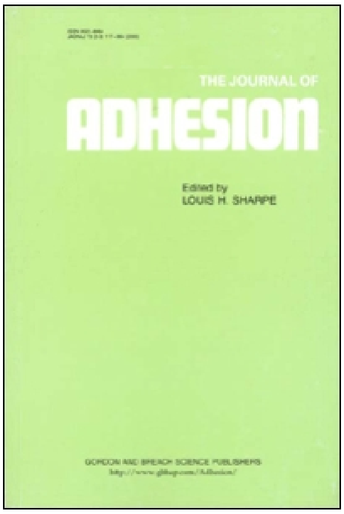


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Wetting Measurements for Identification of Specific Functional Groups Responsible for Adhesion

R. Giles Dillingham[a]; Brietta R. Oakley[a]; Drew Gilpin[a]
[a] Brighton Technologies Group, Inc., Cincinnati, Ohio, USA

To cite this Article Dillingham, R. Giles , Oakley, Brietta R. and Gilpin, Drew(2008) 'Wetting Measurements for Identification of Specific Functional Groups Responsible for Adhesion', The Journal of Adhesion, 84: 12, 1007 — 1022
To link to this Article: DOI: 10.1080/00218460802577191
URL: http://dx.doi.org/10.1080/00218460802577191

The Journal of Adhesion, 84:1007–1022, 2008

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460802577191

Wetting Measurements for Identification of Specific Functional Groups Responsible for Adhesion

R. Giles Dillingham, Brietta R. Oakley, and Drew Gilpin[*]
Brighton Technologies Group, Inc., Cincinnati, Ohio, USA

The relationship between adhesion and surface energy is well established for systems where specific chemical interactions are unlikely, such as pressure sensitive adhesives. However, the relationship of wetting to adhesion in chemically reactive systems is not well understood. This work used atmospheric pressure plasma treatment in air of high density polyethylene to obtain surfaces with a range of electron donor and acceptor character prior to bonding with an amine cured epoxy. Adhesion correlated strongly with the electron donating character of surface energy, and the likely functional groups responsible for this adhesion were amines created by the plasma treatment process. These results indicate that wetting measurements may be useful in detecting the specific chemical interactions important to adhesion in reactive systems.

Keywords: Acid-base; Adhesion; Atmospheric plasma treatment; Plasma treatment; Surface energy

INTRODUCTION

Room temperature (RT) curing paste adhesives are highly desirable joining materials for composite aircraft construction, primarily because these adhesives allow bonding of large and complex structures without autoclaving. However, RT curing adhesives are generally believed to be more sensitive to surface preparation procedures than high temperature curing adhesives [1,2]. This may be related to the low solubility of contaminants in adhesives at low curing temperatures. The combination of high sensitivity to surface conditions prior to bonding and a lack of practical quality assurance tools for surface

---

[*] Present address: Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH.

Received 6 August 2008; in final form 16 October 2008.

Address correspondence to Giles Dillingham, Brighton Technologies Group, Inc., 1006 Kieley Place, Cincinnati, OH 45217, USA. E-mail: gdillingham@btgnow.com

preparation and cleanliness have made it difficult for airframers to adopt RT curing adhesives for flight critical applications.

Developing appropriate quality assurance tools for predicting adhesive bond performance requires a thorough understanding of the relationships between surface treatment, contamination of treated surfaces, and adhesive bond performance. The surface chemistry which determines adhesive bond performance is very sensitive to both treatment conditions and to any exposure history that occurs between treatment and adhesive bonding. Currently there is no practical method that we are aware of for evaluating surface chemistry immediately prior to adhesive bonding in manufacturing environments. Work in our laboratory has indicated that a properly executed surface energy probe can function in this regard [3], but the relationship between wetting behavior, surface treatment and contamination, and adhesive bond performance is still semi-empirical. This paper presents the results of our recent efforts to establish a firmer theoretical relationship between wetting probe measurements and adhesive bond performance.

Adhesion between surfaces that are smooth enough to neglect mechanical interlocking is generally accepted to result from a combination of non-specific intermolecular forces, such as Lifschitz-van der Waals interactions, and specific chemical interactions, defined as interactions that involve some degree of electron transfer. These range from electron donor-acceptor interactions that result in partial electron transfer (acid-base interactions), to interactions that involve electron sharing (covalent bond formation). Small increases in the areal density of sites available for specific bond formation at an interface can dramatically increase the energy required to disrupt an adhesive bond [4–6]. Furthermore, specific chemical interactions across an interface tend to be stable and generally contribute to adhesive joint durability under adverse environmental conditions.

Surface treatments for polymers that improve adhesion generally result in an easily measurable increase in surface energy; contaminating or otherwise restructuring a treated surface reduces this surface energy. Surface energy can be used as a quantitative predictor of adhesive bond fracture toughness in systems where specific chemical interactions such as covalent bonds are highly unlikely [7–9], but the relationship of surface energy to adhesive bond fracture toughness in systems where specific chemical interactions are likely an important component of the adhesive mechanism is not well understood at the current time.

Surface treatments of composite laminates that are currently under investigation are all capable of modifying the surface chemistry in ways that may promote primary chemical bond formation at the interface with the adhesive. Cured epoxy surfaces may have residual curing agent functionality exposed on the surface, such as primary or secondary amines. Mechanical treatments such as grit blasting create free radical sites through fracture that can oxidize to reactive groups such as organic acids or alcohols, or directly react with adhesives. The density of reactive sites created *via* these processes is low, however. Chemical treatments such as corona discharge or plasma treatments create much higher densities of reactive sites through several mechanisms, including ionic bombardment and free radical reactions with activated gas-phase species. These active sites manifest themselves through higher surface energies and improved adhesion, and wettability measurements are frequently used as quality control tools for surface treatments.

Surface energy is related to adhesive bond fracture toughness through the work of adhesion, W_A. One expression of this relationship, developed for viscoelastic adhesives and applicable for a range of testing speeds between about 10^{-10} to 10^{-1} m/s, is shown in Eq. (1) (see [5] and references therein):

$$G = W_A(1 + f(T, v)), \tag{1}$$

where G is the fracture toughness (or energy release rate) and $f(T,v)$ is an energy dissipation term that depends on temperature, T, and crack velocity, v. W_A is a function of the surface energy of the substrate and the adhesive. The way it is evaluated depends upon the paradigm used to express the total surface energy of a substance. One approach is to express the total surface energy of a material as the sum of nonspecific (dispersion) (γ_i^D) and polar (γ_i^P) components. In this treatment, interactions across an interface are presumed to result from the combination of dispersion and polar interactions. In this case, the thermodynamic work of adhesion between an adhesive and a substrate may be expressed by Eq. (2) [10,11]:

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

where the subscripts A and S refer to adhesive and substrate. However, this approach assumes that all polar groups are equally able to interact with one another, within each phase as well as across the interface and, furthermore, makes the assumption that these interactions may be adequately represented *via* the geometric mean of the polar components. However, specific interactions across an interface require specific types of functional groups to be present on the two surfaces. An approach that considers the specific chemical interactions that can occur across an interface expresses the total surface energy as the sum of non-specific interactions and specific chemical interactions, described as electron donor-acceptor interactions [12]. Following Good [13], the Work of Adhesion between an adhesive A and substrate S may be expressed by Eq. (3):

$$W_A = 2\left(\sqrt{\gamma_A^{LW}\gamma_S^{LW}} + \sqrt{\gamma_A^{+}\gamma_S^{-}} + \sqrt{\gamma_A^{-}\gamma_S^{+}}\right). \tag{3}$$

The non-specific interactions ($\gamma_{\mathrm{i}}^{\mathrm{LW}}$for Lifshitz-van der Waals) are ascribed to dispersion force interactions, interactions between permanent dipoles, and permanent dipole-induced dipole interactions. The specific interactions, due to various degrees of valence band interactions, can be considered as a class of acid-base interaction. In this treatment, electron donating (or basic) capacity is expressed as γ_{i}^{-}, and electron accepting (or acid) capacity is expressed as γ_{i}^{+}. Electron donating groups are only capable of interaction with electron accepting groups, either within a phase or across an interface. The contribution of these groups to surface energy may be measured using contact angle techniques [13].

Although there is some discussion in the literature about the details of the functional relationship shown by Eq. (3) [14], it is generally accepted that there is a quantitative relationship between the specific interactions across an interface and the work of adhesion. Because these interactions result from a limited number of specific functional groups, and because these interactions may be quantified *via* wettability measurements, this suggests the possibility of using wetting measurements to gain more understanding about the specific functional groups that are responsible for adhesion in a given system. To this end we have created a series of surfaces with similar morphology and physical properties (such as modulus) but with a range of $\gamma_{\mathrm{i}}^{\mathrm{LW}}$, γ_{i}^{+}, and γ_{i}^{-} parameters through treatment with an atmospheric pressure plasma system. In atmospheric pressure plasma treatment, a plasma is generated remotely from the surface to be treated in a flowing gas stream at atmospheric pressure using a high-frequency discharge. The excited gas, which contains chemically active species such as ions, free electrons, and radicals, is directed from a nozzle over the surface to be treated. This process accomplishes surface cleaning and activation in a similar manner to that obtained in a low-pressure plasma system. To identify the functional groups responsible for various surface energy components, surfaces were analyzed using X-ray photoelectron spectroscopy. Finally, correlation of adhesion with surface energy components allowed determination of the relative importance of the various functional groups.

Adhesion to the prepared surfaces was evaluated using a single lap shear test of adhesive joints constructed from treated polyethylene substrates bonded with a room temperature cure epoxy. Equation (1) was developed for viscoelastic adhesives bonded to elastic substrates, and while using a viscoelastic substrate with a largely elastic adhesive seems like an inversion of this geometry, fundamentally the structures are identical: an elastic phase bonded to a viscoelastic phase through an interface.

Because the functional relationship between joint strength and interfacial fracture toughness is not well understood, lap joints are not generally used for fracture toughness measurements. Joint strength is a strong function of interfacial fracture toughness, however, when interfacial failure is present, and lap joint strength has been shown to correlate with fracture toughness tests [15]. Strength is controlled by crack initiation, which occurs when the applied load generates a local energy release rate larger than the interfacial fracture toughness.

EXPERIMENTAL

Substrates: High density polyethylene (HDPE) sheets conforming to ASTM D4976 (McMaster-Carr, Cleveland, OH, USA), were sheared to 1 × 4 × 3/16 inch (2.5 × 10.2 × 0.48 cm).

Surface preparation: Coupons were rinsed in isopropanol without wiping (to avoid scratches). Plasma treatment was performed using air at atmospheric pressure (single rotary plasma jet RD1004, Plasmatreat North America Inc., Mississauga, ON, Canada). 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 inch/second (15.2 cm/second) while the gun-sample distance was varied from 0.4 to 1.0 inch (1.0 to 2.5 cm) sample/gun distance. Other samples were treated at as received treatment with a 0.4 inch (1.0 cm) fixed sample/gun distance, 1–4 inch/second (2.5–10.2 cm/second) traverse rate. Pitch was held constant at 0.7 inch (1.8 cm). Treatment level was defined as the inverse of the gun-sample distance for experiments where this distance was varied, and as the inverse of the traverse rate (residence time) for experiments where the traverse rate was varied.

Scanning electron microscopy of treated and untreated surfaces showed no detectable change in surface morphology as a result of these treatments.

Surface energy measurements: Advancing contact angles of distilled water (Distillata, Cleveland, OH, USA), diiodomethane (Alfa Aesar, Ward Hill, MA, USA), formamide (Sigma, St. Louis, MO, USA), and ethylene glycol (Sigma) were measured within 1 hour of treatment using a Ramé-Hart Model 100-00 115 contact angle goniometer (Ramé-Hart, Mt: Lakes, NJ, USA). Hamilton Model 700 syringes (Hamilton, Reno, NV, USA) were used to deposit liquids. To ensure a true advancing angle, drops were established by first depositing roughly half the total drop volume (several μL). Measurements were obtained as the remaining volume was added in 0.5–1 μL 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 ± 1°. Acid, base, and Lifshitz-van der Waals components of surface energies were calculated using the method of Good [13].

Adhesive joint fabrication: Single lap joints were constructed of HDPE adherends within 2 hours of treatment (1/2 inch overlap, 0.020 inch bondline) (1.3 cm, 0.051 cm) using a two-part amine cured paste epoxy (EA9394, Henkel-Loctite, Rocky Hill, CT, USA). The adhesive was allowed to cure at room temperature for 12 hours followed with a 1 hr/66°C post cure.

X-ray photoelectron spectroscopy: Spectra were obtained using a Physical Electronics 5300 XPS using Mg K_α radiation (300 watts) (Edeu Priarie, MN, USA). Data processing was performed with AugerScan 3.0 (RBD Instruments, Bend, OR, USA). Curve fitting of C(1s) spectra was preceded by charge referencing the main C(1s) position to 284.6 eV, deconvolution of the X-ray line width, and subtracting a Shirley background. These spectra were then fit to five components representing aliphatic carbon, C-N, $(C\text{-}O + C=N)$, $(C=O + C\equiv N)$, and $O\text{-}C=O$ using binding energy shifts consistent with published data [16,17]. Several constraints on the curve fitting process improved the reliability and reproducibility of the results. Peak shapes and peak widths were established using the main aliphatic C(1s) peak and kept constant for all components within a given curve fit. Also, the total percent of oxidized carbon species was cross-checked against the O/C ratio obtained by atomic composition analysis.

RESULTS AND DISCUSSION

Effect of Treatment on Surface Energy

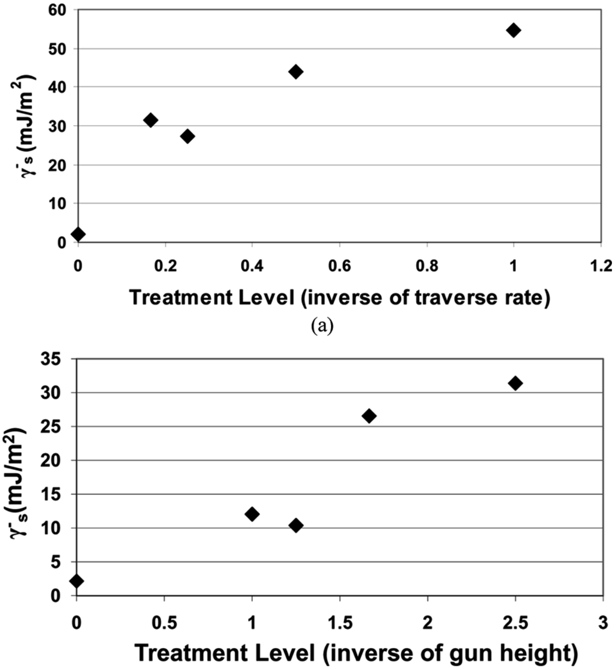
Atmospheric pressure plasma treatment in air increased the electron donating character of the HDPE surfaces in proportion to the residence time in the plasma as well as proximity to the plasma gun. Figure 1 shows base parameters as a function of traverse speed and gun-sample height.

All treatments increased the electron accepting character of the surfaces as well. However, the correlation with treatment level was much weaker (Fig. 2).

Figure 3 shows that the Lifshitz-van der Waals component of HDPE surface energy was increased by ~30–40% due to atmospheric plasma treatment; all treated surfaces showed similar γ^{LW}values.

It is interesting to note that γ^{LW} and γ^{D} are not equivalent. When the contact angle data used to calculate γ^{LW}, γ^{+}, and γ^{-} in Figs. 2–4 is used to calculate γ^{P} and γ^{D} instead, γ^{D} is invariant with plasma treatment. As discussed by Good [13], the Lifshitz-van der Waals component of solid surface energy is comprised of three terms:

$$\gamma^{\mathrm{LW}} = \gamma^{\mathrm{D}} + \gamma^{\mathrm{P}} + \gamma^{\mathrm{ind}},$$



(a)

(b)

FIGURE 1 Base parameter of surface energy *vs*. the inverse of (a) traverse speed or (b) gun-sample height.

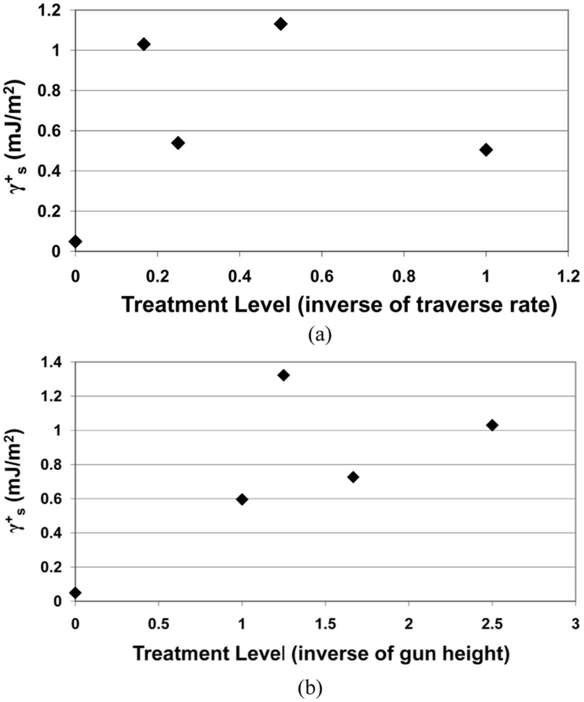


FIGURE 2 Acid component of surface energy *vs*. the inverse of (a) traverse rate or (b) gun-sample height.

where γ^{D} = oscillating temporary dipole interactions, γ^{P} = dipole-dipole interactions, and γ^{ind} = dipole-induced dipole interactions. Plasma treatments introduce polar functional groups such as carbonyls and esters through conversion of nonpolar groups: $(\gamma^{\mathrm{P}} + \gamma^{\mathrm{ind}})$ should increase at the expense of γ^{D}. These data indicate, however, that the increase in $(\gamma^{\mathrm{P}} + \gamma^{\mathrm{ind}})$ is not accompanied by a decrease in γ^{D}.

Effect of Surface Treatment on Adhesion

The relationship between the various components of surface energy and adhesion of HDPE to an amine cured epoxy was evaluated using single lap shear specimens. Figure 4 shows the relationship between γ^{LW} and single lap shear strength. All treatments increased adhesion, but correlation between γ^{LW} and is very weak.

Figure 5 shows the relationship between γ_{s}^{+} and single lap shear strength. As with γ^{LW}, there is no suggestion of correlation between

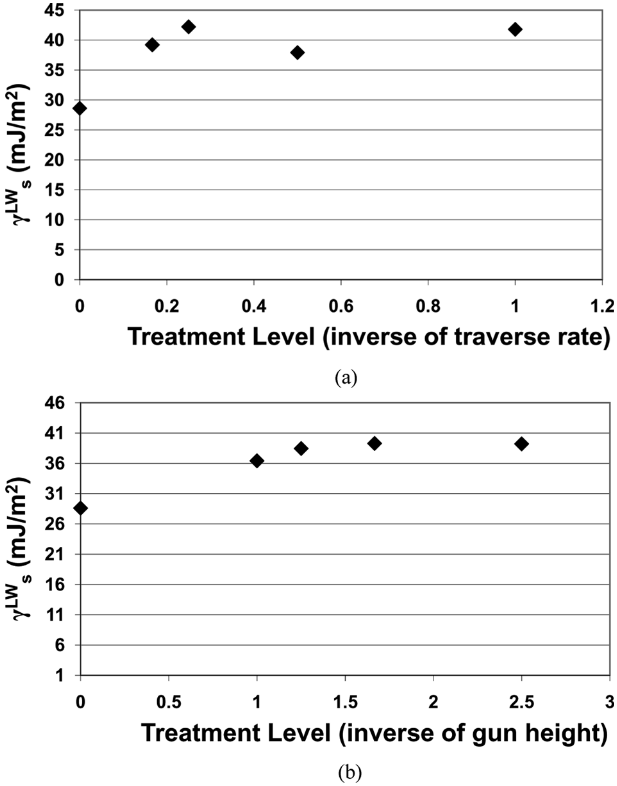


FIGURE 3 Lifshitz-van der Waals surface energy component *vs*. the inverse of (a) traverse rate or (b) gun-sample height.

the electron accepting parameter and adhesion in this system. Figure 6 suggests that there is a strong positive correlation between HDPE lap joint strength and γ_s^-, however. As the base component increases, the single lap joint strength increases as well, until it reaches the ultimate strength of the HDPE, around 500 psi (3.45 MPa).

Visual inspection indicated that many adhesive joint failures were interfacial. However, failure surfaces of samples which demonstrated the highest failure loads were visually frosty. Figure 7 is an SEM image obtained from the adhesive (epoxy) side of one of these specimens, and Fig. 8 is an image obtained from the matching adherend surface. No adhesive is visible in these images, only fibrillated HDPE. This shows that the failures were cohesive within the HDPE substrate, and that the stress transferred by the interface during testing exceeded the cohesive strength of the substrate.

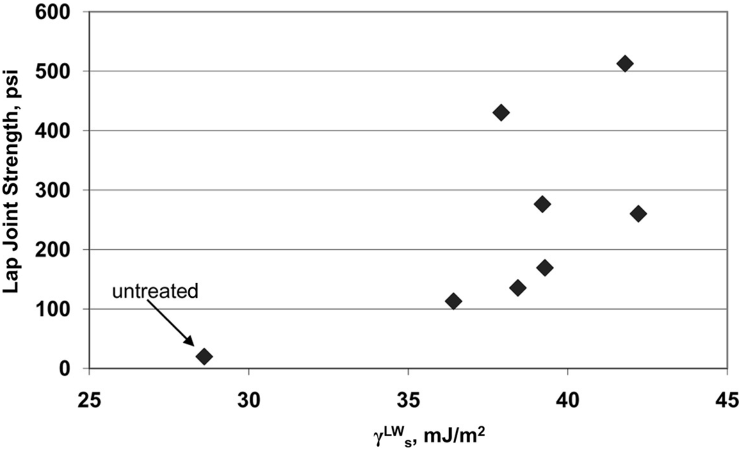


FIGURE 4 Single lap joint strength *vs.* γ^{LW} (100 PSI ≅ 0.69 MPa).

Effect of Treatment on Surface Chemical Composition

Surface energy measurements showed that atmospheric pressure plasma treatments increased all components of surface energy: electron donating, electron accepting, and Lifschitz-van der Waals. The increase in the electron donating character of the surface correlated very well with adhesion. To determine what specific functional groups were responsible for improved adhesion, HDPE surfaces that had been treated at a fixed 0.4 inch (1.0 cm) sample/gun distance and 1–4

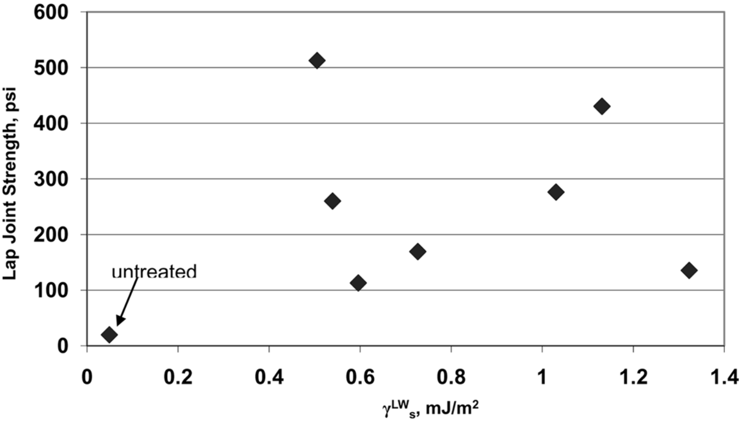


FIGURE 5 Single lap joint strength *vs.* γ_s^+ (100 PSI ≅ 0.69 MPa).

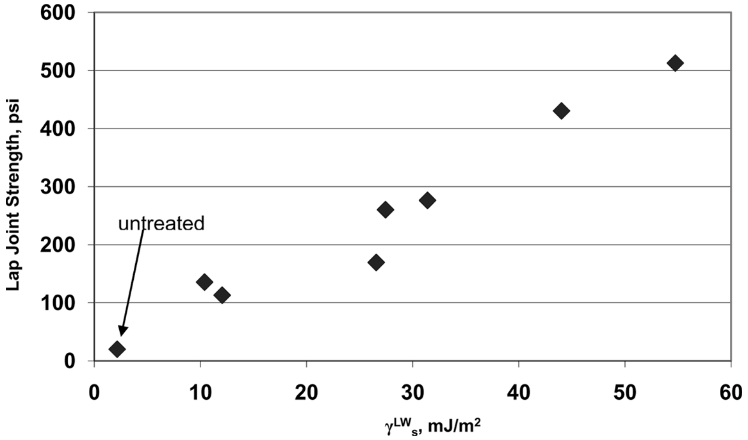


FIGURE 6 Single lap joint strength *vs.* γ_s^- (100 PSI ≅ 0.69 MPa).

inch/second (2.5–10.2 cm) traverse rate (an identical manner to those used to fabricate adhesive joints) were analyzed using X-ray photoelectron spectroscopy. Figure 9 shows that the amount of oxygen and nitrogen incorporated *via* plasma treatment corresponded well with the traverse rate of the treatment head.

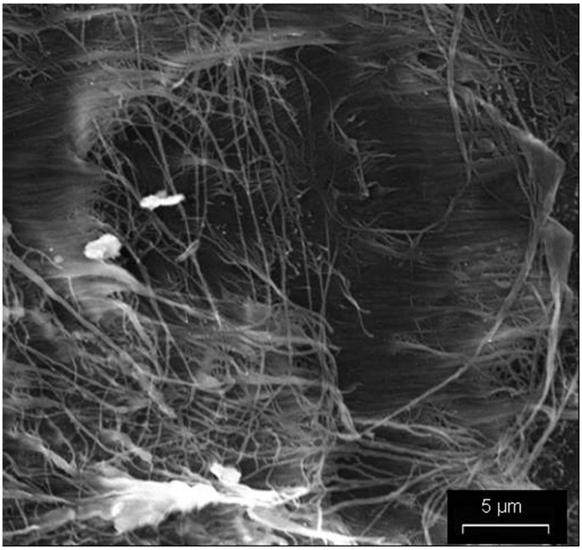


FIGURE 7 Lap joint failure surface, epoxy side, showing fibrils of plastically deformed HDPE. No adhesive is visible in this image. 3000 × 10 kV.

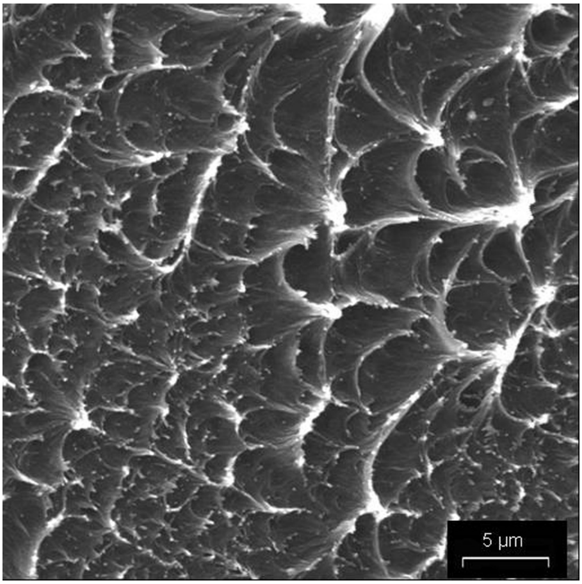


FIGURE 8 Lap joint failure surface, HDPE side, showing fibrils of plastically deformed HDPE. 3000 × 10 kV.

Plasma treatment of polyolefins creates a wide variety of functional groups. When treating in gases such as nitrogen or air, nitrogen is incorporated during plasma treatment primarily in the form of amines and imines, with imines predominating [16,17]. Figure 10 shows the N(1s) spectrum obtained from the most aggressively treated sample

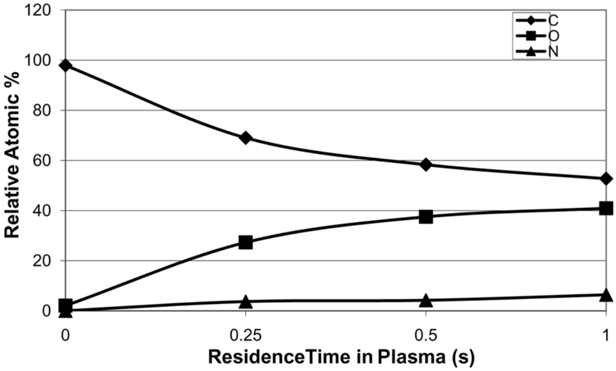


FIGURE 9 Relative atomic composition of surface of plasma-treated HDPE as determined by XPS.

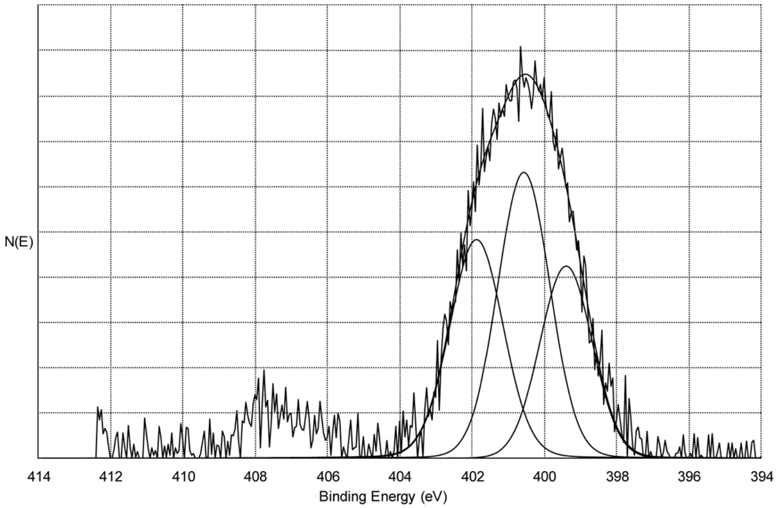


FIGURE 10 N(1s) spectrum obtained from HDPE surface treated in atmospheric plasma [0.4 inch (1.0 cm) sample/gun distance, 1 inch (2.5 cm)/second traverse rate, 0.7 inch (1.8 cm) pitch].

[0.4 inch (1.0 cm) sample/gun distance, 1 inch (2.5 cm)/second traverse rate, 0.7 inch (1.8 cm) pitch]. Consistent with the results of Foerch *et al.* [16] and Liston *et al.* [17], this spectrum was readily resolved into components due to amines (near 399 eV), imines (near 400.5 eV), and higher oxidized species (perhaps C≡N, near 401.5 eV). Imines tend to oxidize to amines during post-deposition exposure to water vapor [16]. This and direct reaction of residual free radicals with oxygen and water vapor accounts for much of the oxygenated species detected in the treated surfaces. Figure 11 shows an example C(1s) curve fit spectrum obtained from the sample with the highest treatment level; the relative peak areas of these components as a function of treatment from all curve fits are presented in Fig. 12. The component labeled O-C = O represents both esters as well as carboxylic acids. Carboxylic acids are the only groups identified in the surface of the treated polymer that are capable of functioning as electron acceptors. The small electron accepting component of surface energy indicates that they are present as a small fraction of the overall surface composition. While carboxylic acids are excellent crosslinking agents for epoxy resins, the lack of correlation of adhesion with this component suggests that they do not play an important role in adhesion.

Most of the groups created *via* plasma treatment are capable of functioning as electron donors, including amines, imines, ketones,

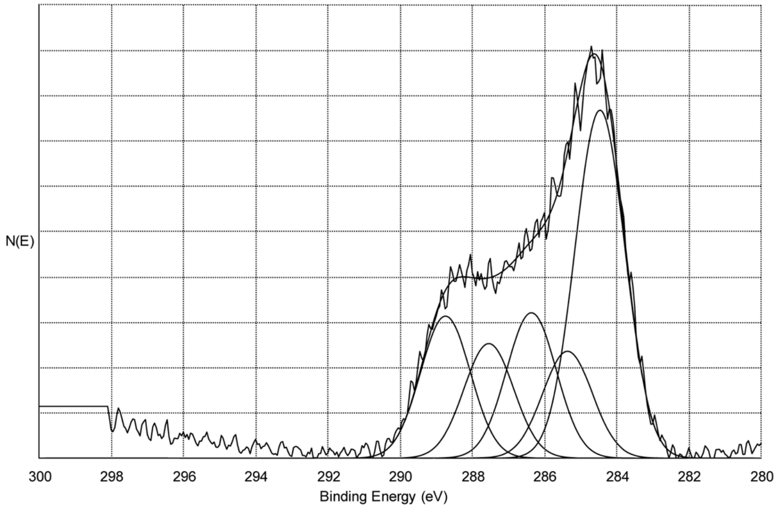


FIGURE 11 C(1s) XPS spectra obtained from HDPE surface treated in atmospheric plasma [0.4 inch (1.0 cm) sample/gun distance, 1 inch (2.5 cm)/second traverse rate, 0.7 inch (1.8 cm) pitch].

esters, alcohols, and ethers. The increase in fraction of these groups with plasma treatment is large, and corresponds to the large increase in this component of surface energy. Interaction of the epoxy with electron donating groups could be through secondary interactions,

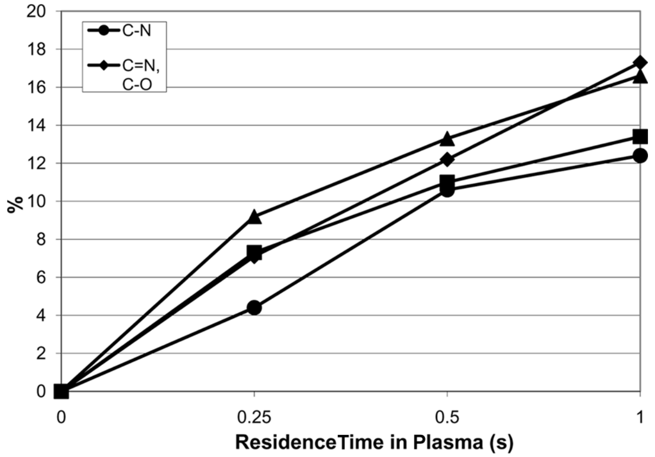


FIGURE 12 Molecular composition of plasma-treated HDPE surfaces as determined by XPS.

especially with esters (consider the relatively high strength of acrylic polymers bonded with epoxies), or through primary chemical bond formation with primary amines and imines (the only electron donating groups capable of covalent bonding with epoxies under the mild curing conditions employed in this work). The relative importance of these groups to adhesion could conceivably be determined by consuming the accessible amines and imines with a monofunctional epoxy prior to forming an adhesive joint; a decrease in adhesive bond strength when compared with the underivatized surfaces would be consistent with a mechanism of adhesion that involved primary amine interactions with the adhesive.

CONCLUSIONS

Surface energies are conveniently measured by contact angle techniques, and the relationship between adhesion and surface energy is well established for systems where specific chemical interactions are unlikely, such as pressure sensitive adhesives. The relationship of wetting to adhesion of chemically reactive systems, such as thermoset adhesives to chemically active surfaces such as plasma treated or even mechanically abraded polymer surfaces, is not as well understood. However, specific interfacial chemical interactions can be treated as classes of electron donor-acceptor reactions, and these may be probed using contact angle techniques; in principle these measurements should have predictive value for adhesion.

This work used atmospheric pressure plasma treatment in air of high density polyethylene to obtain surfaces with a range of surface energies while maintaining similar mechanical properties. It was determined that adhesion correlated strongly with the electron donating character of surface energy, and that the likely functional groups responsible for this adhesion were amines and imines created by the plasma treatment process. The amount of electron accepting groups (such as carboxylic acids) does not correlate to adhesion, suggesting that these groups may not be important to adhesion for this system. These results indicate that wetting measurements may be useful in detecting the specific chemical interactions important to adhesion in reactive systems.

REFERENCES

[1] Hart-Smith, L. J., *Proc. 26th Ann Meeting of The Adhesion Society*, February 23–26, 2003.
[2] Hart-Smith, L. J., *Int. J. Adhesion and Adhesives* **19**, 181–191 (1999).

[3] Dillingham, R. G. and Oakley, B. R., *J. Adhesion* **82**, 407–426 (2006).

[4] Pocius, A. V., *Adhesion and Adhesives Technology: An Introduction*, (Hanser/Gardner, Cincinnati, 1997) pp. 135–137.

[5] Cognard, J., *J. Adhesion* **57**, 31–43 (1996).

[6] Shanahan, M. E. R. and Bourgés-Monnier, C., *Int. J. Adhesion and Adhesives* **16**, 129–135 (1996).

[7] Gent, A. N. and Schultz, J., *J. Adhesion* **3**, 281–294 (1972).

[8] Andrews, E. H., *J. Mat. Sci. Letters* **4**, 887–894 (1974).

[9] Carré, A. and Schultz, J., *J. Adhesion* **17**, 135–156 (1984).

[10] Owens, D. K. and Wendt, R. C., *J. Appl. Polymer Sci.* **13**, 1740 (1969).

[11] Kaelble, D. H. and Uy, K. C., *J. Adhesion* **2**, 50 (1970).

[12] Fowkes, F. M., in *Microscopic Aspects of Adhesion and Lubrication: Proceedings of the 34th International Meeting of the Société de Chimie Physique, Paris, 14–18 September 1981*, J. M. Georges (Ed.) (Elsevier, Amsterdam, 1982) p. 119.

[13] Good, R. J. *J. Adhesion Sci. Technol.* **6**, 1269–1302 (1992).

[14] Greiveldinger, M. and Shanahan, M. E. R., *J. Colloid Interface Sci.* **215**, 170–178 (1999).

[15] Ikegami, K., Fujii, T., Kawagoe, H., Kyogoku, H., Motoie, K., Nohno, K., Sugibayashi, T., and Yoshida, F., *Int. J. Adhesion and Adhesives* **16**, 219–226 (1996).

[16] Foerch, R., McIntyre, N. S., Sodhi, R. N. S., and Hunter, D. H., *J. Appl. Poly. Sci.* **40**, 1903–1915 (1990).

[17] Liston, E. M., Martinu, L., and Wertheimer, M. L., *J. Adhesion Sci. Technol.* **7**, 1091–1127 (1993).