Surface Modification of Cellulose Fibers. II. The Effect of Cellulose Fiber Treatment on the Performance of Cellulose–Polyester Composites

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Synopsis

Cellulose fibers treated with different coupling agents based on trichloro-*s*-triazine have been evaluated in terms of their reinforcement effect on unsaturated polyesters. The treatment with coupling agents containing double bonds resulted in what we believe to be the formation of covalent bonds between fiber and matrix. This has been compared with a treatment, which can only lead to formation of close interfacial molecular contact by wetting. The tensile properties of composites prepared from treated and untreated fibers were studied before and after exposure to water. It was found that all types of fiber treatment decreased water absorption and the reduction of mechanical properties in wet conditions, but that the degradation at the fiber/matrix interface which occurs from immersion in water and drying could only be avoided through the development of covalent bonds between fiber and matrix. Scanning electron microscopy was used to study the adhesion between fiber and matrix. An explanation of the reduction of mechanical properties of cellulose-fiber reinforced polymers in wet conditions is proposed.

INTRODUCTION

In the field of materials, the development of fiber-reinforced polymers is among the most rapidly expanding areas. Glass, the most common reinforcing fiber, has been in use as reinforcement of unsaturated polyesters for more than 40 years. The glass fiber/polymer matrix interface received very early attention, and this led to the development of silane coupling agents.[1] Nowadays glass and other reinforcing fibers, such as carbon[2] and aramide,[3] are surface-treated to promote adhesion. Such treatment affects the mechanical properties of composites, the environmental aging behavior and electrical and optical performance.

In addition to the development of high performance composites reinforced with very strong, stiff fibers, there is a growing interest in light, strong, less expensive composites. Polymers reinforced with natural fibers such as cellulose are among these. However, the use of cellulose as reinforcement has been concentrated to a few polymeric systems, such as amino and phenolic plastics.[4] As we reported in a previous paper,[5] the cellulose fibers were found to be favorable as reinforcement of polyesters, but such composites had poor mechanical properties in wet conditions. Similar behavior was observed in the case of cellulose fiber polyethylene[6] and jute–polyester composites.[7] With polyethylene, mechanical properties were improved in wet conditions when acetylated paper and paper crosslinked with formal-

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dehyde were used. In the case of jute–polyester composites, the degradation of mechanical properties, the percentage water uptake, and percentage increase in thickness could all be decreased by incorporating interfacial agents to give better bonding across the interface. No satisfactory explanation has, to our knowledge, been offered for the reduction of the mechanical properties of cellulose fiber polymer composites after exposure to water.

The aim of this work has been to study the effects of improved adhesion between cellulose fibers and the polyester matrix on the properties of cellulose–polyester composites. In order to improve adhesion, the cellulose fibers were treated with various coupling agents based on trichloro-s-triazine. The chemical reactions occurring during the treatment of cellulose fibers have been discussed in a previous paper.[8] In the present paper we investigate the properties of composites of unsaturated polyester and treated fibers, in particular their environmental aging behavior.

EXPERIMENTAL

Materials

The cellulose fibers used in this study were bleached softwood kraft paper with high porosity and a surface weight of 115 g/m^2, obtained from Klippans Finpappersbruk AB, Sweden. Fiber length and fiber width distribution were determined by measuring 500 fibers in a microscope.
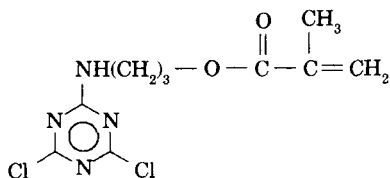
Synthesis of Coupling Agents

Three derivatives of trichloro-s-triazine were synthesized. These are shown below and henceforth referred to as coupling agents A, B, and C.
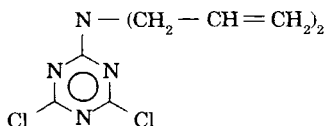
Coupling Agent A. 2-octylamino 4,6-dichloro-s-triazine:

$$NH(CH_2)_7CH_3$$
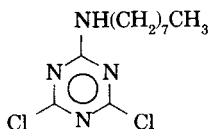
Coupling Agent B. Methacrylic acid, 3-((4,6-dichloro-s-tiazine-2-yl) amino) propyl ester:

$$NH(CH_2)_3 - O - \overset{\overset{\textstyle O}{\|}}{C} - \overset{\overset{\textstyle CH_3}{|}}{C} = CH_2$$

Coupling Agent C. 2-diallylamino 4,6-dichloro-s-triazine:

$$N - (CH_2 - CH = CH_2)_2$$

Coupling agent A (mp 62°C) was synthesized from trichloro-*s*-triazine and octylamine using the Thurston method.[9] Coupling agent B (mp 42°C) was synthesized from trichloro-*s*-triazine and diallylamine using the same method. Coupling agent C (mp 93°C) was prepared from trichloro-*s*-triazine and 3-aminopropyl methacrylate–HCl.

Fiber Treatment

Cellulose fibers in the form of sheets of paper were soaked in a 5% acetone solution of the coupling agents for 3 min. The wet pickup was 100%. After drying for 15 min at 30°C in an oven with air circulation the paper was soaked in an aqueous solution of sodium hydroxide (0.1M) for 3 min. The wet pickup was approximately 300%. The paper was then heated for 1 h at 93°C in a nitrogen atmosphere, and then rinsed several times with distilled water and acetone. Finally, the paper was Soxhlet-extracted with acetone for 20 h to remove compounds not covalently bonded to the fibers and dried in vacuum to constant weight.

Elemental Microanalyses

The nitrogen content was determined with a Carlo Erba ANA 1400 Automatic Analyzer.

Polyester

The polyester used was a commercial unsaturated polyester resin, Norpol PI 2614 made by Jotun A/S, Norway, based on isophthalic acid, with an acid value of 15 g/cm^3, and 40% styrene content.

Composite and Specimen Preparation

The cellulose fibers, in the form of sheets of paper, were impregnated with liquid resin containing 2% benzoyl peroxide (BPO) as curing agent. A 15 mm Hg vacuum was applied for 10 min to remove all air. Stacks of five impregnated sheets of paper were placed between two aluminum plates and restrained using a 150 × 150 × 1 mm steel picture frame mold. Polyester release film was used on both sides of the laminates to ensure a good finish. The laminates were cured at a pressure of 2.5 MPa for 1.5 h at 80°C and postcured at 90°C for 23 h. They were anisotropic because the cellulose fibers were aligned in the machine direction. Samples 10 mm wide in the orientation of the machine were cut for tensile tests and water absorption studies.

Tensile Properties

The tensile strength and tensile modulus of the composite test specimens were determined in an Instron tensile machine Model 1193, equipped with a strain gauge extensometer, at a crosshead speed of 0.5 mm/min. Measurements were made according to ASTM D638 standard with the exception of the dimensions of the test specimens. The samples were tested at 23°C and 50% relative humidity after conditioning for 48 h. The properties in the wet condition were determined for wet samples tested immediately after removal from the immersion tank.

Water Absorption

The samples with unsealed edges were dried at 80°C to constant weight and then placed in an immersion tank with distilled water at 23°C. At chosen time intervals the samples were removed from the tank and weighed using an analytical balance. The water uptake was calculated using the formula

$$W = \frac{W_w - W_0}{W_0} \times 100\%$$

where W_w is the weight of the sample when it has been removed from the immersion chamber and when the surface water has been wiped off and W_0 is the weight of the dry sample. Water uptake was measured on at least three specimens. The average scattering of their mean values is $\pm 0.1\%$.

Scanning Electron Microscopy

Tensile fracture surfaces of the composites were investigated with a Jeol JSM 35 Scanning Electron Microscope, operated at 15 eV at a tilt angle of 30°. The specimens were coated with gold to prevent electrical charging.

RESULTS

Fiber Treatment and Preparation of Composites

The cellulose fibers used in this study were in the form of paper with high porosity. The fibers were ribbon-shaped with average cross-section dimensions 0.034×0.004 mm and an average length of 1.74 mm. The distribution of aspect ratios (calculated as the ratio of length to major axis of the cross section) is shown in Figure 1.

In order to improve adhesion between cellulose fibers and the polyester matrix, the fibers were treated with various coupling agents. In addition to treatments with double bonds containing coupling agents, described previously,[8] the treatment with a compound containing a long alkyl chain
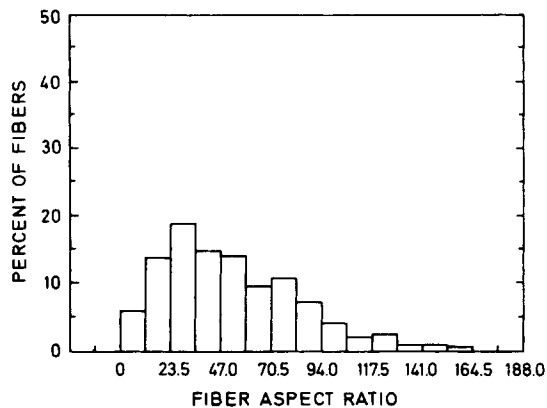

Fig. 1. Histogram showing the distribution of fiber aspect ratios.

(coupling agent A) to promote wetting was applied. Figure 2 presents schematically the possible fiber surface structures which can be formed as a consequence of the various fiber treatments. The nitrogen content of extracted cellulose fibers was 0.1% for paper treated with coupling agent A and 0.4% for B and C.

All treatments resulted in hydrophobic surfaces, as determined by measuring the contact angle between paper surface and water. The contact angle changed from 0° for untreated paper to over 120° for treated surfaces.

Mechanical Properties

The tensile properties were determined of the composites prepared as laminates based on paper composed of untreated fibers and fibers treated with various coupling agents. As shown in an earlier paper,[5] the strength and, even more noticeably, the stiffness of the polyester are increased considerably by incorporation of cellulose fibers. The results summarized in Table I show that there is no significant difference in properties between the composites with untreated fibers and those with fibers treated with coupling agent A, whereas treatments B and C (sample 3 and 4) induce a further increase of strength.

Electron micrographs of tensile fracture surfaces (Fig. 3) illustrate the degree of adhesion. For sample 1 with untreated fibers, some debonding occurs at the interface. However, the fibers are fractured. For sample 2, less debonding occurs, but there are still both adhesive and cohesive failures. Samples 3 and 4 gave results which were so similar that only sample 4 is shown. In sample 4 were observed excellent adhesion, no debonding, and fractured fibers.

Absorption of Water

The samples with unsealed edges were immersed in water at room temperature. Figure 4 shows the plot of water uptake versus immersion time. At saturation, the water uptake (Table II) defined as in Experimental, was
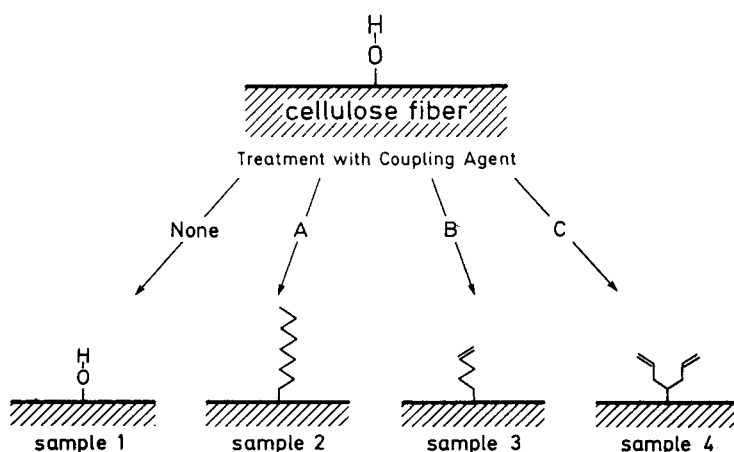
Fig. 2. Simplified molecular surface structures of cellulose fibers treated with trichloro-s-triazine based coupling agents.

TABLE I

Effect of Fiber Surface Treatment on the Tensile Properties[a] of Cellulose–Polyester Composites in Dry and Wet Conditions

Sample	Material	Fiber treatment	Dry				Wet			
			Tensile strength (MPa)	S^b	Tensile modulus (GPa)	S^b	Tensile strength (MPa)	S^b	Tensile modulus (GPa)	S^b
—	Polyester	—	78.5	1.5	3.3	0.1	63.6	2.0	2.5	0.1
1	45% cellulose–polyester	None	117.0	1.2	9.0	0.4	46.3	0.9	2.5	0.2
2	45% cellulose–polyester	Coupling agent A with alkyl chain	112.0	3.2	8.9	0.1	62.4	3.0	3.3	0.1
3	45% cellulose–polyester	Coupling agent B methacrylic	129.6	3.3	9.4	0.4	69.4	2.2	3.4	0.2
4	45% cellulose–polyester	Coupling agent C allylic	136.0	0.5	9.8	0.4	74.5	3.2	3.6	0.1

[a] All results are based on at least five specimens.
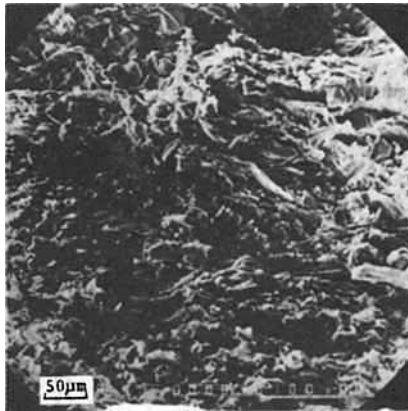[b] S = standard deviation.

(a)

(b)

(c)

Fig. 3.   SEM photomicrographs of tensile fracture surfaces of cellulose–polyester composites: (a) sample 1 (200×); (b) sample 2 (200×); (c) sample 4 (200×).
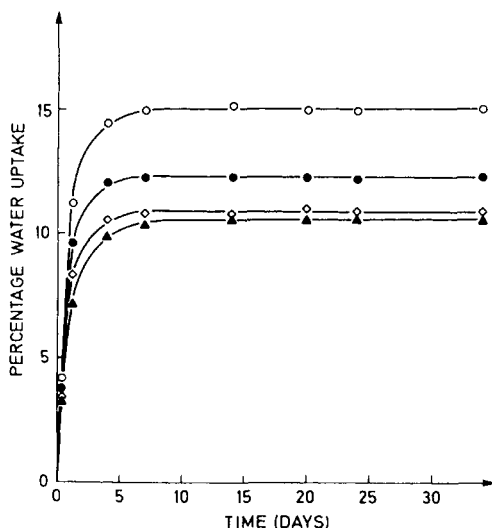
Fig. 4. Water uptake in percent vs. immersion time in water at 23°C. Cellulose-polyester composites: (○) sample 1; (●) sample 2; (◇) sample 3; (▲) sample 4.

dependent on the fiber treatment. The water uptake was decreased by surface treatments. The lowest water uptakes were observed for samples 3 and 4.

The dimensions of the specimens also change during immersion in water, thickness being most affected. The increase in thickness as a function of immersion time is shown in Figure 5. When comparing thickness, increase with weight gain, at the same time (Fig. 6) a linear correlation was found. Thus, the swelling of the fibers can be considered to be responsible for the dimensional change.

Mechanical Properties in the Wet Condition

In order to determine the influence of water on the mechanical properties of cellulose–polyester composites, the tensile properties were tested in the wet condition after immersion in water for 30 days. The results are shown in Table I, and in Figure 7 the "dry" and "wet" tensile strengths are com-

TABLE II
Effect of the Fiber Surface Treatment on the Water Uptake

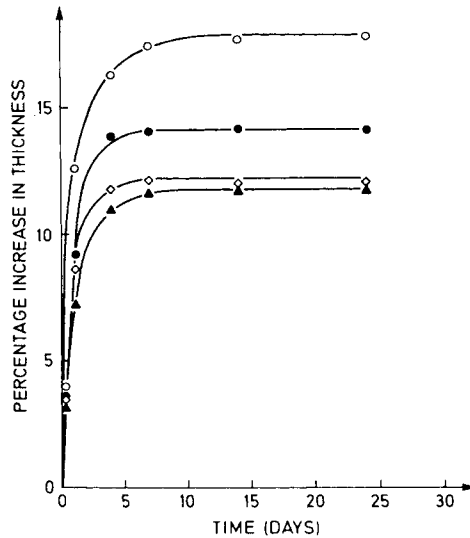| Sample	Material	Fiber treatment	Water uptake (%) at saturation
—	Polyester	—	1.5
1	45% cellulose–polyester	None	15.1
2	45% cellulose–polyester	Coupling agent A with alkyl chain	12.3
3	45% cellulose–polyester	Coupling agent B meth-acrylic	10.9
4	45% cellulose–polyester	Coupling agent C allylic	10.6

Fig. 5.   Percentage increase in thickness of cellulose–polyester composites vs. immersion time in water at 23°C: (○) sample 1; (●) sample 2; (◇) sample 3; (▲) sample 4.

pared for samples with different treatments. The tensile properties of cellulose–polyester composites are strongly affected by immersion in water. There is a dramatic reduction of tensile strength and especially stiffness for all these composites in wet condition. The tensile strength decreases by about one-half and the tensile modulus by nearly two-thirds. This reduction can be decreased by all the surface treatments. Furthermore, treatments B and C imparted superior tensile strength compared with the untreated sample.
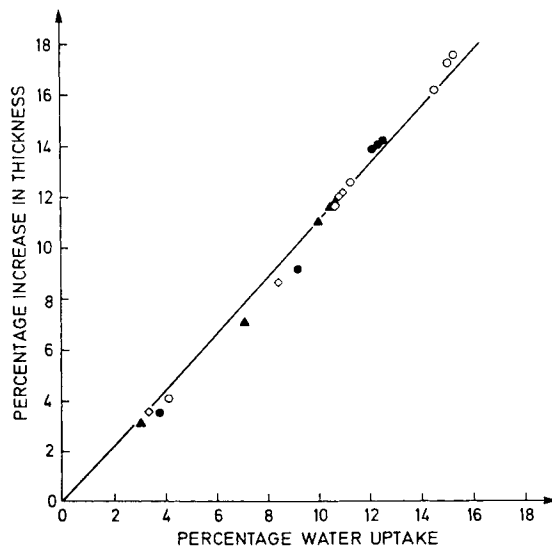

Fig. 6.   Percentage increase in thickness vs. percentage water uptake. Cellulose–polyester composites: (○) sample 1; (●) sample 2; (◇) sample 3; (▲) sample 4.
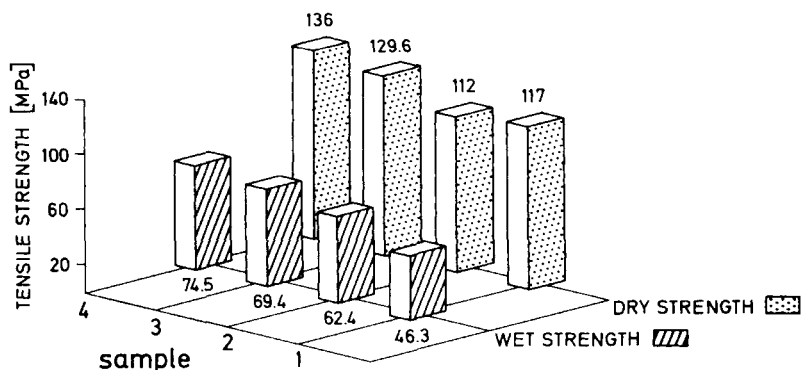
Fig. 7. The effect of fiber treatment on the tensile strength of cellulose–polyester composites in dry and wet conditions.

Scanning Electron Microscopy

Scanning electron microscopy was used to study the failure mode in wet conditions. The samples were dried before testing. The fracture surface of sample 1 (untreated fibers), shown in Figures 8(a) and 8(b), is composed only of fibers. This means that the fibers were pulled out of the matrix under stress, which is evidence of lack of adhesion between fibers and matrix. It should be noted that there are no ruptured fibers, showing that the fibers were not loaded. The fracture surface of sample 2 shown in Figures 8(c) and 8(d), contains fewer fibers on the surface, which indicates a somewhat improved adhesion compared to the untreated sample. The fracture surface of sample 4 shown in Figures 8(e) and (f) indicates excellent adhesion between fibers and matrix in the wet condition. In this case fibers are fractured, as can be observed at the higher magnification [Fig. 8(f)]. Evidently, the fibrils of cellulose fibers were separated during the load bearing.

Desorption Study

While the specimens which had been immersed in water to saturation were being dried, whitening was observed in samples 1 and 2. In both cases delamination and debonding occurred. For samples 3 and 4 no whitening was observed.

DISCUSSION

In fiber-reinforced systems, applied stress is transferred from the matrix to the stronger fibers by shear stress at the fiber/matrix interface.[10] Better shear resistance can result from the formation of chemical links between the modified fiber and the matrix.[11] Due to lack of experimental results dealing with various degrees of adhesion there are different opinions about the contribution of strong interfacial adhesion to the achievement of optimum mechanical properties of composites.

In this investigation, chemical modification of cellulose fibers makes it possible to achieve various interactions between fiber and matrix. The better
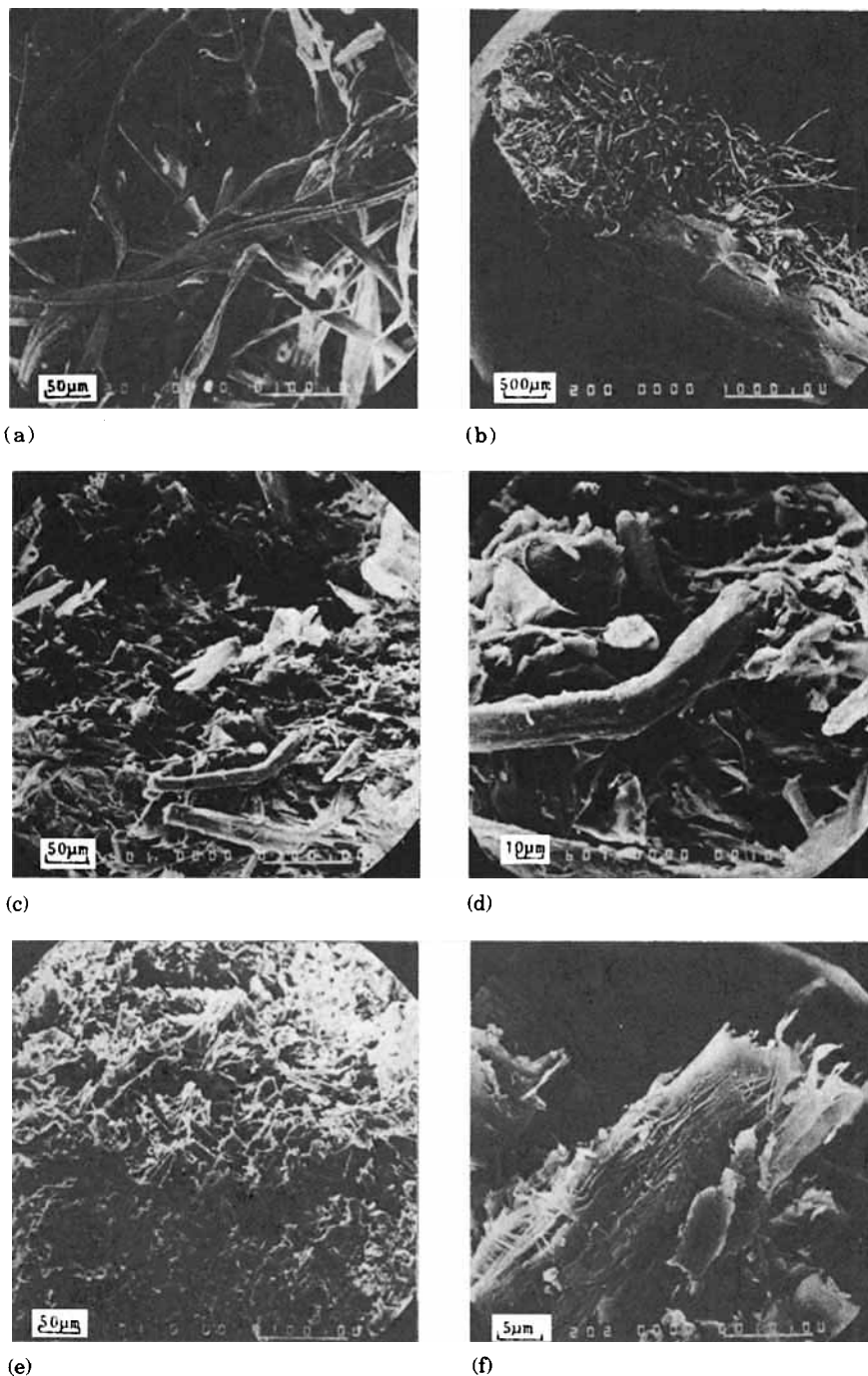
Fig. 8.   SEM photomicrographs of tensile fracture surfaces of cellulose–polyester composites tested in wet condition. (a) sample 1 (200×); (b) sample 1 (20×); (c) sample 2 (200×); (d) sample 2 (600×); (e) sample 4 (200×); (f) sample 4 (2000×).

wetting of fibers by liquid resin in treatment A (sample 2) can lead to closer interfacial molecular contact between cellulose fibers and the polymer matrix. As shown in a previous paper,[8] the cellulose fibers treated with tri-chloro-s-triazine based coupling agents with double bonds copolymerize with styrene. Thus in addition to the good wetting for treatment B (sample 3) and treatment C (sample 4), covalent bonds could possibly be formed between cellulose fibers and polyester matrix.

As was expected, the treatment of cellulose fibers resulted in improved adhesion between cellulose fibers and polyester matrix. SEM of the tensile fracture surfaces which were obtained by testing the samples in dry conditions showed that the fibers were not pulled out of the matrix in the cases when the covalent bonds across the fiber/matrix interface could be formed (samples 3 and 4). Better wetting alone (sample 2) provided adhesion, which was insufficient to prevent the fibers from being pulled out of the matrix. When the influence of the interfacial adhesion on the mechanical properties of short fiber composites is being considered, the effect of the critical aspect ratio has to be taken into account.[12] Since the fibers in the paper have a range of lengths and widths, some of them are certainly below the critical aspect ratio, and are pulled out of the matrix during the loading. Improved adhesion decreases the critical aspect ratio, so that fibers with a lower aspect ratio become sufficiently long to bear the load. The improvement of the strength in samples 3 and 4 can be explained as the consequence of a higher proportion of the fibers exceeding the critical length and thus contributing to the reinforcement.

This study showed that strong interfacial adhesion is particularly important for improved environmental aging behavior of cellulose–polyester composites. Lower water absorption and better dimensional stability of composites based on the treated fibers seems to be caused by restrictions imposed by the polymeric matrix.

The fact that the mechanical properties of composites based on cellulose fibers and polymers are drastically reduced by exposure to water may, on the basis of the results presented above, be explained as follows. Three factors important to the interpretation of the mechanical properties of composites are the matrix properties, the fiber properties, and the fiber/matrix interface properties. It is known that the mechanical properties of the isophthalic-acid-based polyester matrix are affected by immersion in water.[13] We found a reduction in modulus and strength of the polyester in the wet condition (Table I), apparently caused by plasticization by water.

Cellulose fibers, in contrast to other reinforcing fibers, are very sensitive to water. Single fibers can sorb up to 30% of their own weight, which results in swelling.[14] According to recent reports on the influence of water on the mechanical properties of single wood pulp fibers,[15,16] the fiber modulus can decrease by nearly two-thirds or even more for wet fibers. The tensile strength, however, is believed to be less affected by water present in the fibers.[17] It should be mentioned that when wet single cellulose fibers undergo tensile testing, there is some uncertainty in the results because of experimental difficulties.

The interfacial failure in wet conditions, observed with SEM in the sample with untreated fibers, is certainly responsible for the fact that the strength and stiffness of the composite deteriorate. The presence of the water-re-

sistant covalent bonds across the cellulose/polyester interface in the samples 3 and 4 is confirmed further by results from SEM showing excellent adhesion between the fibers and the matrix in wet conditions. Unlike the sample with untreated fibers, the load is transferred from the matrix to the fibers even in wet conditions, and the reinforcement effect is obtained. The fact that strength and, especially, stiffness are reduced in the wet condition can be explained only by poor mechanical properties of the wet cellulose fibers. Actually, an SEM picture illustrating the failure mode of the fiber in wet conditions [Fig. 8(f)] showed that the fibrils of the cellulose fibers were separated under stress. Evidently, amorphous parts of the cellulose fiber become plasticized by water and that is where failure occurs. This finding explains why the presence of water leads to a dramatic reduction in stiffness and strength of the cellulose fibers and hence of the cellulose–polyester composites in spite of excellent interfacial adhesion.

Absorption and desorption studies showed that the delamination and debonding at the cellulose fiber/polyester matrix interface can be avoided only by treating the fiber to develop covalent bonds between fiber and matrix. Further work is in progress to follow water sorption and desorption processes microscopically and to find a molecular explanation for the degradation of the interface by water.

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