

Effect of Corona Modification on the Mechanical Properties of Polypropylene/Cellulose Composites

M. N. BELGACEM,* P. BATAILLE, and S. SAPIEHA

Chemical Engineering Physics Department, École Polytechnique de Montréal, Montréal, Québec, Canada, H3C 3A7

SYNOPSIS

The effect of various corona treatment conditions on the mechanical properties of cellulose fibers/polypropylene composites was studied. The cellulose fibers and polypropylene were modified using a wide range of corona treatment levels and concentrations of oxygen. The treatment level of the fibers was evaluated using the electrical conductance of their aqueous suspensions. The mechanical properties of composites obtained from different combinations of treated or untreated cellulose fibers and polypropylene were characterized by tensile stress-strain measurements; they improved substantially when either the cellulose fibers alone or both components were treated, although composites made from untreated cellulose fibers and treated polypropylene showed a relatively small improvement. The results obtained indicate that dispersive forces are mostly responsible for the enhanced adhesion. The relationship between the electrical conductance of the fibers, the mechanical properties, and the mechanism of improved adhesion is discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Composite materials based on fibers of natural polymers demonstrate remarkable environmental and economical advantages, and they have, therefore, recently attracted much attention.¹⁻¹⁰ It is very well known that the performance, for example, the mechanical properties, of composites depend on the properties of the individual components and their interfacial compatibility. Cellulose fibers, one component of the investigated composites, are strongly polar due to hydroxyl groups and C—O—C links in their structure. This renders cellulose more compatible with polar, acidic, or basic,¹¹ rather than with nonpolar polymers. Because of this inherently poor compatibility between the hydrophilic cellulose fibers and typical hydrophobic commodity thermoplastics, such as polyolefins, a pretreatment of the fiber surfaces,³⁻⁵ of the matrix polymer,⁶ or the incorporation of surface modifiers⁷⁻¹⁰ is generally required.

Our recent work has shown that corona treatment improves the mechanical⁶ and rheological¹² properties of cellulose/polyethylene composites. Such a treatment modifies the surface composition and, therefore, the surface properties, of the composite components. In the case of cellulose fibers, corona increases the surface energy and the acidity and basicity.^{13,14}

In the present study, the mechanical properties of composites obtained by different combinations of untreated or corona-treated cellulose fibers and polypropylene were studied. The treatment level of cellulose fiber surfaces, evaluated by electrical conductance of their aqueous suspensions, has been related to the mechanical properties of the corresponding composites.

EXPERIMENTAL

Materials

The material used in this study is a powder of high alpha, hardwood fiber (cat. No. C8002), a commercial product of Sigma Co. The weighted average length and aspect ratio of the fibers are 0.24 mm

* To whom correspondence should be addressed. Present address: Albatros, Research and Development, 38420 Le Versoud, France.

Table I Description of Samples

Composites	Description
C/PP*	No treatment
TC/PP	Fiber treated only
C/TPP	Polypropylene treated only
TC/TPP	Both fiber and polypropylene treated at the same current

* C = cellulose; PP = polypropylene.

and 10, respectively. The polypropylene matrix was Profax#6531 kindly, supplied by Himont Canada.

Corona Treatment

Cellulose fibres or polypropylene were placed in the corona treatment cell, described elsewhere.⁶ Two independent sets of experiments were performed: in the first set, cellulose fibers or polypropylene were treated for 60 s using a discharge current value between 15 and 35 mA (the corresponding voltage across the treatment cell being 11 and 14 kV, respectively): following this, the corona cell was briefly opened, and the treatment was continued for another 30 s. In the second set of experiments, cellulose fibers were treated for different durations at constant current of 25 mA (voltage 12.0 kV): The cell was

Table II Yield, σ_y , and Rupture, σ_b , Stresses, (MPa) of the Cellulose/Polypropylene Composites

Current Level; mA	TC/PP		C/TPP		TC/TPP	
	σ_y	σ_b	σ_y	σ_b	σ_y	σ_b
Untreated	20.8	20.5	20.8	20.5	20.8	20.5
15	23.0	22.8	21.2	20.8	23.0	22.9
20	23.7	23.7	21.5	21.5	24.0	23.7
25	24.4	24.2	21.6	21.3	24.7	24.0
30	25.1	24.6	21.6	21.5	25.4	25.0
35	25.9	25.4	22.0	21.8	26.3	26.1

Treatment time: 90 s.

opened every 30 s and the total treatment time was 180 s.

The level of corona treatment was evaluated using a method described in detail elsewhere.¹⁵ A suspension of 0.5 g of cellulose fibers in 100 mL of distilled water was prepared for each treatment, following which the electrical conductance of the fiber suspensions was measured using an Omega conductance meter (Model CDH-70).

Sample Preparation and Testing

Composites containing 30% of fiber by weight were prepared using a 60 cm³ Brabender mixer at 210°C,

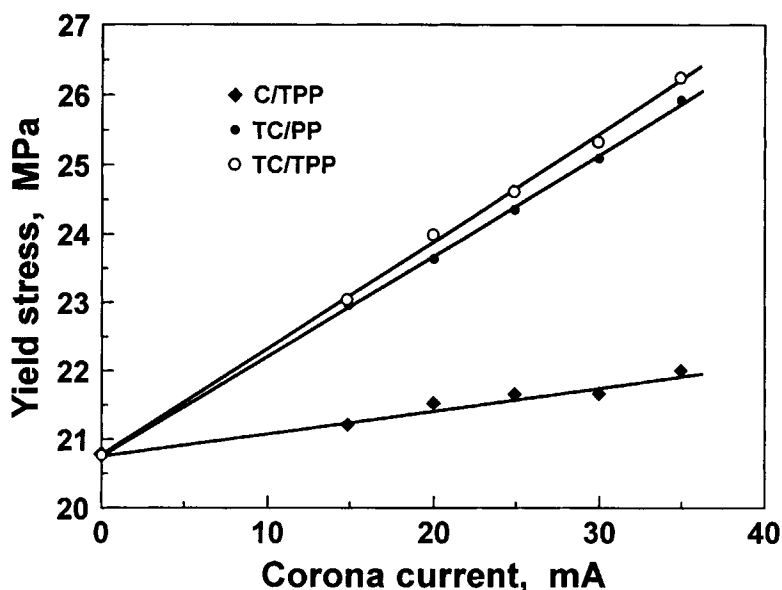


Figure 1 Yield stress of composites as a function of the corona treatment current. Treatment time: 90 s. Both components were treated at the same current.

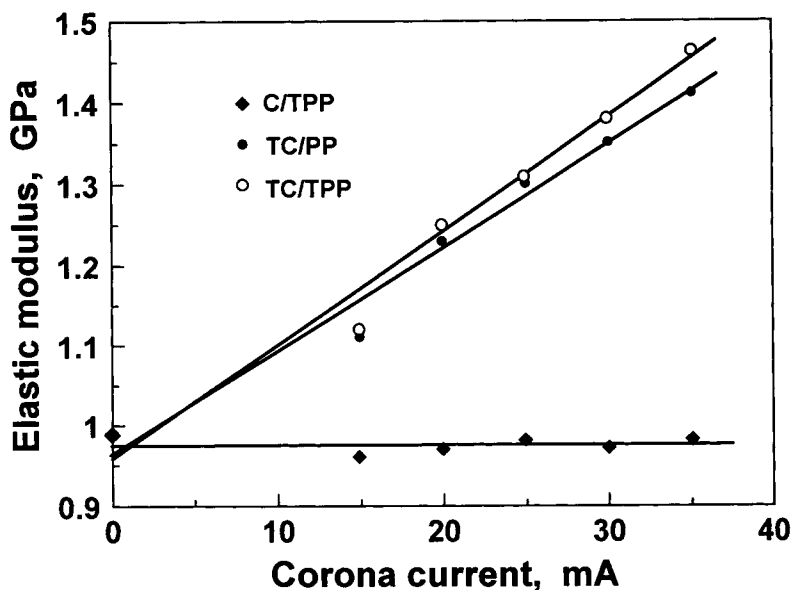


Figure 2 Elastic modulus of composites as a function of the corona treatment current. Treatment time: 90 s. Both components were treated at the same current.

with a screw speed at 40 rpm. The cellulose fibers were predried in the mixing head for 1 min, then polypropylene was slowly added; about 5 min of mixing was required for complete dispersion of the cellulose fibers. The composites were compression molded at 190°C, and then quenched in a cold press for 20 min. The four categories of the composites investigated in this work described in Table I, are designate C/PP, TC/PP, C/TPP, and TC/TPP, where "T" signifies corona treated.

Typical length, width, and thickness of the tested samples were 20 mm, 3.5 mm, and 1.6 mm, respectively. The samples were conditioned before testing for 4 days at room temperature and 50% relative humidity. The tensile stress-strain data were obtained with an Instron tester (Model 4202) at room temperature and at a constant elongation speed of 50 mm/min. The energy to break (W) was calculated from the area under the stress-strain curves. The results presented here are the average values of five tests.

RESULTS AND DISCUSSION

The mechanical properties of cellulose/polypropylene composites were found to improve when either one or both components were modified by corona discharge pretreatment. Mechanical properties of composites made from different combinations of

untreated and treated components are summarized in Table II. A striking result is that modification of cellulose rather than polypropylene yields a greater improvement of the composite properties. The yield stress of composites incorporating treated fibers, shown in Figure 1 as a function of corona current, increased by as much as 24%, although when only polypropylene was treated, the yield strength increased by a mere 6%. This may be at least partially related to a smaller specific surface area of the polypropylene, that is, a larger relative size of the polypropylene particles. Treatment of both components, cellulose fibers and polypropylene, results in composites with only slightly better properties than for cellulose treatment alone (up to 26%, see Fig. 1).

Table III Elastic Modulus (GPa) and Energy to Break (J) of the Composites

Level; mA	TC/PP		C/TPP		TC/TPP	
	E	W	E	W	E	W
0	0.99	1.35	0.99	1.35	0.99	1.35
15	1.11	1.38	0.96	1.36	1.12	1.42
20	1.23	1.40	0.97	1.38	1.25	1.72
25	1.30	1.43	0.98	1.39	1.31	1.85
30	1.35	1.52	0.97	1.41	1.38	1.91
35	1.41	1.70	0.98	1.40	1.46	1.99

Treatment time: 90 s.

Table IV Mechanical Properties of the Cellulose/Polypropylene Composites (TC/PP)

Duration of the Treatment; s	Number of Openings	σ_y MPa	σ_b MPa	E GPa	W J
Untreated	0	20.8	20.5	0.99	1.35
30	0	21.6	21.4	1.17	1.36
60	1	22.1	21.7	1.33	1.41
90	2	23.0	22.9	1.47	1.53
120	3	24.1	24.1	1.52	1.75
150	4	24.6	24.3	1.48	1.88
180	5	25.6	25.5	1.41	2.01
180	0	25.1	24.9	1.38	2.06

Corona current: 25 mA.

The values of elastic modulus (E), and energy to break (W) of the investigated composites are given in Table III. Figure 2 shows that E of TC/PP samples increased linearly with the corona treatment current, although for C/TPP material E remains almost constant. It is somewhat higher for composites where both components were treated. The energy to break as a function of corona current shows a similar behavior.

Mechanical properties of composites obtained at a constant corona current depend on the treatment time (Table IV). The yield stress (Fig. 3) and the energy to break increased the treatment time; the

elastic modulus of these composites reaches a maximum value at about 120 s (Fig. 4).

The interfacial adhesion between a pair of different materials results from dispersive, polar or from acid-base interactions. Figure 1 shows that composites based on nonpolar and (neutral from acid/base point of view) polypropylene (C/PP and TC/PP) are characterized by a significant increase in the yield strength. This clearly indicates that under the experimental conditions used in this work the interfacial adhesion originates mostly from dispersive interactions. For dispersive forces the work of adhesion (W_a) is given by (16):

$$W_a = 2[\gamma_c^d \gamma_{pp}^d]^{1/2} \quad (1)$$

where γ_c^d and γ_{pp}^d are the dispersive components of cellulose fibers and polypropylene, respectively.

Figure 5 shows that the yield stress for TC/PP composites increases linearly with work of adhesion. The values of dispersive energy for the corona-treated cellulose (obtained from IGC measurements) and polypropylene (taken from the literature), and the work of adhesion calculated according to eq. (1) are given in Table V. It is seen that the work of adhesion increases with the treatment level of cellulose. This fact confirms that the dispersive interactions play an important role in improving the mechanical properties.

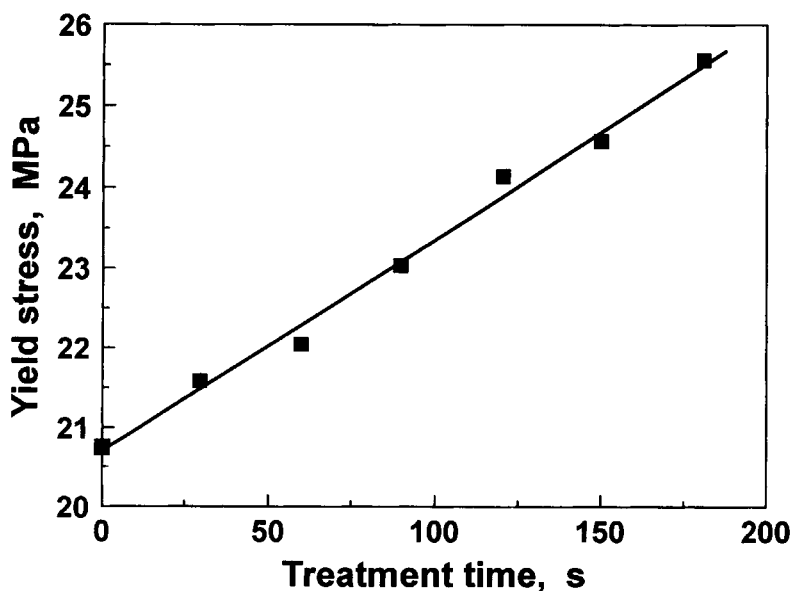


Figure 3 Yield stress of TC/PP composites as a function of the corona treatment time. Corona current: 25 mA.

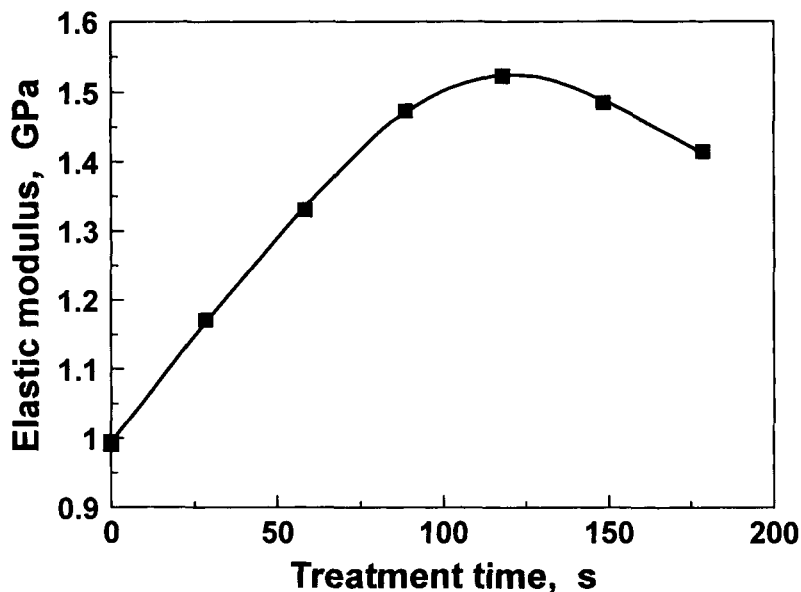


Figure 4 Elastic modulus as a function of corona treatment time. Corona current: 25 mA.

In the case of C/TPP and TC/TPP composites, the adhesive forces are more complex and they include dispersive, polar, and acid-base interaction. However, it was found that the treatment of polypropylene does not contribute significantly to the composite strength. This fact can be partially attributed to a relatively small specific area of the

treated polypropylene particles, which may not come, after melting, into full contact with the fiber.

A correlation was found to exist between the mechanical properties of composites and the electrical conductance of aqueous suspensions of the corona-treated cellulose fibers. The electrical conductance increased with the treatment level of cellulose fibers.

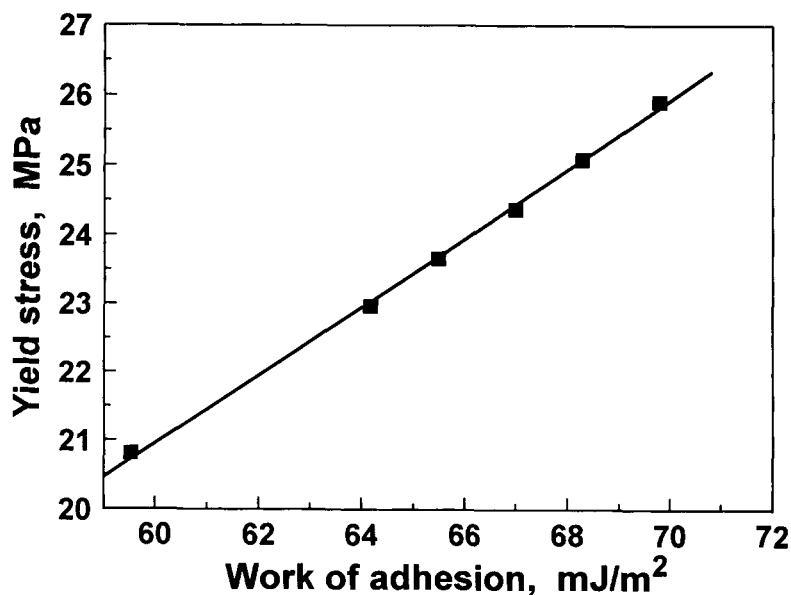


Figure 5 Yield stress as a function of work of adhesion for TC/PP composites. Treatment time: 90 s.

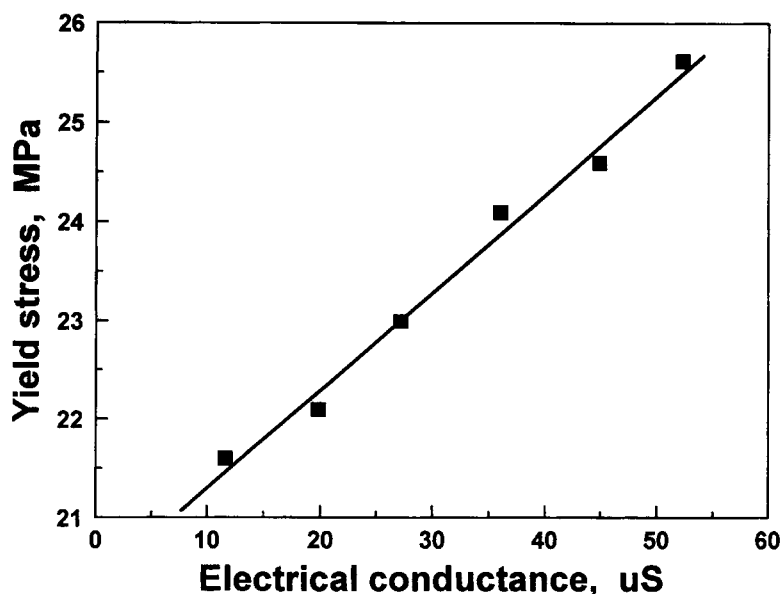


Figure 6 Yield stress as a function of electrical conductance of the fibers. Corona current: 25 mA.

It is expected that the low molecular-weight products formed during treatment are responsible for this effect.¹⁵ These products are mostly of acidic nature and contain carboxylic groups. Figure 6 shows that the yield stress of TC/PP composite increases with electrical conductance of the fiber suspensions. Such a relationship is generally valid for treatments performed under well defined fresh-air supply conditions. For example, composites made of cellulose fibers treated at different fresh-air supply (with or without opening the treatment cell) have similar mechanical properties, whereas the electrical conductance of the suspensions of cellulose fibers for these two treatment conditions may differ to a cer-

tain degree. This topic is being presently pursued in our laboratory.

CONCLUSIONS

The corona treatment of components improves remarkably the mechanical properties of the cellulose/polypropylene composites. The degree of improvement depends on the specific fiber/polypropylene combination and the total treatment energy. The yield stress of composites made of treated cellulose and untreated or treated polypropylene (TC/PP and TC/TPP) are comparable, indicating that the dispersive forces are mainly responsible for the increased interfacial adhesion. In case of this specific composite system, the acid/base interactions seem to have a rather negligible effect on their performance.

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Table V Values of Dispersive Component of Treated Cellulose Fibers, Polypropylene Matrix and Work of Adhesion for TC/PP Composites

Current Level; mA	γ_c^* mJ/m ²	γ_{PP}^{**} mJ/m ²	W_a mJ/m ²
Untreated	31.8	27.0	58.6
15	37.4	—	63.6
20	39.2	—	65.0
25	41.0	—	66.6
30	41.9	—	68.0
35	44.8	—	69.6

Treatment time: 90 s.

* After reference 13; ** After reference 16.

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