

# Assessment of Hindered Phenol Antioxidants on Processing Stability of Peroxide-Cure LDPE by Rheology and DSC Analysis

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**ABSTRACT:** Influence of commercial phenol antioxidants Irganox 300, 1010, 1035, and 1076 on peroxide-cure reaction of low-density polyethylene (LDPE) was evaluated through isothermal dynamic rheological and nonisothermal differential scanning calorimetry (DSC) testing. The results indicated that phenol antioxidants could reduce storage modulus of LDPE completely crosslinked at 175°C while they have a neglectable effect on gel fracture and activity energy of crosslinking reaction. On the other hand, time sweep dynamic rheological test revealed

the antioxidants 1035 and 1076 with low molecular weight and low melting point could significantly depress scorch of crosslinkable LDPE at 135°C. The isothermal time sweep dynamic rheology test method was more sensitive than nonisothermal DSC test for characterizing the influence of phenol antioxidants on crosslinking kinetics of peroxide-cure reaction of LDPE. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** LDPE; DCP; antioxidants; stabilization; kinetics

## INTRODUCTION

Low-density polyethylene (LDPE) with good chemical stabilization and processibility is widely used as cable insulation. However, poor heat resistance due to heat generation of ohmic loss restrains its application greatly.<sup>1</sup> Crosslinked LDPE (XLPE) addresses this problem and gains more popularity.<sup>2,3</sup> Peroxide-cure reaction based on radical couple mechanism is the most common method to prepare XLPE and dicumyl peroxide (DCP) is the most common crosslinking agent used.<sup>4–9</sup> Antioxidants, indispensable additives for XLPE insulation to prevent materials from oxidation and prolong service life, are designed to capture radicals during processing and crosslinking.<sup>7,10,11</sup> Antioxidants could capture radicals and lessen oxidation of polymer effectively<sup>11–15</sup> so that they are usually used to depress scorch in crosslinking systems during processing as well. Primary antioxidants and secondary antioxidants are used in combination to get the greatest effectiveness and synergism. Primary antioxidants, mainly of hindered phenols and hindered aromatic amines, scavenge and destroy the chain propagating peroxy and alkoxy radicals before they react with the polymer; secondary antioxidants (or hydroperoxide decom-

posers) are designed to decompose chain-initiating hydroperoxides to nonradical products to stop the autocatalytic chain propagation step. Some secondary antioxidant could capture radicals as well.<sup>7</sup>

Enough care should be taken to select antioxidants in radical crosslinkable system, for antioxidant can reduce the crosslinking efficiency of DCP greatly. For instance, zinc and nickel dialkyldithiocarbamates even at low dosages strongly reduce the cure extent to an unacceptable level.<sup>10</sup> Interaction between peroxide crosslinking agent and antioxidants has been investigated.<sup>4–7,13,16–20</sup> During crosslinking reaction, primary radicals derived from DCP decomposition deprive hydrogen atoms from polyethylene chains to form macromolecular radicals which undergo coupling reaction, leading to the network formation. Electron spin resonance (ESR) studies showed that phenol antioxidants capture initial radicals and phenol radicals reach maximum concentration before alkyl radicals.<sup>4–7</sup> The effects of antioxidants to crosslinking reaction depend on the molecular structure of antioxidants greatly. In general, amine antioxidants are more powerful than hindered phenols but the oxidation products of amine antioxidants are more discoloring and staining than their hindered phenol counterparts. While phenolic antioxidants are claimed to interfere more with peroxide cures than amine antioxidants, there are exceptions. Molecular structure and molecular weight, which influence mobility of antioxidants in polymer melts, are important factors

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influencing their effects on scorch, for example, the lesser hindered phenols have better effect on scorch.<sup>1</sup> Antioxidants with low molecular weight and small steric hindrance exhibit high mobility, leading to a better effect on scorch, which is more effective in unsaturated elastomers. High molecular weight antioxidants such as Irganox 1010 have high stability so that they are good choices for mineral-filled applications.<sup>10</sup> At high temperatures, antioxidants act effectively to retard the destructive mechanism, slow the rate of chain scission and prevent chain decomposition.<sup>10,16</sup> On the other hand, DCP consumes a lot of antioxidants during crosslinking reaction, leading to a great reduction in oxidation induction time.<sup>21–23</sup> A rather high dosage of antioxidants should be used in crosslinkable systems to guarantee the stabilization in material processing and in service life.

Rheological test, thermal analysis, and ESR are most used in studying the crosslinking reaction kinetics and the influence of antioxidants on peroxide-cure reaction. Both thermal analysis and ESR could not be used to trace the evolution of mechanical properties except for kinetics of free radical generation and crosslinking. Nevertheless, previous investigations using torque rheometer could only provide qualitative information to the crosslinking kinetics. On the other hand, little works have focused on influence of antioxidants on kinetics of peroxide-cure reaction. The combined characterization methods by rheology and differential scanning calorimetry (DSC) analysis are quite interesting to study the influence of antioxidants on kinetics of crosslinking reaction.<sup>24–28</sup> In this article, peroxide-cure kinetics is studied using nonisothermal DSC and isothermal dynamic rheological measurements. Influence of phenol antioxidants on activity energy ( $E_a$ ) and half time ( $K$ ) of crosslinking reaction are reported.

## EXPERIMENTAL

### Materials and preparation

Low-density polyethylene (LDPE, melt flow index 2.12 g/10 min at 2.16 kg and 190°C) is produced by Yanshan, SINOPEC, China. Dicumyl peroxide (DCP) was used as crosslinking agent. Four kinds of commercial primary antioxidants, 4,4'-thio-bis(6-tert-butyl-3-methylphenol) (Irganox 300), tetra-[methylene- $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate] methane (Irganox 1010), 3,5-bis(1,1-dimethylethyl)-4-hydroxyl-hydroxylbenzenepropanoic acid thio-di-2,1-ethanediyl ester (Irganox 1035), and *n*-otadecyl- $\beta$ -(4-hydroxy-3,5-di-tert-butyl-phenyl)-propionate (Irganox 1076) provided by Virtulla Tianjin Tech, China were used as received.

Masterbatch of LDPE containing 5 wt % antioxidant was prepared using a twin-screw extruder (PRISM TSE 16 TC, Thermo Scientific, UK) above melting temperature ( $T_m$ ) of antioxidants. The antioxidant masterbatch, LDPE and DCP were mixed using the twin-screw extruder at 115°C and 22 rpm to prepare crosslinkable LDPE. DCP was 1.5 phr, and antioxidant used was 0.1, 0.2, 0.3, 0.4, and 0.5 phr in crosslinkable LDPE, respectively.

The crosslinkable LDPE was molded into disks of 1.2 mm in thickness and 25 mm in diameter at 15 MPa and 115°C for 5 min and was cooled down under pressure to room temperature for rheological test. Completely crosslinked LDPE sheets were prepared at 15 MPa and 175°C for 10 min.

### Measurement

#### Rheological test

The crosslinkable LDPE disk was placed between the plates of an Advance Rheometric Expansion System (ARES, Rheometrics Sci., USA) in air atmosphere at 120°C. Time sweep was performed at frequency 3.14 rad s<sup>-1</sup> and strain amplitude 1% at 135°C.

#### Gel fracture

Degree of crosslinking was characterized by gel fraction ( $f_{\text{gel}}$ ) determined using a Soxhlet extractor using xylene as solvent for at least 12 h. The crosslinked samples before and after extraction were dried in a vacuum oven to constant weights  $m_1$  and  $m_2$ , and  $f_{\text{gel}}$  was calculated according to  $f_{\text{gel}}(\text{wt}\%) = \frac{m_2}{m_1} \times 100$ .

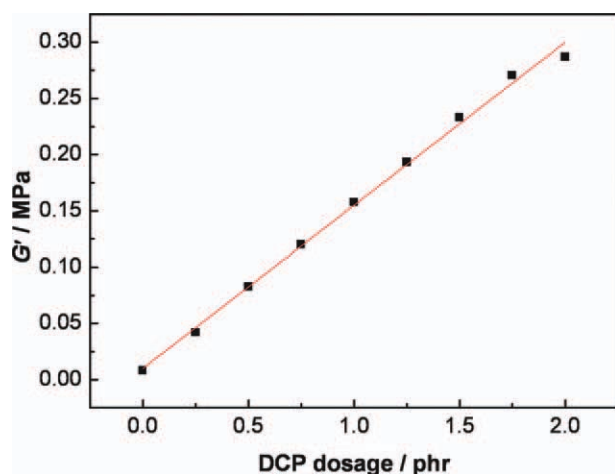
#### DSC test

DSC Q-100 (TA, USA) was used to measure enthalpy of crosslinking reaction. Crosslinkable LDPE of 5–10 mg was heated from 120 to 240°C at a heating rate of 2, 5, 10, and 15°C min<sup>-1</sup>, respectively. Activity energy ( $E_a$ ) of crosslinking reaction was calculated according to the method described elsewhere.<sup>29</sup>

## RESULTS AND DISCUSSION

### Influence of phenol antioxidant on crosslinking

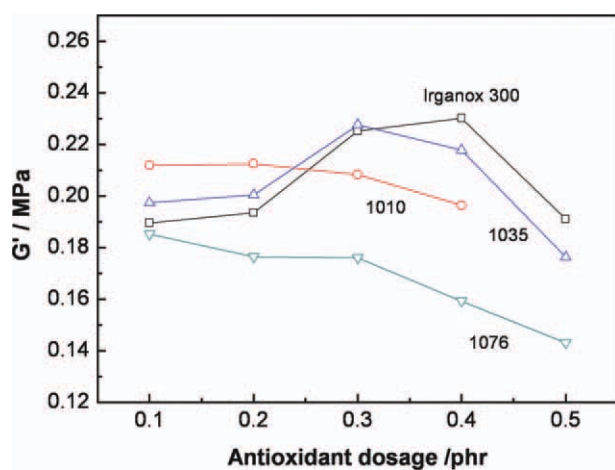
Peroxide-cure reaction proceeds through radical coupling; primary radicals derived from DCP decomposition deprive hydrogen atoms from polyethylene chains to form macromolecular radicals which undergo coupling reaction, leading to the network formation accompanied with great increments in  $G'$  and loss modulus ( $G''$ ).  $G'$  is more sensible to crosslinking degree<sup>27,30</sup> and has a linear relationship with



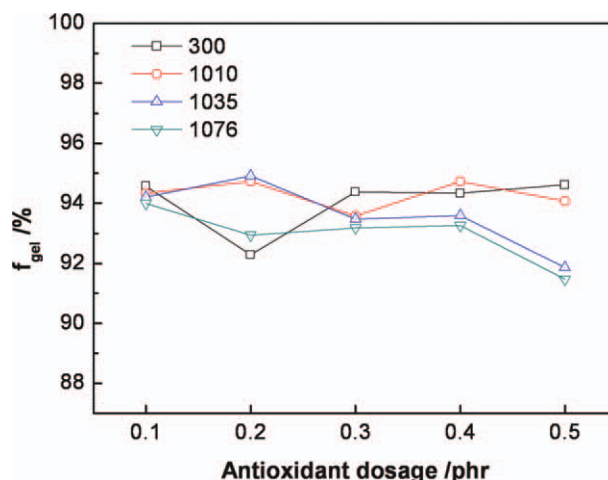
**Figure 1**  $G'$  against DCP dosage for XLPE crosslinked at 175°C for at least 30 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

DCP dosage for LDPE completely crosslinked at 175°C, as shown in Figure 1.

Antioxidants capture radicals during the crosslinking reaction so that  $G'$  of XLPE changes greatly. Figure 2 shows influence of antioxidants on  $G'$  of LDPE crosslinked at 175°C for at least 30 min.  $G'$  of XLPE without antioxidants is 0.23 MPa. Even a small dosage of 0.1 phr antioxidants could decrease  $G'$  significantly.  $G'$  is further reduced with increasing Irganox 1010 and 1076 dosages. On the other hand,  $G'$  of the systems containing Irganox 300 and 1035 reach maximum of about 0.23 MPa at 0.4 and 0.3 phr, respectively. Crosslinking and decomposing reactions of LDPE coexist and compete with each other and chain scission reaction becomes more predominant at high temperatures such as 175°C.<sup>16</sup> Irganox 300 and 1035 containing a bivalent sulfur atom combine



**Figure 2**  $G'$  against antioxidant dosage for XLPE crosslinked with 1.5 phr DCP at 175°C at strain of 1% and frequency of 3.14 rad s<sup>-1</sup>. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3**  $f_{\text{gel}}$  against antioxidant dosage for XLPE crosslinked with 1.5 phr DCP at 175°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

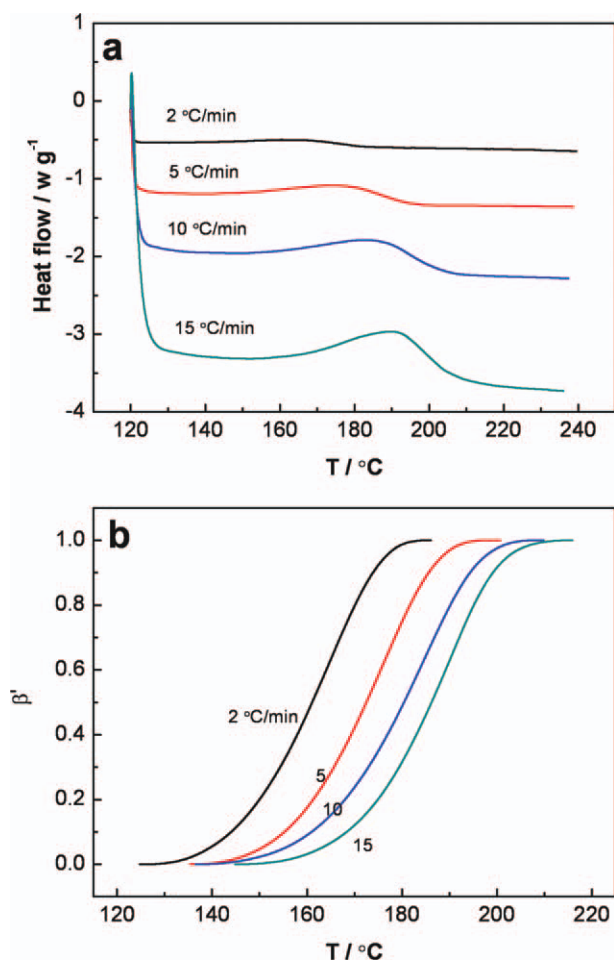
the function of primary and secondary antioxidants.<sup>7,10</sup> As a result, a small dosage of Irganox 300 and 1035 can eliminate the decomposition of LDPE effectively during crosslinking, leading to an increase of  $G'$ . However, a huge dosage of sulfurphenol antioxidant captures a lot of radicals, resulting in a quick decrease of  $G'$ . Nevertheless, antioxidants do not influence  $f_{\text{gel}}$  markedly, as is shown in Figure 3. Investigating influence of DCP dosage on  $f_{\text{gel}}$  revealed that  $f_{\text{gel}}$  increases slightly from 88.7% at 1.0 phr to 91.8% at 1.5 phr DCP dosage. The antioxidants below 0.5 phr may react with free radicals at the end of dangling chains suspending on the network so that they interfere the dangling chains to participate in the network formation (as reflected by the general decreases of  $G'$ ) without marked influence on  $f_{\text{gel}}$ .

### DSC study of crosslinking kinetics

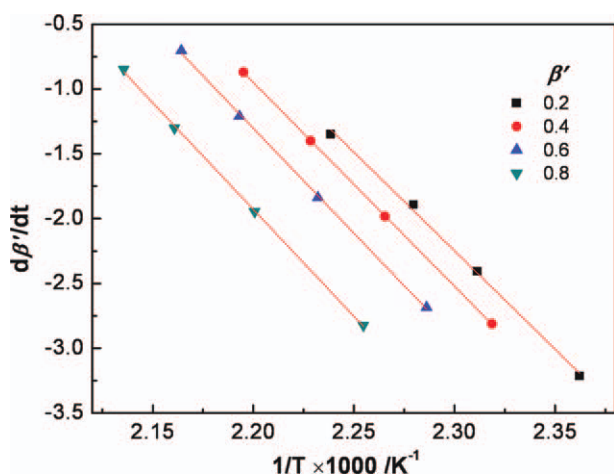
Nonisothermal DSC test was widely used to measure crosslinking reaction and determine  $E_a$ .<sup>29,31</sup> Figure 4(a) shows DSC curves of crosslinkable LDPE without antioxidant at different heating rates. Degree of crosslinking reaction ( $\beta'$ ) was determined according to<sup>32</sup>

$$\beta' = \frac{\int_{T_0}^T (dH/dT)dT}{\int_{T_0}^{T_\infty} (dH/dT)dT}$$

Here,  $dH/dT$  is reaction enthalpy at an infinitesimal temperature  $dT$ , and  $T_0$  and  $T_\infty$  are the initial and final reaction temperatures, respectively. Figure 4(b) shows  $\beta'$  against temperature  $T$  for different heating rates.



**Figure 4** DSC curves (a) and reaction degree  $\beta'$  as a function of  $T$  (b) at different heating rates for crosslinkable LDPE containing 1.5 phr DCP without antioxidants. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

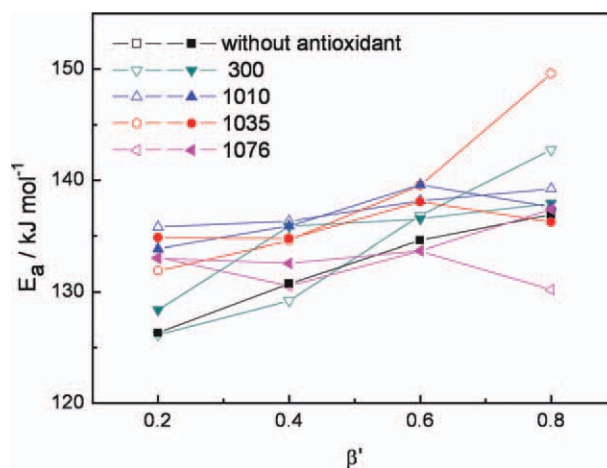


**Figure 5**  $d\beta'/dt \sim 1/T$  curves for crosslinkable LDPE containing 1.5 phr DCP at different reaction degrees  $\beta'$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

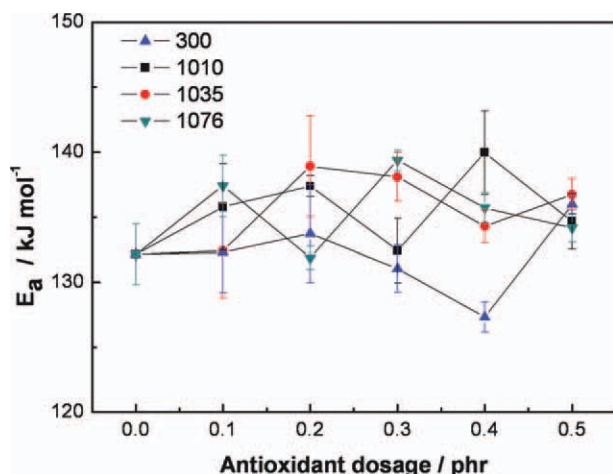
According to Friedman–Reich–Levi equation,<sup>33</sup>

$$\ln \frac{d\beta'}{dt} = \ln Af(\beta') - \frac{E_a}{RT}$$

where  $A$  is preexponential factor and  $f(\beta')$  a kinetic model function. Slope of  $\ln(d\beta'/dT)$  against reciprocal temperature  $1/T$ , as shown in Figure 5, gives  $E_a$ . Figure 6 gives the dependence of  $E_a$  on  $\beta'$  for crosslinkable LDPE containing 0.2 and 0.5 phr antioxidants. The control system without antioxidant exhibits a slight and linear increase of  $E_a$  with increasing  $\beta'$  due to the increased viscosity of crosslinked LDPE.<sup>32</sup> This is quite different from epoxy resin whose  $E_a$  is almost constant in the range of 0.2–0.8 of reaction degree.<sup>29</sup> Dependence of  $E_a$  on  $\beta'$  becomes rather weaker for the systems containing Irganox 1010 and 1076. The systems containing 0.2 phr Irganox 300 and 1035 exhibit enhanced dependence of  $E_a$  on  $\beta'$  while  $E_a$  becomes almost independence on  $\beta'$  at 0.5 phr Irganox 300 and 1035. By ignoring the  $\beta'$ -dependence of  $E_a$ , average value of  $E'$  at  $\beta'$  of 0.2, 0.4, 0.6, and 0.8 was determined and is plotted against antioxidant dosage as shown in Figure 7.  $E_a$  is in the range of 130–140 kJ mol<sup>-1</sup>, being slight lower than that reported at 145–170 kJ mol<sup>-1</sup>.<sup>34,35</sup> A lower  $E_a$  value in the range of 91–107 kJ mol<sup>-1</sup> for crosslinking reaction of EVA could be attributed to the low viscosity of EVA.<sup>32</sup> Antioxidant reacts with the alkyl radicals from thermal decomposition of DCP above 120 °C, which depresses the crosslinking reaction and reduces  $G'$  of XLPE greatly.<sup>4–7</sup> However, antioxidant hardly influences  $E_a$  (Fig. 7) and  $f_{\text{gel}}$  (Fig. 3) within experiment error.  $E_a$  reflects the dynamics of both the coupling reaction between macromolecular free radicals for network formation



**Figure 6**  $E_a$  as a function of  $\beta'$  for crosslinkable LDPE containing 1.5 phr DCP and 0.2 phr (hollow symbols) and 0.5 phr (solid symbols) antioxidants. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

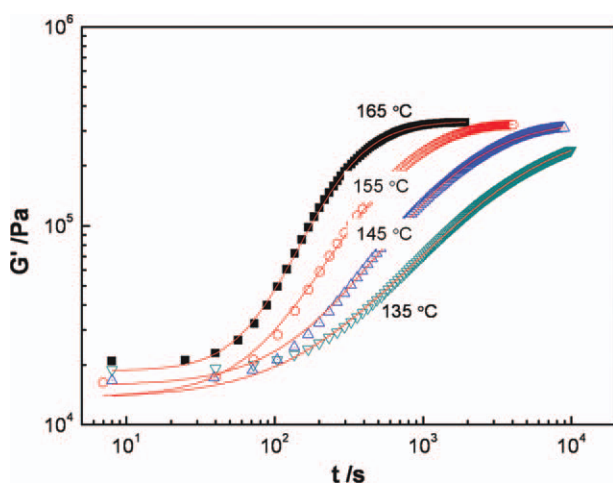


**Figure 7** Influence of antioxidant dosage on  $E_a$  for crosslinkable LDPE containing 1.5 phr DCP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and the reactions of antioxidants as well as decomposed products of DCP with free radicals at the end of dangling chains. In other words, the parameter  $E_a$  could not distinguish the two types of reactions responsible for the network formation and the dangling chain formation. Though antioxidants interfere with the final crosslinking density by plundering free radicals for dangling chain formation,  $E_a$  essentially remains unvaried with antioxidant dosage.

### Rheological testing of crosslinking kinetics

Crosslinking kinetics strongly depends on  $T$ . Figure 8 shows  $G'$  as a function of time ( $t$ ) for LDPE crosslinked with 1.5 phr DCP at different temperatures.



**Figure 8**  $G'$  as a function of  $t$  for crosslinkable LDPE containing 1.5 phr DCP without antioxidants. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Thermal decomposition of DCP follows the first order kinetics,<sup>35,36</sup>

$$\frac{d[\text{DCP}]}{dt} = -k_d[\text{DCP}] \quad (1)$$

or

$$\frac{[\text{DCP}]_t}{[\text{DCP}]_0} = e^{-k_d t} \quad (2)$$

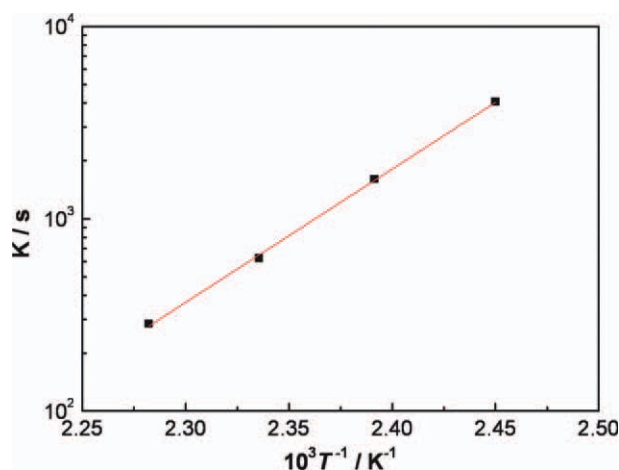
Here,  $k_d = A \exp(-E_a/RT)$  is kinetic constant of DCP decomposition. Assuming that all the decomposed DCP takes part in crosslinking reaction, the degree of crosslinking reaction ( $\beta$ ) has a positive relationship with concentration of decomposed DCP. As  $G'$  of XLPE completely crosslinked at 175°C is linear dependent on DCP dosage as shown in Figure 1, it is proper to write  $\beta$  as the relative change of  $G'$ . Equation (2) is modified as,<sup>37</sup>

$$\beta = \frac{G_t - G_0}{G_\infty - G_0} = 1 - e^{-k_d t} \quad (3)$$

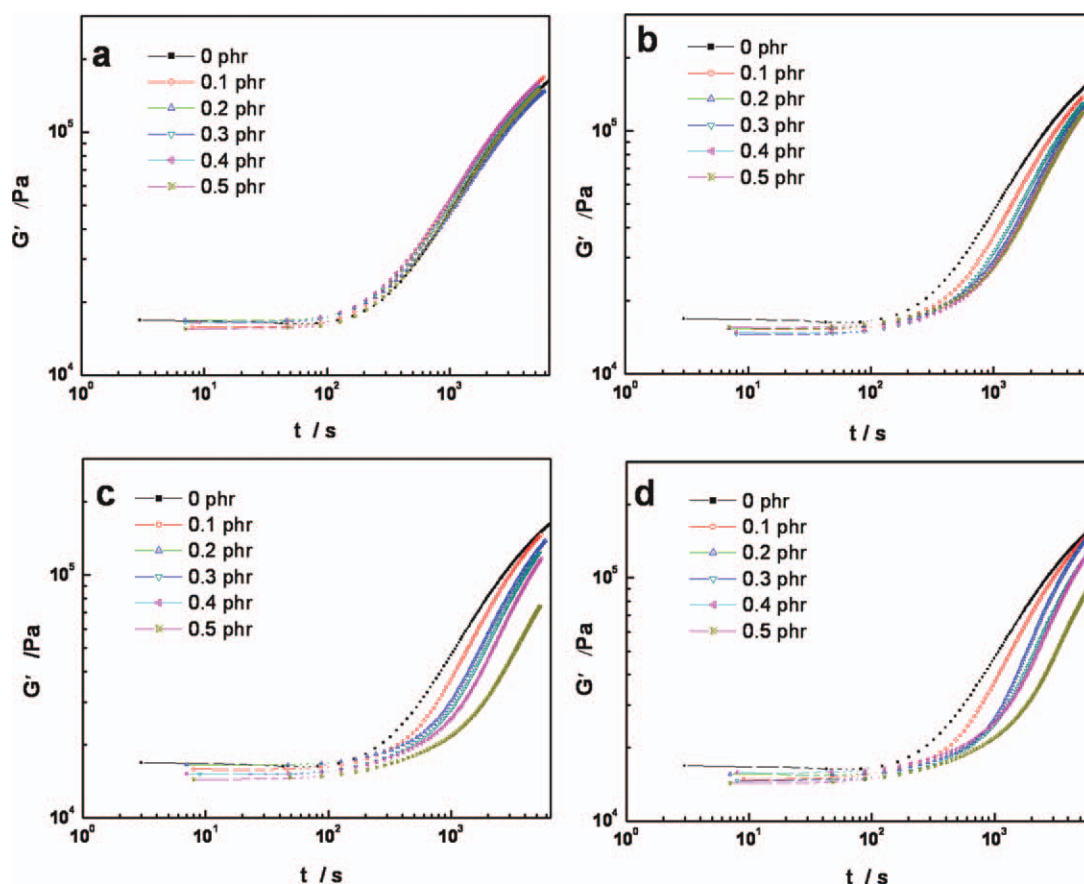
Here,  $G_t$ ,  $G_\infty$ , and  $G_0$  are elastic moduli at time  $t$ , infinite, and zero, respectively. Via Talyer transformation, eq. (3) is approximately reduced to

$$\beta = \frac{G_t - G_0}{G_\infty - G_0} = \frac{t^n}{K^n + t^n} \quad (4)$$

Here,  $K = \ln 2/k_d$  is half time and  $n$  is an exponent depending on  $T$ .  $K$  was estimated through least-square fitting of eq. (4) to the data in Figure 8 and the  $K$  value is plotted against  $1/T$  in Figure 9 in a semilogarithmic plot. The slope gives  $\Delta E_a = 132.8 \pm$



**Figure 9**  $K$  as a function of  $1/T$  for crosslinkable LDPE containing 1.5 phr DCP without antioxidants. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10**  $G'$  as a function of  $t$  for crosslinkable LDPE containing 1.5 phr DCP and various amounts of antioxidants Irganox 300 (a), 1010 (b), 1035(c), and 1076 (d). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

2.4 kJ mol<sup>-1</sup>, being in the range determined from nonisothermal DSC measurement.

Influence of antioxidant on crosslinking kinetics was investigated at 135°C. Figure 10 shows  $G'$  as a function of  $t$  for crosslinkable LDPE with different phenol antioxidants. Antioxidants depress crosslinking reaction depending on their structures. Irganox 300 almost does not influence on crosslinking kinetics. In contrast, Irganox 1010, 1035, and 1076 retard the crosslinking reaction apparently.

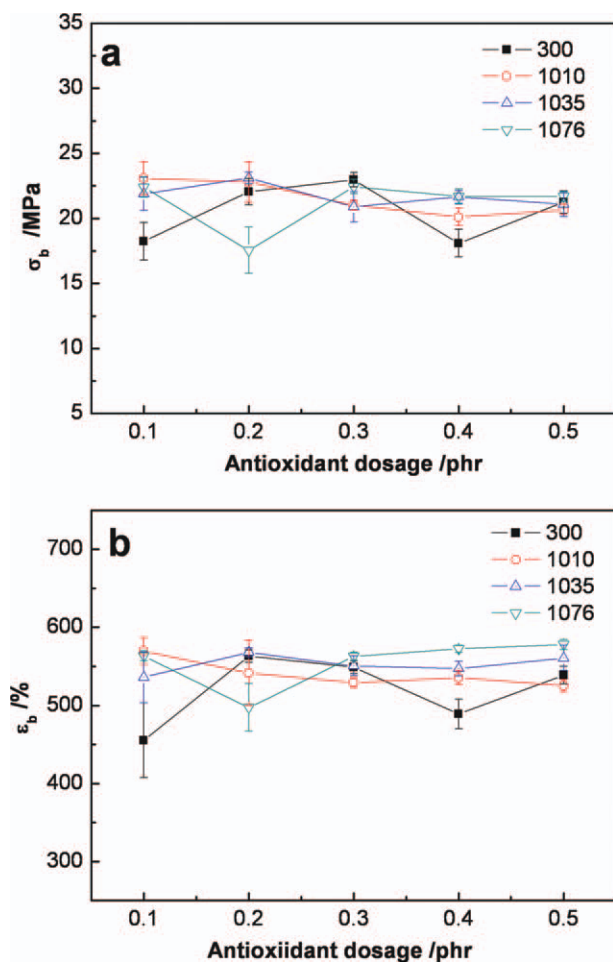
Table I shows the  $K$  values derived from fitting the data of Figure 10 using eq. (4).  $K$  of crosslinkable LDPE without antioxidants is  $62 \pm 0.67$  min. Irganox 300 does not influence the  $K$  value considering experiment error. On the other hand, the other three Irganox 1010, 1035, 1076 cause  $K$  to increase approximately linearly from 63 min at 0.1 phr antioxidants to about 83 min at 0.4 phr antioxidants and there seems no difference in  $K$  for the systems containing these three antioxidants. However, increasing content of Irganox 1035 and 1076 from 0.4 phr to 0.5 phr causes a great increase in  $K$ . This result may attribute to the critical concentration of antioxidants.<sup>38</sup> Antioxidants are consumed during process, and the decomposed antioxidants still remain some resist-

ance to oxidation.<sup>22</sup> A part of initial antioxidants remained could capture radicals more efficiently than the decomposed antioxidants so that the critical concentration appears.

Irganox 300 has a neglectable effect on peroxide-cure reaction in comparison with the other antioxidants. According to diffusion controlled mechanism,<sup>35</sup> antioxidants with a high mobility are the easier to react with radicals. Irganox 300 with  $T_m$  160°C is solid at 135°C so that it hardly affects the DCP crosslinking reaction. The other three antioxidants are in the melt state at 135°C and their effects depend on molecular mobility. Irganox 1010 with molecular weight 1177 g mol<sup>-1</sup> and  $T_m$  119–123°C has four hindered-phenol groups, which limit its

**TABLE I**  
 **$K$  (min) of Crosslinkable LDPE with Different Antioxidants**

Irganox	0.1 phr	0.2 phr	0.3 phr	0.4 phr	0.5 phr
300	63.7	63.5	61.0	60.2	61.7
1010	62.6	76.7	72.1	82.0	84.2
1035	62.9	71.3	78.0	84.5	143.5
1076	63.0	68.5	72.6	83.2	122.9



**Figure 11** Influence of antioxidant on tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) of XLPE crosslinked with 1.5 phr DCP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

mobility in LDPE melt greatly. In contrary, Irganox 1035 and 1076 with both low molecular weight (643 and 531 g mol<sup>-1</sup>) and low melt point (63–67°C and 55°C) can diffuse in the melt of crosslinkable LDPE easily so that they decrease the DCP crosslinking efficiency greatly and improve processing stability.<sup>39</sup> Low molecular weight phenol antioxidants might be easy to volatilize at high temperatures during polymer processing or migrate to surface of materials during the long term service; high molecular weight antioxidants could be more persistent at high temperature due to their low diffusion rate and guarantee the long term service.<sup>10,40</sup> However,  $T_m$  of antioxidants is another important factor influencing kinetics of peroxide-cure systems.

Antioxidants interfere with crosslinking reaction so that they may affect mechanical properties of XLPE. Figure 11 shows tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) of XLPE with 1.5 phr DCP and different antioxidants of less than 0.5 phr. Although antioxidants could retard the crosslinking

reaction, they in the investigation dosage ranges do not influence the mechanical properties considering experimental error.

## CONCLUSIONS

Molecular structure of phenol antioxidants strongly influences their negative effect to peroxide-cure reaction of LDPE. Phenol antioxidants could reduce  $G'$  of XLPE completely crosslinked at 175°C while they have a neglectable effect on  $f_{gel}$  and  $E_a$ . However, time sweep dynamic rheological test reveals that Irganox 1035 and 1076 with low molecular weight and low  $T_m$  could significantly depress scorch of crosslinkable LDPE at 135°C.

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