APPLICATION NOTE

FTIR and Contact Angle Measurements of Surface Modified Polymers

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INTRODUCTION

Polymer materials are ubiquitous in medical devices, automobiles, electronics, food packaging and in a wide range of other industrial and consumer products.[1,2] The surfaces of these materials can be modified to harden the surface, reduce or increase the surface reactivity and alter the surface roughness, etc.[3,4] A common surface modification method involves using plasma to etch the surface or to introduce custom functionality to the surface.[5,6] The modification may be performed for many reasons but it typically needs to impart a specific functional group and be free from contamination. The surface of the sample is altered when a plasma creates energetic species that react with the polymer surface to produce volatile compounds, thereby removing and/or adding molecules to/from the surface. The use of different types of plasma such as oxygen- or fluorine-based plasmas can generate new chemical species on the surface of the polymer and hence change its surface properties.

Fourier Transform Infrared Spectroscopy (FTIR) is a well-established analytical technique for characterizing organic and some inorganic materials.[7,8] FTIR provides chemical bonding information by exciting a material with infrared radiation and measuring the resulting absorption or transmission spectrum. FTIR can be used to monitor changes in the surface composition due to plasma exposure. Similarly, dynamic contact angle tensiometry provides information about the wettability of the surface by measuring the interaction between a surface and water. The combination of two techniques can be useful for gaining a better understanding of the effect of the specific plasma treatment.

SAMPLES

Extruded sheets of polypropylene (PP), polycarbonate (PC), and polyoxymethylene (POM) were investigated before and after exposure to oxygen- and fluorine-based plasmas. Plasma treatment in the presence of O_2 or F_2 gas was carried out for 20 min under specified conditions. The different polymer samples were run together in batches during each plasma treatment process.

ANALYSIS

FTIR data was obtained in attenuated total reflection (ATR) mode using a Thermo-Nicolet 6700 Fourier Transform Infrared (FTIR) spectrometer equipped with a Continuum microscope. A Si crystal was used with a typical depth of penetration on the order of 1 micron. The analytical spot size was approximately 100 microns x 100 microns. OMNIC 8.0 software was used to perform data analysis.

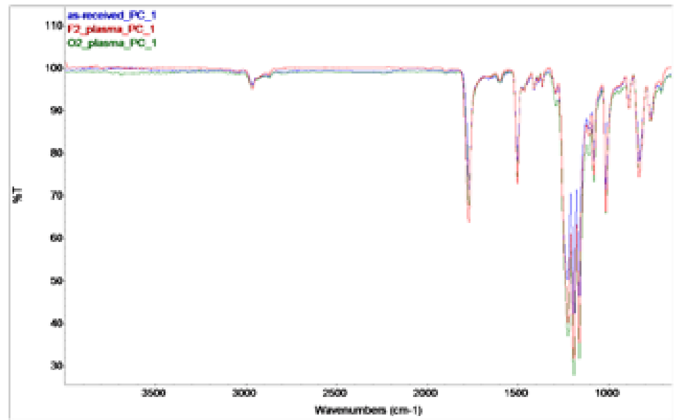

Figure 1: FTIR overlay spectra for POM comparing as received, F_2 plasma, and O_2 plasma treated samples.

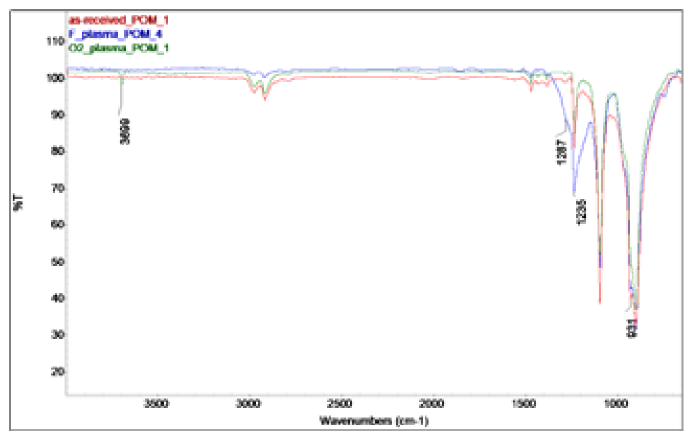

Figure 2: FTIR overlay spectra for polycarbonate comparing as received, F_2 plasma, and O_2 plasma treated samples.

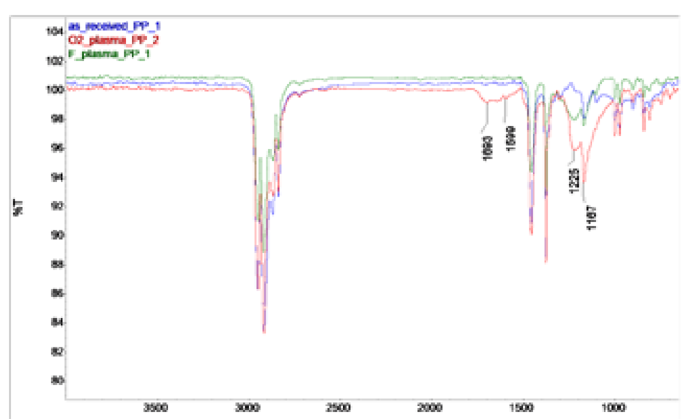

Figure 3: FTIR overlay spectra for polypropylene comparing as received, F_2 plasma, and O_2 plasma treated samples.

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Contact angle measurements provide information about the surface energy of a sample. The degree of tension on a surface moving through a particular liquid indicates the interaction between the functional groups on the surface and those of the liquid. For surfaces modified by plasma treatment this can indicate the degree to which the surface has been altered when compared to untreated samples. A Data Physics DCATS 21 tensiometer was used to measure the dynamic contact angle by dipping each sample into ultrapure water.

RESULTS AND DISCUSSION

The effect of two different types of plasma on three polymers was evaluated using FTIR-ATR, a surface sensitive mode that probes the top micron of the surface. The results are summarized in Table 1.

No obvious differences were observed for plasma-treated versus untreated PC samples as shown in Figure 1. In contrast, treatment of PP and POM samples with F_2 plasma results in the formation of C-O and/or C-F bonds (see Figures 2 and 3). Note that C-O vibrations are typically observed between 1250 and 1050 cm^{-1}, whereas C-F between 1400 – 1000 cm^{-1}, making it difficult to determine the exact functional group responsible for the peak at 1211-1217 cm^{-1}. The presence of probable C-F bonding is supported by previous XPS analysis on these samples, which indicated the presence of CF, CF_2, and CF_3 species.[7]

Oxygen plasma also was shown to have a strong effect on PP and POM polymers. In the case of PP, the treated surfaces show evidence of organic acid (1693 cm^{-1}), possible organic acid salt (1599 cm^{-1}) and possible C-O species (1225 cm^{-1}). In contrast, POM surfaces showed an ester peak at 1736 cm^{-1} and a hydroxide peak at 3699 cm^{-1}. In addition, the peak at 931 cm^{-1}, which may be due to C-H bending vibrations, decreased in intensity compared to the control. These results are related to differences in polymer structures: while PP is composed of C-C and C-H bonds, POM is composed of C-O, C-C and C-H bonds, making it easier to form OH functionalities.

The contact angle results are summarized in Table 2. The F_2 plasma appears to significantly increase the contact angle of PC and POM, but not PP. These results indicate that a more hydrophobic surface is generated on PC and POM due to the fluorine plasma (i.e. the higher the contact angle, the more hydrophobic the surface). The greatest change is observed with POM, where the angle raises from 102 to 156 degrees. In contrast, oxygen plasma introduces a relatively small change in sample wettability (i.e., small increase for POM and PC and decrease for PP).

Based on the testing performed, PC appears to be less sensitive to both types of plasma compared to PP and POM. This higher resistance to the plasma indicates stronger bonding on the surface, which is more resistant to break up by the reactive oxygen and fluorine species in the plasmas.

SUMMARY

In this study, FTIR was shown to be a useful tool for evaluating compositional changes of polymer surfaces following plasma treatment. Likewise, dynamic contact angle measurements provided a quantitative measure of surface energy. This analytical approach can be useful across a variety of industries for evaluating changes in the hydrophobicity/ hydrophilicity of coatings due to surface alterations, including etching, roughening and imparting new surface chemistries.

Other complimentary techniques can be used to investigate the effect of surface modification on surface tension (static contact angle), elemental composition and chemical state (XPS), topography (AFM), and molecular surface chemistry (TOF-SIMS).

Table 1. Summary of FTIR Results

Sample Type	O2 Plasma Treatment	F2 Plasma Treatment
PC	No change	No change
PP	Organic acid (1697 cm^{-1}) Possibly organic acid salt (1598 cm^{-1}) Possibly C-O species (1217 cm^{-1})	Possibly C-O or C-F species (1217 cm^{-1})
POM	Hydroxide (3698 cm^{-1}) Ester (1736 cm^{-1}) Possible change in CH bonding (decrease in 931 cm^{-1})	Possibly C-O or C-F bonding (1211 cm^{-1})

Table 2. Advancing Contact Angle Results

Sample Type	As received	O_2 Plasma Treatment	F_2 Plasma Treatment
PC	103	87	100
PP	102	107	137
POM	102	106	156

REFERENCES:

1. https://www.mddionline.com/surface-modification-using-low-pressure-plasma-technology
2. P. K. Cho, J. Y. Chen, L. P. Wong, N. Huang, Materials Science and Engineering, R36 (2002) 143-206.
3. Polymer Surface Modification: Relevance to Adhesion, K. L. Mittel, 1995, pp 199-212.
4. Miran Mozetic, Surface Modification to Improve Properties of Materials, Materials, 2019, 12, 441.
5. E.M. Liston, L. Martinu & M.R. Wertheimer (1993) Plasma surface modification of polymers for improved adhesion: a critical review, Journal of Adhesion Science and Technology, 7:10, 1091-1127, DOI: 10.1163/156856193X00600
6. Lavanya Jothi and Gomathi Nageswaran, Plasma Modified Polymeric Materials for Biosensors/Biodevice Applications, Non-Thermal Plasma Technology for Polymeric Materials, 10.1016/B978-0-12-813152-7.00015-9, (409-437), (2019).
7. EAG white paper, 2020.
8. N. De Geyter, R. Morent, and C. Leys, Surface characterization of plasma-modified polyethylene by contact angle experiments and ATR-FTIR spectroscopy, Surface and Interface Analysis, 26 November 2007

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