Dicumyl Peroxide-Initiated Crosslinking Reaction of Low Density Polyethylene

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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, radiation crosslinking and silane crosslinking. The chemical crosslinking method was used in this study. The mechanism of peroxide-induced crosslinking of polyethylene which is proposed by A.A. Miller is as follows:

$$I \xrightarrow{k_1} \text{heat} \xrightarrow{R_2 + R_2} \xrightarrow{k_2} RH + P$$

$$R_2 + P \xrightarrow{k_3} R - P$$

$$R_2 + R_2 \xrightarrow{k_4} R - R$$

$$P_2 + P_2 \xrightarrow{k_5} P - P$$

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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 given by assuming \( k_9 = (k_d \cdot k_b)^{1/2} \) and when the reaction is carried out to complete decomposition of the initiator.

\[
[c. \ I] = - \frac{2}{k_d} \left[ \ln(k_d[I]^2 + 1) + (k(I)_{eq}^2 + 1)^{-1} \right] \quad (1)
\]

\[
k = \frac{(k_d k_b)^{1/2}}{k_d[PH]^2}
\]

where \([I]_0\) is the initial initiator concentration and \([PH]\) is the polymer concentration.

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

\[
[c. \ I] = \frac{500(s/PDI - 1)}{M_w (PDI - 1)(1 - s)}
\]

where \( s \) is sol fraction and \( PDI \) is polydispersity index \( (PDI = \frac{M_w}{M_n}) \).

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>
<thead>
<tr>
<th>Designation</th>
<th>( M_w )</th>
<th>PDI</th>
<th>Melt Index</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE A</td>
<td>11,300</td>
<td>7.60</td>
<td>1.0</td>
<td>0.920</td>
</tr>
<tr>
<td>LDPE B</td>
<td>10,600</td>
<td>7.34</td>
<td>1.5</td>
<td>0.920</td>
</tr>
<tr>
<td>LDPE C</td>
<td>9,300</td>
<td>7.19</td>
<td>3.0</td>
<td>0.919</td>
</tr>
<tr>
<td>LDPE D</td>
<td>9,000</td>
<td>7.94</td>
<td>2.0</td>
<td>0.919</td>
</tr>
</tbody>
</table>

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 method.

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 \( (\Delta H_m) \) were measured using a Du Pont Model 910 DSC and Du Pont
Model 990 Thermal Analyzer.

The sample weight was 10 ± 1mg, the heating rate was 10°C min with sensitivity range of 10mV/cm.

The exothermic heat of reaction during crosslinking process was also measured using DSC. Samples were scanned at rates of 0.5°C/min to 50°C/min. The sample weight was 10 ± 1mg, the DCP concentration was fixed at 2.5 PHR. Nitrogen was purged at flow rates of 30ml/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 $\Delta H_m$ from DSC and the density data as follows$^8$:

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

$$W_c = \frac{\rho_c}{\rho} \left( 1 - \frac{\rho_c - \rho_a}{\rho_c} \right) \times 100$$

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

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

The density of the purely amorphous portion, $\rho_a'$ was assumed as 0.85 and that of the purely crystalline portion, $\rho_c'$ was assumed as 1.014. The heat of fusion of the 100% crystalline LDPE, $\Delta H_{100}$ was taken as 72cal/g$^8$.

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 250mm/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 expermental 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).

$$[c. 1] = \frac{2}{3.03^2} \left[ \ln(3.03[I])_e^{1/2} + 1 \right]$$

$$+ \frac{1}{3.03^2[I]_e^{1/2} + 1} - 1$$  (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

\[ T_m = 104.625 - 2.464[I]_0 \] (°C)

As the crosslink concentration increases $T_m$, $\Delta H_m$, 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.

\[ T_m = 104.63 - 2.46[I]_0 \] (°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. 2. Effect of dicumyl peroxide concentration on crystalline melting temperature (LDPE B).

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

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

Fig. 5. Exothermic heat of crosslinking reaction at different scan rates.
from $\Delta H_m$ decreases from 31.7% to 25.9% with increasing DCP concentration (Fig. 4). The differences between the weight % crystallinities calculated from density and $\Delta H_m$ data are dependent on the selection of the literature data of $\Delta H_m$ of 100% crystalline LDPE ($\Delta H_{100}$). The $\Delta H_{100}$ value of 72cal/g° 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 17,705(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 reaction 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.

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

Table 2. Scan Rate, Sensitivity and Heat of Reaction

<table>
<thead>
<tr>
<th>Scan Rate (°C/min)</th>
<th>Sensitivity (mV/cm)</th>
<th>Heat of Reaction (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>10.775</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>11.009</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>15.699</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>17.577</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>17.706</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>15.180</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>12.539</td>
</tr>
</tbody>
</table>

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 $k_a$. 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.

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

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

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

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

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

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

By the integration of this equation, the extent of cure $x$ can be calculated if the reaction time and the reaction temperature are known.

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

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.
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.

$$x = 21.34[c - 1] - 0.0126$$

(6) \hspace{1cm} (x \leq 0.7)

3-5. Tensile Test

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

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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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 170 kg/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 \([I, 0]\).

\[
\begin{align*}
[c, 1] &= \frac{2}{3,03^2} \left( \ln(3,03[I, 0]^{0.5} + 1) \right) \\
&+ \frac{1}{3,03[I, 0]^{0.5} + 1} - 1
\end{align*}
\]

(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 (Rado equation).

\[
[c, 1] = \frac{500(z^{1/PDI} - 1)}{M_n(PDI - 1)(1 - s)}
\]

(2)

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

\[
\frac{dx}{dt} = 1.5521 \times 10^{13} \exp(-30.5/RT)(1-x)^{0.5}
\]

(4)

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

\[
x = 21.34[c, 1] - 0.0126
\]

(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.

$$T_m = 104.63 - 2.46[T]_o$$

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

References


7. ASTM D2765
