

Case study

Determination of the Optimal Plasma Treatment Time of Polypropylene



When applying coatings, inks, adhesives, and other materials to a surface, controlling the surface properties becomes critical. In particular, the wettability – the ability of the process liquid to spread and adhere to the solid surface – needs to be controlled. As more products rely on plastics, from medical devices to automobile bumpers, this concept has grown more important since plastics generally exhibit poor wettability for many liquids. This is due to the low surface free energy of many plastics. For example, polypropylene (PP), a widely used polymer due to its low cost, machinability, good chemical resistance, and mechanical properties, is naturally hydrophobic, causing many water-based liquids to poorly wet the material.

To improve the wettability of a polymer, plasma treatment is typically used [1]. Plasma treatment, in which the surface is placed in a chamber under vacuum and bombarded by an ionized gas, is a safe and effective technique for increasing the wettability without harmful gases or high temperatures, and complex geometries can be easily treated. In the case of polymers like polypropylene (PP), wettability is enhanced by the formation of hydrophilic functional groups such as carbonyl, carboxyl, and hydroxyl at the surface [2].

The purpose of the study is to show how contact angle and surface free energy measurements can be used to determine the optimal plasma treatment time.

Polypropylene samples were treated with air plasma in the Glow Plasma System (Glow Research, Tempe, AZ) for durations ranging from 1 to 120 s. The plasma system operated at 50 W, 100 kHz, and the chamber pressure was 1.0 torr. After treatment, the contact angles of each probe liquid (i.e. DI-water, ethylene glycol, and diiodomethane) were measured using an Attension Theta Flex Optical Tensiometer. Each measurement occurred approximately 2 min after the plasma treatment was finished. Drop volumes were fixed at 2 μl . Using the OneAttension software, the contact angles were used to determine the surface free energy of the polypropylene using the OWRK method.

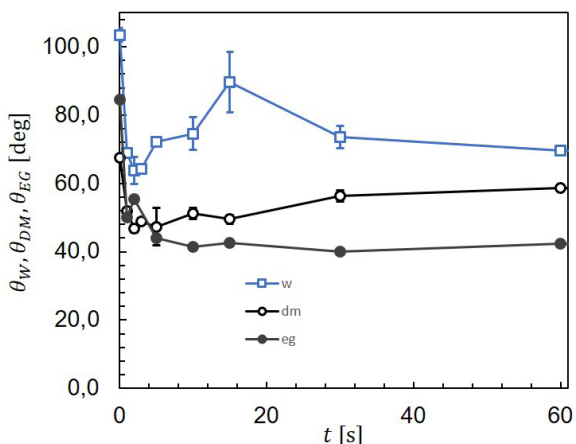


Figure 1 Contact angles as a function of plasma treatment time

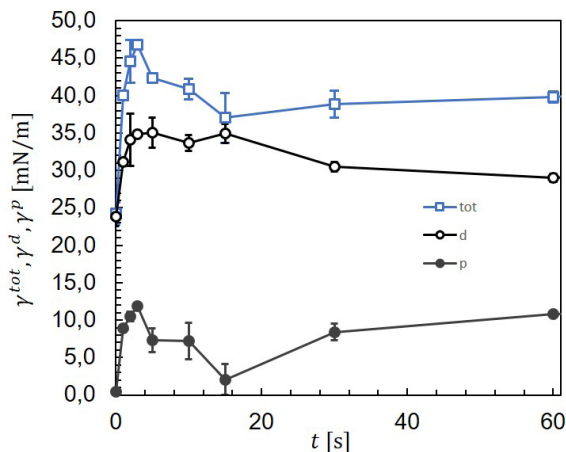


Figure 3 Surface free energy of polypropylene as a function of plasma treatment time

Measurement – Contact angle

The mean contact angles for each probe liquid are plotted versus plasma treatment time in Figure 1. A drastic decrease in contact angles is observed in the first several seconds to 64°, but then the water contact angle increases to a local maximum at 15 s. The diiodomethane contact angle gradually increases for treatment times larger than 4 s, while the ethylene glycol contact angles remain roughly constant for the same treatment times.

Images of drops of probe liquid on the polypropylene surface before and after plasma treatment (120 s) are presented in Figure 2.

Measurement – Surface free energy

Using contact angles in Figure 1, the OWRK method was used to determine the surface

free energy (γ_{tot}) of the polypropylene. The total, polar and dispersive surface free energy as a function of plasma treatment time are presented in Figure 3. Initially $\gamma_{tot}=24.2$ mJ/m² but then increases to 46.8 mJ/m² after 3 s of treatment. The surface free energy then decreases to a local minimum at 15 s and, afterward increases, approaching 40 mJ/m².

The dispersive and especially polar components are also quite dependent on treatment time. Initially, $\gamma_p \sim 0$ as the polypropylene is almost entirely dispersive. After only seconds of plasma exposure, γ_p increases up to 12 mJ/m² while γ_d also increases to about 35 mJ/m². At 15 s though, the polar component drops significantly, corresponding to the drop in γ_{tot} and reduction in hydrophilicity. For treatment times greater than 15 s, γ_p gradually increases while γ_d decreases slightly.

Conclusion

Contact angle and surface free energy measurements prove to be powerful methods to optimize the plasma treatment time. The above results show that the greatest improvement in polypropylene wettability and an increase in surface free energy is achieved with around 3 to 5 s. In addition to plasma treatment time, the effect of plasma pressure and power can also be investigated using the same approach.

References

- [1] F. Awaja, M. Gilbert, G. Kelly, B. Fox, P.J. Pigram. Adhesion of polymers. Prog. Polym. Sci. 34 (2009) 948-968,
- [2] O.-J. Kwon, S. Tang, S.-W. Myung, N. Lu, H.-S. Choi. Surface characteristics of polypropylene film treated by an atmospheric pressure plasma. Surf. Coat. Technol. 192 (2005) 1-10.

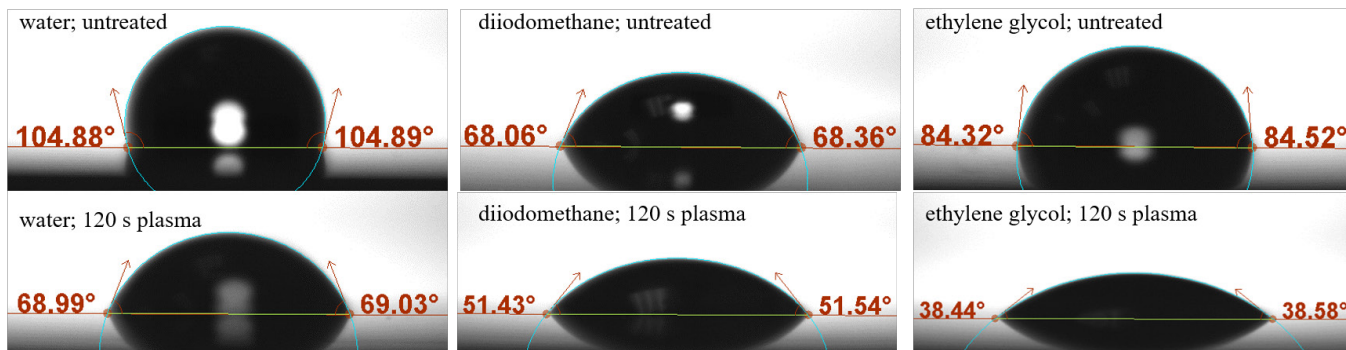


Figure 2 Drops of probe liquids (water, diiodomethane, and ethylene glycol) on untreated and 120 s plasma-treated polypropylene surface