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Effect of Atmosphere on Radiation-Induced Crosslinking of Polyethylene. Part II. Dependency on Dose Rate, Temperature, and Gas Pressure

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INTRODUCTION

As reported recently,[1,2] radiation-induced crosslinking is accelerated in some gas atmospheres, i.e., N_2O. The present paper shows the dependency of the accelerating effect on dose rate, temperature during irradiation, and gas pressure.

Preliminary experiments[2] showed that the accelerating effect is independent of dose rate and is weakened at higher gas pressure. Furthermore, it could be assumed that the species which plays a significant role in the accelerating reaction process is neither the nitrous oxide molecule itself nor radiolytic final products, but is a radiolytic intermediate of some kind. For, the final products, O_2, N_2, NO, and NO_2[4,5] depress the crosslinking, according to our observations.[1,3]

EXPERIMENTAL

The experimental procedure was almost the same as that described in the previous paper.[2] The film used in the present case was limited to Sumikathene L-70, low density polyethylene having a molecular weight of 28,000. Film 0.03 mm. thick was used primarily, but films 0.15 mm. and 0.3 mm. thick were used for comparison. Temperatures during the irradiation were controlled by Dry Ice–methanol mixture for −80°C., Freon gas refrigerant for −40°C., ice water for 0°C., and electric furnace for 60 and 100°C. Again, solubility measurements against xylene were carried out in order to get relative values of the degree of crosslinking.

RESULTS AND DISCUSSION

1. Dose Rate Dependence

Figure 1 shows a plot of gel content versus dose rate for irradiation up to the same total dose. With irradiation in nitrous oxide, the gel content is shown to be independent of dose rate as well as in vacuum. Therefore, the

accelerating effect which should be the difference between the two gel contents can be estimated to be independent of dose rate also.

The depressive effect of oxygen on the crosslinking was reported by Chapiro,[6] Dewhurst,[7] and Okada[2] to be highly dependent on dose rate. It is explained by the former two authors that the oxygen molecule reacts with

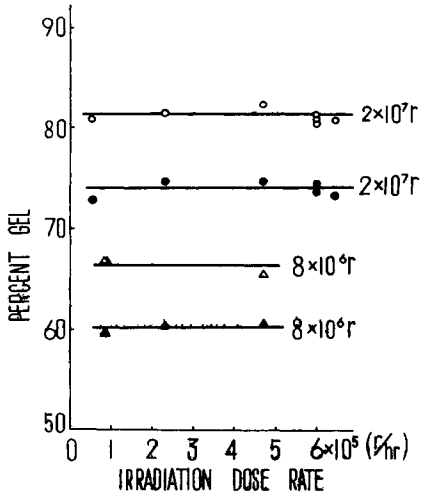

Fig. 1. Gel content *vs.* dose rate for irradiations (○, △) in nitrous oxide atmosphere (600 mm. Hg) and (●, ▲) in vacuum at room temperature.

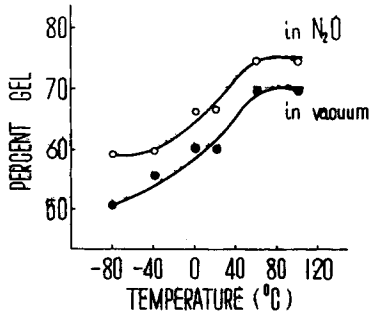

Fig. 2. Gel content vs. temperature during irradiation to a constant dose of 8×10^6 r, at a constant dose rate of 8.4×10^4 r/hr.: (○) in N_2O atmosphere (600 mm. Hg) and (●) in vacuum.

radicals produced in polyethylene and depresses the crosslinking, and the diffusion of oxygen through polymer is a significant factor for the depressive reaction. On the other hand, it is inferred from our results that the diffusion of nitrous oxide would not be so significant for the accelerating reaction. We may then assume that the accelerating process in a solid polymer is considerably more rapid than the depressive process of oxygen.

2. Dependence on Temperature

The variation of gel content with temperature is shown in Figure 2 for the irradiation in nitrous oxide and also in vacuum. Both curves increase with temperature, but the difference between them, the accelerating effect, appears to be independent of temperature within the limit of error.

For the irradiation in vacuum, Lawton et al.[8] previously found that the crosslinking efficiency is highly dependent on temperature in the range between the glass temperature and the crystalline melting temperature. This can be explained to be due to the change in crystallinity of polyethylene with temperature. For the irradiation in nitrous oxide, on the other hand, the accelerating effect may be affected by such complex factors as, the temperature dependency of radiolytic process of nitrous oxide, the change in gas pressure, and the change in gas solubility in polyethylene.

For the radiolysis of nitrous oxide, Wourtzel[4] found a dependency on temperature, but Harteck and Dondes[5] stated that the radiolysis is independent of temperature. However, the formation of radiolytic intermediates which is assumed to play a main role in the accelerating process does not necessarily vary with temperature, whether the total process of radiolysis depends on temperature or not.

Moreover, while the change in gas pressure with temperature cannot be neglected, this is not so significant a factor, since the total gas volume is unchanged.

Finally, Michaels[9] recently showed that the solubility of permanent gases in polyethylene is slightly dependent on temperature. Here we may assume that nitrous oxide shows the same behavior.

3. Dependence on Gas Pressure

The gel content for the irradiation in nitrous oxide is measured at various pressures in the range 0–4560 mm. Hg. In this case, 0.15 and 0.3 mm. thick films are then also used for comparison of influence of thickness among three films. These three films are the same commercial grade, but they cannot be expected to show completely the same solubility against xylene. The comparison of changes in gel content, thus, has only a relative meaning. Therefore, the change in gel content is necessarily shown as the ratio that of film subjected to irradiation in vacuum in Figure 3. It is seen that the gel content rapidly increases with gas pressure, passes through a maximum, and finally falls off. Also, the position of the maximum is shown to shift to the higher pressure region in the case of thicker films.

One can assume from these curves that the accelerating effect is occurring not only on the film surface but also in the interior part of film, since the gel content for the thicker films increases as well as for the thinner film.

The appearance of a maximum in our curves, which cannot be found in the depressive effect of oxygen, would be mainly due to combination of the following three factors: gas concentration in the film, effectiveness of radiolytic intermediates of nitrous oxide for the crosslinking reaction, and total yield of radiolytic final products.

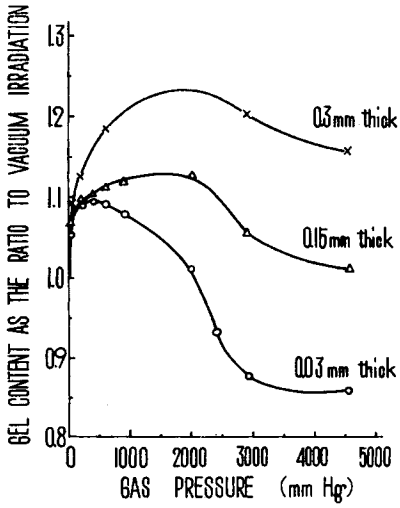

Fig. 3. Variation of gel content with pressure relative to gel content in vacuum irradiation to a constant dose of 2×10^7 r at a constant dose rate of 6.0×10^5 r/hr., at room temperature for various film thicknesses: (○) 0.03 mm. thick; (△) 0.15 mm. thick; (×) 0.3 mm. thick.

Michaels[9] presented evidence that permanent gases are soluble in the amorphous part of polyethylene as well as in liquid paraffin; the gas concentration in the film is thus proportional to the gas pressure outside of the film according to Henry's law, and the gas solubility is nearly zero in the crystalline part. Since the absorbed energy of radiation should be proportional to the gas concentration, the formation of radiolytic intermediates of nitrous oxide in film probably increases with external gas pressure.

The radiolysis of nitrous oxide would appear to be dependent on gas pressure except for the observation of Harteck and Dondes.[5] Burtt and Kircher,[10] for example, showed that the radiolytic yield increases in the low pressure range (under 200 mm. Hg). Furthermore, Johnson[11] noticed that the radiolysis occurs with a very greatly increased yield, corresponding to $G(-N_2O) = 9.4 \times 10^4$, when the gas pressure is reduced to 70 mm. Hg. A chain reaction mechanism due to some intermediates—probably ionic—was assumed for the same pressure region.

Although the overall radiolysis process is known to some extent as just mentioned, nothing is known about the intermediates which are assumed to be the effective species for the accelerating effect. While there should be two reaction courses for the intermediates, i.e., the decomposition to the final products and the acceleration of crosslinking reaction, one can suppose that the reaction ratio between the two courses may change with gas concentration in the film.

Further, N_2, O_2, NO, and NO_2, the final products, are known[1-3] to depress the crosslinking, except for nitrogen. The final products may react with radicals produced in the film, whether the products are formed in the

film or outside of film. Moreover, the total yield of products would increase with gas concentration and with external gas pressure except in the low pressure region. Although $G(-N_2O)$ increases rapidly in the low pressure region as above cited, one cannot estimate the variation of total yield in the same region, since the absorption of radiation energy should be also decreased. While these factors are thus all involved in the appearance of the maximum in our curves, relative effectiveness of each of these factors cannot be estimated at the present.

The shift of position of maximum, on the other hand, appears to be due to diffusion of final radiolytic products from outside of film to inside. A thinner film may be more sensitive to the diffusion of final products than a thicker one when the films are irradiated in the same vessel. Also, the total weight of these three films in the vessel was 0.54 g. and total weight of gas was 0.06 g. at pressures of 1 atm.

CONCLUSION

The accelerating effect of nitrous oxide for the crosslinking is independent of dose rate, and is also nearly independent of temperature during irradiation. Each gel content–pressure curve has at least one point of maximum.

According to our results, it may be considered that the accelerating effect is due to radiolytic intermediates of nitrous oxide which dissolve in polyethylene, and may be rather a fast reaction compared to the depressive effect of oxygen.

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Synopsis

The gel content of polyethylene irradiated in a nitrous oxide atmosphere is higher than when irradiated in vacuum. This is due to an accelerating effect of nitrous oxide on the radiation-induced crosslinking. The dependence of accelerating effect on dose rate, on temperature during irradiation, and on gas pressure is shown. The accelerating effect is independent of dose rate. While various complicated factors are concerned, the effect appears to be also nearly independent of temperature. The gel content rapidly increases with gas pressure, passes through a maximum, and then falls. Moreover, the position of the maximum shifts to a region of higher pressure for thicker films. From

these observations, it may be difficult to explain that the accelerating effect is completely due to a free radical mechanism as shown in the depressive effect of oxygen on the crosslinking.

Résumé

Le degré de gélification du polyéthylène irradié sous atmosphère d'oxyde nitreux est plus élevé que lorsque l'irradition est faite sous vide. La cause réside dans un effet d'accélération par l'oxyde nitreux du processus de pontage provoqué par l'irradition. On montre la dépendance de cet effet d'accéleration en fonction de la dose, de la température en cours de l'irradiation et de la pression du gaz. L'effet d'accélération est indépendant de la dose d'irradition. Alors que divers complexes interviennent, cet, effet semble aussi être presque indépendant de la température. Le degré de gélification augmente rapidement avec la pression en gaz, passe par un maximum puis décroît. De plus, pour les films plus épais, le maximum est déplacé vers la région de pressions plus élevées. A partir de ces observations il pourrait être difficile d'expliquer l'effet d'accélération uniquement par un mécanisme radicalaire, ainsi qui semble l'indiquer le diminution du pontage en présence d'oxygène.

Zusammenfassung

Wie schon früher berichtet wurde, ist der Gelgehalt eines unter Stickoxyd bestrahlten Polyäthylenshöher als bei Bestrahlung in Vakuum. Diese Erscheinung wird durch die beschleunigende Wirkung von Stickoxyd auf die strahlungsinduzierte Vernetzung verursacht. In der vorliegenden Mitteilung wird die Abhängiekeit der beschleunigenden Wirkung von der Dosisleistung, der Temperatur während der Bestrahlung und vom Gasdruck deschrieben. Die beschleunigende Wirkung ist von der Dosisleistung unabhängig. Obgleich verschiedene, unübersichtliche Faktoren beteiligt sind, scheint die Wirkung auch von der Temperatur nahezu unabhängig zu sein. Der Gelgehalt nimmt mit dem Gasdruck rasch zu, geht durch ein Maximum und fällt dann ab. Ausserdem verschiebt sich die Lage des Maximums bei dickeren Filmen zum Bereich höherer Drucke. Diese Beobachtungen lassen es nur schwer verstehen, dass die beschleunigende Wirkung, wie es die Herabsetzung der Vernetzung durch Sauerstoff zeigt, völlig auf einem radikalischen Mechanismus beruhen sollte.

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