Thermogravimetric Analysis of the Effect of Ionizing Radiation on Thermal Stability of Polyethylene

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Synopsis

The effect of radiation on thermal and oxidative degradation of polyethylene was studied by thermogravimetric analysis. It was found that the thermal stability of polyethylene irradiated in a vacuum and in air at room temperature decreases with increasing radiation dose. In nitrogen the thermal decomposition of irradiated polyethylenes occurs in one stage without marked influences of the irradiation atmosphere. In the presence of air, oxidative degradation takes place in three stages, on which irradiation atmosphere has great effect. This is due to the difference in the chemical structure of irradiated polyethylenes.

INTRODUCTION

A number of experiments have been carried out on the thermal degradation of high polymers by use of the thermobalance, both isothermally[1-4] and thermoanalytically.[5-7] The effect of radiation on high polymers has also been studied by many workers.[8,9] Little work has been done, however, on the thermal degradation of the irradiated crosslinked polyethylenes, and their thermal stability is not yet understood in detail. By comparing the decomposition of linear polymethylene with that of polyethylene crosslinked by radiation, Wall et al.[10] concluded that crosslinking had little effect on the rate of thermal decomposition of polyethylene.

The present paper is devoted primarily to a study of the effect of radiation on thermal stability of polyethylene by thermogravimetric analysis.

The irradiation was carried out in air and in vacuum in order to investigate the effect of the atmosphere during irradiation on the thermal stability of irradiated polyethylene. Thermal decomposition of the irradiated polyethylenes was also carried out in air and in nitrogen.

EXPERIMENTAL

Apparatus for Thermogravimetric Analysis

The apparatus for thermogravimetric analysis (TGA) was designed and constructed in our laboratory.[11] It is essentially an automatic recording
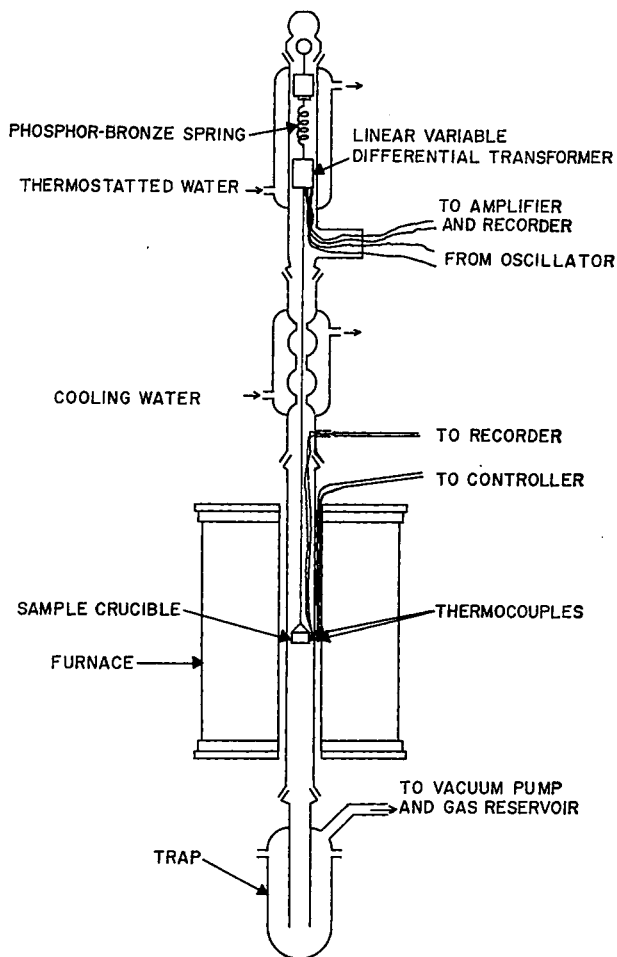
Fig. 1. Automatic recording thermobalance.

thermobalance with a phosphor–bronze helical spring and a linear variable differential transformer, and is similar to that reported by Hooley.[12] Its schematic diagram is shown in Figure 1.

A sample crucible is suspended by a glass thread to a core of the differential transformer which, in turn, is suspended by another thread to the tungsten spring. The primary coil of transformer is usually excited by an alternating current of 2 v. in 400 cycles/sec. The differential transformer generates an alternating current signal which is directly proportional to the linear displacement of the core from the electrical center of the transformer. This output is amplified, converted to direct current by a diode type phase discriminating converter, and fed into the first channel of a six-channel recorder. The recorder used is a 10 mv. electronic potentiometer.

The temperature of a cylindrical electric furnace is controlled by an electrical program controller, which senses the furnace temperature by means of a chromel–alumel thermocouple located between the furnace wall and a glass tube covering the sample crucible.

The temperature of the sample is measured with another chromel–alumel thermocouple located near the sample crucible in the glass tube, and the output of this thermocouple is recorded on the second channel of the recorder. The third channel of the recorder is used to monitor the temperature of the water circulating from a thermostatted bath through a jacket enclosing the spring and the differential transformer coil.

Preparation of Samples

The polymer used was a polyethylene (Sholex-50) supplied without additives by Showa Denko Co., Tokyo. This polymer, which is similar to Marlex-50, was reported to have a number-average molecular weight of 520,000.

Molded sheets of the polymer, 0.027 mm. thick, were placed in glass ampules and evacuated for several hours. The ampules were then sealed and irradiated with γ-rays from a Co^{60} source at room temperature for the required length of time. The dose rate in these experiments was approximately 4.1×10^5 r/hr. Some polymers were irradiated in air at room temperature.

A highly branched polyethylene (Sumikathene F-70), manufactured by Sumitomo Chemicals Co., was purified by precipitation and used without irradiation in comparison with the irradiated samples.

The samples investigated are summarized in Table I.

TABLE I
Conditions of Irradiation of Polyethylenes at Room Temperature

Sample	Radiation dose, Mr	Dose rate, r/hr. $\times 10^{-4}$	
		In vacuum	In air
Sholex-50[a]	Unirradiated		
	1	41	
	1.8		7.5
	5.2	41	11
	11	41	
	22		49
	30	60	60
	55	41	60
Sumikathene F-70[b]	Unirradiated		

[a] Linear polyethylene.
[b] Commercial high pressure polyethylene.

Experimental Procedure

In all runs, a sample of about 90 mg. was placed in a glass crucible and then the furnace temperature was continuously increased at a constant

rate of 1°C./min. from room temperature to approximately 450°C. in air or in nitrogen. The change in weight of sample is recorded as a function of temperature for the thermogravimetric analysis (TGA) curve. By a graphical differentiation of weight loss curve the rates of relative weight loss (in per cent/°C.) are plotted against the temperature for the derivative thermogravimetric analysis (DTGA) curve.

Amounts of gel fraction were determined by extracting the irradiated polymers to constant weight with boiling toluene.

RESULTS AND DISCUSSION

Thermogravimetric Analysis in Nitrogen

Polyethylene irradiated in a vacuum, unirradiated, and unirradiated highly branched polymers are decomposed in nitrogen at ambient pressure from 350 to 450°C. Their DTGA curves are shown in Figure 2. The curve of polyethylene irradiated at 55 Mr is similar to that of highly branched polymer, but different from the curve of unirradiated sample. This shows that the effect of irradiation on the thermal decomposition of polyethylene is similar to that of chain branching. A linear polyethylene is thermally more stable than a highly branched polyethylene, in agreement with the conclusion of the isothermal experiments by Wall and Straus.[4]

DTGA curves in nitrogen for two polyethylenes irradiated in air (at 5.2 and 22 Mr) are shown in Figure 3. It seems that the effect of irradiation in air on the thermal decomposition of polyethylene is the same as that of irradiation in a vacuum, but infrared spectra of the former samples in-
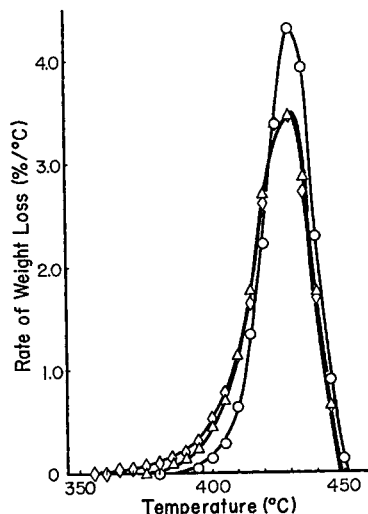

Fig. 2. Thermogravimetric analysis curves of irradiated polyethylenes in nitrogen: (O) unirradiated; (△) irradiated at 55 Mr in a vacuum; (◇) highly branched.
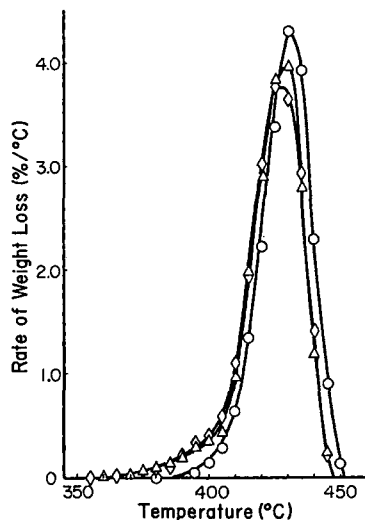
Fig. 3. Thermogravimetric analysis curves of irradiated polyethylenes in nitrogen: (O) unirradiated; (◊) at 5.2 Mr in air; (△) at 22 Mr in air.
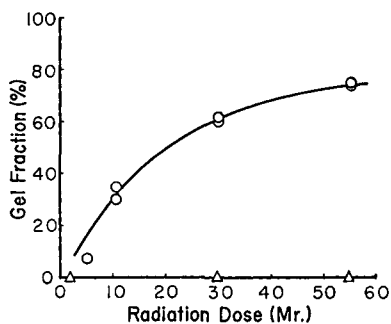

Fig. 4. Variation of gel fraction of polyethylene with radiation dose: (O) irradiated in a vacuum; (△) irradiated in air.

dicate that the carbonyl groups increase in the polymer with increasing radiation dose, while the latter does not show any carbonyl absorption. Polyethylene is reported to react with oxygen during irradiation in air.[13] Infrared spectra revealed also the increase in vinylene and decrease in vinyl type double bonds in polyethylenes irradiated in a vacuum with increasing radiation dose.[14]   The same trend was observed in polyethylenes irradiated in air.   In Figure 4 and in Table II we have shown the gel fraction of irradiated polyethylenes as a function of radiation dose.   The results show that the gel fraction increases with radiation dose in a vacuum. The sample irradiated in air did not show any gel content.   However, these differences in the molecular structure of each irradiated polyethylene were not revealed in DTGA curves.   This is because the decomposition of polyethylenes in nitrogen over these temperature ranges is principally due

TABLE II
Crosslinking Index and Oxidizability of Polyethylenes Irradiated in a Vacuum

Radiation dose, Mr	Gel fraction	Crosslinking index	Weight loss in TGA, %	
			First stage	Second stage
Unirradiated			4.0	12.3
5.2	0.07	0.82	6.8	19.0
11	0.30, 0.35	1.2	6.0	16.9
30	0.60, 0.61	3.0	12.3	27.0
55	0.74, 0.75	14.4	16.9	35.3
	0.74[a]			

[a] Extraction with boiling xylene.

to the main-chain scission of polymer molecules, and structural differences as such crosslinking, unsaturation, carbonyl groups, etc., have only a minor effect on the weight loss by thermal decomposition.

In view of the above results, it can be concluded that irradiated polyethylene is thermally more unstable than unirradiated polymer, irrespective of the atmosphere during irradiation.

Thermogravimetric Analysis in Air

In order to investigate the effects of the atmosphere during irradiation and the radiation dose on the oxidative degradation of irradiated polyethylenes, thermogravimetric analyses were carried out in air.

In Figure 5 are shown some typical DTGA curves of polyethylenes irradiated in a vacuum at various doses of radiation, in comparison with an unirradiated sample. In the presence of air, degradation takes place in three stages; the first stage occurs over a temperature range from ca. 200 to 300°C., the second from ca. 300 to 390°C., and the third from ca. 390 to 450°C. The former two peaks were not observed for the thermal decomposition in nitrogen (Fig. 2). Therefore, it is obvious that two low temperature stages of weight loss in air are due to the oxidative degradation of polyethylenes.

In Figure 6 are shown some typical DTGA curves of polyethylenes irradiated in air. The three stages of oxidative degradation are also observed in these curves.

From Figures 5 and 6 it is clear that polyethylenes irradiated both in a vacuum and in air are more susceptible to oxidative degradation than unirradiated polymer. However, the weight loss by oxidative degradation of polyethylenes irradiated in a vacuum is larger than that of samples irradiated in the presence of air. This is shown in Table III.

In Figure 7 the weight loss for each oxidative degradation stage is plotted against radiation dose. It is found from Figure 7 that weight loss by oxidative degradation increases linearly with radiation dose. The effect of irradiation in a vacuum is much more pronounced than that in air, however.

TABLE III
Thermogravimetric Analyses of Irradiated Polyethylenes in Air

Atmosphere during irradiation	Radiation dose, Mr	Weight loss, %			Residue, %
		First stage	Second stage	Third stage	
In vacuum	Unirradiated	4.0	12.3	79.8	3.9
	1	2.8	16.6	76.6	4.0
	5.2	6.8	19.0	68.9	5.3
	11	6.0	16.9	69.9	7.2
	30	12.3	27.0	51.4	9.3
	55	16.9	35.3	36.9	10.9
In air	5.2	6.5	15.3	72.7	5.5
	22	5.1	11.6	78.1	5.2
	30	4.5	19.5	71.2	4.8
	55	7.6	20.3	64.6	7.5

From the sol fraction s of the polymer we calculated the crosslinking index γ, number of crosslinked units per number-average primary molecule, for each sample irradiated at various doses R by using the two following equations:[9]

$$\gamma = \alpha u_1 R \qquad (1)$$

and

$$s + \sqrt{s} = \beta/\alpha + 1/\alpha u_1 R \qquad (2)$$

where α and β are constants relating to crosslinking and scission of the chain molecule, and u_1 is the initial molecular weight of polymer.

The values of crosslinking index are also listed in Table II. We can calculate the number of tertiary hydrogen atoms from the initial molecular weight of sample, for example, when $\gamma = 10$ it is estimated to be 0.3 per 1000 carbon atoms. As already mentioned, polyethylenes irradiated in air give carbonyl groups and have no crosslinks.

These findings support the view that, in the case of polyethylene irradiated in a vacuum, crosslinks with tertiary hydrogen atoms and unsaturations, the number of which is nearly proportional to radiation dose, make the polyethylene more subject to oxidative degradation. In the case of polyethylene irradiated in air, carbonyl groups and unsaturations may slightly promote the oxidation. These differences may be attributed mainly to the tertiary hydrogen atoms in the crosslinked units.

In summary, the thermal stability of the irradiated polyethylenes decrease with increasing radiation dose. There are some differences in the chemical structure between the polyethylene irradiated in the presence of air and that irradiated in the absence of air; the former does not have crosslinks but carbonyl groups. However, the derivative thermogravimetric analysis curves for their thermal decomposition in nitrogen show little difference. In this case, the thermal decomposition occurs in one
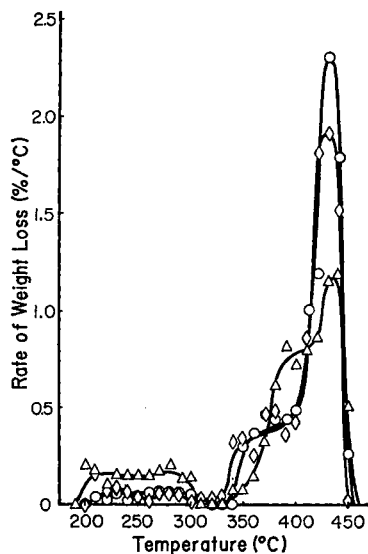
Fig. 5. Thermogravimetric analysis curves of irradiated polyethylenes in air: (O) unir-
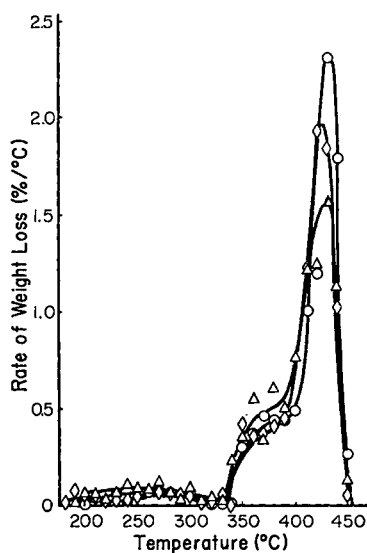radiated; (◇) at 5.2 Mr in vacuum; (△) at 55 Mr in vacuum.

Fig. 6. Thermogravimetric analysis curves of irradiated polyethylenes in air: (O) un-
irradiated; (◇) at 5.2 Mr in air; (△) at 55 Mr in air.

stage over the range from about 350 to 450°C.; however, in air, degrada-
tion takes place in three stages, i.e., ca. 200–300°C., ca. 300–390°C., and
ca. 390–450°C. Each weight loss at the first two stages by oxidative
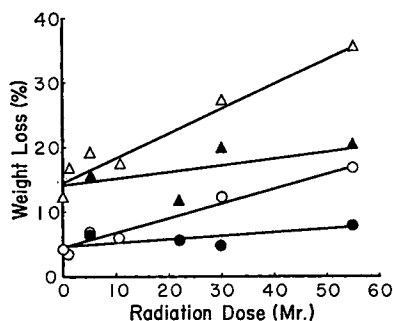degradation increases with increasing radiation dose. In particular, it

Fig. 7. Variation of weight losses with radiation dose at each stage of degradation of irradiated polyethylenes: (O) irradiated in vacuum, first stage; (△) irradiated in vacuum, second stage; (●) irradiated in air; first stage; (▲) irradiated in air, second stage.

is found that the crosslinked polyethylene is more susceptible to oxidation than the polymer irradiated in air.

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Résumé

On a étudié par analyse thermogravimétrique l'effet des radiations sur la dégradation thermique et oxydante du polyéthylène. On a trouvé que la stabilité thermique du polyéthyléne irradié dans le vide et dans l'air, à température de chambre, diminue avec l'augmentation de la dose d'irradiation. Sous azote, la décomposition thermique des polyéthylènes irradiés se produit en une étape sans influence importante de l'atmosphère d'irradiation. En présence d'air, la dégradation oxydante se déroule en trois étapes sur lesquelles l'atmosphère d'irradiation exerce une grande influence. Ceci est dû à la différence de structure chimique des polyéthylènes irradiés.

Zusammenfassung

Der Einfluss von Strahlung auf den thermischen und oxydativen Abbau von Polyäthylen wurde durch thermogravimetrische Analyse untersucht. Die thermische Stabilität von im Vakuum und in Luft bei Raumtemperatur bestrahltem Polyäthylen nimmt mit steigender Strahlungsdosis ab. Während die thermische Zersetzung von bestrahltem Polyäthylen in Stickstoff in einem Schritt verläuft und von der Bestrahlungsatmosphäre nicht merklich beeinfluss wird, wurde bei dem in drei Schritten verlaufenden oxydativen Abbau in Gegenwart von Luft ein starker Einfluss der Bestrahlungsatmosphäre festgestellt. Dies wird auf Unterschiede der chemischen Struktur des bestrahlten Polyäthylens zurückgeführt.