Modification of Ethylene—Vinyl Acetate Copolymer by Acrylamide in Solid State*

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Mechanochemical modification of ethylene—vinyl acetate copolymer by acrylamide in solid state has been studied. When radicals were introduced into the system by preirradiation of acrylamide, the modification reaction proceeded in just the same way as with non-irradiated acrylamide. Instability of acrylamide radicals was observed. In the course of modification the spectrum of peroxide radical or superposed spectrum of acrylamide and peroxide radicals have been found.

The acrylamide (AA) polymerization in solid state has been studied by various authors [1—5]. They found that after $\gamma$ irradiation the AA polymerization proceeds for quite a long time. Adler et al. [6] found that at $-196^\circ$C the radical formed from irradiated acrylamide does not change after 16 hours, its e.s.r. spectrum corresponding to that of monomer radical. The spectrum of the growth radical, most frequently observed at room temperature, can be observed at temperatures as low as $-20^\circ$C. At low conversions the AA polymerization rate decreases rapidly, whereas, for long polymerization times ($25^\circ$C $10^4$ sec approx.) the polymer yield is linear in the logarithm of time after irradiation [4].

It was the aim of the present paper to study more thoroughly some of the peculiarities of acrylamide polymerization (copolymerization) in polymer matrix. Some of these peculiarities connected with the use of acrylamide in solid state for polymer modification have been referred to in a previous contribution [7].

**Experimental**

For the purpose of modification acrylamide of m.p. 86.5°C, ethylene—vinyl acetate copolymer (EVAc), commercial tradename LEVAPREN, content of ethylene component 50%, $M_n 4.73 \times 10^4$; $T_G -30^\circ$C were used.

Acrylamide was irradiated by means of a $^{60}$Co source in the course of 6 hours at the temperature of liquid nitrogen. Dose rate was 0.357 Mr/hr.

Both the mechanical degradation and the mechanochemical modification were carried out on a laboratory plasticator [8] at 20°C and 300 r.p.m. For degradation studies oxygen was employed as an acceptor. Molecular weight was determined osmometrically.

The modification was made using a mixture of acrylamide (irradiated or non-irradiated) and ethylene—vinyl acetate copolymer in the ratio 0.3 : 0.7 in nitrogen atmosphere.

The separation of the product modified from the starting compounds was performed by dissolution of unaltered part of ethylene—vinyl acetate copolymer in toluene and, to remove unchanged acrylamide, the insoluble part was subjected to further extraction by methanol.

The conversion of irradiated AA was determined by dissolution of monomer in methanol. The e.s.r. measurements were carried out on an ER-9 (Zeiss, Jena) spectrometer.

AA content in hybrid (EVAc modified) was determined from that of nitrogen using Perkin—Elmer Model 240 analyzer.

Results

Fig. 1 shows the time dependence of ethylene—vinyl acetate copolymer (EVAc) degradation. After 4 hours degradation of about 50% of macromolecules was obtained. The time dependent amount of scission calculated from curve on Fig. 1 is shown in Table 1.

![Fig. 1. The time dependence of mechanical degradation of ethylene—vinyl acetate copolymer at 20°C.](image)

The amount of scission $Z$ was calculated from the relation [9]

$$Z = m N_A \left( \frac{1}{M_\tau} - \frac{1}{M_0} \right),$$

<table>
<thead>
<tr>
<th>$\tau$ [min]</th>
<th>$Z \times 10^{-18}$ [spin/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.174</td>
</tr>
<tr>
<td>30</td>
<td>1.957</td>
</tr>
<tr>
<td>45</td>
<td>2.91</td>
</tr>
<tr>
<td>60</td>
<td>3.24</td>
</tr>
<tr>
<td>75</td>
<td>4.00</td>
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</tbody>
</table>
where \( m \) = amount of polymer in g,
\[ N_A = \text{Avogadro's number}, \]
\[ M_0, M_\tau = \text{molecular weight of polymer at time } 0 \text{ and } \tau. \]

Conversion of ethylene—vinyl acetate copolymer as a function of modification time is shown in Fig. 2. Initially, the conversion increases rapidly, stabilizing, however, at the value of 50—60\% after 15 minutes. There was no difference in conversion using either irradiated or non-irradiated acrylamide. Polyacrylamide content in the hybrid was about 31\% in both cases, independently of modification time.

![Fig. 2. Conversion of ethylene—vinyl acetate copolymer as a function of modification time using irradiated (○) and non-irradiated (●) acrylamide.](image)

**Fig. 3.** The e.s.r. spectra of acrylamide obtained under the same conditions.

a) crystalline acrylamide irradiated for 6 hours at —196°C by doses of 0.357 Mr/hr;

b) just as sub a) and rubbed in mill.

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The e.s.r. spectra indicating free radical concentration after the acrylamide irradiation and hybridization are shown in Figs. 3 and 4.

Fig. 3 shows the spectra of irradiated acrylamide obtained under the same conditions. Mechanical crushing of crystals leads to the decrease of radical concentration when compared with the original concentration.

![Fig. 3](image1)

**Fig. 4.** The e.s.r. spectra of samples after mechanical modification of ethylene—vinyl acetate copolymer by acrylamide.

a) irradiated acrylamide; b) non-irradiated acrylamide.

Fig. 4 shows the e.s.r. spectra obtained after EVAc modification by acrylamide. The spectrum obtained when using irradiated acrylamide does not correspond to the spectrum of AA radical and it may well be attributed to peroxide radical (Fig. 4a). Its concentration is very low. The spectrum obtained when using non-irradiated acrylamide is the superposition of acrylamide and peroxide spectrum (Fig. 4b).

**Discussion**

Mechanochemical modification of polymers is determined by macroradical generation in the place of polymer chain scission, under the influence of mechanical forces. Should an appropriate monomer be present in the system, the macroradicals might well initiate the polymerization resulting in the formation of hybrid (usually block polymer).

It follows from the data given in Fig. 1 or Table 1 that after 15 minutes the scission of approximately 10% of the original macromolecules takes place. However, the conversion of EVAc after 15 minutes is higher than 50%. This may be due to the following factors:

a) In the modification the degradation of the main polymer proceeds more rapidly owing to the change of physical properties of the system in the presence of acrylamide (filler effect).

b) The presence of acrylamide might be more efficient in hindering the recombination of macroradicals arising by destruction of EVAc.

c) Transfer reactions with polymer chain.

The last factor, however, contradicts the fact that in using irradiated AA (radical concentration $1.1 \times 10^{18}$ spin/g) the conversion does not further increase. It is possible
that the radicals introduced into the system by irradiated acrylamide are not in a position to make the transfer reactions. The effect of AA radicals obtained by irradiation on the modification should be manifested by using a polymer of sufficiently low molecular weight not degrading any more under given conditions. In the experiments of this type the modification was not observed. In this connection it should be noted that in the course of mechanochemical modification, crushing of acrylamide crystals and hence the stripping of radical centres take place. In mechanochemical modification quite a considerable decrease (Figs. 3 and 4) was observed in the spectrum. This suggests a particular course of AA polymerization in mechanochemical modification when compared with AA polymerization after its irradiation. It seems that in the present case, the macroradical of rubber component is effective. Should AA polymerization mostly proceed at crystal defects [4, 5] then the rubber chain mobility might affect crystal configuration destructively.

AA radical instability is another peculiarity when compared with AA polymerization in solid state. The papers [10, 11] state oxygen not to have any substantial influence on acrylamide radical stability. According to Kuri [10] it might well be due to weak hydrogen bonds. In the case of mechanochemical modification peroxidic radical at room temperature (Fig. 4) and, when irradiated AA was used, both the acrylamide and peroxidic radicals have been observed. By crushing the irradiated AA the radical concentration decreases but the spectrum shape does not change. The superposition observed may be assumed to be a specific case of the modification and the mechanochemical polymerization of AA may be supported by a mechanism other than post solid-state irradiation.

References


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