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Water contact angle as a quantitative measure of total polyethylene surface energy

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A wide variety of plasma treatments was performed on polyethylene surfaces, resulting in a wide range of total surface energies. The linear correlation of γ_S^p with $\cos \theta$ was discussed in light of the Young–Dupré equation. Hundred percent of the surface energy variation was accounted for by the polar component of surface energy; the dispersive component was not affected by surface treatment. These data show that for this polymer the contact angle of a single polar liquid can be used as a robust quantitative indicator of treatment level, and because of its excellent linear correlation with total surface energy for this system, can be used as a quantitative measure of total surface energy.

Keywords: surface energy; contact angle; surface treatment; wetting tension; adhesion

Introduction

To have predictable strength and therefore to be useful in structural applications, adhesive bonds must not fail interfacially. Failure must be cohesive in the substrate or in the adhesive. This means that the interfacial fracture toughness must be maximized. Interfacial fracture toughness (G) depends on the thermodynamic Work of Adhesion (W_A) [1]:

$$G = W_A(1 + f(T, \nu)) \quad (1)$$

where $f(t, \nu)$ is the term that accounts for the viscoelastic deformation that accompanies crack growth and fracture. W_A is frequently expressed as a function of the polar and dispersive components of the surface tension of the substrate and adhesive [2,3]:

$$W_A = 2 \left(\sqrt{\gamma_A^D \gamma_S^D} + \sqrt{\gamma_A^P \gamma_S^P} \right) \quad (2)$$

where subscripts A and S refer to adhesive and substrate, and superscripts D and P refer to dispersive and polar components of surface energy. A primary goal of surface treatment is to maximize W_A by maximizing γ_S^D and γ_S^P . In practice, one way to accomplish this goal is by plasma treatment to increase γ_S^P . For inorganic substrates such as metals and ceramics, plasma treatment increases γ_S^P primarily by removal of low-energy contaminants, usually hydrocarbons. For organic substrates (such as polymers), plasma

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treatment increases γ_S^P via oxidation of C–H and C–C groups to groups such as hydroxyls and, to a lesser extent, carbonyls and carboxyls [4].

Knowledge of surface energy is important in many industrial processes because of its direct influence on practical adhesion through Equation (1). Surface energies of solids may be measured using several techniques [5], but the most common method is based on obtaining contact angle measurements of multiple fluids [2,3,6]. Although it is an indirect approach, the results have been shown to correlate very well with more fundamental methods [7].

However, obtaining contact angles with multiple fluids can be cumbersome, and many of the common nonwater fluids used in these analyses present health and safety issues to the technician. Furthermore, because many of these nonwater fluids are organic solvents they can damage common surfaces. For this reason surface energy measurements frequently qualify as destructive tests.

This paper presents an argument for using water contact angle measurements as a robust estimator of total surface energy. Similar approaches have been discussed before in the context of estimating surface wetting tension [8,9], but the correlations are empirical and the relation between wetting tension and surface energy is not clear.

The contact angle of a fluid is fundamentally related to the surface free energy of the solid surface, the liquid, and the interface through the Young–Dupré equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \quad (3)$$

Where the cosine of the liquid contact angle varies with the solid surface energy. The precise form of the relationship between γ_S and $\cos \theta$ is unknown because the form of the dependence of γ_{SL} on γ_S is unknown. However, for a given substrate and liquid chemistry, it is reasonable to expect it to be linear, that is, as γ_S is varied by changing functional group concentration, γ_{SL} (which depends on the molar concentration of functional groups at the interface) should vary in proportion. Therefore, a plot of γ_S versus $\cos \theta$ should be linear. This implies that a plot of the cosine of the contact angles of a single liquid against a homologous series of surfaces of varying surface energy should be linear. In one sense, this concept represents the inverse of the seminal work by Zisman [5,10], which showed that a plot of $\cos \theta$ versus γ_L for a series of homologous liquids on a surface of fixed γ_S is linear.

Due to its capacity for hydrogen bonding, water is a very polar liquid: $\gamma_L^D = 22 \text{ mJ/m}^2$ and $\gamma_L^P = 50.2 \text{ mJ/m}^2$. Therefore, it is expected that the contact angle formed by water with prepared polymer surfaces should be determined primarily through polar–polar interactions. This report discusses contact angles of water formed with polyethylene surfaces that were treated to different levels of polarity using atmospheric pressure plasma treatments in air and vacuum plasma treatments in a variety of gasses. It is shown that the cosine of the contact angle of water has a strong linear correlation with the polar component of surface energy. Because of this excellent correlation, water contact angles can be used as a convenient single-point measure of surface polarity in these instances.

Experimental

Substrate preparation

High density polyethylene (HDPE) sheets conforming to ASTM D4976 (McMaster-Carr, Cleveland, OH), were sheared to $1'' \times 4'' \times 3/16''$. Coupons were selected for plasma treatment by visually inspecting their surfaces for scratches. HDPE coupons

which showed at least one surface with minimal surface scratches were selected for plasma treatment. Coupons destined for vacuum plasma treatments had a small hole drilled near the top of the coupon to allow suspension by copper wire in the plasma reactor. After drilling, coupons were gently washed with detergent in hot tap water, and then rinsed with distilled water followed by a rinse in isopropanol and air drying. Earlier tests had shown wiping with a laboratory tissue wiper was sufficient to impart visible scratching to the surface; therefore, no wiping was performed on the HDPE coupons.

Plasma treatment

Some plasma treatments were performed using air at atmospheric pressure (single rotary plasma jet RD1004, Plasmatreat North America Inc., Mississauga, ON). With this apparatus an electrode gun that produces a stream of low temperature ionized gas is mounted on a robotic arm with controllable traverse rate, pitch (lateral distance between successive traverses), and sample/gun distance. Some samples received treatment with a fixed traverse rate of 6"/second, while the gun-sample distance was varied from 0.4" to 1.0" sample/gun distance. Other samples were treated at a 0.4" fixed sample/gun distance while varying the traverse rate between 1 and 4"/s. Pitch was held constant at 0.7". Scanning electron microscopy of treated and untreated surfaces showed no detectable change in surface morphology as a result of these treatments.

Other plasma treatments were performed in vacuum using a 1001 Advanced Plasma Systems B6 RF reactor (13.56 MHz) under varying conditions (1–20 min, 50 W, 65–120 mTorr) in O₂, H₂O₂/H₂O, N₂, N₂/H₂, Ar, or H₂ atmospheres.

Surface energy measurements

Advancing contact angles of distilled water (Distillata brand), diiodomethane (Alfa Aesar L00472), formamide (Sigma F9037), and ethylene glycol (Sigma 324558) were measured within 1 h of treatment using a Ramé-Hart Model 100-00 115 contact angle goniometer. Hamilton Model 700 syringes were used to deposit liquids. To ensure a true advancing angle, drops were established by first depositing roughly half the total drop volume (several μ l). Measurements were obtained as the remaining volume was added in 0.5–1 μ l increments. Images of probe fluid drops were captured using a digital camera fitted to the eyepiece of the goniometer. The digital image of the drop on the sample surface was then analyzed using software which returned the average value of the contact angles on both sides of the drop. Contact angle measurements were repeatable within $\pm 1^\circ$. Polar and dispersive values of surface energies were calculated using the Kaelble method [3] as extended by Boerio et al. [6] to make use of the added precision available from employing more than two liquids.

Results and discussion

Tables 1 and 2 show the various surface treatments used along with the calculated values for γ_S^D and γ_S^P . Total surface energies ranged from a low of 28.2 mJ/m² for untreated HDPE to a high of 60.1 mJ/m² for material that was treated with a two-step process consisting of an Ar plasma followed by a H₂ plasma. Some treatment conditions were repeated; in general, the repeated runs provided surface energy values that were within a few % of each other.

Table 1. Process conditions and surface energy values for atmospheric pressure plasma treatment of HDPE. Treatments performed using a Plasmacreat RD1004 with air as the process gas. Surface energies were determined as described in Refs. [3] and [6].

Atmospheric pressure plasma treatment				Surface energy (mJ/m ²)		
Process	Plasma–surface distance (in)	Traverse rate (in/s)	Plasma–surface distance (in)	γ_S^D	γ_S^P	γ_S^T
1	0.4	4	0.4	32.6	17.7	50.4
2	0.4	2	0.4	25.8	30.2	56.0
3	0.4	1	0.4	29.1	29.6	58.7
4	0.6	6	0.6	28.5	23.2	51.7
5	0.6	6	0.6	29.8	18.8	48.5
6	0.8	6	0.8	30.9	13.1	44.0
7	1.0	6	1.0	31.4	6.6	38.1
Untreated control				28.4	0.4	28.8

Table 2. Process conditions and surface energy values for vacuum plasma treatment of HDPE. Treatments performed in vacuum 13.56 MHz. Surface energies were determined as described in Refs. [3] and [6].

Vacuum plasma treatment						Surface energy (mJ/m ²)		
Process	Duration (min)	Pressure (mTorr)	Power (W)	Gas	Flow (sccm)	γ_S^D	γ_S^P	γ_S^T
1	10	85	50	H ₂ O ₂ +O ₂	100	30.5	23.8	54.3
2	10	70	50	H ₂ O ₂ +H ₂ O	100	26.1	31.7	57.9
3	10	85	50	H ₂ O ₂ +O ₂	100	30.5	22.6	53.1
4	10	125	50	1:3 N ₂ :H ₂	100	28.3	28.6	56.9
5	10	85	50	N ₂	100	28.9	29.3	58.3
6	10	120	50	1:3 N ₂ :H ₂	100	34.3	23.1	57.4
7	20	85	50	O ₂	100	31.3	22.8	54.1
8	15	85	50	O ₂	100	33.1	21.6	54.7
9	10	85	50	O ₂	100	29.9	25.0	55.0
10	10	85	50	O ₂	100	30.4	23.8	54.3
11	1	85	50	O ₂	100	29.2	19.3	48.4
12	10	65	50	Ar	100	36.5	23.6	60.1
	15	120	50	H ₂	100			

Figure 1 shows the total, polar, and dispersive components of surface energies from Tables 1 and 2 vs. the cosine of the water contact angle for the various treated polyethylene surfaces. The total surface energies vary linearly with the cosine of the water contact angle, as predicted by Equation (2), with $R^2 = 0.982$.

Figure 1 also shows the dependence of the dispersive (γ_S^D) and polar components (γ_S^P) of surface energy on the cosine of the water contact angle. It is seen that these treatments had little or no effect on γ_S^D , and that these treatments served only to increase the polar component of surface energy of the HDPE. This figure indicates that a single parameter, the water contact angle, is extremely sensitive to the changes in total surface energy undergone by a polyolefin surface as a result of a wide variety of plasma treatments.

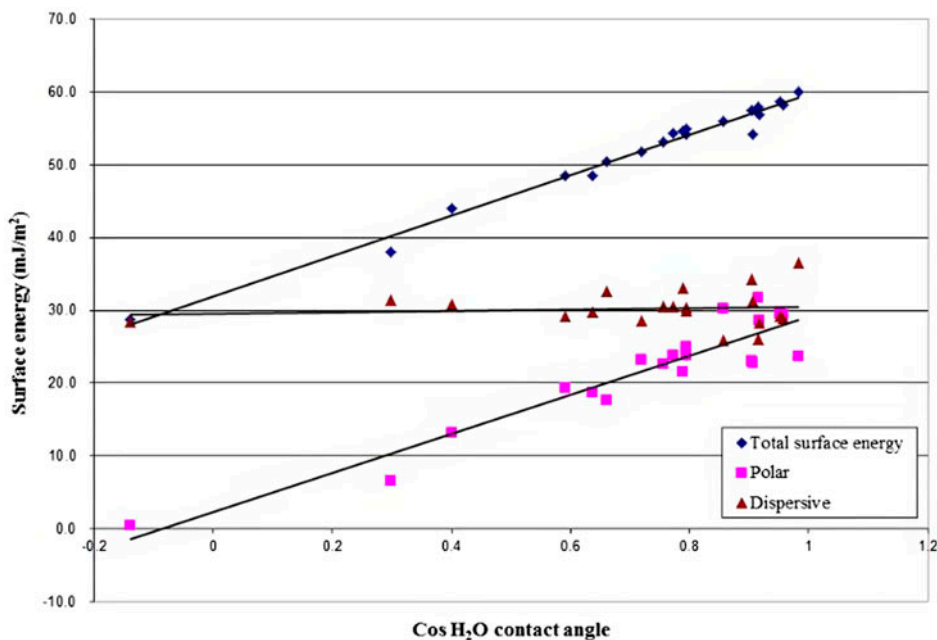


Figure 1. Surface energy and surface energy components of plasma treatment polyethylene versus the cosine of the advancing water contact angle. Total surface energy: \blacklozenge , polar component: \blacksquare , and dispersive component: \blacktriangle .

In other work, these treated substrates were used to create adhesive joints which allowed analysis of the surface energy components that were important for adhesion with an epoxy [11]. In the cited paper, it was concluded that the electron donating (i.e. basic) nature of the polar groups influenced adhesion the most.

Several conclusions were drawn from this data:

- (1) A wide variety of plasma treatments resulted in an increase in the polar component of surface energy but had no discernible effect on the dispersive component.
- (2) The cosine of the water contact angle showed strong linear correlation with the polar component of surface energy.
- (3) The linear correlation of γ_S with $\cos \theta$ was linear as predicted by the Young–Dupré equation.
- (4) For this system, the contact angle of water can be used as a quantitative measure of total surface energy.

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