

Epoxy-Pretreated Asbestos Composites: Solution Based versus Interfacial Polymerization Pretreatment Process

C. D. PAPASPYRIDES* and T. DUVIS, *Laboratory of Special Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, 42 Patission Street, Athens 106 82, Greece*

Synopsis

Epoxy-resin-based composites filled with treated asbestos fibers were made. The asbestos, of chrysotile variety, was coated by impregnation in poly(hexamethylene adipamide) solution and the results of testing the tensile properties of the asbestos/polyamide/epoxy composite system are presented. The interest was focused on the influence of the asbestos content in the composite together with that of the polyamide content deposited on asbestos. No satisfactory reinforcing effect was found, especially when comparing with previous studies on coating the chrysotile by *in situ* interfacial polymerization. Nevertheless, a qualitative model was proposed to correlate the effect of the different phases contained in the composite with the experimental behavior encountered.

INTRODUCTION

Chrysotile, a hydrated magnesium silicate [$Mg_3Si_2O_5(OH)_4$], comprises the most commercially used asbestos fibers in the reinforced plastics industry, representing over 90% of the asbestos world production.¹ Chrysotile fibers, as technological reinforcing material, have a wide range of applications in the aircraft, space, automotive, chemical, and building fields due to the unique combination of excellent properties.^{2,3} The flame and heat resistance is outstanding together with satisfactory behavior in mechanical tests, as the fibers have a good engineering balance of stiffness and strength and a specific stiffness more than twice that of E glass fibers.⁴ Very low cost completes this image.⁵

The aforementioned advantages are not always exploited as the fibers are not satisfactorily wetted by the matrix employed. This is due to the high surface area of the asbestos and the high length/diameter ratio.^{1,6,7} Also this high potential aspect ratio is not always realized in practice because the fibers break in length to fine diameters.⁸ This very considerable new surface created makes successful wetting difficult or impossible. As a result, pretreatment of the fibers seems crucial in order to increase the cooperation between asbestos and matrix. On the other hand, another serious problem faced is concerned with health hazards caused by these fibers. Not only are the miners exposed to that danger, but also the end-users of products, such as car brakes or insulation laminates.

Nowadays the industry would continue to accept asbestos, at least temporarily, if it was possible to considerably reduce these problems. Some investi-

* To whom correspondence should be addressed.

gators are considering the possibilities of encapsulating the fibers by elastomeric membranes.⁹ On the other hand, alternative materials, such as combinations of asbestos with aramid fibers, have been proposed¹⁰⁻¹⁴ but aspects like high price or insufficient balance of properties comprise serious obstacles to their commercial use.

In our laboratory the possibility of coating the fibers with a polyamide phase has been thoroughly investigated.^{15,16} This coating was accomplished by two different experimental procedures: (a) *in situ* polyamidation and (b) solution coating. In the first case, based on the principles of interfacial polymerization, the fibers were treated successively with an aqueous solution of hexamethylenediamine and an adipoyl chloride solution in carbon tetrachloride. Nevertheless, serial application to the asbestos of these two immiscible solutions involves two cases, i.e., diamine can be applied before or after dichloride. The former comprises the interfacial process I or Case I¹⁵ and the latter the interfacial process II or Case II.¹⁶

In a following experimental stage, interest was focused on asbestos-epoxy composites comprising materials of increased industrial importance.¹⁷ The polyamide-coated asbestos was employed because of the well-known compatibility between polyamide and epoxy phases. Initially, the interfacial polymerization technique was applied and results from mechanical^{18,20} and thermal tests^{19,21} were presented. To explain the nonlinear behavior encountered, a qualitative model was proposed, based on the presence of three different phases in the composite, epoxy, nylon, and asbestos, and therefore of two interphases, asbestos-nylon and nylon-epoxy. Their contribution was studied by means of the parameters C_A and C_N . The former represents the asbestos content in the composite expressed in phr: weight parts of *treated* asbestos per 100 weight parts of epoxy system (epoxy resin + curing agent + plasticizer). On the other hand, C_N is defined as the polyamide content on asbestos expressed similarly in phr: polyamide weight parts per 100 weight parts of untreated dried ("pure") asbestos.

An analysis based on correlating tensile modulus (E) and strength at break (σ_u) of the composite with the ratio C_N/C_A was then attempted. Three stages were distinguished: In the first stage of low values of this ratio, meaning composites rich in asbestos of low polyamide concentration, all the polyamide phase is expected to interact chemically with the epoxy,^{22,23} nevertheless, as seen now, a quite unprovable phenomenon from our experimental conditions. Due to the coating procedure followed good adhesion between asbestos and polyamide is further ensured and both elasticity modulus and ultimate strength increase.^{18,20}

In the second stage with higher values of the ratio C_N/C_A , excess nylon, noninteracted with epoxy, acts as a plasticizer, decreasing both E and σ_u . Then, in the last stage with even higher C_N/C_A values, resulting in composites of high polyamide concentration but poor in asbestos, regions of pure nylon, dispersed separately in the matrix or partly adhered to the fibers, are likely to exist. Possibly, this polyamide excess acts as a second reinforcing material and this may explain the increase again of both E and σ_u .^{18,20}

In the present paper the behavior of epoxy composites when asbestos fibers coated by the alternative solution method¹⁵ are employed (Case III) is studied. We call these fibers type III asbestos. The experimental data are also treated in a different way, in order to have a better approach to the net effect of the

different existing phases. Thus, a more realistic version of the mechanism already presented is proposed while a comparison with interfacial polymerization based results is further attempted.

EXPERIMENTAL

Fiber Coating Procedure

The dried fibers were treated in a Werner mixer with a nylon 6,6 solution in formic acid. After 1 h mixing, complete wetting was assumed. The product was dispersed in water and washed several times until neutral pH was established. Finally the fibers were dried at 110°C for 2 h and stored in a desiccator above calcium chloride. Characterization of the modified asbestos fibers was based on evaluating the nylon 6,6 content deposited by weight loss, either on ignition in a crucible or by 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.¹⁵

Epoxide Molding Preparation

A similar procedure as described elsewhere was followed¹⁸⁻²¹: 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 P at 25°C.

Triethylenetetramine (TETA) was employed as curing agent, added at a concentration of 8 weight parts per 100 weight parts (phr) of epoxy resin.

To reduce viscosity (i.e. to allow more asbestos to be incorporated with the resin and improve wetting), dibutyl phthalate (DBP) was used, at the level of 15 phr by weight, on epoxy plus TETA basis. Under these conditions, the maximum filler content effected (C_A), on epoxy system (resin + TETA + DPB) basis, was found equal to about 9 phr, instead of the limit of 6 phr encountered in previous studies.¹⁸⁻²¹ It should be mentioned that 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. Under continuous stirring, proper amounts of diluent, asbestos, and curing agent were then added, but the latter after allowing the temperature to decrease to 60°C. The mixture 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. After 24 h at room temperature and 2 h at 50°C, the molding was removed and subjected to a 48 h thermal treatment at 100°C to effect storage independent properties.

Treated asbestos of type III was available at five different qualities, depending on the nylon content deposited (C_N equals 0.8, 2, 4.5, 6.9, or 9 phr).¹⁵ Control moldings were made with uncoated asbestos and also one blank unfilled (matrix). Fiber content (C_A) was kept at the levels of 0.9, 2.6, 5.2, and 8.7 phr. Thus the complete series had 25 different kinds of specimens.

It is worthwhile mentioning here the observation that, independently of C_A , low polyamide contents on asbestos contribute to easier molding process in terms of total viscosity. This is not the case when C_N takes higher values.

Tensile Breaking Tests

All tensile measurements were carried out with a T30K tensile machine (J. J. Lloyd Instruments) at room temperature. The specimens were tested according to the 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%.

Calculations

In this study data from tensile tests are not correlated with C_N and C_A as previously.¹⁸⁻²¹ The reasons are the following: By means of the parameter C_A the effect of the pure asbestos is not "separated" from that of the polyamide phase present as C_A is, by definition, the content of *treated* asbestos in the composite system. On the other hand, C_N does not represent the content of the polyamide phase *in the composite system*, but on the treated fibers. Accordingly, two new parameters are now introduced, C'_A and C'_N , while the basis of our calculations is defined as 100 weight parts of epoxy system (epoxy resin + TETA + DBP).

C'_N represents the polyamide content in the composite system and it is calculated as follows:

$$C'_N = C_N \times [C_A / (100 + C_N)] \quad (1)$$

C'_N is expressed in phr: weight parts of polyamide per 100 weight parts of epoxy system. Obviously, the polyamide phase is introduced in the composite system through the addition of the C_A weight parts of treated fibers per 100 weight parts of epoxy system.

C'_A represents the pure asbestos content in the composite system, i.e., when the polyamide phase contained is excluded. Obviously,

$$C'_A = C_A - C'_N = C_A \times [1 - C_N / (100 + C_N)] \quad (2)$$

Similarly with C'_N and C'_A is expressed in weight parts of pure dried asbestos per 100 weight parts of epoxy system.

RESULTS AND DISCUSSION

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 61.7 MPa, respectively. The subscript m denotes a matrix property, and c , a composite property.

The primary data for epoxy/asbestos III composites are given in Figures 1 and 2, showing the E_c/E_m and $\sigma_{u_c}/\sigma_{u_m}$ values as a function of C'_A for a given value of C_N (nylon content on asbestos).

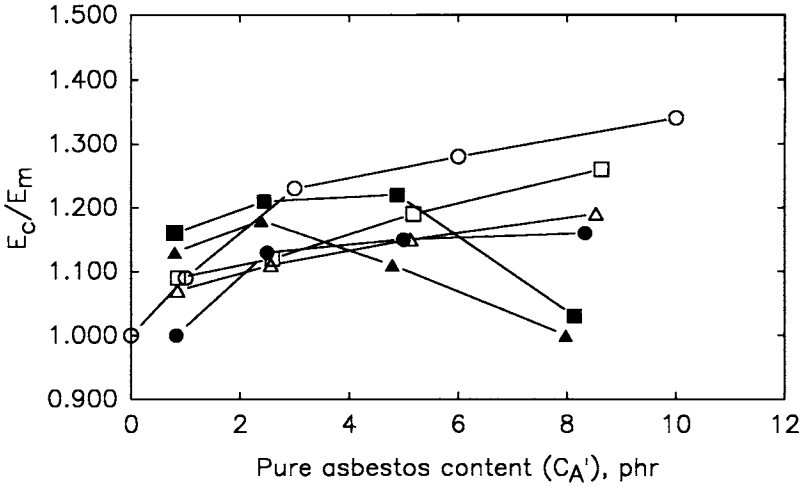


Fig. 1. Plots of relative modulus of elasticity (E_c/E_m) vs. pure asbestos content in the composite system (C_A') at constant polyamide content on the fibers (C_N): (\circ) untreated; (\square) 0.8 phr; (\triangle) 2 phr; (\bullet) 4.5 phr; (\blacksquare) 6.9 phr; (\blacktriangle) 9 phr.

Figure 1 indicates that the modulus of the composite filled with untreated asbestos increases with asbestos content. Similar behavior is encountered from composites based on treated asbestos, but only for low polyamide content values. On the contrary, for C_N more than 4.5 phr a maximum appears, but not at the same C_A' value: The maximum shifts to lower C_A' values as C_N increases.

Turning now to reinforcing aspects, it should be mentioned that the presence of the coating does not result in any improvement with the exception of the highest polyamide contents at very low C_A' values.

In Figure 2 it is shown that all values of ultimate strength (σ_{uc}) for filled

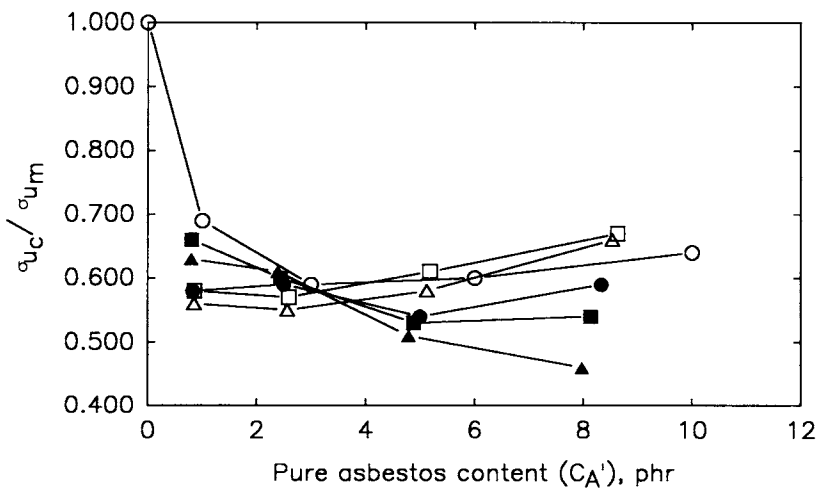


Fig. 2. Plots of relative ultimate strength (σ_{uc}/σ_{um}) vs. pure asbestos content in the composite system (C_A') at constant polyamide content on the fibers (C_N): (\circ) untreated; (\square) 0.8 phr; (\triangle) 2 phr; (\bullet) 4.5 phr; (\blacksquare) 6.9 phr; (\blacktriangle) 9 phr.

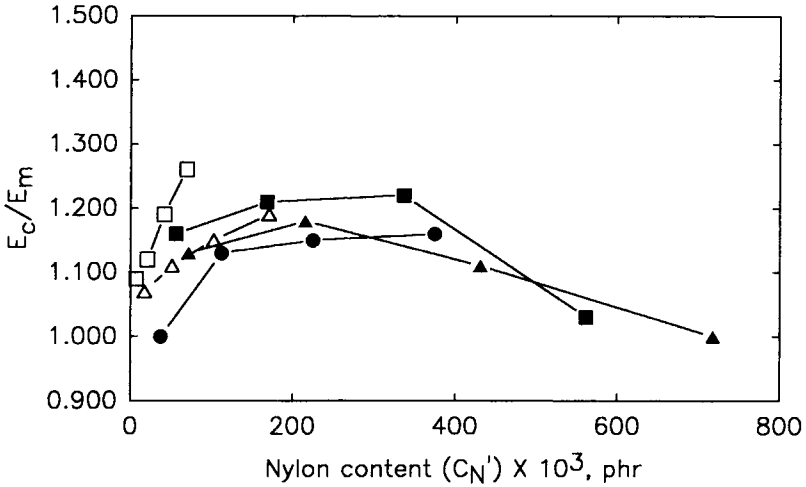


Fig. 3. Plots of relative modulus of elasticity (E_c/E_m) vs. polyamide content in the composite system (C'_N) at constant polyamide content on the fibers (C_N): (\square) 0.8 phr; (Δ) 2 phr; (\bullet) 4.5 phr; (\blacksquare) 6.9 phr; (\blacktriangle) 9 phr.

epoxy specimens are obviously lower than the corresponding value for the matrix (σ_{u_m}) in agreement with similar behavior encountered already.²⁰ Furthermore, specimens with untreated asbestos or of low C_N present a kind of minimum, whereas specimens with the highest C_N values seem not to suggest a minimum but a continuously decreasing trend.

Figures 3 and 4 were made to detect the influence of the total nylon phase C'_N contained in the composite system as a function of the nylon content C_N deposited on the fibers. In Figure 3 it is observed that the modulus increases with C'_N , but only for low C_N values. Afterwards, the slope decreases and even-

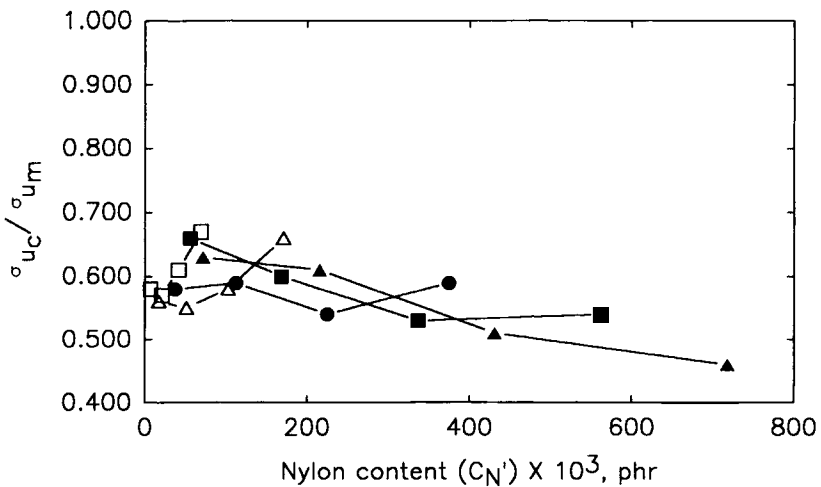


Fig. 4. Plots of relative ultimate strength ($\sigma_{u_c}/\sigma_{u_m}$) vs. polyamide content in the composite system (C'_N) at constant polyamide content on the fibers (C_N): (\square) 0.8 phr; (Δ) 2 phr; (\bullet) 4.5 phr; (\blacksquare) 6.9 phr; (\blacktriangle) 9 phr.

tually a maximum appears. It should be mentioned that for the highest polyamide contents in the system the modulus becomes very low, quite the same with that of unfilled epoxy resin.

In Figure 4 a similar behavior appears. The ratio σ_{uc}/σ_{um} for composites filled with coated asbestos of low C_N (0.8 or 2 phr) increases with the total polyamide content. This is not the case at the highest C_N values where the relative strength shows a continuously decreasing behavior.

Qualitative Model

As already mentioned, 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. 5). On this basis, an attempt to examine cooperation at interface regions becomes of critical importance^{7,8,24-26} for establishing a mechanism fitting the data obtained and also similar when asbestos of type I or II is employed. Accordingly, the following aspects can be considered:

(a) The degree of cooperation between the asbestos and the nylon phase: It is a well-known fact that the coating process followed has a definite influence on the quality of the cooperation effected.^{15,16} In the present case (solution method), it was necessary to deal with viscous polyamide solutions. Such high viscosities are expected to make successful bonding between the high surface area asbestos and the nylon phase deposited quite difficult due to insufficient wetting.

(b) The influence of the molding process: Even if a plasticizer was added and the temperature was increased, the mixture epoxy-coated asbestos still becomes very viscous, and now this makes the wetting of the fibers by the epoxy difficult, probably leading to the appearance of "defects" between the nylon and the epoxy phases.

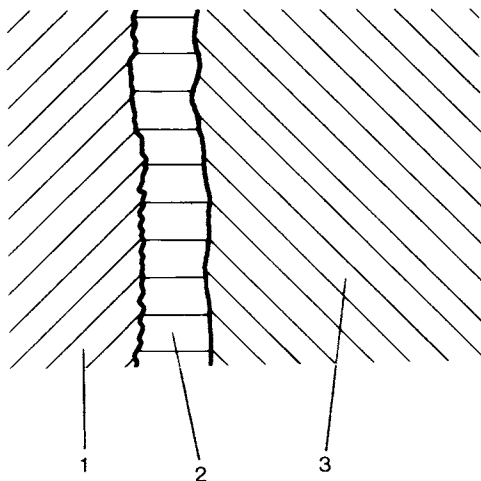


Fig. 5. Representative element of the polyphase materials considered in this study: (1) asbestos; (2) nylon; (3) epoxy.

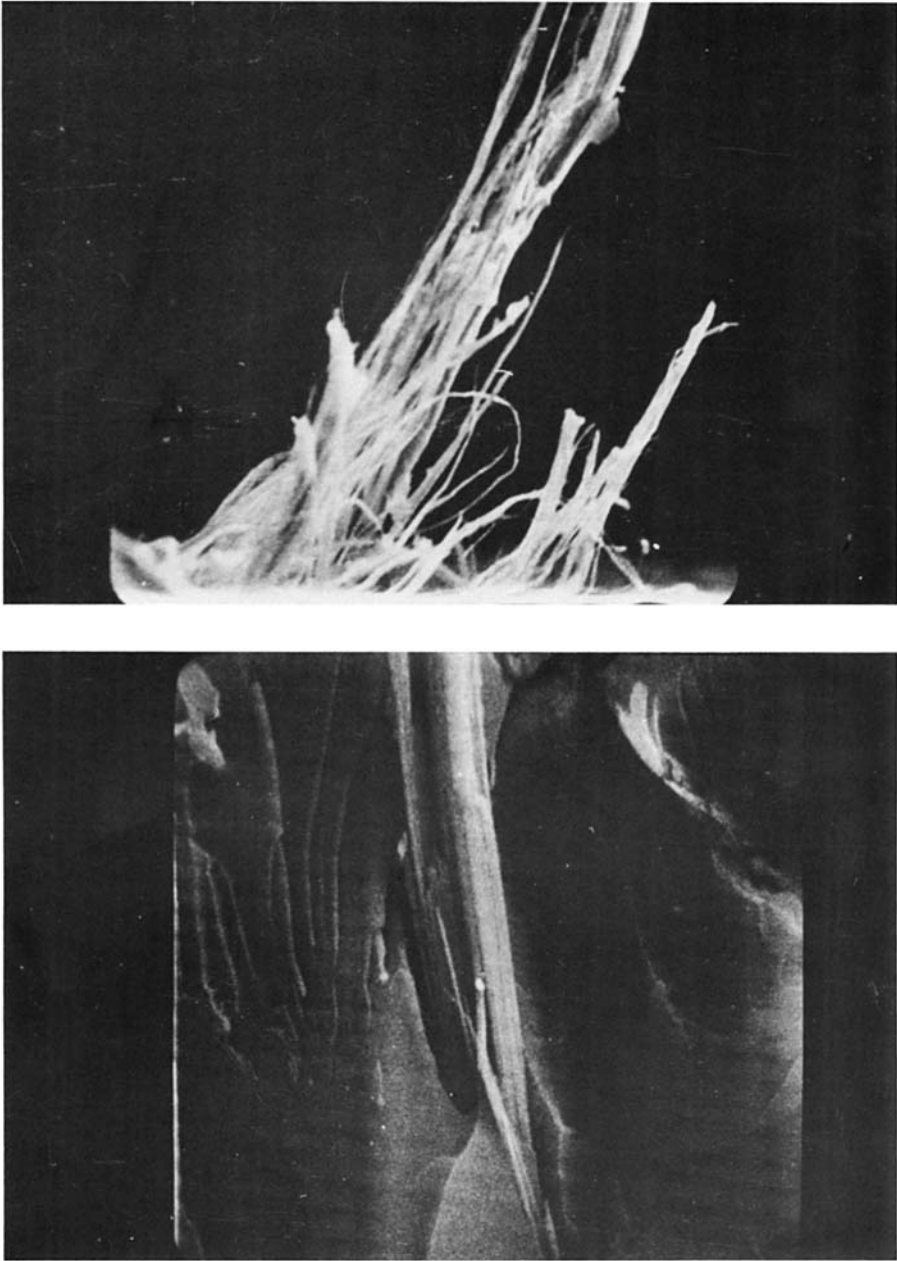


Fig. 6. Chrysotile bundles: (a) untreated ($\times 750$); (b) solution treated ($C_N = 4.5$ phr) ($\times 1000$); (c) interfacially treated ($C_N = 5.8$ phr, Case I) ($\times 450$).²⁰

(c) The fiber roughness. Untreated asbestos provides a high surface area leading to wetting problems, as already referred. Nevertheless, the coating may result in considerable smoothing of the surface with opposite effect on the fiber-matrix cooperation.⁸

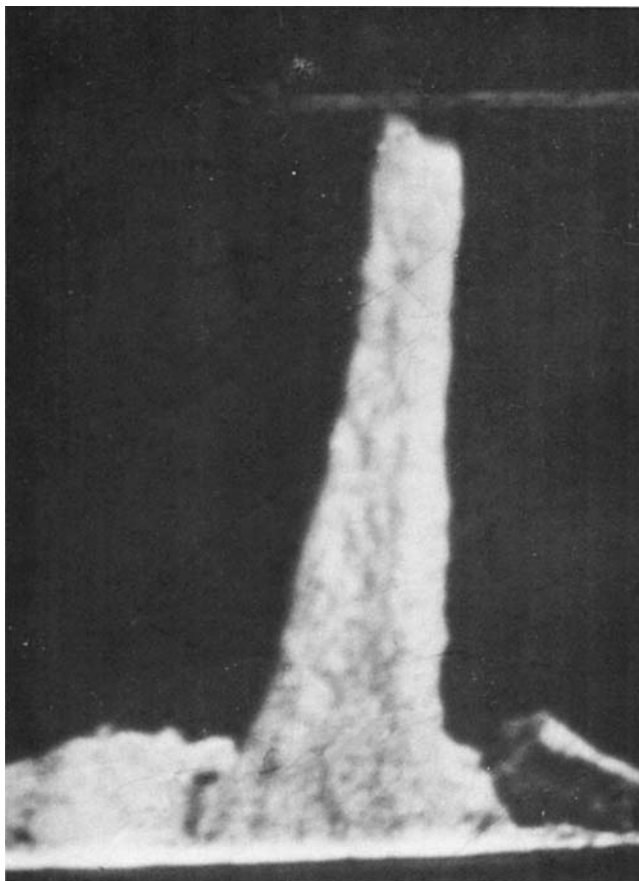


Fig. 6. (Continued from previous page.)

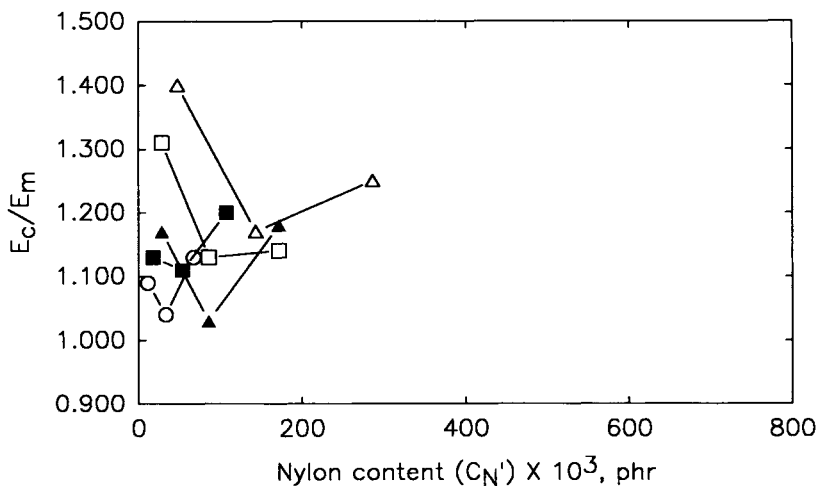


Fig. 7. Interfacial polymerization based pretreatment: Plots of relative modulus of elasticity (E_c/E_m) vs. polyamide content in the composite system (C_N') at constant polyamide content on the fibers (C_N). Case I: (○) 1.3 phr; (□) 3.4 phr; (△) 5.8 phr. Case II: (■) 2.1 phr; (▲) 3.4 phr.

Based on the above points and in order to explain the behavior of E_c/E_m against C'_N (Fig. 3) [or equally against C_A , formula (1)], it is useful to consider that, for the lowest C_N value (0.2 phr), the previously mentioned viscosity problems should not be very important: Neither the polyamide solution during the coating process¹⁵ nor the epoxy-asbestos mixture during molding (see Epoxy Molding Preparation in the Experimental section) were significantly viscous. Thus, no voids are expected and both interphases are satisfactory. The good total bonding obtained, for this asbestos quality, becomes the predominant aspect up to high asbestos contents and an improving tendency is observed.

When C_N increases the picture changes: The higher viscosity of the nylon solution employed to treat the fibers results in the formation of weak points (voids, etc.) between asbestos and nylon. Thus, the nylon phase is easier debonded and the improvement is gradually reduced. For very high C_A values, at a given C_N , the viscosity of the epoxy-treated asbestos mixture increases, wetting problems arise also in the second interphase (epoxy-nylon) and the modulus passes through a maximum. Probably, this maximum could also be observed for low C_N values, but for much higher C_A contents.

It should be mentioned that elasticity modulus in general is lower than the corresponding moduli of composites filled with untreated fibers (Fig. 1). A possible explanation for this behavior is concerned with the roughness factor (c): The solution-based pretreatment results in some smoothing of the asbestos surface, especially at higher C_N values, so that the epoxy coating cannot cooperate very well with the contained treated fibers.⁸ In Figure 6 typical microphotographs of differently treated chrysotile bundles can be seen, arising from the fracture surface of a tensile specimen. Obviously, the solution technique [Fig. 6(b)] seems to result in smoother coating than the interfacial treatment [Fig. 6(c)].

A similar discussion may apply for the σ_{uc}/σ_{um} vs. C'_N plots (Fig. 4). Composites at the lowest C_N value have no voids in the interphases and the improving effect is maintained when C_A increases, i.e., σ_{uc}/σ_{um} increases with C_A or equally with C'_N . On the other hand, at moderate C_N values this improving effect becomes less effective according to the mechanism already proposed while for even higher C_N values the results show negative influence.

The aforementioned suppositions may also explain the mechanical behavior of composites filled with asbestos of type I or II (i.e., coated by the alternative method of *in situ* interfacial polyamidation).^{15,16} As seen in Figure 7, where a similar treatment of the experimental data presented in Ref. 20 is now applied, the modulus values at a given C_N content pass through a minimum as C_A (or equally C'_N) increases. This is valid for all C_N values and both types of interfacial treatment.

It is worth mentioning that for the case of the interfacial polymerization no viscosity problem was observed while coating the fibers. In other words, independently of the C_N value eventually accomplished, the solutions employed (diamine/water and dichloride/ CCl_4) are low viscosity liquids very well impregnating the asbestos structure.^{15,16} Therefore, any increase of C_N is not correlated with viscosity aspects, as for the solution technique where the concentration of the polyamide has a considerable effect on the viscosity of the solution used. In this way, the good bonding between asbestos fibers and nylon phase deposited is always ensured, independently of C_N value. The latter point has

been also previously confirmed by means of extraction experiments and subsequent DSC analysis.¹⁶ This was not the case for solution coated chrysotile.¹⁵

If the above picture given is correct, then one can conclude that for the interfacial polymerization treatment only the interphase between nylon and epoxy is critical to the end properties of the composite system, in contrast with the solution technique where both interphases (Fig. 5) play a significant role. Consequently, turning back to Figure 7, the following interpretation may be given: At low C_A values, independently of C_N , no problem (voids, etc.) in the nylon-epoxy interphase arises and the composite provides a modulus value well above the modulus of the untreated asbestos-epoxy system.^{18,20} Also no considerable "smoothing" of the asbestos surface occurs as the interfacial polyamidation ensures the surface profile of the latter²⁰ (also Fig. 6); i.e., very good cooperation between treated fibers and epoxy is accomplished.

In the same figure when C_A increases, at a given C_N value, the mixture-treated asbestos-epoxy becomes more viscous, and the interphase between coated asbestos and epoxy becomes less satisfactory. This results in decrease of the modulus as C_A increases. Eventually, at even higher C_A values, the asbestos content seems to be a more predominant factor than the problems at the nylon-epoxy interphase leading to a new reinforcing effect.

CONCLUSION

The solution-based coating process does not lead to any noteworthy results, as the tensile performance of the composites prepared is practically worse than that of the untreated fiber-epoxy system. On the contrary, the interfacial polyamidation technique remains a more attractive method for improving the tensile modulus of asbestos-nylon-epoxy composites. Furthermore, correlation of the tensile tests data with the parameters C'_A and C'_N , while taking into account processing stages, seems to allow a more realistic approach for understanding competitive aspects prevailing when the components of the three-species composite system are varied.

References

1. G. L. Wicker, *Composites*, **2**, 221 (1971).
2. S. S. Oleesky and J. G. Mohr, *Handbook of Reinforced Plastics*, Reinhold, New York, 1964, Chap. III-2.
3. C. A. Rader and A. M. Schwartz, NASA Contract. Rep. NASA CR-893, 1967.
4. B. L. Hollingsworth, *Composites*, **1**, 28 (1969).
5. D. C. Phillips and B. Harris, in *Polymer Engineering Composites, Material Science Series*, M. O. W. Richardson, Ed., Applied Science, London, 1977, p. 45.
6. F. L. Pundsack and W. O. Jackson, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley-Interscience, New York, 1967, Vol. 6, pp. 671-690.
7. P. Ehrburger and J. B. Donner, *Phil. Trans. R. Soc. London Ser. A*, **294**, 495 (1980).
8. J. H. Davis, *Plast. Polym.*, 137 (1970).
9. C. Lewis, *Kunst. Plast.*, **32**(7), 6 (1985).
10. J. Hunt, *Eng. Mat. Des.*, **29**(12), 20 (1985).
11. P. Steinau, *Gummi Fas. Kunst.*, **37**(11), 567 (1984).
12. H. J. Schultz, *Gummi Fas. Kunst.*, **37**(11), 558 (1984).
13. H. Roehrens and K. Hillermeier, *Gummi Fas. Kunst.*, **37**(11), 547 (1984).

14. K. Schmauder, *Gummi Fas. Kunst.*, **37**(11), 540 (1984).
15. C. D. Papaspyrides and A. G. Andreopoulos, *Mater. Sci. Monogr.*, **21**, 415 (1984).
16. E. M. Kampouris and C. D. Papaspyrides, *J. Appl. Polym. Sci.*, **33**, 205 (1987).
17. W. G. Potter, *Epoxy Resins*, Iliffe Books, London, 1970, pp. 144-236.
18. G. C. Papanicolaou and C. D. Papaspyrides, *Mater. Chem. Phys.*, **17**, 453 (1987).
19. C. D. Papaspyrides, T. Duvis, and G. C. Papanicolaou, *Mater. Chem. Phys.*, **17**, 531 (1987).
20. C. D. Papaspyrides and G. C. Papanicolaou, *J. Appl. Polym. Sci.*, **36**, 309 (1988).
21. G. C. Papanicolaou and C. D. Papaspyrides, *Compos. Sci. Technol.*, **31**, 261 (1988).
22. B. S. Gorton, *J. Appl. Polym. Sci.*, **8**, 1287 (1964).
23. Y. Y. Wang and S. A. Chen, *Polym. Eng. Sci.*, **20**, 823 (1980).
24. D. B. Eagles, B. F. Blumentritt, and S. L. Cooper, *J. Appl. Polym. Sci.*, **20**, 435 (1976).
25. F. J. McGarry and M. K. Tse, *Elastomer Coated Filler as Toughness Modifier in Glassy Polymers*, MIT, Cambridge, MA, 1985, p. 69.
26. J. L. Kardos, in *Molecular Characterization of Composite Interfaces*, H. Ishida and G. Kumar, Eds., Plenum, New York, 1985, pp. 1-11.

Received February 27, 1989

Accepted September 25, 1989