SPECTROSCOPIC ANALYSIS OF POLYPROPYLENE USING AN $H_2$ GLOW DISCHARGE

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Abstract

Results obtained by optical emission spectroscopy of active species formed during the process of degradation of the polypropylene (PP) using a glow discharge are presented in this work. The discharge configuration used consisted in a confined cathode-anode geometry, with the PP placed on the anode. In order to correlate the interaction of active species with the degradation of PP measurements by emission spectroscopy ($H_2^*$, CH(A-X), Hα) were carried out as a function of plasma parameters. An increase in the intensity of the CH band was observed in the first 30 minutes of heating. It is shown that the degradation of PP is related to CH band intensity. The offset of the process can be determined by using the optical emission spectroscopy technique.

Keywords: polypropylene degradation, plasma dc discharge, optical spectroscopy.

1. Introduction

Binder removal is the critical step in the manufacturing of injection-molded parts in that the formation of defects is quite likely to take place. The extraction can be basically processed chemically, thermally, or under vacuum [1-3]. During thermal degradation, the time of extraction is extremely long to avoid cracks and distortions in the component. Recent studies performed in our laboratories have shown the efficiency of plasma thermal degradation of PP. In this work a process of degradation of PP using a hydrogen abnormal glow discharge is presented.

2. Experimental

The plasma reactor consisted of a cylindrical pyrex vacuum chamber closed in both ends by stainless steel lids. The electrodes were configured in a confined cathode-anode system as shown in Figure 1. The discharge was generated by a square pulse power supply in which the voltage was applied to the rectangular cathode. The sample worked as the grounded anode placed inside the rectangular cathode where it was heated by radiation. The temperature was adjusted by varying the pulse time on ($t_{on}$) and was measured using a chromel-alumel (type K) thermocouple. The PP, in the form of spheres of 4 to 6 mm in diameter, was degraded in a discharge of pure hydrogen at 2 Torr flowing at 3.3 scm/s.
2.1. Polypropylene Degradation

Polypropylene was degraded in discharge of pure hydrogen flowing at 3.3 Scm⁻³/s. The pressure was set to 2 Torr and the temperature varied between 300 and 400°C. For each temperature investigated times between 15 and 120 minutes were used. An analytical balance (precision of 10⁻⁵g) was used to measure the mass loss of the polypropylene samples.

2.2. Discharge Characterization

The degradation of polypropylene was monitored by optical emission spectroscopy using a Jobin-Yvon HR 640 monochromator. The instrument is capable of scanning the spectral domain from 190 to 900 nm. A Hamamatsu R928 photomultiplier with maximum quantum yield at λ = 400 nm was attached to the monochromator. The luminous radiation originated at the discharge entered an optic fiber cable 0.5 mm thick. Data control and acquisition was carried out using the PRISM computer program installed in a 486DX2 personal computer. A Spectralink interface provided communication between monochromator and computer. The temporal evolution of the intensity of H⁺⁺, CH (A-X), and H₂ bands and peaks was investigated as a function of the plasma parameters.

3. Results and Interpretation

The results summarized in Table 1 showed that the total degradation of PP occurred in 60 minutes at 350°C, whereas at 380°C it was achieved in 30 min.

Table 1. PP mass loss (in %) using a pure H₂ glow discharge

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
</tr>
</thead>
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<tr>
<td>300</td>
<td></td>
<td>2.70</td>
<td>5.80</td>
<td>10.01</td>
<td>25.20</td>
<td>35.71</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>25.00</td>
<td>55.48</td>
<td>95.99</td>
<td>99.97</td>
<td>99.84</td>
</tr>
<tr>
<td>360</td>
<td></td>
<td>44.05</td>
<td>86.97</td>
<td>99.85</td>
<td>99.98</td>
<td>100.00</td>
</tr>
<tr>
<td>370</td>
<td></td>
<td>49.15</td>
<td>95.23</td>
<td>99.91</td>
<td>99.99</td>
<td>100.00</td>
</tr>
<tr>
<td>380</td>
<td></td>
<td>54.32</td>
<td>99.93</td>
<td>99.97</td>
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<td>100.00</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>61.87</td>
<td>99.95</td>
<td>99.98</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
The CH (A-X, λ = 431.4 nm) band and H₂ peak (λ = 434.15 nm) were monitored during the degradation of P.P (Figure 2). The intensity of the CH(A-X) band increased as a result of P.P degradation in the H₂ plasma. The maximum amount of CH formed in the discharge took place between 160 and 280 °C, where the polymer reaches its softening temperature and evaporates. The intensity of that band decreased with increasing the temperature. No changes were observed for the H peak.

![Figure 2 – Emission pattern of CH(A-X) and H₂ bands during the degradation of P.P at different temperatures.](image)

Figure 3 shows the temporal evolution of the CH(A-X) band as a function of the temperature. The graph shows a good agreement with the results discussed previously. The intensity of that band significantly increased during the first 30 min of the process up to the point where the temperature reached 350 °C. This was related to the intense mass loss of P.P during that period. After 40 min the intensity of the band remained constant and showed hysteresis, i.e., it did not resume its original value. This effect was attributed to carbon deposited on the walls of the reactor chamber. The carbon residues returned to the volume of the plasma by desorption and combined with atomic hydrogen generated in the discharge thus forming CH radicals.
Figure 3 – Evolution of the intensity of CH(A-X) band and temperature as a function of the degradation time of PP in a H₂ plasma at 2 Torr.

Figure 4-a shows an abrupt increase of the temperature for t_on between 50 and 75 µs and simultaneously an increase in the intensity of the emission bands of CH(A-X), H₂* and of the H₅ line (Fig. 4-b). At 50 µs, the beginning of the degradation of PP was observed. At t_on = 150 µs a decrease of the CH band intensity indicated the end point of the process.

Collisions of electrons with molecules of the gaseous mixture produced reactive species (CH₃, H, H₂) that contributed to the efficiency of the PP degradation. This degradation produced new CH₃ radicals, heavier than hydrogen, whose ions caused an increase of the cathode temperature thus increasing the gas temperature. This can also be observed in Figure 4-a, where the current and voltage are both linear functions of t_on whereas the temperature undergoes an abrupt increase.

The significant increase in the H₅ intensity (Fig. 4-b) was attributed to the high concentration of H and H₂ species also resulting from the PP degradation.
Figure 4 - (a) Variation of discharge parameters $I_{\text{dis}}$ and (b) intensities of CH, H₂ and H as a function of $I_{\text{on}}$.

4. CONCLUSIONS

Optical spectroscopic analysis of CH, H₂, and H₂⁺ species confirmed the efficient degradation of polypropylene in hydrogen plasma. It was shown that this technique is suitable to identify both the onset and offset of the process.

5. REFERENCES
