Nitric Acid Digestion and Crystallinity of Ethylene–Vinyl Acetate Copolymers

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Synopsis

Nitric acid digestion studies of ethylene–vinyl acetate copolymers indicated that copolymers containing identical amounts of vinyl acetate but varying in melt index differed in crystallinity. These results were confirmed by x-ray analysis. The differences in crystallinity were interpreted as showing a variation in the degree of short-chain branching in the polyethylene segments of the copolymer chain. This variation was correlated with the conditions of synthesis.

Introduction

During an investigation of the morphology of ethylene–vinyl acetate copolymers in which digestion by nitric acid[1] was employed to remove the amorphous material, some unexpected results were observed.

It is known that the vinyl acetate content controls the crystallinity of the system, and digestion experiments showed, as expected, that the ultimate weight loss of a copolymer was related to the vinyl acetate content. However, when samples of identical vinyl acetate content but different melt index were examined, anomalous results were obtained, i.e., as the molecular weight of the copolymer increased, as reflected by the drop in melt index, its crystallinity increased. These results were subsequently confirmed by x-ray analysis at room temperature.

Experimental

The nitric acid digestion technique involves suspending the polymer in 95% nitric acid at 70°C., which results in the preferential digestion of the amorphous material. The per cent weight loss is plotted against digestion time. The curve levels off when practically all the amorphous material is consumed, and at this point an estimate can be made of the relative crystallinities of the materials at the digestion temperature.

The method employed to calculate the crystallinity of the copolymers from the x-ray data was that described by Kamath and Wakefield.[2]

The copolymers used in this study were all prepared under similar conditions, i.e., at high pressure with a free-radical initiator in the absence of a chain-transfer agent. It was assumed that any data obtained concerning

the random nature and molecular weight distribution of one of the copoly-
mers could be applied equally to all the copolymers.

It is known from the reactivity ratios for the free-radical copolymeriza-
tion of ethylene with vinyl acetate that the copolymers will be random.
However, in order to confirm that the copolymers were homogeneous, two
of them, A and E, were fractionated, and a few fractions were taken at
random and analyzed for vinyl acetate content. As expected, the results
shown in Table I confirmed that the vinyl acetate was randomly distributed
throughout the copolymer.

TABLE I
Fraction of Copolymers A and E for Examination of Homogeneity

Copolymer A			Copolymer E		
Fraction number	Inherent viscosity, dl./g.[a]	Vinyl acetate, wt.-%	Fraction number	Inherent viscosity, dl./g.[a]	Vinyl acetate, wt.-%
1	0.23	21	1	0.25	26
3	0.34	20	3	0.52	26
7	0.58	20	8	0.82	25
10	0.01	20	12	1.37	25
12	1.63	21	15	1.93	25
Whole polymer	0.99	20.5	Whole polymer	0.88	25.5

[a] Inherent viscosities were measured in decalin at 135°C. at a concentration of 0.1
g./dl.

In order to confirm that melt index was a measure of molecular weight for
these particular copolymers, three copolymers covering a wide range of
melt index were analyzed by gel permeation chromatography (GPC).
The curves obtained are shown in Figure 1, and the number-average and
weight-average molecular sizes calculated from the distribution curves are
given in Table II.

TABLE II
Molecular Sizes and Melt Indices of Ethylene–Vinyl Acetate Copolymers[a]

Copolymer	Vinyl acetate, %	Melt index, g./10 min.	A_n	A_w	$R = A_w/A_n$
A	20.5	1.4	2408	5831	2.42
B	20.0	25	1510	4408	2.92
C	20.3	180	1347	3609	2.68

[a] A_n = number-average molecular size (proportional to number-average molecular
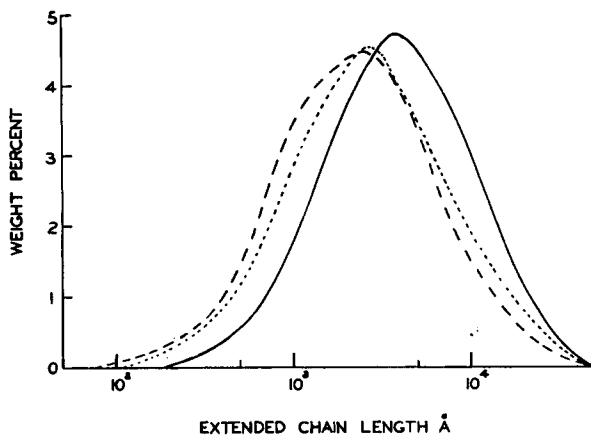weight); A_w = weight-average molecular size (proportional to weight-average molecu-
lar weight).

Fig. 1. GPC curves for copolymers A, B, and C: (——) copolymer A; (- - -) copolymer B; (· · ·) copolymer C.

It is apparent from Figure 1 that all the copolymers exhibit a symmetrical molecular weight distribution. From Table II one can qualitatively say that for the copolymers used in this study that melt index is an indication of the molecular weight of the material.

Results and Discussion

Three ethylene–vinyl acetate copolymers having similar vinyl acetate contents but differing widely in melt index were subjected to nitric acid digestion. The weight loss versus time curves are shown in Figure 2, and their vinyl acetate contents and melt indices are listed in Table III.

It can be seen that a decrease in the molecular weight, as reflected by an increase in the melt index, results in higher weight loss instead of a constant weight loss. This may be interpreted as showing that the material of low molecular weight is degraded to a soluble entity more rapidly than material of high molecular weight as a consequence of the shorter chain length of the former. However, if this were true, each copolymer would have the same ultimate weight loss. A second explanation could be that the copolymers are not homogeneous, i.e., the vinyl acetate is not randomly distributed throughout all the polymer chains but is concentrated in the lower molecular weight fractions which could lead to the results shown

TABLE III
Copolymers Digested in Nitric Acid

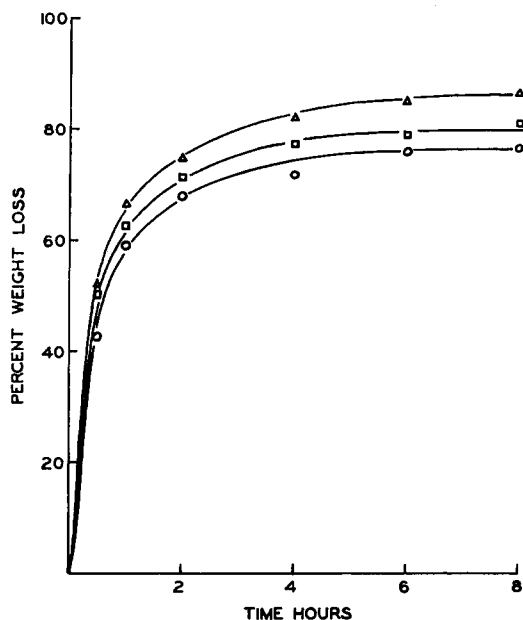| Copolymer	Vinyl acetate, %	Melt index, g./10 min.
A	20.5	1.4
B	20.0	25
C	20.3	180

Fig. 2. Nitric acid digestion of ethylene–vinyl acetate copolymers of varying melt index: (O) copolymer A; (□) copolymer B; (△) copolymer C.

in Figure 1. However, it has already been shown that the copolymers are homogeneous in this respect. A third explanation is that there are subtle differences in the chain structure which allows the higher molecular weight material to attain a greater degree of crystallinity than the other copolymers.

In order to verify the latter, x-ray measurements were performed on a series of copolymers of various vinyl acetate contents and melt indices. The copolymers used in this investigation are listed in Table IV, and the x-ray crystallinity results are plotted as a function of the vinyl acetate content in Figure 3.

TABLE IV
Copolymer Composition and Melt Index

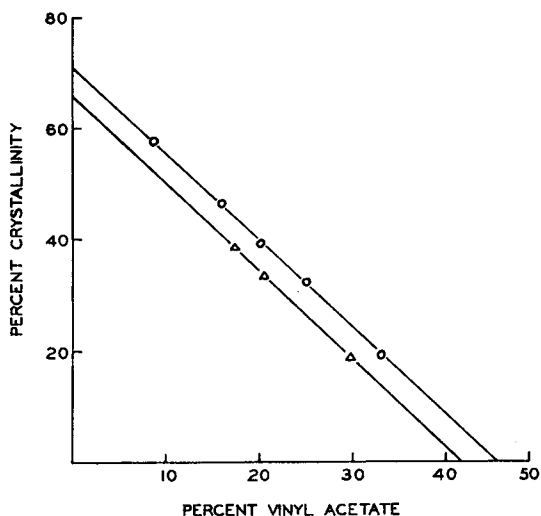| Copolymer	Vinyl acetate, %	Melt index, g./10 min.	Crystallinity, %
J	8.9	1.7	57.5
D	16.8	1.0	46.9
A	20.5	1.4	39.7
E	26.0	2.6	32.8
F	33.6	12.9	19.0
G	17.4	240	38.7
C	20.3	180	33.7
H	30.0	139	19.2

Fig. 3. X-ray crystallinities of ethylene–vinyl acetate copolymers: (△) copolymer melt index = >100 g./10 min.; (○) copolymer melt index 1–13 g./10 min.

In the ethylene–vinyl acetate copolymer system only the polyethylene segments are crystallizable; therefore, the major factor controlling the crystallinity is the vinyl acetate. However, it is readily seen in Figure 3, that the higher molecular weight copolymers achieve greater crystallinity than other copolymers of the same vinyl acetate content. This indicates that there are differences in the structure of the polyethylene segments. These differences have been attributed to short-chain branching, since it is known that the crystallinity of polyethylene is inversely dependent upon the degree of branching.[3]

In order to produce polyethylene of high molecular weight it is necessary to use low temperatures and high pressures. These conditions also minimize the number of branches introduced onto the polymer backbone. The molecular weight of the copolymers is controlled likewise. Therefore, it is probable that the polyethylene segments vary similarly in their degree of short-chain branching, which results in the variation of crystallinity for copolymers having identical vinyl acetate contents but differing molecular weights.

This work illustrates the sensitivity of the nitric acid digestion technique in detecting subtle differences in polymer structure, even in materials of relatively low crystalline content.

References

1. R. P. Palmer and A. J. Cobbold, *Makromol. Chem.*, **74**, 174 (1964).
2. P. M. Kamath and R. W. Wakefield, *J. Appl. Polymer Sci.*, **9**, 3153 (1965).
3. W. M. D. Bryant and R. C. Voter, *J. Am. Chem. Soc.*, **75**, 6113 (1953).

Résumé

Des études de digestion de l'acide nitrique de copolymères d'acétate de vinyle–ethylène indiquaient que les copolymères contenant des quantités égales d'acétate de vinyle mais d'indice de fusion variable différaient du point de vue de la cristallinité. Ces résultats sont confirmés par analyse aux rayons-X. Les différences de cristallinité ont été interpréteés comme indiquant une variation dans le degré deramification courte des chaînes dans les segments de polyéthylène de la chaîne copolymérique. Cette variation était reliée aux conditions de synthèse.

Zusammenfassung

Untersuchungen über die Einwirkung von Salpetersäure auf Äthylen–Vinylacetat-copolymere zeigten, dass Copolymer mit identischem Gehalt an Vinylacetat aber ver-schiedenem Schmelzindex sich in ihrer Kristallinität unterscheiden. Diese Ergebnisse wurden durch Röntgenanalyse bestätigt. Die Kristallinitätsunterschiede wurden als ein Hinweis auf eine Variation des Kurzketten-Verzweigungsgrades in den Polyäthylen-segmenten der Copolymerkette interpretiert. Diese Variation wurde zu den Synthese-bedingungen in Beziehung gebracht.