

Response of Polyethylene to Acid Etching

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Synopsis

Several samples of polyethylene were exposed to attack by fuming nitric acid and the resulting changes in density, infrared absorption, and visual appearance were recorded. The motivation for this investigation lies in the possibility of using acid etching as a means of studying the structure of interspherulitic regions in polyethylene and the relations between these and structure-sensitive properties such as stress-crack resistance. The results indicate that certain parts of the samples were attacked preferentially by the acid; the residual material, though of a porous gross structure, was of higher density than that of the average initial material. The differences in visual appearance were the most dramatic and appear to correlate with stress-crack resistance. Insofar as quantitative characterization of interspherulitic regions are concerned, the merits of this method of investigation are still in doubt and await further study.

Introduction

It is generally accepted that the microscopic structure of crystalline polymers, such as polyethylene, consists of crystalline regions which are further organized into larger morphological units, namely spherulites.¹⁻³ Impurities, including molecular weight fractions or portions of the molecule which act as impurities, are present mainly in the noncrystalline interspherulitic regions. It is to be expected that certain physical properties of these polymers will be sensitive to minor changes in the composition and arrangement of the interspherulitic regions. However, there is no existing method by which changes in the structure of these regions can be characterized and consequently no way of investigating such relations, even if they do exist. In view of this need, it was felt that acid etching could be used as a technique for selectively characterizing such morphological aspects of the crystalline polymers.^{4,5} It was anticipated that fuming nitric acid would preferentially attack the less crystalline and less organized portions first, leaving the more crystalline material unharmed and suitable for detailed study. In this manner the relationship between physical properties and polymer structure could be explored in a meaningful way.

In this investigation three samples of polyethylene of different molecular weights, densities, and melt indices were exposed to fuming nitric acid for periods of time ranging from 15 min. to 16 hr. at 60, 70, 80, and 90°C. Changes in density, infrared spectra, and visual appearance were followed and are reported in this memorandum. Electron micrographs and x-ray

diffraction patterns were also obtained on the samples exposed for 16 hr. at 90°C.; however, these data did not reveal significant differences between polymers and are not included in this report. It is anticipated, however, that with appropriate changes, including the uniaxial stressing or biaxial stressing of the polymer, more pertinent data may be obtained.

Eleven other well characterized experimental polyethylenes obtained from E. I. du Pont de Nemours and Company were also investigated. The preliminary density changes after exposure at 70°C. are reported here. As in the case of the other three polymers, these density changes reflect principally the amount of extremely low molecular weight fraction present in the polymer but until other appropriate data become available no firm conclusion can be drawn.

Experimental

Three samples of polyethylene, Alathon 5B, Alathon 17, and PE 3553, manufactured by E. I. du Pont de Nemours and Company, were used in this investigation. Polymer pellets were molded into 0.050 in. sheets and

TABLE I
Changes in Density of Polyethylene after Acid Etching Treatment

Temp., °C.	Time, hr.	Alathon 5B (original y = 0.9170 g./cc.)		Alathon 17 (original y = 0.9250 g./cc.)		PE 3553 (original y = 0.9195 g./cc.)	
		y , g./cc.	Δy , g./cc.	y , g./cc.	Δy , g./cc.	y , g./cc.	Δy , g./cc.
60	1/4	0.9190	0.0020	0.9250	0.0000	0.9200	0.0005
	1	0.9200	0.0030	0.9250	0.0000	0.9200	0.0005
	2	0.9270	0.0100	0.9260	0.0010	0.9215	0.0020
	4	0.9280	0.0110	0.9280	0.0030	0.9235	0.0040
	8	0.9310	0.0140	0.9315	0.0065	0.9305	0.0110
	16	0.9410	0.0240	0.9380	0.0130	0.9385	0.0190
70	1/4	0.9200	0.0030	0.9250	0.0000	0.9200	0.0005
	1	0.9210	0.0040	0.9260	0.0010	0.9200	0.0005
	2	0.9220	0.0050	0.9270	0.0020	0.9230	0.0035
	4	0.9280	0.0110	0.9280	0.0030	0.9210	0.0025
	8	0.9420	0.0250	0.9405	0.0155	0.9385	0.0190
	16	0.9800	0.0630	0.9705	0.0455	0.9715	0.0520
80	1/4	0.9190	0.0020	0.9280	0.0030	0.9235	0.0040
	1	0.9210	0.0040	0.9305	0.0055	0.9280	0.0085
	2	0.9250	0.0080	0.9375	0.0125	0.9380	0.0185
	4	0.9780	0.0510	0.9625	0.0375	0.9600	0.0405
	8	0.9855	0.0685	0.9860	0.0610	0.9875	0.0680
	16	1.0105	0.0935	1.0063	0.0813	1.0085	0.0890
90	1/4	0.9210	0.0040	0.9285	0.0035	0.9245	0.0050
	1	0.9245	0.0075	0.9319	0.0069	0.9290	0.0095
	2	0.9265	0.0095	0.9380	0.0130	0.9390	0.0195
	4	0.9868	0.0698	0.9640	0.0390	0.9660	0.0465
	8	0.9945	0.0775	0.9965	0.0715	0.9950	0.0755
	16	1.0250	0.1080	1.0280	0.1030	1.0290	0.1095

also into 0.002 in. films. Rectangular specimens (1.0 × 0.50 in.) were cut from the sheets and films respectively, and placed in flasks containing fuming nitric acid. These flasks and their contents were maintained at constant temperatures to within $\pm 2^\circ\text{C}$. by means of a circulated oil bath. Water-cooled condensers were used to prevent loss of acid vapor. After the prescribed period of time, the samples were removed from the flasks, washed in distilled water for 24 hr. or until the pH was 7. Prior to the density measurements the specimens were dried in a vacuum oven for about 16 hr. at 50°C .

Infrared spectra were obtained on the thin films with the Perkin-Elmer Model 21 dual-beam infrared spectrometer. The visual appearance of the treated materials was examined with an optical microscope.

Results and Discussion

The density changes caused by the acid etching of three polyethylenes are found in Table I and Figures 1-3. In general, the densities γ of the treated samples increased with increase in exposure time and temperature. The density differences ($\Delta\gamma$) divided sharply when the samples were exposed for more than 2 hr. and at above 80°C . (Figs. 1-3). It is readily seen in Table I that there is a very small change between the 60 and 70°C . densities especially if one omits the 16-hr. exposure. In viewing the density differences in Figures 1-3 it is apparent that the Alathon 17 shows the smallest net changes, next the PE 3553 and the Alathon 5B shows the greatest differences at most exposure levels. This indicates that the Al-

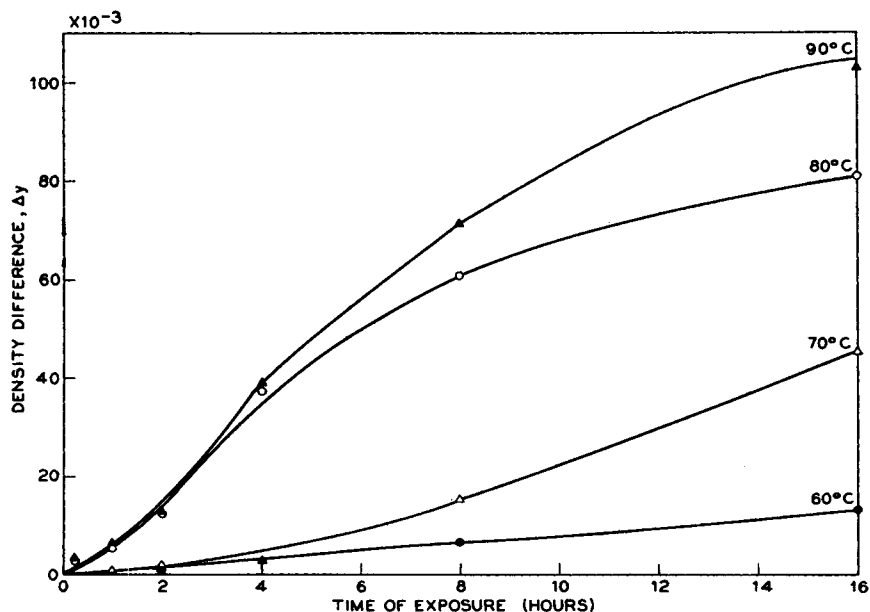


Fig. 1. Density difference for Alathon 17 after exposure to fuming nitric acid.

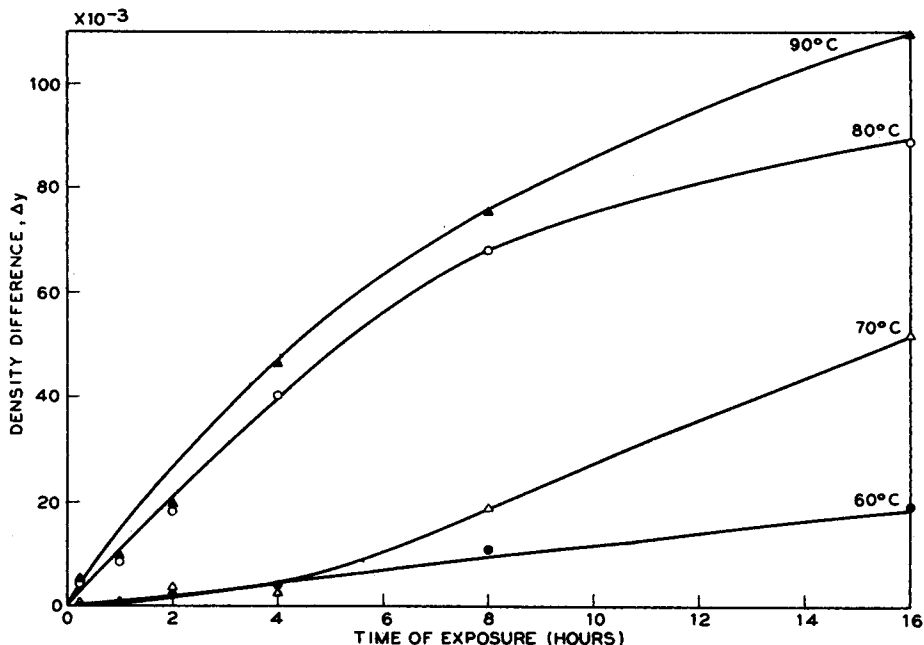


Fig. 2. Density difference for PE 3553 after exposure to fuming nitric acid.

athon 17 contains the smallest amount of low molecular weight material and Alathon 5B the largest.

In addition, eleven other du Pont experimental samples were exposed to fuming nitric for periods of time ranging from 15 min. to 4 hr. at 70°C. only. The measured density changes found in Table II show wide variations among the samples investigated. It is concluded and expected that the materials with the lower original density (0.9160–0.9225 g./cc.) show greater $\Delta\gamma$ values than those having the higher original density. The preliminary density variation of these eleven materials is tabulated mainly for comparison.

One noteworthy observation was that the three materials investigated appeared to be "eroded" after the nitric acid treatment of greater than 4 hr. and 80°C. This was especially noticeable after the prolonged and rigorous 16 hr. and 90°C. treatment. The Alathon 5B was usually the first one in the series to disintegrate or be fragmented in the acid flask.

The most noticeable changes in the typical infrared spectra are exhibited in Figure 4. The increase in the intensity of an N=O group at 6.12–6.15 μ is probably due to attack of the polymer by the nitric acid. The acid treatment apparently caused the formation of this N=O group to increase with time and/or temperature. The increase in the intensity of the 7.83 μ band was also apparently due to the nitric acid etching; however, the band is not easily identified. Another N—O vibration, appearing at 11.7 μ , is broad and is not shown in Figure 4. The polymers were certainly

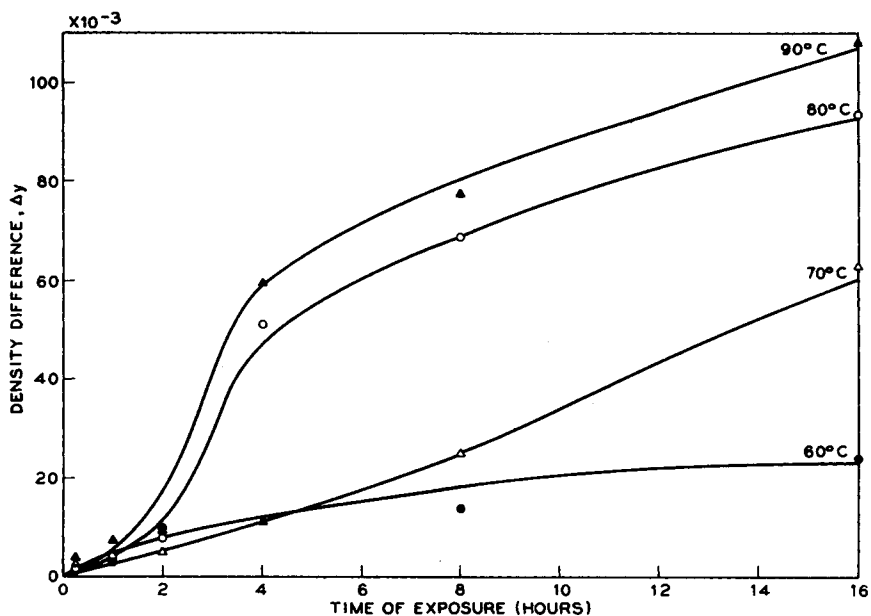


Fig. 3. Density difference for Alathon 5B after exposure to fuming nitric acid.

nitration and part of the density changes are due to nitration; however, although the effect of the nitro groups is small, no quantitative results are included in this report. A further examination of the infrared spectra indicates that HOH was present. Due to the fact that the samples contained water from the washing operation it is no consequence to this particular characterization.

The visual effects of 4 hr. of nitric acid treatment at 90°C. are shown in Figure 5. The photograph in the upper left is a 10× magnification of the three samples prior to treatment and the other photographs are 50× magnifications after etching. The differences evidenced by these photographs correlate with chloroform-extractable content of these polymers, that of Alathon 5B being the largest (Table III).

Conclusions

Three polyethylenes etched with fuming nitric acid increased in density with increased exposure of time and temperature. The average density of the polyethylenes increased from 0.9200 to 1.0270 g./cc. after etching for 16 hr. at 90°C. with nitric acid. It appears that the acid preferentially attacks the lower molecular weight fraction, leaving the higher density, more crystalline material untouched.

Further changes are recorded in photographs of the microscopic uniqueness of the surface structure of these materials. The photographs indicate that the surfaces of the treated samples were porous and coarse in texture, whereas the original samples were smooth, even and clear of cracks or

TABLE II
Density Changes of du Pont Experimental Samples after Acid Etching at 70°C.

Sample no.	Etching time, hr.	γ , g./cc.	$\Delta\gamma$, g./cc.
75	0	0.9160	—
	1/4	0.9155	0.0005
	1	0.9175	0.0015
	2	0.9223	0.0063
	4	0.9223	0.0063
76	0	0.9221	—
	1/4	0.9225	0.0004
	1	0.9238	0.0017
	2	0.9267	0.0046
	4	0.9270	0.0049
77	0	0.9210	—
	1/4	0.9210	0.0000
	1	0.9223	0.0013
	2	0.9238	0.0028
	4	0.9260	0.0050
78	0	0.9225	—
	1/4	0.9230	0.0005
	1	0.9240	0.0015
	2	0.9270	0.0045
	4	0.9276	0.0051
79	0	0.9223	—
	1/4	0.9220	0.0003
	1	0.9238	0.0015
	2	0.9267	0.0044
	4	0.9260	0.0037
80	0	0.9223	—
	1/4	0.9225	0.0002
	1	0.9232	0.0009
	2	0.9267	0.0044
	4	0.9264	0.0041
81	0	0.9203	—
	1/4	0.9208	0.0005
	1	0.9223	0.0020
	2	0.9238	0.0035
	4	0.9251	0.0048
82	0	0.9183	—
	1/4	0.9195	0.0012
	1	0.9207	0.0024
	2	0.9230	0.0047
	4	0.9238	0.0055
83	0	0.9330	—
	1/4	0.9339	0.0009
	1	0.9342	0.0012
	2	0.9345	0.0015
	4	0.9349	0.0019

TABLE II (continued)

Sample no.	Etching time, hr.	y , g./cc.	Δy , g./cc.
84	0	0.9512	—
	1/4	0.9518	0.0006
	1	0.9522	0.0010
	2	0.9520	0.0008
	4	0.9520	0.0008
85	0	0.9532	—
	1/4	0.9540	0.0008
	1	0.9544	0.0012
	2	0.9544	0.0012
	4	0.9550	0.0018

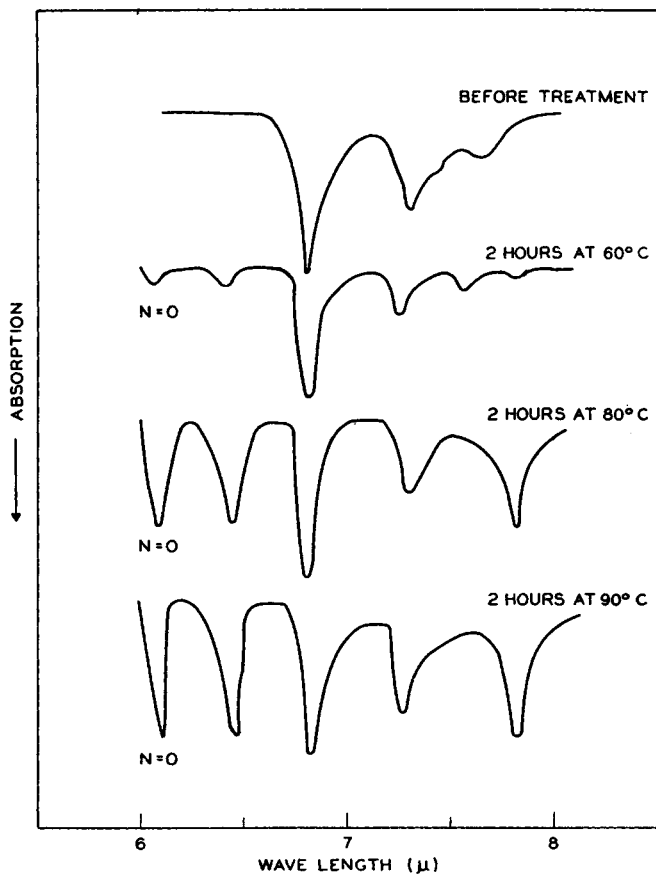


Fig. 4. Infrared spectra of polyethylenes exposed to fuming nitric acid.

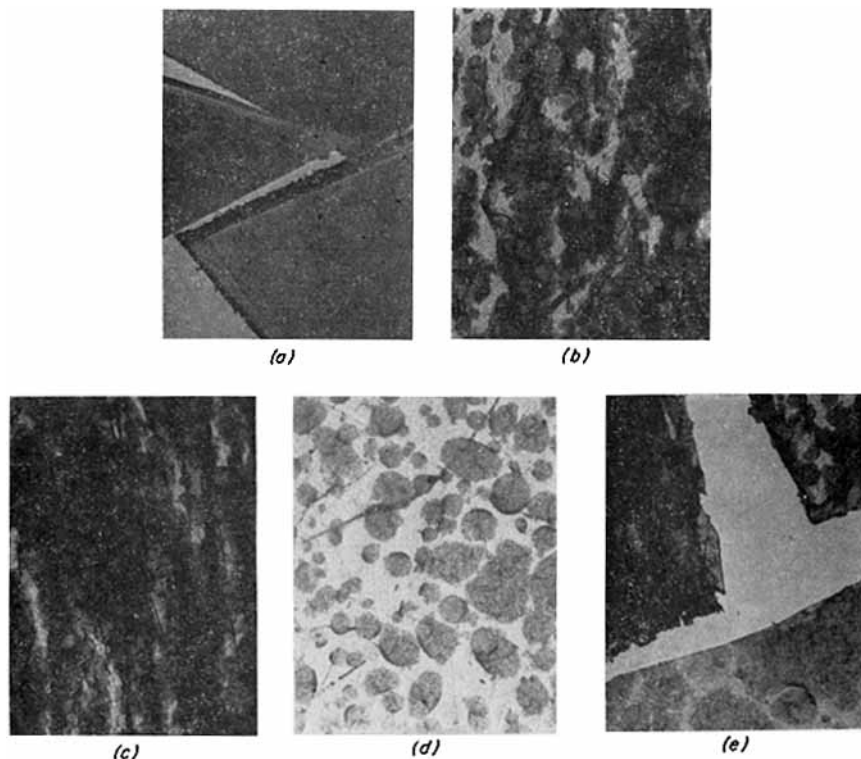


Fig. 5. Surfaces of the polymers before and after nitric acid etching: (a) composite before treatment (upper, Alathon 17; lower, Alathon 5B; left side, PE 3553), 10 \times ; (b) Alathon 5B, treated 4 hr. at 90°C., 50 \times ; (c) Alathon 17, treated 4 hr. at 90°C., 50 \times ; (d) PE 3553, treated 4 hr. at 90°C., 50 \times ; (e) composite after treatment (upper left, Alathon 17; upper right, Alathon 5B; lower, PE 3553), 50 \times .

fissures. Alathon 5B was noticeably the more readily attacked by the acid, next was Alathon 17, and PE 3553 appeared the most resistant to the vigorous etching mechanism. These findings correlate with chloroform extractable results of the polyethylenes under investigation.

The infrared data show that N=O and N—O are formed in the chemical treatment of the polymer films. The interpretations of the changes in density are complicated by the incorporation of the nitrogen and

TABLE III

	Melt index	Chloroform extractables, % ^a
Alathon 5B	1.4	7.6
Alathon 17	22.6	1.6
PE 3553	0.27	0.8

^a Information supplied by M. P. Schard, Jr., of our laboratory.

oxygen which undoubtedly adds to it. It is possible that with quantitative spectral information this component could be subtracted from the gross change. The remaining component then perhaps would reflect not only the extractable or amorphous content but also the manner in which they are incorporated into the interspherulitic regions. One might suggest that under biaxial stress acid etching would help to reveal the more subtle morphological differences.

It is clear that this method of study shows considerable promise insofar as investigations of polymer structures are concerned, but considerable further characterization work needs to be done.

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Résumé

Plusieurs échantillons de polyéthylène ont été soumis à l'attaque par l'acide nitrique fumant et on a enregistré les changements qui en résultent dans la densité, l'absorption infrarouge et l'aspect visuel. La justification de cette étude est liée à la possibilité d'utiliser l'attaque par l'acide comme moyen pour étudier la structure des régions intersphérolitiques dans le polyéthylène et les relations entre ces régions et les propriétés sensibles à la structure telles que la résistance à la cassure sous un effort de tension. Les résultats montrent que certaines parties des échantillons sont attaquées préférentiellement par l'acide; le produit résiduel, bien que d'une structure poreuse grossière, est d'une densité plus élevée que celle du matériau initial. Les différences dans l'aspect visuel sont les plus dramatiques et semblent être liées à la résistance à la cassure sous un effort de tension. Dans la mesure où on ne peut pas caractériser d'une façon quantitative les régions intersphérolitiques, les mérites de cette méthode sont encore douteux et attendent une étude plus poussée.

Zusammenfassung

Einige Polyäthylenproben wurden dem Angriff rauchender Salpetersäure ausgesetzt und die entstehenden Änderungen der Dichte, der Infrarotabsorption und des Aussehens festgestellt. Der Grund für diese Untersuchung liegt in der Möglichkeit, Säureätzung als Mittel zur Untersuchung der Struktur der Zwischensphärolithbereiche in Polyäthylenen und Beziehungen zwischen diesen Bereichen und strukturempfindlichen Eigenschaften wie Spannungsrissbeständigkeit zu verwenden. Die Ergebnisse zeigen, dass bestimmte Teile der Proben bevorzugt durch die Säure angegriffen wurden; das zurückbleibende Material besaß zwar eine poröse Gesamtstruktur, hatte jedoch eine höhere Dichte als dem Mittelwert des Ausgangsmaterials entspricht. Die Unterschiede im Aussehen waren am auffallendsten und scheinen zur Spannungsrissbeständigkeit in Beziehung zu stehen. Was die quantitative Charakterisierung der Zwischensphärolithbereiche betrifft, so ist die Brauchbarkeit dieser Methode hoch zweifelhaft und bedarf einer weiteren Untersuchung.

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