EFFECT OF ATMOSPHERIC PLASMA TREATMENT ON POLYMER SURFACE ENERGY AND ADHESION*

Rachel M. Thurston, John D. Clay† and Michael D. Schulte
Battelle Memorial Institute, Advanced Materials Applications
505 King Avenue, Columbus, Ohio 43201, USA

ABSTRACT: This study describes experiments to quantify polymer surface energy changes after exposure to atmospheric plasma. Atmospheric plasma treatment permits surface functionalization at near-ambient temperatures. Polyethylene and polystyrene are treated with an atmospheric plasma unit. The increased surface energy and improved wetting characteristics lead to a significant adhesion improvement with adhesives that cannot be used without surface treatment.

KEY WORDS: surface modification, plasma treatment, contact angle, lap shear tests, medium density PE, polystyrene.

BACKGROUND

PLASTICS ARE NOTORIOUSLY difficult to adhere to, especially polyethylene (PE). This is due to the low surface energy, which reduces surface wetting by the adhesive during application, resulting in a poor bond. Complex surface treatments often are required to optimize material adherence to a plastic part. Plasma treatment offers a fast, simple plastic surface treatment method that increases surface energy and improves adhesion. Atmospheric plasma is particularly beneficial because it operates at near-ambient temperatures without a vacuum.

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† Author to whom correspondence should be addressed. E-mail: clayj@battelle.org
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Surface Tension and Surface Energy

Wetting is the extent to which a liquid makes contact with a surface. Wetting is often quantified by measuring the contact angle a liquid makes at equilibrium with a solid surface. A lower surface tension fluid and a higher surface energy solid will result in improved wetting.

The major thermodynamic quantity that characterizes a surface or interface is the reversible work, $\gamma$, required to create a unit area of new surface. The specific surface work is more commonly called the surface tension or surface energy. A liquid’s surface tension minimizes the surface energy by keeping the drop spherical. A solid’s surface energy may spread a liquid drop over the surface if the liquid wets the surface. Surface tension is the sum of two distinct components: a dispersive component and a polar component (Equation (1)).

$$\gamma_i = \gamma_i^d + \gamma_i^p.$$  \hspace{1cm} (1)

A common and useful surface wetability measure is the contact angle. Contact angle measurements provide average surface property information and are determined by the outermost exposed atoms ($\approx 1$ nm or 10 Å) of a surface [1]. The contact angle is the result of a force balance at the three-phase interface between the solid, liquid, and vapor (air). The drop shape changes until the sum of interfacial free energies is a minimum. When a liquid drop contacts a plane and is at equilibrium, the system is described by Young’s equation [2] as shown in Equation (2).

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$  \hspace{1cm} (2)

where:

- $\gamma_{sv}$ = solid surface energy
- $\gamma_{sl}$ = solid–liquid interfacial tension
- $\gamma_{lv}$ = liquid surface tension
- $\theta$ = angle between the solid–liquid and liquid–air interfaces at the contact line.

To measure the solid surface energy, a liquid drop is placed on the surface. After the drop reaches equilibrium, a goniometer is used to measure the three-phase interface angle. Solid surface energies are obtained by contact angle measurements with at least two fluids of known surface tensions. When a solid and liquid are in contact, the interfacial energies of the two substances interact to produce...
an interfacial tension. The interfacial tension is the sum of the interfacial energies and interaction terms between the polar and dispersive components (Equation (3)). A harmonic mean average of the interfacial energy components gives accurate predictions for polymer systems [2].

\[
\gamma_{si} = \gamma_{sv} + \gamma_{lv} - 4 \left( \frac{\gamma_{sv}^d \gamma_{lv}^d}{\gamma_{sv}^d + \gamma_{lv}^d} \right) - 4 \left( \frac{\gamma_{sv}^p \gamma_{lv}^p}{\gamma_{sv}^p + \gamma_{lv}^p} \right).
\] (3)

By combining Equations (1)–(3), an expression is obtained with two unknowns, \( \gamma_{sv}^p \) and \( \gamma_{sv}^d \). The contact angle on the solid is measured with two probe liquids to evaluate these unknowns.

**Plasma Treatment and Atmospheric Plasma**

Plasma, the fourth state of matter, is an ionized gas with an essentially equal density of positive and negative charges. Plasma, which is spatially neutral, has free electrons and positive ions comprising most negative and positive species. Well-known plasmas are the solar corona, lightning, flames, and fluorescent lights. Owing to the constituent species’ high reactivity, plasma treatments may be used for cleaning or chemically modifying surfaces. For these reasons, plasma treatment should have significant benefits for adhesive systems by minimizing contamination and imparting favorable chemical moieties at the surface. It is well known that surface treatment of plastic surfaces generates polar functional groups. Often, surface analysis techniques, such as electron spectroscopy for chemical analysis (ESCA) are used to quantify the chemistry changes at the surface [3]. ESCA was not performed on the samples in this work. Atmospheric plasma treatment for improved bonding is desirable as surface chemistry can be tuned to achieve functionalities that are conducive to various adhesive cure chemistries. In particular, it is believed that the increase in surface energy is especially beneficial.

Traditionally, plasmas have been generated using high temperatures and in a low-pressure environment. Recent advances have permitted plasmas to be generated at ambient temperatures and atmospheric pressure. Helium is used as a carrier gas, based on its inert nature and high thermal conductivity. Adding oxygen at low levels yields a plasma that oxidizes both surface groups and contaminants. Other gases can be
used in conjunction with the helium carrier to produce additional effects, such as surface reduction or surface functionalization.

The Atomflo™ atmospheric plasma unit manufactured by Surfx Technologies LLC uses technology licensed from the University of California, Los Angeles. This atmospheric plasma unit is a source of atoms and radicals that are carefully selected for surface treatment, cleaning, etching, or depositing thin coatings. One of the most attractive features of this technology is its effectiveness at low temperatures without the need for reduced pressure (vacuum).

There has been a large amount of work in the new field of atmospheric plasma treatment. Much of the work has focused on increasing the wettability of materials [4, 5]. A complete survey of the literature and comparisons with alternate plasma techniques are outside of the scope of this work.

Adhesives

Silicone adhesive sealants, commonly known as RTVs, are liquid rubbers that vulcanize at room temperature. Their characteristics include:

- Excellent resistance to oxidation and ultraviolet (UV) degradation
- High gas permeability
- High chemical and thermal stability
- Low-temperature flexibility

As a result, silicone elastomeric sealants are used in:

- Manufacturing
- Automotive
- Aerospace
- Construction

Silicone-based elastomeric joint sealants, like other adhesives, are known to have characteristically poor adhesive properties to untreated PE substrates.

The main component in silicone RTV adhesives is typically a silanol-terminated polydimethylsiloxane (PDMS) with a repeat unit, $n$, between 300 and 1600 molecular weight [6]. The cross-linking component is often a multifunctional silane, such as methyltrimethoxysilane. Together, these components react using a condensation catalyst, such as stannous octanoate or a titanate. In the presence of atmospheric moisture, the silane undergoes hydrolysis and condenses with silanol
groups, yielding a cross-linked silicone rubber and liberating a condensation product, such as methanol.

Epoxy adhesives can cure over a wide range and are resistant to organic solvents and moisture. Their favorable wetting characteristics result in good adhesion to most substrates with the exception of low-surface energy, untreated plastics, and elastomers. Epoxy molecules are based on an oxygen-containing three-membered ring. Many epoxy adhesive systems use the diglycidyl ether of bisphenol A (DGEBA). This resin may be cured with amines or polyamides for room temperature setting systems [6].

Aziridine-based adhesives have proven useful for bonding low surface energy materials, such as PE. These adhesives use a polyfunctional aziridine (40–60%) and tetra(ethylene glycol) (20–30%) as active ingredients. Each aziridine group can react with an active proton (H\(^+\)). The resulting reaction protonates and opens the aziridine ring, forming a cross-linked network.

**OBJECTIVES OF THIS WORK**

The objective of this work was to quantify the surface energy changes in two different polymers (PE and PS) after exposure to an atmospheric plasma treatment. A contact angle technique was used to quantify surface energy changes over time after exposure to the atmospheric plasma. To relate these changes to functional performance, the lap shear strength was measured for samples before and after exposure to the atmospheric plasma.

**EXPERIMENTAL DETAILS**

**Sample Preparation**

Two different substrates were used to assess the surface energy change associated with atmospheric plasma treatment. The first substrate was Novapol TR0535U, a medium-density polyethylene (PE) from Nova Chemical (Calgary, Alberta, Canada). Polyethylene has a very low surface energy and is a notoriously difficult polymer to bond. Styron 666D, a polystyrene (PS) material from Dow Chemical (Midland, MI), was selected as the second substrate. For the two polymers, injection molded samples cut to appropriate dimensions were used as test articles. Samples for contact angle
measurements were \( \approx 50 \text{mm} \) by \( 12.5 \text{mm} \) by 3mm. Lap shear samples were \( \approx 125 \times 12.5 \times 3 \text{mm} \) for each side. A small hole was drilled in the center of each sample on one end, permitting samples to be hung from a copper wire after cleaning and plasma treatment. Before testing or plasma treatment, all samples were rinsed with HPLC-grade methanol from Sigma-Aldrich and allowed to dry for 24 h in a controlled temperature and humidity room at 22°C and 48% relative humidity.

Samples were plasma treated using the Atomflo\textsuperscript{TM} for 30 s per side with a 0.5 cm separation from the plasma head (Figure 1). The gas was 5% oxygen in a helium carrier. Plasma conditions were optimized according to the manufacturer’s instructions. In particular, the dial for RF power was adjusted to achieve the peak reflected power output and the brightest plasma output.

Lap shear samples were prepared by first cleaning with methanol (for untreated samples) or plasma treatment (for treated samples) as described above. Tongue depressors were used as spacers to create a consistent bond area of \( \approx 13 \times 18 \text{mm} \) on each sample, with an adhesive thickness around 3 mm. All adhesives were applied in excess and allowed to cure for a minimum of 24 h. The three commercially available adhesive systems selected for evaluation were:

- Silicone RTVs represented by the off-the-shelf GE RTV 162.
- Epoxies represented by DP-460 from 3M.
- Two-part aziridine-based adhesives represented by Loctite 3030.

![Figure 1. Low-temperature, atmospheric (a) plasma head and (b) power supply used to modify the surface energy of PS and PE substrates.](image-url)
Contact Angle Measurements

Contact angle measurements were made on a ThermoCahn Radian 315 dynamic contact angle instrument from ThermoMaterials Characterization (Figure 2). This method determines contact angle from the forces as a sample of known dimensions is immersed (advancing) and then withdrawn (receding) from a fluid of known surface tension. The samples were immersed to a depth of 8.0 mm at a speed of 80 microns/second. Contact angle was determined by the WinDCA32 software, using only the steady-state portion of the force-position curve during the advancing and receding stages.

The surface energy and its polar and dispersive components were calculated from the advancing contact angles in water and formamide [7]. The water was HPLC grade from Sigma-Aldrich, with a surface tension of 72.8 mN/m. The formamide was of 99.5+% purity from Sigma-Aldrich, with a surface tension of 58.2 mN/m.

Figure 2. Thermo Cahn dynamic contact angle instrument used to determine surface energy of control and plasma-treated substrates.
Lap Shear Testing

Lap shear tests were conducted on an Instron model 5564 testing machine running Series IX software (Figure 3). Tests were conducted using a 1.0 kN (224 lb) load cell and pneumatic grips with 12.5 × 25 mm faces. All tests were run at a 1.5 mm/min cross-head speed. Testing was conducted according to ASTM method D3163. While spacers helped align the lap shear samples in the grips so that the load was parallel to
the adhesive layer, a slight misalignment occurred in most tests. The maximum load stress was recorded for each test.

**RESULTS AND DISCUSSION**

**Contact Angle and Surface Energy**

The surface energy and its polar and dispersive components were calculated from the advancing contact angles in water and formamide. These baseline results are shown in Table 1 and Figure 4. Both PE and PS have a rather low surface energy, making it difficult to achieve surface wetting.

To quantify contact angle changes over time, samples were treated with the Atomflo™ and kept in a constant temperature and humidity room until tested. Figure 5 shows how the water contact angle changed over time for the polyethylene (PE) and polystyrene (PS) samples. Two samples were tested at each time increment, with the average result plotted.

At the earliest measurement period (1.5 h after plasma treatment), the PS sample had an initial zero degree contact angle in water and formamide. After 3 h of aging, the average contact angle was $45^\circ$ and continued to increase over time.

The PE sample exhibited a drop in contact angle after plasma treatment from 102 to $48^\circ$. As with the PS sample, the PE samples exhibited a slow increase in contact angle over time. This suggests that the surface slowly reverts to its original nature, losing the polar functional groups created by plasma treatment. However, the change is slow enough that even a delay of several hours between plasma treatment and adhesive bonding would still leave the surface energy high enough to improve adhesion.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface energy (mN/m)</th>
<th>Polar</th>
<th>Dispersive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline PE</td>
<td>24.3</td>
<td>4.4</td>
<td>19.9</td>
</tr>
<tr>
<td>Baseline PS</td>
<td>30.6</td>
<td>2.9</td>
<td>27.7</td>
</tr>
<tr>
<td>Plasma PE</td>
<td>54.6</td>
<td>29.0</td>
<td>25.6</td>
</tr>
<tr>
<td>Plasma PS</td>
<td>&gt;72.8</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Lap shear tests were conducted to assess how atmospheric plasma treatment affects adhesion. Figure 6 shows that plasma treatment increases the maximum stress for RTV and epoxy resins (DP-460) when used to bond both PE and PS substrates. All lap shear test results are summarized in Table 2. Three to five specimens were tested for each sample set. The increases in adhesion are hypothesized to be primarily due to chemical changes at the surfaces of the samples. However, it has been noted [8] that the surface roughness of samples can be increased after plasma treatment. This could also augment the adhesion of the samples. Surface roughness measurements were not made on samples in this study.

Cohesive failure modes were observed for treated substrates bonded with RTV silicone. This resulted in average maximum stresses of 0.81 and 1.51 MPa for treated PE and PS substrates, respectively. Figure 7 depicts tested lap shear specimens that had been adhered with RTV silicone. Cohesive failure modes are shown (arrows) in Figure 7a and c.
for PS and PE substrates, respectively. Adhesive failure modes were observed for untreated PS (Figure 7b) and PE (not shown) substrates. The PE control sample is not pictured because the bond was so weak that they literally fell apart when handled, so they were not tested.

The most significant improvement in adhesive strength was observed for epoxy resin applied to treated specimens. In these cases, the average maximum stresses for PS and PE were 1.89 and 1.84 MPa, respectively. Mixed but predominantly cohesive failure modes were observed for both plasma-treated PS (Figure 8a) and PE (Figure 8c) adhered with DP 460, as shown by arrows. Control specimens exhibited only adhesive failure modes as represented by the single PS specimen shown in Figure 8b. The average maximum stress of the PS control was about 25% lower than the plasma treated samples. Again, the PE control was not tested or pictured because the adhesion was so poor that it literally fell apart.

The aziridine-based adhesive (Loctite 3030) performed very well on untreated PE with an average maximum stress of 1.60 MPa. Plasma treatment had the primary effect of changing the failure mode from mixed-mode to purely cohesive and increasing the average maximum stress to 2.0 MPa. Loctite 3030 is not recommended for joining PS as the resin readily solubilizes the matrix.
Table 2. Lap shear adhesive test results.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Adhesive</th>
<th>Failure mode</th>
<th>Treatment</th>
<th>Stress max load (MPa)</th>
<th>SD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>GE RTV 162</td>
<td>Cohesive</td>
<td>Plasma</td>
<td>0.81</td>
<td>0.14</td>
</tr>
<tr>
<td>PE</td>
<td>GE RTV 162</td>
<td>Adhesive</td>
<td>Control</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PS</td>
<td>GE RTV 162</td>
<td>Cohesive</td>
<td>Plasma</td>
<td>1.51</td>
<td>0.09</td>
</tr>
<tr>
<td>PS</td>
<td>GE RTV 162</td>
<td>Mixed</td>
<td>Control</td>
<td>0.46</td>
<td>0.10</td>
</tr>
<tr>
<td>PE</td>
<td>DP-460</td>
<td>Mixed</td>
<td>Plasma</td>
<td>1.84</td>
<td>0.12</td>
</tr>
<tr>
<td>PE</td>
<td>DP-460</td>
<td>Adhesive</td>
<td>Control</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>PS</td>
<td>DP-460</td>
<td>Mixed</td>
<td>Plasma</td>
<td>1.89</td>
<td>0.20</td>
</tr>
<tr>
<td>PS</td>
<td>DP-460</td>
<td>Adhesive</td>
<td>Control</td>
<td>0.46</td>
<td>0.13</td>
</tr>
<tr>
<td>PE</td>
<td>Loctite 3030</td>
<td>Cohesive</td>
<td>Plasma</td>
<td>2.00</td>
<td>0.05</td>
</tr>
<tr>
<td>PE</td>
<td>Loctite 3030</td>
<td>Mixed</td>
<td>Control</td>
<td>1.60</td>
<td>0.44</td>
</tr>
<tr>
<td>PS</td>
<td>Loctite 3030</td>
<td>N/A</td>
<td>Plasma</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>PS</td>
<td>Loctite 3030</td>
<td>N/A</td>
<td>Control</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 6. Maximum stress of lap shear adhesion of controls versus samples made after plasma treatment of the substrate. Substrates are polyethylene (PE) and polystyrene (PS).
Figure 7. Lap shear specimens bonded with RTV silicone which had been subjected to tensile testing. Plasma-treated polystyrene (PS) and polyethylene (PE) substrates (a and c, respectively) displayed cohesive failure modes as depicted by arrows. Control specimens of PS (b) and PE (not shown) exhibited only adhesive failure modes.

Figure 8. Lap shear specimens bonded with DP 460 epoxy which had been subjected to tensile testing. Plasma-treated polystyrene (PS) and polyethylene (PE) substrates (a and c, respectively) displayed mixed failure modes as depicted by arrows. Control specimens of PS (b) and PE (not shown) revealed adhesive failure modes only.
CONCLUSIONS

Plasma treatment of low-surface-energy polymers (polyethylene and polystyrene) has been shown to increase the surface energy and improve the wetting characteristics. This wetting improvement leads to a concurrent, significant improvement in adhesion to these polymer surfaces, allowing bonding with adhesives that cannot be used with these polymers without surface treatment. The changes in surface energy and the increases in adhesion are primarily due to the chemical changes at the surface induced by exposure to the plasma.

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REFERENCES

BIOGRAPHIES

Rachel M. Thurston

Rachel M. Thurston holds a BS in Materials Science and Engineering from MIT and an MS in Macromolecular Science from Case Western Reserve University. For the past 8 years, she has worked as a Principal Research Scientist in the Advanced Materials Applications group at Battelle Memorial Institute. Her research areas are widely varied, from environmental stress cracking of polymers to novel rheology and tensile tests for very small samples (less than a gram). She holds two patents, one for an improved wallboard joint compound, and one for formulations for improved aerosols for inhaled medications. Recent publications include four papers at ANTEC, the most recent being adapted for this article.

Dr John D. Clay

Dr John D. Clay is a Senior Research Scientist at Battelle Memorial Institute. He received a BSChE from the University of Toledo, and a PhD in Chemical Engineering from The Ohio State University in 1997. Since then, he has been employed at Battelle. Currently, Dr Clay manages the Characterization group in the Advanced Materials Applications (AMA) product line. His specialties are in the areas of rheology, polymer characterization, failure analysis, and injection molding. Dr Clay manages commercial and government programs in the areas of precision injection molding, interface control and manipulation, biomedical materials, and rheological modification of solutions. His work has resulted in numerous publications, invention reports, and increased business volume for AMA.

Dr Michael D. Schulte

Dr Michael D. Schulte has spent the last 12 years investigating composite materials for biomedical, aerospace, and automotive applications. He holds a BS in Materials Engineering, an MS in Materials Science, and a PhD in Polymer Science, all from the University of Cincinnati. His experience includes research at Wright-Patterson AFB in the Laser-Hardened Materials branch where he worked as a materials scientist with interests in monomer synthesis, characterization, and processing materials for nanocomposite applications. Before joining
General Electric Aircraft Engines in 2005, he worked as a Principal Research Scientist in the Advanced Materials Applications group at Battelle Memorial Institute. His present interests include high temperature polymeric composite matrices and structure–property relationships of carbon-fiber reinforced composites.