

Dicumyl Peroxide-Initiated Crosslinking Reaction of Low Density Polyethylene

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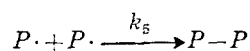
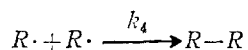
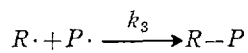
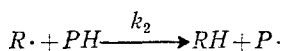
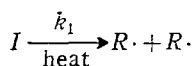
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Abstract : Low density polyethylene (LDPE) was crosslinked with dicumyl peroxide (DCP) by the gas (nitrogen) curing method. In order to prevent the formation of microvoids, crosslinking reactions were carried out under 50 psi pressure. The reaction kinetics of the crosslinking process was evaluated by dynamic differential scanning calorimetry (DSC) method (measuring exothermic heat of reaction during crosslinking process). An empirical correlation was obtained between the extent of reaction and the soluble fraction in the crosslinked polymer. Thus one can calculate the expected sol fraction of a specific crosslinking process if the reaction temperature, time, DCP concentration, number average molecular weight (\bar{M}_n) and polydispersity index of LDPE are known. The degree of crosslinking, density, crystallinity and mechanical properties of the crosslinked polymers were also studied. The degree of crystallinity and density of the crosslinked polymers decreased with increasing DCP concentration. The elongation at break and tensile strength were found to be influenced by the combined effect of crosslink concentration and crystallinity change. The elongation at break reached maximum at 1.0 PHR DCP concentration and decreased as the crosslinked polymer became brittle at higher crosslink concentration. The melting point depression was also noted as the degree of crosslinking increased and an empirical equation was derived correlating T_m and the concentration of the crosslinking initiator.

1. Introduction

The crosslinked low density polyethylene has been used as an insulation material with the excellent electrical properties as well as thermal, chemical and environmental properties. There are three methods in crosslinking polyethylene; chemical crosslinking^{1,2}, radiation crosslinking³ and silane crosslinking⁴. The chemical crosslinking method was used in this study. The mechanism of peroxide-induced

crosslinking of polyethylene which is proposed by A.A. Miller⁵ is as follows :



where I represents initiator, PH represents polymer and $P-P$ represents crosslinked polymer. The crosslink concentration ($[c. I]$) derived from the steady-state kinetic analysis of this free-radical process is given⁶ by assuming $k_3 = (k_4 \cdot k_5)^{1/2}$ and when the reaction is carried out to complete decomposition of the initiator.

$$[c. I] = \frac{2}{k^2} \{ \ln(k[I]_0^{1/2} + 1) + (k[I]_0^{1/2} + 1)^{-1} - 1 \} \quad (1)$$

$$k = \frac{(k_4 k_5)^{1/2}}{k_2 [PH]}$$

where $[I]_0$ is the initial initiator concentration and $[PH]$ is the polymer concentration.

The crosslink concentration which is proposed by R. Rado⁶ is given by

$$[c. I] = \frac{500(s^{1/PDI} - 1)}{M_n(PDI - 1)(1 - s)} \quad (2)$$

where s is sol fraction and PDI is polydispersity index ($PDI = \frac{\bar{M}_w}{\bar{M}_n}$).

In this study, the kinetic equation was derived on the basis of a dynamic DSC method and the degree of crosslinking, density, crystallinity and mechanical properties of the crosslinked polymers were measured.

The relationship between the conversion x and the sol fraction in the crosslinked polymer was also investigated.

2. Experimental

2-1. Materials

Four different grades of commercial low density polyethylenes were used. LDPE A, B and C have similar polydispersity index (PDI) but they are differing in molecular weight. LDPE C and D are differing in polydispersity index with similar molecular weight (Table 1).

Dicumyl peroxide (DCP) was used as the free radical initiator and xylene was used as a solvent for the measurement of soluble fractions.

Table 1. Low Density Polyethylene

Designation	\bar{M}_n	PDI ($=\bar{M}_w/\bar{M}_n$)	Melt Index	Density (g/cm^3)
LDPE A	11,300	7.60	1.0	0.920
LDPE B	10,600	7.34	1.5	0.920
LDPE C	9,300	7.19	3.0	0.919
LDPE D	9,000	9.74	2.0	0.919

2-2. Blending and Extrusion

LDPE and DCP were mixed by dry blending method. Blending was carried out at 50°C for 30 minutes. The amount of DCP was varied from 0.5 to 3.5 PHR. The mixture was extruded by a Brabender extruder type 2003 with barrel diameter of 3/4", L/D ratio of 20 : 1 and the compression ratio of 3 : 1. The 1" x 0.02" ribbon die was used for the tape extrusion. The temperature of the extruder was controlled at 120°C (heat zone 1), 125°C (heat zone 2) and 125°C (die). The screw rpm was set at 40 rpm.

2-3. Crosslinking Reaction

The crosslinking reaction was carried out with the Parr instruments No. 4552 and No. 4521 pressure reactors.

The high purity (99.995%) N_2 gas was used as the heating medium and the crosslinking reaction was carried out at 160°C for one hour under 50 psig pressure.

2-4. Testing

2-4-1. Extraction

The soluble fraction was measured by the extraction test according to ASTM D2765 method⁷.

Specimens (approximately 2mm x 2mm x 0.9 mm size and 0.300 ± 0.015g weight) were extracted in boiling xylene for 12 hours and dried at 100°C for 12 hours in vacuum oven.

2-4-2. DSC

The crystalline melting temperature (T_m) and the heat of fusion (ΔH_m) were measured using a Du Pont Model 910 DSC and Du Pont

Model 990 Thermal Analyzer.

The sample weight was 10 ± 1 mg, the heating rate was $10^\circ\text{C}/\text{min}$ with sensitivity range of $10\text{mV}/\text{cm}$.

The exothermic heat of reaction during crosslinking process was also measured using DSC. Samples were scanned at rates of $0.5^\circ\text{C}/\text{min}$ to $50^\circ\text{C}/\text{min}$. The sample weight was 10 ± 1 mg, the DCP concentration was fixed at 2.5 PHR. Nitrogen was purged at flow rates of $30\text{ml}/\text{min}$.

2-4-3. Density and Crystallinity

Density was measured by the buoyancy method using isopropyl alcohol as immersion medium. The crystallinity was calculated using both ΔH_m from DSC and the density data as follows⁸,

$$V_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \times 100$$

$$W_c = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \times 100$$

$$W_c' = \frac{\Delta H_m}{\Delta H_{100}} \times 100$$

where V_c and W_c are the percent crystallinity by volume and by weight.

The density of the purely amorphous portion, ρ_a' was assumed as 0.85 and that of the purely crystalline portion, ρ_c' was assumed as 1.014. The heat of fusion of the 100% crystalline LDPE, ΔH_{100} was taken as $72\text{cal}/\text{g}^\circ$.

2-4-4. Tensile Test

The % elongation at break, ultimate tensile strength and Young's modulus were measured with Instron tensile tester (Model 1130) with the crosshead speed of $250\text{mm}/\text{min}$.

The microtensile specimens for tensile test were prepared according to ASTM D1708.

3. Results and Discussion

3-1. The Degree of Crosslinking

The sol fraction of samples crosslinked at 160°C for one hour under 50 psig pressure

were correlated with the crosslink concentration $[c. 1]$ using eq. (1) and eq. (2).

The $[c. 1]$ value obtained from eq. (2) was substituted to eq. (1) and the overall rate constant k was obtained by trial-and-error method to minimize the sum of squares of the differences between the calculated s from eq. (2) and the experimental s for the four different resins. The k value obtained was 3.03 and it became possible to calculate the crosslink concentration according to eq. (3).

$$[c. 1] = \frac{2}{3.03^2} \{ \ln(3.03[I]_0^{1/2} + 1) + \frac{1}{3.03[I]_0^{1/2} + 1} - 1 \} \quad (3)$$

The combination of eq. (3) and eq. (2) would allow us to predict sol fractions at a given initiator concentration when the crosslinking reaction was carried out to complete reaction.

Figure 1 shows the comparison between the

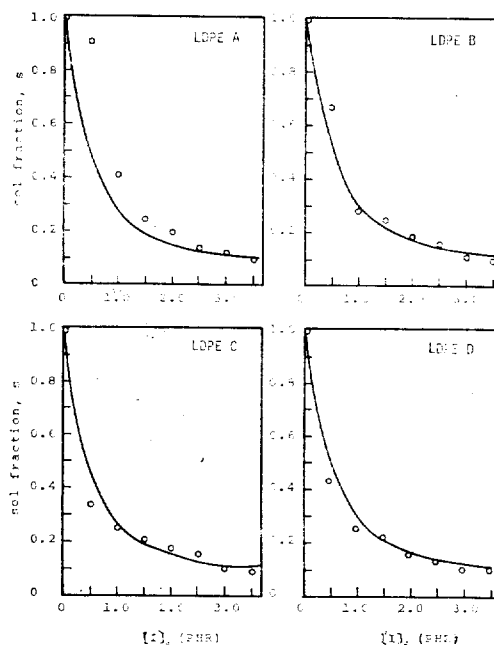


Fig. 1. Experimental and predicted sol fractions of samples crosslinked at 160°C , 1 hr, under 50 psig (circle represents experiment data and line represents predicted value).

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experimental s value and the calculated s value. They coincide quite well except at 0.5 PHR DCP concentration. It seems that it would be difficult to correlate the degree of crosslinking and the sol fraction at low initiator concentration.

3-2. Melting Temperature and Crystallinity

T_m , and % crystallinity versus the initial

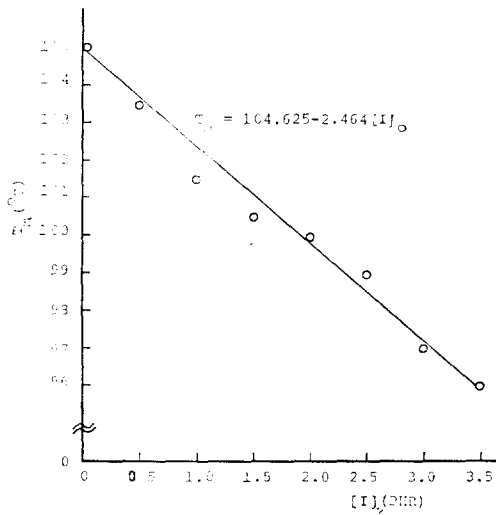


Fig. 2. Effect of dicumyl peroxide concentration on crystalline melting temperature (LDPE B).

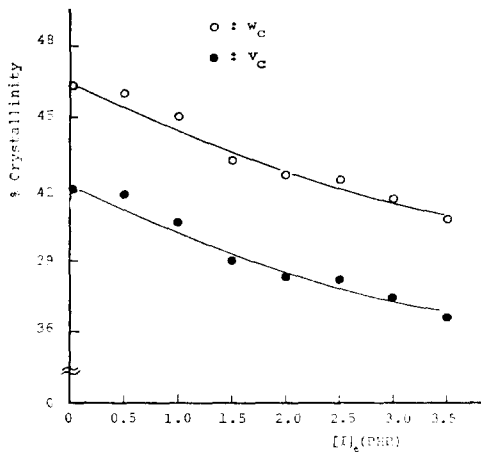


Fig. 3. % Crystallinity change with increasing amounts of dicumyl peroxide (LDPE B).

DCP concentration of the samples crosslinked at 160°C for 1 hr under 50 psig pressure are shown in Figure 2, 3, and 4.

As the crosslink concentration increases T_m , ΔH_m , density and % crystallinity decrease because of the formation of crystalline defects. An empirical equation between T_m and DCP concentration was obtained from Figure 2 when the crosslinking reaction was completed.

$$T_m = 104.63 - 2.46[I]_0 \text{ (}^\circ\text{C)}$$

The weight % crystallinity calculated from the density data decreases from 46.3% to 40.8% with increasing DCP concentration (Fig. 3) and the weight % crystallinity calculated

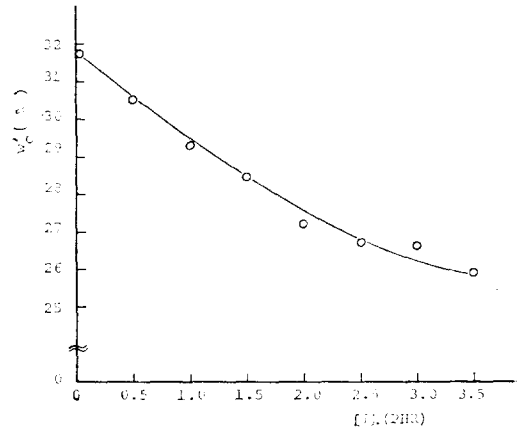


Fig. 4. % Crystallinity change with increasing amounts of dicumyl peroxide (LDPE B).

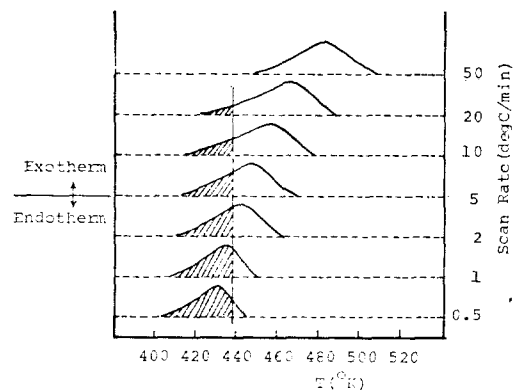


Fig. 5. Exothermic heat of crosslinking reaction at different scan rates.

from ΔH_m decreases from 31.7% to 25.9% with increasing DCP concentration (Fig. 4). The differences between the weight % crystallinities calculated from density and ΔH_m data are dependent on the selection of the literature data of ΔH_m of 100% crystalline LDPE (ΔH_{100}). The ΔH_{100} value of 72cal/g⁹ is used for the study.

3-3. Crosslinking Reaction Rate by Dynamic DSC Method

The DSC thermograms for exothermic heat of crosslinking reaction at different heating rates are shown in Figure 5. As scan rate increases from 0.5°C/min to 50°C/min, exothermic peak temperature shifts toward high temperature due to the dependence of crosslinking reaction on time and temperature. Table 2 shows the experimental conditions and the heat of reaction.

The heat of reaction varies with the scan rate. It reaches maximum value of 17.706(J/g) at the scan rate of 10°C/min. It seems that at low scan rates, there remains some residual crystallites at the initial stage of crosslinking reaction (127°C–150°C), and the decomposed DCP is not fully reacted. The efficiency of DCP reaction reaches maximum at the temperature ranges of 145–210°C when the scan rate is 10°C/min. At high scan rates, there may be some endothermic decomposition reac-

Table 2. Scan Rate, Sensitivity and Heat of Reaction

Scan Rate (°C/min)	Sensitivity (mV/cm)	Heat of Reaction (J/g)
0.5	0.5	10.775
1	0.5	11.009
2	0.5	15.699
5	1	17.577
10	2	17.706
20	5	15.180
50	20	12.539

tion to occur at high temperature range (210–240°C) to reduce the heat of reaction.

The exothermic peak temperature is shifted from 157°C to 208°C when the scan rate is changed from 0.5°C/min to 50°C/min.

The crosslinking reaction rate is obtained from the dynamic DSC thermograms by the following procedure :

1. To find the $[d(H/H_0)/dt]^{-1}$ vs. H/H_0 plot, the partial heat of reaction H calculated from the shaded area in Figure 5 is normalized by the total heat of reaction H_0 calculated from the total exothermic heat area in Figure 5. The above values are obtained at 160°C, 170°C, 180°C and 190°C (Fig. 6).

2. The reaction time t is calculated from the area below the curve in Figure 6. Figure 7 shows the relation between the extent of cure $x(=H/H_0)$ and the reaction time.

$$\int_0^x \frac{dt}{dx} \cdot dx = t(\text{time required to reach } x)$$

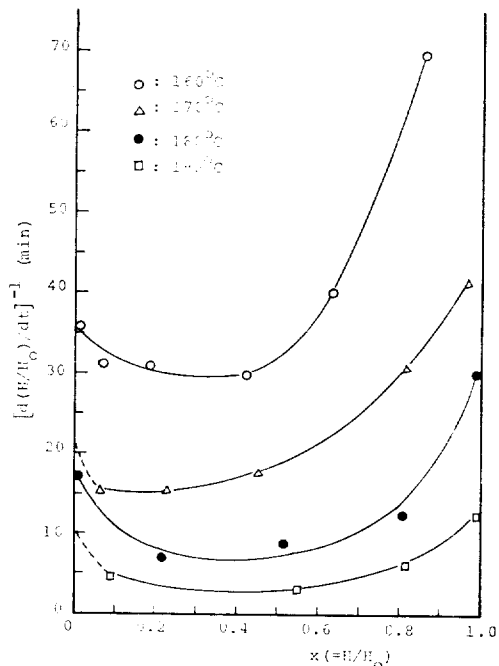


Fig. 6. Plot of the reciprocal reaction rate vs. the extent of cure.

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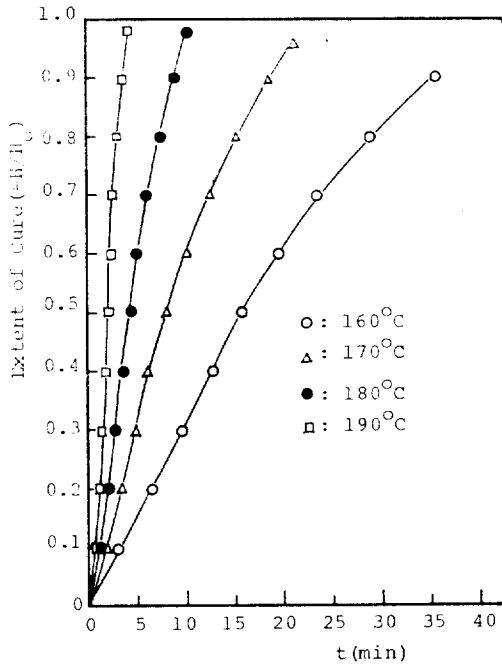


Fig. 7. Plot of extent of cure vs. reaction time.

3. Express the crosslinking reaction rate as equation (4), and obtain the best fitting n value and the reaction rate constant k_d . Figure 8 shows the linear relationship when n is assumed as 0.5. The reaction rate constant k is obtained from the slope in Fig. 8.

$$\frac{dx}{dt} = k_d(1-x)^n \quad (4)$$

4. The reaction rate constant is expressed in the Arrhenius type form.

$$k_d = A \exp\left(-\frac{E}{RT}\right)$$

The activation energy (E) is obtained by plotting $-\ln k_d$ versus $\frac{1,000}{T}$ (Fig. 9). The activation energy is 30.5 Kcal/mol and the frequency factor A is $1.5521 \times 10^{12} \text{ sec}^{-1}$.

The final kinetic equation describing the crosslinking reaction is as follows.

$$\frac{dx}{dt} = 1.5521 \times 10^{12} \exp(-30.5/RT) (1-x)^{0.5} \quad (\text{sec}^{-1})$$

By the integration of this equation, the ex-

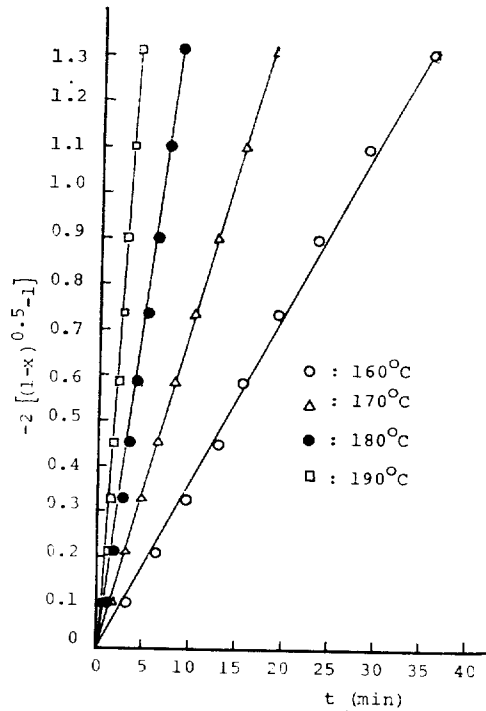


Fig. 8. Plot of $-2[(1-x)^{0.5}-1]$ vs. reaction time

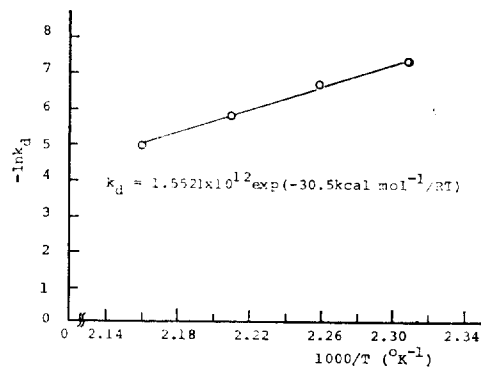


Fig. 9. Plot of $-\ln k_d$ vs. $1,000/T$

tent of cure x can be calculated if the reaction time and the reaction temperature are known

$$-2[(1-x)^{0.5}-1] = 1.5521 \times 10^{12} \exp(-30.5/RT) (1-x)^{0.5} t \quad (5)$$

3-4. Relationship between the Degree of Crosslinking and the Extent of Cure

Samples reacted at 150°C and 160°C for 10–50 min under 50 psig pressure were analyzed

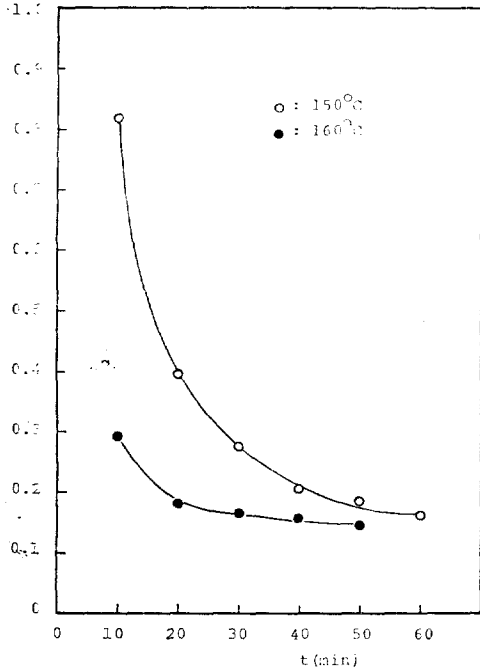


Fig. 10. Reaction time dependence of sol fraction (LDPE B).

to correlate the degree of crosslinking and the extent of cure. Figure 10 shows the sol fraction obtained at different reaction times. As the reaction time increases, sol fraction decreases with increasing extent of cure. The extent of cure, x , is calculated from the given reaction time and temperature. The sol fraction at given reaction time is converted to the crosslink concentration using equation (2).

The plot of the extent of cure and the crosslink concentration (Fig. 11) shows amazingly linear correlations when the extent of cure is below 0.7. At high x value, there is deviation from the linear plot. An empirical correlation is obtained as follows.

$$x = 21.34[c. 1] - 0.0126 \quad (6)$$

$(x \leq 0.7)$

3-5. Tensile Test

The % elongation at break, ultimate tensile strength and Young's modulus are shown in

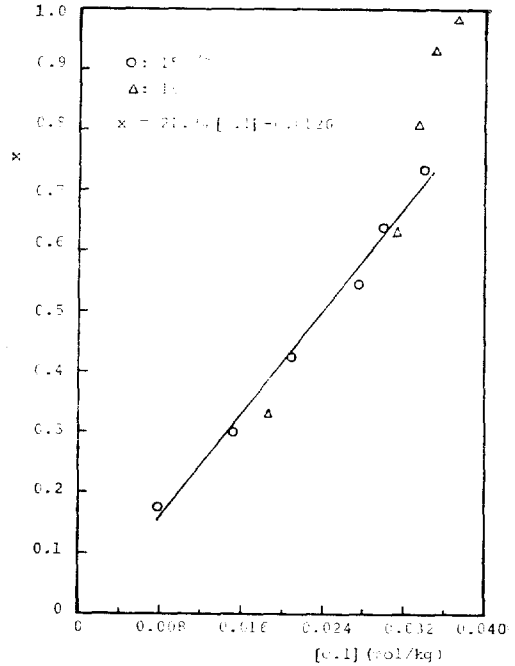


Fig. 11. Relation between the extent of cure and the crosslink concentration.

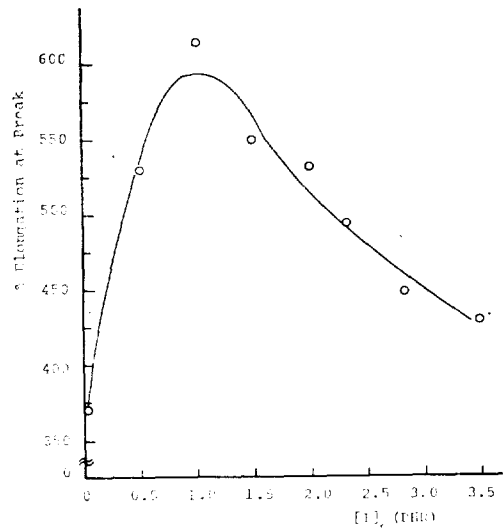


Fig. 12. Effect of dicumyl peroxide concentration on % elongation at break (LDPE B).

Figure 12, 13, and 14.

The % elongation at break and ultimate tensile strength are found to be influenced by

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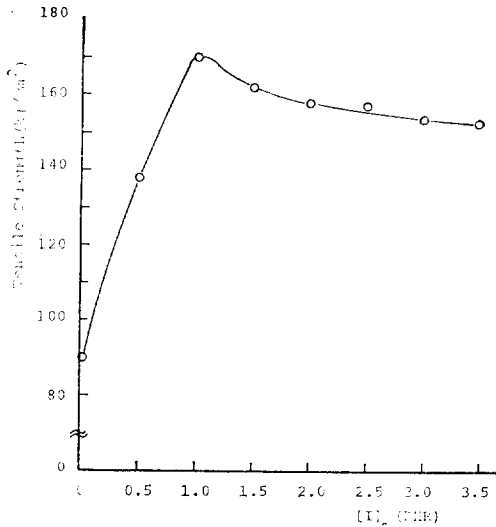


Fig. 13. Effect of dicumyl peroxide concentration on tensile strength (LDPE B).

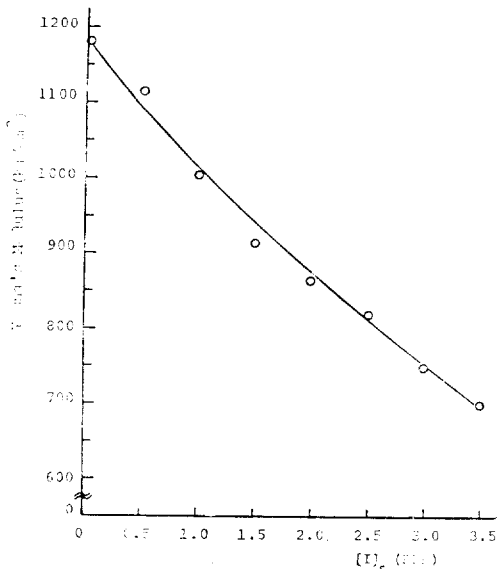


Fig. 14. Effect of dicumyl peroxide concentration on Young's modulus (LDPE B).

the combined effect of crosslink concentration and crystallinity change. The % elongation at break reaches maximum at 1.0 PHR DCP concentration and decreases as the crosslink concentration increases. The maximum value obtained was 615%.

The ultimate tensile strength reaches maximum at 1.0 PHR DCP concentration and decreases as the crosslinked polymer becomes brittle at higher crosslink concentration. The maximum value obtained was 170kg/cm². The Young's modulus decreases as the DCP concentration increases due to the decrease in crystallinity.

4. Conclusion

A series of empirical equations are obtained to describe the dicumyl peroxide initiated crosslinking reactions of LDPE. First, when the reaction is carried out to completion (peroxide is completely decomposed), the crosslink concentration $[c. 1]$ is correlated with the initial DCP concentration $[I]_0$.

$$[c. 1] = \frac{2}{3.03^2} \{ \ln(3.03[I]_0^{0.5} + 1) + \frac{1}{3.03[I]_0^{0.5} + 1} - 1 \} \quad (3)$$

This crosslink concentration can be correlated with the sol fraction of the crosslinked polymer when the molecular weight and the molecular weight distribution are known (Radoequation).

$$[c. 1] = \frac{500(s^{1/PDI} - 1)}{\bar{M}_n(PDI - 1)(1 - s)} \quad (2)$$

The reaction rate equation for the crosslinking reaction is also obtained.

$$\frac{dx}{dt} = 1.5521 \times 10^{12} \exp(-30.5/RT) (1-x)^{0.5} \quad (4)$$

The extent of cure x which can be calculated by intergrating the above equation at given reaction temperature and time, is also correlated to the crosslink concentration when x is below 0.7.

$$x = 21.34[c. 1] - 0.0126 \quad (6)$$

Thus we can predict the sol fraction when the reaction is carried out to completion using eq. (2) and (3), and if the reaction is not

completed ($x \leq 0.7$) we can also predict the sol fraction from eq. (4), (6) and (2).

The crystalline melting point, T_m , decreases linearly with increasing DCP concentration when the reaction is carried out to completion.

$$T_m = 104.63 - 2.46[I]_0$$

The % elongation at break and ultimate tensile strength both reach maximum value at DCP concentration of 1 PHR.

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