

Surface Energy of Untreated and Surface-Modified Cellulose Fibers

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Synopsis

Average advancing and receding contact angles made against cotton and glass fibers by a set of probe liquids are determined using the Wilhelmy technique. The dispersive and polar components of the surface energy are calculated from the measured contact angles using both the geometric and the harmonic mean methods. It is found that these components are similar for untreated cellulose and glass fibers, and that they both have a high polar component, corresponding to a hydrophilic surface. Changes in surface energy caused by treatment of the cellulose fiber surfaces with melamine, polyethyleneimine (PEI), and a silane coupling agent are reported. It is found in particular that polyethyleneimine treatment of cellulose significantly reduces the polar component of its surface energy. While treatment of glass fibers with a silane coupling agent reduces the polar component and increases the dispersive component of the surface energy, it shows little effect on the surface energy of cellulose.

INTRODUCTION

Synthetic polymers are playing an increasingly important role in the manufacture of materials based on cellulose. For example, a polymer is commonly added as a binder to hold the fibers in place in dry-formed papers,^{1,2} and polymer films are often extrusion coated on paper boards used in the packaging industry.³ Conversely, cellulose fibers show increasing promise as reinforcing materials in plastics,^{4,5} and the development of a variety of cellulose fiber-polymer matrix composite materials appears imminent. Critical to the properties of such materials is the nature of adhesion between cellulose fibers and synthetic polymers, and an understanding of polymer-cellulose interactions is essential for predicting and improving product performance. Although very many factors may be involved in the formation of an adhesive bond, a *necessary* condition for good adhesion between two materials appears to be compatibility between their surface energies. In the simplest cases, where chemical reaction between the two materials does not occur, such compatibility means rough equality between both the total magnitude and the makeup ("polarity fraction") of the surface energies. Both the "interfacial defect" and the "fracture energy" models of adhesion lead to these criteria.⁶

Many attempts have been made to improve the adhesion of cellulose fibers to a polymer matrix by surface modification of the cellulose fibers or by modifying the polymer matrix. For example, treatment of cellulose fibers with

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polyethyleneimine (PEI) and protein or surface modification of the fibers with triazine enhances the mechanical strength of cellulose-epoxy composites.⁵ A similar improvement in strength is obtained by triazine treatment of the fibers of cellulose-polyester composites.⁷ On the other hand, the strength of fiber-reinforced polypropylene is improved by substituting maleic anhydride-modified polypropylene for part of the polypropylene matrix.⁴ Such results have not generally been examined in terms of surface energy criteria. The consideration of surface energetics in adhesion between surface-modified *glass* fibers and polymer matrices, however, has been useful in the interpretation of the effectiveness of silane coupling agents.⁸⁻¹¹ Wesson et al.^{10,11} attribute the improvement in adhesion effected by the coupling agent in part to a reduction in the polar component of the fiber surface energy. They also point out how important this is for reducing the hydrogen bonding capability of the fiber surface in order to increase the wet strength of the composite.

Application of surface energy criteria is practicable because surface energies may be determined independently using wetting and surface tension measurements.¹² As detailed below, one may obtain the values for dispersive and polar components, σ^d and σ^p , respectively, of the surface energy of a given solid from the measured contact angles made against it by probe liquids. The surface tensions and surface tension components of the probe liquids are measured independently.

The objective of the present work is to use wetting measurements to determine the dispersive and polar components of the surface energy of cotton cellulose fibers and to investigate how some compounds physically adsorbed to the surface may affect these properties. The adsorbates studied were melamine, PEI and a silane coupling agent. Melamine was chosen because its amino groups were expected to confer added hydrophilicity to the cellulose surface, while PEI was chosen for its anticipated opposite effect. The latter material is also of interest because of its common usage as a wet and dry strength additive and as an agent to improve filler retention in papermaking.¹³ Finally, PEI has shown efficacy in combination with proteins for improving the strength of cellulose fiber-epoxy composites. Silane coupling agents are included because of their well-known effect on the adhesion of glass fibers to synthetic polymers. For comparison, glass fibers are thus included in the present investigation.

EXPERIMENT

Materials

The fibers used were of purified cotton from Parke-Davis, and the glass fibers were uncoated Evanite 523 from Evans Glass Fiber. The adsorbates used for surface treating of the cellulose fibers were: polyethyleneimine (PEI) $(C_2H_4NH)_n$ with a molecular weight of ca. 60,000 from BASF Inc. (Polymine P), melamine $C_3N_3(NH_2)_3$ purified at the College of Forest Resources, University of Washington, and a silane coupling agent, A-174, from Union Carbide (8-methacryloxypropyltrimethoxysilane) $CH_2C_3H_3OOCH_2CH_2CH_2Si(OCH_3)_3$. The glass fibers were treated only with the silane coupling agent. The fiber-wetting experiments were carried out in hexadecane purified to 99%, diiodomethane 99%, and triply distilled water.

Surface Treatments

The solutions used for the fiber surface treatments were prepared as follows:

Polyethyleneimine: diluted to 0.2 wt% in water and adjusted to pH 9.5 with HCl.

Melamine: powder dissolved in water to 0.2 wt%, giving a pH of 7.2.

Silane: 0.5 silane added to a 50 mL mixture of 90 vol% methanol and 10 vol% water and adjusted to pH 4 with acetic acid.

Treatment was according to the following scheme:

Stir gently 0.1 g of fibers for 1 h in a 50 mL treatment solution prepared immediately before use.

Transfer fibers onto a filter paper and drain excess amount of water or solvent.

Dry and cure fibers at 110°C for 1 h.

Preparation of Fiber Test Samples

Individual cellulose fibers were mounted by pinching their ends in a folded aluminum foil of several layers thickness described in detail elsewhere.¹⁴ The glass fibers, because of their brittleness, were mounted instead between two rectangular pieces of adhesive aluminum foil. For suspending from the hang-down wire of the electrobalance, a hole was punched in the foil of each sample at the opposite side from where the fiber protruded. The fibers were cut approximately 5 mm from the edge of the foil. Eight to ten fiber test specimens were prepared and used for each fiber and treatment.

Measuring the Advancing and Receding Force

The contact angles between the fiber and the wetting liquid as well as the surface tension of the wetting liquids were measured with a microbalance by the Wilhelmy technique, as described in detail elsewhere.^{12,14} The method is similar to that used by Wesson et al.^{10,11} and Mason et al.¹⁵ The principle is to measure the downward force of surface tension on the wetted interline around the fiber (or rod or plate) as the liquid is raised or lowered over the length of the test specimen. The advancing and receding contact angles are calculated from the advancing and receding force if both the perimeter of the test specimen and the surface tension of the wetting liquid are known. The apparatus used consisted of a Cahn model RG 2000 electrobalance, a Burleigh Instruments Model IW 601-2 translator, a Hewlett-Packard HP87 computer, and a telescope for observing the fiber-liquid system. The wetting liquid was inside a small cup ($d = 20$ mm) of aluminum or Teflon in an environmental chamber placed on top of a vertically movable stage connected to the translator. The aluminum cup was used for hexadecane and diiodomethane in order to minimize electrostatic effects. Teflon was used for water since electrostatic effects were not detected for this liquid in the wetting experiments. The test specimen hung freely on the hangdown wire from the microbalance a short distance above the liquid surface at the start of a measurement cycle. The air

in the environmental chamber was humidified to 100% relative humidity (RH) with a wet filter paper wick inside. The computer was used to raise and lower the liquid in accord with the prescribed schedule, involving one to several cycles, to record data output (at a sampling rate of 5/s) and to compute contact angles, surface tension, or perimeter, as required. Approximately the same part of the fiber was measured for all wetting liquids. The depth of fiber immersion (hence the axial excursion) was approximately 1000 μm in all cases, and the rate of excursion was set at 11 $\mu\text{m/s}$. The untreated and treated cellulose and glass fibers were cycled twice in hexadecane and diiodomethane and ten times in triply distilled water.

Calculating the Contact Angles

The wetted perimeter, liquid surface tension, and the contact angle are related to the measured downward force (relative to the weight of the suspended system in air) by Eq. (1).¹²

$$F = p\sigma \cos \theta - \rho_1 gAh \quad (1)$$

where

F = advancing (a) or receding (r) force

p = wetted perimeter

σ = surface tension of liquid

θ = advancing or receding contact angle

ρ_1 = liquid density

g = gravitational acceleration

A = cross-sectional area of fiber, rod, or plate

h = immersion depth

The buoyancy term $\rho_1 gAh$ is negligible (because A is so small) in the present measurements on fibers. The perimeter of the fiber and the surface tension of the liquid need to be known in order to calculate the advancing and receding contact angles. The fiber perimeter can be obtained from a wetting experiment with a liquid having a low surface tension (giving a wet-out condition, $\theta = 0^\circ$) and with no swelling effect on the fiber. Under these conditions, the only unknown in Eq. (1) is the perimeter. The advancing and receding contact angles are then calculated from the advancing and receding force in a wetting experiment with any test liquid (if it does not swell the fiber and change the perimeter). Hexadecane ($\sigma = 27.6$ dynes/cm) was used to obtain the perimeter of the glass fibers. Possible swelling was a problem with cellulose,^{16,17} so it was possible to obtain only an apparent perimeter for cellulose fibers in contact angle calculations. In wetting experiments with cellulose fibers and with diiodomethane, the apparent perimeter was obtained from the receding force in hexadecane, the assumption being that there is no difference in swelling behavior on cellulose between these two liquids. Perimeters obtained with hexadecane were also used in wetting experiments with PEI and silane-treated cellulose fibers in water. For untreated and melamine-treated cellulose fibers in water, the apparent perimeter was obtained from the receding force in

water. The assumption was that the receding contact angle in water was zero for these two fibers. The criterion for choosing the apparent perimeter for cellulose fibers in the advancing contact angle calculations for water was to use the larger value obtained from the receding force in either hexadecane or water.

The Surface Tension of the Liquids

The surface tension of the wetting liquids was measured before and after each set of measurements using a roughened platinized platinum rod,¹⁸ which is wet out by most liquids. The surface tension check consisted of cycling the liquid level up and down a distance of 1000 μm at a speed of 11 $\mu\text{m/s}$. The rod end had an area-to-perimeter ratio large enough to make buoyancy correction necessary. The reference level from which the height in the buoyancy term is calculated is the point where the rod end is aligned with the undisturbed liquid level, determined automatically by the computer. The surface tensions of the wetting liquids were hexadecane: 28.0 ± 0.2 , diiodomethane: 51.4 ± 0.7 , and triply distilled water: 73.0 ± 1.0 dynes/cm. No significant change in the surface tension of the wetting liquids was found after fiber testing.

RESULTS AND DISCUSSION

Force Curves from Fiber-Wetting Experiments

Pen recorder curves obtained from wetting experiments on one single fiber in three different liquids for the first two cycles are shown in Figures 1 and 2. The forces acting on the fibers are drawn as a function of time. The curves are divided into four zones: the advancing and receding of the liquid front along the length of the fiber for Cycles 1 and 2. Figure 1 shows the force curves for an untreated cellulose fiber, and Figure 2 for an untreated glass fiber in hexadecane, diiodomethane, and triply distilled water. A drift in baseline was noted when fibers mounted on an adhesive aluminum foil were tested with diiodomethane. This can be seen in Figure 2, and it was attributed to sorption of the high density diiodomethane (3.325 g/cm^3) onto the adhesive layer. In order to compensate for this, the baseline value was taken before and after each measurement and subtracted from the curve by assuming a linear sorption rate. The slight drift in baseline was observed only for the fibers mounted with adhesive aluminum foil.

The noise in the wetting profiles can be attributed to both chemical and geometric heterogeneities on the fiber surface.¹² However, for a liquid which fully wets out the fiber (such as hexadecane), only geometric heterogeneities will be evident. This is observed in Figures 1 and 2 by comparing the wetting profiles for hexadecane and diiodomethane. The frequency of fluctuations in the wetting curves for hexadecane is not as great as for diiodomethane. Water, as a wetting liquid, has a frequency dependent upon whether the liquid is advancing or receding. In general, the lower the contact angle, the less important are chemical heterogeneities in the wetting profile. Somewhat higher frequency was also present in the advancing compared to the receding force curves for untreated glass fibers. Only a small difference in the frequency between advancing and receding branches of the wetting force curves was

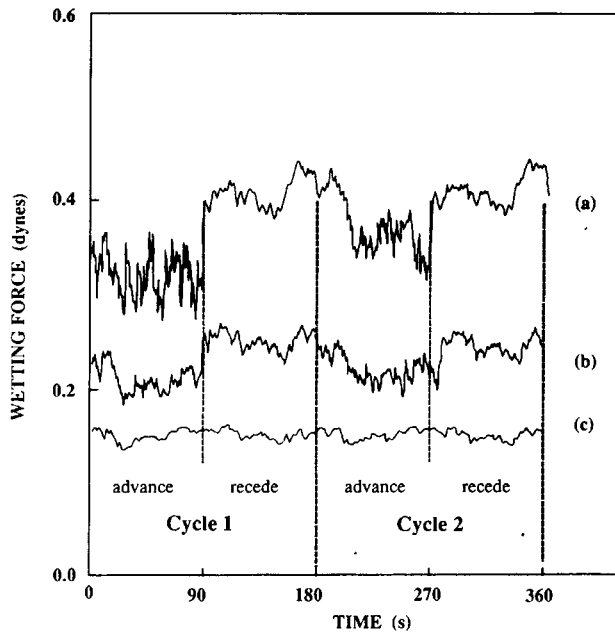


Fig. 1. Wetting force as a function of time for an untreated cellulose fiber tested in water (a), diiodomethane (b), and hexadecane (c) for the initial two wetting cycles. Each cycle consists of an advancing and receding 1-mm excursion of the liquid front over the same part of the fiber surface.

observed in cases where wetting was poor, viz., polyethyleneimine-treated cellulose and silane-treated glass with water, as shown in Figure 3. The treatments increased the high frequency components in the receding force and made the frequency content in the receding force look similar to that of the advancing force. The treatments made the fibers more hydrophobic and increased the receding contact angle, suggesting that chemical heterogeneities

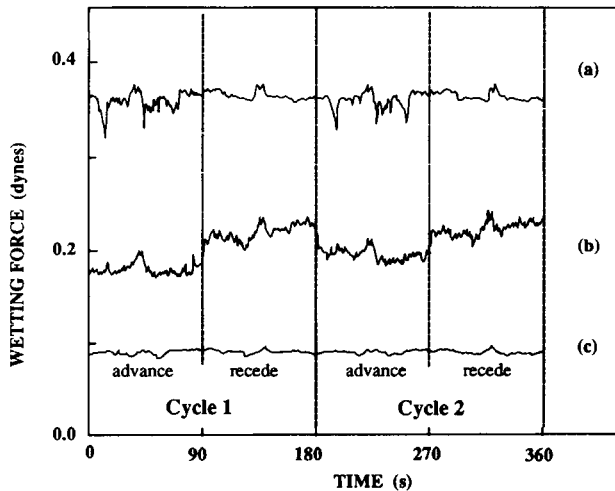


Fig. 2. Wetting force as a function of time for a glass fiber tested in the same liquids as in Figure 1.

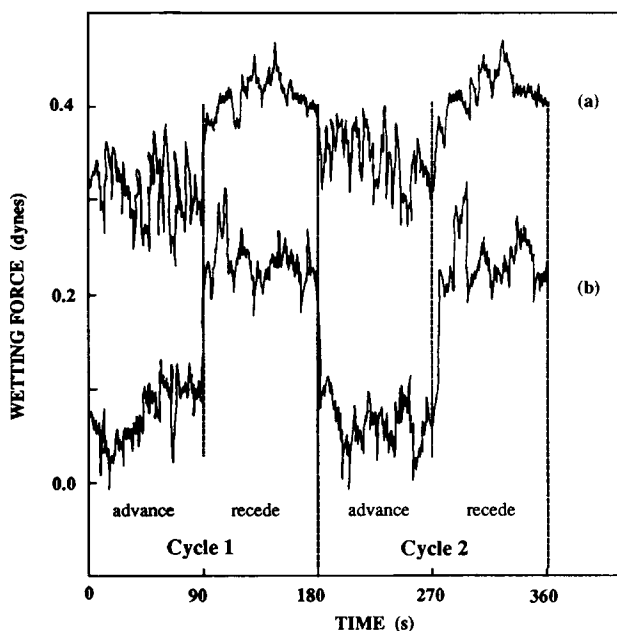


Fig. 3. Wetting force profiles for a PEI-treated cellulose fiber (a) and a silane-treated glass fiber (b) in water.

influenced the receding force profile. Melamine and silane treatments of the cellulose fibers had no influence on the frequency components when water was used as the wetting liquid.

Average advancing and receding contact angles were computed from the measured force traces using Eq. (1) for up to 10 cycles for each fiber-liquid combination. The advancing angles, as shown in terms of their cosine (Figs. 4–7), show gradual change as the sample is repeatedly cycled. Each cycle required approximately 180 s so that the 10-cycle experiment spanned a total time of 30 min. In each case, steady-state conditions were achieved over this period. Each data point shown corresponds to one cycle, with the cycle-average force used to compute $\cos \theta$, and the different data shown for the same cycle number correspond to repeat runs with different fibers of identical type and treatment. The solid lines show the average of all repeat runs, while the dashed curves show the 95% confidence limits. While significant scatter is evident, the trends are unmistakable.

Untreated cellulose fibers showed an average, first-cycle advancing contact angle of 40° ($\cos \theta_a = 0.76$) in water, leveling out after 10 cycles to 20° (Fig. 4). The opposite trend was found for untreated glass fibers (Fig. 6), which showed a first-cycle contact angle of 11° ($\cos \theta_a = 0.98$) followed by a small increase over time to 18° ($\cos \theta_a = 0.95$). Figure 5 shows results for PEI-treated cellulose fibers in water: a significant decrease in $\cos \theta_a$ (i.e., increase in contact angle) in comparison to the untreated fibers. This parallels the comparison obtained between untreated and silane-treated glass fibers in water (Figs. 6 and 7). The measured receding force showed no change with cycle number for any of the cases studied.

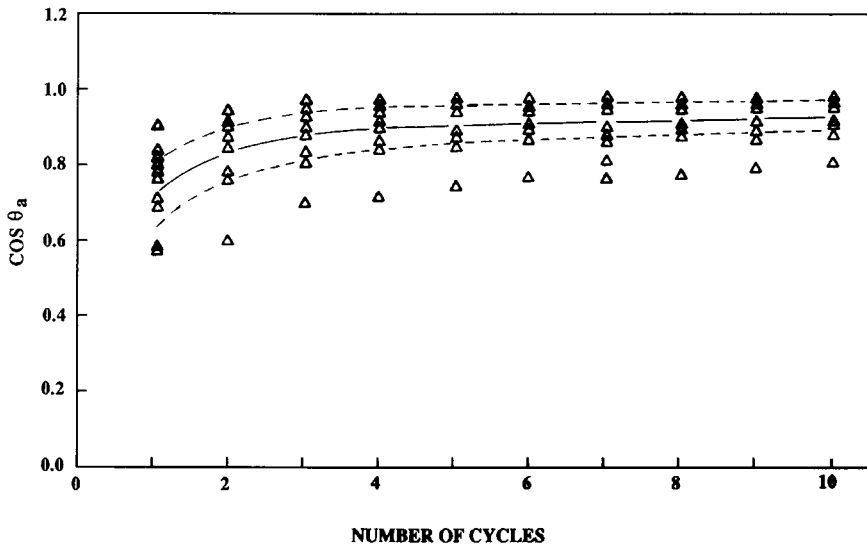


Fig. 4. Cosine of the advancing contact angle for untreated cellulose fibers in water as a function of cycle number. Each data point corresponds to a cycle-averaged value for one fiber. The continuous line is the average value for all fibers, and the dashed lines are the upper and lower 95% confidence limits.

Figure 8 summarizes the wetting results for treated and untreated fibers in both water and diiodomethane. The water results are taken from the tenth cycle, and those for diiodomethane from the second cycle. The data showed little difference between the untreated, melamine-treated and silane-treated cellulose fibers. Only the PEI treatment significantly decreased the wettabil-

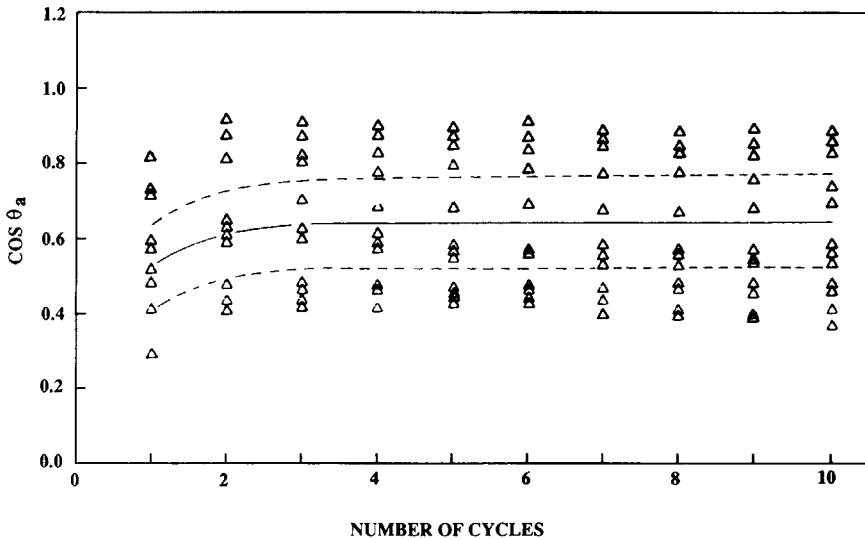


Fig. 5. Cosine of the advancing contact angle for PEI-treated cellulose fibers in water as a function of cycle number. The data points and lines have the same significance as in Figure 4.

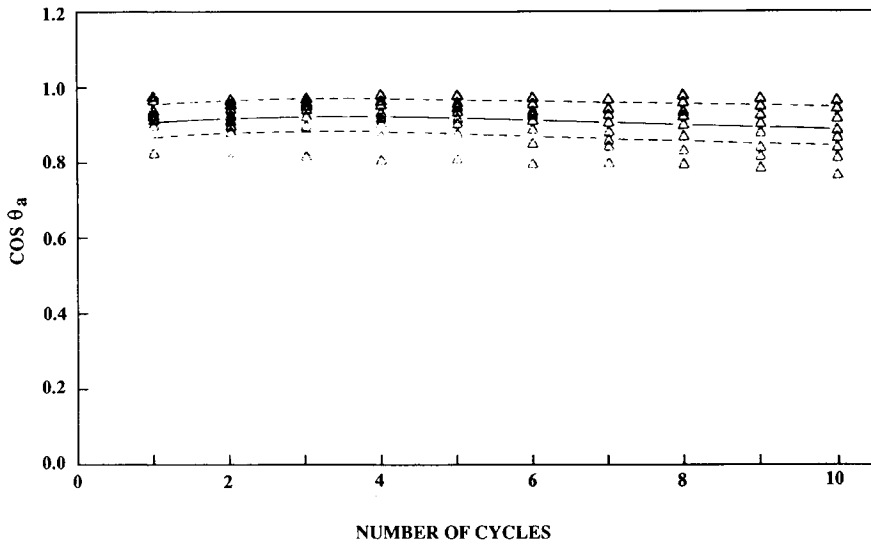


Fig. 6. Cosine of the advancing contact angle for untreated glass fibers in water as a function of cycle number. The data points and lines have the same significance as in Figure 4.

ity of these fibers, in parallel with but less pronounced than the effect observed for silane treatment of the glass fibers.

The permanence of the PEI treatment of the cellulose fibers and the silane treatment of the glass fibers was examined by washing them. The treated fibers were rinsed five times in water and once in acetone. The results, shown in Figure 9, indicated that the changes effected in water wettability were in neither case permanent.

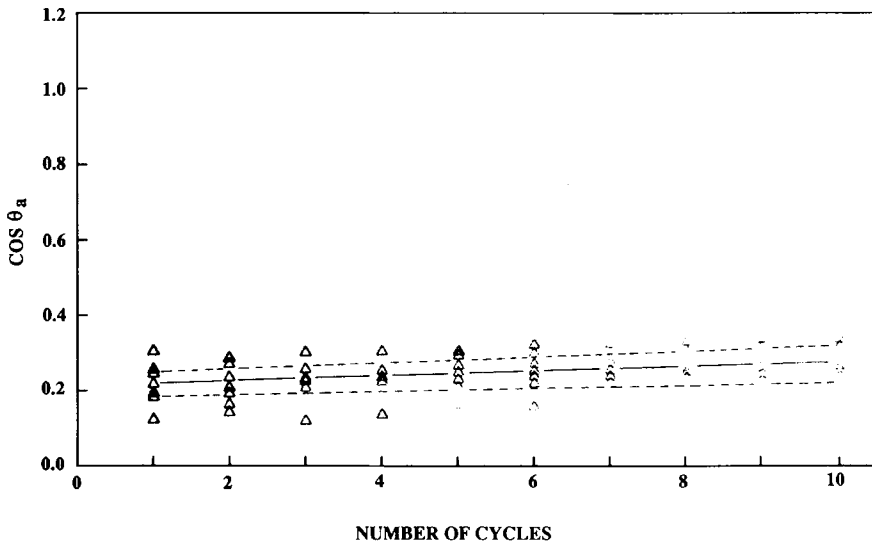


Fig. 7. Cosine of the advancing contact angle for silane-treated glass fibers in water as a function of cycle number. The data points and lines have the same significance as in Figure 4.

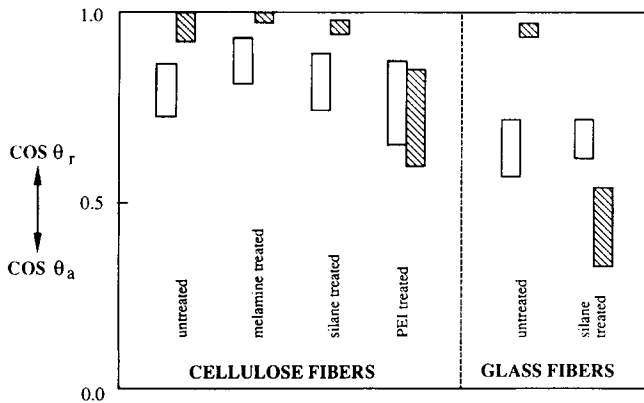


Fig. 8. Summary of the advancing and receding contact angles (in terms of their cosines) for untreated and treated cellulose and glass fibers. The unfilled and cross-hatched bars refer to the contact angles in diiodomethane and water, resp., where the lower and upper ends of the bars correspond to the advancing and receding contact angles, respectively.

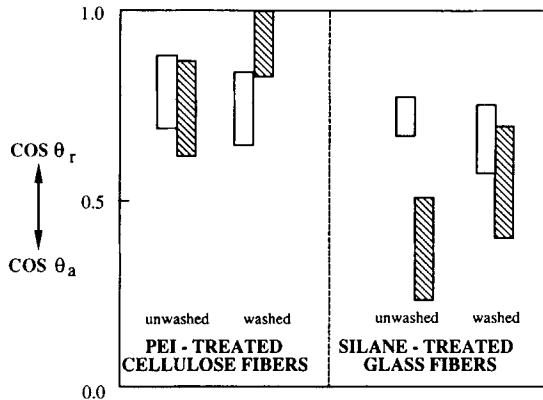


Fig. 9. The effect of washing on the advancing and receding contact angles for PEI-treated cellulose fibers and silane-treated glass fibers. The unfilled and cross-hatched bars are labelled the same as in Figure 8.

Surface Energy of the Fibers

The surface energies of materials may be split into dispersive and polar components, as suggested by Fowkes:¹⁹

$$\sigma = \sigma^d + \sigma^p \quad (2)$$

If hydrogen bonding or other specific interactions occur between the two phases forming the interface, either additional terms must be added to the right hand side of Eq. (2) or such terms must be lumped into σ^p . The method most often used for extracting the values of σ^d and σ^p for a solid surface from contact angle and surface tension data is that proposed by Kaelble.^{20,21} Contact angles θ_i and θ_j , are measured for two liquids, i and j , for which the surface tension components, σ_i^d , σ_i^p , σ_j^d , and σ_j^p are known. Assuming that

both the dispersive and polar interacting across the solid-liquid interface conform to geometric mean mixing rules, the solid-liquid interfacial energies may be expressed as:

$$\sigma_{si} = \sigma_s + \sigma_{li} - 2\sqrt{\sigma_s^d \sigma_{li}^d} - 2\sqrt{\sigma_s^p \sigma_{li}^p}, \quad (3a)$$

and

$$\sigma_{sj} = \sigma_s + \sigma_{lj} - 2\sqrt{\sigma_s^d \sigma_{lj}^d} - 2\sqrt{\sigma_s^p \sigma_{lj}^p} \quad (3b)$$

Substitution of Young's equation for each solid-liquid combination:

$$\sigma_{si} - \sigma_s = -\sigma_{li} \cos \theta_i \quad (4a)$$

and

$$\sigma_{sj} - \sigma_s = -\sigma_{lj} \cos \theta_j \quad (4b)$$

permits simultaneous solution of the resulting pair of equations for σ_s^d and σ_s^p in terms of the known or independently measurable properties: θ_i , θ_j , σ_{li}^d , σ_{li}^p , σ_{lj}^d , and σ_{lj}^p . Wu⁶ suggested that the geometric mean mixing rules of Eq. (3) should be replaced by harmonic mean mixing rules under some circumstances. In the present study, both procedures were used to analyze the wetting data (advancing contact angles) for the cellulose and glass fibers with diiodomethane and water. The required data for these probe liquids are given in Table I, and the results for the cellulose and glass using both the geometric and harmonic mean methods are given in Table II. The results obtained using the two methods were not significantly different. Literature data²² for the surface energy of highly crystalline cellulose (Avicel) are 29.1 and 34.8 ergs/cm² for the dispersive and polar components, respectively, in reasonable agreement with the results obtained for untreated cotton fibers in this study.

It is seen that neither the melamine nor the PEI or silane treatments had a significant effect on the dispersive component of the surface energy of the cellulose and that only PEI produced a significant change (reduction) in the polar component of the surface energy. The silane treatment of the glass fibers produced a slight increase in the dispersive component of the glass surface energy and a large reduction in the polar component. Thus the use of PEI treatment of cellulose fibers should significantly aid in the bonding of apolar materials to the fibers just as silane treatment of glass fibers aids in their adhesion to apolar materials.

TABLE I
Dispersive and Polar Components of the Surface Tension for Diiodomethane and Water Calculated by the Geometric and Harmonic Mean Methods

Liquid	Geometric mean		Harmonic mean	
	σ^d (dynes/cm)	σ^p	σ^d (dynes/cm)	σ^p
Diiodomethane	49.5	1.3	44.1	6.7
Triply distilled water	21.8	51.0	22.1	50.7

TABLE II
Dispersive and Polar Components of Untreated and Treated Cellulose and Glass Fibers
Calculated from Wetting Data for Diiodomethane and Water Using Both the
Geometric and Harmonic Mean Methods, with 95% Confidence Limits

Fiber	Geometric mean		Harmonic mean	
	σ^d	σ^p	σ^d	σ^p
	(erg/cm ²)		(erg/cm ²)	
Cellulose, untreated	27.5 ± 1.5	41.0 ± 2.9	26.5 ± 1.1	43.0 ± 2.4
Cellulose, melamine treated	31.0 ± 1.9	47.0 ± 1.5	29.0 ± 1.5	44.0 ± 1.1
Cellulose, silane treated	28.5 ± 1.3	42.0 ± 5.9	26.5 ± 1.3	44.0 ± 5.4
Cellulose, PEI treated	28.0 ± 1.4	24.0 ± 6.3	25.0 ± 1.2	28.0 ± 5.5
Glass, untreated	23.0 ± 1.2	47.5 ± 5.5	22.0 ± 1.2	47.5 ± 4.8
Glass, silane treated	31.5 ± 1.1	9.0 ± 1.3	27.5 ± 0.9	14.0 ± 1.4

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