SURFACE ENGINEERING OF POLYMER SURFACES USING ATMOSPHERIC PRESSURE PLASMA

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Abstract

Atmospheric pressure plasmas are becoming more widely available for the surface engineering of materials. We report on a microwave coupled non-equilibrium atmospheric pressure plasma that is currently being investigated in a collaboration between the University of Surrey and EA Technology Ltd. [1,2]. After successfully demonstrating that the atmospheric pressure plasma could be used to modify the surfaces of commercially important polymers (such as polyolefins, poly(ethylene terephthalate) and poly(methyl methacrylate)) [3,4], atmospheric plasma assisted deposition have also been performed.

In this paper after introducing the atmospheric pressure plasma we are exploring, we outline an experimental arrangement for the preparation of atmospheric plasma assisted deposited materials highlighting some of the difficulties encountered due to operation at atmospheric pressure. Analysis of the surfaces generated has been done by Fourier Transform infrared spectroscopy and optical microscopy.

1. Introduction

An introduction to APNEP, atmospheric versus vacuum plasmas and the apparatus and instrumentation used in this study are presented elsewhere at this conference [3] and in the authors' previous publications [4-7].

<table>
<thead>
<tr>
<th>'Monomer'</th>
<th>Technique*</th>
<th>Deposited material</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>PP</td>
<td>Hydrocarbon</td>
<td>[14]</td>
</tr>
<tr>
<td>(CH₃)₃Si-O-Si(CH₃)₃</td>
<td>PP</td>
<td>Si-(CH₃)₃, Si-O-CH₃, SiO₂</td>
<td>[15]</td>
</tr>
<tr>
<td>C₆F₆</td>
<td>PP</td>
<td>Perfluorinated alkyl benzene, CₓFᵧ</td>
<td>[16]</td>
</tr>
<tr>
<td>Gold</td>
<td>Vacuum sputtering</td>
<td>Gold</td>
<td></td>
</tr>
<tr>
<td>SiH₄ + NH₃</td>
<td>LPCVD</td>
<td>SiNx</td>
<td>[9]</td>
</tr>
</tbody>
</table>

Table 1: Materials deposited in a vacuum environment.
* PP - plasma polymerisation; LPCVD - low-pressure chemical vapour deposition

A wide variety of materials may be deposited by using vacuum techniques such as plasma polymerization [8], sputtering or low-pressure chemical vapour deposition [9], see Table 1.
Recently, a variety of atmospheric pressure non-equilibrium plasmas have been developed [10-13]. Although many applications have involved surface treatments, examples of using these plasmas to deposit materials are now emerging, see Table 2.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Technique*</th>
<th>Deposited material</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-(OCH₂CH₃)₄, N₂O, He</td>
<td>APG</td>
<td>Silica</td>
<td>[17]</td>
</tr>
<tr>
<td>CF₃CF=CF₂</td>
<td>APG</td>
<td>Fluoro-polymer</td>
<td>[18]</td>
</tr>
<tr>
<td>Si-(OCH₂)₄, H₂, Ar</td>
<td>Cold plasma torch</td>
<td>SiO₂</td>
<td>[19]</td>
</tr>
<tr>
<td>Ti-(OCH₂CH₃)₄, H₂, He</td>
<td>Cold plasma torch</td>
<td>TiO₂</td>
<td>[20]</td>
</tr>
</tbody>
</table>

Table 2: Materials deposited using atmospheric plasmas. *APG - atmospheric pressure plasma glow.

Preliminary results using APNEP indicate that this atmospheric plasma may also be used to deposit materials [3]. Hence the aim of the work outlined here is to scope a selection of monomers for deposition using atmospheric pressure plasma and compare the properties and characteristics of the deposited materials with those deposited by vacuum plasma methods.

2. Experimental

2.1. Atmospheric Plasma Deposition

The operation of APNEP used for surface modification has been described elsewhere [4-7]. However, for surface deposition experiments, the downstream reactor is modified to enable the introduction of the monomer, see Figure 1. The monomer, octamethylcyclosiloxane (D₈, supplied by Dow Corning) is placed in a bubbler and nitrogen is flowed through it. For the surface deposition experiment performed in this study, a 2.5 dm³ min⁻¹ nitrogen APNEP was generated, and D₈ vapour (in 0.5 dm³ min⁻¹ nitrogen) was introduced. The plasma on time was 5 minutes. Low-density polyethylene (LDPE, from Goodfellow Ltd.) substrate was placed 200 mm downstream from the plasma exhaust to avoid thermally induced degradation.

2.2. Analysis

Optical microscopy images were recorded on a Zeiss optical microscope in reflectance mode at magnifications from x20 to x80. Attenuated total reflection Fourier Transform infrared (ATR-FT-IR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR from 4000 - 600 cm⁻¹ at a resolution of 4 cm⁻¹. A Graseby Specac single reflection diamond ATR was used to analyse approximately the surface 2 x 2 mm² of the polymers to a depth of about 2 μm.
3. Results

Optical microscope analysis of the LDPE after exposure to the downstream of the nitrogen/D$_4$ plasma revealed the presence of a deposited material, see Figure 2b. The optical microscope image from the untreated polymer is shown in Figure 2a.

![Figure 2: Optical microscope images of a) untreated LDPE and b) LDPE deposited with D$_4$ from the downstream of an atmospheric plasma, both images recorded at a magnification of x32.](image)

The size of the deposited islands of material range from in excess of 100 $\mu$m to under a micron in diameter, see Figures 3a and 3b. Furthermore, the type of material may be classified as a mixture of white crystallites or grey 'dust'. ATR-FT-IR analysis indicated that the crystallites were likely to be composed of a significant amount of SiO$_x$ due to the characteristic Si-O-Si absorbance of this material seen around 1100 - 1000 cm$^{-1}$ although there was an indication that Si-C was also present; see Figure 4 with peak assignments in Table 3. We believe the grey dust is carbon-rich layer, although further investigations into the composition of both deposited materials are continuing.

The ATR-FT-IR spectra also indicate that complete coverage of the underlying LDPE was not achieved under these conditions. However, material was spread throughout the APNEP apparatus and with greater control of the reaction conditions, controlled high-deposition rates may be achievable.
Figure 3: Optical microscope images of LDPE coated with a D₄ deposited from the downstream of atmospheric plasma, images a) and b) recorded at a magnifications of x20 and x80 respectively.

Figure 4: ATR-FT-IR spectra of a) virgin LDPE and b) APNEP-enhanced-CVD of D₄ on LDPE.

<table>
<thead>
<tr>
<th>Peak /cm⁻¹</th>
<th>Assignment</th>
<th>Peak /cm⁻¹</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>720</td>
<td>C-H, LDPE</td>
<td>1100 - 1000</td>
<td>Si-O-Si</td>
</tr>
<tr>
<td>810</td>
<td>Si-(CH₃)₂</td>
<td>1470</td>
<td>C-H, LDPE</td>
</tr>
<tr>
<td>865</td>
<td>Si-(CH₃)₂</td>
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<td></td>
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</tbody>
</table>

Table 3: Peak assignments for LDPE and APNEP-enhanced-CVD of D₄ [21].

4. Summary

When D₄ was being fed in to the downstream of the atmospheric plasma, some D₄ was entrained in to the APNEP glow discharge. This resulted in the plasma increasing in intensity and changing to a yellow turbulent glow. Pure nitrogen APNEP has a stable mauve glow [5].
Furthermore, the silica containment vessel and to a lesser extent, the downstream reactor, were coated in a grey deposit. This grey deposit, which was also deposited on the LDPE substrate, is likely to be amorphous carbon.

Under the conditions used here, APNEP-enhanced CVD of D₄ has resulted in significant degradation of the monomer producing a mixture of carbonaceous and glassy deposits. However, it is possible to produce milder conditions by introducing the monomer further downstream or by activating the surface with the plasma, then exposing the active surface to a monomer in the absence of the plasma. These approaches, as well as the use of other candidate monomers (hydrocarbons, fluorocarbons, siloxanes and metal chlorides) are currently under investigation by the authors.

5. Acknowledgements

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References
