Surface Modification of Cellulose Fibers III. Durability of Cellulose–Polyester Composites Under Environmental Aging

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Synopsis

The effects of improved interfacial adhesion on the environmental aging behavior of cellulose–polyester composites were studied. The reduction in maximum water content of the composites upon immersion in water which occurs for surface-treated fibers is explained by the restrictions from fiber/matrix network. Whitening of the specimens based on the untreated fibers, or on fibers treated but not covalently bonded to the matrix, was found to be due to the formation of debonding cracks. Such cracks were formed on drying the material. When the fiber and the matrix are covalently bonded, the matrix follows the fiber during shrinking, and thus no cracks are formed.

INTRODUCTION

Fiber-reinforced polymers are widely used for structural applications. These composites are exposed to various environments during their service life. The behavior of glass–fiber polyesters under exposure to water is already quite well understood.[1-5] We recently reported on the properties of cellulose-reinforced polyesters.[6] Due to the hydrophilic nature of a cellulose fiber and its hygroexpansivity, it is very important to study the response of cellulose-based composites to environmental aging, in particular exposure to water. For this reason the effects of immersion in water on the properties of cellulose–polyester composites have been investigated.

In a previous paper,[7] we reported on the effects of surface treatments of cellulose fibers using triazine-based coupling agents, on the mechanical properties of cellulose–polyester composites in dry and wet conditions, their water absorption, and dimensional changes. It has also been mentioned that the degradation process induced by water was only prevented by the formation of covalent bonds between fibers and matrix.

In the present work, debonding at the fiber/matrix interface is observed using both optical and scanning electron microscopy. This paper also includes a proposed mechanism concerning crack formation during environmental aging, which is based on fiber swelling, fiber shrinkage, and lack of bonding between the cellulose fiber and the polyester matrix.

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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.

Synthesis of Coupling Agents

Coupling agents based on trichloro-*s*-triazine; 2-octylamino 4,6-dichloro-*s*-triazine (Coupling agent A), Methacrylic acid, 3-((4,6-dichloro - s-triazine-2-yl) amino) propyl ester (coupling agent B) and 2-diallylamino 4,6-dichloro-*s*-triazine (coupling agent C) were synthesized from trichloro-*s*-triazine using the Thurston method.[8]

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 (0.1 m) 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.

Polyester

The polyester used was a commercial unsaturated polyester resin, Norpol PI 2614 made by Jotun A/S, Norway, based on isophtalic 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 water absorption studies.

Table I shows the compositions of the materials.

Water Absorption

The samples of composites with unsealed edges were dried at 80°C to constant weight and then placed in an immersion tank with distilled water

TABLE I
Specifications of Samples

Sample	1	2	3	4
Reinforcement	Cellulose fibers in the form of paper			
Surface treatment	None	Coupling agent A	Coupling agent B	Coupling agent C
Matrix	Unsaturated polyester NORPOL PI 2614			
Fiber content (wt %)	45	45	45	45
State of interface	No interactions	Improved molecular contact	Covalent bonds	Covalent bonds

at 23°C. The water content was calculated using the formula

$$W = \frac{W_w - W_0}{W_0} 100\% \tag{1}$$

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 the weight of the dry sample.

Moisture Absorption

Untreated and treated paper sheets were dried to constant weight and then placed in a closed chamber containing a reservoir with distilled water. The relative humidity of the air surrounding the paper samples was 100%. The weight gain was measured by weighing them periodically on a Mettler Analytical Balance. The moisture content was calculated using the formula (1). The results are the average of three data within ±5%.

UV Microscopy

The cross section of the composite was analyzed with a Zeiss UV microscope with additional equipment as described elsewhere.[9] Absorbance measurements were made at 280 nm with a spectral bandwidth of 6 nm.

Scanning Electron Microscopy

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

Microscopy

The cross section of the composite was embedded in the epoxy resin, Epikote 812, Shell Chemicals, Holland. When the epoxy resin has cured, sections of uniform thickness were cut on a microtome and investigated in dry, wet, and redried conditions using polarizing optics in a Leitz-Zetopan microscope.

RESULTS AND DISCUSSION

The Fiber Component of Wood and Composite

In Figure 1 a cross section of wood is shown. The cell walls are seen as grey areas and lumina are seen as white areas. Figure 2 shows a SEM photograph of a paper sheet like those used in the preparation of the composite. The fibers of the paper exhibit a collapsed, flattened appearance, as can be seen in Figure 2, as a result of the removal of "natural" (lignin) matrix materials during the pulping process.[10]

The specimens of cellulose–polyester composites prepared by the method previously described were translucent, which indicates that no voids were present in the material. Investigation of such composites using UV microscopy showed that the polyester matrix was present in a lumen of the fiber (Fig. 3). The shapes of the fibers in the composite are definitely more like those of the wood than those of the paper sheet.

Water Absorption

The specimens of composites were immersed in water to saturation. The extent of water absorbed by the composites, as shown in Table II, decreased significantly when the fibers were treated with coupling agents. By assuming that the presence of cellulose fibers does not affect the water absorption of the polyester matrix, and that water is present only in the matrix and in the fibers, the water content of the composite, W, may be given by the expression

$$W = m_m W_m + m_f W_f \tag{2}$$

where m_m is the weight fraction of the matrix, m_f is the weight fraction of the fibers, and W_m and W_f are the maximum water contents of the matrix and the fibers, respectively.

The maximum water content of the cellulose fibers, W_f, in each sample were calculated, and the results are summarized in Table II. The maximum water content of untreated fibers in the composite is more than 30%, which is normal for pulped cellulose fiber. Thus the behavior of cellulose fibers

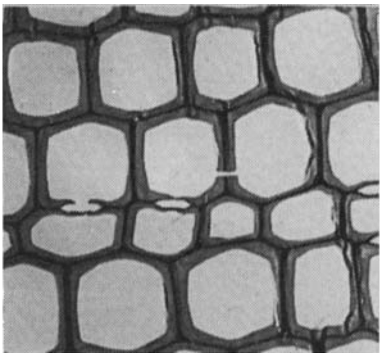

Fig. 1. UV photomicrograph of a cross section of wood.

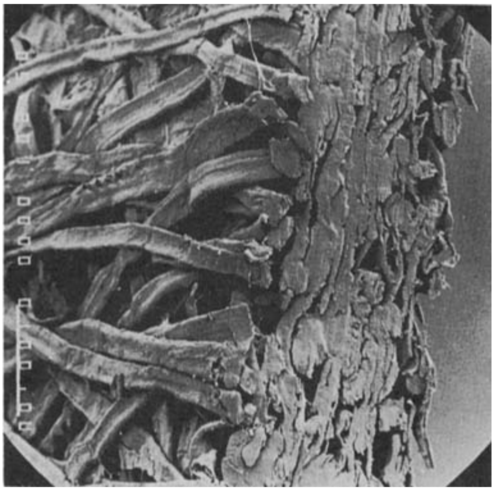

Fig. 2. Top and cross section of a paper sheet (magnification 200×).

Fig. 3. UV photomicrograph of the cross section of the 45% cellulose–polyester composite.

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

Sample	Material	Fiber treatment	Max water content (%)	Water content of fibers calcd by eq. (2)
—	Polyester	—	1.5	—
1	45% Cellulose–polyester	None	15.1	31.7
2	45% Cellulose–polyester	Coupling agent A with alkyl chain	12.3	25.5
3	45% Cellulose–polyester	Coupling agent B methacrylic	10.9	22.4
4	45% Cellulose–polyester	Coupling agent C allylic	10.6	21.7

regarding water absorption and subsequent swelling seems not to be affected by the fact that the fibers are surrounded by a polyester matrix. This indicates that the swelling pressure of untreated fibers is greater than the strength of the wet polyester matrix.

The lower water absorption by composites with surface-treated fibers may be explained by two phenomena. First, the fiber treatment reduces the number of available hydroxyl groups of the cellulose; second, surface treatment of the fibers induces interactions between the fiber and the polyester matrix in the composite, and thus the swelling of the fiber is restricted by the arrangement of the fiber and matrix in a crosslinked network. In order to determine which phenomenon is responsible for the reduction in water absorption, untreated and treated cellulose fibers in the form of paper were exposed to 100% moisture, and a moisture content was determined as a weight gain. The results (see Table III) show that the fiber treatments did not induce any reduction in moisture content of the fibers at saturation. Thus the model based on the restriction from the network seems to be a valid explanation for the reduced water absorption of the composites.

Water Desorption

During drying of the wet specimens, whitening occurred in samples 1 and 2 very soon (about 1 h) after removing the specimens from the immersion chamber. Whitening is due to the scattered reflection of light caused by voids formed by debonding at the interface between fiber and matrix.

Figure 4 shows the edge of the redried specimen 1, investigated by SEM. The disk-shaped cracks can be clearly recognized. In a higher magnification, it can be seen that the cracks are present around the fibers in the regions between the fiber and the matrix.

Formation of Cracks

In order to find out when the cracks are formed, sample 1 was investigated by microscopy before exposure to water, after saturation and after subsequent drying. The same area of the specimen 1 in the different conditions is shown in Figure 5. Swelling of the cellulose fibers in the composite due to exposure to water is clearly seen in Figure 5(b). However, there are no cracks present in the material. They appear first in the redried state [see Fig. 5(c)]. Two cracks can be seen in the regions with high concentrations of fibers. The same procedure was carried out on a sample with covalent

TABLE III
Effect of Surface Treatment on the Moisture Absorption of Cellulose Fibers

Fiber treatment	Maximum moisture content
None	32.5
Coupling agent A with alkyl chain	31.7
Coupling agent B methacrylic	32.4
Coupling agent C allylic	31.2

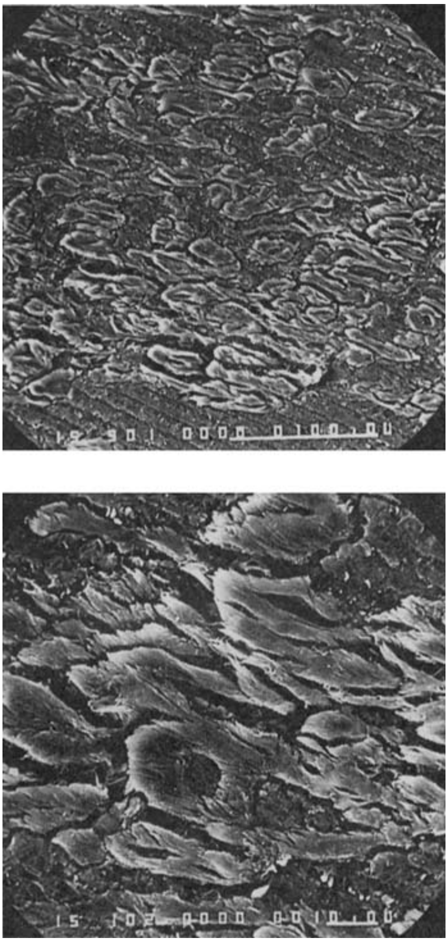

Fig. 4. SEM photomicrographs of the edge of the 45% cellulose–polyester composite.

bonds across interface, samples 3 and 4, and no cracks were found in those cases.

Mechanism of Crack Formation

Previous studies of environmental aging of glass–fiber-reinforced polyesters showed that whitening was caused by the presence of debonding cracks in the material.[11] This disruption has been attributed to the osmotic pressure generated at the fiber/matrix interface.[12]

A mechanism for crack formation in the cellulose–polyester composite, based on the results presented above, is now proposed. The hydrophilic nature of cellulose fibers is certainly responsible for the fact that cellulose–polyester composites perform differently from glass-fiber-polyester. The driving force for water absorption of the cellulose–polyester composite is the affinity of the cellulose fiber for water. When water is absorbed, the polyester matrix is placed under stress by the swelling of the fibers. Cracks are first nucleated, however, when the material without bonds between the

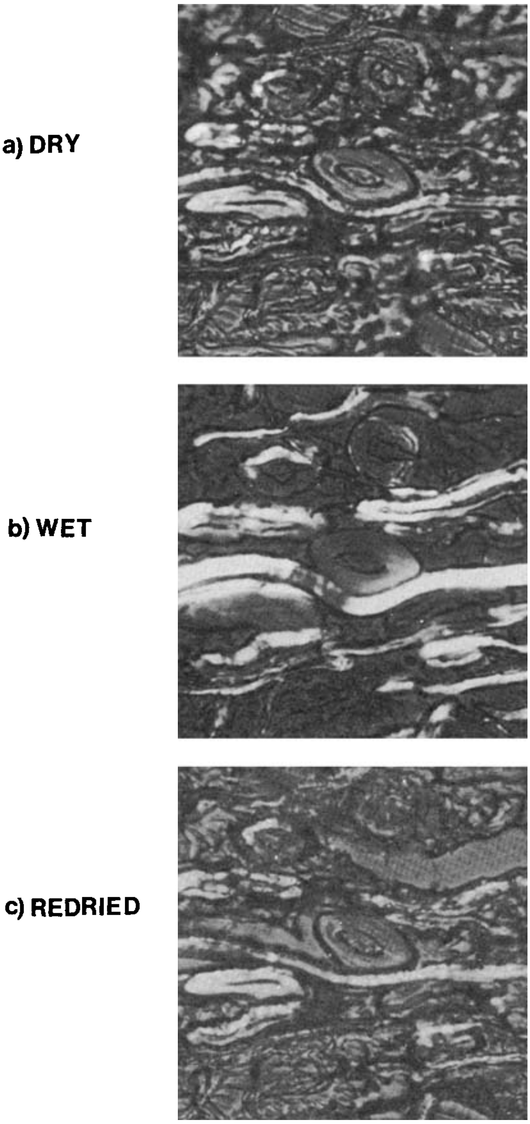

Fig. 5. Photomicrograph of the cross section of the composite in various conditions: (a) dry; (b) wet; (c) redried.

fiber and the matrix is drying. Subsequent desorption results in rapid shrinkage of the fibers and propagation of the debonding cracks. When the fiber and matrix are covalently bonded, no cracks are formed, as the strong bonds force the matrix to follow the fiber upon shrinkage.

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