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Characterization of the interface between cellulosic fibers and a thermoplastic matrix

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Abstract—The applicability of the microbond test to evaluate the interfacial properties between cellulosic fibers and thermoplastics was studied. Acetylation and heat treatment were applied to modify the surface of cellulosic fibers (rayon, cotton, and wood). The apparent diameters and surface free energies of the fibers were estimated by dynamic contact angle (DCA) analysis. Interfacial shear strengths between the cellulosic fibers and the polystyrene matrix were determined using the microbond test method. The test results indicate that acetylation increases the total surface free energy of the wood fibers, whereas heat treatment dramatically decreases the surface free energy of all cellulosic fibers tested. For heat treated and acetylated fibers, the greater the surface free energy, the greater the interfacial shear strength (ISS) regardless of fiber types. For control group fibers, a low ISS exists even though the fibers have high surface free energies because of the formation of a weak boundary layer. The high ISS between the acetylated wood fiber and the polystyrene matrix is attributed to the improved wetting and spreading of the melting polystyrene on the acetylated wood fiber surfaces. As such, the interfacial properties between the cellulosic fibers and polystyrene matrix system can be successfully characterized by dynamic contact angle and microbond test.

Keywords: Acetylation; dynamic contact angle (DCA) analysis; microbond test; surface free energy; cellulosic fiber; polystyrene.

1. INTRODUCTION

Recently, environmental and social interest in recycling has provided impetus for making reinforced thermoplastic composities with cellulosic fibers. However, the use of recycled cellulosic fibers for reinforced thermoplastic composites has been limited by poor interfacial adhesion between the hydrophilic cellulosic fibers and hydrophobic matrices [1, 2]. The interface plays a significant role in the effective transfer of

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stress between the thermoplastic matrix and fibers [3]. Most of the methodologies used to improve the compatibility of fiber surfaces and polymer matrices involve the modification of the fiber surface, matrix, or both. For example, plasma treatment [4] and chemical coupling [5] have had some success in the chemical modification of fiber surfaces. Acetic anhydride is used to modify the cell wall of wood to stabilize the wood products [6]. Graft copolymerization and coupling agents (isocyanates) have been used to improve the compatibility of the cellulosic fiber/thermoplastic matrix [7, 8].

A wealth of information has been generated on bulk properties of wood-fiber/polymer composites with different fiber surface modifications [2, 3, 7–10]. However, little research has addressed the physical performance of the fiber/matrix interface directly. Three tests are currently used in synthetic fiber reinforced composites to determine composite interfacial performance:

1. Fiber pull-out.
2. Critical fiber length.
3. Microbond test.

In the fiber pull-out test, an individual fiber is embedded to a predetermined distance in a polymer plug. The force required to extract the fiber from the plug is then recorded. Although this test has been widely used with synthetic fibers [11], the complex stress fields that develop around the tapered ends of natural fibers complicate the interpretation of results. In addition, the short length of many natural fibers often presents difficulties in precisely embedding fibers.

The critical fiber length test has been used to characterize the interface between a wood fiber with polyurethane [12] and polypropylene [13] matrices. In this test, an individual fiber is embedded in a matrix film. The film is then loaded in tension along the fiber axis. The fiber then fragments into lengths that are inversely related to the quality of the fiber/matrix interface. Although this test alleviates some of the experimental difficulties present for the fiber pull-out test, it is difficult to produce samples with straight fibers and it only produces an indirect measure of interface quality. In addition, this technique is best for samples with well developed interfaces to produce many fiber fragments. These conditions are often not possible for natural fibers with short lengths and poor interfaces.

The microbond test, developed by Miller and Gaur [14, 15], involves the removal of a small polymer droplet that is placed on the surface of the fiber. The test generates not only a maximum interfacial shear strength, but also a force-displacement diagram that can be used to interpret failure modes. In addition, the fiber droplet assembly can be examined after failure with a microscope to confirm failure mechanisms. The limitation of this test is that droplets as small as 30 μm are often necessary to prevent fiber breaking when interfaces are well developed. Such an extremely small polymer droplet is often difficult to produce on fibers.

This paper presents efforts at characterizing the interface between cellulosic fibers and synthetic thermoplastics. Specifically, wood, cotton, and rayon fibers were used with polystyrene droplets as both model and realistic material systems. All fibers were tested in a control, heat-treated, and acetylated form to produce various surface conditions. The specific objectives of the research were:

1. To determine the applicability of the microbond test to natural fiber composites.
2. To correlate interfacial shear strength of the fiber/polystyrene matrix to surface free energy measurements using dynamic contact angle analysis (DCA).

2. MATERIAL AND EXPERIMENTAL DETAIL

2.1. Material

Rayon, cotton, and wood fibers were evaluated as three model fibers. Rayon and cotton (medical grade) fibers were obtained commercially. Wood fibers were produced in our laboratory by macerating spruce (*Picea* spp.), following Franklin's procedure [16]. The macerated wood fibers were stored in distilled water for later acetylation and testing. The unmodified fibers are termed control fibers and tested as received.

Acetic anhydride used in acetylation was ACS analytical pure grade. Water and glycerol used for DCA experiments were pure HPLC grade. The test liquid surface tensions are listed in Table 1. The polystyrene number average molecular weight (MW) was 25 000 (Polyscience Inc.).

2.2. Fiber treatment procedure

Rayon, cotton, and wood fibers were acetylated using the technique of Rowell *et al.* [6]. The fibers were cleaned in an ultrasonic bath for 2 min before acetylation. In addition, fibers were heat treated with the same techniques used in acetylation without addition of acetic anhydride. The weight percent gain (WPG) from acetylation was calculated based on the oven dried weight of the untreated fibers. After weighing, both acetylated and heat treated fibers were extracted (Ext.) for 2 h in Soxhlet extractors with refluxing benzene/ethanol (1/1, v/v). After ovendrying, weight loss was determined. The samples were kept in a dark desiccator for later use. Control fibers were treated as received without extraction or ultrasonic cleaning.

Table 1.
Probe liquid surface tension (dynes/cm)

Methodology	Component	Water	Glycerol
Geometric	Dispersive	22.5	37
	Polar	50.3	26.4
	Total	72.8	63.4
Harmonic	Dispersive	22.1	40.6
	Polar	50.7	22.8
	Total	72.8	63.4

2.3. *Dynamic contact angle (DCA) tests*

DCA measurements were made using a Cahn Instrument DCA 322. Each DCA test consisted of measuring the advancing and receding angles over a 2 mm section of the fiber at a constant velocity of 12 μm/sec [17]. A small metal strip was used to minimize the electrostatic effects during the test.

Each test fiber was attached to a 35 × 10 mm^2 mylar strip with pressure sensitive tape. The fiber was carefully aligned to be perpendicular to the liquid surface during testing. This method held the sample more securely than the crimped aluminum foil method specified by Hodgson and Berg [17]. Forceps were used to handle the fibers at all times. For each treatment condition, five samples were tested for calculating the surface free energy.

The Wilhelmy equation was used to determine the dynamic contact angles of the fibers.

$$F = \gamma_{lv} P \cos(\theta), \tag{1}$$

where: F = force; γ_{lv} = probe liquid surface tension; P = perimeter; θ = dynamic contact angle.

The advancing contact angles were calculated using equation (2):

$$\cos(\theta) \quad \frac{F_a}{F_r}, \tag{2}$$

where: F_a = force for advancing; F_r = force for receding.

Each fiber was scanned and the perimeter and advancing contact angle were determined. The dispersive force, γ_s^d, and polar force, γ_s^p, were determined by measuring the contact angles of the probe liquids, water and glycerol, with different values of γ_L^d and γ_L^p against the single fiber, respectively. The sum of these components was used as an approximation of the total fiber surface free energy, γ_s [18]. Equation (3) was used to calculate the surface free energies of different fibers:

$$\gamma_{LV}\bigl(1 + \cos(\theta)\bigr) = \frac{4\gamma_s^d \gamma_{LV}^d}{\gamma_s^d + \gamma_{LV}^d} + \frac{4\gamma_s^p \gamma_{LV}^p}{\gamma_s^p + \gamma_{LV}^p} \tag{3}$$

2.4. *Microbond test procedure*

Polystyrene films (thickness 50–75 μm) were solution cast on a clean glass slide from a 20% solution of polystyrene. After 48 h, the polystyrene films were cut into 10 × 2 mm^2 pieces under a dissecting microscope. A longitudinal cut was made in the center of each film, following Miller and Gaur's procedure [14, 15]. The two halves were joined, like a pair of trousers, at one end in a distance of about 50–100 μm. The trouser films were peeled from the glass slide and dried for an additional 24 h.

After DCA analysis, each fiber was mounted on a piece of paperboard (45 × 60 mm^2) with a 30 × 5 mm^2 slit. The fiber was fixed to the paperboard support on one end by taping the transparent film end for DCA testing. A drop of epoxy resin was used to bond the free end of the fiber.

To form a microdroplet on the fiber, a polystyrene trouser film was hung on the horizontal fiber. Samples were placed in oven at 200°C for 1 min. Upon melting, droplets of uniform sizes were obtained on the fibers. The embedded lengths of microdroplets were measured optically. The fiber diameters were obtained by both optical and DCA scans. The contact angles of the polystyrene microdroplets on the fiber were measured optically with an image analysis system.

The microbond samples were tested in a screw-driven, universal testing machine equipped with a 50 g load cell. A vice with precision ground jaws was used to contact the microdroplet. Force and displacement data were acquired by computer. The maximum force (F_{max}) was recorded to calculate the maximum interfacial shear strength (τ_{max}) using equation (4):

$$\tau_{max} = \frac{F_{max}}{\pi DL} \tag{4}$$

where D and L are fiber diameter and droplet length, respectively.

3. RESULTS AND DISCUSSIONS

3.1. Fiber surface free energy

Because the surface free energies of fibers depend highly upon the treatment of their surfaces, it is worthwhile to specify the three treatments of fibers before further discussion. Firstly, the rayon, cotton, and wood fibers as received are defined as control group fibers (ctrl.). Secondly, fibers were cleaned ultrasonically and subsequently acetylated using the technique of Rowell *et al.* [6]. The acetylation procedure involves the fiber being ovendried for 12 h, acetylated at 120°C for 2 h, extracted for another 2 h in Soxhlet extractors with refluxing benzene/ethanol (1/1, v/v), and finally re-oven-dried for 12 h. In this process, both chemical acetylation and physical heat treatment were introduced. These chemically treated rayon, cotton, and wood fibers are defined as acetylated fibers (acet.). Thirdly, to separate the effect of heat tratment from acetylation, rayon, cotton, and wood fibers were cleaned with an ultrasonic bath and treated following the same procedure as acetylation without adding acetic anhydride. These rayon, cotton, and wood fibers are defined as heat treated fibers.

Extended heat treatment or high temperature can cause the fiber surfaces to age and lead to a low surface free energy [19, 20]. Our experimental results on surface free energy further confirm this conclusion. It is seen in Fig. 1 that the total surface free energy in heat-treated groups for all types of fibers is lower than that in control groups. A large difference in the surface free energy exists between the control and heat-treated groups for both rayon and cotton fibers. This may result from the reduction of hydroxyl groups on the cellulosic fiber surfaces. The hydroxyl groups on the crystalline surface and in the amorphous regions of cellulose in rayon and cotton fibers form sorption sites. High temperature treatment causes these sorption sites to

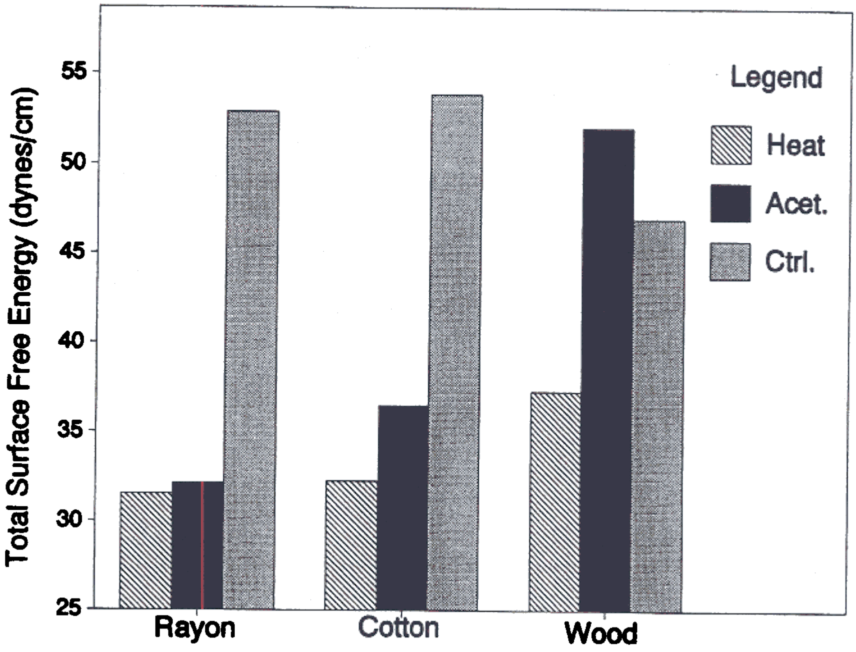

Figure 1. Total surface free energy for different fiber types and treatments.

lose their bound water. This provides good opportunities for two separate hydroxyl groups to contact intimately and form new hydrogen bonding, which is difficult to reverse. The sorption sites in this situation will permanently decrease. In contrast, hemicelluloses play an important role in the determination of fiber sorption sites for wood fibers. Few inter- and intra-hydrogen bonds occur in hemicelluloses because of their branched structures. When water is removed during the heat treatment of wood fibers, the hydroxyl groups in wood fibers may remain free. Therefore, the decrease in surface free energy with heat treatment is less for wood fibers than for either cotton or rayon fibers, which lack hemicelluloses.

The total surface free energies of fibers in acetylated groups are enhanced compared with the heat-treated fibers as shown in Fig. 1. The reason for this increase is that acetylation exhibits the combined effects of both heat and fiber surface chemical reaction. During acetylation, partial hydroxyl groups on the fiber surface were replaced by acetyl groups. These acetyl groups may prevent the formation of hydrogen bonding between the neighboring hydroxyl groups. With a high grafting percentage, the fiber surfaces are dominated by the $-COO-$ ester configuration instead of free hydroxyl groups. Since the polarity of an ester bond is higher than that of the hydroxyl group, the surface free energy of the ester compound is higher than that of the corresponding hydroxyl compound from the wettability 'spectrum' for selected surfaces [21]. This causes the total surface free energy of acetylated fibers to increase.

As shown in Fig. 2, the total surface free energy is mainly dominated by the polar force components. This explanation is supported by research on synthetic polymers. Ko *et al.* [22] found that the total surface free energy of polymers increases as the

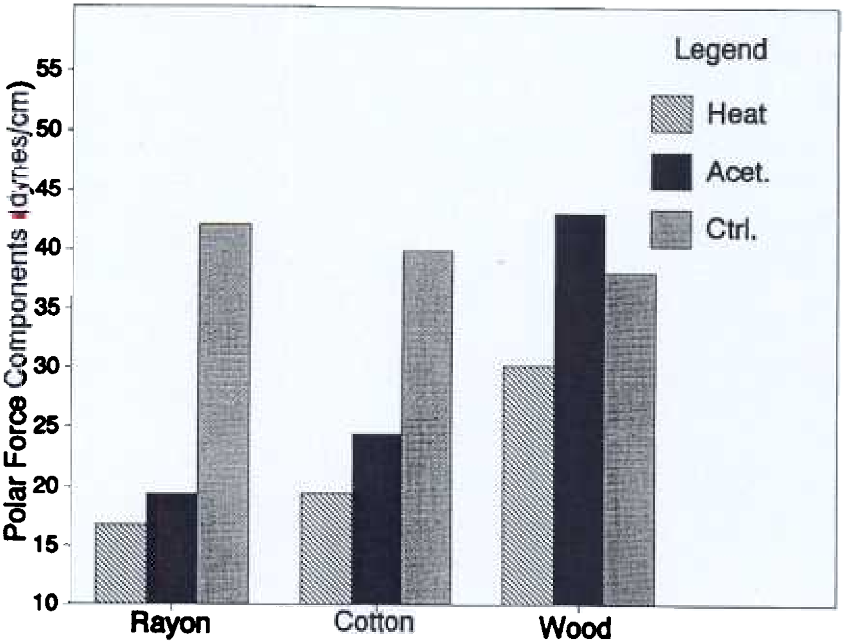

Figure 2. Comparison of polar force components with dispersive components for different fiber types and treatments.

ratio of hydrophilic functional groups to hydrophobic functional groups increases. In both treated glass fibers and polythylene films, the O/C ratio is positively correlated with the polar contribution of total surface free energy on the fiber surface [4, 23]. Using X-ray photoelectron spectroscopy (XPS), Gardner [24] found that acetylation of yellow-poplar and red oak increases the oxygen/carbon (O/C) ratio [23]. Therefore, the polar force components play a dominant role in controlling the total surface free energy of fibers.

Table 2 shows that both total surface free energy and polar force components in acetylated group fibers are in the order: acetyl wood > acetyl cotton > acetyl rayon. Experimental results indicated that the acetylation of wood fibers resulted in a weight percent gain (WPG) of 11.27 with an acetyl content of 10.37% similar to that found by Gardner [24] for yellow-poplar and red oak. A low WPG was found for both acetylated cotton (0.82%) and acetylated rayon (undetectable) fibers. The different acetyl contents can be attributed to the different reactivities and surface morphologies among the different types of fibers. For example, each β-D-glucopyranose unit within the cellulose chain has three reactive hydroxyl groups, two secondary (HO-2 and HO-3) and one primary (HO-6). For esterification, the primary hydroxyl group (HO-6) possesses the highest reactivity. In addition, the morphology of cellulose has a profound effect on its reactivity. The hydroxyl groups located in the amorphous regions are highly accessible and react readily, whereas those in crystalline regions with close packing and strong interchain bonding can be completely inaccessible [25]. Both rayon and cotton fibers are highly crystalline polymers which provide few free hydroxyl groups

Table 2.

Surface free energy means and variances for different types of fibers under different treatment conditions

Type	Sources	Harmonic means (dynes/cm)		
		Dispers.	Polar	Total
Rayon	Ctrl.	10.78 ± 0.78	42.10 ± 3.26	52.89 ± 1.40
	Heat	14.79 ± 2.46	16.73 ± 2.96	31.55 ± 1.03
	Acet.	12.58 ± 0.75	19.42 ± 1.87	32.13 ± 1.32
Cotton	Ctrl.	13.79 ± 3.88	39.91 ± 10.43	53.86 ± 8.49
	Heat	12.79 ± 3.58	19.47 ± 1.99	32.26 ± 3.57
	Acet.	12.07 ± 2.84	24.45 ± 5.62	36.52 ± 3.67
Wood	Ctrl.	8.89 ± 2.79	38.10 ± 5.19	46.99 ± 4.85
	Heat	7.07 ± 3.09	30.24 ± 7.77	37.31 ± 5.96
	Acet.	8.99 ± 3.40	43.05 ± 4.85	52.04 ± 3.00

for reaction. However, wood fiber is made up of cellulose and hemicellulose. Most of its lignin was removed during maceration. Large amorphous components exist in wood fibers and these amorphous components cause wood fibers to have a much higher reactivity for acetylation than that exhibited by rayon and cotton fibers. As such, the difference in morphology and chemical composition of the fiber surfaces results in the different amount of acetylation and different surface free energy state.

3.2. Microbond test

The interfacial shear strength (ISS) was calculated from maximum load and interfacial area using equation (4). It is seen that the ISS is determined by the accurate measurement of the microdroplet length, perimeter, and applied shear force. In addition, the validity of equation (4) should be confirmed before equation (4) can be used to calculate the ISS.

The length of fibers can be easily determined optically. The perimeters of rayon fibers may be also measured optically. For cotton and wood fibers, an accurate value of the perimeter presents a difficult problem because of their irregular shape. It has been found that the receding contact angle of many liquids including water on cellulosic fibers is zero [17, 18, 26–28]. Therefore, the Wilhelmy equation (1) can be reduced to determine fiber perimeter (P) by:

$$P = \frac{F_r}{\gamma_{lv}}. \tag{5}$$

Table 3 lists the comparison of fiber diameter values measured by DCA scan and optical microscope. The mean diameters for rayon fibers determined using optical measurements and DCA scans are similar because of their smooth and uniform surfaces. We believe that the means of fiber diameters measured by DCA scan are more reliable and accurate than those obtained by the optical method because the necessary

Table 3.
Means of fiber diameters using DCA and optical methods

Methodology	No. sample	Means of fiber diameters (μm)		Standard deviation of fiber diameters (μm)	
Fiber type		DCA	Micro.	DCA	Micro.
Wood fiber	18	22.16	28.57	4.4	4.7
Cotton fiber	10	16.24	15.3	1.32	1.4
Rayon fiber	10	27.76	27.5	1.34	2.1

assumption for optical measurement, which is that the cross-section of a wood fiber is perfectly circular, is unrealistic. Therefore, before microbond testing, all fibers were scanned using DCA analysis and perimeters were determined by equation (5).

Figure 3 shows a typical load-deformation diagram for the microbond test. The maximum forces in Fig. 3 were used to calculate the ISS from equation (4). As with microbond testing on synthetic fibers [14, 15], no consistent relationship was found between the ISS and the embedded length of the microdroplet in the range examined. This indicates that equation (4) can be used to calculate the interface shear strength between fibers and matrices [14, 15]. The interfacial shear strengths for each fiber type are summarized in Table 4. A one-way analysis of variance (ANOVA) was used to determine whether fiber treatment had a statistically significant influence on the ISS ($P > 0.01$). The differences of the ISS means for fiber groups were determined using Duncan's multiple range test and are shown in Table 4. The results

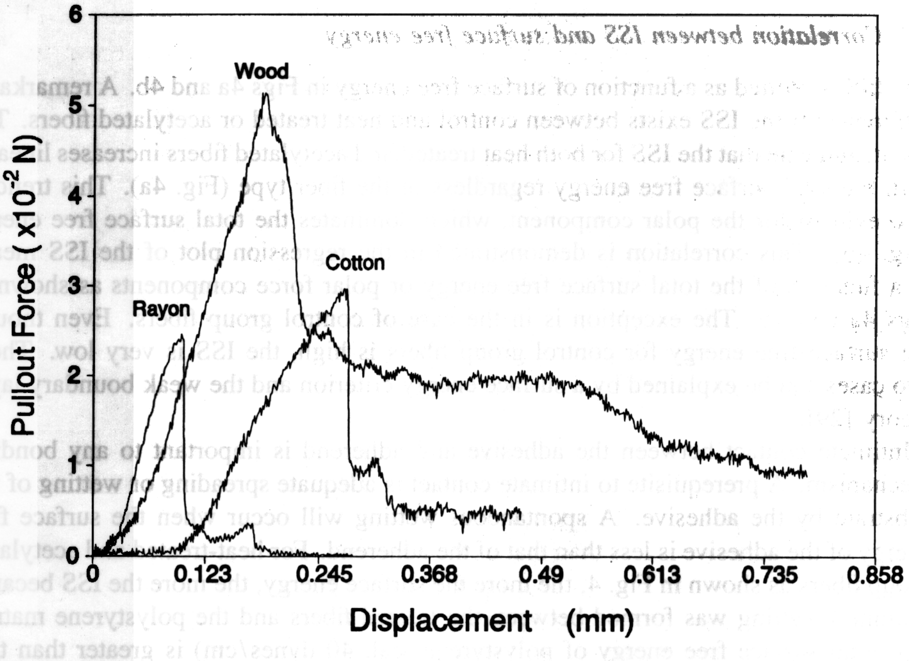

Figure 3. Typical force/displacement diagram for microbond test.

Table 4.
Summary of the interfacial shear strengths between the cellulosic fiber/polystyrene matrix system

Type	Source	Shear strength (MPa)	No.	Group
Rayon	Ctrl.	3.06 ± 1.44	78	D&E
	Heat	3.72 ± 1.26	18	D&C&E
	Acet.	2.87 ± 1.47	12	E
Cotton	Ctrl.	3.36 ± 1.30	36	D&C&E
	Heat	4.52 ± 0.97	13	C
	Acet.	6.46 ± 2.84	6	B
Wood	Ctrl.	3.06 ± 1.44	14	C&D&E
	Heat	6.29 ± 1.57	12	B
	Acet.	10.00 ± 4.47	9	A
Total		3.95 ± 2.36	198	

Note: Means with the same letter are not significantly different. The shear strength decreases in A, B, C, D, E order.

indicate that the acetylated wood fiber group has significantly higher shear strengths (ca. 10.0 MPa) compared with all other groups. Acetylation also improved the ISS for cotton, although to a lesser degree. No differences were found in ISS with fiber treatments for rayon. Even though large variabilities exist in different group fibers, a significant difference in the ISS is illustrated in Table 4.

3.3. Correlation between ISS and surface free energy

The ISS is plotted as a function of surface free energy in Figs 4a and 4b. A remarkable difference of the ISS exists between control and heat treated or acetylated fibers. The results indicate that the ISS for both heat treated and acetylated fibers increases linearly with the total surface free energy regardless of the fiber type (Fig. 4a). This trend is also evident for the polar component, which dominates the total surface free energy (Fig. 4b). This correlation is demonstrated in the regression plot of the ISS means as a function of the total surface free energy or polar force components as shown in Figs 4a and 4b. The exception is in the case of control group fibers. Even though the surface free energy for control group fibers is high, the ISS is very low. These two cases can be explained by a surface energy criterion and the weak boundary layer theory [29].

Intimate contact between the adhesive and adherend is important to any bonding mechanism. A prerequisite to intimate contact is adequate spreading or wetting of the substrate by the adhesive. A spontaneous wetting will occur when the surface free energy of the adhesive is less than that of the adherend. For heat-treated and acetylated group fibers as shown in Fig. 4, the more the surface energy, the more the ISS because a limited wetting was formed between the treated fibers and the polystyrene matrix. The total surface free energy of polystyrene (cal. 40 dynes/cm) is greater than that of all fiber types except acetylated wood fibers and the total surface free energies for

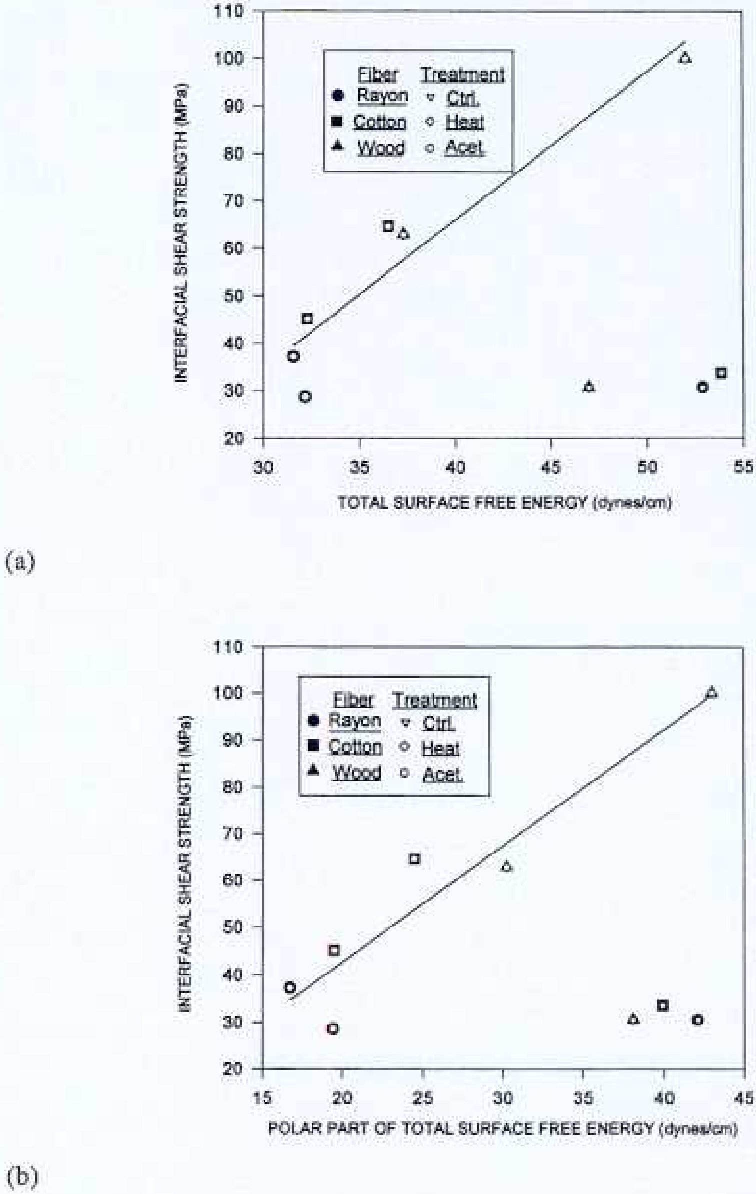

Figure 4. Relationship between interfacial shear strength (ISS) and surface free energy: (a) ISS vs. total surface free energy; (b) ISS vs. polar component of surface free energy.

wood fibers are in the order: acet. wood > ctrl. wood > heat wood. Figure 5 illustrates the microdroplet on control and acetylated wood fibers. The average contact angle of the polystyrene microdroplet on the wood fibers is 9.6 ± 3.6 degree for the acetylated groups and 26.9 ± 5.7 degree for control groups, respectively. This suggests that the difference of ISS between acetylated, heat-treated, and control group wood fibers can

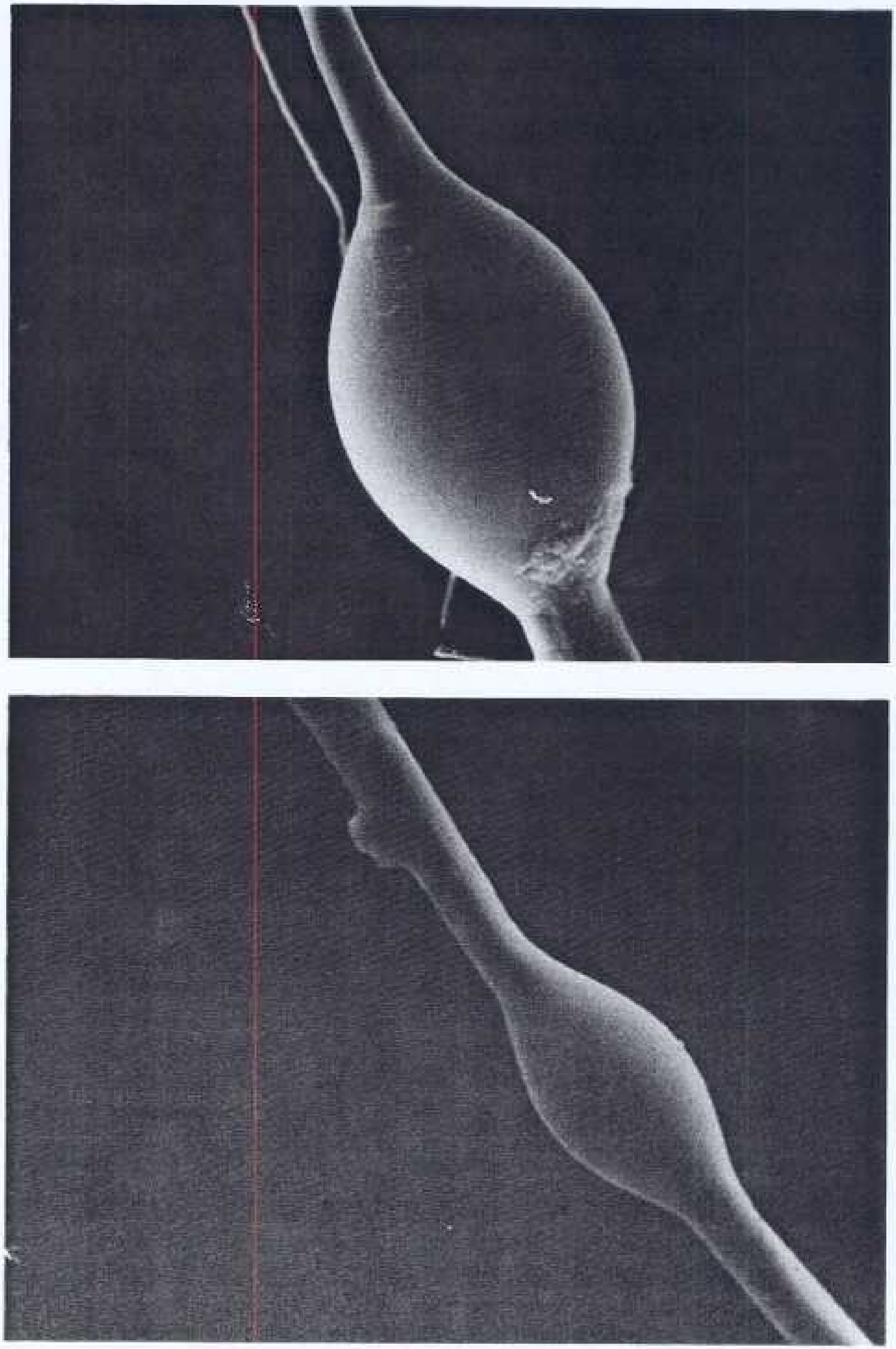

Figure 5. Topomicrographs of microdroplet on the wood fiber surfaces: (a) before acetylation (magnitude: 200×); (b) after acetylation (magnitude: 200×).

be partially attributed to the better wetting and spreading of polystyrene film on the wood fiber surfaces. The surface modification of wood fibers improves the wetting of polystyrene on the fiber surface, thereby increasing the work of adhesion.

In contrast, the interfacial shear strengths (cal. 3.0 MPa) between the control fibers and polystyrene do not follow the same trend with surface free energy as do the treated fibers as shown in Fig. 4. Even though high surface free energies exist in control group fibers, low ISSs present in all control groups of fibers. It is believed that a weak boundary layer may exist in these control fibers. Weak boundary layers refer to layers in the interphase with lower cohesive or adhesive properties than their bulk substrates due to entrapped gas, contaminants, and structural anomalies of the substrates. Contaminants are generally detrimental to adhesion and can prevent formation of strong adhesion although extensive interfacial contact might be present. During ultrasonic treatment, acetylation, and extraction, the fiber surfaces may add new functional groups and remove contaminants from the fiber surface so that different fiber surfaces are present in heat-treated and acetylated fibers. The significant increases of the ISS indicate that the surface treatment of fibers is an effective approach to obtaining high performance composites.

4. CONCLUSIONS

The combination of dynamic contact angle (DCA) analysis with the microbond test method can directly characterize the fiber surface thermodynamics and the mechanical performance of fiber and matrix strength interface. Determining surface free energy presents a simple and quantitative evaluation of the wettability of cellulosic fibers. Heat treatment leads to surface free energy decreases. The surface free energy of acetylated wood fibers is 52 dyne/cm, which is 40% higher than that of heat treated wood fibers. This increase is assigned to the acetyl group polar contribution increase.

For heat and acetylation treated fibers, the correlation between the surface characteristics of the fibers and the ISS can be estimated by the surface energy criterion. The higher the total surface free energy, the greater the ISS regardless of fiber type. The total surface free energy of acetylated wood fibers, which drives the polystyrene to wet and spread on its surface, is the dominant reason that leads to high interfacial shear strength between the acetylated wood fiber and polystyrene matrix. On the other hand, a low ISS for control group fibers exists even though the fiber surface has a high surface free energy regardless of fiber types. A weak boundary layer is postulated as an important factor which dominates the untreated cellulosic fiber and polystyrene composite interface. Fiber surface treatment may add new functional groups, remove fiber surface contaminants, and improve the interfacial shear strengths.

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