Novel Wetting Measurements for Rapid Quality Assurance of Surface Treatment for Adhesion on Polymers

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Abstract

The theoretical relationship between surface energies and adhesion are briefly reviewed. Surface energies obtained from contact angle measurements can be extremely useful but difficult to obtain in manufacturing and field environments. A novel technique for probing surface energies via liquid drops created using ballistic deposition is discussed. This approach provides a contact angle measurement that overcomes problems associated with chemical and physical heterogeneity of the surface. The technique simplifies obtaining precise wetting measurements from industrially important surfaces. The use of this technique as a quality assurance tool for surface treatment of packaging materials is discussed.

Introduction

Quantitative relationship between wetting and adhesion. The tendency of a liquid to either spread or bead up on a surface (termed *wetting*) is a necessary prerequisite for adhesion. The quantitative relationship between *wetting* and *adhesion* for pressure sensitive adhesives is well established [1-4]. Surface energy is related to adhesive bond fracture toughness through the work of adhesion W_A. An expression of this relationship, applicable for a range of testing speeds between about 10^{-10} to 10^{-1} ms^{-1} [1], is shown in equation 1:

$$G_{int} = W_A(1 + f(T,v)) \qquad (1)$$

Where G_{int} is the interfacial fracture toughness, $f(T,v)$ is a viscoelastic energy dissipation term, and T and v are temperature and crack velocity. G is a fundamental measure of adhesion that is a material parameter independent of specimen geometry. W_A is a thermodynamic parameter that represents the reduction in free energy that occurs when an adhesive or coating is placed in contact with a surface. It may be measured directly through the contact angle that the adhesive or coating makes with the surface:

$$W_A = \gamma_l(1 + \cos\Theta) \qquad (2)$$

Where γ_l is the surface tension of the liquid adhesive or coating. Note that as wetting of the substrate by the adhesive improves, $\theta \rightarrow 0$ and $W_A \rightarrow 2\gamma_l$. $2\gamma_l$ represents the minimum cohesive fracture toughness of the adhesive. This is the goal of surface treatment.

Equations 1 and 2 show the direct relationship between the contact angle and adhesion. Through these equations, wetting measurements can be used for *quantitative* prediction of interfacial adhesion.

It is important to note that equations 1 and 2 predict the *interfacial* strength of a composite system: paint/substrate, adhesive/adherend, etc. If wetting is improved to the point where $G_{int} > G_s$, the toughness of substrate or bulk adhesive, failure will no longer occur at the interface. Further improvements in the interface via surface treatment will not result in improved adhesive joint strength.

Figure 1 shows Mode I fracture toughness for adhesive joints constructed from 177°C cure epoxy laminates bonded with a RT cure paste adhesive. The Work of Adhesion (W_A) was controlled in these samples by applying small amounts of a silicone mold release to the substrate after grit blasting. This simulates the type of contamination that might be expected to occur in an industrial setting. In the region of interfacial failure, the relationship between adhesion and W_A is linear, as predicted by Equation 1. For uncontaminated or lightly contaminated substrates, W_A is high enough that failure is cohesive in the adhesive or substrate and G is no longer predicted by surface properties.

Similar plots of adhesion vs W_A are obtained for a variety of substrates, surface treatments, and adhesion, indicating that equations 1 and 2 are indeed universal. It remains to develop techniques for conveniently obtaining quantitative wetting measurements in industrial settings.

Wetting measurements in manufacturing environments. Printing of food packaging material provides an excellent application for these wetting

measurements. Food packaging typically consists of low surface energy polymers, such as oriented polypropylene film. These materials are low cost with excellent mechanical properties, but the low surface energies of the untreated materials (ca. 32 dynes/cm) mandate the use of surface treatment such as flame or corona treatment to achieve adhesion of inks and adhesives. Monitoring of surface energy is an important component of quality assurance programs.
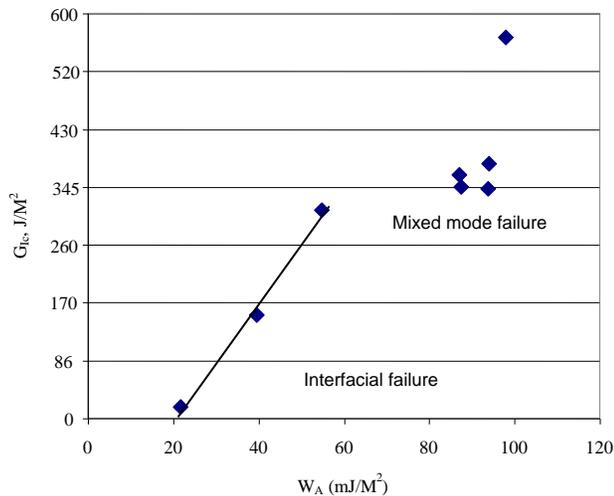

Figure 1. Mode I fracture toughness obtained from double cantilever beam tests, grit blasted 177°C cure epoxy/carbon fiber laminates bonded with RT cure epoxy. W_A was controlled via contamination of the laminate surfaces with silicone mold release.

Surface energy measurements in the food packaging and printing industries are typically accomplished via dyne solutions. These are mixtures of two miscible liquids in different proportions to obtain a range of surface tensions. Surface energy is estimated by the lowest surface tension mixture which will remain spread on the surface under a particular set of application conditions [5]. The surface energy number is termed the wetting tension and approximates Zisman's critical surface tension γ_c [6]. The approach generates numbers that correlate with surface treatment level, but the results depend strongly on the technique of the individual operator. Interlaboratory reproducibility is very poor. Although contact angle techniques are more precise and reproducible, they generally require a trained operator, a laboratory environment, and a small sample cut from the treated web.

Recently we have developed an alternative approach for characterizing surface energetics that overcomes these problems. This approach

incorporates a novel technique for establishing equilibrium liquid/solid contact. Instead of depositing a droplet by transfer from the tip of a syringe needle, the probe liquid drop is constructed on the surface from a high frequency stream of nanoliter-sized pulses from a jeweled nozzle located several cm remote from the surface. This technique is termed ballistic deposition. Because the stream of droplet pulses imparts vibration to the growing drop, the drop tends to spread more readily to its equilibrium size [7]. Because of this, ballistic deposition can result in a more robust characterization of wetting of surfaces exhibiting physical or chemical heterogeneity.

Rather than directly measuring contact angles, this approach calculates the contact angle from a diameter measurement of a small droplet of probe liquid of precisely known volume that the device deposits on the surface; this simplifies the imaging and image analysis requirements, and obtains a contact angle value which represents an average value for the entire drop perimeter. The contact angle calculated using this approach is probably more robust and more representative of the average surface energy around the drop perimeter. These measurements can be obtained using a hand-held surface energy probe, a device that can be carried on an operator's belt and can obtain wetting measurements from an object of any size or orientation in almost any environment.

This work presents the results of investigations into the ability of the ballistic drop deposition technique to measure surface treatment in corona and flame treated oriented polypropylene films. The existence of a quantitative relationship between wetting and surface energy is demonstrated for a range of treatments. These measurements uncovered variation in surface energy of both treated and untreated material along the machine direction of the web, suggesting that more precise control of treatment level could result in a more uniform product.

Experimentation

Samples of treated and untreated biaxially oriented polypropylene (BOPP) were analyzed beginning approximately one week after manufacture and treatment. Samples were obtained by coring a 10m wide roll to obtain a stack of 8.5"x11" sheets, each sheet representing a sample from approximately 3 meters further along the machine direction. Wetting tension measurements were obtained immediately after receipt according to [5] using a Wetting

Tension Test Kit obtained from Wedor Corporation (1907 S. 89th Street, West Allis, WI 53227). Surface energies were also measured through contact angles of five probe fluids using a Ramé-Hart NRL 100 contact angle goniometer. Polar, dispersive, and total surface energies were calculated from this data using the method of Kaelble [8].

In addition, 2µl water droplets were ballistically deposited onto the surfaces using the BTG Labs Surface Analyst™ surface energy probe. Image analysis of the drops provided contact angles through the Bikerman equation [9].

Results

Comparison of wetting tension measurements obtained in different laboratories. Wetting tension values obtained in our laboratory were within about 2 dynes/com of the reported values, with the exception of the values for a metallized surface. In this case, the value measured in our facility was about 6 dynes/com lower than the reported value. This is probably due to adsorption of contaminants by the active metal surface during the elapsed time between the two sets of measurements. Clean metal surfaces absorb contaminants from the atmosphere much more quickly and to a greater extent than a treated polymer surface.

Correlation of contact angle measurements with wetting tension measurements. The correlation of cosine θ_{H2O} (contact angle of water) to wetting tension is shown in Figure 2. The correlation is not strong, and was not significantly better for any of the other probe fluids investigated (ethylene glycol, dimethyl sulfoxide, formamide, and dioodomethane.
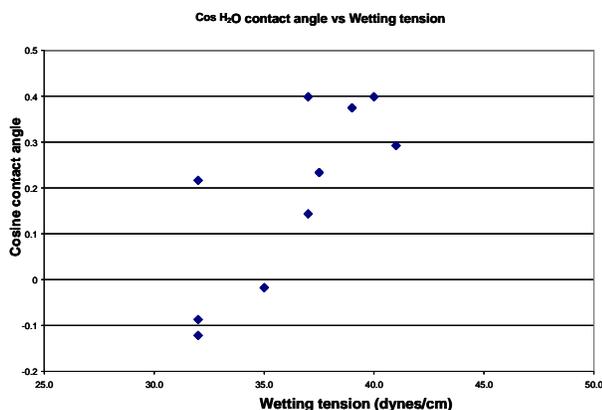

Figure 2. Correlation of cosine of water contact angle with wetting tension measurements.

The relationship between contact angle and wetting tension measurements has been investigated before. At least two references indicate a useful level of correlation between water contact angle measurements and wetting tension measurements [10,11]. The correlation demonstrated in [10], very similar to that in Figure 2, is claimed to be sufficient to warrant using contact angle measurements of water in place of wetting tension measurements as a metric of treatment level. ASTM D5946 is based on this correlation.

Variation in surface *energy along the machine direction.* Figure 3 shows the variation in wetting tension (determined via dyne solutions) as a function of distance along the machine direction for the treated and untreated sides. The untreated side provided a constant wetting tension number of 32 dynes/cm. The treated side showed a higher level of wetting tension; about 44-45 dynes/cm until the 6th meter along the machine direction when it showed an increase to about 47 dynes/cm. These results are typical for treated BOPP films.
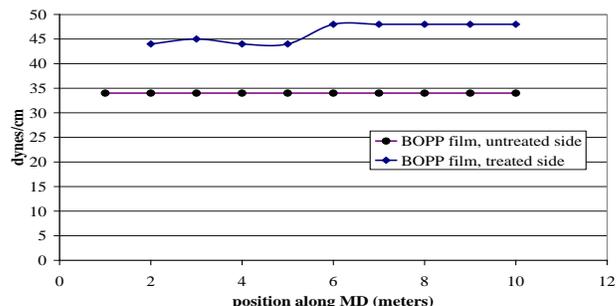

Figure 3. Wetting tension as a function along machine direction for untreated and corona treated BOPP.

However, the surface energy of these samples showed large variation along the machine direction not picked up by the wetting tension measurements. Figure 4 shows the total surface energy of these same samples as determined by the multi-fluid contact angle technique.
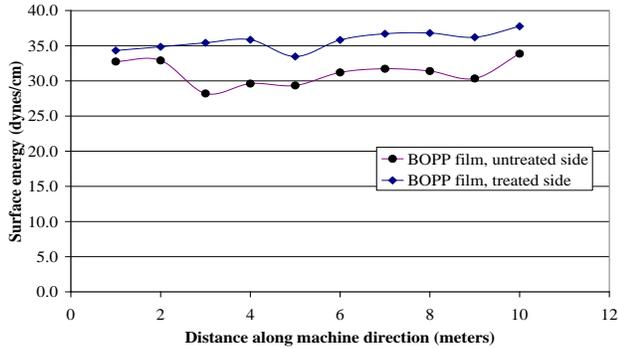
Figure 4. Total surface energies of samples in Figure 3 measured using multi-fluid contact angle technique.

Interestingly, there is a sinusoidal variation in the surface energy of the untreated material along the MD that is reflected in the surface energy of the treated side. It is clear that providing constant treatment intensity to a substrate that is varying in surface energy creates a treated surface that varies in a similar manner. Ideally, a closed loop feedback in the treatment system would correct for this to create a treated product having a uniform level of treatment along the MD.

Ballistically deposited liquid as a surface energy probe. Figure 5 shows the contact angle of ballistically deposited water drops along the MD of the same samples shown in Figures 3 and 4. The sinusoidal variation in surface energy seen in Figure 4 causes a similar variation in the water contact angle.
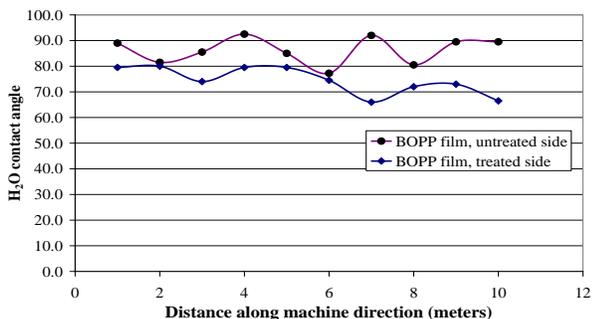

Figure 5. Variation in contact angle of ballistically deposited water drops along the machine direction of the samples from Figures 3 and 4.

Conclusions

Wettability has been used as a tool for interrogating surface energetics for many decades. Although inherently quantitative, implementation of wettability probes for quality assurance purposes has been difficult. The concept of a ballistically deposited probe fluid drop to interrogate surface energetics is new. From a quality assurance standpoint, it generates robust data that has good predictive capability in regards to processes such as surface treatment, and the technique lends itself to a simple handheld device. The technique returns a useful parameter (water contact angle) that is closely related to surface energy and adhesion, and shows potential as a tool for quantitative quality control in surface treatment, adhesive bonding, and printing operations. The ease of data collection (due to a simple, robust tool) allows for the collection of statistical process control data. Trends in wettability that occur as a result of changes in operators, techniques, raw materials, climate, etc. can be identified and corrected before these process drifts result in deterioration of adhesive bond performance.

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