

Analysis of Plasma Treated Polymers

Key Words

- Angle Resolved XPS
- Co-axial Charge Compensation
- High Resolution XPS spectra
- Surface Analysis

Surface modification of polymers is an important and emerging technology. In this example surface treatment is required so that polymer surfaces become more suitable for use as prosthetic veins.

The approach used here to modify the polymer surfaces is to expose them to plasmas containing a variety of gases. Following this treatment their surface texture, wettability, and chemical composition needs to be established.

One of the most common complaints about the use of synthetic grafts is occlusion (blockage). If the graft diameter is greater than 6 mm blood flow is unimpeded. If, however, the graft diameter is less than 6 mm then thrombosis results. One cause of thrombosis is the build up of macrophage on the walls of the graft which causes an inflammation reaction with the polymer.

The inside of natural blood vessels (lumen) are lined with endothelial cells (endothelium) which are inert to blood and so thrombosis does not occur. The aim of this work is to engineer a surface which will support the growth of these cells and avoid inflammation and blockage. An important factor in the modification of these surfaces is their wettability, cells cannot grow on a highly hydrophobic surface.

Surfaces of PTFE were treated in a plasma containing an active gas. Gases used were nitrous oxide, oxygen, air, nitrogen, argon and ammonia.

The surfaces were then characterized using XPS, AFM and DCA.

AFM Analysis

The AFM data show that, regardless of plasma used, the surface roughness increases as a result of the plasma treatment. Figure 1 shows the effect of a 1 minute ammonia plasma treatment on PTFE.

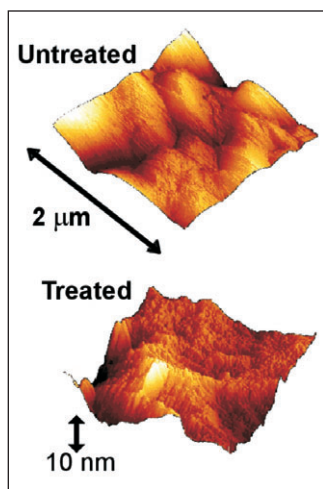


Figure 1: AFM measurements of PTFE before and after treatment with an ammonia plasma

Contact Angle Measurements

The dynamic contact angle (DCA) measurements for all of the treated polymers showed that the plasma treatment increased the wettability of the surfaces (i.e. both advancing and receding contact angles decreased).

The extent of the decrease in contact angle depended upon the treatment time and the nature of the gas in the plasma. Oxygen treatment had the smallest effect on wettability and ammonia the largest.

XPS Measurements

The XPS data were taken on a Thermo Scientific Theta Probe instrument. The C 1s spectra from the treated and untreated PTFE are shown in figure 2. The plasma treatment was for two minutes in each case. The effect of the plasma on the composition of the polymer can be seen in the spectra. All of the plasma treatments cause defluorination but the ammonia plasma treatment has the greatest effect.

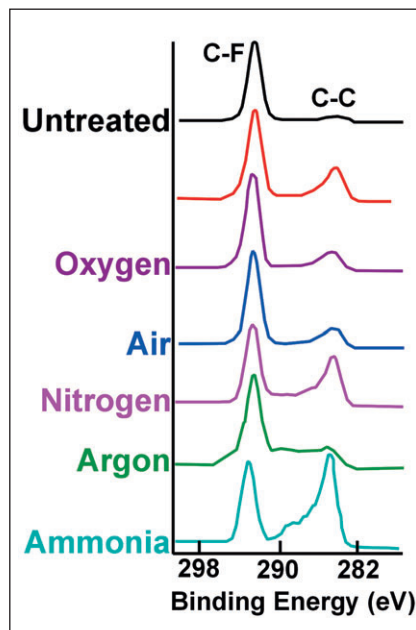


Figure 2: The C 1s region from the XPS spectra of untreated and plasma treated PTFE

Correlation of XPS with DCA Measurements

The spectra in figure 2 can be quantified and atomic ratios calculated. The atomic ratios can then be compared with the contact angle measurements. The results of this comparison are shown in figure 3.

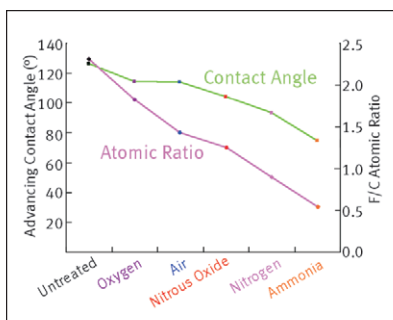


Figure 3: Comparison of XPS and DCA measurements for PTFE

For PTFE, the fluorine content correlates with contact angle, and thus to the wettability. The spectra in figure 2 show that, as the fluorine content decreases there is an increase in oxygen and nitrogen at the polymer surface.

It seems likely that incorporation of oxygen-containing and nitrogen-containing species into the polymer molecules during the plasma treatment is responsible for increasing the hydrophilic character of the polymer surface.

Angle Resolved XPS

The XPS data in figure 2 show the changes in the chemistry of the near surface region of the polymer surfaces as a result of their exposure to a plasma. The data give no indication whether the change in chemistry is uniform within the information depth or whether there is a more gradual change in the composition as a function of depth.

To determine the changes in composition with depth, Theta Probe was operated in its angle resolving mode.

The spectra in figure 4 were collected simultaneously without tilting the sample.

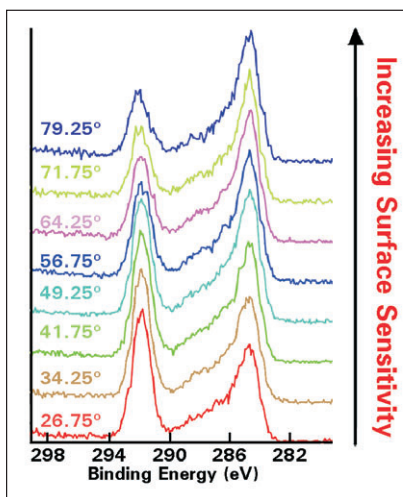


Figure 4: Angle resolved XPS spectra from ammonia plasma treated PTFE

It is clear from the spectra that the depletion of fluorine and the build up of C-C, C-O and C-N species in the polymer is greatest near to the surface and decrease with

increasing depth. Similar phenomena were observed when PTFE was exposed to a nitrogen plasma.

Figure 5 shows the atomic concentrations measured as a function of emission angle (measured with respect to the surface normal) for nitrogen plasma treated PTFE.

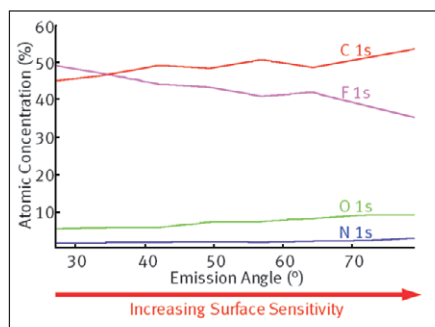


Figure 5: Quantification of ARXPS data from PTFE exposed to a nitrogen plasma

Again this shows that fluorine is depleted near the surface to be partially replaced by oxygen and nitrogen.

Similar effects were observed following treatment with other gases and when plasma treated PET was analyzed.

Conclusions

XPS provides important surface information concerning the surface modification of PTFE. The XPS data provide an explanation for the changes in contact angle determined by the DCA experiments, the increase in the concentration of functional groups causes an increase in the hydrophilic character of the surface and the contact angle decreases.

ARXPS provides more surface sensitive information and shows the variation of the extent of the surface modification as a function of depth. As might be expected, the extent of the polymer modification is greatest near the surface but the ARXPS spectra show that some of the original characteristics of the polymer remain (e.g. there is a CF₂ peak in all of the spectra in figure 4, including those which were taken at grazing emergence angles).

Ammonia treated PTFE displays the most significant surface modification.

These experiments have shown that ARXPS is a valuable technique in the development of surface modified polymers. Not only can the chemical composition be ascertained from the results but the variation of the composition with depth can also be measured.

Acknowledgement:

Thermo Fisher Scientific would like to thank Dr R L Williams and Dr T Markkula, Department of Clinical Engineering, University of Liverpool, UK for their permission to reproduce these data.

www.thermo.com/surfaceanalysis

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa
+43 1 333 5034 127

Australia
+61 2 8844 9500

Austria
+43 1 333 50340

Belgium
+32 2 482 30 30

Canada
+1 800 530 8447

China
+86 10 8419 3588

Denmark
+45 70 23 62 60

Europe - Other
+43 1 333 5034 127

France
+33 1 60 92 48 00

Germany
+49 6103 408 1014

India
+91 22 6742 9434

Italy
+39 02 950 591

Japan
+81 45 453 9100

Latin America
+1 608 276 5659

Middle East
+43 1 333 5034 127

Netherlands
+31 76 579 55 55

South Africa
+27 11 570 1840

Spain
+34 914 845 965

Sweden/Norway/Finland
+46 8 556 468 00

Switzerland
+41 61 48784 00

UK
+44 1442 233555

USA
+1 800 532 4752

www.thermo.com



VG Systems Ltd. Trading as Thermo Fisher Scientific, East Grinstead, UK is ISO Certified.

AN31010_E 04/08M