

TRANSITION PROPERTIES OF PRETREATED ASBESTOS-FILLED EPOXY POLYMERS

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ABSTRACT

By means of interfacial *in situ* polymerization poly(hexamethylene adipamide) was deposited on chrysotile fibres to ensure a strong interphase bond. The filler treated fibres were incorporated into epoxy resin using dibutyl phthalate as diluent to overcome viscosity effects and the resulting composite material was examined. Transition properties were considered while varying fibre volume fraction and concentration of the polyamide coating.

INTRODUCTION

As it is well known the addition of well dispersed asbestos fibres in polymeric matrices leads to composites with improved mechanical properties.

Asbestos fibres are available in a variety of forms, of which chrysotile asbestos is the most popular reinforcement due to its high modulus, mechanical strength, excellent heat and chemical resistance and also good electrical and thermal properties.

Asbestos-epoxy composites are widely used for both structural and non-structural applications. However, despite their widespread use little or no work on their transition properties has been published in the literature [1,2].

Thermal expansion behaviour of fibre-reinforced composites is strongly influenced by the fibre volume fraction, orientation and distribution of fibres, nature of matrix and fibres, adhesion efficiency between the two phases, and also by the process of fabrication of the test specimens. In the case of asbestos-phenolic composites, imperfect post-cure may result in high porosity and severe delamination may be observed, probably caused

by the presence and thermal expansion of occluded water which comprises one of the products of the cure reaction [1].

Thermal expansion behaviour can be important when it is necessary to match the thermal expansion of one structural component with another or when studying load transfer from fibre to fibre by the matrix at a range of temperatures. In particular, according to the shrink-fit theory [3], during the polymerization or cure of the resin matrix material and for the case of higher coefficient of thermal expansion a_m of the matrix compared to the respective coefficient a_f of the reinforcement, the matrix shrinks around the reinforcement with sufficient force providing frictional resistance to movement of the fibre through the cured resin. Thus the resulting differential rates lead to the development of stresses in the composite which, in many cases, lead in turn to the appearance of microcracks at the filler-matrix interphase [10]. These microcracks and internal stresses can be important not only in the fabrication of the composite but also in determining its subsequent behaviour [11]. On the other hand, if $a_m < a_f$ and the temperature of an initially stress-free composite is raised, a normal tensile stress will be developed at the interphase which may lead to debonding [4-9].

In many cases, in order to improve the load transfer between the fibres, a separate coupling agent is used, one part of which reacts with the reinforcement and another part of which reacts with the polymer matrix [3]. In the model system, epoxy resin-glass beads covered with poly(butylmethacrylate) [12], the formation of an interphase region was established with its own relaxation maximum, the structure of which was supposed to be a kind of semi-interpenetrating network formed by crosslinked linear polymers. The properties and the extent of the interphase for particulate composites were calculated as a function of the respective properties of the filler, the matrix and the composite [13], while from experimental findings [16] the thermomechanical behaviour of this layer was investigated [15]. The properties of the interphase were considered to vary in a continuous way from the filler surface to the bulk matrix [17,18], while in [14] an approximation was introduced assuming that the interphase is extended to infinity, penetrating into the matrix. Based on the conceptions of Kerner's model and the properties and the extent of the interphase, a model suitable for the determination of the cubic thermal expansion coefficient of particulate composites was then developed [19].

The investigation to be described was undertaken in order to enhance the understanding of the role of surface treatment in the case of typical asbestos fibre-reinforced plastics in which chrysotile fibres were employed.

EXPERIMENTAL

The resin employed as matrix in the present study was a diglycidyl ether of bisphenol A, Epikote 828 (Shell Co.), with an epoxy equivalent 185-192, a molecular weight between 370 and 384 and a viscosity of 15000 cP at 25°C.

As curing agent, 8 phr by weight of diethylenetriamine (DTA) were employed.

As diluent, in order to allow more asbestos to be incorporated with the resin and give better impregnation, dibutyl phthalate (DBP) was used at the level of 15 phr by weight on epoxy plus DTA basis.

Asbestos fibres were in situ pretreated with poly(hexamethyleneadipamide), according to the principles of interfacial polymerization, i.e. the asbestos was first impregnated by a diamine solution and then by one of dichloride. Full details on the experimental procedure followed have been given elsewhere [20,21]. The polyamide phase deposited on asbestos is expected to enhance interfacial cooperation with epoxy due to the well known compatibility between polyamides and epoxies [22,23].

Mouldings were prepared as follows : the epoxide resin was heated up to about 100°C to cause a further viscosity decrease. Proper amounts of diluent, asbestos and curing agent were then added, and the mixture, after being stirred thoroughly, was left in a vacuum chamber for degassing. Subsequently, it was put in a rectangular PMMA mold, 250x250x3mm, internally coated with silicone oil to facilitate removal of the moulding. The latter after 24 h at room temperature and 2 h at 50°C was removed, to be then subjected to a 48 h thermal treatment at 100°C, in order to have complete curing, i.e. storage-independent properties.

In order to study the effect of both filler and polyamide coating concentration on the transient properties of asbestos-epoxy composites, specimens with various concentrations of asbestos and nylon were manufactured as above and their compositions are shown in Table I. On the other hand, some of the physical and mechanical properties of the constituent materials are tabulated in Table II.

The materials were tested on a du Pont 990 thermomechanical analyzer (TMA) in order to determine linear thermal expansion coefficients and glass transition temperatures.

Static properties of the same materials were also obtained by means of an Instron tester at room temperature and the results were presented in [24].

Table I. Specimens composition.

Type of Specimens	1	2	3	4	5	6	7	8	9
DGEBA weight parts	100	100	100	100	100	100	100	100	100
DTA weight parts	8	8	8	8	8	8	8	8	8
Nylon 6,6 weight parts*	1.3	3.4	5.8	1.3	3.4	5.8	1.3	3.4	5.8
Asbestos weight parts	0.9	0.9	0.9	2.8	2.8	2.8	5.6	5.6	5.6
DBP weight parts	13.9	13.9	13.9	13.9	13.9	13.9	13.9	13.9	13.9

* Weight parts of Nylon 6,6 per 100 parts of dry asbestos

Table II. Properties of the constituent materials (average values).

PROPERTIES	Epoxy Matrix	Nylon 6,6	Asbestos
Density ρ (Mg.m ⁻³)	1.2	1.14	2.5
Strength σ_u (GPa)	62.1	70	5500
Young's Modulus E (GPa)	1.6	2	160
Coef. of Thermal Expansion α ($^{\circ}\text{C}^{-1} \times 10^{-6}$)	47 (T<T _g) 122 (T>T _g)	85 (T<T _g) 120 (T>T _g)	50
Glass Transition Temperature T _g ($^{\circ}\text{C}$)	67	50	-

RESULTS AND DISCUSSION

Figure 1 shows the variation of the glass transition temperature T_g of the composites prepared as a function of the nylon concentration c_N divided by the asbestos concentration c_A . From this figure one may observe that with increasing c_N/c_A , T_g increases, passes through a maximum, then decreases showing a minimum and finally increases again. It is worthwhile to mention that exactly the same behaviour has been also detected versus c_N/c_A for the relative modulus of elasticity (E_c/E_m) of the composites considered (Fig. 2) [24].

The explanation of this variation of T_g with c_N/c_A may be attributed to the complex structure of the composites under investigation. More precisely in the region between bulk epoxy matrix and nylon coating an interphase is developed which is supposed to be a kind of interpenetrating polymeric network (IPN), consisting of epoxy resin and nylon. In fact, as it has been observed in [22,23], amide hydrogens in nylon chains may interact with epoxy rings to form a crosslinked network, so that in the interphase

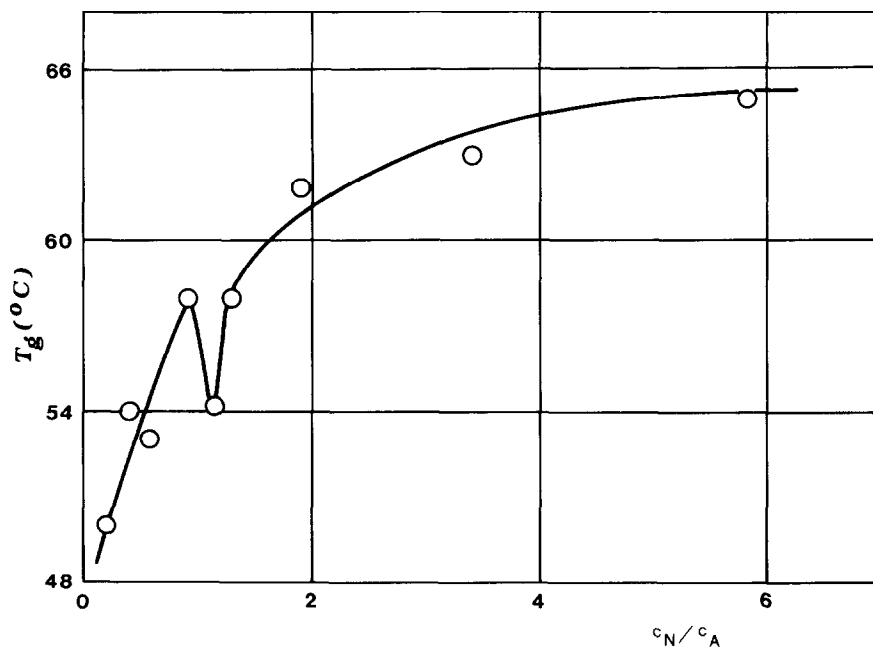


Fig. 1. Variation of T_g values for composite specimens as a function of the relative concentration c_N/c_A .

area three phases are in general met, namely pure nylon, crosslinked nylon-epoxy and crosslinked epoxy (Fig. 3). At low values of the ratio c_N/c_A all the nylon available is expected to interact with the epoxy matrix while no pure nylon phase exists. Given the good adhesion effected between asbestos and polyamide [21] this explains why T_g increases. However, as

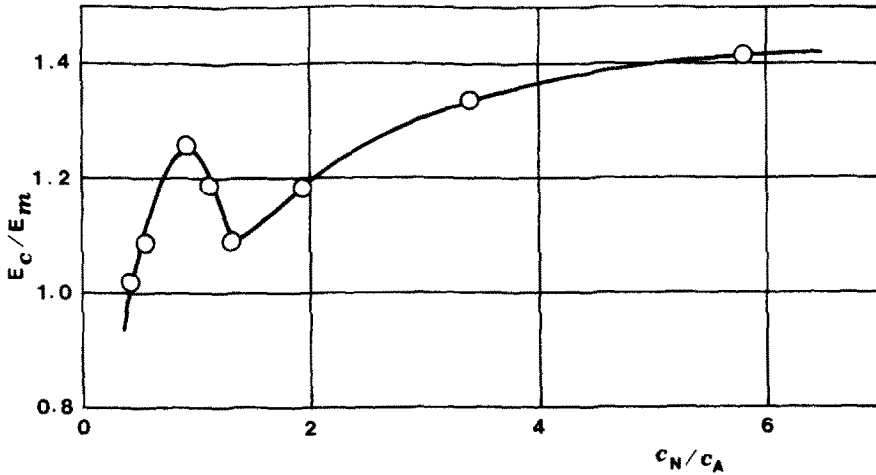


Fig. 2. Plot of relative modulus of elasticity (E_c/E_m) versus the contents ratio c_N/c_A (24).

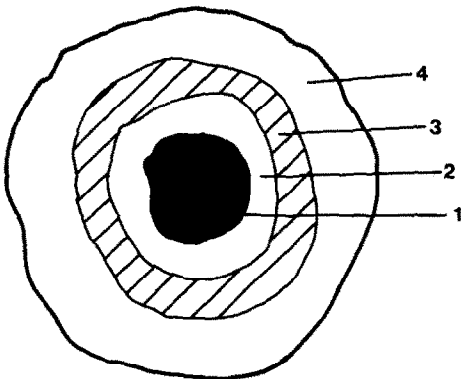


Fig. 3. Representative volume element of the polyphase material considered in the present study. 1= Asbestos; 2= Nylon; 3= Nylon-epoxy interphase; 4= Epoxy.

the value of c_N/c_A is further increased, the pure nylon phase then formed has a plasticizing effect [22,24], leading to a decrease of the T_g . Furthermore, for even higher values of the ratio c_N/c_A parts of the excess nylon contained start acting independently [21,24] and the interphase regions are increased (Fig. 4). If this is the case and further supposing that these regions are characterized by a higher crosslink density than that in the bulk matrix, an interpretation of the observed increase of the T_g is then provided.

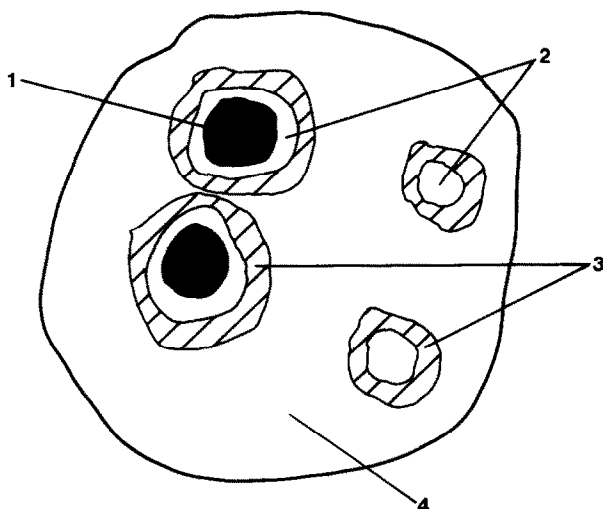


Fig. 4. Theoretical representation of the composite under investigation having an excess in nylon phase. 1= Asbestos; 2= Nylon; 3= Nylon-epoxy interphase; 4= Epoxy.

Turning now to the thermal expansion behaviour of the composites prepared, Fig. 5 and 6 show the variation of thermal expansion coefficient below and above T_g respectively, again as a function of the relative concentration c_N/c_A . It can be observed that the variation of the thermal expansion coefficients are similar in nature. More precisely at the beginning, as the ratio c_N/c_A increases, it passes through a maximum, then decreases and finally for higher values of c_N/c_A increases again. This kind of behaviour may be also explained according to the previously mentioned reinforcing mechanism.

As it is well known, thermal expansion involves the transmission of stresses across an interphase and should thus be connected with the degree of

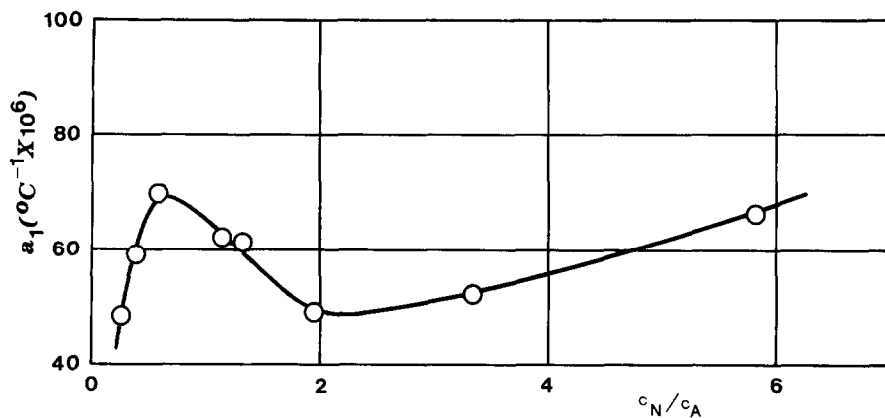


Fig. 5. Variation of thermal expansion coefficient a_1 ($T < T_g$) as a function of the relative concentration c_N/c_A .

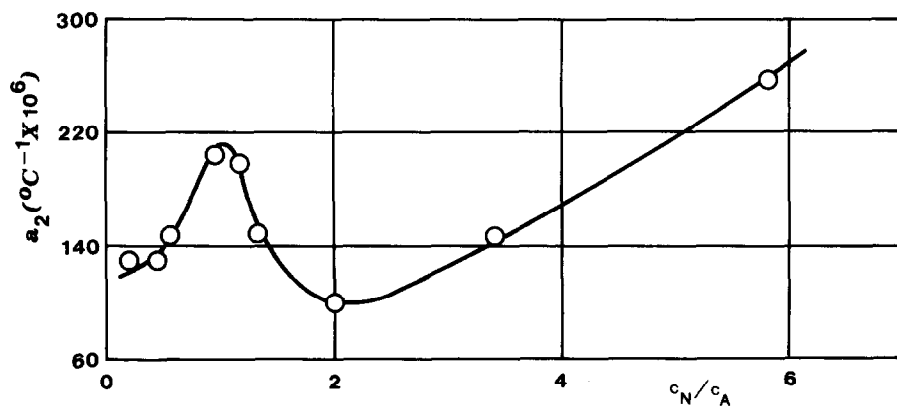


Fig. 6. Variation of thermal expansion coefficient a_2 ($T > T_g$) as a function of the relative concentration c_N/c_A .

adhesion between the phases. In our case, with increasing c_N/c_A there is a first increase in α (Figs. 5 and 6), due to the good adhesion bond developed between matrix and inclusions at this range of c_N/c_A values [16] (see also Table II). For higher values of c_N/c_A , where the nylon phase starts existing in the close vicinity of the asbestos fibres, a clear decrease in α values is observed with increasing c_N/c_A because of considerable deterioration of the adhesion between the two main phases of the composite, i.e. the asbestos fibres and the epoxy matrix. Finally, as c_N/c_A is increased further, this excessive nylon phase starts playing the role of independent reinforcing material (Fig. 4) with a higher thermal expansion coefficient, so that there is again an increase in α values.

CONCLUSIONS

In the present work, transition properties of pretreated asbestos-filled epoxy polymers were investigated. It has been established that both T_g and thermal expansion coefficient are strongly dependent on the relative concentration ratio c_N/c_A . The results may be explained qualitatively by means of a theoretical model which takes seriously into account the existence of a boundary interphase consisting of pure nylon, crosslinked nylon-epoxy and crosslinked epoxy phase.

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