

**In: Rowell, Roger M.; Laufenberg, Theodore L.;
Rowell, Judith K., eds. Materials interactions relevant to
recycling of wood-based materials: Proceedings of Materials
Research Society symposium; 1992 April 27-29; San Francisco, CA. 113
Pittsburg, PA: Materials Research Society; 1992: 113-126. Vol. 266.**

SURFACE ENERGY COMPATIBILITIES OF CELLULOSE
AND POLYPROPYLENE

DANIEL T. QUILLIN*, DANIEL F. CAULFIELD**, and JAMES A. KOUTSKY*

*University of Wisconsin-Madison, 1415 Johnson St., Madison, WI 53706

** USDA Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705

ABSTRACT

In addition to its use in recycled paper products, recovered lignocellulosic fiber can be used as a reinforcement filler in composites with polyolefins. However, problems in both processing and product performance are often caused by the incompatibilities of surface energies between hydrophilic cellulose and non-polar polyolefin. This poor match in surface polarities is detrimental to strong adhesive bonding between olefin and cellulose. This work examines the effect of surface energy on the adhesion properties of polypropylene and cellulose. In particular, three materials accepted as paper-sizing agents were used to change the cellulosic fiber's surface energy to make it more compatible with the surface energy of polypropylene.

Cellulose fibers were treated by various methods with (1) alkyl ketene dimer, (2) alkenyl succinic anhydride, and (3) stearic acid and were characterized by their surface energies as determined by single fiber wettability measurements using the Wilhelmy technique. These measurements are discussed in detail. Results from these measurements can be related to differences in adhesion between treated cellulose and polypropylene, which can be measured by internal bond tests on hot-pressed composite sheets.

Results indicate that the use of sizing agents reduces the acid/base (hydrogen bonding) character of the cellulose surface. Interactions involving hydrogen bonding are important in cellulose/modified-polypropylene composites. Reduction of these interactions appears to lead to a corresponding reduction in adhesion between cellulose and polypropylene.

INTRODUCTION

The recent trend in environmental awareness has created a need for waste management. Of the current waste stream, the major components are paper and plastics. Developing a use for these materials in commercial products could prove to be rewarding, both financially and environmentally.

One possible application for reclaimed cellulose-based material is in composites with thermoplastic polyolefins, such as polyethylene and polypropylene. Significant research efforts have already been conducted in this area [1-6] to overcome fundamental problems. Of these problems, the most significant is lack of compatibility between hydrophilic, polar cellulose and hydrophobic, non-polar polyolefin. Differences in surface polarities have a profound influence on the compatibility and the nature of the interactions between materials and led to deBruyne's rule of adhesion [7]. This rule states that strong joints can never be made to polar adherents with non-polar adhesives, or to non-polar adherents with polar adhesives. Incompatibility leads to poor stress transfer between matrix and filler (due to

lack of intimate contact) and poor dispersion. The methods most often used to overcome these problems are grafting and the use of compatibilizers or coupling agents.

The focus of this research was to investigate the role of surface energy in determining compatibility and adhesion between cellulose (both unmodified and surface-modified) and surface-modified polypropylene.

PURPOSE AND NATURE OF THE STUDY

In the modern papermaking process, the use of chemical-sizing agents is known to change the hydrophilic surface of the cellulosic fibers of paper to a surface that is more hydrophobic. Some of these sizes react chemically with cellulose and have a dual polarity (i.e., both a hydrophilic and hydrophobic end). The chemicals used in this study are stearic acid, alkyl ketene dimer (AKD), and alkenyl succinic anhydride (ASA), all of which have dual polarity. In the manner applied, stearic acid is believed to impart its sizing effect without a covalent chemical bond to the cellulosic surface. In contrast, both AKD and ASA have been shown to react with cellulose [26,27] through covalent bonds. This study employed these three chemicals as treatments to α -cellulose fibers.

Next, the acid/base [i.e., hydrogen bonding] surface characteristics of untreated and treated fibers were analyzed by single fiber wetting measurements in various liquids. The liquids used were methylene iodide (neutral), formamide (a Lewis base), ethylene glycol, glycerol (Lewis acids), and water (bi-functional). These liquids are not, unfortunately, completely acidic or basic (in a Lewis sense) and show amphoteric behavior. Data from these wetting measurements were used to evaluate the work of adhesion.

In addition, composite sheets were formed using untreated or treated cellulose fiber and Pulpex¹ (Hercules), a surface-modified polypropylene fiber. Surface modification (i.e., incorporation of about 1 wt. % poly(vinyl alcohol) on the surface) during manufacture of these polypropylene fibers was originally designed to improve Pulpex's wettability and dispersibility in water for use as a synthetic pulp. These properties are important for the wet forming and uniformity of the composite sheets. In subsequent hot pressing of the composite sheets, however, the hydrophilic characteristic of the Pulpex is lost as the melted polymer surface composition approaches that of bulk polypropylene. The flow and dispersion of the melting polypropylene through the composite are affected by its surface characteristics, and those of the cellulose which together determine the level of adhesive interaction.

To assess adhesion in the composite, internal bond tests were then performed on samples taken from the composite sheets. Correlations between surface characteristics and mechanical properties are then used to infer the nature of the surface interactions needed for good adhesive bonding and composite properties.

1) The use of trade or firm names is for the readers' convenience and does not institute endorsement by the USDA of any product or service to the exclusion of others which may be suitable.

BACKGROUND

The role of surface chemistry in adhesion has been studied for some time. The importance of direct covalent chemical bonding has often been emphasized. Another necessary condition for good interaction and adhesion between two components is compatibility of their surface energies [8]. In simplest terms, such compatibility means rough equality between both the polar and non-polar characteristics of the components' surfaces. Thus, it is important to understand and control the surface energy characteristics of the interacting component surfaces and to relate those energy characteristics to the processability and properties of the composite. Hence, the ability to monitor the surface characteristics of the fiber component may provide valuable guidelines and predictors of composite performance.

During the past three decades, the methods and theories used in investigating adhesion have undergone considerable refinement. In particular, the area of wetting and contact angle analysis has developed more sensitive techniques and broader theory to better describe surface characteristics.

The earliest notions of surface energy and contact angle for a liquid drop on a solid surface (where the spreading pressure of the liquid's vapor on the solid is negligible) are expressed by the familiar Young's equation

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\Theta \quad (1)$$

where γ_{sv} is the surface energy of the solid, γ_{lv} is the surface tension of the liquid, and γ_{sl} is the interfacial tension between solid and liquid. In general terms, the thermodynamic energy of interaction, W_a (equivalent to the work of adhesion) is given by the reversible energy difference on separating a liquid from a solid:

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \quad (2)$$

Combining Equations (1) and (2) yields

$$W_a = \gamma_{lv}(1 + \cos\Theta) \quad (3)$$

Hence, the thermodynamic energy of interaction at an interface is readily determined from the contact angle measured with a liquid of known surface tension.

One of the first breakthroughs in surface energy and interfacial tension theory came when Fowkes [9-11] postulated that the surface energy of a material could be broken into parts, corresponding to various contributions from different interactions:

$$\gamma = \gamma^d + \gamma^p \quad (4)$$

or, more generally, in terms of work of adhesion:

$$W_a = W_a^d + W_a^p + W_a^h + W_a^i \quad (5)$$

where the superscript d refers to dispersive forces, p to dipole-dipole interactions, h to hydrogen bonding, and i to induced dipole interactions. In addition, the attractive forces acting across the interface of two non-polar materials can be represented as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} \quad (6)$$

Since Fowkes' initial suggestion, several different forms of Equation (6) have been proposed [12] to account for 'polar' interactions, with the most widely used being

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2}, \quad (7)$$

proposed by Kaelble and Uy [13]. This equation has been criticized repeatedly [11, 14, 24, 25], but remains widely used.

Since the dipole (p) and induction (i) forces are usually quite small, Equation (5) is more generally expressed as

$$W_a = W_a^{LW} + W_a^{ab} \quad (8)$$

where the dispersion forces are combined with the dipole and induced dipole contributions and are designated Lifshitz-van der Waals (LW) forces. All other forces can be described as acid/base (ab) interactions. Lewis acid/base interactions cover any interaction that involves the sharing of an electron pair, including hydrogen bonding. This corrects the notion that 'polar' interactions are dependent solely on the dipoles of materials, which is not the case [14]. Furthermore, attempts to model acid/base interactions with a geometric mean representation (such as Eq. (7)) are incorrect, as noted by Fowkes [11, 14, 24]. Acid/base concepts have continued to develop, and today are widely accepted and researched [14-18]. In the case of cellulose, with a surface dominated by hydroxyl groups, acid/base interactions can be described as predominantly hydrogen bonding.

Recently, Vrbanac and Berg [15] proposed a method using contact angle measurements to determine the acid/base contribution to the work of adhesion, W_a^{ab} :

$$W_a^{ab} = \gamma_1(1 + \cos\Theta) - 2(\gamma_s^{LW} \gamma_1^{LW})^{1/2} \quad (9)$$

where the first term on the right-hand side represents the total work of adhesion, and the second term represents interactions as a result of Lifshitz-van der Waals forces. To evaluate W_a^{ab} in Equation (9), it is assumed that the Lifshitz-van der Waals contribution to

the surface energy of the solid can be obtained by measuring the contact angle of a neutral, non-self-associating probe liquid (i.e., one with no acid/base character) against the solid. Since $\gamma_s = \gamma_s^{LW} = \gamma_{\text{probe}}$, Equation (9) becomes

$$\gamma_s^{LW} = \gamma_{\text{probe}}(1 + \cos\Theta)^2 / 4 \quad (10)$$

Wetting experiments have been used to investigate wood and cellulose surfaces for some time. An early paper by Herczeg [30] measured the critical surface tension of Douglas-fir as well as the effects of exposure time. Luner and Sandell [31] and Lee and Luner [32] investigated the wetting behavior of cellulose, hemicellulose, and lignin. A 1972 review by Collett [33] gives an overview of the importance of wetting in the adhesion of wood. Young [21], Klungness [38], and Hodgson and Berg [34] used the Wilhelmy technique to measure surface characteristics of various types of pulp fibers, while Westerlind and Berg [19] used the method to measure the effects of surface treatments on the surface properties of cellulose. Toussaint and Luner [29] also investigated the effects of surface modification on the wetting properties of cellulose films using sessile drop methods. In a recent review of polymer-paper adhesion, Borch [35] details the role of surface energy as measured by wetting experiments.

EXPERIMENTAL

Materials

The polypropylene used in composite samples was Hercules Pulpex P AD-H, which contains a surface treatment of < 1.0 wt.% poly(vinyl alcohol) for better water dispersibility.

Bleached kraft α -cellulose fiber (Ultranier-J) obtained from ITT Rayonier was used for all wetting measurements. Fibers used were generally about 2 mm long and 60-80 μm in perimeter.

Aquapel 364 (Hercules), a dry AKD wax was used in all AKD/toluene solutions. Hercon 70, also provided by Hercules, was diluted with water to prepare the AKD emulsions for the study.

ACCOSIZE 18 synthetic size (American Cyanamid) was used both in toluene solutions and in water-based emulsions. ASA emulsions were produced with ACCOSIZE 18 and ACCOSIZE 72 cationic starch (1:3 starch) as an emulsifier dissolved in water.

Stearic acid (99+ %, Aldrich) was used in stearic acid/toluene solutions.

Spectrophotometric grade formamide (99+%) and glycerol (99.5+%), as well as hexadecane (99%), methylene iodide (99%), and ethylene glycol (99+%) were obtained from Aldrich and used without further purification.

Sample Preparation

Individual α -cellulose fibers were mounted to small metal hooks using a cellulose nitrate-based glue (Stevens Industries). Scanning electron micrographs of the glued area showed no evidence of glue spreading down the fiber. Eight to twelve fibers were mounted for each treatment.

Fiber Surface Treatments

Batches of six mounted fibers were suspended in AKD, ASA, or stearic acid treatments for 10 minutes. Solution or emulsions contained approximately 0.1 wt. % of the surface active agent, which should be sufficient to give complete surface coverage [36]. After treatment, fibers were allowed to air-dry in a laboratory hood for 15 minutes. AKD- or ASA-treated fibers also underwent a further 15 minute curing stage in a $104 \pm 2^\circ$ C circulating oven. Perimeters for all fibers were obtained before treatments, as the following describes, except for fibers measured in formamide.

Wetting Measurements

The Wilhelmy method of contact angle measurement has been widely used to measure fiber surface characteristics [15,19-23]. This technique [12], involves using a very sensitive microbalance to measure the downward force that a liquid's surface tension exerts on a fiber or rod submerged vertically in the liquid. With an elevator, a beaker containing a probe liquid can be raised and lowered over the fiber surface, while advancing and receding force are measured. From these data, advancing contact angles can be measured. The relevant equation is

$$F = P\gamma_l \cos\Theta \quad (11)$$

where F is the measured force, P is the fiber perimeter, and γ_l is the probe liquid's surface tension. Because the cross-sectional area of the fibers is small, no correction was made for buoyancy effects.

Perimeters of fibers can be measured by this technique if the probe liquid is a neutral (non-self-associating), low surface tension liquid. Hexadecane, as used in this study, is a perfect example, because it completely wets out the fibers ($\cos\Theta = 1$), allowing the perimeters to be calculated. For cellulose fibers in formamide, rapid swelling proved to be a problem, so perimeters measured in hexadecane were not useful. Instead, perimeters were calculated from the receding force in formamide, because formamide yields a receding angle of $\cos\Theta = 1$.

Measurements were performed by placing a mounted fiber at the end of a hangdown wire attached to one side of the electrobalance arm. The electrobalance used was a Cahn model RG electrobalance, connected to an Esterline Angus model LI101S chart recorder. A beaker of the probe liquid was placed on a small elevator below the hanging fiber. The

elevator speed was controlled by a variable speed motor at approximately $40 \pm 5 \mu\text{m/s}$. Fibers were cycled five times in each liquid (except methylene iodide), although only data from the first cycle were used in all calculations. Table 1 gives the surface energy values used for the probe liquids. Surface tension measurements were done on the liquids using a small plate cut from a glass cover slip or a small length of glass fiber optic cable. Good agreement ($\pm 2 \text{ mJ/m}^2$) was found between measured and literature values, with literature values being used in all calculations. The measurement apparatus was used in a conditioned room ($72 \pm 3^\circ \text{ F}$, $50 \pm 5\% \text{ RH}$) to minimize environmental effects.

Table 1: Surface Energy Properties of Probe Liquids^a

Liquid	γ_l	γ_l^{LW}	γ_l^{P}	Reference
Hexadecane	28.0	28.0	0	--
Ethylene glycol	48.3	29.3	19.0	23
Methylene iodide	50.8	49.5	1.3	19
Formamide	58.3	32.3	26.0	23
Glycerol	63.4	37.0	26.4	9
Water	72.2	22.0	50.2	11

a) Units are mJ/m^2

Composite Formation and Testing

To study the mechanical properties of cellulose/polypropylene composites, paper-like sheets containing 70% cellulose fiber and 30% Pulpex polypropylene fiber were wet-formed into handsheets, treated with the treatments previously mentioned at a 1.5 wt%/cellulose fiber wt. level, and hot-pressed as described elsewhere [28]. Internal bond (z-direction) strength and density were also measured as described elsewhere [28].

RESULTS AND DISCUSSION

Table 2 and Figures 1 and 2 show the results of calculations involving Equations (9) and (10) and the liquids methylene iodide, formamide, ethylene glycol, and glycerol. Table 2 relates values of γ_s^{LW} calculated from wetting data in methylene iodide and Equation (10), as well as values of $W_a [= \gamma_l(1+\cos\Theta)]$. These data were then used in Equation (9) to calculate values in Figures 1 and 2. As can be seen in Figure 1, untreated cellulose has significant interactions with both the acidic and basic probe liquids and can hence be characterized as bi-functional. This result matches findings of Good, *et al.* [37] that also show cellulose to be bi-functional. As might be expected, cellulose treated with a mobile molecule (stearic acid) shows virtually identical behavior. ASA solution treatments also appear to be ineffective in covering up hydrogen bonding moieties of the cellulose,

resulting in strong interactions with both acidic and basic probes. AKD and ASA emulsion treatments appear to cover the acidic sites on the cellulose (resulting in negative W_{a}^{ab} with formamide), but do not completely cover basic sites (resulting in small positive values of W_{a}^{ab} for ethylene glycol or glycerol). Differences between solution and emulsion treatments appear to be quite significant, with emulsion treatments giving much lower, even negative, values of W_{a}^{ab} .

Table 2: Lifshitz-van der Waals Surface Energy Component and Work of Adhesion for Treated and Untreated Cellulose (1st cycle data)^a

Treatment	γ_s^{LW}	$\gamma_{form}(1+\cos\Theta)$	$\gamma_{EG}(1+\cos\Theta)$	$\gamma_{glyc}(1+\cos\Theta)$
Untreated	38.5	105.4	89.3	114.5
AKD solution	19.7	75.1	68.1	60.3
ASA solution	28.0	107.7	92.4	90.0
AKD emulsion	24.9	44.0	64.7	56.7
ASA emulsion	28.8	50.3	49.4	72.4
Stearic acid solution	39.0	104.8	79.8	114.3

a) Units are mf/m^2 ; form=formamide, EG=ethylene glycol, glyc=glycerol
 γ_s^{LW} calculated using methylene iodide

Negative values of W_{a}^{ab} , some of which may actually be zero when experimental error is considered, have two possible causes. The first is a base-base (or acid-acid) interaction that is actually repulsive in nature. Hence, these surfaces should show a positive interaction with a liquid of the opposite type. The second cause may be just the result of a relatively high surface tension liquid trying to move over the surface of a lower energy solid. This may be energetically unfavorable and result in negative values for the acid/base work of adhesion calculation, even though acid/base interactions between solid and liquid are occurring.

Figure 3 is a representative curve showing the effects of cycling a treated fiber in and out of a probe liquid five times. Note the difference between the first and second cycles. As can be seen, the value of $\cos\Theta$ changes significantly. This change is an indication of the amount of unreacted surface modifier initially on the fiber surface. After the first cycle, the unreacted portion of the treatment will be washed off the cellulose fiber surface, revealing a more hydrophilic surface. This new surface will be more readily wet by the probe liquid, resulting in much greater values of $\cos\Theta$. For the treatments previously mentioned, AKD solution treatments showed the greatest change between the first and second cycles.

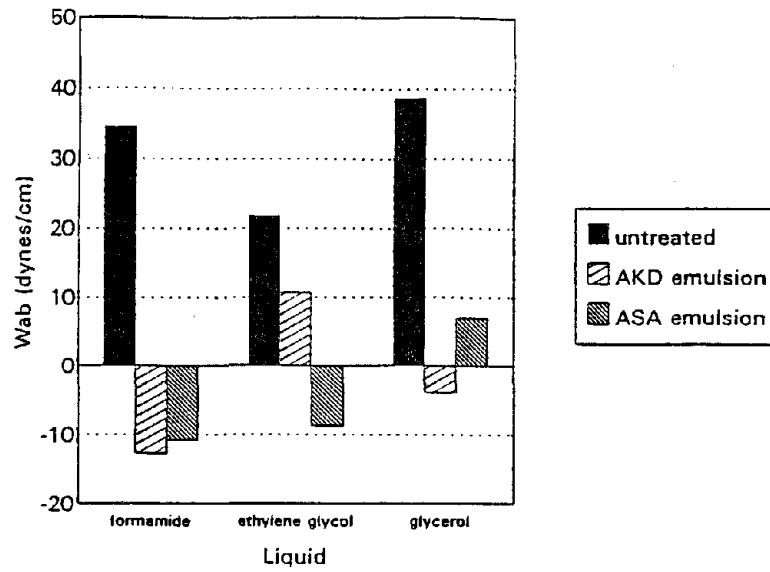


Figure 1: Acid/Base Work of Adhesion for Untreated and Emulsion-Treated Cellulose Fibers in Various Liquids

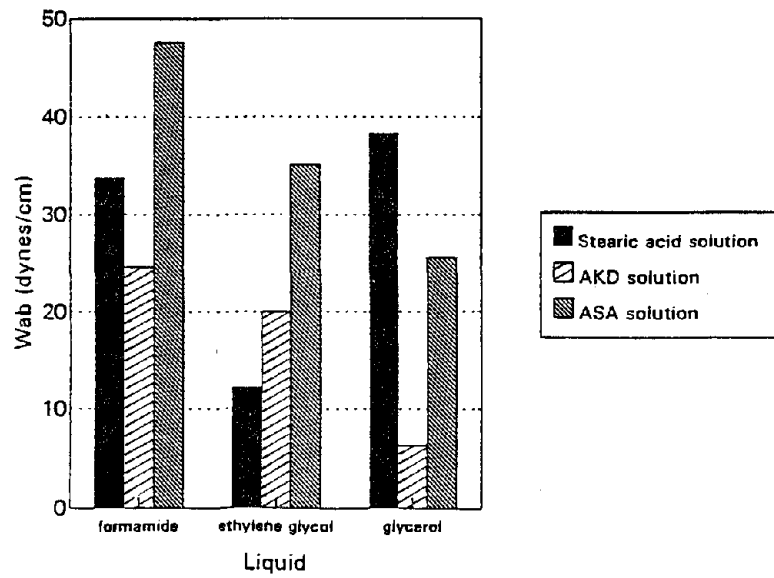


Figure 2: Acid/Base Work of Adhesion for Solution-Treated Cellulose Fibers in Various Liquids

Table 3: Comparison of Current Acid/Base Work of Adhesion Data with Literature Data^a

Liquid	Cellulose		AKD-Treated Cellulose	
	Toussaint & Luner ^b W_a^{ab} (mJ/m ²)	Quillin, <i>et al.</i> W_a^{ab} (mJ/m ²)	Toussaint & Luner ^b W_a^{ab} (mJ/m ²)	Quillin, <i>et al.</i> W_a^{ab} (mJ/m ²)
Water	77.5	73.0	28.1	()
Glycerol	42.3	38.8	14.8	6.3
Ethylene glycol	()	21.9	5.4	20.0
Formamide	41.9	34.6	11.6	24.6

a) () indicates no data.

b) Values calculated using data from ref. [29] for AKD-II treated regenerated cellulose films.

70/30 cellulose/polypropylene composite sheets. Specific internal bond strength is used to compensate for the effects of density. It should be noted that untreated and stearic acid-treated cellulose/polypropylene composites have the highest specific bond strength.

The next step is to see if any correlation exists between measured acid/base interactions between a probe liquid and cellulose, and actual composite performance. In an ideal case, molten polypropylene should be used as a probe liquid. However, in our case the melting process would destroy the surface characteristics [i.e., poly(vinyl alcohol) surface layer] that give the Pulpex fibers their unique properties. If these pre-melted surface characteristics of the polypropylene are important in the hot-pressing step of composite sheet formation, as we believe they are, then wetting measurements using a probe liquid with similar surface characteristics could reveal something about the role surface interactions play in actual composite performance. As the Pulpex melts and flows during the hot-pressing operation, the expectation would be that fresh unmodified polypropylene is uncovered and the polar surface becomes buried in the bulk of the polypropylene. Instead, when Pulpex is in close proximity with cellulose, it is believed that during the melting process, a preferential migration of the surface hydroxyl groups occurs towards the interface between cellulose and molten polymer. Insertion of a covalently bonded hydrophobic-size molecule at the interface can impede this migration and replace a potential hydrogen bond with a weaker, dispersive interaction between non-polar molecules. In contrast, stearic acid molecules and unreacted AKD and ASA molecules are not bonded to the fiber surface and hence can be swept away with the flowing polymer, resulting in a stronger interfacial bond between exposed cellulose and polymer. Hence, a suitable probe liquid may be glycerol, which also contains pendant hydroxyl groups similar to poly(vinyl alcohol).

By using data from Figures 1 and 2 and Table 4, Figure 4 was constructed. This figure plots the acid/base work of adhesion for

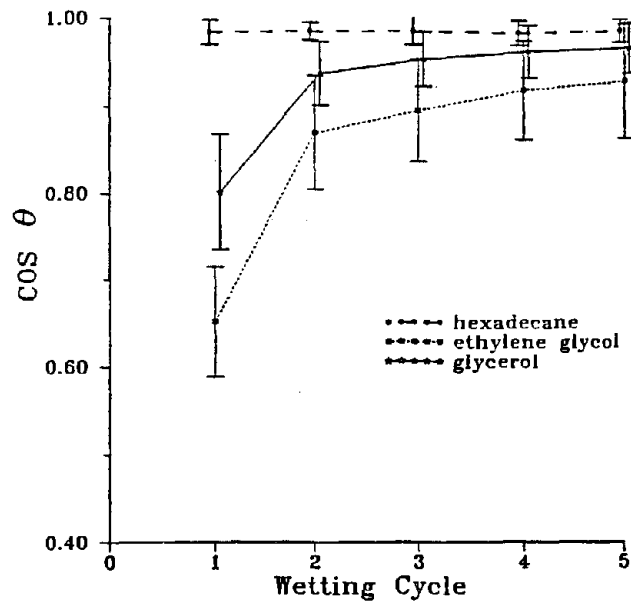


Figure 3: Change in Contact Angle with Cycling a Treated Fiber (stearic acid solution) in Various Liquids (error bars = std. dev.)

To check the validity of single fiber wetting measurements for cellulose, a comparison can be made with data obtained through static wetting measurements on cellulose films. Table 3 gives a comparison between results from this work and results calculated from other literature data [29]. As can be seen, agreement between the two is good, although data for AKD-treated cellulose wetted with ethylene glycol and formamide are different. This is not completely unexpected because of the differences in treatment methods and retained (i.e., unreacted) AKD in a cellulose film compared to a single fiber.

The next step is to determine if acid/base interactions play a role in bonding and adhesion in actual composite samples. To do this, an internal bond test was used as a means of determining the effect of the above treatments on the adhesion of cellulose and (surface-modified) polypropylene. The internal bond test should be a valid measure of the adhesion between fiber and matrix if the sample to be measured is of a random, two-dimensional nature (i.e., no orientation in the z-direction). This is the case for the paper-like composite sheets produced for this study. Table 4 lists internal bond properties of the

Table 4: Internal Bond Properties of Cellulose/Polypropylene Composite Sheets^a

Treatment	Bond Strength (MPa)	Density (g/cm ³)	Specific Bond Strength (MPa-cm ³ /g)
Untreated	1.50 (0.16)	0.81 (0.04)	1.85 (0.22)
AKD solution	1.26 (0.21)	0.72 (0.03)	1.75 (0.30)
ASA solution	1.29 (0.15)	0.73 (0.02)	1.77 (0.21)
AKD emulsion	1.07 (0.17)	0.77 (0.05)	1.39 (0.24)
ASA emulsion	1.17 (0.17)	0.78 (0.05)	1.50 (0.24)
Stearic acid solution	1.67 (0.16)	0.84 (0.03)	1.99 (0.20)

a) (standard deviation).

glycerol with the treated and untreated cellulose compared to the specific internal bond strength measured from cellulose/polypropylene composite sheets. As can be seen, a fairly strong correlation exists between the acid/base work of adhesion and actual composite strength. As the acid/base interactions increase, so does the adhesion between the two components. This result reinforces the results found by various other studies [39-42] that link the polarity of the interacting surfaces to the strength of their interactions. It has been reported that paper adheres better to presumably "non-polar" plastics (i.e., polyethylene)

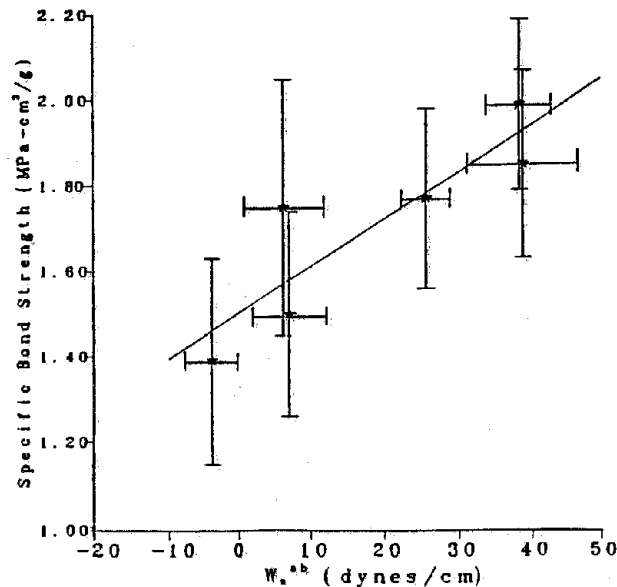


Figure 4: correlation Between Acid/Base Work of Adhesion in Glycerol and Specific Internal Bond Strength (error bars = std. dev.)

when the surface energy of the paper increases. This increased adhesion of the paper likely results from better interaction with the adventitious surface contaminants on the polymer that have a polar (acid/base) character. This literature also suggests that improvements in adhesion resulting from corona treatment of plastic film and paper are also best explained in these terms. Results from literature and this study also reinforce the idea that hydrogen bonding, even when present in low concentrations, can play a very significant role in the overall strength of a composite.

CONCLUSIONS

The main effect of modifying the surface of cellulose with hydrophobic sizes such as AKD or ASA appears to be decreased adhesion with modified polypropylene (Pulpex) as a result of a reduction of strong, non-dispersive (acid/base) interactions. Wetting measurements prove that treating cellulose with AKD, ASA, or stearic acid results in a hydrophobic surface, but a portion of that hydrophobicity is a result of unreacted, and hence removable, species. It is largely the covalently bonded surface-size molecule that appears to impede the migration of hydroxyl groups from the molten Pulpex fiber surface to the cellulose/polymer interface during the hot-pressing step. Coupled surface energy and internal bond strength measurements indicate a strong correlation between the extent of hydroxyl-rich (acid/base) interface and good adhesive properties. To improve adhesion between cellulose and polypropylene (or other polyolefins), the recommendation would be to modify the hydrophobic polymer in a way that introduces chemical moieties on its surface that are capable of producing strong acid/base (hydrogen bonding) interactions with similar groups on the cellulose surface.

ACKNOWLEDGMENTS

We are most grateful to Paul Clark for his help with a large portion of the fiber wetting measurements. Financial support for the project was provided by USDA Competitive Grant No. 90-37291-5773 and through a S. C. Johnson Fellowship (DTQ).

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