

## Atmospheric Plasma Surface Modification of Medical Plastics

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### Medical Plastics and Applications

Most plastics are hydrophobic and have low surface energy (~30-40 dyne/cm). By increasing the hydrophilic character and the surface energy of the plastic, its adhesive bond strength can be improved dramatically. Acetal copolymer (AC), polycarbonate (PC), polyethylene terephthalate (PET), poly(tetrafluoroethylene) (PTFE), poly(etheretherketone) (PEEK), poly(dimethylsiloxane) (PDMS silicone) possess attractive physical properties that are desirable to the medical device industry.

Acetal copolymer (e.g. Celcon<sup>®</sup>) is used in drug delivery systems such as dry powder inhalers, nebulizers, prefilled syringes, insulin injection pens, needleless syringes and metered dose inhalers.

Polycarbonate materials based on bisphenol A (for example, Diflon<sup>®</sup>, Macrolon<sup>®</sup>, Lexan<sup>®</sup>, and so on) are used for lenses, cell-culture containers, blood oxygenators and filters, surgical instruments and IV connectors.

Polyethylene terephthalate (e.g. Ertalyte<sup>®</sup>, Eastar Copolyester MN100) is used for vascular grafts, implantable sutures, surgical mesh, and components for heart valves.

By enabling medical plastics to bond well with other materials, more convenient and functional medical devices can be fabricated.

### Problems with Adhesion

Surface energy, or “surface wettability”, relates to the ability of a physical surface to wet out practical industrial liquids, such as inks, coatings, or adhesives. Low-surface energy plastics (typically 30 – 40 dynes/cm) have difficulty bonding to the surfaces of other materials (e.g. metals, other plastics, ceramics). By raising the surface energy to 60 – 70 dynes/cm, one can hope to achieve stronger adhesive bonds and improve the reliability and durability of the medical devices.

### The Surfx Atomflo™ Solution

Recently, there has been increased interest in the use of atmospheric pressure plasmas for materials processing. These devices take advantage of tunable gas chemistry and ambient pressure conditions (no vacuum chambers) to create effective surface treatment of medical polymers. High-speed treatment of surfaces of many shapes and sizes can be applied prior to bonding, marking, painting, and coating. The Atomflo™ capacitive discharge plasma operates at temperatures slightly above room temperature and up to 300°C under atmospheric pressure with either helium or argon as the primary gas, and a reactive gas such as oxygen, hydrogen, nitrogen, or carbon tetrafluoride. The process chemistry is determined by the reagent gas employed. The Atomflo™ atmospheric plasma system shown in

Figure 1 was developed by Surfx Technologies LLC for surface activation of plastics.



Figure 1. Atomflo™ 400 with XYZ robot

#### *How the Atomflo™ Works*

An inert carrier gas mixture of argon or helium and oxygen is fed between two electrodes in the plasma source with a constant radio-frequency (RF) power setting. Stable plasmas are achieved under concentrations of 0.1 – 0.8 vol % O<sub>2</sub> with argon and 1.6 – 3.8 vol % O<sub>2</sub> with helium. Flow rates of the carrier gas range from 10 to 30 L/min, depending on the applicator used. A variety of plasma sources are available to treat 3D plastic parts of many different sizes and shapes. The AH-500L produces a 2-inch wide beam and operates at 120 to 220W applied power with oxygen and helium.

Surface treatment of a 3D object is best accomplished by scanning the beam over the surface with an XYZ robot (see Figure 1). The plasma source is held within 10 mm of the sample. Scan rates are adjustable from 0.1 to 800 mm/s.

#### *Proving Surface Activation*

Dyne pens (rated from 30 to 70 dynes/cm) offer a quick qualitative means of evaluating the surface energy of a material. The behavior of applied strips of ink indicates a narrow range of surface energy values. A more

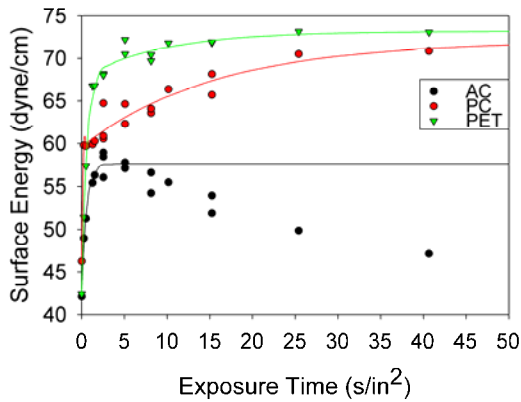
quantitative method of surface energy evaluation is through goniometry or the measurement of contact angles of liquids that are laid upon a test surface. Water contact angle data alone is useful in determining whether a surface has become more hydrophilic or hydrophobic. Contact angle measurements of other liquids in addition to water allow an accurate calculation of the surface energy.

In order to assess the capabilities of the Atomflo™ helium and oxygen plasma, we have undertaken a detailed study of surface activation and adhesion promotion for three specific polymers. This application note highlights the best results achieved. For more information see Reference [1].

## **Results**

### *Exposure*

Acetal copolymer (AC), polycarbonate (PC) and polyethylene terephthalate (PET) were treated with the Surfx Atomflo™ system using the two-inch plasma beam source (AH-500L) with 2.9 vol% O<sub>2</sub> and helium under 200 W of RF power. Surface activation was rapid, occurring within 5 to 10 s/in<sup>2</sup> of exposure. As shown in Figure 2 the surface energy of the acetal copolymer jumped from 42 to 58 dyne/cm and then declined gradually with further plasma exposure. The PC and PET surface energies rapidly increased within 5 s/in<sup>2</sup> of the plasma treatment. Values >70 dyne/cm were achieved beyond 20 s/in<sup>2</sup>, and calculated values of PC and PET were 70.9 and 73.1 dyne/cm after 40 s/in<sup>2</sup>, respectively.

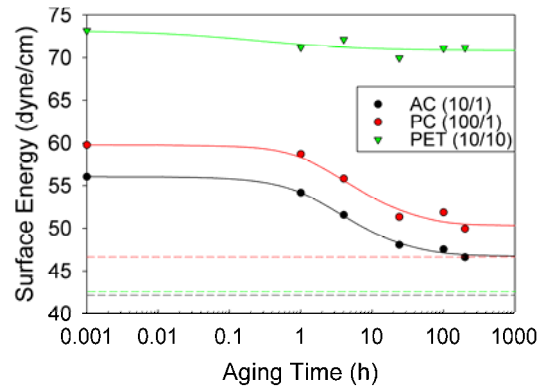


**Figure 2. The effect of the oxygen-helium plasma on the surface energy of the polymers.**

### Aging

The aging behavior of the plasma-treated polymers was analyzed as follows. Four different scans were performed on each material: 10 mm/s at 1 scan (10/1), 10 mm/s at 10 scans (10/10), 100 mm/s at 1 scan (100/1) and 100 mm/s at 10 scans (100/10). The 100/1 and 10/10 conditions represented a “short” (0.25 s/in<sup>2</sup>) and “long” (25.4 s/in<sup>2</sup>) exposure to the oxygen-helium plasma, respectively. The 100/10 and 10/1 conditions were “medium” scans at approximately 2.54 s/in<sup>2</sup> of exposure. The aging behavior of each polymer with the least degree of change in surface energy is displayed in Figure 3 up to 200 hours of aging.

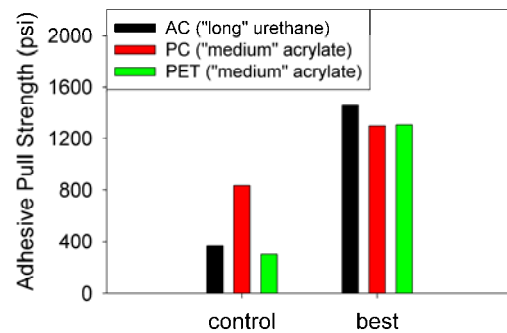
The AC material aged the least when exposed to a “medium” scan. It showed a 17% drop in surface energy after 200 hours while remaining above its untreated value of 42 dyne/cm. The PC material exhibited a similar 17% decrease in surface energy after the “short” scan, and it also maintained a value above the untreated case. The PET material had the best aging behavior after the “long” scan condition. Its surface energy declined by only about 3% after 200 hours.



**Figure 3. The aging behavior of plasma-treated polymers (dashed lines indicate the untreated values).**

### Adhesive Pull Strength

Each plastic was bonded to an aluminum “dolly” with three adhesives: epoxy, urethane and acrylate. The best results achieved are presented in Figure 4. The AC polymer exhibited a 4.0x increase in bond strength using the urethane adhesive and a “long” plasma exposure of 40 s/in<sup>2</sup>. The adhesive pull strength of PC increased a maximum of 1.6 times using a “medium” plasma exposure, about 8 s/in<sup>2</sup>, with the acrylate adhesive. The PET material’s adhesive strength was enhanced for all the adhesives tested. The greatest improvement was 4.4 times with the acrylate adhesive following a 8 s/in<sup>2</sup> plasma treatment.



**Figure 4. Adhesion pull test data for AC, PC and PET with the best combination of adhesive and plasma treatment.**

## Conclusions

The acetal copolymer, polycarbonate and polyethylene terephthalate polymers responded well to the plasma treatment. Surface energies of the AC, PC and PET increased to 57.5, 72.1 and 73.1 dyne/cm, respectively. The surface energy of the acetal copolymer decreased with time from the initial plasma-treated value in a similar manner at each exposure condition. PC's surface energy recovered towards the untreated value faster under long exposure times, showing poor aging. By increasing the exposure time, the PET polymer exhibited improved stability against aging. In general, the AC, PC and PET polymers showed dramatic improvements in adhesive bond strength with all three adhesives. The AC and PET gave rise to roughly fourfold increases under "long" treatment conditions, whereas the PC showed a 50% strength enhancement.

## References

1. PC Guschl,"Atmospheric Plasma Surface Modification of Medical Plastics," Surfx Technical Report (2008).