31G05

Wetting Characteristics and Surface Energy Properties of Fibers

Hyun Suk Whang

North Carolina State University
Raleigh, NC 27695

1. Introduction

Surface wetting characteristics affects textiles in both applications and manufacturing processes: adhesion in coating and composite applications, wettability in wipes, dressings and personal hygiene products, dyeing and finishing of textiles. Wetting behavior can be used to characterize surfaces and to determine solid/liquid/vapor interactions. The equilibrium contact angle between a liquid and a solid surface is an important parameter that determines wettability. Another parameter important in determining surface behavior of a solid is surface energy. Knowledge of surface energy is important in understanding the surface behavior and in evaluating the degree and durability of a given surface modification.

The Wilhelmy dynamic method, which measures the vertical component of the advancing and receding attractive forces across the interface between a liquid surface and a partially immersed solid can be the most accurate way to measure the contact angle values. Application of the wilhelmy technique to fibers originated in 1947 for measuring perimeters [1]. Since then many other investigators [2,3] have carried out contact angle studies, the more recent ones taking advantages of the availability of modern recording microbalances to ungrade the sensitivity of the force measurements. The first effective method for estimating surface energy of a solid, introduced by Zisman [4], is still in use today. The best method available for determining the polar and the dispersion components of surface energy is the measurement of the contact angles of two dissimilar liquids whose dispersive and polar contributions to their surface tension are known [5].

In this study, surface characteristics of several different fibers, including cotton, Galaxy and regular rayons, cellulose acetate, polyester, and polypropylene fibers, were examined. The variables were fiber type, cross-sectional shape, denier, and finishes.

2. Experimental

The materials used in the dynamic wetting experiments are listed in Table 1. All fibers except cotton were extracted using the Soxhelet extraction method (AATCC Test Method 97-1995). Cotton fiber was scoured.

Table 1 Details of fibers used in the investigation

Fiber	Denier	Cross sectional Shape	Supplier
Cotton*	1.4	crenulated	Barnhandt
Cellulose diacetate	2.7	trilobal	Hoechst Celanese
Galaxy rayon	3.0	trilobal	Courtaulds
Regular rayon	3.0	crenulated	Courtaulds
Polyester	4.4	round	Dupont
Polypropylene	3.1	bullet, delta, round, and Y	Amoco
"	5.1	bullet, round, and Y	Amoco

* Cotton fiber has DMDHEU finish and oleic acid finish

The wetting force test on single fibers was conducted with a Cahn C-2000 electrobalance using a developed sample mounting method and the Wilhelmy technique. The fiber to which a sinker was attached was suspended from an electrobalance by a hangdown wire. The wetting liquid is pulled over the fiber at a constant speed of 750 µm/min via a computer-controlled stage.

The liquid container is moved up and down mechanically. As the liquid is raised and lowered at a constant speed, the weight decrease and increase, measured by the electrobalance, are used to calculate the advancing contact angle (θ_a) and the receding contact angle (θ_r), respectively. The wettability experiments were carried out using Deionized Ultra Filtered water (DIUF water) and methylene iodide (CH_2I_2). Test conditions used were controlled at 50 ± 2 % humidity and 21 ± 1 ° C. To convert the measured wetting force to values of contact angles, perimeters of fiber were determined using image anaylsis of scanning electron micrographs (SEM) of the fiber cross sections.

3. The Wetting Parameters

According to the formula of Wilhelmy [6], the pull exerted on a solid rod inserted into a mass of liquid is expressed by:

$$F_W = \gamma_{LV} \, P \cos\theta$$

where F_W = wetting force ($N \times 10^{-5}$), γ_{LV} = surface tension of liquid (mN/m), P = perimeter of the solid (cm), and θ = contact angle between liquid and solid interface. Therefore, the contact angle of a liquid /fiber can be calculated from the wetting forces, measured perimeters of the test specimen, and known values of the surface tension of the wetting liquid.

The surfaces of solids are often characterized for their interaction with liquids in terms of the parameter called the work of adhesion (W_A). It is given by:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

where the γ_{SV}, γ_{LV}, and γ_{SL} terms are the interfacial tensions at solid-vapor, liquid-vapor, and solid-liquid interfaces, respectively. By combining the above equation with the Dupre-Young equation ($\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$) and solving simultaneously for W_A, the following relation results:

$$W_A = \gamma_{LV}(1 + \cos\theta)$$

Measuring contact angles with liquids of known surface tension provides a means for quantifying the interaction between solids and liquids.

The total surface energy ($\gamma_s = \gamma_s^{d} + \gamma_s^{P}$), which is the sum of the dispersive component (γ_s^{d}) and the polar component (γ_s^{P}), is determined by measuring the contact angles of a solid with two dissimilar liquids (DIUF water, and methylene iodide), whose dispersive and polar contributions to surface tension were known. Assuming that both the dispersive and the polar interactions across the solid-liquid interface conform to geometric mean mixing rule, one can express the solid-liquid interfacial energies as:

$$\gamma_{SLi} = \gamma_S + \gamma_{Li} - 2\,(\gamma_S^{d}\,\gamma_{Li}^{d})^{0.5} - 2\,(\gamma_S^{P}\,\gamma_{Li}^{P})^{0.5}$$
$$\gamma_{SLj} = \gamma_S + \gamma_{Lj} - 2\,(\gamma_S^{d}\,\gamma_{Lj}^{d})^{0.5} - 2\,(\gamma_S^{P}\,\gamma_{Lj}^{P})^{0.5}$$

Substitution of these equations into Young's equation yields relations for determining the surface free energy of a solid:

$$-\gamma_S + \gamma_{SLi} = -\gamma_{Li} \cos\theta_i$$
$$-\gamma_S + \gamma_{SLj} = -\gamma_{Lj} \cos\theta_j$$

These four equations are solved simultaneously for the dispersive and the polar components of the surface energy of the fibers.

4. Result and Discussion

4.1 Effect of Fiber Cross-Sectional Shape and Fiber Size for Wetting Characteristics in Water

Figure 1 gives plots of the advancing and the receding forces against perimeter for polypropylene fibers. Excellent correlation is found between both the advancing and the receding wetting forces and the perimeters irrespective of the cross sectional shapes and deniers of the fibers. Table 1 shows the average values of wetting parameters of polypropylene fibers of different cross sectional shapes and deniers. As is expected from these results, the values of the contact angle and the work of adhesion appear largely independent of the size and shape of fiber.

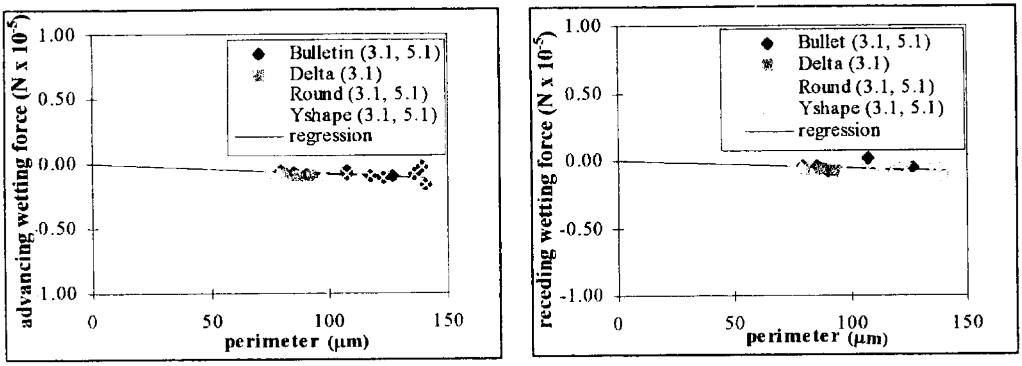


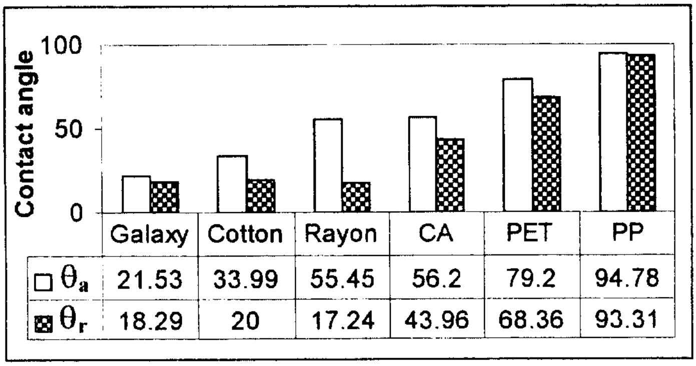
Figure 1 Correlation between the wetting force and the perimeter for polypropylene (parenthesis represents denier)

Table 1. Average wetting parameters for polypropylene fibers in water

Denier	Cross sectional shape	Advancing Contact angle $(\theta_a, ^\circ)$	Advancing Work of adhesion (W_a, mN/m)	Receding Contact angle $(\theta_r, ^\circ)$	Receding Work of adhesion (W_r, mN/m)
3.1	Bullet	96.41	64.67	94.97	66.49
3.1	Delta	98.45	62.10	96.72	64.28
3.1	Round	98.32	62.27	96.55	64.50
3.1	Y shape	96.91	64.04	94.57	67.00
5.1	Bullet	91.99	70.28	87.48	75.98
5.1	Round	95.65	65.64	91.15	71.34
5.1	Y shape	95.25	66.15	91.70	70.64

4. 2. Effect of Fiber Type for Wetting Characteristics in Water

Contact angle of various fibers are shown in Figure 2. Examining the results of wettability on cellulosic fibers, Galaxy rayon has the highest wettability among all the cellulosic fibers. However, the receding values of the various parameters was nearly the same for all cellulosic fibers. Galaxy rayon has lower advancing contact angle than that of regular rayon. On the other hand, receding contact angles of the two fibers are nearly the same. This indicates that two rayons behave differently in the dry state, but they behave nearly the same when wetted. This is possibly due to difference in the structures at the surface of the two rayons. Cellulosic fibers show better wetting characteristics than cellulose acetate. Acetylation of the cellulosic materials, which is less hydrophilic, leads to decreased wettability. The wettability properties of polyester are better than those of polypropylene due possibility to the presence of relatively more polar ester groups and benzene rings in the former. Polypropylene has the lowest wettability among all the fibers. This is due to the fact that polypropylene is a hydrocarbon and does not have polar groups.



	Galaxy	Cotton	Rayon	CA	PET	PP
□ θ_a	21.53	33.99	55.45	56.2	79.2	94.78
▨ θ_r	18.29	20	17.24	43.96	68.36	93.31

Figure 2. Effect of the fiber type on the values of contact angles

4.3. Effect of Finish for Wetting Characteristics in Water

Figure 3 shows the wetting property of scoured, DMDHEU, and oleic acid finish on cotton.

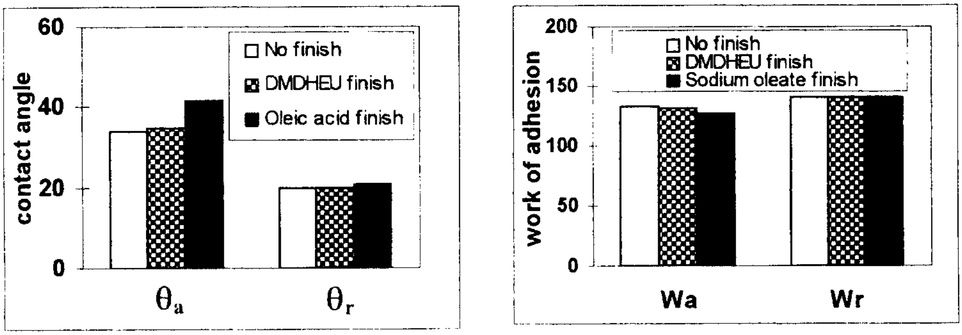
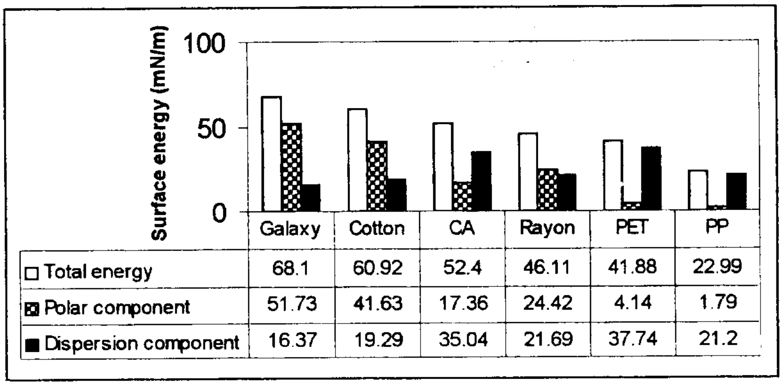


Figure 3. Effect of finish on the wetting parameters of cotton fibers

DMDHEU reagent generates resilience in cotton fiber by cross-linking with hydroxyl groups of cellulose in the amorphous regions of the fiber microstructure. The crosslinks restrict the imbibition of water into the fiber. The results, however, showed that the contact angle of the DMDHEU finished cotton was nearly the same as that of the scoured cotton, indicating that the wettability was not affected by the DMDHEU finish. A possible explanation for this is that the durable-press reagents themselves containing hydroxyl groups readily interact with water. Oleic acid finished cotton has a slightly higher advancing contact angle than that of the scoured cotton fiber. Oleic acid produced one of the fatty acids present in cotton wax and is expected to coat the surface of the fibers. Being hydrophobic in character, it causes the advancing contact angle to be increased and, thus, wettability to decrease.

4.4. Surface Energy Properties of the Fibers

The surface energy results for the fibers are given in Figure 4. It is evident that higher surface energy is correlated with higher wettability. Among the two rayons, Galaxy rayon has a higher polar component and low dispersion component than does regular rayon. This indicates that these two materials have different surface structures with Galaxy rayon having a more polar surface. Cotton fiber has a lower surface energy than Galaxy rayon, but a higher surface energy than regular rayon. Cellulose acetate fiber exhibits smaller polar component and higher dispersion component than does regular rayon. Substitution of the hydrogen atoms of celulosic fibers by the more hydrophobic acetyl groups led to a large increase in the dispersion force component and a large decrease in the polar component. Polyester and polypropylene are characterized by a hydrophobic surface. The critical surface tension of polyester and polypropylene are reported to be 40 mN/m and 28 mN/m, respectively. The values of the dispersion component of polyester and polypropylene found here are about 38 mN/m and 21 mN/m, respectively, which agree well with reported values of the critical surface tension.



	Galaxy	Cotton	CA	Rayon	PET	PP
□ Total energy	68.1	60.92	52.4	46.11	41.88	22.99
▨ Polar component	51.73	41.63	17.36	24.42	4.14	1.79
■ Dispersion component	16.37	19.29	35.04	21.69	37.74	21.2

Figure 4. Comparison of surface energies of different fibers

5. Conclusions

Wetting characteristics - contact angle and work of adhesion – are independent of cross-sectional shapes and deniers, but they are dependent on fiber type and finish applied. Among the fibers studied, the wettability decreased in the order as follows: Galaxy rayon maximum wettability), cotton, regular rayon, cellulose acetate, polyester, and polypropylene (minimum wettability). The durable press finish on cotton fiber did not change wettability, but oleic acid finish on cotton caused a decrease in the values. Surface energy datas for fibers indicate that surface energy correlated with wettability. Galaxy rayon, which had the lowest value of contact angle, also had the highest value of surface energy. Likewise, polypropylene, which had the lowest wettability, also had the lowest surface energy of the fibers studied here.

6. References

1. G. E. Collins, A Surface Tension Method for Measuring the perimeter of Fibers and the Contact Angles of Liquids against Fibers, J. Textile. Inst., 38, T73, 1947.
2. R. L. Bendure, Dynamic Adhesion Tension Measurement, J. Colloid Interface Sci., 42, 137-144, 1973.
3. R. A. Young, wettability of Wool Pulp Fibers, Wool and Fiber, 8(2), 120, 1976.
4. W. A. Zisman, Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution in Contact angle, Wettability and Adhesion, Advances in Chemistry Series, 43, 1-51, 1963.
5. D. H. Kaeble, Dispersion-Polar Surface Tension Properties of Organic Solids, J. Adhesion, 2, 50, 1970.
6. J. Wilhelmy, Under die Abhangigkeit der Capillaritats Constanten des Alkohols von Substanz und Gestalt des benetzten festen Korpers, Ann Physik, 119, 177-217, 1863.