

A Qualitative Model for the Mechanical Behavior of Pretreated Asbestos-Epoxy Composites

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Synopsis

The aim of the present work was to investigate the effect of fiber pretreatment, fiber content, coating concentration, and also pretreatment procedure on the tensile properties of asbestos-epoxy composites. These composites comprise materials of considerable industrial importance. Asbestos exhibits unique properties. Occasionally it is difficult to disperse asbestos properly because the individual fibrils are very small and tend to agglomerate, but there is no evidence that asbestos is not easily wetted out by all systems. However, the higher potential aspect ratio of asbestos fibers compared with glass is not always realized in practice because the fibers break in length to fine diameters. Accordingly, the very considerable new surface created makes successful wetting difficult or impossible. For this reason, asbestos was precoated with a well adhered film of poly(hexamethylene adipamide), a polymer especially compatible with the epoxy phase. The pretreatment procedure followed was based on the principles of the interfacial polymerization involving the serial application to the asbestos of two immiscible solutions of hexamethylenediamine and adipoyl chloride. Accordingly, epoxy-nylon-chrysotile composites were made while varying pretreated fiber volume fraction, concentration of the polyamide coating, and reactants application order. Results obtained from tensile measurements proved quite interesting: Relative modulus of elasticity and relative ultimate strength exhibited a similar behavior when correlated with the ratio of polyamide to asbestos concentration. The corresponding curves pass through distinct maxima at which severe improvement of the material performance is effected. A thorough interpretation of these results is also included.

INTRODUCTION

Asbestos has been used in combination with plastics for more than 60 years, provided in a variety of forms, such as bulk (both reinforcing and filler grades), paper, felt, and mat, roving, and fabric and cloth.^{1,2}

Asbestos in all four main varieties—chrysotile (white asbestos), crocidolite (blue asbestos), amosite, and anthophyllite—consists of short, discontinuous fibers of high length/diameter ratio and high surface area.³ Of these, chrysotile asbestos, a hydrated magnesium silicate [$Mg_3Si_2O_5(OH)_4$] represents a great percentage of the annual consumption of asbestos in plastics. Asbestos fibers referred to in this article are of the chrysotile variety. Asbestos was used

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in the form of fiber bundles of varying diameter containing thousands of individual fibers with diameters in chrysotile of around $0.03 \mu\text{m}$.

Chrysotile fibers have a good engineering balance of stiffness and strength, and a specific stiffness more than twice that of E glass fibers.⁴ The elevated temperature properties are equally significant due to the presence of approximately 14% water in the chemical constitution of chrysotile. Considerable quantities of thermal energy to effect its release and elimination from the unit structure are required, so that elevated temperature strengths and structures of asbestos-reinforced plastics may be preserved for extended periods of time.⁵

Due to the high surface area of asbestos, we are greatly concerned with the wetting aspect during fabrication of asbestos-reinforced plastics. In fact, the high potential aspect ratio of asbestos fibers is not always realized in practice because the fibers break in length to fine diameters.⁶ The very considerable new surface created makes successful wetting difficult or impossible. Accordingly, particular interest should be focused on the structure and properties of the asbestos-matrix interphase, since the stresses acting on the matrix are transmitted to the fiber across this interphase.^{6,7} Composite materials with weak interphases have relatively low strength and stiffness but high resistance to fracture, whereas materials with strong interphases have high strength and stiffness but are very brittle. The effect is related to the ease of debonding and pull-out of fibers from the matrix during crack propagation.

Previous efforts on these affinity problems were mainly concentrated on pretreating the asbestos fibers with a suitable coupling agent to effect better dispersion.^{8,9} On the other hand, in two contributions from our laboratory^{10,11} the case of the nylon-asbestos composites interphase was first examined. To improve affinity between matrix and asbestos fibers, the latter were pretreated in situ with poly (hexamethylene adipamide) according to the principles of interfacial polymerization.¹² This pretreatment should increase the cooperation between asbestos and polyamide matrix, while further fibrillation of the asbestos is diminished together with concurrent health problems.

In this article, results are presented from studying the mechanical behavior of asbestos-epoxy composites comprising materials of increased industrial importance.^{2,13-26} Chrysotile fibers employed were treated interfacially as above due to the well-known compatibility between polyamide and epoxy phase.^{27,28} More precisely, while varying pretreated asbestos fiber fraction, concentration of the polyamide coating, and pretreatment procedure, the tensile properties of the result and epoxy-nylon-asbestos composites were investigated. A qualitative model for explaining the results presented has also been included.

EXPERIMENTAL

Asbestos Fibers Pretreatment

After drying at 110°C for 2h, 200 g of chrysotile fibers were treated in a Werner mixer to ensure homogeneous wetting with an aqueous solution of hexamethylenediamine and an adipoyl chloride solution in carbon tetrachloride. Treatment with hexamethylenediamine was accompanied by addition of

sodium carbonate in a quantity twice that of the diamine. The ratio K of the reactants molar concentration (diamine/dichloride) was always kept equal to 2.5. On the other hand, serial application to the asbestos of these two immiscible solutions involves two cases, namely diamine can be applied before or after dichloride. The former comprises the interfacial process I or Case I and the latter the interfacial process II or Case II.

After addition of reactants, mixing was continued for some time, the reaction product was dispersed in water, and then washed several times in a centrifugal separator until neutral pH. Finally, the treated fibers were thoroughly dried and stored in a desiccator above calcium chloride.

Characterization of the modified asbestos fibers was based mainly on evaluating the nylon 6, 6 content deposited by weight loss, either on ignition in a crucible or by means of differential thermal analysis, as well as by solvent extraction, infrared spectroscopy, and microscopy studies. The exact experimental procedures together with typical results obtained have been given elsewhere.^{10,11}

Epoxide Moldings Preparation

As prepolymer for the thermoset system, a diglycidyl ether of bisphenol A resin was used, Epikote 828 (Shell Co.), with an epoxy equivalent between 182 and 194 and a viscosity between 100 and 150 poise at 25°C.

Diethylenetriamine (DTA) was employed as curing agent (i.e., a low viscosity and highly reactive primary aliphatic amine, capable of curing diglycidyl ethers at room temperature). DTA was added at a concentration of 8 weight parts per one hundred weight parts (phr) of epoxy resin.

To reduce viscosity (i.e., to allow more asbestos to be incorporated with the resin and improve wetting), xylene or alternatively dibutyl phtalate (DBP) were used, at the levels of 5 and 15 phr by weight, respectively, on epoxy plus DTA basis. Under these conditions, the maximum filler content effected for a pourable mixture, on the same basis, was found equal to about 6 phr. Accordingly, asbestos fibers either treated (grades I and II from processes I and II, respectively) or untreated were employed at the contents of 1, 3, and 6 phr. In all cases the fiber size was kept at the level of minus 16 mesh (US Sieve Series).

Moldings were prepared as follows: The epoxide resin was heated to about 100–110°C to effect further viscosity decrease. Proper amounts of diluent, asbestos, and curing agent were then added, and the mixture, after being stirred thoroughly, was left for 5 min in a vacuum chamber for degassing. Subsequently, it was put in a rectangular PMMA mold, 250 × 250 × 5 mm, coated internally with silicone oil to facilitate removal of the molding. The latter, after 24 h at room temperature and 2 h at 50°C was removed and subjected to a 48 h thermal treatment at 100°C, well above the glass transition point of the material,²⁹ in order to effect storage independent properties.²

Tensile Breaking Tests

Tensile measurements were carried out with a conventional Instron type tester at room temperature. The specimens were tested according to the

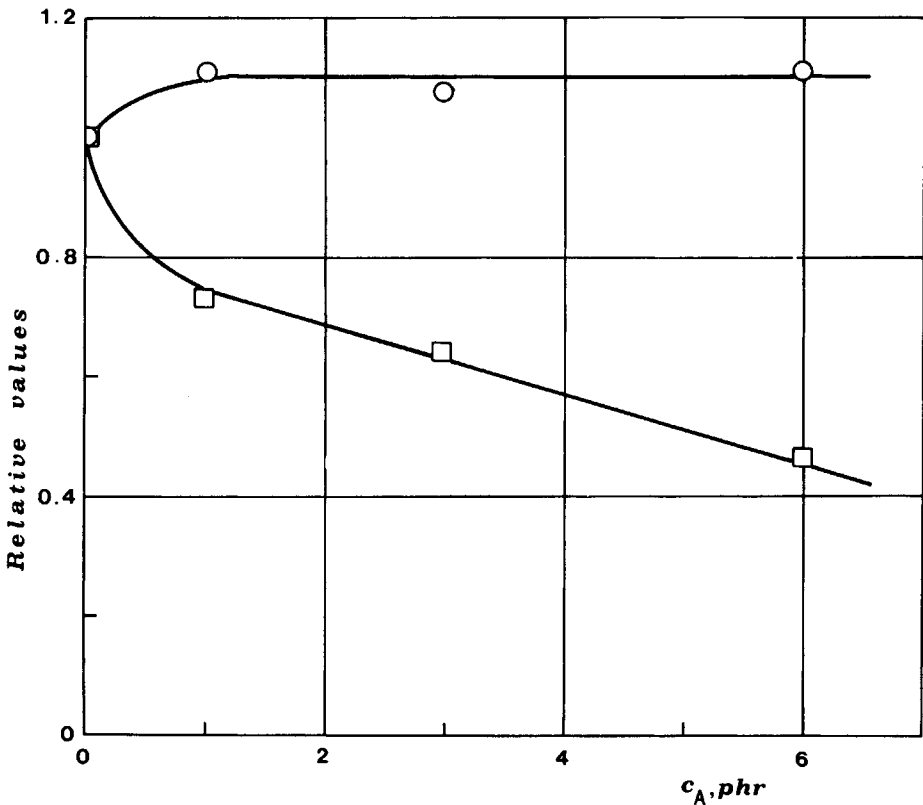


Fig. 1. Untreated asbestos composites: plots of relative modulus of elasticity (E_c/E_m) (○) and relative ultimate strength ($\sigma_{u_c}/\sigma_{u_m}$) (□) versus asbestos content (c_A).

D638-76 ASTM at a rate of extension equal to 1.0×10^{-3} m/min. All the results obtained were within an experimental error of the order of 2–3%.

RESULTS AND DISCUSSION

Nonmodified Asbestos Fibers

Preliminary moldings containing xylene as diluent were eventually characterized by the presence of numerous small bubbles. The phenomenon was clearly evident after the thermal treatment followed, due to solvent volatilization. Therefore, it seemed worthwhile to continue the investigation by using DBP exclusively, at the level already mentioned. In this case, modulus of elasticity (E_m) and tensile strength at break (σ_{u_m}) for the unfilled epoxy resin (matrix) were found equal to 1.6 GPa and 62.10 MPa, respectively. Subscript m denotes a matrix property, f denotes a filler property, and c a composite property.

When untreated asbestos is added to the resin the effect on relative modulus (E_c/E_m) and relative ultimate strength ($\sigma_{u_c}/\sigma_{u_m}$) is shown in Figure 1: Relative modulus increases slightly and is maintained independent of asbestos content (c_A), while tensile strength decreases considerably. The de-

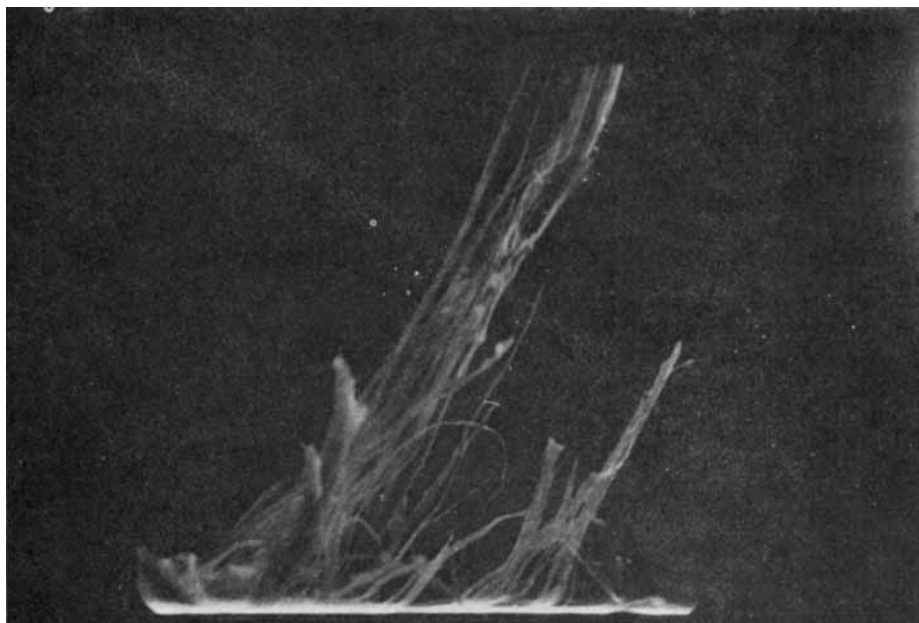


Fig. 2. Untreated chrysotile bundles ($c_N, c_A = 0, 6$ phr, respectively) (magnification $\times 750$).

pression of the latter is typical of the adhesion problem between fibers and matrix, due to bad wetting of the asbestos by the epoxy phase.² In fact, in Figure 2, a microphotograph of untreated fiber bundles arising from the fracture surface of a tensile specimen is provided. The difficulty of successfully wetting this fiber aggregation is quite evident.

Modified Asbestos Fibers

What happens when treated asbestos is used (i.e., when a polyphase (epoxy-nylon-asbestos) composite is faced), can be seen in Figures 3 to 6. Figures 3 and 4 correspond to asbestos of Case I, while Figures 5 and 6 correspond to the alternative grade of Case II. Primary data of E_c and σ_{u_c} are given versus c_A for different values of the polyamide content c_N deposited on the chrysotile fibers used. c_N takes the values of 1.3, 3.4, and 5.8 phr (polyamide weight parts per 100 weight parts of dried asbestos) for grade I, and 0.3, 2.1, and 3.4 phr for grade II.

Turning first to the modulus effect it is clear again that incorporation of treated asbestos, either grade I or II, results in increasing E_c . Furthermore, in both cases (Figs. 3 and 5), when c_A increases, the curve of E_c passes through a maximum and then, depending on grade and c_N , starts increasing again. On the other hand, the magnitude of the maximum appearing at the lower c_A values seems related positively with c_N , especially for Case I asbestos grade.

The effect of pretreatment on ultimate strength (Figs. 4 and 6) does not result in variation of the mode encountered with the untreated chrysotile (Fig. 1) (i.e., in all cases σ_{u_c} remains below σ_{u_m}). Nevertheless, when c_A increases, at constant c_N , σ_{u_c} seems to pass through a broad minimum.

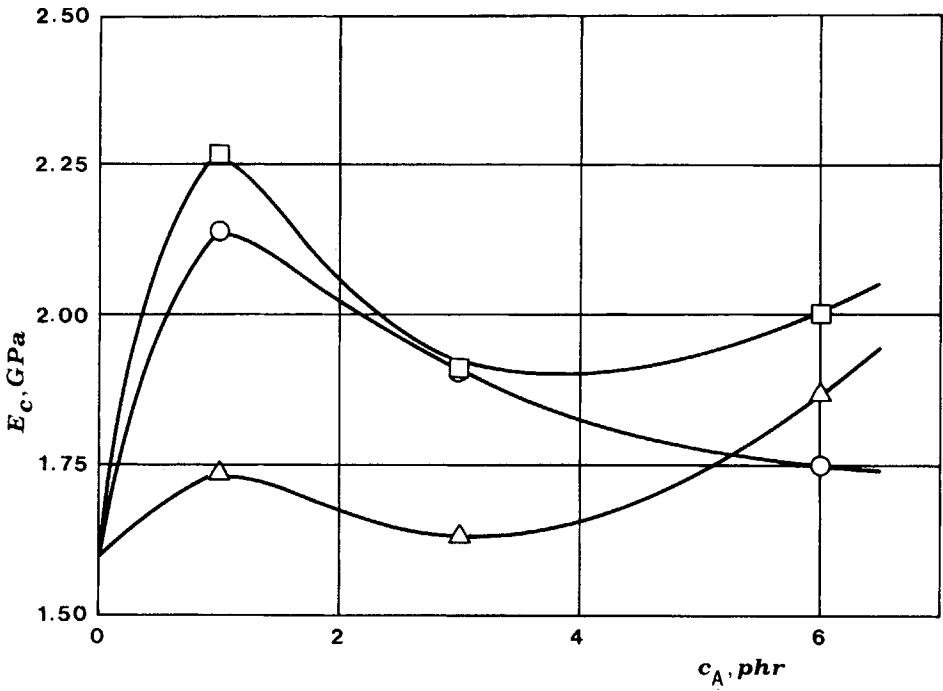


Fig. 3. Case I asbestos composites. Plots of modulus of elasticity (E_c) versus asbestos content (c_A) at constant nylon content (c_N): (Δ), 1.3 phr; (\circ), 3.4 phr; (\square), 5.8 phr.

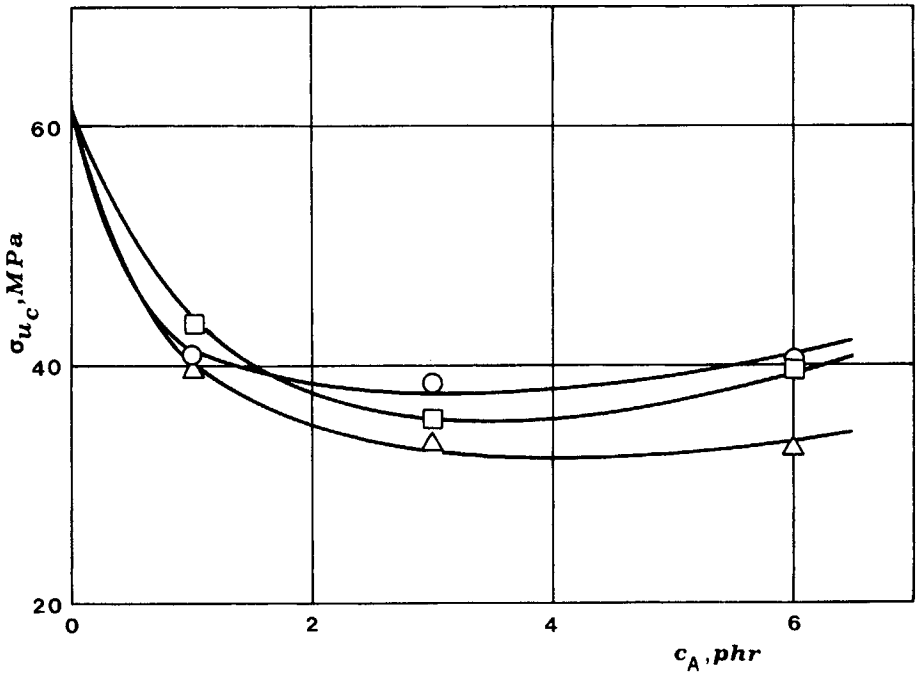


Fig. 4. Case I asbestos composites. Plots of ultimate strength (σ_{uc}) versus asbestos content (c_A) at constant nylon content (c_N): (Δ), 1.3 phr; (\circ), 3.4 phr; (\square), 5.8 phr.

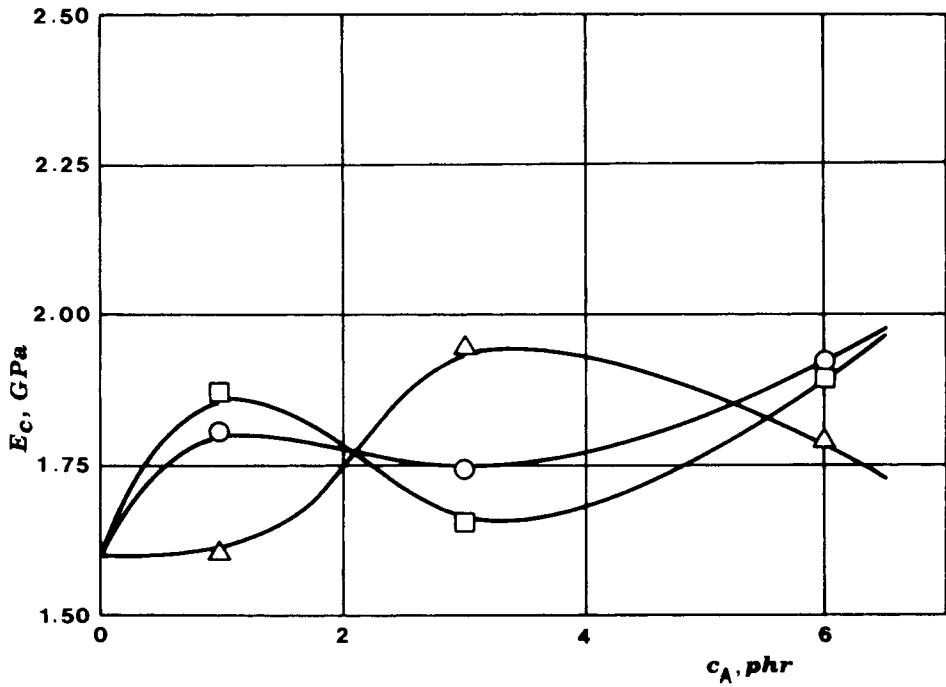


Fig. 5. Case II asbestos composites. Plots of modulus of elasticity (E_c) versus asbestos content (c_A) at constant nylon content (c_N): (Δ), 0.3 phr; (\circ), 2.1 phr; (\square), 3.4 phr.

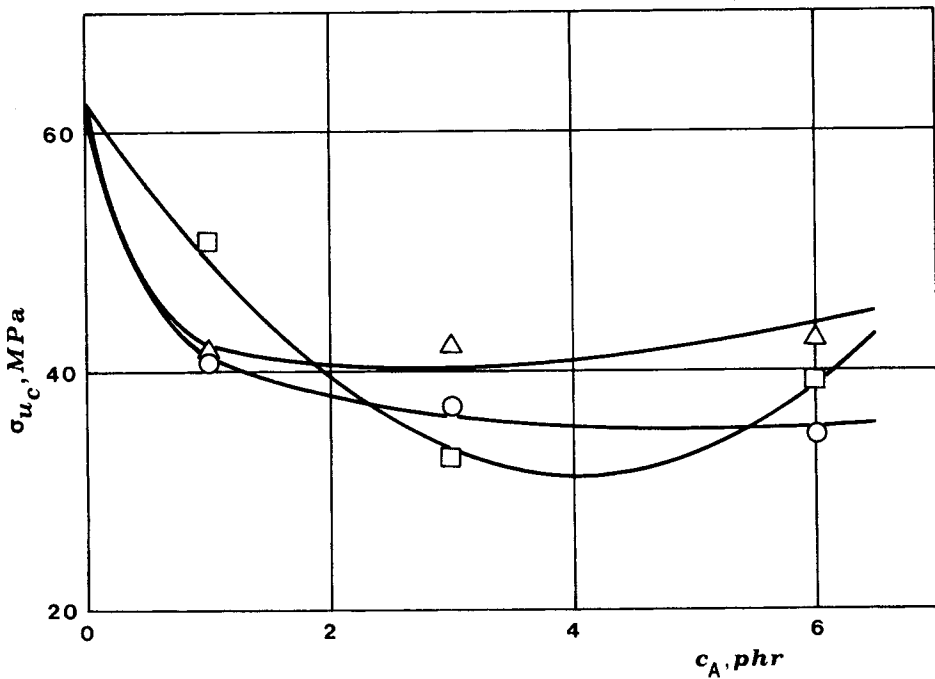


Fig. 6. Case II asbestos composites. Plots of ultimate strength (σ_{uc}) versus asbestos content (c_A) at constant nylon content (c_N): (Δ), 0.3 phr; (\circ), 2.1 phr; (\square), 3.4 phr.

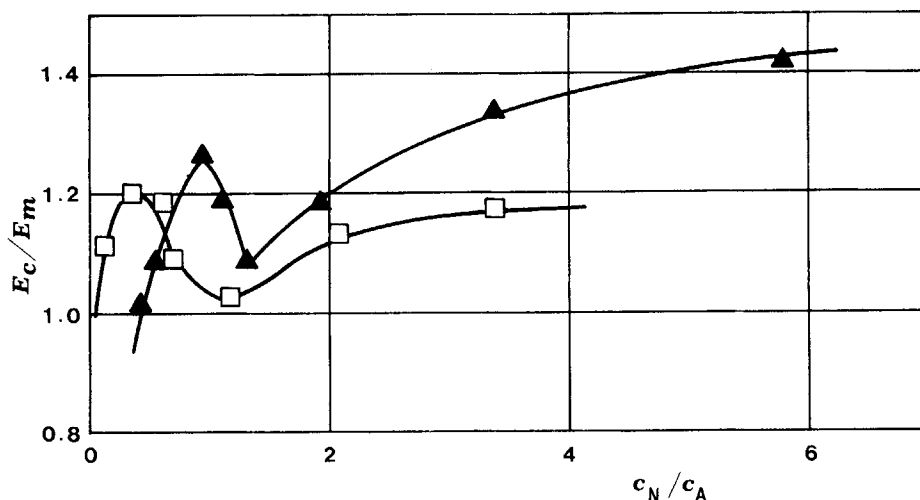


Fig. 7. Treated asbestos composites. Plots of relative modulus of elasticity (E_c/E_m) versus the contents ratio c_N/c_A . (\blacktriangle), Case I asbestos; (\square), Case II asbestos.

"Relative Concentration" Effect

In a previous paper³⁰ dealing with the influence on epoxy-asbestos composites of Case I pretreatment of chrysotile, it proved quite worthwhile correlating the relative values E_c/E_m and $\sigma_{u_c}/\sigma_{u_m}$ with the "relative concentration" c_N/c_A , on the grounds of the supposition that asbestos and polyamide phases may play competitive roles in the composite performance. The curves obtained are shown in Figures 7 and 8 together with similar grade II asbestos data. Obviously, both grades of asbestos provide the same exact behavior in qualitative terms: Both curves of E_c/E_m and $\sigma_{u_c}/\sigma_{u_m}$ pass through a maximum with increasing c_N/c_A and, after considerable reduction, an increase is again noticed at higher relative concentrations. Nevertheless, from a quantitative point of view, shift from type I to type II grade of asbestos clearly results in shifting the curve a bit to the left along the c_N/c_A axis, that is, for grade II if c_A is supposed constant, lower values of c_N become effective in increasing modulus and strength. On the other hand, in both figures, no considerable differences are evident as far as the magnitude of these peaks is concerned.

Reinforcement Mechanism

It is essential to realize that these composite materials contain three main species (i.e., epoxy, nylon, and asbestos), and therefore provide two interfaces, the one between asbestos and nylon and the other between nylon and epoxy [Fig. 9(A)]. On this basis, an attempt to examine further possible interactions at interface regions becomes of critical importance for establishing a mechanism fitting the data obtained.³¹

Interfacial aspects between asbestos and nylon, according to the in situ polymerization technique followed,^{10,11} can be summarized in that controlled deposition of polymer on asbestos is feasible, accompanied by the develop-

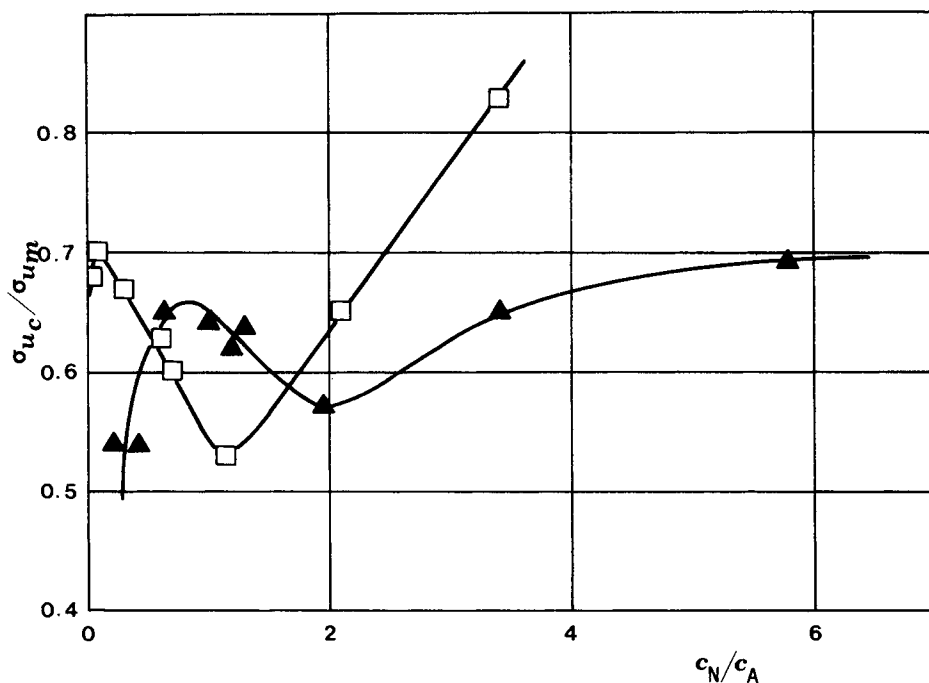


Fig. 8. Treated asbestos composites. Plots of relative ultimate strength ($\sigma_{u_c}/\sigma_{u_m}$) versus the contents ratio c_N/c_A . (\blacktriangle), Case I asbestos; (\square), Case II asbestos.

ment of a strong interface bond while filling the existing pores. In Figure 10, a microphotograph of a fiber bundle fully coated with nylon can be seen, again as arising from the fracture surface of a tensile specimen. On the other hand, turning to the epoxy-nylon interface it is known from the literature²⁸ that in nylon—bisphenol A-based epoxy blends appear to have three phases, the relative percentage of which, however, depends on the nylon/epoxy ratio: nylon phase, crosslinked nylon-epoxy phase (N-Ep), and crosslinked epoxy phase. The N-Ep phase mainly comprises a crosslinking network formed by reaction of epoxy rings with amide hydrogens in nylon chains. This possibility has been also studied intensively by Gorton.²⁷

Taking into account the above findings the behavior encountered in Figures 7 and 8 can be basically explained as follows: Let us consider again Figure 9(A). The simplified model shown of some asbestos particles surrounded by nylon and then epoxy phase, can be corrected in such a manner so that the N-Ep phase is also included [Fig. 9(B)]. Accordingly, at the low level region of c_N/c_A the composite appears rich in asbestos of low polyamide concentration. If this is the case, then most of the polyamide phase contained is expected to interact with the epoxy material, resulting in the development only of a N-Ep phase between asbestos and epoxy resin. Therefore, the typical model of Figure 9(B) turns to that of Figure 9(C), while good cooperation between epoxy and nylon is ensured. Given also the good adhesion effected between asbestos and polyamide deposited¹¹ this explains why both modulus and strength increase.

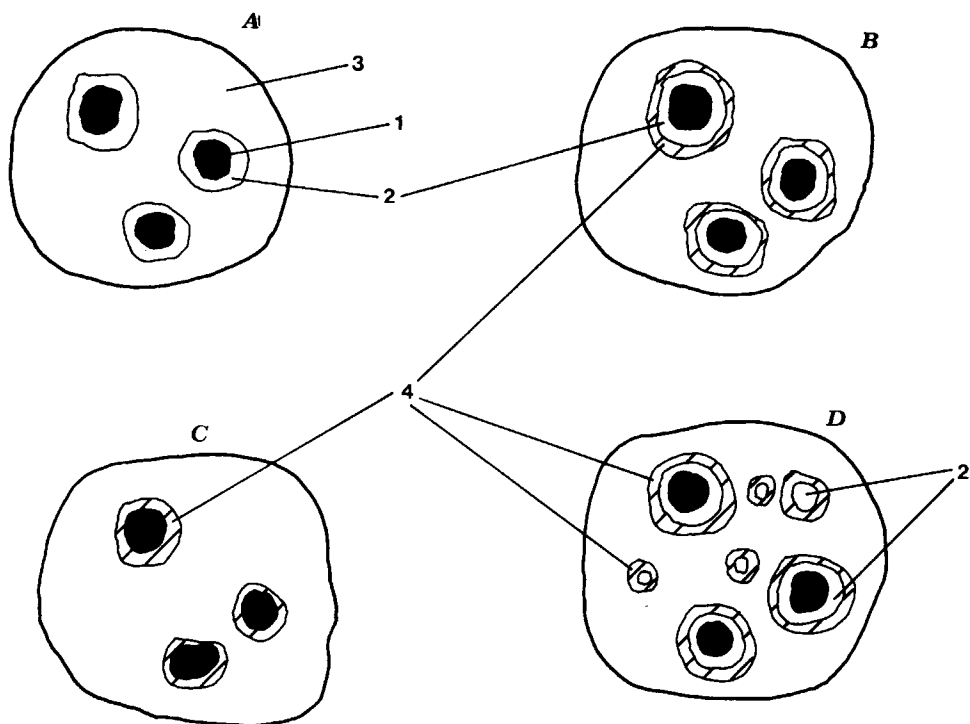


Fig. 9. Representative volume elements of the polyphase materials considered in this study. 1 = Asbestos; 2 = Nylon; 3 = Epoxy; 4 = Nylon-epoxy phase.

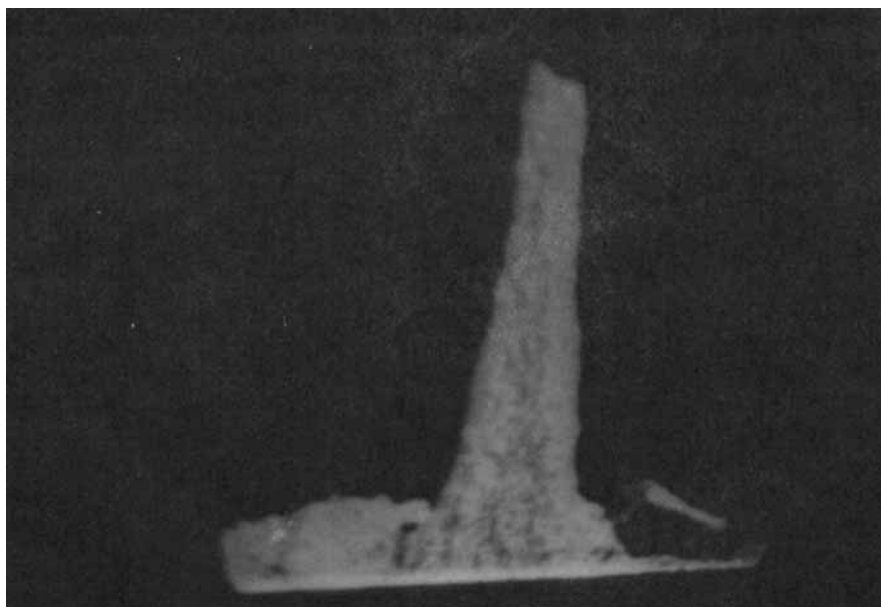


Fig. 10. Treated chrysotile bundle ($c_N, c_A = 5.8$ (I), 6 phr, respectively) (magnification $\times 450$).

Further increase of c_N/c_A results in the appearance of a nylon phase [Figure 9(B)], non interacted with the epoxy resin. This excessive nylon content is expected to result in some plasticization of the material, a situation similar with that detected by Wang et al.²⁸ leading accordingly to degradation of modulus and strength. On the other hand, formation of voids within this pure nylon phase, during its deposition, cannot be excluded and indeed, results from thermal expansion studies of the same materials fit well to this supposition.²⁹

In order to explain the quite right part of the curves of Figures 7 and 8 it has to be underlined that great values of c_N/c_A simply mean that there exist considerable quantity of nylon phase, in comparison with asbestos, and even more that it is not all necessarily adhered to asbestos. In other words, a percentage of polyamide phase may remain quite free near or around asbestos. In fact, it is this phase which after excessive extraction of the treated fibers with formic acid is swept out, so that only nearly 20% of the polyamide quantity deposited in the high polyamide contents region remains strongly adhered to the asbestos.^{10,11} Consequently, if this is the case, when epoxy resin is added these excessive polyamide particles comprise, through interaction with the epoxy resin, independent reinforcing material well adhered to the epoxy [Figure 9(D)], so that increase of modulus and ultimate strength is again effected.

Finally, regarding the earlier appearance of the first maximum in the curves E_c/E_m or σ_u/σ_{u_m} versus c_N/c_A (Figs. 7 and 8), for the grade II asbestos, the interpretation seems quite simple: The preparation of Case II asbestos involves first use of dichloride and then of diamine. Dichloride is pretty reactive with the basic in nature chrysotile effecting a stronger interfacial bond between the resulting polyamide and the inorganic material.¹¹ For this reason, the polyamide phase deposited is then more effective in establishing a good adhesion situation between asbestos and epoxy in comparison with treated fibers according to the interfacial process I.

CONCLUSIONS

In this study the influence of asbestos fiber pretreatment on the tensile properties of asbestos-epoxy composites has been investigated. The pretreatment followed comprises a controlled deposition of poly (hexamethylene adipamide) on asbestos, in situ, according to the principles of the interfacial polymerization. Two alternative processes, I and II, were applied and the results obtained can be summarized as follows:

1. When untreated asbestos is employed the relative modulus of elasticity increases with asbestos concentration while the ultimate strength decreases considerably.
2. Better correlation, due to the presence of the polyamide phase, can be effected when the variation of the relative modulus and the relative strength is examined versus the polyamide and asbestos contents ratio c_N/c_A . In this case, both relative values increase initially, with c_N/c_A , passing through a maximum and then start increasing again.
3. The model proposed may explain in qualitative terms the behavior encountered. The role of the interactions at the two interfaces regions has been seriously taken into account.
4. The effect of alternating the two types of asbestos pretreatment was simply a shift to the left on the c_N/c_A axis of the two curves, E_c/E_m or σ_u/σ_{u_m} versus c_N/c_A .

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