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Wettability Tests of Polymer Films and Fabrics and Determination of Their Surface Energy by Contact-Angle Methods

by Daphne Pappas, Craig Copeland, and Robert Jensen

ARL-TR-4052   **March 2007**

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
March 2007	Progress	June 2006–December 2006

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Wettability Tests of Polymer Films and Fabrics and Determination of Their Surface Energy by Contact-Angle Methods	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Daphne Pappas, Craig Copeland, and Robert Jensen	AH84
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army Research Laboratory ATTN: AMSRD-ARL-WM-MA Aberdeen Proving Ground, MD 21005-5069	ARL-TR-4052

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In this research, wettability testing was performed for nylon-6 and polyethylene films and ultra-high molecular weight polyethylene woven fabrics to examine the effects of surface atmospheric plasma treatment.

15. SUBJECT TERMS

atmospheric plasma, surface energy, contact angle, wetting, UHMWPE, nylon

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Daphne Pappas
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED	UL	18	19b. TELEPHONE NUMBER (Include area code) (410) 306-0966

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1. Introduction

High-strength polymer materials are a useful component in many multifunctional materials applications. However, because of low reactivity, their use is inhibited in many processing techniques. Polymer films and fibers possess low surface energies and need to be modified through surface activation prior to being used in composite systems where adhesive bonding is an issue. Treatment of polymer materials through plasma processing is one route to greatly increase surface reactivity (*1*, *2*). Once the surface has been plasma-modified, wettability by liquids can be examined to determine the treatment effects on the polymer material's surface reactivity.

The surface energy of solids cannot be measured directly. Instead, contact angle is measured when various test liquids are placed on the solid material. Many theories have been applied to link the solid surface energy to the liquid-vapor tensions as a function of contact angle. Among the theories are the one-liquid method by Good, Girifalco, and Neumann, the two-liquid method where only dispersive and polar contributions determine the interfacial tensions, and the Lifshitz-Vanderwaals three-liquid method that considers acid-base interactions (*3*). As reported in literature, all methods are sensitive to the choice of test liquids used. More consistent results are obtained if a polar liquid and two or more liquids besides water are used.

In this research, wettability testing of nylon-6 (*4*) and polyethylene film and ultra-high molecular weight polyethylene (UHMWPE) woven fabrics was performed to examine the effects of surface plasma treatment. Each material was plasma-treated under varying treatment times, flow rates, and compositions of helium and oxygen plasmas (*5*).

2. Experimental

2.1 Plasma Modification of Polymer Surfaces

The atmospheric plasma system used for the surface treatments was an industrial scale plasma system from Sigma Technologies. The gases (He and He-O_2 in this case) were injected into the electrode at atmospheric pressure and allowed to diffuse, forming a filamentary glow discharge. Helium is typically used to initiate and generate the plasma at atmospheric pressure before another gas is introduced to the system. The operating frequency was 90 kHz with an operating power of 1050 W.

UHMWPE fibers (with an average diameter of 100 μm), UHMWPE films (Goodfellow, 75 μm thick), and nylon-6 films (Goodfellow, 75 μm thick) were exposed to the plasma created between the just described electrode and a second electrode covered by an alumina layer.

2.2   Wettability Testing

Wettability testing was carried out using one of two methods described in this section. For films, a static contact-angle setup using the sessile drop method was utilized. The setup consists of a micrometer-controlled syringe held in place above a moveable stage (shown in figure 1). Contact angles were recorded using a goniometer equipped with a charge-coupled-device camera and using an image capture program employing LabVIEW* software. Contact angles were measured by defining a circle around the drop and recording the tangent angle formed at the substrate surface. The LabVIEW program measures this angle on the left and right sides of the snapshot and then averages them for a final contact-angle value.
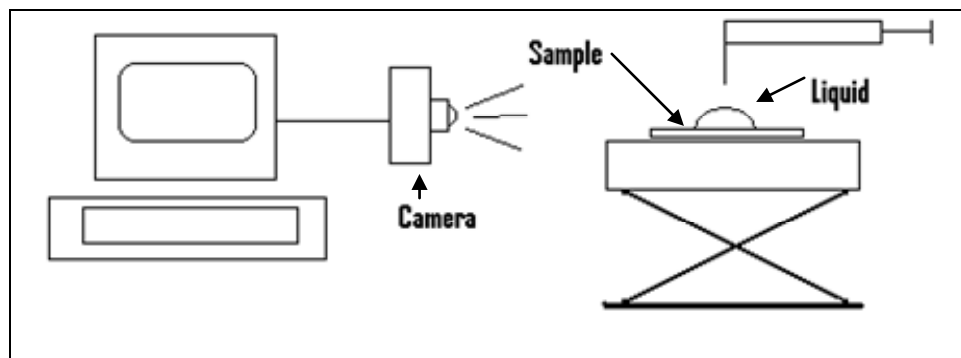
Figure 1. Contact-angle goniometer setup at the U.S. Army Research Laboratory.

For static contact-angle measurements on films, small strips (5 × 1 cm) of the sample film are cut and placed onto a glass microscope slide using double-sided tape to ensure a flat viewing surface. The glass slide is placed onto the stage where a 5-μL drop is measured out from the syringe and dropped to the film surface. The drop is allowed to reach equilibrium before the measurement is recorded and before evaporation occurs. Once the drop has been measured, the slide is moved to allow another drop to be placed on the sample surface. We used between three and five drops for each sample, averaging the values for our final contact-angle value. This exact process was then repeated using methylene iodide, ethanol, and formamide. These liquids were chosen to cover a wide range of polarity, as listed in table 1 (*6*).

Table 1. Surface tension γ_{LV}, density ρ_L, and viscosity η_L of the test liquids.

Test Liquid	γ_{LV} (mN/m)	ρ_L (g/cm^3)	η_L (mPa s)
Water	72.8	0.998	1.002
Formamide	58.2	1.133	3.812
Methylene iodide	50.8	3.332	2.762
Ethanol	23.0	0.789	1.162

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* LabVIEW is a trademark of National Instruments Corporation.

The work of adhesion W_a at the interface of solid-liquid-vapor systems can be derived from the following equation:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL},\tag{1}$$

where γ_{SV} and γ_{LV} represent the surface energies of the solid and liquid phases, respectively, and γ_{SL} is the energy of the solid liquid interface. The work of adhesion represents the energy per unit area of interaction between dissimilar phases.

According to Young's equation, if θ, the solid-liquid contact angle is known, the energy of the solid-liquid interface can be calculated using the following expression:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos\theta.\tag{2}$$

Therefore, the combination of equations one and two leads to the determination of work of adhesion W_a:

$$W_a = \gamma_{LV}\,(1 + \cos\theta).\tag{3}$$

The intramolecular attraction that is expressed through γ consists of two components: one attributed to polar interactions, γ^p, and one that can be correlated to dispersion forces, γ^d. Fowkes stated that the intermolecular forces acting in the interface are partly a result of the London dispersive forces and that their contribution to the surface energy is represented by γ^d, while dipole-dipole interactions and hydrogen bond forces can be expressed through γ^p (7). According to Good and Girifalco (8), the attraction energy between different molecules is the geometric mean of the attraction energy between pairs of like molecules. Thus, the work of adhesion that corresponds to the interaction energy between dissimilar phases, such as in solid-liquid systems, is given as the following:

$$W_a = W_a^d + W_a^p = 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} + 2(\gamma_{SV}^p \gamma_{LV}^p)^{1/2}$$

$$\Rightarrow \frac{W_a}{2 \cdot (\gamma_{LV}^p)^{1/2}} = (\gamma_{SV}^d)^{1/2}\left(\frac{\gamma_{LV}^d}{\gamma_{LV}^p}\right)^{1/2} + (\gamma_{SV}^p)^{1/2}.\tag{4}$$

Once W_a has been calculated, a plot of $W_a / 2(\gamma_{LV}^p)^{1/2}$ vs. $(\gamma^d_{LV}/\gamma^p_{LV})^{1/2}$ for multiple test liquids will yield a linear fit with slope of $(\gamma_{SV}^d)^{1/2}$ and intercept equaling $(\gamma_{SV}^p)^{1/2}$. Squaring and adding these two values gives the total surface tension of the solid.

When measuring the liquid-solid contact angle for fabrics, the static contact-angle setup can't be used, as fabric roughness causes absorption of the single drop. To measure the liquid-solid contact angle for fabrics, we use the Wilhelmy balance method setup. This setup consists of a LabVIEW interface allowing for computer control of a moveable stage and simultaneous reading from a microbalance.

For fabric testing using the Wilhelmy balance setup (shown in figure 2), small, equal-width strips of each fabric to be tested are cut and attached by tape to a straight piece of wire with a hooked opposite end. This wire is suspended from the underside of the microbalance, which must then be tared. Single fiber tests are not preferred because extraction of a single fiber may result in an uneven distribution of finishes and sizings. A small vessel of testing liquid is placed on the moveable stage directly beneath the hanging fabric strip, ~1 mm from the fabric end. The stage is then moved upward toward the fabric at a speed of 10 μm/s. Immediately upon liquid-solid contact, which must be viewed directly, the stage progression is stopped. This leaves the sample edge only a few micrometers below the liquid surface. As the sample is partially immersed in a liquid, the liquid either rises or depresses along the strip, resulting in a wetting force F_w on the solid (9):

$$F_w = \gamma_{LV} \, P \cos \theta , \qquad (5)$$

where γ_{LV} is the surface tension of the liquid, P is the perimeter dimension of the solid-liquid interface, and θ is the contact angle between liquid and solid interface.
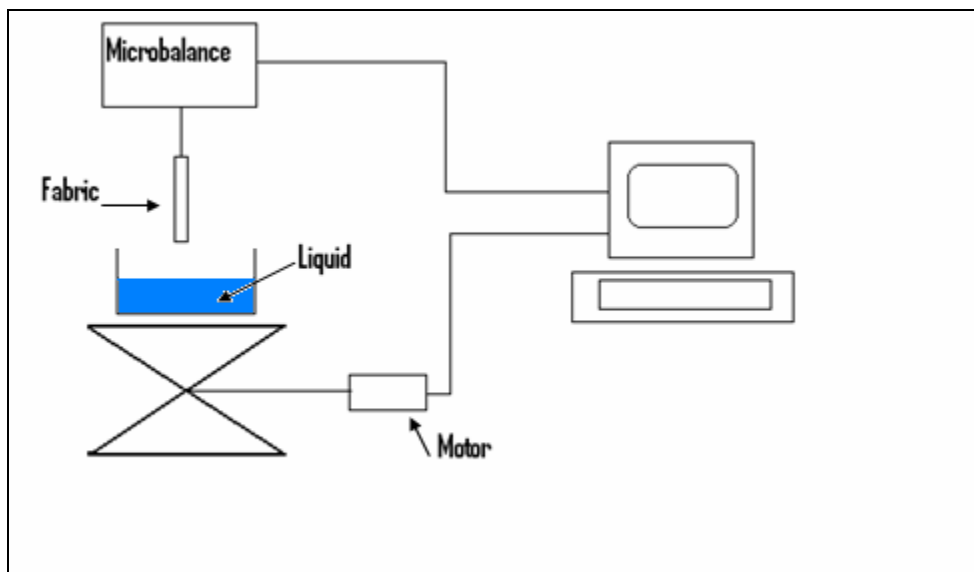
Figure 2. Wilhelmy microbalance setup for fabric liquid—solid contact-angle measurements.

The perimeter P can be derived from equation 5 from the force measurement in a total wetting liquid, such as hexane, where $\cos \theta = 1$. The microbalance will display a mass reading that is due to liquid uptake and the wetting force exerted on the perimeter of the fabric by the liquid. To attain an accurate value for the wetting force, liquid uptake must be subtracted from the force value given by the microbalance. To accomplish this, liquid uptake must be allowed to continue to saturation, at which point the microbalance reading will be nearly stable. This value is the advancing steady-state force F_{ADV}. The stage is then moved down at 80 μm/s until the fabric is free of the liquid surface. As soon as separation occurs, the mass value must again be taken,

corresponding to the total liquid retention W_t. The wetting force F_W is then given by the following:

$$F_W = F_{ADV} - W_t .$$ (6)

Combined with equation 5, the contact angles between the fabric and the various test liquids are obtained.

3. Results

Polyethylene films were exposed to helium plasmas containing oxygen at atmospheric pressure conditions. The total helium flow was 15,000 sccm[*], and oxygen was diluted in it in the following volume percentages: 0.6%, 2%, and 6%. Through the collisions and reactions occurring in the gas phase, atomic oxygen is generated that is highly reactive and causes oxidation and mild etching of the polymer surface. X-ray photoelectron spectroscopy (XPS) studies (5) show that hydroxylic and carboxylic functionalities are grafted on the surface, modifying its chemical character.

Besides functionalizing the surface, these polar groups are expected to decrease the water contact angle of the surface (compared to the control sample) and increase its energy. Figure 3 depicts the effect of plasma exposure on a polyethylene film. Prior to plasma exposure, a drop of water was placed on the film and the contact angle was 98°. In this case, the surface can be characterized as hydrophobic. Then, the film was treated under a helium-oxygen plasma for a few seconds and the water contact angle dropped to 25°, revealing a very hydrophilic surface.
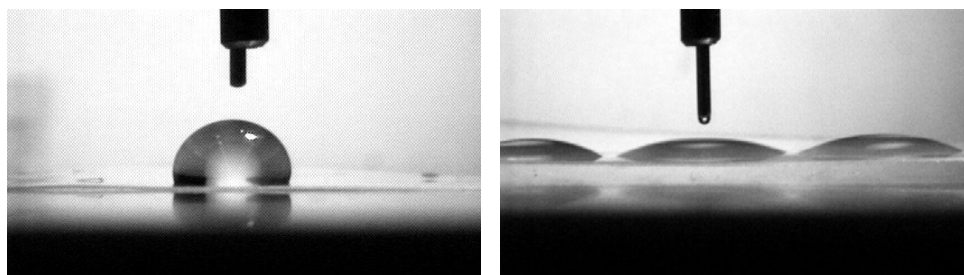

Figure 3. Water droplets on the control polyethylene film before plasma exposure (left) and after helium-oxygen plasma treatment (right).

Figure 4 shows the observed water contact angles for the three polyethylene films treated under helium-oxygen plasmas and the film treated under pure helium plasma.

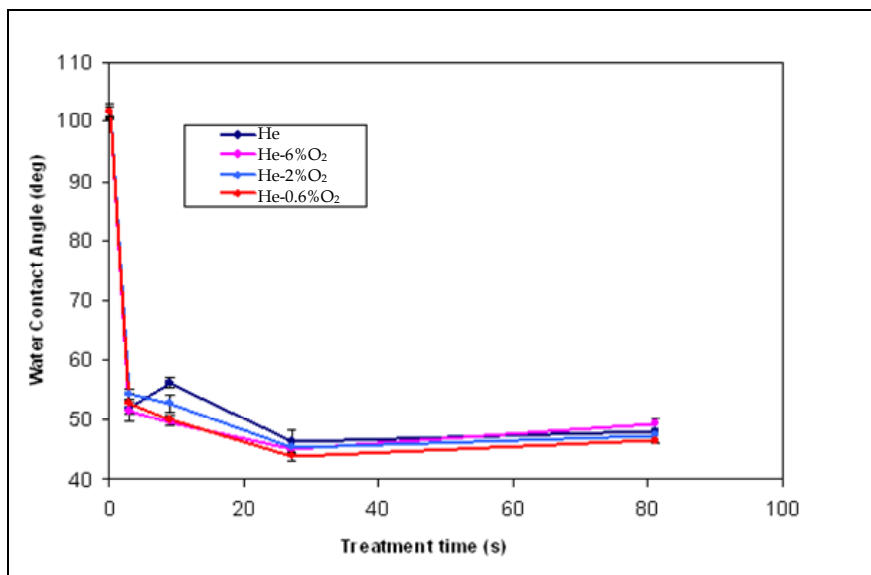[*] sccm = standard cubic centimeters per minute.

Figure 4. Water contact angle vs. plasma treatment time for polyethylene films.

The water contact angles were measured directly following the plasma exposure. The water contact angle for the control sample was 102°. After a short plasma treatment of 3 s, it decreased to 52°. The recorded values are similar for all samples studied, indicating that under these experimental conditions (power, gas composition, gas flow) the plasma has similar impact on the treated surfaces. The reduction of the water contact angle is a result of two combined effects due to the plasma exposure: chemical modification (oxidation) of the surface as described earlier and morphological changes on the surface as a rougher surface is created.

Similar results were found for nylon-6 films treated under He-O_2 plasmas, as shown in table 2. In this case, the average water contact angle for the control sample was found to be 75° and depending on the gas composition and treatment time, the contact angle of the modified surface can be as low as 26.4°.

Table 2. Water contact-angle values for plasma-modified nylon films treated under helium and helium-oxygen plasmas.

	Treatment Time (s)			
Gas	**3**	**9**	**27**	**81**
He-0%O_2	43.2° ± 0.9°	37.5° ± 0.5°	29.8° ± 0.2°	26.4° ± 1.2°
He-6%O_2	47.2° ± 0.3°	36.1° ± 1.5°	34.3° ± 0.2°	35.5° ± 0.9°
He-2%O_2	44.5° ± 0.7°	41.4° ± 1.0°	39.3° ± 1.6°	32.4° ± 1.1°
He-0.6%O_2	41.6° ± 1.6°	37.3° ± 1.2°	35.7° ± 0.5°	31.6° ± 1.9°

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The static contact-angle measurements are then used to calculate the surface tension of the polymer films. The theory described in section 2.2 was used to calculate the surface tension of polyethylene films using three test liquids. Plotting equation (4) allowed us to calculate the two components of the film surface energy, γ^p and γ^d. Then, the total surface tension for each sample was calculated, and the results were plotted in terms of treatment time. As seen in figure 5, we observed a significant increase of the polar component γ^p depending on the plasma treatment time, which ranged from 3 to 30 s. The dispersive component γ^d shows a small decrease and remains stable for longer exposure times. The steep increase of the polar component of the surface energy reveals that new polar groups are grafted on the film surface, as confirmed earlier by XPS results, and are responsible for the improved hydrophilicity of the surface.
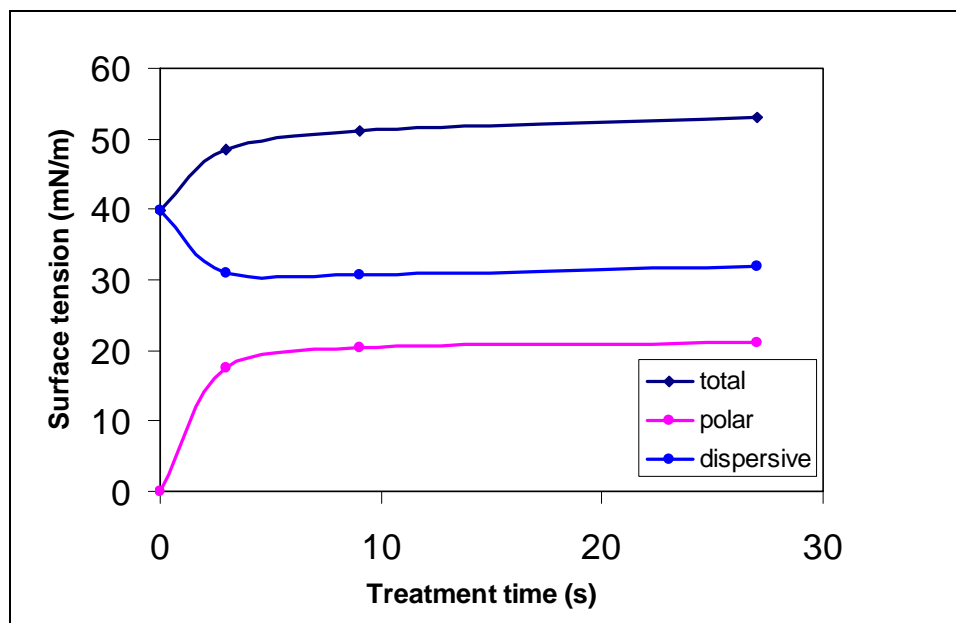

Figure 5. Surface energy of polyethylene and its polar and dispersive components in terms of treatment time.

Wettability studies on UHMWPE woven fabrics were also performed. Small strips of the material were cut and immersed in water, methylene iodide, and ethanol, while a microbalance monitored the total force and liquid uptake. The wetting force and, finally, the contact angles were calculated using the theory in section 2.2; the results are shown in table 3. The water contact angle of polyethylene fibers was 65° and decreased to 23.7° for ethanol, as expected.

Table 3. Results for polyethylene woven fabric from the wettability test using the microbalance method.

Test Liquid	Wetting Force F_w (10^{-4} N)	Contact Angle
Water	5.99 ± 0.21	$64.3° \pm 1.0°$
Methylene iodide	5.62 ± 0.30	$54.4° \pm 2.2°$
Ethanol	3.89 ± 0.06	$22.2° \pm 2.0°$

4. Conclusions

Two different wettability test methods were applied at U.S. Army Research Laboratory to measure and calculate liquid-polymer contact angles and polymer surface tension. The polymeric materials studied were polyethylene and nylon thin films and polyethylene woven fabric. For the films, three to five drops of each test liquid was averaged, giving consistent results for the liquid-solid contact angle and providing data for the surface tension calculation. Results obtained for the control films were compared with those of the plasma-modified surfaces, proving that the surface chemistry is altered and more hydrophilic surfaces are formed through plasma exposure. For the woven fabrics, small strips of the control fabrics were tested, and the microbalance method was employed to give an estimate of the liquid-solid contact angle.

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