Treated Aramid Fibers as Reinforcement in Nonpolar Matrices

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Synopsis

Crosslinked polyethylene finds extensive use in applications where improved thermal resistance is required. Furthermore, reinforced and crosslinked polyethylene presents high strength at elevated temperatures, so that the field of applications of such materials is considerably enlarged. Aramid fibers seem to be a promising reinforcement for the above materials since they combine high modulus with thermal resistance and light weight. The development of an adequate adhesive bond between aramid fiber and polyethylene matrix is of course the main problem, taking into consideration that both polyethylene and aramid present reduced chemical affinity to other substances. Thus, fiber pretreatment was performed in order to insert unsaturated groups in the aramid chain. These groups could be, in turn, grafted in the polyethylene backbone during the crosslinking reaction. The aramid fibers were treated with methacryloyl chloride, and then dispersed under stirring in 2% aqueous sodium hydroxide containing 0.5% of a nonionic surfactant. After washing and drying, the fibers were dry blended with polyethylene powder containing 2 phr dicumyl peroxide. The mixture was melt-blended in a Brabender plasticorder and tensile specimens were prepared. Tensile measurements and microscopy on the fracture surface were carried out in order to evaluate changes introduced in the fiber by surface treatment.

INTRODUCTION

It is well known that crosslinking of polyethylene (PE) is a modification leading to products with improved thermal stability. This fact allows the introduction of PE to applications requiring dimensional stability and strength at elevated temperatures, such as hot water pipelines, etc.[1,2] Many authors studied the existing techniques, i.e., chemical or radiation-induced crosslinking, the changes of properties, the final product behavior, etc. However, the reinforcing of crosslinked PE with fibrous materials is not extensively studied whereas many data are available concerning reinforcing with particulate fillers.

The incorporation of fibers into crosslinked PE is expected to improve significantly its mechanical strength at elevated temperatures where the final product could find extensive use. Thus, a recommended reinforcement for this case must combine high strength and modulus with heat resistance and, among the organic fibers, the aramid seem to be the most promising reinforcing agent.

Aramid fibers are made of aromatic polyamides and present high 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
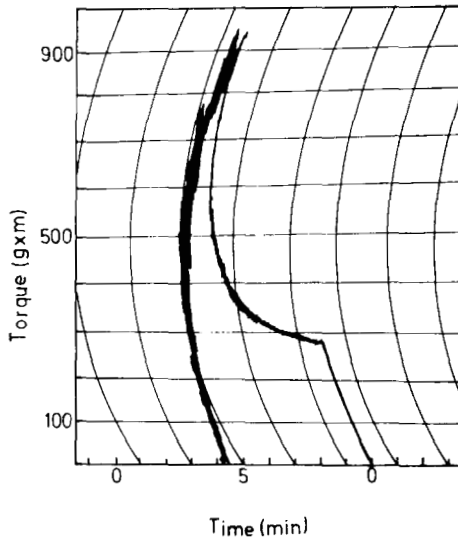
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Fig. 1. Typical mixing torque-time curve from Brabender Plasticorder.

of fibers, a new generic term for fibers from aromatic polyamides was re-
quested by DuPont 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
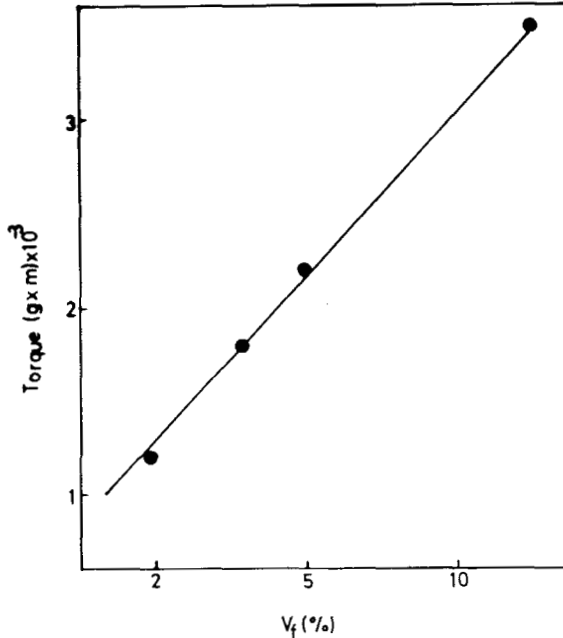($-CO-NH-$) linkages are attached directly to two aromatic rings."[3]

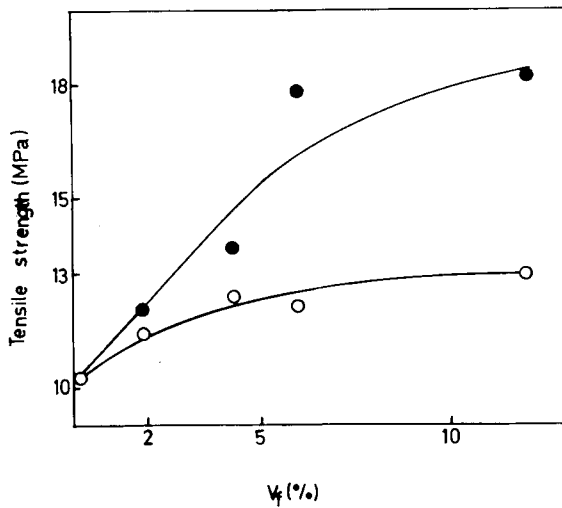Fig. 2. The mixing torque as a function of filler volume fraction.

Fig. 3. The tensile strength versus V_f, for specimens reinforced with treated and untreated aramid fibers. ●: treated, ○: untreated.

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.[4] A comparative study comprising aramid, carbon, and glass fibers as well as their composites, was presented by von Hillermeier.[5] Vaughan investigated the interfacial adhesion between aramid fibers and epoxy or polyester matrices.[6] Many studies deal with the mechanical behavior and fiber–matrix interactions[7-9] whereas enough data are reported on the physicochemical and structure properties of aramid fibers.[10-13]
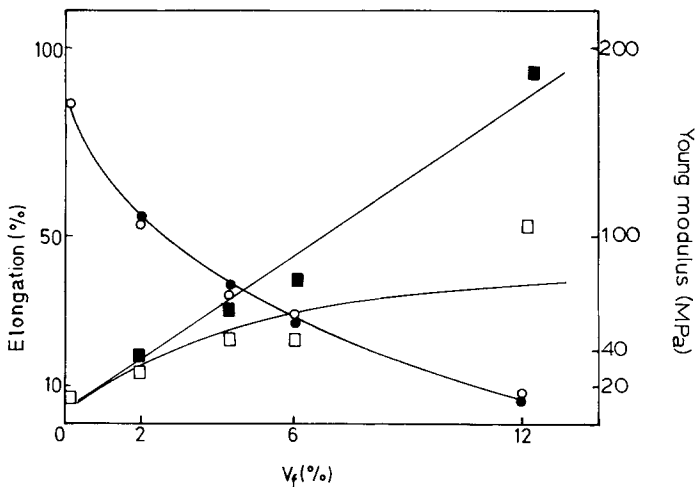

Fig. 4. The percentage elongation as a function of filler volume fraction. ○: untreated fibers, ●: treated fibers, □: untreated fibers, ■: treated fibers.

Although aramid fibers are a reinforcement which could readily combine with most resins used in composites manufacture, experience has shown that their poor interfacial adhesion to the resin matrix can lead to compressive breakdown. In order that the excellent properties of aramid fibers may be fully utilized as reinforcing agents, it is apparent that improvement must be made in the area of interlaminar adhesion. Thus, Vaughan[6] applied a number of commercial coupling agents and obtained some improvement. Eagles, Blumentritt, and Cooper[14] studied the adhesion of Kevlar 49 monofilaments to thermoplastic polymers. They performed three different surface treatments and concluded that boiling in water improves adhesion but to a lower degree than the fiber sizing with a suitable commercial product.

The surface modification proposed by Takayanagi, Kajiyama, and Katayose[15, 16] seems to be very effective, improving remarkably the mechanical properties of the composites prepared from discontinuous aramid fibers dispersed in an ionomer matrix. Mai and Castino[17] compared two commercial varnishes as aramid fiber coatings and note that the silicone-based material is superior to the polyurethane coating.

Finally, Breznick et al.[18] proposed a surface treatment technique which provides the attack of aramid fiber by bromine water. This technique leads to the surface roughening, resulting in a fiber strength loss accompanied by a considerable improvement in the interlaminar shear strength.

In a recent work,[19] an attempt was made to modify aramid fibers by treatment with methacryloyl chloride. This chemical reagent could be possibly grafted in the polymer chain so that the fiber could be chemically attached to matrices containing unsaturation, such as thermosetting polyesters. Although the grafting of methacryloyl chloride has not been proved in this study, a remarkable increase of the fiber–matrix adhesive bond was clear as indicated by mechanical tests and optical microscopy.
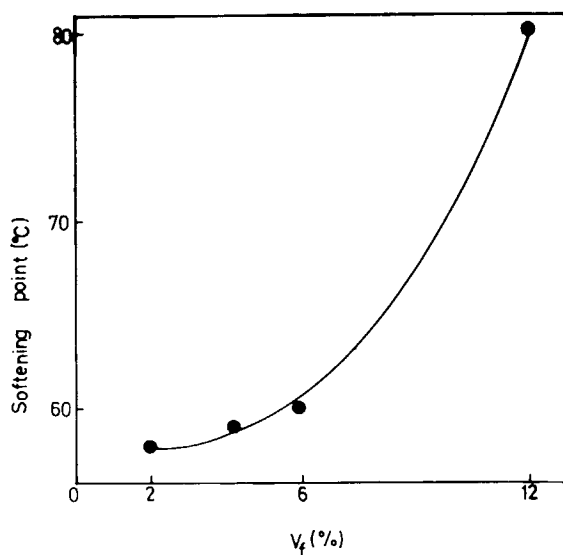

Fig. 5. The Vicat Softening Point, versus filler volume fraction.

In this work, Kevlar pulp was used as a reinforcement, in comparison with chloride-treated pulp. This investigation could provide more information about the chemical reactions or the polar–polar interactions occurring between treated aramid fibers and various matrices.

EXPERIMENTAL

Materials

A low density PE (LDPE) in powder form was used, having density 0.921 and MFI 70 g/10 min. Dicumyl peroxide (DCP) [MERCK-Schuchardt, bis(α,α-dimethyl benzyl) peroxide], for synthesis was used as the crosslinking agent in concentration 2 phr.[20]

Discontinuous aramid fibers were selected as reinforcing agent, since the incorporation technique was based on melt mixing, a method very common for thermoplastics. Thus, Kevlar pulp (DuPont) was used. The aramid surface treatment was carried out using methacryloyl chloride (purum, Fluka A. G.) as well as chemical pure carbon tetrachloride and sodium hydroxide.

(a)

Fig. 6a. Pull-out of untreated aramid fibers.

Method

The treatment of Kevlar pulp with methacryloyl chloride was carried out as follows: A 5% (w/w) solution of methacryloyl chloride in carbon tetrachloride was added to 20 g of pulp and allowed to sit for 1 h. Carbon tetrachloride was then removed by evaporation at 40°C and the pulp was transferred to 1 L of water containing 20 g sodium hydroxide and 5 g nonionic surfactant and stirred for 30 min. This process is necessary to neutralize any unreacted chloride as well as to produce fiber disentangling. The wet pulp was then filtered, repeatedly washed with deionized water, and, finally, dried for 2 h in an air circulating oven at 80°C.

The preparation of the reinforced crosslinked specimens included the following steps: First, a premixing of the fibers and PE was necessary. Since dry blending was proved inadequate, wet blending was performed dispersing the resin powder and the fibers in water, stirring for 30 min, and then filtering and drying. DCP was subsequently added and the mixture was ready for melt mixing.

The second step was carried out in a Brabender plasticorder equipped with a 50 mL mixing head. Mixing temperature and time were 140°C and 5 min,

(b)

Fig. 6b. (*Continued from the previous page.*)

respectively. These conditions were selected in order to exclude the beginning of the crosslinking reaction during the melt mixing step.

The final step includes the curing of the mixed specimens during the molding in a heated plates hydraulic press (Dake and Co., Michigan). The molding conditions were the following: temperature 160°C, time 10 min, pressure 1000–1200 psi, cooling time (to 25°C) 30 min. The molded specimens were obtained in the form of plaques of 1–3 mm thickness.

Tensile Measurements

For the tensile tests, the ASTM D 638[21] designation was followed using type IV dumbbell specimens. A JJ Instrument tensile machine was used, working at a grip separation speed of 50 mm/min.

Vicat Softening Point Determination

The determination of the Vicat softening point was carried out according to the ASTM D 1525 designation, using a Ceast (Italy) machine. The rate of temperature increase was 55°C/h and the load imposed 5 kg. The tempera-
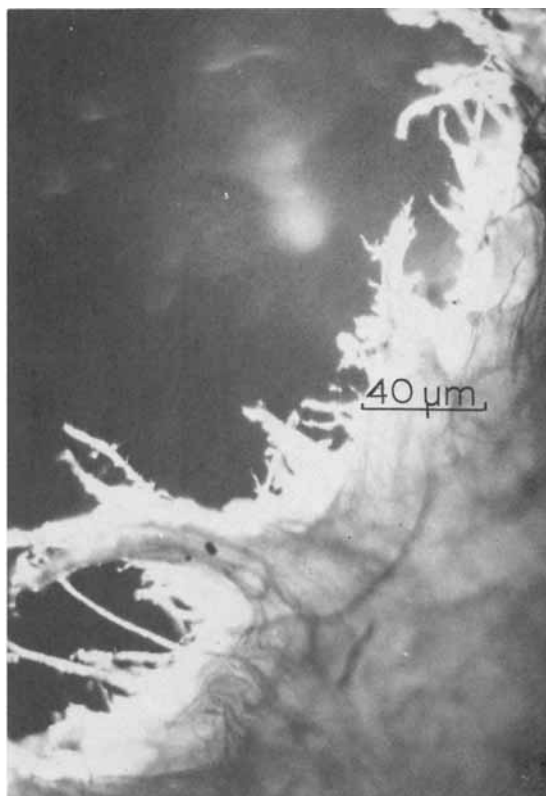
(a)

Fig. 7a.   Fiber-matrix interaction in case of chloride treated fibers.

ture at which the needle penetrates the specimen to a thickness of 1 mm is considered as the softening point.

Optical Microscopy

The fracture surfaces were observed using an Amplival optical microscope (Jenoptik Jena GmbH) equipped with a camera to record and reproduce micrographic images by photographic means. The aim of such observation under magnification is to determine visually the fiber–matrix interactions in the cases of treated and untreated fibers.

RESULTS AND DISCUSSION

The typical torque–time curve, deriving from the mixing operations in the Brabender plasticorder, is presented in Figure 1, which is a copy of the recorder chart with curvilinear coordinates. It is evident that maximum torque is reached when polymer fusion occurs and then an equilibrium effect is observed. In all cases a 5-min mixing time is enough to achieve torque stability. These ultimate torque values are plotted vs the volume fraction of
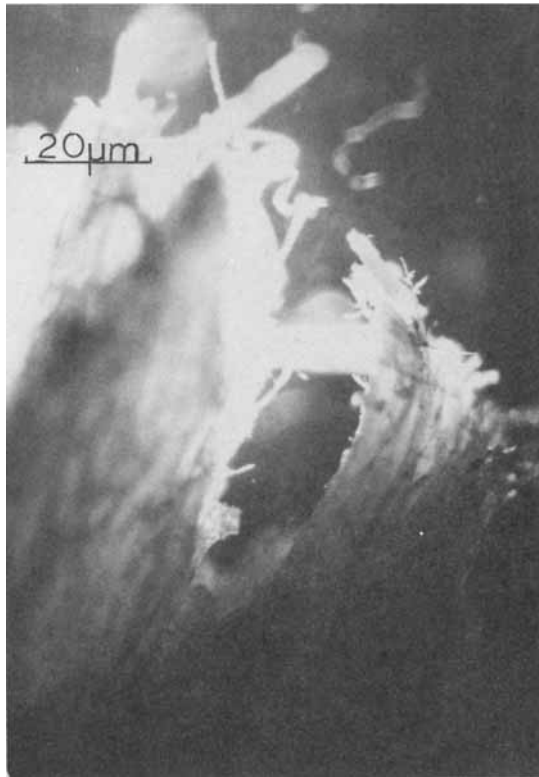
(b)

Fig. 7b. (Continued from the previous page.)

fibers, in Figure 2. The volume fractions of the polymer and reinforcement were determined using the formulas

$$V_p = \frac{d_f W_p}{d_p W_f + d_f W_p}$$
(1)

and

$$V_f = \frac{d_p W_f}{d_p W_f + d_f W_p}$$
(2)

where V_p and V_f are the volume fractions of the polymer and filler, respectively, d_p and d_f the densities, and W_p and W_f the weight of each one of the
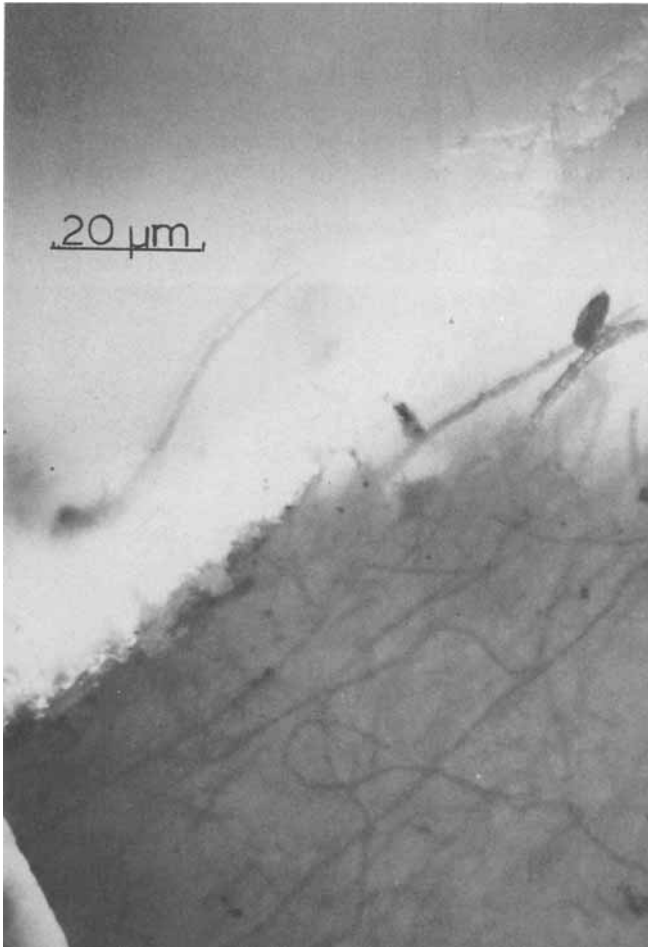

Fig. 8. Dispersion of aramid fibers, for $V_f = 1.9\%$.

phases. As Figure 2 indicates there is an essentially linear increase of the torque with increasing reinforcement volume fraction. Furthermore, the treatment of fibers with methacryloyl chloride seems to have no effect on the mixing torque.

The results obtained by mechanical tests are presented, as a function of filler volume fraction, in Figures 3 and 4. The curves of Figure 3 indicate that in both series of specimens the strength increases with increasing filler content up to 4%. After this point, a rather limiting effect is observed. This behavior could possibly be attributed to dispersion difficulties arising as the percentage of fibers increases. The PE melt is perhaps unable to ensure a proper fiber wetting when filler volume fraction (V_f) surpasses the limit of 4%, so that the tensile strength increase (expected from the law of mixtures) is balanced by the poor dispersion. In addition, a clear difference exists between the reinforcing effect of treated and untreated fibers. This fact is probably a consequence of the improved adhesion between fiber and matrix, in the case of chloride-treated fibers. It also should be noted that the load–extension curve presents a typical viscoelastic behavior for low filler volume fractions, whereas a linear relationship is clear for higher filler percentages.

Figure 4 presents the elongation at break and the moduli of elasticity for the two series of specimens. It is clear that deformation decreases with increasing V_f and this decrease is essentially the same for both types of reinforcement, i.e., treated or untreated fibers. On the other hand, the modulus of elasticity increases with V_f. In the case of treated aramid, the in-
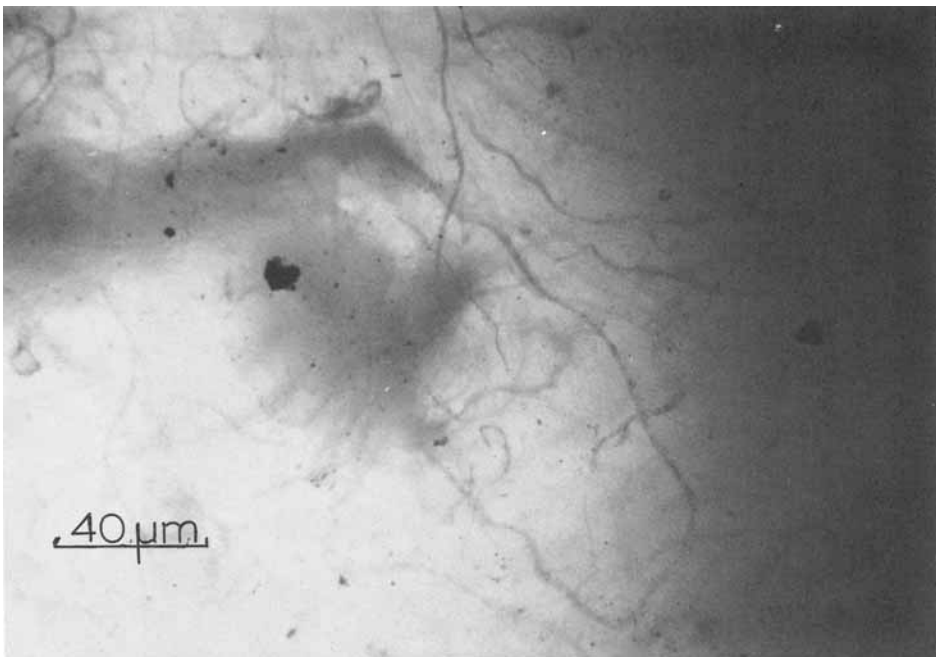

Fig. 9.   Dispersion of aramid fibers, for $V_f = 6\%$.

crease is higher and a linear relationship is present possibly due to the higher fiber–matrix adherence.

The Vicat softening point, as a function of V_f, is also presented in Figure 5. As the curve of this figure indicates, there is an increase of softening point with increasing V_f but especially the high fiber content can lead to remarkable effects.

The fracture surfaces of the tensile specimens are shown in Figures 6 and 7. In the case of untreated fibers (Fig. 6) pullout is evident whereas in the case of chloride-treated fibers (Fig. 7) the fiber–matrix separation is considerably eliminated. This difference must be combined with the already observed improvement of tensile strength, when treated fibers are used. It is, therefore, obvious that methacryloyl chloride promotes fiber–matrix adhesion and this interaction is probably due to the grafting of chloride molecules to the aramid chain and the subsequent grafting of the unsaturated methacrylic group to the PE network, during the crosslinking reaction.

Finally, Figures 8 and 9 present the fiber distribution in thin polymer samples with different V_f. As it is evident in Figure 8, the lower filler content (1.9%) results in a more uniform dispersion in comparison with V_f as high as 6% (Fig. 9). This fact is again in agreement with the limiting effect observed for the tensile strength increase with increasing V_f.

CONCLUSIONS

The above discussion can lead to the following conclusions:

1. Aramid pulp is an efficient reinforcing agent for crosslinked PE, improving its mechanical properties and thermal stability.
2. Filler volume fractions higher than 4% are difficult to be dispersed in the PE melt. Thus, special care should be taken for the preparation of an homogeneous sample.
3. The fiber treatment with methacryloyl chloride seems to be a very effective technique to promote fiber–matrix adhesion. Since PE is a nonpolar polymer, this adhesion must be attributed rather to chemical grafting than to polar–polar interactions.

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