Surface Activation of Conventional Polymers Using Atmospheric Pressure Plasmas

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Polymers and Applications

Surface activation of conventional polymeric materials or plastics, has been an area of considerable attention over many decades. These materials have gained a nearly omnipresence character in today's industrial global economy in numerous fields like medical devices, aerospace and automotive applications, household appliances, consumer electronics and semiconductors, recreational equipment, etc. Often the ability to effectively bond one polymer to another polymer or to dissimilar material dictates the development and implementation of particular products for a given application.

Polyethylene is available in several forms in industry [low-density (LDPE), linear low-density, high-density (HDPE), ultrahigh molecular weight (UHMWPE)]. This material is known for its toughness, impact resistance, ductility, tensile strength, and relative low cost. Polypropylene (PP) has similar properties as polyethylene with the additional benefit of slightly higher temperature application.

Polystyrene (PS) is a rigid, transparent thermoplastic and found readily in plastic model assembly kits, license plate frames, plastic cutlery, CD cases, etc.

Nylon or polyamide 6 (PA 6) is a tough thermoplastic that is useful in fiber form, possessing high tensile strength, high elasticity and luster, a high resistance to abrasion and chemical inertness. The fibers are wrinkle-proof and have high water absorption.

Polyethylene terephthalate (PET) is a polyester thermoplastic that is most familiar as synthetic fibers and containers for liquid or food. This material can be rigid, very lightweight and strong. It is a good gas barrier and a fair moisture barrier with resistance to alcohols and other solvents and is recyclable.

Polyetheretherketone (PEEK) is known for its extraordinary mechanical properties and high-temperature performance with tremendous resistance to thermal degradation. Although it tends to be an expensive material, PEEK proves worthy of use in both organic and aqueous environments, and is often used in bearings, piston parts, pumps, compressor plate valves, cable insulation, and, recently, medical implants.

Polycarbonate (PC) is a thermoplastic with properties much like PS, such as impact resistance and optical transperancy (bullet-proof glass), but its scratch and temperature resistance offer additional applications.

Silicone compounds are heat-resistant, nonstick and rubberlike oils, greases, and elastomers. They are frequently used in cookware, medical devices, sealants, lubricants and insulation. They possess excellent thermal stability with resistance to water, oxygen, ozone and sunlight, are flexible, and exhibit low electrical conductivity, chemical reactivity and toxicity.

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, adhesives, or aqueous solutions. Low-surface energy plastics (typically 30 – 40 dynes/cm), have difficulty bonding to the surfaces of other materials (e.g. metals, plastics, ceramics, etc.). By raising the energy to 60 – 70 dynes/cm, one can hope to achieve stronger adhesive bonds to other substrates. Therefore, viable methods are needed for treating plastic surfaces in a cost-effective, environmentally-friendly way with minimal process time.

The Surfx Atomflo™ Solution and Methodology

Recently, there has been increased interest in the use of atmospheric pressure plasmas for materials processing. These particular devices take advantage of tunable gas chemistries and ambient pressure conditions (no vacuum chambers necessary) to create effective surface treatments of plastic materials. 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 can operate at temperatures slightly above room temperature and up to 300^{o}C under atmospheric pressure with either helium or argon as the primary gas, and a reactive gas such as oxygen, hydrogen, nitrogen, carbon tetrafluoride, etc. The process chemistry is determined by the reagent gas employed. The Atomflo™ atmospheric plasma system was developed at Surfx Technologies LLC for several applications in materials processing such as surface activation, etching/cleaning (contaminant removal) and plasma-assisted chemical vapor deposition (PECVD).

Figure 1. Surfx Atomflo™ AH-250C "showerhead" plasma source.

How the Atomflo™ Works

A gas mixture of argon or helium and oxygen (the most common reactive gas used) is fed between two electrodes in a plasma source with a constant radio-frequency (RF) power setting. The stable plasmas are achieved under concentrations of 0.1 – 0.8 vol % O_2 with argon and 1.6 – 3.8 vol % O_2 with helium. Flow rates of the carrier gas range from 10 – 30 L/min, depending on the applicator used. A variety of available plasma sources provide many degrees of freedom with RF powers and gas flow rates. The AH-250C operates at 60 – 180W with the oxygen-helium plasma.

Application techniques can involve stationary or translational motion with the aid of an XYZ robot underneath the active plasma source within 10 mm of separation. Stationary exposures can be treated at various dwell times of the substrate under the source. Translation rates are adjustable from 0.1 – 800 mm/s and may entail multiple scans.

Proving Surface Activation

Ideally, an effective means of determining whether or not a surface has been altered by plasma exposure is desirable. Dyne pens (rated from 30 – 70 dynes/cm) offer a quick qualitative method of evaluating surface energy. The behavior of applied strips of ink indicates a narrow range of surface energy values within seconds of application. 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 representing whether a surface is hydrophilic or hydrophobic. Contact angle measurements of other liquids in addition to water allow an accurate calculation of the surface energy. Ultimately, the adhesive properties of glues, inks, coatings, etc. are improved as surface energy is increased.

In order to assess the capabilities of the Atomflo™ with argon and helium carrier gases, we have undertaken a study of material surface activation. The following objectives are explored in this report: 1) comparison of argon and helium plasmas, 2) effect of treatment distance on surface activation, 3) effect of treatment time, and 4) the relative ease of surface activation among different polymers.

Results

The oxygen concentration was maintained at 0.2% and 2.0% for the argon and helium plasmas, respectively. Both plasmas were ignited at 125 W. The plasma source was kept 5 mm above the test specimens while the exposure times were varied. The best results, which were based on average surface energy values determined through dyne pen tests, are presented in this application note. For a more detailed technical report, please see Reference [1].

From Figure 2 one can see that the argon and helium plasmas are effective at treating the four plastics, LDPE, HDPE, PP and PS. Every plastic after treatment show values of at least 60 dyne/cm within 20 seconds of exposure.

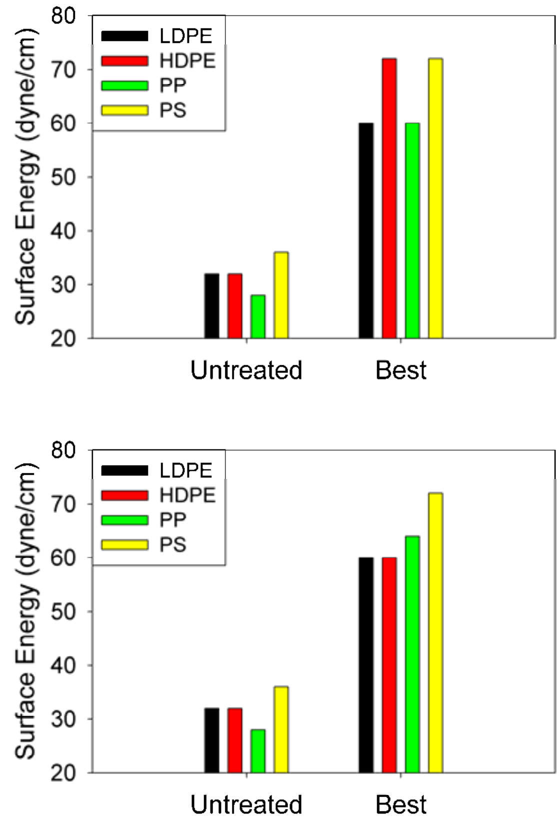
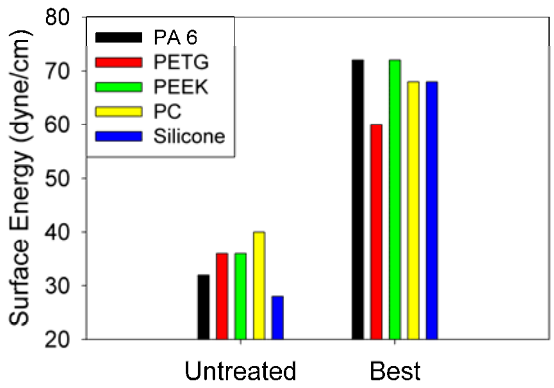


Figure 2. Improvements in average surface energy of four polymers due to argon (top) and helium (bottom) plasma treatment.

Figure 3 displays similar results for the PA 6, PETG, PEEK, PC and Silicone materials. Little to no differences existed for these five plastics when comparing the two plasma types. Higher exit temperatures for the helium can give rise to warping of some of the film samples. This can be prevented by mounting the samples on a stage with sufficient heat-sinking capability.



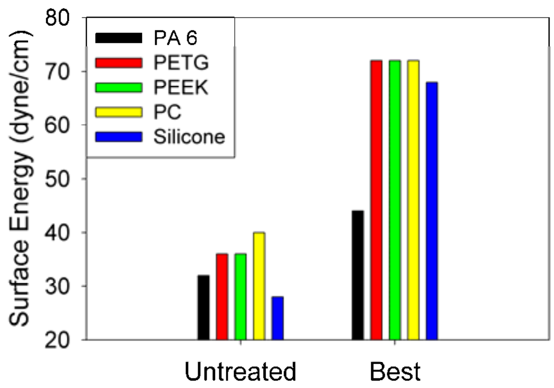


Figure 3. Improvements in surface energy of five polymers due to argon (top) and helium (bottom) plasma.

Conclusions

All the polymers tested showed significant improvements in surface energy when exposed to the oxygen-argon and oxygen-helium plasmas. Surface energies increased as much as 44 dynes/cm for the plasma-treated materials. Although the changes in surface energy were similar for both plasma types, the HDPE, PA 6 and Silicone responded best to the argon plasma, whereas the LDPE, PP and PETG activated better under the helium plasma. If thermal effects are a concern, argon can offer effective treatment at temperatures around 110^{o}C.

Surfx engineers will assist you in developing a recipe that is tailored to your specific material needs.

References

1. PC Guschl and S Babayan, "A Dyne Pen Test Analysis of the Surface Activation of Polymers Using Argon and Helium Atmospheric Pressure Plasmas", Surfx Technical Report (2008)