Fluorine Gas Plasma Treatment of Polypropylene Film

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Abstract: Polypropylene (PP) film surfaces can be treated using fluorine (F₂) plasmas. Analysis of plasma-fluorinated PP surfaces indicates a surface modification process that is initially quite rapid, but then slows sharply as the fluorination progresses. Results from a two-dimensional plasma hydrodynamics model of PP fluorination suggest that the surface reaction mechanism includes a hierarchy of H abstraction and F/F₂ passivation reactions, while the effects of energetic ion and photon fluxes are minimal at short exposure times. Both experimental and modeling results indicate that the increasingly fluorinated PP surface becomes less reactive to the plasma as the surface develops a fully fluorinated, crosslinked surface layer that eventually extends to the full ESCA sampling depth.

Keywords: fluorination, modeling, surface modification, polymer film

1. Introduction

In this paper, we present results from experimental and computational investigations of gas-phase and surface reactions occurring during the fluorination of polypropylene (PP) films in a low-pressure capacitively coupled F₂/Ar plasma. The relatively simple reaction chemistry of F₂/Ar plasmas, combined with surface analysis techniques that can distinguish fine differences in fluorinated polymer surfaces, allows for detailed characterization of the fluorination reaction.

2. Techniques Used

Biaxially oriented PP film was treated using a parallel plate, capacitively coupled plasma reactor built by 3M Company. The large-area electrodes were driven by a 13.56 MHz supply that provided 0.18 W·cm⁻² of electrode area. The film typically passed through the center of the 2.54 cm electrode gap. Gas pressures were 0.5 torr. Plasma-treated polymer films treated were analyzed by ESCA and AFM. All reported data from ESCA were acquired at a photoelectron take-off angle of 90°. The integrated plasma equipment-surface kinetics model used in this investigation, the Hybrid Plasma Equipment Model, is described Refs [1, 2].

A surface reaction mechanism for the fluorination of PP films was developed, incorporated into a 2-dimensional model for gas and surface processes, and applied to a capacitively coupled plasma (CCP) reactor. To adequately characterize the reaction mechanism using a reasonable number of parameters, we implemented a reaction hierarchy in our model that addresses the major pathways in a systematic way while also accounting for secondary pathways. (See Ref. [3].) In short, F atoms abstract H atoms from the surface of the PP film, creating a free radical site. These free radical sites can be passivated by either F atoms or F₂ molecules. As the sites on the PP backbone originally having H atoms are filled with F atoms, deactivation occurs, which slows the rate of subsequent H abstraction and passivation. Free radical sites can also form cross-links between polymer chains, consuming bonds that might otherwise be passivated by F atoms.

3. Results

The ESCA F/C ratio of fluorinated PP samples, as a function of exposure time, is shown in Fig. 1. These representative samples indicate that fluorination to an F/C of ca. 1.2 occurs within a few seconds for treatments using an F₂/Ar = 60/40 gas mixture. These data further indicate that the rate of change of the F/C ratio with increasing exposure time decreases rapidly after an F/C of about 1.4 is attained.
The percentages of total carbon atoms in each functional group, as derived from the ESCA C 1s spectra, are shown in Fig. 2. This data set shows general trends of decreasing CHₙ species and increasing CF, CF₂, and CF₃ species. The β-shift CHₙ signal rises early in the fluorination and then decreases as the fluorination process ends. Representative AFM images of treated PP films are shown in Fig. 3. While the AFM image shown in Fig. 3a was collected from a PP film sample with an F/C ratio of 0.61, the characteristic fibrillar structure of the PP film seen in this image is nearly identical to previously reported images of an untreated PP surface [4] and to all samples with lower amounts of fluorination. This result indicates that no discernable topographical change occurs on fluorinated PP surfaces with F/C ratios of ca. 0.6 or less.

A comparison of functional group surface coverages from computed and experimental results after 6 s and after 26 s of treatment is shown in Table 1. The predicted F/C ratio agrees well with the experiment. The discrimination between CH and β–C in our model is somewhat arbitrary because of the finite number of modeled configurations. If we compare the sum of CH and β–C with experiment, the agreement is better. The excess of estimated CF and deficit of CF₃ most likely originates from the approximate manner in which F atom diffusion into the surface layers is addressed. Another source of discrepancy is that the F/C ratios obtained from the experimental ESCA measurements arise from analysis of the outermost 6-8 nm of the surface, which does not directly correspond to the effective depth addressed in the simulation.

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Surface Fractional Coverage and F/C</th>
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<tr>
<td></td>
<td>6 s Treatment</td>
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<tr>
<td></td>
<td>Simulation</td>
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<tr>
<td>CH</td>
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<tr>
<td>β–C</td>
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<tr>
<td>CF</td>
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<tr>
<td>CF₃</td>
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<tr>
<td>F/C</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 1. Comparison of modeled surface coverage and experimental ESCA F/C ratios.
Figure 4. Simulated functionalization of a surface of the PP film as a function of position for a web speed of 9 cm-s^{-1}, or a total exposure time of 6 sec. (Ar/F_{2}=60/40, 500 mtorr, 600 W at 10 MHz) (a) coverage of functional groups, and (b) F/C ratio.

The fractional coverages of functional groups and the F/C ratio indicated by our model are shown in Fig. 4 as a function of position for a PP surface translating through an F_{2}/Ar plasma. The persistence of small fractions of CH results from the ablation of C_{S} and C_{T} groups (secondary and tertiary carbon on the PP backbone) by ion bombardment and the slow rates of fluorination of the underlying PP backbone. In the absence of cross-linking, we would expect CF, CF_{2}, and CF_{3} to each have 1/3 of the fractional coverage at reaction completion. The dominance of CF_{2} (0.37 coverage) is largely attributed to the cross-linking of C_{P} (primary carbon) sites, which limits possible CF_{3} group formation. The cross-linking of C_{T} converts it to a β-C site by eliminating the possibility of F attachment and this conversion contributes to the high coverage of β-C (0.19) at the exit of the reactor. The cross-linked C_{T} sites have no F or H bonding and are bonded to only other C atoms.

Our computed results show that the F/C ratio first undergoes a rapid increase in the first 10 s, and then stabilizes at about 1.7 between 10 and 26 s. This stabilization can be attributed to two effects. First, the top PP surface is highly fluorinated and cross-linked after the first 10 s. Second, ion bombardment and the slow fluorination of exposed fresh backbone also reach a balance beyond 10 s.

4. Discussion

In this system, the observed rate of the fluorination varies significantly, occurring rapidly at first and then more slowly as the PP surface becomes progressively fluorinated. This observation appears to be the effect of two distinct mechanisms: a decrease in reactivity as the PP becomes fluorinated and a gradient of fluorination into the bulk of the PP polymer that spans the ESCA sampling depth.

In addition to the overall deactivation effect of the fluorination process, the high relative concentration of CF_{2} on the partially fluorinated PP surface also indicates that the multi-step process required to fully fluorinate the PP on the very surface occurs faster than the progression of the fluorination reactions into the bulk of the polymer film. The relatively low level of CF can be explained by the outer “layers” of the PP surface (within the ESCA sampling depth) becoming fully fluorinated more quickly than layers that are further into the bulk of the PP sample, but still within the ESCA sampling depth.

While ESCA analysis suggests that the average chemical composition of the outermost layers does not change in the final stages of the fluorination process, AFM images of PP films with longer plasma exposure indicate significant changes in the surface topography. The surface nodules that are seen to develop in the AFM images of the more highly fluorinated samples are consistent with a change to a less linear (more-crosslinked) polymer structure.

Fluorine atoms reacting with the polymer surface can not directly develop a cross-linked structure in the modified polymer, so cross-links must develop through the reaction of carbon radicals generated on the polymer. However, the polymer fluorination reaction occurs simultaneously through this same pathway, so that any cross-linking reactions will necessarily compete with the fluorine-substitution reaction. However, our results show evidence of cross-linking in what appears to be the “end state” of
the modified polymer. In the samples with the highest level of fluorination, ESCA shows a remnant β-shifted CH₃ signal of ca. 10% of the carbon atoms detected. SIMS analysis of these surfaces [5] shows extremely small amounts of hydrogen remaining on the end-state modified polymer. These results demonstrate the presence of polymer carbon atoms without either hydrogen or fluorine attached, something that is possible only by new C-C bonds developing in the starting polymer. This cross-linking of up to 10% of the carbon atoms partially accounts for the lack of full fluorination, that is, the fact that F/C is < 2 even after long plasma exposure.

Simulation results indicate that at one early point during the fluorination reaction, 9% of the PP carbon atoms in the surface layers are in the form of free radicals. The presence of so many radicals that have not yet reacted with F and F₂ significantly increases the probability of reaction between surface free radicals and is likely the reason why cross-linking is so prevalent. It is reasonably assumed that the non-fluorinated cross-linked carbon would most likely be C_T and not C_P because of the large number of non-fluorination reactions involved to develop cross-links involving the C_P atom.

For films electrically floating in the plasma (and not in contact with an electrode) and with moderate exposure times (< tens of s), ion bombardment and photon-induced reactions do not have a significant effect on the final F/C ratio. However, given longer exposure time or placement of the film on an electrode, ion sputtering produces significant changes in surface composition.

4. Conclusions

In summary, our results indicate that the first reactions of a PP film surface in a F₂/Ar plasma are fast (significant fluorination in less than 1 s) and form some cross-links, but generally retain the polypropylene structure. The majority of the fluorination process proceeds through hydrogen abstraction and subsequent fluorination of polymer radicals. This fluorination process is accompanied by infrequent, but slowly accumulating, breaks in the polymer backbone and scission of pendant methyl groups from ion exposure. Particular observed effects include:

(1) The initial fluorination reactions are fast. Our numerical simulation shows that after only 1.1 s of processing in a F₂/Ar 40/60 plasma, 97% of the PP units have at least one F atom added. After only 6 s of processing 96% of the surface H atoms have been removed. Our experimental sample with 1.8 s of exposure to an F₂/Ar 60/40 plasma showed an ESCA F/C of 1.2.

(2) The fluorination reaction develops a treatment gradient within the ESCA sampling depth of ca. 10 nm. The evolution of the surface chemistry indicated by ESCA indicates deactivation of the increasingly fluorinated polymer surface and demonstrates that fluorination “across” PP “layers” progresses more rapidly than fluorination into the bulk of the polymer.

(3) Significant numbers of cross-links develop as a result of the fluorination process. About 70% of the PP units are involved with cross-linking near the end of the reaction. About 10% of all of the PP units are cross-linked through C_T, which leads to the large β-shift C in the end-state ESCA spectra.

(4) The “end-state” of PP exposed to F₂ plasma is a highly fluorinated surface with a significant amount of cross-links between original polymer chains.

References


