

A New Coupling Agent for Aramid Fibers

A. G. ANDREOPOULOS, *Laboratory of Special Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, 42 Patission Str., 106 82 Athens, Greece*

Synopsis

Various compounds were used for the surface treatment of aramid fibers in order to promote adhesion to polymeric matrices. The improvement of adhesive bond could be based either on the roughness of fiber surface or on chemical modification introduced by grafting. The compounds used are more or less reactive to the secondary amide groups, present on the aramid chain. Thus, the fibers were impregnated with acetic acid anhydride, sulfuric acid-acrylamide, and methacryloyl chloride. The effect of such treatment was first evaluated by optical microscopy and infrared analysis. Tensile measurements were also carried out in order to define any changes of strength and modulus. Finally, tensile specimens were prepared using unsaturated polyester reinforced with aramid fibers and the effect of chemical treatment on the tensile strength was determined. From the above study, methacryloyl chloride was proved an effective coupling agent with possible grafting to aramid fibers.

INTRODUCTION

The fibers made of aromatic polyamides present superhigh tensile modulus and high strength accompanied by exceptional heat and flame resistance. Since the physical properties differences between fibers of aromatic and aliphatic polyamides are greater than those between other existing classes of fibers, a new generic term for fibers from aromatic polyamides was requested by the E. I. du Pont de Nemours and Co. in 1971. The U.S. Federal Trade Commission has adopted, in 1974, the term "aramid" for designating fibers of the aromatic polyamide type: "Aramid—a manufactured fiber in which the fiber forming substance is a long-chain synthetic polyamide in which at least 85% of the amide ($-\text{CO}-\text{NH}-$) linkages are attached directly to two aromatic rings."¹

Many works have already been published dealing with the behavior, handling, and properties of aramid fibers. Thus, Preston studied the flame resistance of a large number of aromatic polyamides.² A comparative study comprising aramid, carbon, and glass fibers as well as their composites, was presented by von Hillermeier.³ Vaughan investigated the interfacial adhesion between aramid fibers and epoxy or polyester matrices.⁴ Many studies deal with the mechanical behavior and fiber-matrix interactions⁵⁻⁷ whereas enough data are reported on the physicochemical and structure properties of aramid fibers.⁸⁻¹¹

Some attempts are reported to reinforce acrylic polymers by the incorporation of aramide fibers,¹² but some discouraging results have, also, been

EXPERIMENTAL**Materials**

The two types of aramid fibers used were Kevlar 49 and Kevlar pulp, products provided by E. I. du Pont de Nemours and Co. These two types of reinforcement differ only in the spinning process. Kevlar 49 aramid fiber are continuous with a diameter of about $12\ \mu\text{m}$ whereas Kevlar pulp is consisted of discontinuous fibers with $12\text{--}15\ \mu\text{m}$ diameter. The chemicals used to attack aramid fibers and cause grafting are as follows:

- a. acetic acid anhydride (Puro, Carlo Erba);
- b. methacryloyl chloride (Purum, Fluka AG);

TABLE I
Effect of Treatment on the Tensile Strength of Kevlar 49

Fiber	Tensile load at break (N)	Strength loss (%)
Kevlar 49	232 ± 5	—
Acetic-anhydride-treated	139 ± 14	40
Chloride-treated	188 ± 11	19
Sulfuric-acid-treated	56 ± 8	75.9

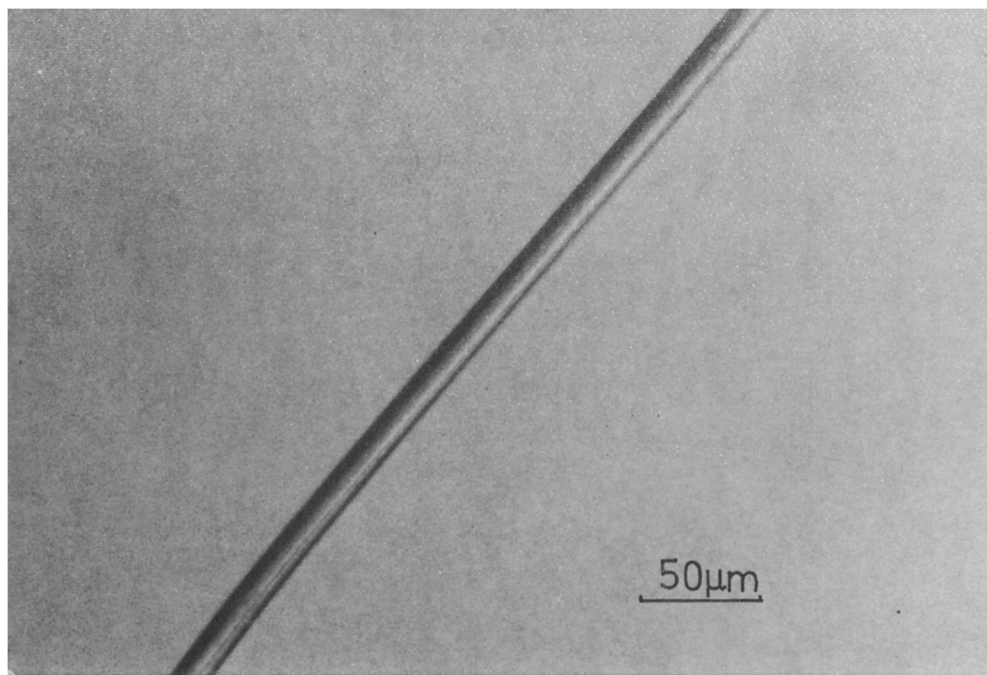


Fig. 2. Micrograph of Kevlar 49 monofilament.

- c. sulfuric acid (analytical reagent, Mallinckrodt Chemical Works);
- d. acrylamide (97%, Aldrich Chemical Co.).

Method

The treatment of Kevlar 49 fibers with acetic acid anhydride provides boiling for 1 h whereas methacryloyl chloride was allowed to react with fibers at room temperature. The above process is expected to lead to grafting of the reactive chemicals in the aramid chain.

An attempt for the grafting of acrylamide units was also made, in the following way. A 20% solution of sulfuric acid in propylene glycol was used to impregnate the Kevlar 49 fibers. After washing with water, the fiber were treated with a 10% acrylamide solution in isopropanol. The fibers were then dried and then cured in a vacuum oven at 85°C and 200 mm Hg. Kevlar pulp was only reacted with methacryloyl chloride.

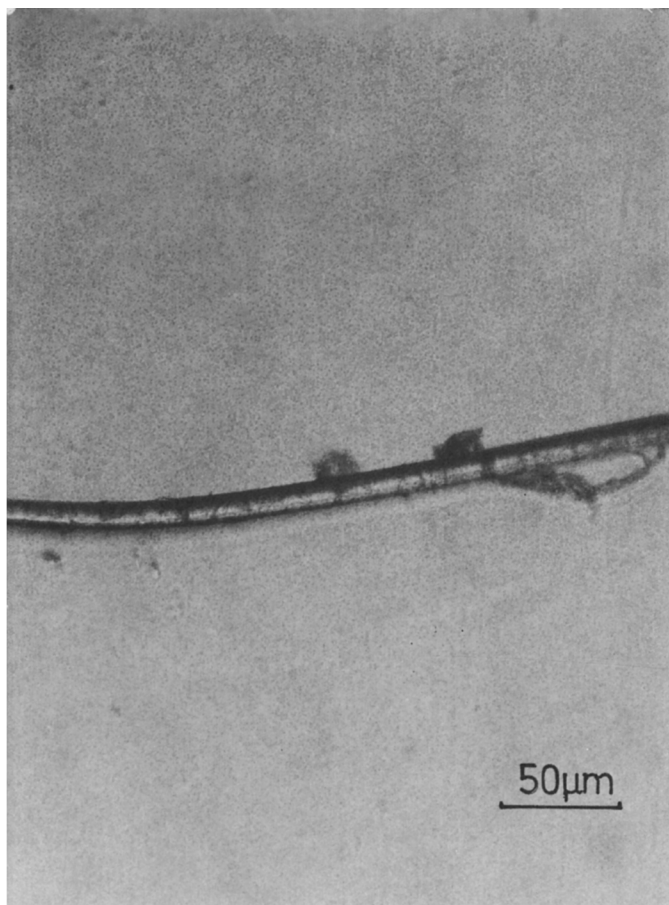


Fig. 3. Fiber treated with methacryloyl chloride.

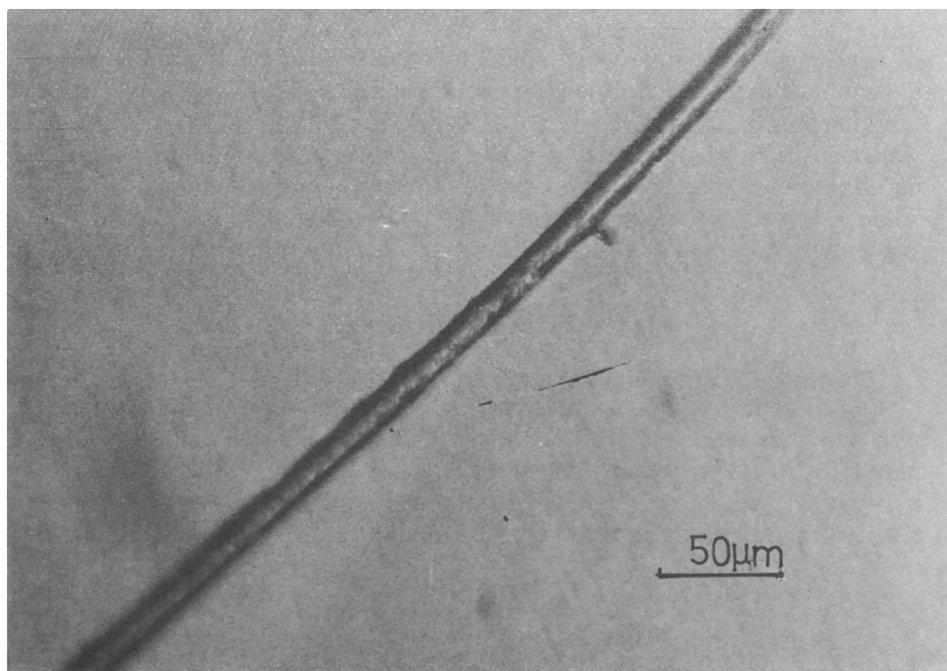


Fig. 4. Fiber treated with acetic acid anhydride.

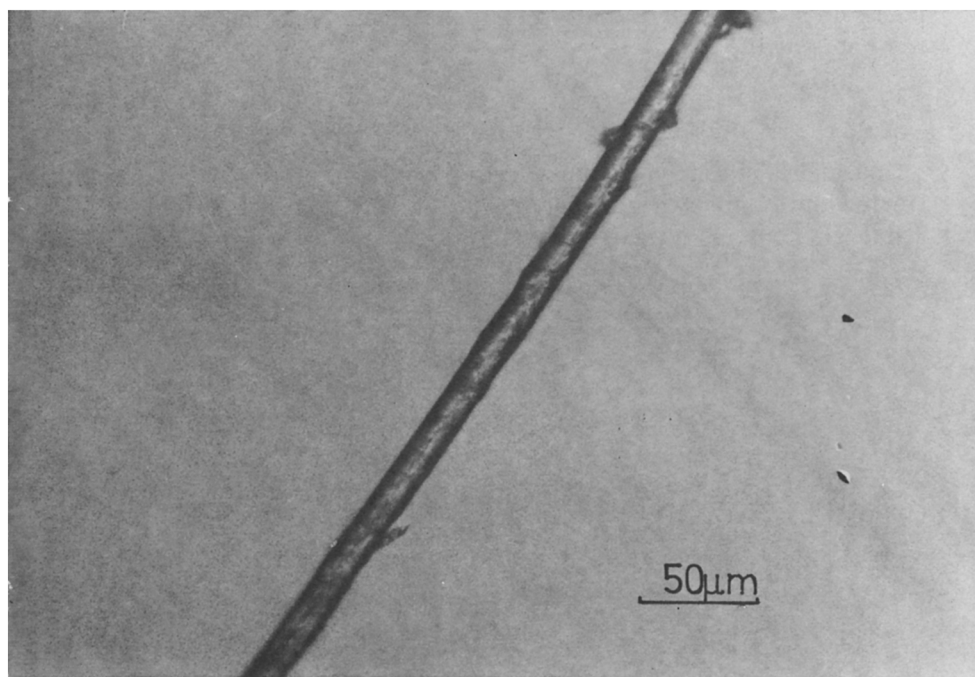


Fig. 5. Fiber treated with sulfuric acid-acrylamide.

Tensile Measurements

The tensile strength of the above-treated fibers was measured in order to determine the degree of strength loss. The specimens were prepared using 15 cm long multifilaments, mounted at both ends between polyester sheets, as shown in Figure 1. Mounting was carried out using unsaturated polyester as an adhesive, covering the ends enough in order to surpass the critical length. This is necessary to ensure fracture instead of pulling out and must be accompanied by proper fiber alignment in order to obtain reliable results.

Optical Microscopy

The treated fibers were observed using a Amplival Optical Microscope (Jenoptik Jena GmbH) equipped with a camera to record and reproduce by photographic means microscopic images. The aim of such observation under magnification is to determine visually any changes of the fibers shape caused by etching. We obtain, therefore, an indicative picture of the surface roughness which can lead to improved adhesion, but also to reduced fiber strength.

Infrared Spectroscopy

Infrared transmission spectroscopy was performed in order to detect any grafted group. The treated fibers were thoroughly washed with ethanol and water to remove the unreacted chemicals. After drying at 100°C for 4 h, the fibers were finely divided using a microtome blade and mixed with potassium bromide to a weight ratio approximately 3 : 1000. The tablets prepared were placed in a Perkin-Elmer 283B spectrophotometer, and the respective spectra were obtained.

Preparation of Reinforced Polyester Specimens

Specimens of reinforced unsaturated polyester were prepared using untreated and treated with methacryloyl chloride Kevlar pulp. Specimens A (see Table II) contain untreated Kevlar pulp, which was dispersed as received

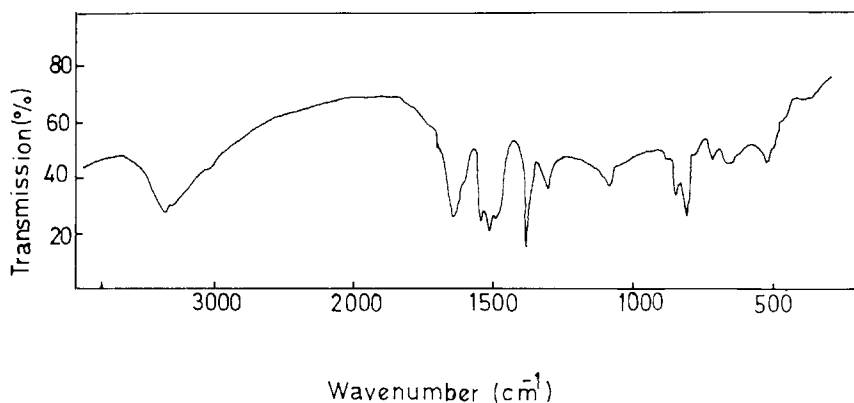


Fig. 6. Infrared spectrum for the original and acetic-acid-anhydride-treated Kevlar 49 fiber.

within the polyester matrix. Specimens B and C contain untreated and chloride-treated fibers, respectively, but the incorporation was carried out after dispersion of the Kevlar pulp into water. For the dispersion 10 g of fibers were added to 250 mL of water containing 0.5% of a nonionic surfactant and thoroughly stirred for 30 min. The wet pulp was then filtered and repeatedly washed with water and methanol and, finally, dried in an air circulating oven at 80°C for 1 h. The above process allows the disentangling of the fibers ensuring better dispersion in the polymer matrix. In all cases, the polyester/fibers weight ratio was 100/3.

For the tensile tests, the ASTM D 638²⁰ specification was followed, using type IV dumbbell specimens. A JJ Instrument tensile machine was used with a common type of grips and working at a separation speed 50 mm/min. In all cases five specimens were tested, and the mean values were determined.

RESULTS AND DISCUSSION

The results obtained from the tensile tests on treated Kevlar 49 fibers are shown in Table I. It is evident that the tensile strength decreases in all cases of treatment. This fact is a result of the etching, created to a higher or lower degree, by the chemical agents used. The selection of these chemicals is, of course, based on their reactivity to the secondary amide group, so that a possible grafting could be expected. Nevertheless, the reactivity of the compounds used could result in a rough fiber surface, reducing its original strength.

The most important weakening is caused by concentrated sulfuric acid which is also a solvent for aramid. This dramatic strength loss is, of course, prohibitive for any further fiber application.

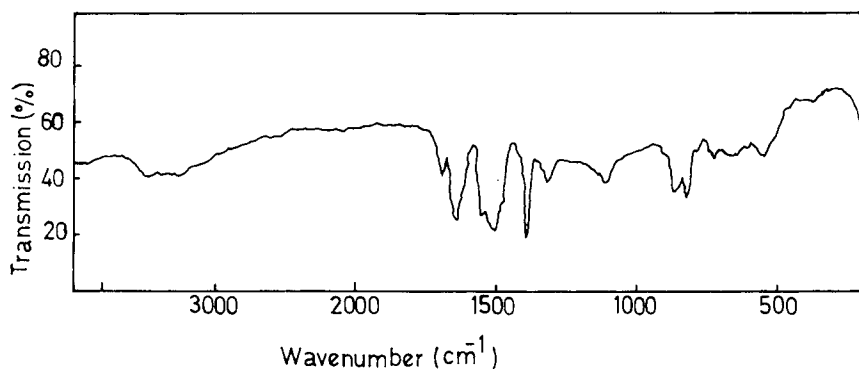


Fig. 7. Infrared spectrum for chloride-treated Kevlar 49 fiber.

TABLE II
Tensile Strength of Reinforced Polyester Specimens

Sample	Tensile strength (MPa)	Strength increase (%)
A	25.0 ± 2.7	—
B	28.2 ± 1.9	12.8
C	41.5 ± 3.7	64.8



Fig. 8. Fracture surface for sample A.



Fig. 9. Isolated fiber on the fracture surface of sample A.

The treated fibers under magnification, are shown in the micrographs of Figures 2-5, which were obtained by the optical microscopy. It is clear that chemical treatment develops a surface roughness whereas untreated Kevlar 49 present an almost perfect cylindrical shape (Fig. 2). Intermediate degree of roughness is shown in Figures 3 and 4, which correspond to treatment with methacryloyl chloride and acetic acid anhydride, respectively, but the most severe etching is caused by sulfuric acid-acrylamide treatment, as Figure 5 presents. The view of the Kevlar fiber after the sulfuric acid treatment combined with the extremely low mechanical strength means that any further study on these fibers is rather worthless.

The infrared spectrum of Kevlar 49 fibers is shown in Figure 6, but also the fibers treated with acetic acid anhydride present essentially the same spectrum pattern. The spectrum taken from the chloride treated fibers can be seen

in Figure 7, where some changes appear in respect with Figure 6. First, a decrease in the intensity of 3440 cm^{-1} absorption band (due to the secondary amide group) can be observed, accompanied by the appearance of a band at 1720 cm^{-1} due to the group $-\text{CH}=\text{CH}-\text{CO}-\text{O}-$. However, no evidence exists about the development of tertiary amide groups, as a result of the direct amidation of the group $-\text{NH}-\text{CO}-$ by methacryloyl chloride. This fact could be possibly attributed to the overlapping of the 1650 cm^{-1} band by absorption bands already present in the spectrum of untreated Kevlar fibers.

Finally, the results of the tensile measurements on reinforced polyester specimens, are presented in Table II. It is clear that best results are given by the treated Kevlar pulp. As a matter of fact, sample C presents 65% improved tensile strength in comparison with sample A, which contains untreated Kevlar. An intermediate strength increase is, also, presented by sample B which contains Kevlar pulp formerly suspended in water for fiber disentan-



Fig. 10. Fracture surface of sample B.



Fig. 11. Fracture surface of sample C.

gling. The micrographs of the fracture surfaces of the above samples A, B, and C are shown in Figures 8–11.

Figures 8 and 9 present the isolated Kevlar fibers on the fracture surface of sample A. This is a result of the poor adhesion of the untreated fibers to the polymer matrix. Similarly, Figure 10 indicates isolated fibers, but the disentangling occurred by the suspension in water is also clear. Finally, Figure 11 presents fibers covered with matrix fragments, as a result of the strong adhesion or the chemical bonding.

CONCLUSIONS

The above discussion can lead to the following conclusions:

1. Strong chemical means, such as sulfuric acid, acetic anhydride, and methacryloyl chloride, are suitable for the etching of aramid fibers.
2. Sulfuric acid dramatically reduces fiber strength.
3. Acetic acid anhydride produces surface roughness on the surface of the aramid fibers, but there is no evidence for chemical reaction.

4. Methacryloyl chloride creates intermediate roughness and possibly chemical grafting, but, in any case, the adherence of the chloride-treated aramid fibers to an unsaturated polymer matrix is considerably favored.

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