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Ethylene-Acrylic Acid Copolymers via Thermal Cracking

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ABSTRACT

It has been found that ethylene-acrylic acid copolymers can be prepared by extruder cracking of ethylene-isopropyl acrylate copolymers. The cracking of the ester to the acid goes very smoothly to give 90-100% conversion; however, the melt index behavior of the product is quite complex. The melt index of the starting ester copolymer was 2.0, but the melt index of the thermally cracked product immediately after extrusion was only 0.1. On standing, the melt index of the product slowly increased to 30.0. This complex melt index behavior is related to anhydride formation and chain scission reaction in the extruder. The anhydride linkages give a pseudocross-linked structure and lead to an initial low melt index value. On standing, the anhydride groups are hydrolyzed with water from the atmosphere to give an uncross-linked acid copolymer. After the acid is formed, the main chain polymer scissions that have occurred during extrusion become evident and the high melt index value is observed.

INTRODUCTION

Production of ethylene-acrylic acid copolymers is usually accomplished by the direct, free radical polymerization of the monomers

[1] or by saponification of an ethylene-alkyl acrylate copolymer [2]. In the first process, high-temperature, high-pressure corrosion problems exist, while the second process involves multiple steps.

A third possible route to the production of the ethylene-acrylic acid copolymers is thermal cracking of ethylene-alkyl acrylate copolymers. Literature references concerning the thermal stability of alkyl acrylate homopolymers [3], together with preliminary thermal gravimetric analysis studies on various ethylene-alkyl acrylate copolymers, revealed that the methyl and ethyl esters are stable whereas the isopropyl and t-butyl esters can be thermally decomposed to yield acrylic acid.

Isopropyl acrylate has a lower molecular weight than t-butyl acrylate; therefore, a lower weight percent isopropyl ester is required to yield a given acrylic acid level than if the t-butyl ester was used in the starting copolymer. It is for this reason that ethylene-isopropyl acrylate was chosen for use in this study. In fact, the results reported in this paper are limited to a study of a 30 wt% isopropyl acrylate-ethylene copolymer prepared by a conventional autoclave polymerization process using a peroxide initiator. Complete thermal cracking of this copolymer should yield a 21% acrylic acid-ethylene copolymer. Both the polymerization and thermal cracking reactions are shown in Fig. 1. As no unusual problems were encountered in the polymerization reaction, this paper will only be concerned with the thermal cracking reaction.

EXPERIMENTAL

Extruder

All of the cracking was carried out using a 2 $\frac{1}{2}$ in. Black Clawson vented extruder. Variables that were investigated included temperature, screw speed, feed rate, and water injection. The percent conversion of the acrylate ester to acrylic acid was used to measure the effect of the various variables on the extruder cracking.

Infrared Method

Infrared measurements proved to be a rapid and convenient way of determining the percent conversion in the polymer samples. However, infrared is not a primary standard technique, and in order to use it, calibration curves must be constructed. These were prepared using carefully purified ethylene copolymers that were analyzed for oxygen via neutron activation analysis to obtain their composition. The infrared calibration curves are shown in Fig. 2, and the percent conversion of the thermally cracked copolymers were calculated from these curves using the following formula:

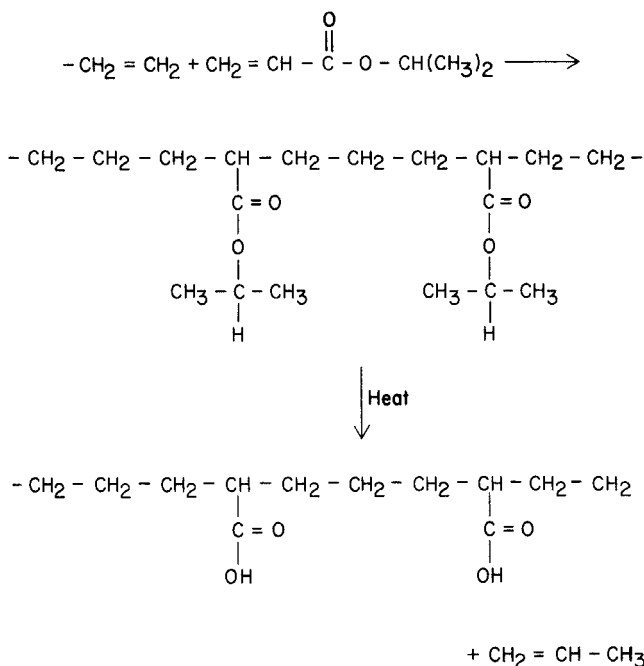


FIG. 1. Thermal cracking route to ethylene-acrylic acid.

$$\% \text{ conversion} = \frac{\text{wt}\% \text{ acrylic acid}}{\text{wt}\% \text{ acrylic acid} \times 0.63 (\text{wt}\% \text{ isopropyl acrylate})}$$

Analytical Methods

Melt index measurements were made according to ASTM procedure D-1238-70 for polyethylene at 190°C. Solution viscosities were made using a 3:1 xylene:acetic acid solvent at 70°C. Other polymer characterization, chromatographic, and infrared techniques reported in this paper are by standard analytical procedures.

RESULTS AND DISCUSSION

Extruder Variables

The effects of temperature, screw speed, and feed rate on the conversion of the isopropyl acrylate group to acrylic acid are given in Fig. 3. As expected, the results in Fig. 3 indicate the higher the

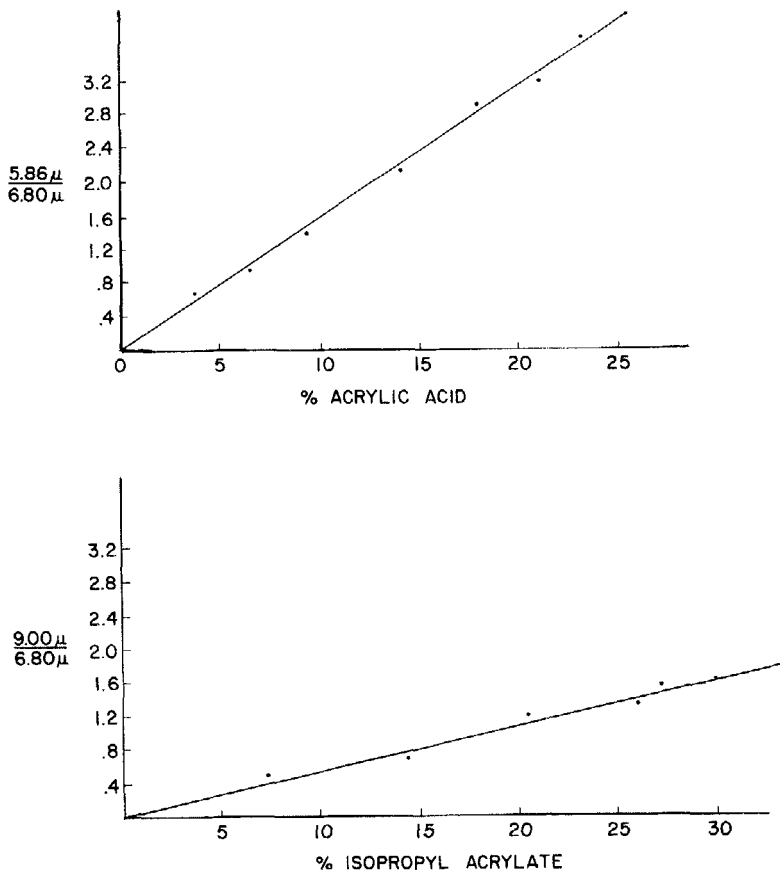


FIG. 2. Infrared calibration curves.

temperature, the greater the conversion. While not precisely defined, it would appear that temperatures in the 380-390°C range are needed for significant thermal cracking to occur.

An unexpected key variable turns out to be the feed rate. The lower the feed rate, the higher the conversion. This no doubt shows that a long residence time at the cracking temperature is needed to obtain the desired thermal decomposition. The low feed rate needed to obtain high conversion certainly will be a challenging engineering problem if the process is to be scaled to commercial-sized production.

From Fig. 3 it can be seen that the extruder speed has only a minor effect on the results. The other extruder variable that was investigated involved water injection and it had no effect on the results.

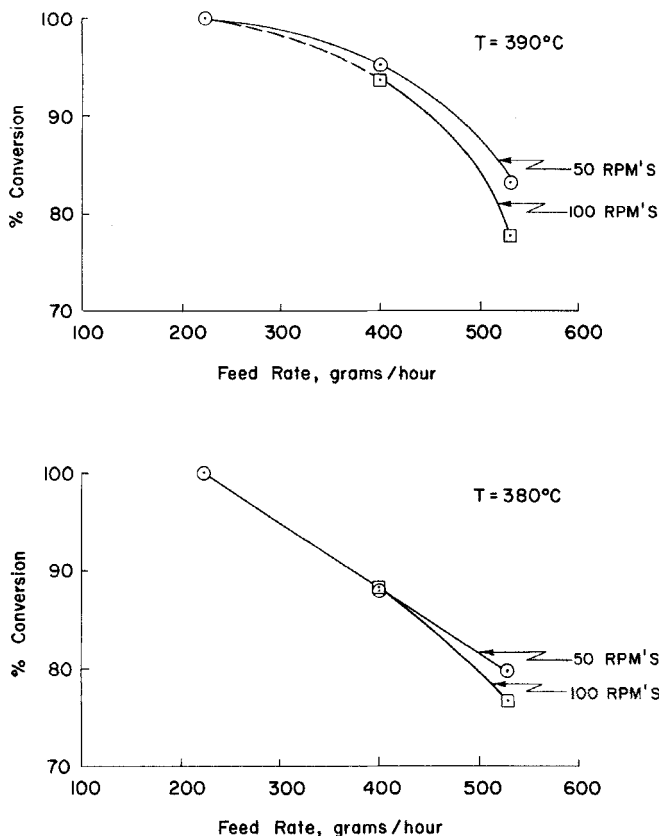


FIG. 3. Effect of extruder variables on percent conversion.

Vent Gas Analysis

If the extruder cracking is carried out at 390°C using a feed rate of 400 g/hr, Fig. 3 indicates about 95% conversion of the isopropyl groups to acid groups. Examination of the equation shown in Fig. 1 indicates that if the cracking is proceeding in the indicated manner, then a large amount of propylene should be produced. To see if this was actually occurring, a sample of the vent gas was obtained and analyzed by gas chromatography. Results are given in Table 1, where it is noted that the majority of the vent gas is indeed propylene. This result indicates that the isopropyl acrylate cracking is proceeding as expected in the extruder.

TABLE 1. Analysis of Vent Gas

Gas chromatograph results	
Propylene	98.8%
Butane	1.0
Ethylene	0.2
Methane	0.01
Carbon monoxide	0
Carbon dioxide	0

Melt Index

The melt index of the starting isopropyl acrylate copolymer was 2.0 and it was expected that the cracked product would have a similar melt index. However, the initial melt index of the product was very low, but the melt index of the cracked product slowly increased from 0.1 to 30 on standing.

Further study of this intriguing melt index result showed that the rate of increase of melt index with time depended on the environment to which the polymer pellets were exposed. These results are shown in Fig. 4. If the pellets are kept absolutely dry, no increase in melt index occurs, while a humid atmosphere gives a rapid increase in melt index to its equilibrium value.

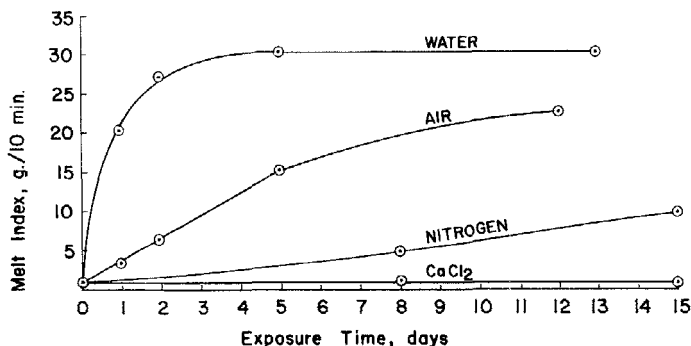


FIG. 4. Effect of environment on the melt index of EAA copolymers.

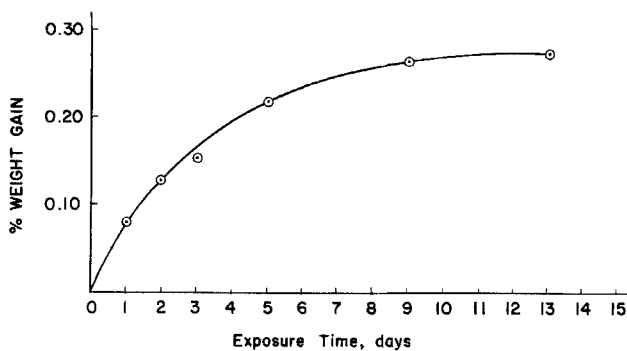


FIG. 5. Weight change of EAA copolymers exposed to 50% relative humidity at 70° F.

Weight Increase

The above results suggest that the thermally cracked polymer as produced in the extruder is an anhydride cross-linked structure that slowly reacts with water from the air to give an uncross-linked polymer. If this were true, a small weight gain would be expected if the polymer pellets were stored in a humid atmosphere. This is what was observed, as Fig. 5 indicates.

Infrared Analyses

The films pressed for the measurements of percent conversion by infrared showed no indication of anhydride linkages. This is probably the result of the films' being compression molded in a humid atmosphere. Very careful fabrication of infrared films under anhydrous condition gave spectra which had small peaks at 5.59, 5.70, and 9.8 μm . These are probably due to anhydride linkages [4]. Exposure of these films to water vapor caused these peaks to disappear, while exposure to vapors of heavy water caused these peaks to disappear and new peaks at 4.35 and 4.8 μm to appear. These new peaks are probably caused by $-\text{OD}$ structure [5] on the acid group.

Solution Viscosities

The anhydride formation probably explains the low initial melt index values, but the final melt index value is much higher than what would be expected if just the ester groups were removed during the extruder cracking. The most logical explanation for the high ultimate melt index is that the main polymer chains are undergoing scissions

TABLE 2. Copolymer Properties

	Isopropyl acrylate copolymers	Acrylic acid copolymer	
		Saponification	Thermal cracking
Melt index	2	0.5	30
Solution viscosity	-	0.945	0.368
Unsaturation:			
Vinylene	0	0	0.46
Vinyl	0	0	0.29

during the extruder cracking, thus leading to a lower molecular weight product. To investigate this possibility, the solution viscosities of ethylene-acrylic acid copolymers derived from the same starting ethylene-isopropyl acrylate copolymer via the thermal cracking route and via saponification were measured. These results, together with the melt index of the two products, are given in Table 2. From these data it is clear that the polymer chains have undergone some degradation during the extruder cracking.

Unsaturation

Further proof that the thermally cracked polymer has undergone some chain scission is seen in the unsaturation values reported in Table 2. These were obtained by infrared techniques and clearly show that the unsaturation values are higher for the cracked copolymer than the saponification copolymer product. Nevertheless, the unsaturation values for the thermally cracked product are in the range found in some commercial grades of polyethylene [6]. Indeed, none of the indications of polymer degradation during extrusion suggests that the resultant product is not of commercial interest.

SUMMARY

It has been shown that an ethylene-isopropyl acrylate copolymer can be thermally cracked in an extruder to yield an ethylene-acrylic acid copolymer. The mechanism of extruder cracking causes anhydride formation and chain scission, as well as removal of propylene from the polymer. The anhydride formation manifests itself as a low melt index product that initially comes from the extruder. On standing, the anhydride groups are hydrolyzed with water from the atmosphere to give the ethylene-acrylic acid copolymer. The ultimate

ethylene-acrylic acid copolymer has a high melt index which reflects that chain scission has occurred during the extruder cracking.

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