

Crosslinking Kinetics of Polyethylene with Small Amount of Peroxide and Its Influence on the Subsequent Crystallization Behaviors^{*}

Yan-hua Niu^{a, b**}, Wen-bin Liang^b, Yin-ling Zhang^b, Xue-lian Chen^b, Shih-yaw Lai^b,
Guang-xian Li^a and Du-jin Wang^c

^a College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering of China, Sichuan University, Chengdu 610065, China

^b Performance Material Center, National Institute of Clean-and-low-carbon Energy (NICE), Beijing 102209, China

^c CAS Key Laboratory of Engineering Plastics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract Crosslinking reactions of high density polyethylene with low peroxide concentrations ranging from 0.1 wt% to 1.0 wt% at temperatures of 170, 180 and 190 °C were monitored by rheological measurements. A critical gel forms at the peroxide concentration of 0.2 wt%, where the transition from long chain branching generation to crosslinking network formation could occur. Rheokinetics of crosslinking can be fitted well by Ding-Leonov's model. The curing rate k_2 at the earlier stage exhibits about 3 times acceleration per 10 °C with increasing temperature, while the equilibrium modulus G' at the fully cured stage is almost independent of temperature. Influences of crosslinking on the subsequent crystallization behaviors were detected by DSC measurements. Above the critical gel concentration, crystallization is largely retarded as evidenced by the lower crystallization temperature T_c and crystallinity X_c due to the network formation. The secondary crystallization valley located at the temperature near 80 °C can be observed above the critical concentration, which becomes more evident with the increasing peroxide concentration and curing temperature. This phenomenon provides another evidence of crystallization retardation by the crosslinking network.

Keywords: Polyethylene; Rheology; Crosslinking kinetics; Crystallization.

INTRODUCTION

Polyethylene (PE) as one of the most widely used thermoplastics has gained increasing attractions during the past decades due to its excellent chemical and physical properties, superior processability and low cost. However, some shortcomings such as the relatively low melting point, swelling in hydrocarbons and tendency to crack under stress limit its applications at elevated temperature or under some harsher environments. Crosslinking of PE realized either by chemical agents like organic peroxides and silanes, or high energy irradiation methods, can overcome these above disadvantages and achieve improved thermal performance, impact strength, and environmental resistance^[1–3]. Peroxides crosslinking is the most frequently used method in industry to obtain polymers with desired properties. This method is based on the formation of free radicals by thermal decomposition of peroxide, generation of polymer radicals *via* abstraction of hydrogen atoms from the polymer chains by free radicals, and the combination of two polymer radicals to form crosslinking, long chain

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^{**} Corresponding author: Yan-hua Niu (牛艳华), E-mail: yhnui@scu.edu.cn

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branching (LCB) and chain extension^[4]. Tremendous attention has been made to investigate the reaction mechanisms of crosslinking based on various molecular structures of PE, for example different molecular weight and distribution, vinyl content, and the number of tertiary carbons^[5, 6].

Determination of reaction kinetics during crosslinking or curing is very important for both the industrial processing control and fundamental research. Kinetic characterizations can be phenomenally monitored by differential scanning calorimetry (DSC), electron spin resonance (ESR) and rheological measurements^[7, 8], among which rheology was considered as the most sensitive and popular method. Various kinetic models based on rheological measurements were developed. Ding and Leonov^[9] derived a simplified but more realistic model to continuously simulate the induction, curing, and overcure periods for natural rubber compound by taking account of the reversion process. Han *et al.*^[10] proposed a cure kinetic model based on the Arrhenius type equations for rubber compounds to describe the commonly observed reversion and induction periods, which showed excellent agreement with the rheometric torque curves. Yu *et al.*^[11] proposed a new expression correlating the reaction kinetic rate and the rheological conversion to simulate the rheokinetics of the high density polyethylene (HDPE) with dicumyl peroxide under flow field, and it was found that large strain can significantly accelerate the curing rate. In Whelan's book^[7], a curing kinetic model under real processing conditions based on the evolution of viscosity was established. It is seen that rheological parameters are more sensitive and effective for developing curing kinetic models of polymers under either statistic conditions or taking account of the shear fields.

Upon crosslinking, three dimensional network connected by chemical bonds is formed. Crosslink density is an important parameter governing the properties of the crosslinked network, such as the hardness, chemical resistance, tensile modulus, and impact strength^[12]. For crosslinked polyethylene, these above mentioned properties are not only correlated to the network structure but also influenced by the subsequent crystallization behavior of the system. It was found that crosslinking could affect both the crystallization kinetics and the crystal cell parameters in the microstructure of the condensed phase^[13–16]. Phillips *et al.*^[13, 17–19] published a series of work to discuss the influences of controlled crosslink density on the crystal structure parameters, crystallization kinetics and crystalline morphology of crosslinked low density polyethylene (LDPE) with dicumyl peroxide based on the analysis of extracted sol and gel fractions. They demonstrated that crystallization structures from the melt of a randomly crosslinked network were quite different from those of irradiated polyethylene in solid state. Khonakdar *et al.*^[4] showed that increase in the degree of crosslinking led to the restriction in chain packing, and consequently, resulted in the reduction in the heat of fusion, crystallinity, and melting or crystallization temperature of HDPE. Nilsson *et al.*^[3] presented the similar results in crosslinked LDPE based on the restraining effect of the incorporated crosslinks.

All of the above studies investigated crosslinked polyethylene with relatively high peroxide concentration and the changes in the crystallization parameters were attributed to the condensed network formation. At very low peroxide concentrations, there in fact, exists a transition from long chain branching (LCB) to the 3-dimensional network. The crosslinking kinetics below and above this transition and its influence on the crystallization behaviors have not been reported to our knowledge. Furthermore, the relationship between crosslinking and the constrained crystallization at relatively lower crosslinking degree is very important for industry application. In this study, the crosslinking kinetics of HDPE with relatively low peroxide concentrations (0.1 wt%–1.0 wt%) were investigated by dynamic rheological measurements and the corresponding kinetic parameters were derived by simulation of the Ding-Leonov (DL) model^[9]. The influence of crosslinking and critical gel formation on the subsequent crystallization of HDPE was demonstrated by thermal analyses. Some new results and insights are expected to shed on the fundamental investigation and application development for crosslinked polyethylene.

EXPERIMENTAL

Materials and Samples Preparation

The high density polyethylene (HDPE) with commercial code DGDA8007 was purchased from Dow Chemical. The mass averaged molecular weight M_w and polydispersity index are 77000 g/mol and 3.76, respectively, determined by Polytech PL-220 high temperature GPC. The melt index of the polymer is 8.5 g/10min (190 °C/2.16kg) and the density is 0.963 g/cm³. The peroxide 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (Trigonox 101) was supplied by Aldrich and the half time of decomposition is 60 min at 138 °C.

Samples of HDPE with different levels of peroxide 0.1 wt%, 0.2 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt%, were prepared by a Haake mixer at 137 °C and 50 r/min for 6–8 min. The sample names are defined as P0.1wt%, P0.2wt%, P0.5wt%, P1.0wt%, and P1.5wt% in the following sections, in which “P” represents the peroxide and the numeric value denotes the peroxide concentration. Circular-shaped samples of 25 mm in diameter and 1.0 mm in thickness were compression-molded under vacuumed condition at 135 °C for 5 min to avoid pre-curing. The prepared disks were used for rheological measurements.

Rheological Measurements

Rheological experiments were conducted on a TA DHR-2 rheometer. Frequency sweeps ranging from 0.1 rad/s to 500 rad/s were performed at 150 °C with the fixed strain of 2% within the linear range for samples with different peroxide concentrations P0.1wt%, P0.2wt%, P0.5wt%, P1.0wt%. Time scans were conducted at 170, 180, and 190 °C with fixed frequency of 1.0 rad/s and strain of 1% to monitor the curing kinetics, before which the samples were loaded and compressed between the two plates at 150 °C to avoid pre-curing.

Differential Scanning Calorimetry (DSC)

Crystallization behaviors of samples with different levels of peroxide P0.1wt%, P0.2wt%, P0.5wt%, P1.0wt% and P1.5wt% were investigated by a TA Q2000 DSC instrument. The samples were first pre-crosslinked at different temperatures of 170, 180, and 190 °C for 10 min and then the subsequent cooling and heating processes with the cooling and heating rates of 10 K/min were conducted. The sample weight is about 3.0–5.0 mg and all the experiments were conducted under nitrogen purge. The crystallinity X_c can be calculated as

$$X_c = \frac{\Delta H_m}{\Delta H_{\text{fusion}}} \times 100\%, \text{ in which } \Delta H_m \text{ is the melting enthalpy of tested sample and } \Delta H_{\text{fusion}} \text{ denotes the enthalpy}$$

of 100% crystalline polyethylene. According to the report by Wunderlich *et al.*^[20], a value for ΔH_{fusion} of 293.6 J/g was used.

RESULTS AND DISCUSSION

Rheological Properties of HDPE during Crosslinking

Figure 1 shows the frequency sweep curves for pure HDPE and samples with different peroxide concentrations of 0.1 wt%, 0.2 wt%, 0.5 wt% and 1.0 wt% at 150 °C. In Fig. 1(a), one can see that for pure HDPE at the terminal region, the storage modulus G' and loss modulus G'' follow the scaling relation $G' \sim \omega^2$, and $G'' \sim \omega$ ^[21]. With the addition and increase of peroxide concentration, G' shows slight increase and deviates a little bit from the scaling relation in the low frequency region. The deviation becomes more evident for sample P1.0wt% with the highest peroxide. At high frequencies, the crossover of G' and G'' represents the longest relaxation of a single polymer chain with monodispersion, which is a measurement of polymer molecular weight M_w . In an experimental way for polydispersed polymers, the reciprocal of frequency $1/\omega_c$ where $G' = G''$ represents the longest relaxation time τ_r of the majority of molecular chains. More specifically, τ_r is about 2.4 ms for pure HDPE and the addition of peroxide has almost no influence on the relaxation time, indicating that crosslinking can hardly occur at this lower temperature for relatively shorter time. Correspondingly, the complex viscosity $|\eta^*|$ is another parameter involving the information of M_w , molecular weight distribution and even long chain branching. In Fig. 1(b), frequency dependence of $|\eta^*|$ for pure HDPE and samples with different peroxide concentrations was depicted. Similar to the variation of G' , with increasing peroxide concentration, the slight

deviation from Newtonian plateau can be observed. In the non-Newtonian region, shear thinning also becomes somewhat serious for samples with peroxide addition, which indicates the appearance of slight long chain branching (LCB)^[22]. It should be noted that for both G' and $|\eta^*|$ the deviation phenomena all occur at frequency lower than 1.0 rad/s, above which the influence of slight LCB can be neglected. Therefore, in the next section, crosslinking kinetics was detected by time sweeps with fixed frequency 1.0 rad/s to avoid or minimize the pre-cure effects. Since the global time of the frequency sweeps from high to low (500–0.1 rad/s) are about 10 min, it is thus proven that at 150 °C, the samples kept for 5–8 min are safety enough and the pre-curing can be neglected. Nevertheless, during the heating process from 150 °C to the target curing temperature (170, 180 and 190 °C), pre-curing is inevitably involved, which will be discussed in Fig. 2.

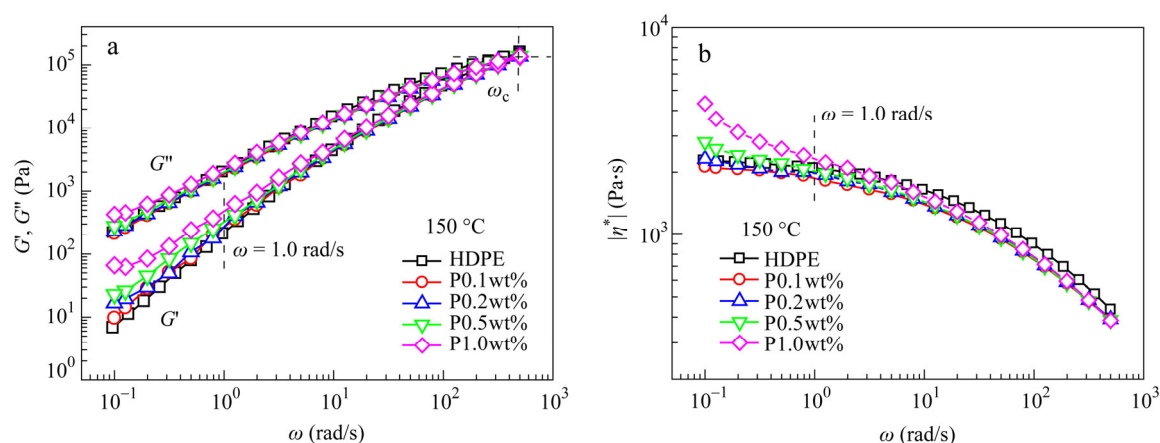


Fig. 1 Frequency dependences of (a) storage moduli G' and loss moduli G'' and (b) complex viscosity $|\eta^*|$ for pure HDPE and samples with different peroxide concentrations of 0.1 wt%, 0.2 wt%, 0.5 wt% and 1.0 wt% at 150 °C (before curing) with the fixed strain of 2% within the linear range

Figure 2 shows the time evolution of G' and G'' of HDPE with various peroxide concentrations ranging from 0.1 wt% to 1.0 wt% at different curing temperatures of 170, 180 and 190 °C. The selected frequency 1.0 rad/s is sensitive enough to detect the progress of crosslinking and meanwhile ensures that the influence of those slight LCBs formed during sample loading at 150 °C could be excluded. Under ideal situations, the crosslinking kinetic curves show typical “S” shapes including the induction, curing, and even over-cure stages. In our cases, however, the induction stage cannot be observed because pre-cure might occur during the heating process from 150 °C to the target curing temperatures. In Fig. 2(a), it can be seen that at all the temperatures during both the curing and over cure stages, G'' is always larger than G' . This indicates that the lower peroxide concentration 0.1 wt% is only introduced into some LCB or isolated crosslinking fractions and the HDPE melts still show liquid behavior. With the increase of curing temperature, the pre-cure becomes more serious and the curing rate also becomes faster. At the late over-cure stage, however, the equilibrium moduli almost reach the same level and are almost independent of temperature. This suggests that the curing temperature only influences the curing rate while the peroxide concentration determines the equilibrium moduli. At the peroxide concentration of 0.2 wt% as shown in Fig. 2(b), $G' < G''$ can be observed at the early curing stage. At the late stages, the G' and G'' almost overlap with each other at all curing temperatures, which indicates that the critical gel at which polymer chains connected into a three-dimensional network forms at this peroxide concentration^[23]. Near the gel point, another phenomenon that the equilibrium moduli at higher curing temperature, e.g. 190 °C, are even slightly lower than that at lower temperature of 180 °C can be observed. This temperature independent phenomenon was also reported by other researchers^[24–26], and the tentative explanation is that at higher temperatures both the crosslinking and termination are more complex due to the possible degradation of peroxide. It was basically assumed that during the curing process, crosslinking and reversion/scission could occur simultaneously, and at higher curing temperature the reversion process became more prominent, which as

a result led to lower equilibrium moduli^[9, 10, 25]. When the peroxide concentration reaches 0.5 wt% in Fig. 2(c), a transition from liquid to solid state can be observed. At the lower temperature of 170 and 180 °C, a crossover between G' and G'' can be found at the early curing stage indicating a transient gel formation. With increasing temperature the crossover shifts to shorter time indicating the faster curing rate. At the late stage of curing, $G' > G''$ at all temperatures is persisted. With further increase in peroxide concentration, G' becomes much higher than G'' and at the late over-cure stage the moduli tend to approach the same level as shown in Fig. 2(d).

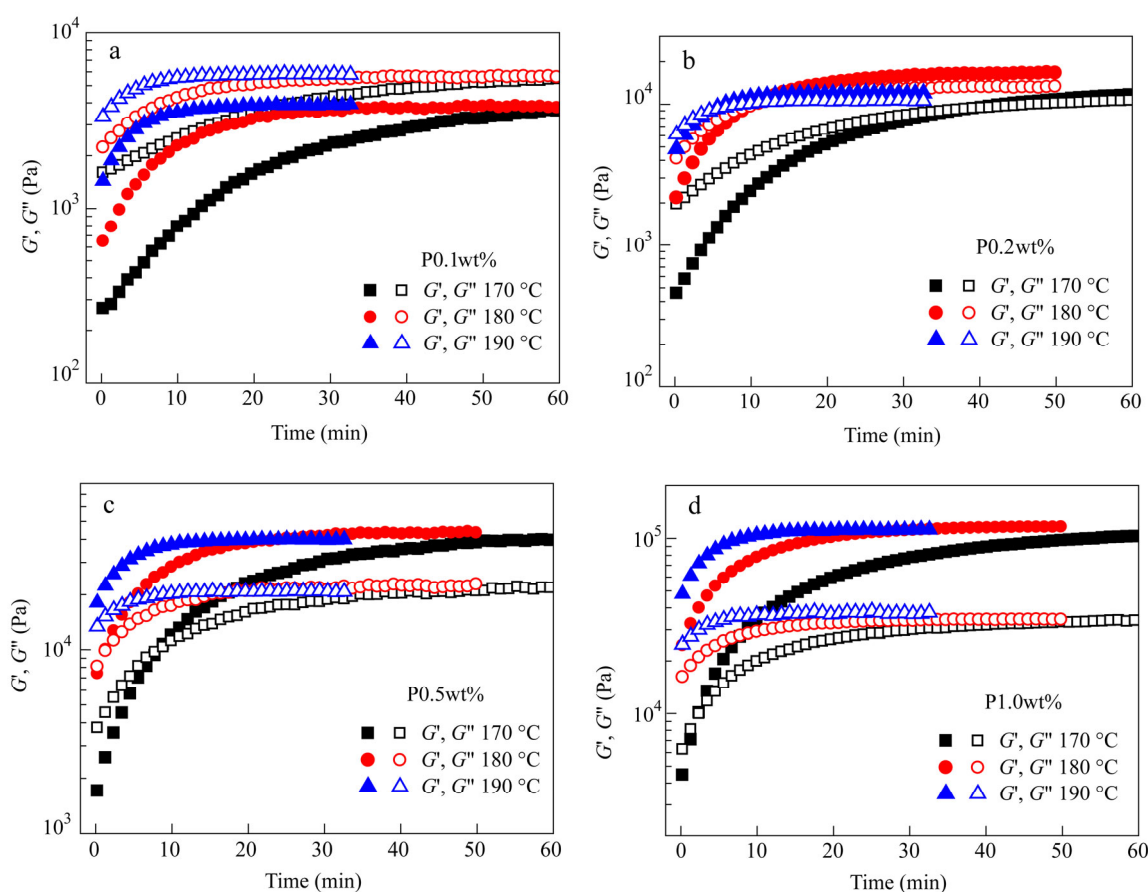


Fig. 2 Time evolution of storage moduli G' and loss moduli G'' at various curing temperatures for HDPE with different peroxide concentrations (a) 0.1 wt%, (b) 0.2 wt%, (c) 0.5 wt%, and (d) 1.0 wt%. The filled symbols represent G' and the blank symbols represent G'' , respectively.

The loss tangent $\tan\delta = G''/G'$ is another rheological parameter to determine the critical gel point and the sol-gel transition behavior. Figure 3 shows the evolution of $\tan\delta$ at various curing temperatures for HDPE with different peroxide concentrations. Consistent with the evolution of G' and G'' , with the progress of crosslinking, $\tan\delta$ sharply decreases at the early curing stage and then reaches an equilibrium plateau. With the increase of curing temperature, the initial value of $\tan\delta$ decreases, which is ascribed to the pre-cure during heating. At the lowest peroxide concentration 0.1 wt% in Fig. 3(a), the values of $\tan\delta$ at all curing temperatures are higher than 1. With the increasing peroxide concentration, the curves of $\tan\delta$ at different temperatures coherently shift to lower values indicating the more elastic behavior induced by increasing crosslink density. If we only concentrate on $\tan\delta$ at the late equilibrium stages, one can see that for samples with the peroxide concentration of 0.2 wt% in Fig. 3(b), $\tan\delta$ is approximately equal to 1 and independent of temperature, which indicates that the critical gel could be formed at this concentration. As the peroxide concentration increased to 0.5 wt% and 1.0 wt% as shown in Figs. 3(c) and 3(d), the $\tan\delta$ values under different temperatures become lower than 1. Although $\tan\delta$ at the

equilibrium stage is almost independent of the curing temperature, the transition from curing stage to equilibrium over-cure stage as marked in Fig. 3(b) retract to shorter times as the temperature increasing, indicating the faster curing rate.

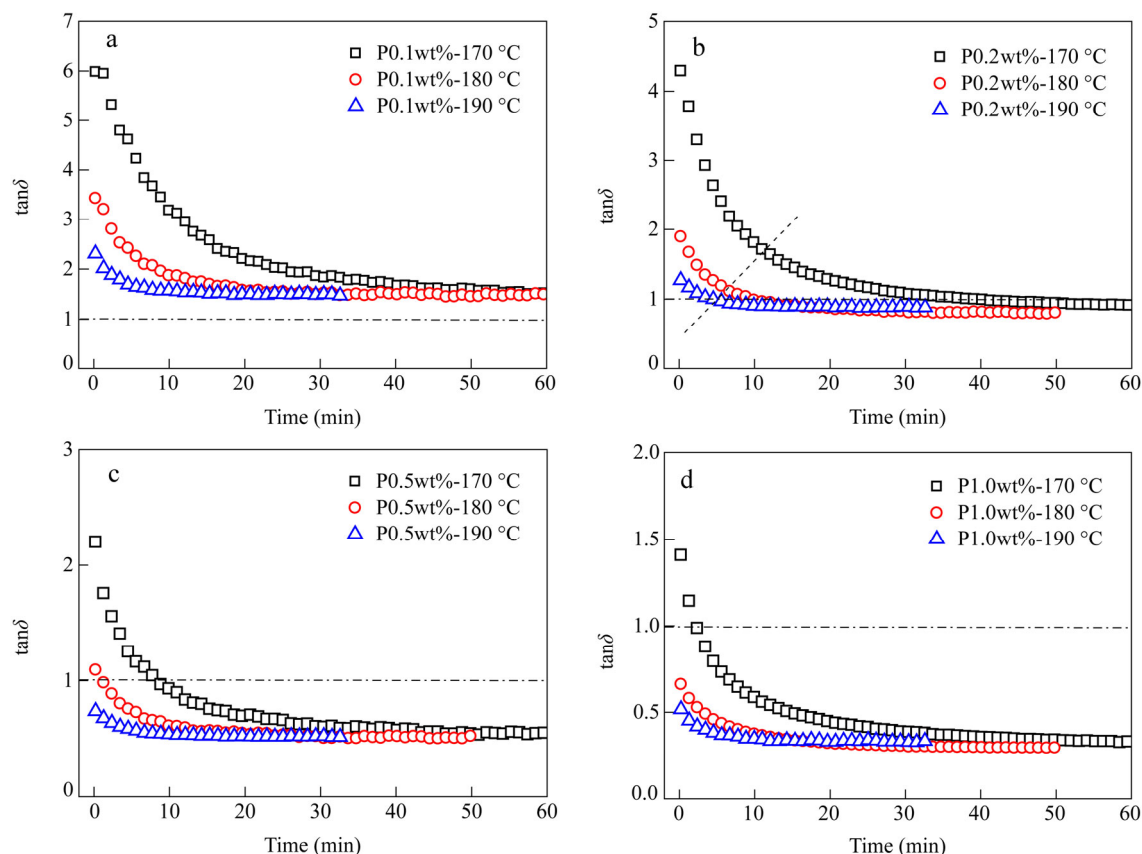


Fig. 3 Time evolution loss tangent ($\tan\delta$) at various curing temperatures for HDPE with different peroxide concentrations (a) 0.1 wt%, (b) 0.2 wt%, (c) 0.5 wt% and (d) 1.0 wt%

Figure 4 shows the influence of peroxide concentration on the equilibrium storage modulus G' at the over-cure stage, which is a measurement of the crosslinking degree. The data of original HDPE without peroxide were obtained from the temperature ramp at the same frequency of 1.0 rad/s. With the increasing peroxide concentrations, the equilibrium G' first sharply increase at lower concentration below 0.2 wt% and then slightly increase with further peroxide increasing. As marked in the Fig. 4, 0.2 wt% is a critical peroxide concentration, at which it is hypothesized that a transition from long chain branching to un-reversed crosslinking network occurs. The curves of G' versus peroxide concentration are similar to the gel content dependence of the peroxide concentration as previously reported^[3]. Compared to the peroxide concentration, curing temperature has almost no influence on equilibrium G' . Although it was discussed that higher curing temperature would lead to lower G' as shown in Fig. 2 and explained by simultaneous reversion process, at larger scale covering all the concentration range, this difference became more subtle. This also indicates that the curing temperature is more efficient on the curing stages and the peroxide concentration is the prominent factor to influence the final equilibrium stage.

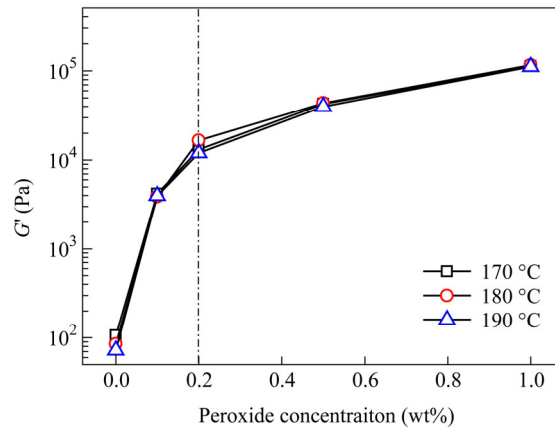
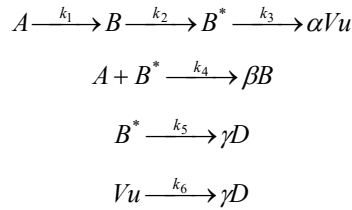


Fig. 4 Influence of peroxide concentration on the crosslinking degree represented by equilibrium storage modulus G' at various curing temperatures
The values of equilibrium G' for each crosslinked sample was determined from G' at the late-stage plateau regions in Fig. 2.

Crosslinking Kinetics

Taking account of the induction, curing and even the reversion process during over-cure stages, Ding-Leonov (D-L)^[9] used the following scheme to describe the crosslinking kinetic process,



where A is the accelerator and/or its reaction products; B is a precursor to crosslinks, probably polymeric; B^* is an activated form of B ; Vu is a crosslink; D is inactive side products; α , β and γ are adjustable stoichiometric parameters; and k_i ($i = 1, 2, \dots, 6$) is the rate constant of each step.

Based on the above scheme and mass balance, and assuming that $\frac{k_2}{k_3} \ll 1$, $\frac{k_4}{k_3} = \varphi$, $\frac{k_5}{k_3} = \psi$, the rate equations were derived as:

$$\begin{aligned}
 dVu / dt' &= A_0 k_2 [\exp(-k_2 t')] / (1 + \psi) - k_6 Vu \\
 Vu(t' = 0) &= 0
 \end{aligned} \tag{1}$$

The solution of Eq. (1) can be written as:

$$Vu = A_0 k_2 [\exp(-k_2 t') - \exp(-k_6 t')] / [(1 + \psi) - (k_6 - k_2)] \tag{2}$$

Consider the maximum cure at $t = t_m$ or $t' = t_m - t_i$, we have

$$dVu/dt' = 0 \text{ at } t' = t_m - t_i \tag{3}$$

which leads to

$$t_m - t_i = \frac{\ln k_2 / k_6}{k_2 - k_6} \tag{4}$$

The fitting procedure using isothermal data is as follows: first, using Eqs. (2) and (4), k_2 and ψ can be obtained by knowing two characteristic points in the over-cure region. Then k_6 is automatically calculated

according to Eq. (4). k_1 and ϕ can be determined from induction time t_i and the initial slope of the cure curve in the curing period.

Generally, the rate constant k_i ($i = 1, 2, 6$) and ψ parameter take the forms of Arrhenius type relation

$$k_i = k_{i0} \exp(-E_i/RT) \quad (5)$$

$$\psi = a \exp(b/T) \quad (6)$$

where E is the active energy, T is absolute temperature, and a and b are material constants.

Figure 5 illustrates the fitting results for P0.5 wt% sample curing at different temperatures of 170, 180 and 190 °C through the above deduced D-L model. Evidently, the fitting results look quite well at all the curing temperatures. Through fitting, the induction time t_i , initial accelerator number A_0 , curing rate k_2 , reversion rate k_6 , and ϕ can be determined as summarized in Table 1. It can be seen that at higher curing temperatures, *e.g.* 180 and 190 °C, the induction time t_i is 0. This is due to the pre-cure during the heating process. At the lower curing temperature of 170 °C, the influence of pre-cure can be neglected and t_i is determined to be 1.52 min. The reversion at all curing temperatures can also be neglected as evidenced by the zero values of k_6 . The parameter ϕ characterizes the initial rate of curing reaction immediately after the induction period, and is observed to be insensitive to temperature. The decreased values of A_0 with the increase of curing temperature indicate that more accelerators were consumed during the pre-cure. k_2 is the key parameter describing the curing rate at different temperatures. One can see that with the increasing temperature of per 10 °C, the curing rate is almost 3 times acceleration. Therefore, by adjusting these kinetic parameters, the crosslinking process and final properties can be well controlled.

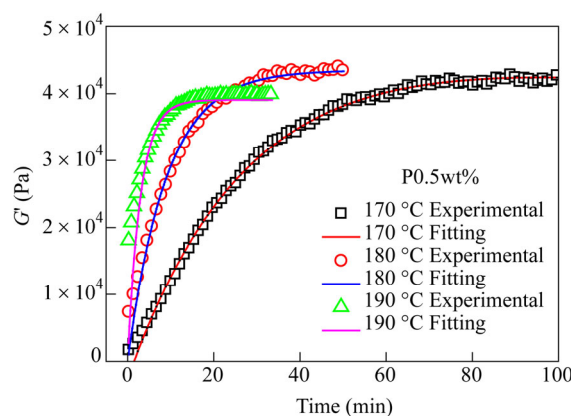


Fig. 5 Time evolution of storage modulus G' (symbols) and the fitting results (lines) for P0.5 wt% sample curing at different temperatures of 170, 180 and 190 °C

Table 1. The fitting parameters of P0.5 wt% sample cured at different temperatures of 170, 180 and 190 °C

Fitting parameters	t_i (min)	A_0	k_2 (1/min)	k_6 (1/min)	ϕ (mol/m ³) ⁻¹
P0.5wt%-170 °C	1.52	48120	0.036	0	1.93×10^{-5}
P0.5wt%-180 °C	0	43487	0.11	0	1.97×10^{-5}
P0.5wt%-190 °C	0	39066	0.33	0	1.93×10^{-5}

Influence of Crosslinking on the Subsequent Crystallization

The influence of crosslinking on the crystallization behavior was detected by DSC measurements. Samples were first cured at different temperatures of 170, 180, and 190 °C for 10 min, and then the subsequent cooling and heating processes were recorded. Figure 6 shows the influence of curing temperature, at which crosslinking with different curing rates occurred, on the crystallization and melting behaviors for HDPE samples with various peroxide concentrations ranging from 0.1 wt% to 1.0 wt%. It is seen that at lower peroxide concentration, both the crystallization and the melting behaviors are not influenced by the curing temperature as shown in Fig. 6(a).

Above the critical peroxide concentration of P0.2wt%, the higher curing temperature leads to the slightly decreased crystallization temperature and reduced peak areas. The melting temperature and the corresponding peak area of these samples with higher peroxide concentrations of P0.5wt% and P1.0wt% also decrease with the increase of curing temperature. This indicates that the network formation during the curing process could more or less hinder the crystallization process. For the sample of P0.2wt% as shown in Fig. 6(b), the sharp crystallization and melting peaks at lower curing temperature of 170 °C might be due to the dominant nucleation effect of the peroxide addition compared with the crosslinking.

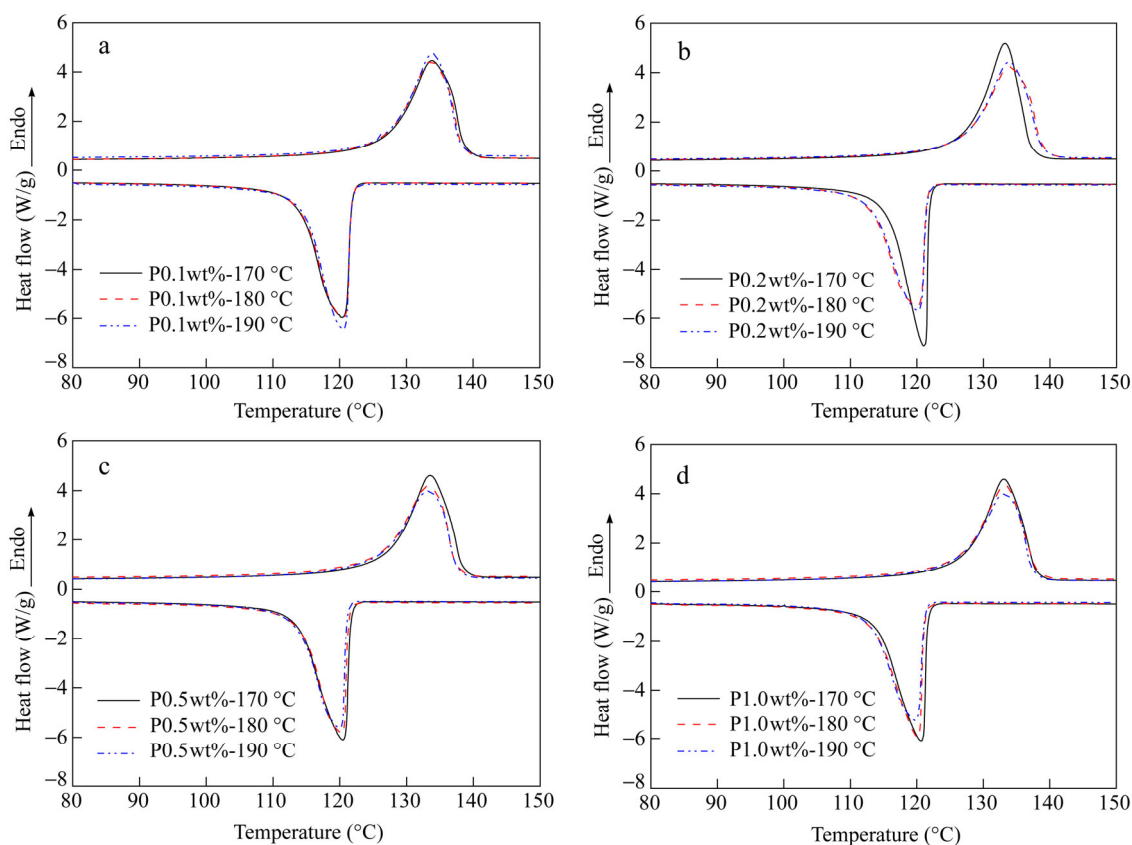


Fig. 6 DSC cooling and heating scan traces for samples with different peroxide concentrations (a) 0.1 wt%, (b) 0.2 wt%, (c) 0.5 wt% and (d) 1.0 wt% after pre-annealed at various temperatures of 170, 180 and 190 °C for 10 min

Besides the changes of the main peaks influenced by crosslinking, a faint low temperature valley around 80 °C can also be observed at higher peroxide concentration *e.g.* 1.5 wt% as marked in the dashed square area in Fig. 7(a). This small valley is very common in the crystallization of ethylene copolymers, which is reported to be related to the crystallization of shorter ethylene sequence between two short chain branches^[28]. For clarity, Fig. 7(b) illustrates the enlarged low temperature cooling trace of samples with peroxide concentrations ranging from 0.1 wt% to 1.5 wt% pre-annealed at various temperatures of 170, 180 and 190 °C for 10 min. The influence of curing temperature and peroxide concentration on the progress of low temperature valley can be obviously seen. At the lowest peroxide level of P0.1wt%, the low temperature crystallization valley cannot be observed. At the critical gel concentration of 0.2 wt%, this crystallization valley starts to appear at higher curing temperature of 190 °C. With the increase of peroxide concentration, the higher curing temperature evidently leads to larger crystallization valleys. This indicates that below the critical gel, long chain branching has little influence on the subsequent crystallization behavior. Above the critical gel peroxide concentration, the restraints of crosslinks become more prominent at the higher curing temperatures and the secondary crystallization valley becomes

more distinguishable. At lower annealing temperature of 170 °C, the secondary crystallization valley is very faint even at higher peroxide concentrations indicating lower degree of crosslinking. For polyethylene copolymers, the low temperature valley can be interpreted from the disruption of chain regularity or different ethylene sequence lengths between each two neighboring branching points^[28]. For the crosslinked system, it is likely that the different ethylene sequence length is attributed to the neighboring crosslinks formed during the curing process. The readily formed crosslinks can act as anchors to limit chain relaxation and thus could hinder the crystallization of nearby sequences and/or chains. As a consequence, the restricted sequences crystallize at much lower temperature with larger super cooling degree and thus the low temperature valley can be observed. The same phenomenon was also reported in Péreza *et al.*'s study^[29], in which the small exotherm peak was explained to be associated to the secondary crystallization process.

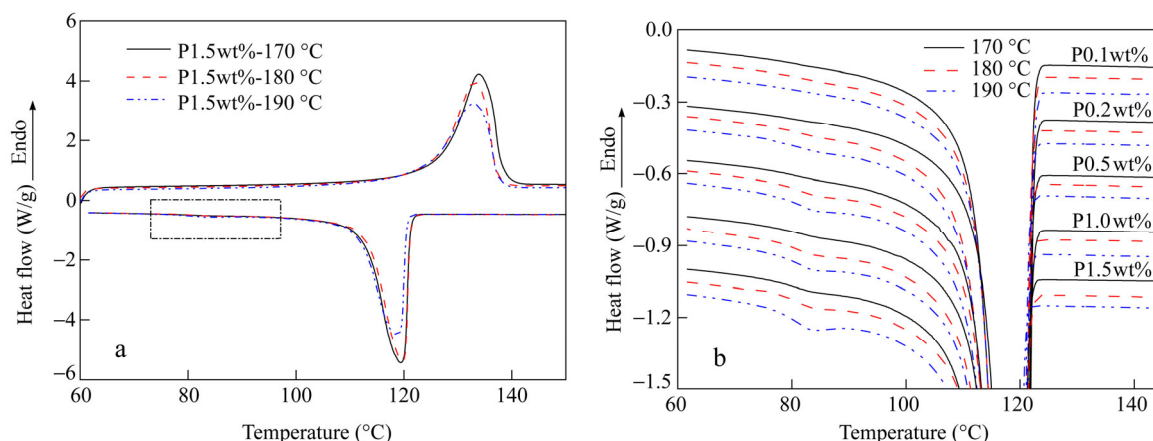


Fig. 7 (a) DSC cooling and heating scan traces for samples with peroxide concentration of 1.5 wt%, and (b) enlarged cooling traces of samples with peroxide concentrations ranging from 0.1 wt% to 1.5 wt% pre-annealed at various temperatures of 170, 180 and 190 °C for 10 min

Figure 8 shows the dependence of the crystallization temperature T_c and crystallinity X_c on the peroxide concentration. In Fig. 8(a), it is seen that below the critical gel concentration of 0.2 wt%, T_c shows a small increase with the increasing peroxide concentration at the lower curing temperature of 170 °C; while at the elevating curing temperatures of 180 and 190 °C, T_c decreases with the increasing peroxide concentration. This phenomenon might be attributed to the competition between the accelerated crystallization by peroxide addition as the nucleation agent and the retarded crystallization induced by crosslinking. At lower curing temperature the acceleration is dominated, whereas at higher curing temperatures the retardation is predominant due to the cross-linked network formation. With the increase of peroxide concentration, T_c shows approximately the decreasing trend, which becomes more evident at higher curing temperature. It is seen that there is a transition from nucleation effect to the crosslinking restricted crystallization at the critical gel point. At the same peroxide level above the critical point, T_c decreases with the elevation of annealing temperature and the difference becomes more evident at higher peroxide level. Similar to the variation of the T_c , the effect of peroxide concentration on crystallinity X_c is shown in Fig. 8(b). At relatively lower annealing temperature of 170 °C, X_c only slightly decreases with the peroxide concentration. With increasing curing temperature, the decrease of X_c becomes more prominent. At the highest curing temperature of 190 °C, X_c decreases significantly from 73% to 63% with the increasing peroxide concentration. Above the critical gel point, the decrease of T_c and X_c was also frequently reported by other researchers^[3, 18]. This might has great influence on the toughness control of crosslinkable polyethylene products.

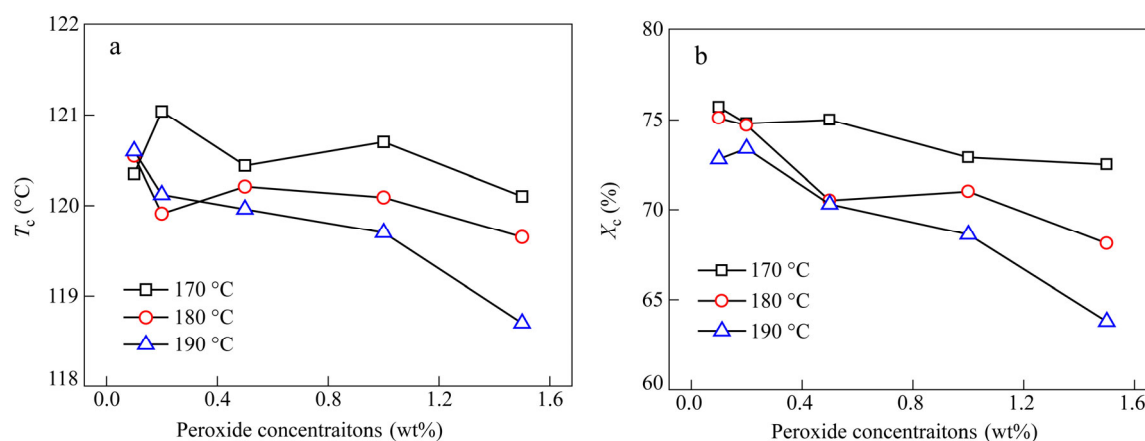


Fig. 8 Peroxide concentration dependences of (a) crystallization temperature T_c and (b) crystallinity X_c of samples pre-annealed at various temperature of 170, 180 and 190 °C for 10 min

CONCLUSIONS

The effects of peroxide concentration and curing temperature on the crosslinking kinetics and the subsequent crystallization behaviors of polyethylene have been investigated. Rheological results indicate that there is a critical gel concentration of peroxide at about 0.2 wt%, below which peroxide decomposition predominantly introduce long chain branching (LCB), and above which crosslinking network can be developed. With the increase of curing temperature, the crosslinking process could be prominently accelerated at the earlier stages while the equilibrium late stage modulus is almost independent of the curing temperature. Crosslinking kinetics can be fitted well by Ding-Leonov's model and the curing rate k_2 is determined to be almost 3 times increasing per 10 °C within the temperature range of 170–190 °C. Influences of crosslinking on the subsequent crystallization behaviors were detected by DSC measurements. Below the critical gel concentration of 0.2 wt%, there exists a competition between peroxide (as the nucleation agent) induced crystallization and crosslinking retarded crystallization. Above the critical gel concentration, crystallization was almost retarded as evidenced by the decrease of crystallization temperature T_c and crystallinity X_c . With the increase of curing temperature, the retardation of crystallization becomes more prominent. The exothermic small valley at temperature of 80 °C is found to be related to the crystallization of shorter ethylene sequence between the neighboring crosslinks. This secondary crystallization of constrained shorter chains becomes more evident with increasing curing temperature and peroxide concentration above the critical gel point.

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