

RHEOLOGIC STUDIES ON CHEMICAL CROSS-LINKING KINETICS FOR LDPE*

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Abstract Crosslinking reaction of LDPE resin in the presence of dicumyl peroxide (DCP) was studied by isothermal rheological measurements at different temperatures and non-isothermal differential scanning calorimetry (DSC) technique with different heating rates. The kinetic parameters of crosslinking reaction were calculated by both rheological and DSC measurements. The results reveal that with the increase of DCP contents, the apparent activation energy, E_a , ranges from about 140 kJ/mol to 170 kJ/mol and the order of crosslinking reaction, $\bar{n}$, approaches unity. The influence of measurement frequency, ω on crosslinking reaction was also investigated. It can be found that $\bar{n}$ does not change with the increase of ω and E_a decreases slightly with the increase of ω .

Keywords: Crosslinking kinetic; LDPE; Rheological measurement; DSC measurement.

INTRODUCTION

Low density polyethylene (LDPE) is commonly used as an electrical insulator of high voltage cables due to its low cost, excellent electrical properties, good chemical resistance and easy processing^[1–3]. While crosslinked polyethylene (XLPE) has progressively replaced LDPE used in extruded cable insulation^[4, 5] over the past two decades on the basis that XLPE exhibits superior mechanical properties and chemical resistance owing to its three-dimensional network structure^[6–8].

The physical properties of XLPE are determined by the network structure, which depends on the extent of cure and processing conditions such as the time and temperature of crosslinking^[9]. Crosslinking kinetics of the resin, an efficient method to track the extent of chemical crosslinking reaction for the given crosslinking time, could provide basis for obtaining high quality product and optimizing process.

One of the most widely used methods for studying the kinetics of crosslinking reaction is the thermal analysis by differential scanning calorimetry (DSC) in isothermal or non-isothermal modes^[10–13].

It is worth noting that rheological measurement, as an important testing method, can give us a lot of valuable information about polymer morphologies and structures, especially viscoelastic properties of polymers and their corresponding structural evolution during processing^[14–16]. Fenouillot *et al.*^[17] investigated the rheological behavior of thermoset/thermoplastic blends during isothermal curing, and proposed a rheokinetic model to predict the viscoelastic behavior of the system. Ciardelli *et al.*^[18] monitored the chemical crosslinking reaction of propylene polymer through rheological testing. Zhou *et al.*^[19] examined the rheokinetics of melt poly(ethylene- α -octene) elastomer with dicumyl peroxide. Rosca *et al.*^[20–21] investigated the cure process of

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rubbers through the moving die rheometer in scanning mode, and the kinetic parameters were obtained.

In this study, the chemical crosslinking reaction of LDPE was investigated through rheological and DSC measurements. The kinetic parameters of the crosslinking reaction were obtained from isothermal rheological measurements, and the apparent activation energy was calculated from non-isothermal DSC measurements.

THEORETICAL

Mathematical Treatment for the Rheological Measurement in Isothermal Scanning Mode

Storage modulus (G') is sensitive to the formation of network structure and can be used to monitor the crosslinking process. The degree of relative conversion for crosslinking reaction is given by^[18]

$$\beta = \frac{G'(t) - G'(0)}{G'(\infty) - G'(0)} \quad (1)$$

where $G'(\infty)$ is the final value of G' at the end of crosslinking process, $G'(t)$ is the value of G' at a certain time t during crosslinking process, and $G'(0)$ is the value of G' at the beginning of crosslinking process.

A general expression for the reaction rate as a function of temperature is

$$\frac{d\beta}{dt} = K(T) \cdot f(\beta) \quad (2)$$

where $d\beta/dt$ is the rate of relative conversion, $f(\beta)$ stands for a function of degree of relative conversion which implies the reaction mechanism. For n -order kinetics, we assumed $f(\beta)$ in Eq. (2) is expressed by^[22]

$$f(\beta) = (1 - \beta)^n \quad (3)$$

where n is the reaction order. $K(T)$ is a temperature dependent reaction rate constant and is given by the expression

$$K(T) = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where k_0 is a constant, R is the gas constant and E_a is the apparent activation energy.

By combining Eqs. (2), (3) and (4), the following equation is obtained:

$$\frac{d\beta}{dt} = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \beta)^n \quad (5)$$

The kinetic parameters of the crosslinking reaction are calculated by the logarithmic form of Eq. (5):

$$\ln \frac{d\beta}{dt} = \ln k_0 - \frac{E_a}{RT} + n \ln(1 - \beta) \quad (6)$$

The slope of $\ln(d\beta/dt)$ versus $\ln(1 - \beta)$ gives the value of n and the intercept is $\ln K(T)$. The pre-exponential factor k_0 and activation energy E_a can be calculated finally in Eq. (4).

Mathematical Treatment for the DSC Measurement in Non-isothermal Scanning Mode

The degree of relative conversion β for crosslinking reaction is given by

$$\beta = \frac{\Delta H_T}{\Delta H_0} \quad (7)$$

where ΔH_T is the heat flow generated up to time t or temperature T , and ΔH_0 is the total heat flow generated during the entire crosslinking reaction. Eq. (2) and Eq. (4) are valid for the moment and Eq. (3) may be invalid because temperature and time both change in the non-isothermal scanning mode. But $f(\beta)$ still stands for a function of degree of relative conversion. By combining Eqs. (2) and (4), the following equation is obtained:

$$\frac{d\beta}{dt} = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\beta) \quad (8)$$

The E_a is obtained using the logarithmic form of Eq. (8)

$$\ln \frac{d\beta}{dt} = \ln[k_0 \cdot f(\beta)] - \frac{E_a}{RT} \quad (9)$$

The slope of $\ln(d\beta/dt)$ versus $1/T$ for the same value of β gives the value of E_a .

EXPERIMENTAL

Materials

Two kinds of low density polyethylene resin (PE-1, $M_n = 15000$, $M_w = 82600$, PE-2, $M_n = 13300$, $M_w = 77500$) were purchased from Yanshan Petrochemical Corporation (Beijing, China). Antioxidant 300 and dicumyl peroxide (DCP) were bought as additives, and all the materials were used directly without further purification. The mixing formulations are shown in Table 1.

Table 1. Mixing formulations for different samples

Sample number	LDPE:Antioxidant 300:DCP (weight ratio)
PE-12	100:0.5:1.0
PE-13	100:0.5:1.5
PE-14	100:0.5:2.0
PE-22	100:0.5:1.0
PE-23	100:0.5:1.5
PE-24	100:0.5:2.0

Sample Preparation

LDPE and antioxidant 300 as shown in Table 1 were melting mixed in a twin-screw extruder (PRISM TSE 16TC, Thermo Fisher, German) with a speed of 33 r/min at 160°C. Then the mixture and DCP in different ratios were melting mixed with a speed of 20 r/min at 115°C. Disks of 1.2 mm in thickness and 25 mm in diameter were made by compression moulding from pellets of the formulations for rheological tests. The pellets were pressed at 115°C and 15 MPa in a hot-press (XLB 25-D, China). Afterwards, the samples were cooled in air under 16 MPa for 10 min.

Measurements

DSC measurements

DSC measurements were carried out in a DSC Q100 (TA Instruments, USA), and experiments were conducted in dynamic mode under nitrogen atmosphere. Runs at a constant heating rate were performed in a temperature range from 120°C to 240°C for each sample. The ramp rates were 2, 5, 10 and 15 K/min, respectively.

Rheological measurements

The rheological tests were performed using an advanced rheometric expansion system (ARES, TA Instruments, USA) in air atmosphere and the system was operated under conditions: (1) frequency $\omega = 10$ rad/s in dynamic strain sweep, (2) $\omega = 0.5$ rad/s, $\gamma = 1\%$, at different temperatures in dynamic time sweep.

RESULTS AND DISCUSSION

Isothermal strain sweeps were carried out from 0.1% to 100% with fixed frequency 10 rad/s to determine the linear viscoelastic region of PE-1 and PE-2. The results show that PE-1 and PE-2 are in a linear viscoelastic region when the strain is below 20%. $\gamma = 1\%$ was chosen for all the dynamic rheological measurements.

Thermal oxidation may induce the formation of network structure and make G' increase. Dynamic time sweeps were carried out first for PE-1 and PE-2 resins with antioxidant at 150°C for 2.5 h to rule out the effects of thermal oxidation on experimental results. The dependence of G' and G'' on time can be obtained as shown in

Fig. 1. G' and G'' almost didn't change during the test, which means that there is no thermal oxidation reaction during the test.

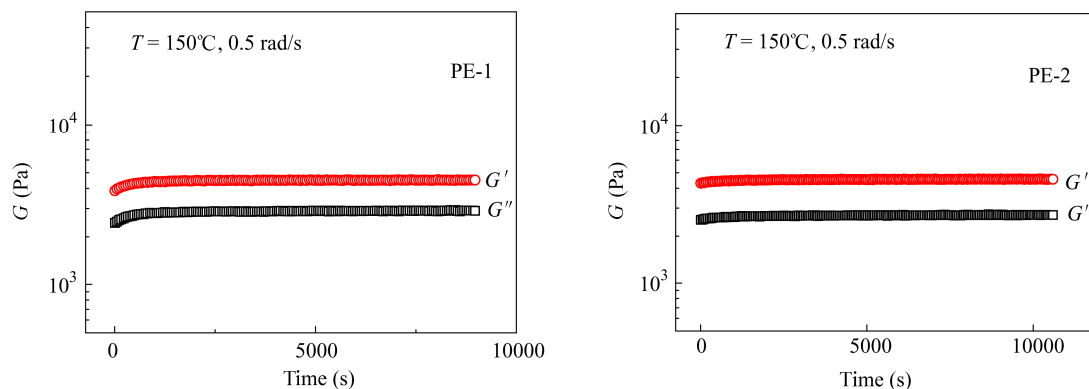


Fig. 1 Dependence of storage modulus G' and loss modulus G'' on time for PE-1 and PE-2 resins with antioxidant at 150°C with a frequency $\omega = 0.5$ rad/s

The dynamic viscoelasticity of polymer melts at low ω is considerably sensitive to the formation or evolution of network structure. Figure 2 shows that the increase of temperature increases the reaction rate clearly and the increase of DCP content increases the crosslinking density.

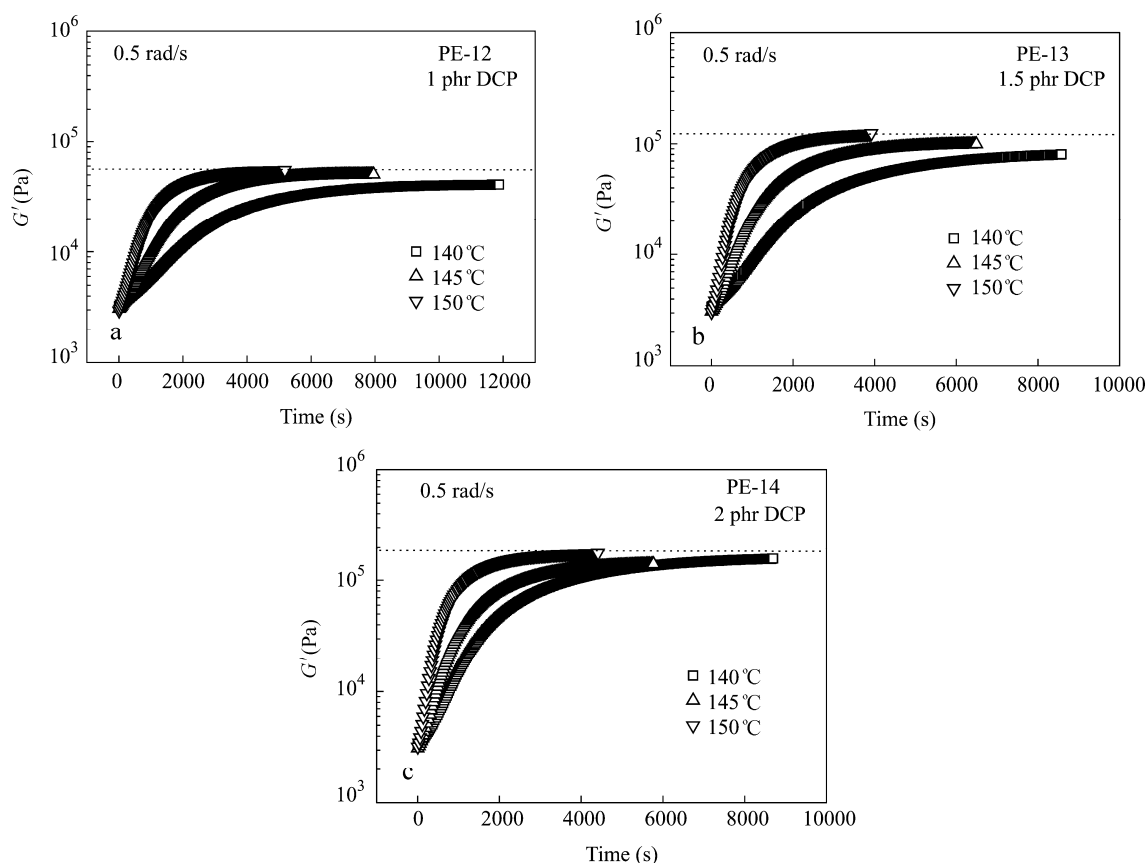


Fig. 2 Dependence of storage modulus G' on time for PE-1 samples with different DCP contents at different temperatures of 140°C , 145°C , 150°C , respectively

Data of dynamic time sweep were all analyzed by using Eq. (1) to Eq. (6). In Fig. 3, a straight line is well fitted at each temperature when $\ln(1-\beta) < -0.5$. This fact occurs when $\beta > 0.35$. Slope of the straight line is the order of crosslinking reaction, n , and intercept is $\ln K(T)$. The fitting line is in a serious deviation when $\beta < 0.35$, which means the model $f(\beta) = (1-\beta)^n$ is not suitable for the reaction stage where $\beta < 0.35$.

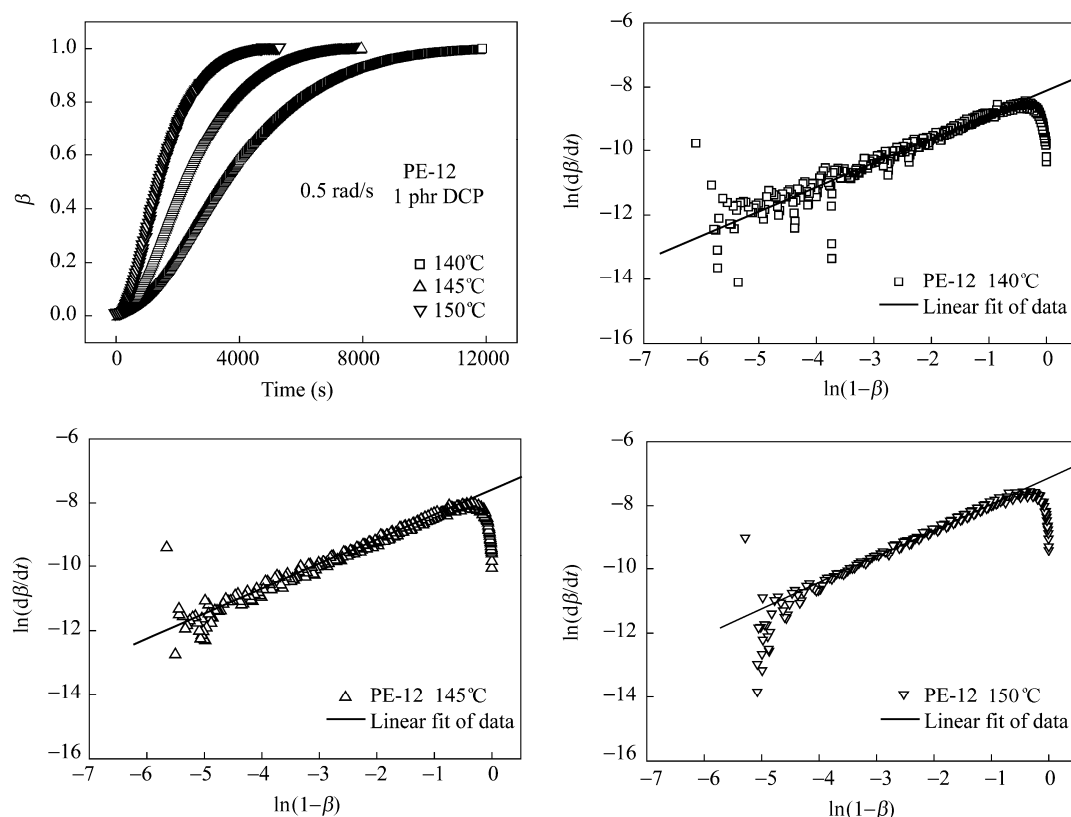


Fig. 3 Dependence of β on time and relationship between $\ln(d\beta/dt)$ and $\ln(1-\beta)$ for PE-12 sample at different temperatures

Based on Eq. (4), the apparent activation energy is calculated by plotting $\ln K(T)$ versus reciprocal absolute temperature. As shown in Fig. 4, the slope of straight lines is the apparent activation energy (E_a/R), and the intercept is the pre-exponential factor ($\ln k_0$).

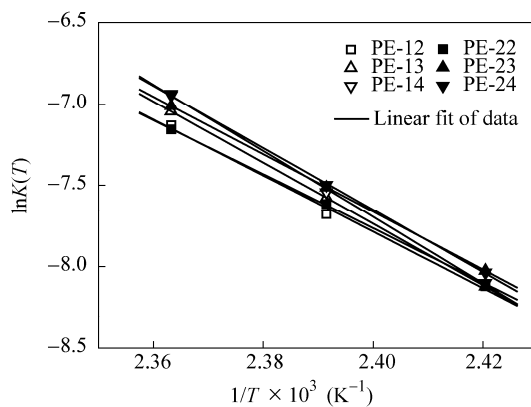


Fig. 4 $\ln K-1/T$ curves for different samples

The kinetic parameters of different samples are shown in Table 2. The order of crosslinking reaction, n , ranges from 0.7 to 0.8, approaches 1, which means it is a first order reaction. Activation energy, E_a , and pre-exponential factor, $\ln k_0$, increase with the increase of DCP content for PE-1 and PE-2 samples, and E_a ranges from 140 kJ/mol to 170 kJ/mol.

Table 2. Kinetic parameters of different samples at different temperatures

Item	$T_{\text{test}} (^{\circ}\text{C})$	n	$\bar{n}$	$\ln K(T)$	$\ln k_0$	$-E_a/R$ (K)	E_a (kJ/mol)
PE-24	140	0.73	0.78	-8.04	38.17	-19090	159
	145	0.80		-7.50			
	150	0.82		-6.95			
PE-23	140	0.76	0.75	-8.03	34.89	-17730	147
	145	0.75		-7.51			
	150	0.75		-7.01			
PE-22	140	0.68	0.70	-8.11	32.23	-16660	139
	145	0.71		-7.62			
	150	0.71		-7.16			
PE-14	140	0.67	0.77	-8.10	41.16	-20350	169
	145	0.75		-7.54			
	150	0.89		-6.94			
PE-13	140	0.65	0.75	-8.12	37.49	-18850	157
	145	0.77		-7.58			
	150	0.82		-7.04			
PE-12	140	0.76	0.78	-8.12	33.71	-17290	144
	145	0.76		-7.68			
	150	0.82		-7.13			

The crosslinking reaction happened under dynamic shear. Table 3 shows the kinetic parameters of PE-24 and PE-14 samples under different ω . E_a and $\ln k_0$ decrease slightly with ω increasing but $\bar{n}$ almost does not change. When E_a and $\ln k_0$ are constant, half-life of reaction ($t_{1/2}$) can be calculated at a given temperature, and vice versa.

Table 3. Kinetic parameters of PE-14 and PE-24 samples under different measurement frequencies

Item	$T_{\text{test}} (^{\circ}\text{C})$	n	$\bar{n}$	$\ln K(T)$	$\ln k_0$	$-E_a/R$ (K)	E_a (kJ/mol)
PE-24 -0.5 rad/s	140	0.73	0.78	-8.04	38.17	-19090	159
	145	0.80		-7.50			
	150	0.82		-6.95			
PE-24 -3.14 rad/s	140	0.77	0.80	-7.97	36.99	-18580	155
	145	0.80		-7.48			
	150	0.82		-6.91			
PE-24 -10 rad/s	140	0.78	0.80	-7.98	36.37	-18330	152
	145	0.80		-7.47			
	150	0.81		-6.93			
PE-14 -0.5 rad/s	140	0.67	0.77	-8.10	41.16	-20350	169
	145	0.75		-7.54			
	150	0.89		-6.94			
PE-14 -3.14 rad/s	140	0.70	0.77	-8.06	39.23	-19550	163
	145	0.76		-7.53			
	150	0.84		-6.94			
PE-14 -10 rad/s	140	0.70	0.78	-8.04	37.92	-18980	158
	145	0.81		-7.48			
	150	0.83		-6.95			

In industry, the reaction rate is estimated by the temperature at which $t_{1/2} = 60$ s. Table 4 shows crosslinking temperature with $t_{1/2} = 60$ s and $t_{1/2}$ at 180°C for different samples. It is found that both the crosslinking temperature with $t_{1/2} = 60$ s and $t_{1/2}$ at 180°C decrease with the increase of DCP content for each sample. It seems that the reaction rate of PE-1 sample is a little higher than that of PE-2 sample with the same DCP content, due to the different structure of PE-1 and PE-2. Our other study results show that the content of the terminal double bond of PE-1 sample decreases faster than that of PE-2 sample in the process of cross-linking reaction, which means that the terminal double bond of PE-1 sample has a higher reactivity on the cross-linking reaction than that of PE-2 sample. But further study will be needed to find out the exact reason.

Table 4. Crosslinking temperature with $t_{1/2} = 60$ s and $t_{1/2}$ at 180°C for different samples

Item	T ($t_{1/2} = 60$ s)	$t_{1/2}$ ($T = 180^\circ\text{C}$)
PE-24	175°C	36 s
PE-23	177°C	48 s
PE-22	181°C	64 s
PE-14	173°C	30 s
PE-13	176°C	42 s
PE-12	180°C	59 s

DSC measurement is a common method to study kinetic parameters of crosslinking reaction. Figure 5 shows that the temperature at which the heat flow is up to the top value increases with the increase of ramp rate. All the data are analyzed according to Eq. (7) and Eq. (9), and the results are shown in Figs. 6 and 7. The straight line is obtained by plotting $\ln(d\beta/dt)$ versus $1/T$ at different ramp rates when the value of β is constant as shown in Fig. 7. The slope is equal to activation energy (E_a/R).

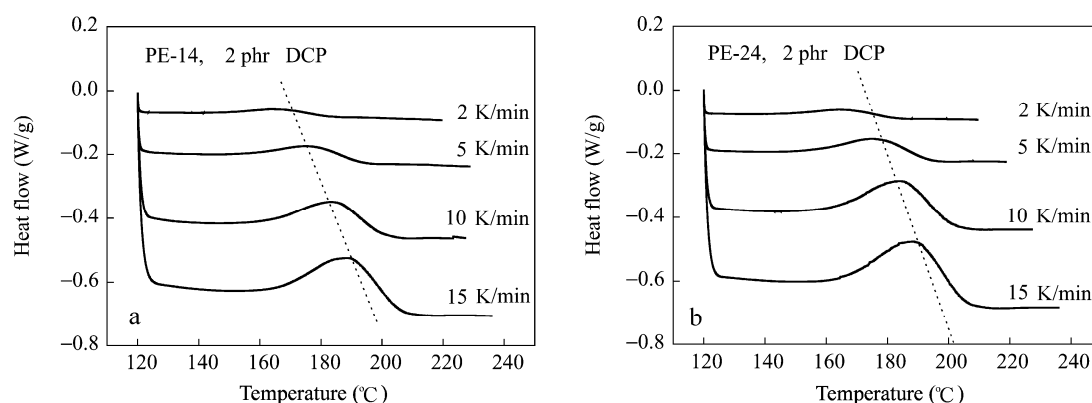


Fig. 5 DSC curves of crosslinking reaction for PE-14 and PE-24 samples at different ramp rates

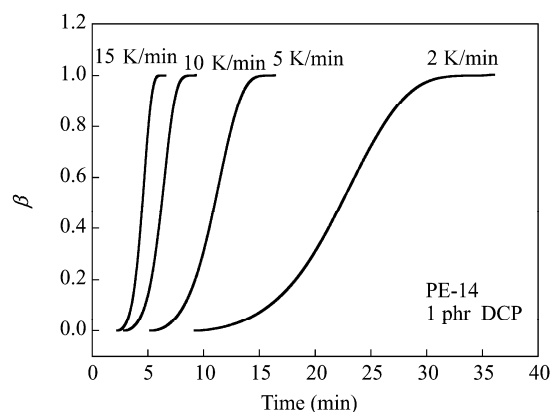


Fig. 6 Dependence of β on time for PE-14 sample at different ramp rates

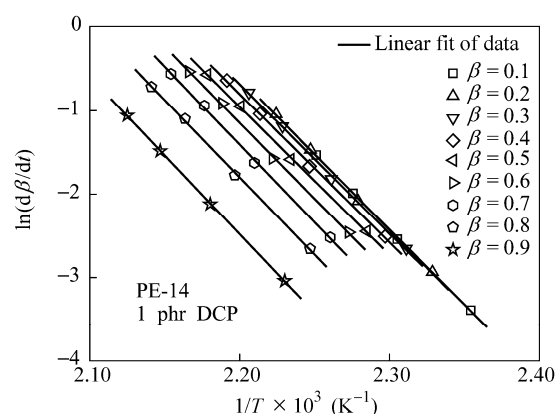


Fig. 7 Evaluation of the activation energy for PE-14 sample at different ramp rates

Figure 8 shows E_a ranges from 140 kJ/mol to 160 kJ/mol, and E_a increases a little with increase of DCP content at the same β value for PE-1 sample and PE-2 sample respectively. It is similar to the results obtained by rheological measurements. E_a probably gets minimum value when $\beta = 0.4$, but the variation is slight as β ranges from 0.1 to 0.9.

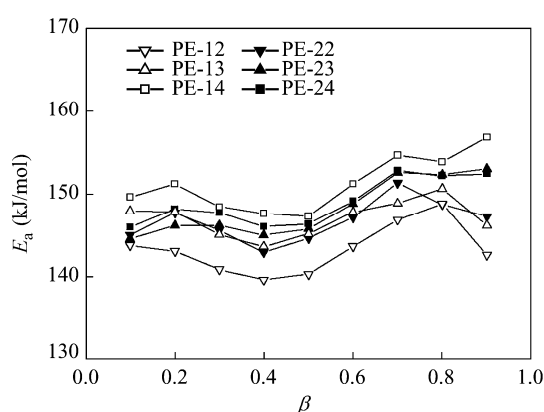


Fig. 8 Variation of apparent activation energy E_a versus relative conversion degree β for different samples

CONCLUSIONS

Two kinds of LDPE granules with different DCP contents were prepared, and the crosslinking reaction was studied by isothermal rheological measurements at different temperatures and non-isothermal DSC technique at different heating rates. The kinetic parameters of the crosslinking reaction were calculated by rheological measurements. The apparent activation energy ranges from 140 kJ/mol to 170 kJ/mol with the increase of DCP contents, and the order of crosslinking reaction approaches unity. Reaction order does not change with the increase of frequency, and activation energy decreases slightly with the increase of frequency. Samples with 2 phr DCP have the higher reaction rate. Activation energy obtained by DSC and rheological measurements is similar. Rheological method can well apply to studies on chemical cross-linking kinetics for LDPE.

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