

# The Influence of Fiber Pretreatment on the Mechanical Properties of Nylon 6,6-Asbestos Composites. II. Interfacial Coating of Asbestos Fibers with a Thin Film of Nylon 6,6

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

## Synopsis

Nylon-asbestos composites comprise a significant proportion of reinforced nylon thermoplastics. To improve the cooperation between matrix and fibers the coating of the asbestos by interfacial *in situ* polymerization is proposed. Previous work on the system chrysotile-nylon 6,6 is extended so that the reactants application order is now inverted, in order to consider any differences in the extraction resistance and the polymerization yield, in conjunction with thermal analysis studies. Experimental results gathered provide severe, but indirect, indications for the development of a strong interface bond between polymer and asbestos fibers.

## INTRODUCTION

Although glass fiber is still the most widely used reinforcing filler for thermoplastics, a wide range of alternative fillers has been proposed. Asbestos fibers should be classified among the most promising inorganic materials giving fiber-filled thermoplastics with properties at least comparable with those of the glass-filled analogues.<sup>1-4</sup> Glass fiber has satisfactory tensile properties, but its stiffness is low. On the contrary, asbestos fibers exhibit an attractive balance of stiffness and strength, a specific stiffness more than twice that of E glass fibers and further, they are cheaper than glass. Asbestos-reinforced plastics have been used for many years in the engineering, aircraft, automotive, chemical, and shipbuilding industries. Chrysotile asbestos, a hydrated magnesium silicate ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) is considered to be the most commercially important. Asbestos referred to in this article is of the chrysotile variety.

Unidirectional composites reinforced with high modulus fibers show an excellent behavior along the direction of reinforcement. However, stress transfer at the interface requires good affinity between matrix and fibers,<sup>5</sup> but also needs to be optimized to prevent the appearance of a worse impact strength.<sup>6</sup>

Good affinity between matrix and fibers depends mainly upon the following three factors:<sup>5)</sup>

- (a) Area of contact (aspect ratio) of the fiber.
- (b) Frictional properties arising from the geometry of the fiber, the nature of the surface, and the degree of gripping of the fiber in the matrix.

- (c) Positive bonding depending upon the chemical nature of the matrix and fiber, and the surface treatment of the latter.

According to Ehrburger and Donnet<sup>6</sup> the above classification is equivalent, by distinguishing the "mechanical bonding model," involving mainly wetting, from the "physical coupling model," involving development of secondary forces, and the "chemical coupling model," in which the adsorption of chemical groups, and the formation of true covalent bonds between fiber and matrix are assumed.

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.<sup>5</sup> Accordingly, the very considerable new surface created makes successful wetting difficult or impossible. For this reason pretreatment of the fibers with a suitable coupling agent has been proposed to effect better dispersion.<sup>7</sup>

Nylon-asbestos composites comprise materials of increased industrial importance.<sup>3,8-10</sup> Focusing our interest on the affinity problem and first on its wetting aspect during the incorporation process, it seemed worthwhile to precoat the asbestos fibers with a strongly adhered film of Nylon 6,6 before utilizing them as reinforcing agents in polyamide matrices. This pretreatment may increase the cooperation between asbestos and polyamide matrix, assuming thorough wetting and development of a strong interface bond between asbestos and coating. On the other hand, further fibrillation of the asbestos may seriously be diminished together with concurrent health problems.

In a previous work<sup>11</sup> we started examining this possibility by proposing two alternative processes, i.e., either interfacial formation of the polymer *in situ* on the fibers or impregnation of the latter with a Nylon 6,6 solution and removal of the solvent. The interfacial process, based on the principles of the interfacial polymerization, involves the serial application to the asbestos of two immiscible solutions of hexamethylenediamine and adipoyl chloride. Diamine can be applied before or after dichloride. The first case (interfacial process I) has already been studied,<sup>11</sup> and in this paper results are presented on the other (interfacial process II), while considering, also in conjunction with thermal analysis studies, any differences arising.

## EXPERIMENTAL

**Coating Procedure.** After drying at 110°C for 2 h, 200 g of chrysotile asbestos were treated in a Werner mixer to ensure homogeneous wetting for 10 min with an adipoyl chloride solution in carbon tetrachloride (40 mL)\*. Subsequently, an aqueous solution of hexamethylenediamine (80 mL) was added together with pulverized sodium carbonate. Mixing was continued for 30 min, the reaction product was dispersed in about 10 L of water, and then washed several times in a centrifugal separator until neutral pH. Finally, the treated fibers were dried in a circulating air oven at 110°C for 2 h and stored in a dessicator above calcium chloride.

\*Volumes or concentrations of solutions are given on solvent basis, i.e., before the addition of the reactant.

**Characterization.** The characterization of the modified asbestos fibers was based on the following physical and chemical methods: (a) Determination of Nylon 6,6 content by weight loss on ignition; (b) determination of nongrafted Nylon 6,6 content by extraction; (c) infrared spectroscopy; (d) microscopy studies and (e) differential thermal analysis. The experimental procedures followed have already been reported,<sup>11</sup> except for DTA: Fiber samples of 70–80 mg were heated in air atmosphere at a rate of 10°C/min from room temperature to 1000°C. A Netzsch STA Model 429 instrument was employed.

## RESULTS AND DISCUSSION

Interfacial (II) coating of chrysotile fibers with Nylon 6,6 was studied according to the experimental conditions given in Table I. The ratio  $K$  of the reactants molar concentrations (diamine/dichloride) was again kept equal to 2.5,<sup>11</sup> as any considerable deviation from this value is not accompanied with higher yields.<sup>12</sup> The quantity of sodium carbonate added was twice that of the diamine.

Asbestos fibers treated as above were extracted with typical polyamide solvents, either formic acid or hot benzyl alcohol. The polymer dissolved was reprecipitated in a nonsolvent, such as water or methanol, and identified by infrared spectroscopy. A typical polyamide spectrum was obtained, i.e., a significant absorbance at 1640  $\text{cm}^{-1}$ , however characteristic also of the chrysotile,<sup>13</sup> together with absorbances at 3300 and 1540  $\text{cm}^{-1}$ .

In Table I also are given results of weight loss on ignition determinations for unmodified and modified asbestos. From these data the polymer content of the fibers can be easily calculated (expressed in g of polymer per 100 g of untreated asbestos). Furthermore, microscopy studies before and after treatment revealed, in accordance with process I,<sup>11</sup> that the modified material seems to be composed of fibers entrapped into a polymer matrix.

**Extraction Studies.** Extraction tests for studying the nature of the interfacial bond developed between coating and substrate are varied.<sup>14</sup> In Figure 1 a correlation is shown between the polyamide content remaining after the extraction process, either with formic acid or benzyl alcohol, and that initially present. All data quoted are based on weight loss on ignition determinations and correspond to successive extractions of the same sample until constant

TABLE I  
Interfacial (II) Formation of Nylon 6,6 on Chrysotile Fibers

Coating run	Dichloride concentration (g/dL $\text{CCl}_4$ )	Diamine concentration (g/dL $\text{H}_2\text{O}$ )	Weight loss (% w/w)	Polyamide content determined (phr)
Unmodified	—	—	14.0(0.9)*	0.0
1	34.75	55.00	14.3(1.7)	0.3
2	50.00	79.25	15.7(0.5)	2.1
3	62.50	99.00	16.8(0.9)	3.4
4	75.00	118.88	16.7(1.1)	3.3

\*Standard deviation of weight loss measurements (%).

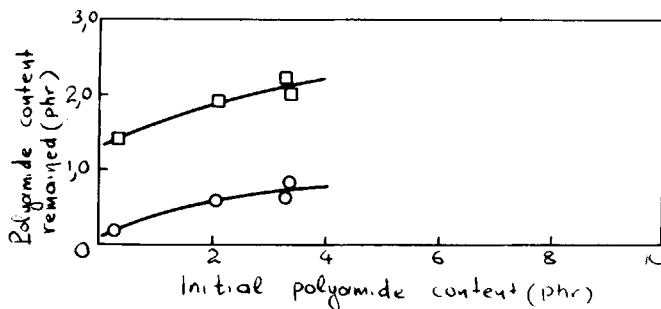


Fig. 1. Polyamide content remained after extraction versus that initially present. (O) Formic acid; (□), benzyl alcohol.

weight loss.\* Clearly, formic acid shows a greater effectiveness compared with benzyl alcohol; nevertheless, under the experimental conditions followed, a considerable amount of polymer formed resists removal out of the fibers. In addition, this residual polyamide content seems to increase slightly over that initially contained, which is in agreement with similar results obtained with procedure I.<sup>11</sup> In other words, the interfacial method, either I or II, is clearly differentiated from the "solution" one,<sup>11</sup> as in the latter case formic acid has a much greater sweeping influence on the coated fibers.

Asbestos treated interfacially (II) and then extracted, either with formic acid or benzyl alcohol, was further studied by infrared spectroscopy. The well known absorbances at 3300 and 1540  $\text{cm}^{-1}$  were not clearly distinguished. In accordance with interfacial process I,<sup>11</sup> this is possibly due to the very low concentrations of the polymer matter still present. Furthermore, microscopy studies did not lead to any clearer results.

**DTA Studies.** To investigate further the modification process followed, it seemed worthwhile to study the treated asbestos fibers by a technique more sensitive than infrared spectroscopy. Accordingly, differential thermal analysis was chosen: The presence of Nylon 6,6 resistant to washing out could be definitely confirmed by a fiber thermogram in which the typical characteristics of this particular polymer would appear.<sup>15,16</sup>

DTA studies included asbestos fibers coated interfacially (either I or II) and then extracted with formic acid. On the other hand, uncoated asbestos, treated simply with formic acid and then washed and dried, was used as a reference sample in all tests to exclude any solvents' effects. In Table II a brief description of typical samples studied is given, together with data on weight loss either by ignition in a crucible or DTA. Clearly, no significant deviation arises between the two techniques and therefore the values of the organic content already referred to are considerably reliable.

In Figure 2 are shown DTA thermograms recorded from the typical samples of Table II. The curves are extended within the temperature range of interest, i.e., between 150 and 600°C.<sup>17</sup> Figure 2(a) corresponds to the reference sample containing no polymer. The absence of a distinct peak is evident. On the

\*Usually two extractions are sufficient.

TABLE II  
 Typical Results on Characterization of Asbestos Samples Treated Interfacially and  
 Then Extracted with Formic Acid

Sample ref. code	Sample description	Weight loss (20–1000°C)		Polyamide content (phr)
		Ignition <sup>11</sup> (% w/w)	DTA (% w/w)	
a	Asbestos treated with formic acid (Reference sample)	13.1	13.0	—
b	Asbestos treated interfacially (I)	18.7	18.6	5.8
c	Sample (b) extracted 3 successive times	14.2	14.3	1.2
d	Asbestos treated interfacially (II)	16.8	16.8	3.4
e	Sample (d) extracted 3 successive times	13.8	13.7	0.8

contrary, an asbestos sample rich in polyamide content and prepared according to the interfacial process I [Fig. 2(b)] gives a strong exothermic peak at 340°C. This particular peak has been interpreted as revealing the oxidative degradation of Nylon 6,6,<sup>17</sup> and it is also present in the thermogram of the typical sample (d) [Fig. 2(d)] prepared by the interfacial procedure II.

It is of great importance that after three successive extractions with formic acid the peak considered has not been eliminated [Fig. 2(c) and (e) corresponding to the extracted samples (b) and (d), respectively]. Furthermore, its size seems to be proportional to the remaining polyamide content.

At 405°C another exothermic peak has been detected for the case of the Nylon 6,6 tested in air atmosphere.<sup>17</sup> This peak should correspond to the weak exotherm appeared at 420°C in our thermograms [Fig. 2(b) and (d)], but not easily detected in the extracted fibers [Fig. 2(c) and (e)]. The nature of the substrate may be responsible for the temperature shift observed.

**Yield Aspects of the Interfacial Process II.** From the data already quoted (Table I) yield values of the polymerization runs carried out were

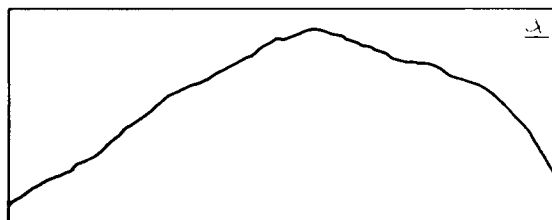


Fig. 2. DTA thermograms (150 to 600°C shown) of asbestos samples coated interfacially and then extracted three successive times with formic acid: (a) Reference sample (a) (Table II); (b) Sample (b), polyamide content 5.8 phr, process I; (c) Sample (c), after extraction, polyamide content 1.2 phr; (d) Sample (d), polyamide content 3.4 phr, process II; (e) Sample (e), after extraction, polyamide content 0.8 phr.

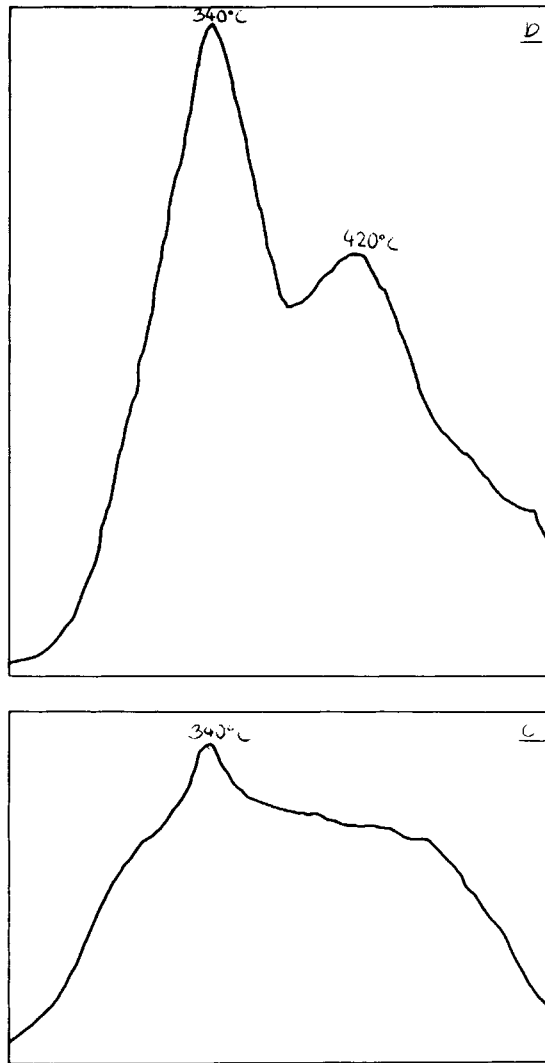


Fig. 2. (Continued from previous page.)

determined as follows:

When complete conversion to polymer of the reactant not in excess (dichloride) is supposed, the "expected" polyamide content ( $c_e$ ) of the fibers is easily calculated and then the corresponding yield of the interfacial reaction through the value of the polymer content determined ( $c_d$ ). Accordingly, in Figure 3 the relationship between  $c_d$  and  $c_e$  is shown, while in Figure 4 a correlation between yield and reactant concentration is attempted. For comparison similar results are presented from interfacial process I.<sup>11</sup>

From Figures 3 or 4 important differences appear: It is significantly more difficult to increase the yield by following interfacial process II. In other words, more concentrated solutions should be employed for considerable polyamide contents maintained lower than those corresponding to interfacial

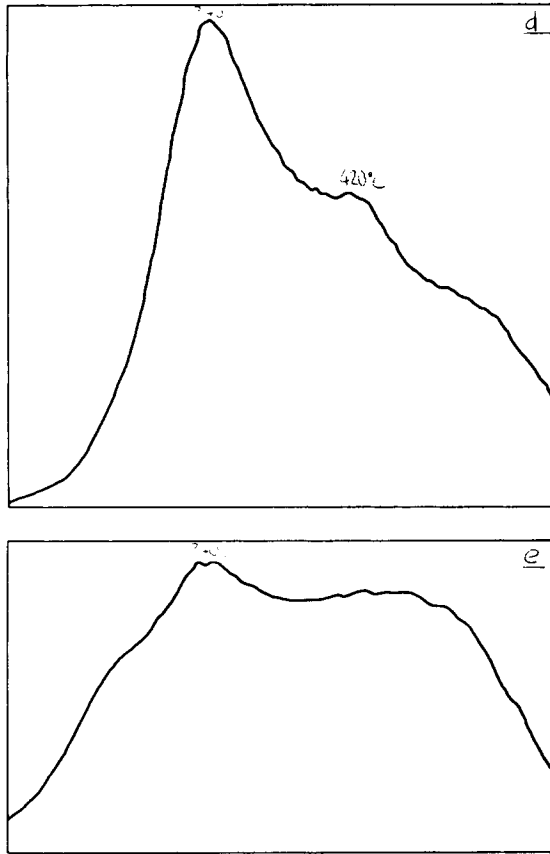


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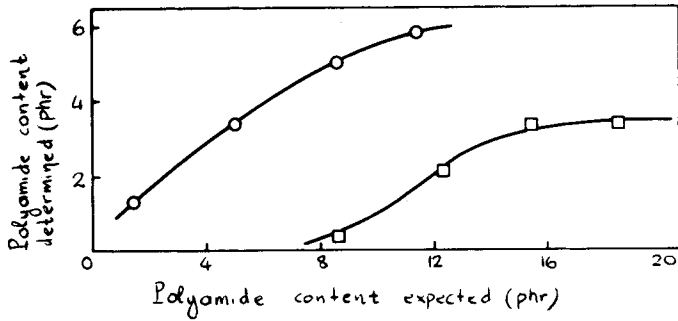


Fig. 3. Correlation between polyamide content expected and determined: (○) Interfacial process I; (□) interfacial process II.

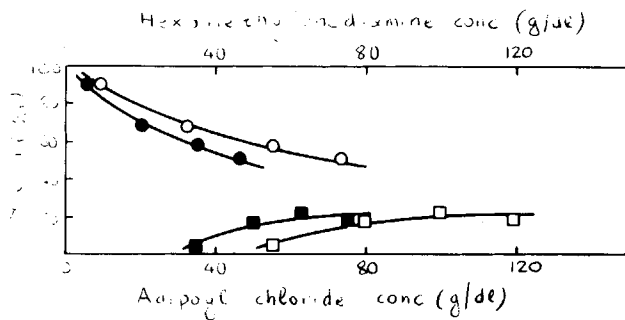


Fig. 4. Yield of the interfacial processes I and II versus reactants concentration: (○) Diamine, I; (●) dichloride, I; (□) diamine, II; (■) dichloride, II.

process I. Furthermore, the yield of interfacial polymerization II increases with reactant concentration in contrast with polymerization I.

This different behavior could be explained in terms of the chemical response of the asbestos fibers when they are combined with organic polymers. It is well known that the dominant chemical feature of chrysotile is its strongly basic nature.<sup>18</sup> Accordingly, when process II is applied significant hydrolysis of the dichloride leading to negligible polymerization yields should be expected.<sup>19,20</sup> Furthermore, the yield seems to increase in a parabolic way versus dichloride concentration [Fig. 4(II)], but still the values attained are very low. In other words, the fiber substrate appears to "consume" considerable quantities of the reactant. On the other hand, when the basic hexamethylenediamine is applied first (process I), such interactions between fiber and reactant are expected to be significantly lower, and indeed the yield of the interfacial polymerization reaches high values. However, by increasing the quantity of the reactants added, the diffusion of the diamine into the organic phase becomes slower and therefore the yield continuously decreases [Fig. 4(I)].<sup>21</sup>

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