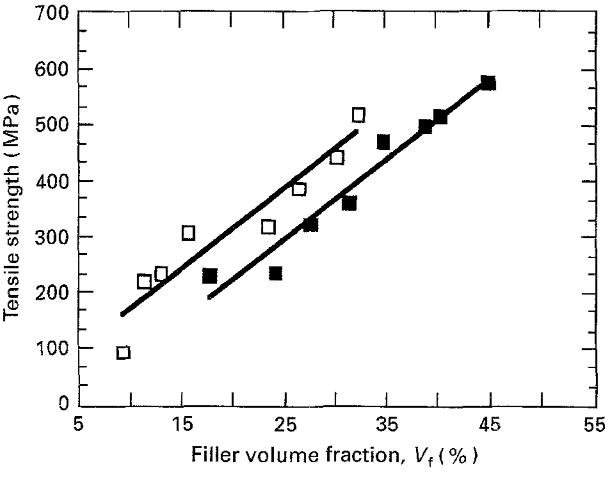

Figure 7 Tensile strength as a function of filler volume fraction: (■) prepreg compound, (□) Epikote 828/Epilink compound.

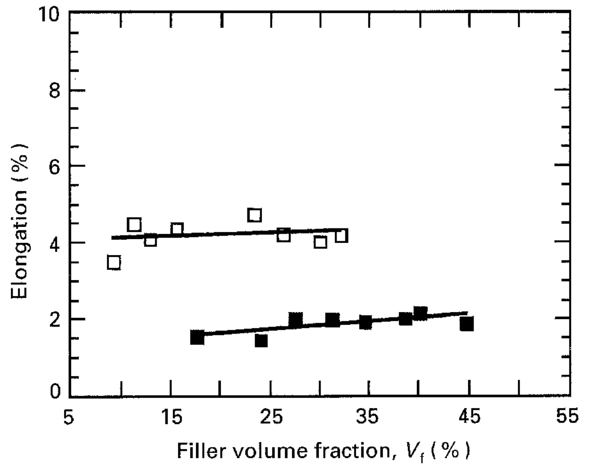

Figure 8 Elongation as a function of filler volume fraction: (☐) prepreg compound, (■) Epikote 828/Epilink compound.

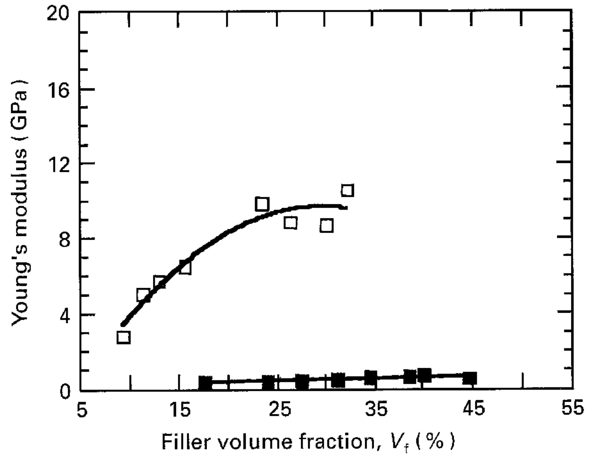

Figure 9 Modulus of elasticity as a function of filler volume fraction: (■) prepreg compound, (☐) Epikote 828/Epilink compound.

increase of the tensile strength with filler volume fraction can be seen for both types of specimen, in Fig. 7. Also, the prepreg compound seems to give products with reduced strength in comparison with the one-step curing systems Epikote/Epilink, probably due to its inherent strength properties.

The filler volume fraction has a small effect on the elongation of both types of specimens, as shown in Fig. 8. From this same figure, one can observe that the elongation of prepregs is higher than that of the one-step specimens which can be attributed to the matrix characteristics. As a result, the Young's moduli of the two series of specimens show significant differences as the curves of Fig. 9 display.

4. Conclusion

Regardless of the fact that mechanical properties are dependent on the type of matrix used in the preparation of a composite specimen, it can be clearly seen that prepregs display sufficient strength which increases as the reinforcement content increases, up to volume fractions of 40%.

Systems containing *o*-phenylenediamine as cross-linker are homogeneous and safe to storage conditions, because propagation of the thermosetting reaction occurs at sufficiently high temperatures. On the other hand, the various types of anhydride tested are not compatible with the solid epoxy phase, resulting in the dispersion of crystals. Drying conditions must be adjusted in order to obtain systems with adequate homogeneity.

The preparation of composite structures with prepregs using a two-stage technique, i.e. impregnation of the reinforcing fibres in a solution of polymeric matrix and then curing in a further step, appears versatile, because it allows handling and tailoring without the risk of premature cross-linking.

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