ELECTROCHEMICAL REDUCTION OF FUNCTIONAL GROUPS IN THE CATHODIC EXFOLIATION OF AN ETHYLENE-VINYL ACETATE COPOLYMER

A. A. Korzhenko, G. S. Shapoval, and V. G. Syromyatnikov

UDC 541.13.183;541.64.678

A study was carried out on the electrochemical processes involving the functional groups of an ethylene—vinyl acetate copolymer upon its cathodic exfoliation from metal. Electron transfer to the polymer is facilitated by the activation effect of an adhesion interaction with the metal.

Studies of electrochemical reactions of polymer functional groups during exfoliation of protective polymer coatings from cathodically-polarized metal surfaces in aqueous media involve considerable experimental difficulties due to electrochemical processes with participation of electrolyte components and the accumulation of the products of such reactions on the cathode surface.

One of the major products of the oxygen and hydrogen depolarization is alkali, which accumulates in the electrode layer on the metal—coating—electrolyte phase separation boundary (PSB), over which the exfoliation front propagates. Thus, the most common concepts concerning the nature of the dissociation of the metal—coating adhesive interaction reduce to alkaline hydrolysis of the surface functional groups of the polymer [1, 2].

However, in our opinion, direct electron transfer is possible since the contact of the cathodically polarized metal—polymer separation surface with a conducting aqueous medium provides favorable conditions for such transfer, which would permit the electrochemical reductive decomposition (ECRD) of the polymer, which has mainly been studied in nonaqueous media [3]. Only Pud et al. [4] have observed ECRD upon prolonged electrolysis of the ethylene—vinyl acetate copolymer (EVAC) with 45% vinyl acetate groups (EVAC-45) at −2.0 V (s. c. e.), while EVAC with a lower VA content was resistant to the action of cathodic polarization.

We have found ECRD in an ethylene—vinyl acetate copolymer with only 12% VA groups (EVAC-12) upon its cathodic exfoliation in aqueous medium.

A rapid measurement technique and an instrument for studying cathodic exfoliation (CE) [5, 6] were used. An advantage of this method is that the exfoliated segment of the polymer is bent off the polarization base by a small static force, thereby preventing the accumulation of corrosive products of the electrochemical reactions below the coating and the reaction of such products with the polymer surface. The short duration of the experiment permits us to neglect diffusion of the electrolyte through the coating. As a consequence of these advantages of the present method relative to the existing methods, we were able, to some extent, to eliminate the action of the products of electrochemical reactions on the polymer surface and observe those changes in the functional composition due to electron transfer.

An ethylene—vinyl acetate copolymer with 12% VA groups provided by Miravithen was used. The copolymer was deposited onto a steel plate (Steel 3) by hot pressing at 150°C and 0.003 MPa over 30 min, using a PE coating as the upper layer. We also studied EVAC-12 films maintained in an electrolyte solution (0.5 mole/liter NaCl) and in an alkaline solution over 15 min (the mean exfoliation time of the sample).

The exfoliation was carried out at −1.2 V (Ag/AgCl), which was applied using a PI-50-1 potentiostat. A carbon rod served as the auxiliary electrode, while 0.5 mole/liter NaCl in distilled water served as the electrolyte. The change in the functional composition of the polymer surface was evaluated by MFTIR IR spectroscopy using a Specord M-80 spectrometer.
TABLE 1. Reduced Integral Intensities of the Analytical MFTIR IR Bands of an EVAC-12 Film Subjected to Various Treatments

<table>
<thead>
<tr>
<th>$A_n$</th>
<th>Without treatment</th>
<th>After maintenance in 0.5 mole/liter NaCl</th>
<th>After maintenance in alkali (pH 14)</th>
<th>After CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$ (O---H)</td>
<td>0.40 ± 0.10</td>
<td>0.40 ± 0.15</td>
<td>0.40 ± 0.20</td>
<td>0.80 ± 0.20</td>
</tr>
<tr>
<td>$A_2$ (C=O)</td>
<td>1.37 ± 0.05</td>
<td>1.37 ± 0.10</td>
<td>1.39 ± 0.10</td>
<td>1.14 ± 0.10</td>
</tr>
<tr>
<td>$A_3$ (C=C)</td>
<td>0.13 ± 0.02</td>
<td>---</td>
<td>---</td>
<td>0.14 ± 0.05</td>
</tr>
<tr>
<td>$A_4$ (−CH₃)</td>
<td>0.55 ± 0.02</td>
<td>0.55 ± 0.02</td>
<td>0.55 ± 0.02</td>
<td>0.47 ± 0.05</td>
</tr>
<tr>
<td>$A_5$ (C−O)</td>
<td>2.70 ± 0.20</td>
<td>2.70 ± 0.20</td>
<td>2.70 ± 0.20</td>
<td>3.10 ± 0.40</td>
</tr>
</tbody>
</table>

KRS-5 material with 45° working angle and number of internal reflections equal to 15 was used as the internal reflection element. A total of six spectra were taken for each of the samples studied. These spectra were integrated and treated statistically.

The changes in the surface layers of the polymer were studied relative to the integral intensity ($A_n$) in the following absorption regions: 1) O−H (3100-3600 cm⁻¹), 2) C=O (1739 cm⁻¹), 3) C=C (1600-1700 cm⁻¹), 4) CH₃ (1372 cm⁻¹), and 5) C−O (1237 cm⁻¹), which were examined in comparison with the CH₂ group deformation bands (1464 cm⁻¹). This band may be used conveniently as an internal standard for monitoring the functional composition of EVAC [7].

Analysis of the IR data for EVAC-12 films after CE indicated marked differences from the control reflected by the relative integral band intensities (Table 1): an increase in the content of O−H groups and C−O bonds and decrease in the amount of carbonyl and methyl groups. No changes were seen after maintaining the EVAC-12 films in 0.5 mole/liter NaCl and alkali.

Table 1 shows that there are steady changes in the functional composition of EVAC-12 after cathodic exfoliation but these changes are slight, i.e., only a small fraction of the acetate fragments is altered.

This finding as well as the stability of the copolymer studied during prolonged electrolysis of samples clamped rather than pressed to the cathode surface [4] suggest specific decomposition of the acetate groups, which participate in the adhesion bonds to the metal.

According to Michaels [8], the metal−ester group adhesion bond is achieved by means of an Fe−OH interaction on the metal surface with the carbonyl oxygen of the acetate. This interaction is approximately 30% ionic [8]. Thus, it is quite likely that this activation, which is enhanced by the strong electric field of the double electric field on the PSB, clearly creates the preconditions for direct electron transfer to the acetate groups with their subsequent decomposition.

In all likelihood, the specific result of such electron transfer is cleavage of the adhesion bonds with loss of acetate groups, which may occur through the formation of a radical−anion:

![Chemical Structure]

This hypothesis is indicated by the drop in the amount of C−O bonds and methyl groups in the polymer. However, the formation of C=C bonds in the major chain of the copolymer, as in the case of EVAC-45 [4], does not occur since the double bond absorption region (Table 1) remains at the level of background noise. This discrepancy is probably related to the different structure of EVAC-12 and EVAC-45 and the different decomposition conditions. In the case of Pud et al. [4], electron transfer to the polymer is facilitated due to a high concentration of VA and continuous contact of the polymer with a strongly polarized cathode, while in our case, electron transfer to the acetate group is facilitated by a direct bond with the cathode and the radical−anion formed at such a potential and in the presence of such an activator depolarizer as water is incapable of delocalizing to the polymer chain. Thus, the decomposition of the radical−anion occurs, in all probability, specifically with