

# Influence of Binary Combined Systems of Antioxidants on the Stabilization of Peroxide-Cured Low-Density Polyethylene

Xiaohu Zhang, Hongmei Yang, Yihu Song, Qiang Zheng

Ministry of Education Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received 9 October 2011; accepted 5 January 2012

DOI 10.1002/app.36754

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The secondary antioxidants Irganox 168 and 242 and dilaurylthiodipropionate (didodecyl-3,3'-thiodipropionate) (DLTP) were chosen to be combined with the primary phenol antioxidants Irganox 300, 1010, 1035, and 1076, and the effects of the binary combined systems of antioxidants on the peroxide curing reaction and the long-term stability of crosslinked low-density polyethylene (XLPE) were studied through isothermal dynamic rheological and mechanical testing. The results show that the primary phenol antioxidants with lower melting points had better resistance to scorching and exhibited good synergistic effects with the secondary antioxidants. Irganox 168 had little resistance to scorching, whereas Irganox DLTP

had moderate resistance, and Irganox 242 had the greatest resistance. Irganox 168 and DLTP guaranteed the mechanical properties well, whereas Irganox 242 reduced the tensile strength obviously. Irganox 300 and 1035 combined with secondary antioxidants performed poorly in long-term thermal aging test, whereas Irganox 1076 in combination with secondary antioxidants displayed a moderate effect of aging resistance, and Irganox 1010 showed the best effect. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**Key words:** ageing; antioxidants; crosslinking; polyethylene (PE)

## INTRODUCTION

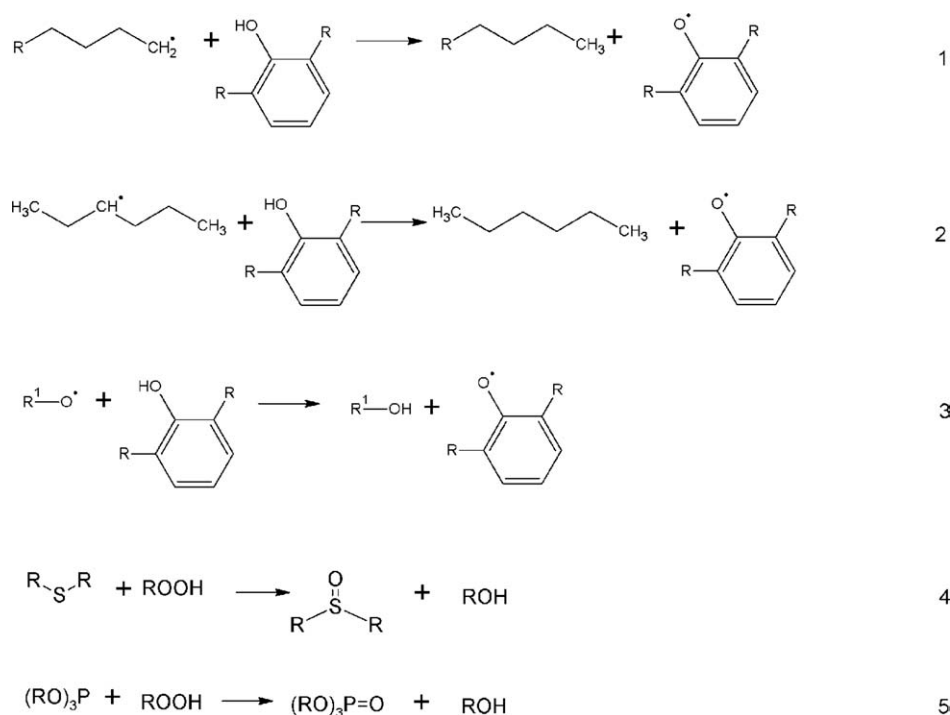
Low-density polyethylene (LDPE) is widely used as an insulation material for cables. However, a poor heat resistance due to a low melting temperature ( $T_m$ ) restrains its application greatly. Crosslinked low-density polyethylene (XLPE) addresses this problem and has gained more popularity.<sup>1</sup> Dicumyl peroxide (DCP), the most prevalent crosslinking agent used to cure LDPE, is easy to decompose above 120°C so that scorching is likely to occur during XLPE processing. Impurities, such as aggregates of antioxidants, and the scorching of LDPE can lead to electrical breakdown during cable service.<sup>2–4</sup> Consequently, care should be taken to select antioxidants to stabilize XLPE.

The peroxide curing reaction proceeds through a radical coupling reaction. Primary radicals derived from DCP decomposition deprive hydrogen atoms from polyethylene chains to form macromolecular radicals, which undergo a coupling reaction, which leads to network formation.<sup>5–9</sup> Antioxidants are designed to scavenge radicals to prohibit scorching during processing and to prevent cables from oxida-

tion during long-term service.<sup>10–13</sup> Primary and secondary antioxidants are used in combination to obtain the greatest effectiveness and synergism effects. Primary antioxidants, mainly hindered phenols and aromatic amines, scavenge chain-propagating peroxy and alkoxy radicals before they react with the polymer, as shown in formulas (1)–(3) in Scheme 1; secondary antioxidants, mainly phosphorous- and sulfur-type antioxidants as hydroperoxide decomposers, are designed to decompose chain-initiating hydroperoxides to nonradical products to stop the autocatalytic chain-propagation step, as shown in eqs. (4) and (5) in Scheme 1.

Negative synergistic effects between crosslinking agents and antioxidants in polyolefins have been investigated extensively.<sup>6–12,14–17</sup> Electron spin resonance (ESR) studies have shown that phenol radicals reach a maximum concentration before alkyl radicals when antioxidants are added to peroxide curing systems.<sup>6–9</sup> The molecular structure influences the ability of antioxidants to capture radicals. Some researchers have pointed out that lesser hindered phenols have better effects on scorching.<sup>1</sup> On the other hand, the mobility of antioxidants in the LDPE melt is another important factor that influences their effect on scorching.<sup>17</sup> Antioxidants with low  $T_m$ 's and small steric hindrances exhibit a high mobility; this leads to better effects on scorching at low

Correspondence to: Y. Song (s\_yh0411@zju.edu.cn).



**Scheme 1** Reactions of the primary antioxidants with radicals (formulas 1, 2, and 3) and secondary antioxidants with hydroperoxides (formulas 4 and 5)

temperatures. At high temperatures, antioxidants act effectively to retard the destructive mechanism, slow the rate of chain scission, and prevent chain decomposition.<sup>14,17,18</sup> Although secondary antioxidants are designed to decompose oxidation products and hinder the autocatalytic reaction, some secondary antioxidants can also capture radicals significantly.<sup>9,19</sup> For example, the commercial antioxidant tris(mixdomono or dinonylphenyl) phosphite (Irganox 329K) reduces the radical concentration to such an extent that it is difficult to analyze the reaction by ESR. Sulfur-type antioxidants have a high ability to capture radicals as well, but an ESR investigation could not distinguish the different effects between different sulfur-type antioxidants on radicals.<sup>9</sup> DCP consumes a lot of antioxidants during the crosslinking reaction; this leads to a great reduction in the oxidation induction time. A rather high dosage of antioxidants should be used in crosslinkable systems to guarantee the stabilization of service life.<sup>20,21</sup>

Although the synergism effects of primary and secondary antioxidants on oxidation have been studied widely, their effects on crosslinking reactions have rarely been reported. In this study, we chose four kinds of hindered phenol-type primary antioxidants and three kinds of secondary antioxidants to study the effects of binary combined systems of antioxidants on the crosslinking reaction and thermal aging behavior of XLPE. We were aiming to find a balance among the crosslinking efficiency, scorching resistance, and stability during the thermal aging of XLPE.

## EXPERIMENTAL

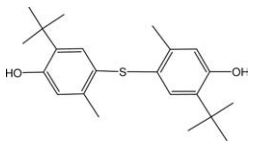
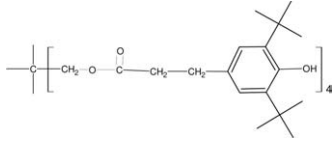
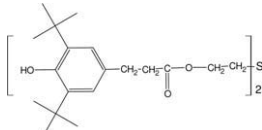
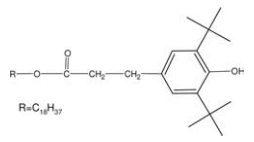
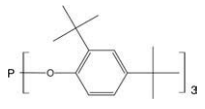
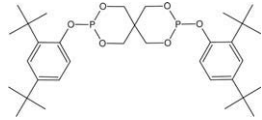
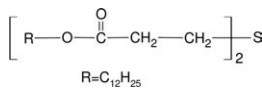
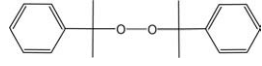
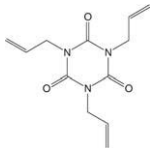
### Materials

The low-density polyethylene (LDPE; LD100BW, melt flow index = 2.038 g/10 min, 2.16 kg, 190°C) was produced by Yanshan Co. (Sinopec, China). DCP and triallyl isocyanurate (TAIC) were used as crosslinking agents. Four commercial Irganoxes, Irganox 300, Irganox 1010, Irganox 1035, and Irganox 1076, were used as primary antioxidants. Three commercial Irganoxes, Irganox 168, Irganox 242, and Irganox dilaurylthiodipropionate (didodecyl-3,3'-thiodipropionate) (DLTP), were used as secondary antioxidants. The crosslinking agents and the antioxidants were provided by Virtulla Tianjin Technology Co., Ltd. (Tianjin, China). Xylene (analytical reagent) as a solvent was produced by Hangzhou Chemical Agent Co., Ltd. (Hangzhou, China). Table I lists the chemical names and structures of the additives used. All of the materials were used as received.

### Sample preparation

Master batches of 5 wt % antioxidants were prepared with a twin-screw extruder (PRISM TSE 16 TC, Thermo Scientific, Waltham, United Kingdom) at temperatures above the  $T_m$ 's of the antioxidants at a screw rate 20 rpm. LDPE (100 phr), DCP (1.5 phr), and master batches of antioxidant (primary and secondary antioxidants, both at 0.2 phr) were mixed in the twin-screw extruder at 115°C and pelleted into

TABLE I  
Structures and Chemical Names of the Chemicals Used

Commercial name	Chemical name	Structure
Irganox 300	4,4'-Thiobis(6-tertbutyl-3-methylphenol)	
Irganox 1010	Tetra[methylene-β-(3,5-ditertbutyl-4-hydroxyphenyl)-propionate] methane	
Irganox 1035	3,5-Bis(1,1-dimethylethyl)-4-hydroxyhydroxybenzenepropanoic acid thiodi-2,1-ethanediyl ester	
Irganox 1076	<i>n</i> -Octadecyl-β-(4-hydroxy-3,5-ditertbutylphenyl) propionate	
Irganox 168	Tris(2,4-ditertbutyl) phosphate	
Irganox 242	2,4-Ditertbutylphenyl phosphate	
Irganox DLTP	Dilaurylthiodipropionate (didodecyl-3,3'-thiodipropionate)	
DCP	Dicumyl peroxide	
TAIC	Triallyl isocyanurate	

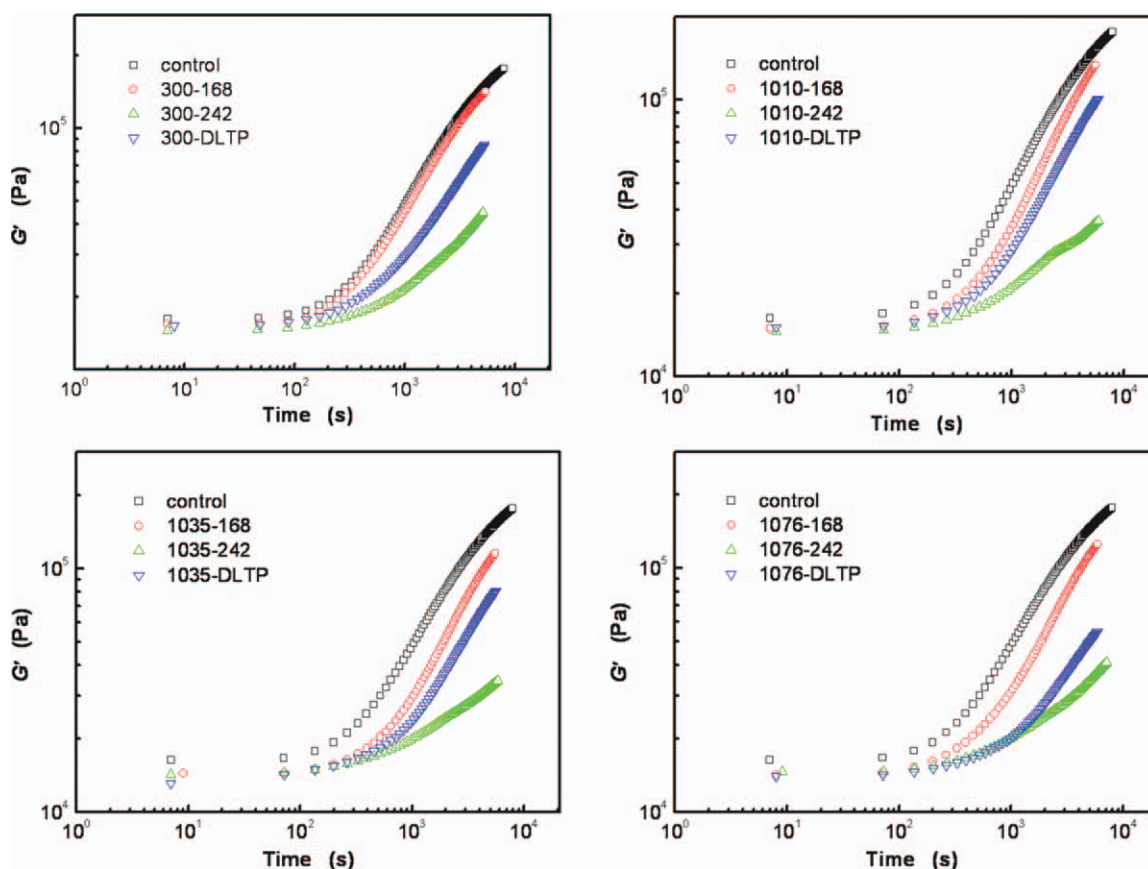
granules. The granules were molded into disks 1.2 mm in thickness and 25 mm in diameter at 15 MPa and at 115°C for 5 min, and the disks were cooled down to room temperature under pressure and were used for rheological testing. Completely crosslinked XLPE sheets of 1.2 mm in thickness were prepared under 15 MPa and at 175°C for 10 min. The sheets were cooled down to room temperature under pressure and were cut into dumbbell-shaped specimens for tensile, aging, and gel fraction ( $f_{gel}$ ) tests. Crosslinkable PE and completely crosslinked XLPE with

DCP (0.5 phr) and TAIC (1.0 phr) as crosslinking agents were prepared with the method described previously. All specimens were stored at room temperature for at least 48 h before testing.

## Measurements

### Rheological tests

The crosslinkable LDPE disk was placed between the two plates of an Advance Rheometric Expansion System (ARES; Rheometrics Scientific, Inc., USA) in



**Figure 1**  $G'$  as a function of  $t$  for LDPE with different primary and secondary antioxidants. DCP (1.5 phr) was used as crosslinking agent in the control sample. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

an air atmosphere at 120°C. A time sweep was performed at a frequency 3.14 rad/s and a strain amplitude of 1% at 135°C. The storage modulus ( $G'$ ), reflecting the elastic properties, was recorded as a function of time to trace the crosslinking reaction.

#### Gel fraction test

The degree of crosslinking was characterized by  $f_{\text{gel}}$  and was determined with a Soxhlet extractor with boiled xylene as solvent for at least 12 h. The XLPE samples before and after extraction were dried in a vacuum oven to constant weights ( $m_1$  and  $m_2$ , respectively), and  $f_{\text{gel}}$  was calculated according to the following equation:

$$f_{\text{gel}}(\text{wt}\%) = m_2/m_1 \times 100$$

#### Mechanical properties

The tensile tests of XLPE were performed on dumbbell-shaped specimens with a universal testing machine (CMT 4204, Shenzhen SANS Test Machine Co., Ltd., Shenzhen, China) according to GB/T 2591-2008. The average value of six replicates for each sample is reported.

#### Aging test

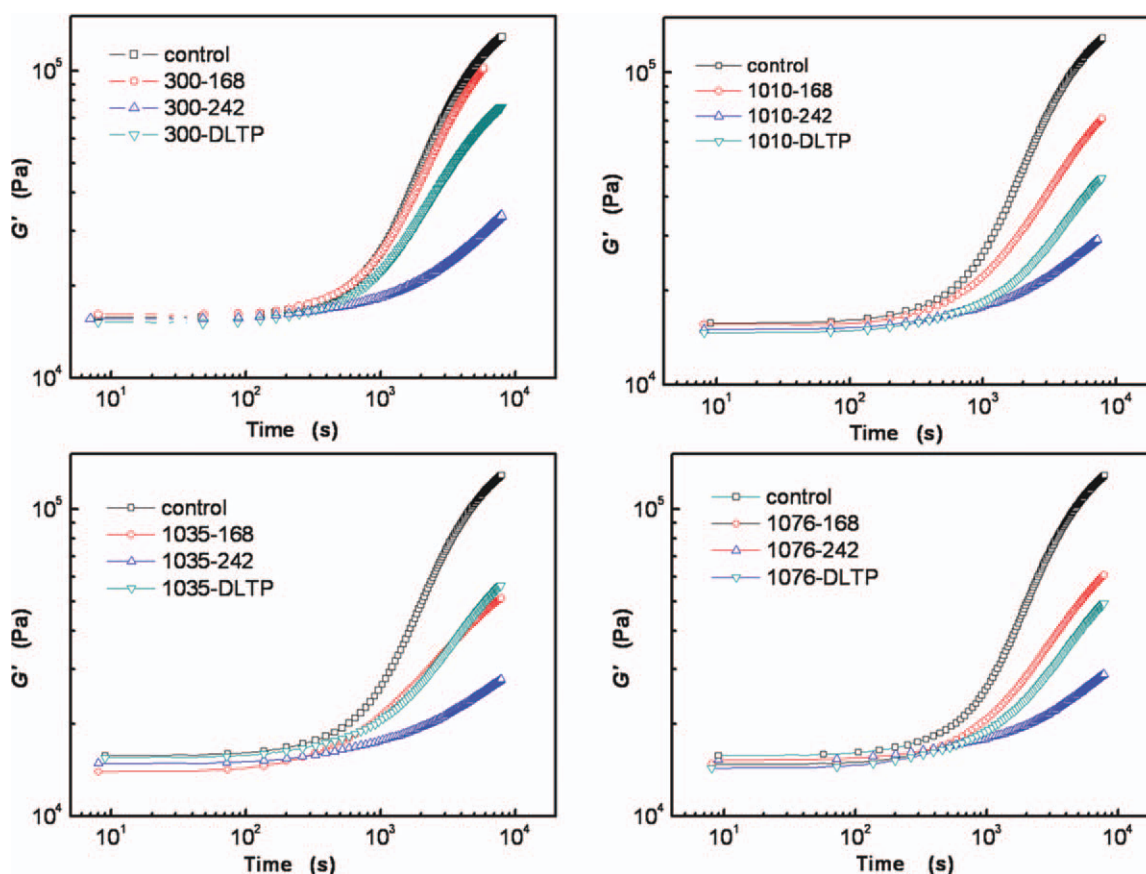
Accelerated aging tests were carried out on dumbbell-shaped XLPE specimens in an air-aging oven without any forced aeration at 135°C for 168 h. The aged specimens were used for mechanical testing, and the change in the mechanical properties was used to characterize the aging behavior of XLPE.

## RESULTS AND DISCUSSION

### Influence of antioxidants on the crosslinking reaction

$G'$  of the completely crosslinked XLPE was proportional to the DCP dosage. The dependence of  $G'$  on time ( $t$ ) was used to evaluate the effects of DCP and the evaluated antioxidants on the crosslinking reaction.<sup>18</sup> Figures 1 and 2 show  $G'$  as a function of  $t$  at 135°C with DCP or DCP/TAIC as crosslinking agents. In comparison with the control system without antioxidants, the initial elastic modulus ( $G'_0$ ) decreased with the addition of the binary combined systems of antioxidants. The binary combined systems of antioxidants also retarded the induction time of the crosslinking reaction and reduced the





**Figure 2**  $G'$  as a function of  $t$  for LDPE with different primary and secondary antioxidants. DCP (0.5 phr) and TAIC (1.0 phr) were used as crosslinking agents in the control sample. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

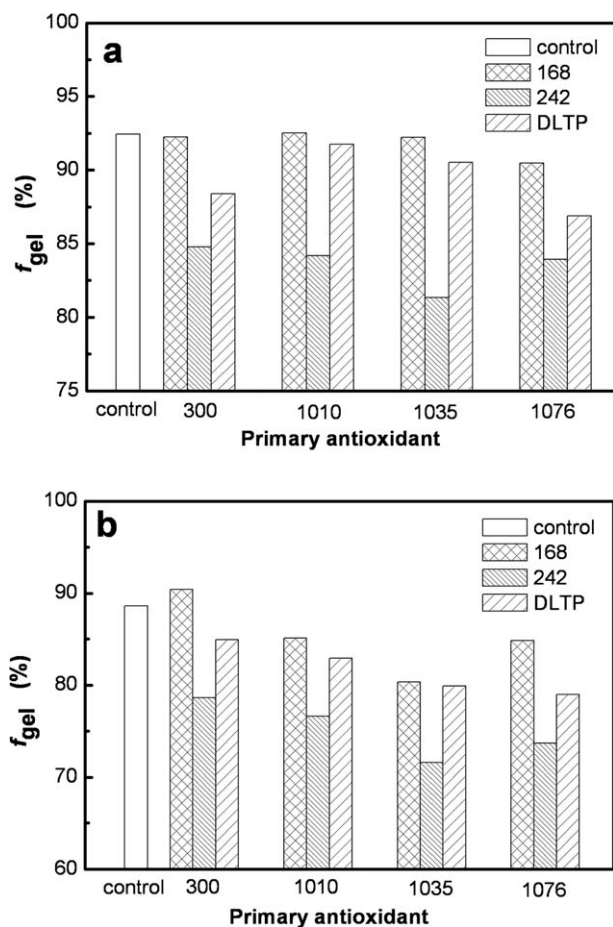
crosslinking rate greatly. The primary antioxidants Irganox 1035 and 1076 with low  $T_m$ 's showed better depression of the crosslinking reaction. With the same primary antioxidants, the secondary antioxidants Irganox 168 and 242 showed the least and greatest depressing effects, respectively.

Figure 3 shows influence of the binary combined systems of antioxidants on  $f_{gel}$  for the XLPE crosslinked with DCP or DCP/TAIC. In comparison with the control system without antioxidants, the binary combined systems of antioxidants caused a reduction in  $f_{gel}$ . With the same primary antioxidants, Irganox 168 had the least effect on  $f_{gel}$ , whereas Irganox 242 reduced  $f_{gel}$  by about 10%. The sulfur antioxidant Irganox DLTP had a moderate influence on  $f_{gel}$ .

According to the first-order kinetics of the crosslinking reaction, the relative change in the elastic modulus ( $\beta$ ) is used to characterize the crosslinking reaction as a function of time ( $t$ )<sup>18</sup> and can be calculated from the following equation:

$$\beta = \frac{G'_t - G'_0}{G'_\infty - G'_0} = \frac{t^n}{K^n + t^n} \quad (1)$$

where  $G'_0$ ,  $G'_t$ , and  $G'_\infty$  are the elastic moduli at times zero,  $t$ , and infinity, respectively;  $K (= \ln 2/k_d)$  is the half-time;  $k_d = A \exp(-E_a/RT)$  is the kinetic constant;  $E_a$  is the activation energy;  $R$  is the gas constant; and  $n$  is an exponent that is dependent on temperature ( $T$ ).  $K$  was estimated through the least-squares fitting of Eq. (1) to the data in Figures 1 and 2. Table II shows the derived  $K$ ,  $G'_0$ , and  $G'_\infty$  values with different primary and secondary antioxidants for the crosslinkable LDPE containing DCP or DCP/TAIC crosslinking agents. The crosslinkable LDPE without antioxidants showed values of  $K = 62.0$  min and  $G'_0 = 15.0$  kPa.  $K$  values of 63.5, 77.3, 71.2, and 68.5 min were determined for the crosslinkable systems only containing 0.2 phr of the primary antioxidants Irganox 300, 1010, 1035, and 1076, respectively (data not listed in Table II). In the systems containing binary combined systems of antioxidants, Irganox 168 showed the least resistance to scorching, and the increase in  $K$  ( $\Delta K$ ) was less than 10 min, except for the system with Irganox 1076 as the primary antioxidant. A combination of the primary antioxidant Irganox 1076 with the secondary antioxidant Irganox 168 caused a large  $\Delta K$  of about 30 min.



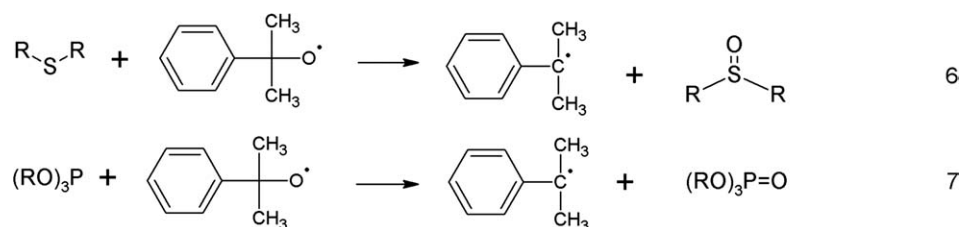
**Figure 3** Influence of the binary combined systems of antioxidants on  $f_{gel}$  of LDPE crosslinked with (a) DCP and (b) DCP/TAIC.

Irganox DLTP had a moderate synergistic effect in combination with the primary antioxidants for retarding the crosslinking reaction, resulting in a  $\Delta K$  value ranging from 10 to 40 min. A combination of Irganox 242 with Irganox 1035, 300, and 1076 gave rise to pronounced synergistic effects corresponding to  $\Delta K$  values of 75, 92, and 274 min, respectively. Irganox 242 showed a lesser synergistic effect with Irganox 1010, with a  $\Delta K$  value of 21 min. The chemical structures and  $T_m$  values had a great influence on the synergism between the primary and secondary antioxidants. Large synergism effects were observed in the combinations of primary phenol antioxidants of low  $T_m$  with secondary antioxidants.  $G'_\infty$  had a positive relationship with crosslinking density so that it could be used to characterize the crosslinking degree of XLPE.<sup>18</sup> The secondary antioxidant Irganox 168 in combination with primary phenol antioxidants and the Irganox 300–DLTP binary combined system of antioxidants had a negligible effect on  $G'_\infty$ . Irganox 242 reduced  $G'_\infty$  significantly, and DLTP showed a moderate effect.

When 0.5 phr DCP and 1.0 phr TAIC were used as the crosslinking agents, the binary combined

**TABLE II**  
**Rheological Parameters of the Crosslinkable LDPE Containing Different Binary Combined Systems of Antioxidants**

Primary antioxidant	Secondary antioxidant	Control		Irganox 168		Irganox 242		Irganox 300		Irganox 1010		Irganox 1035		Irganox 1076			
		K (min)	$\Delta K$ (min)	$G'_0$ (kPa)	$G'_\infty$ (kPa)	K (min)	$\Delta K$ (min)	$G'_0$ (kPa)	$G'_\infty$ (kPa)	K (min)	$\Delta K$ (min)	$G'_0$ (kPa)	$G'_\infty$ (kPa)	K (min)	$\Delta K$ (min)	$G'_0$ (kPa)	$G'_\infty$ (kPa)
DCP	K (min)	62.0	0	63.5	231.4	63.5	231.4	63.5	231.4	63.5	231.4	63.5	231.4	63.5	231.4	63.5	231.4
	$\Delta K$ (min)	0	15.2	1.5	221.8	1.5	221.8	1.5	221.8	1.5	221.8	1.5	221.8	1.5	221.8	1.5	221.8
DCP/TAIC	$G'_0$ (kPa)	15.2	231.4	14.3	231.4	14.3	231.4	14.3	231.4	14.3	231.4	14.3	231.4	14.3	231.4	14.3	231.4
	$G'_\infty$ (kPa)	231.4	62.1	221.8	62.1	221.8	62.1	62.1	221.8	62.1	62.1	221.8	62.1	62.1	221.8	62.1	62.1



**Scheme 2** Reactions of the secondary antioxidants with initial radicals derived from the decomposition of DCP (formulas 6 and 7).

systems of antioxidants had the same influence on the crosslinking reaction, but the  $\Delta K$  values were in the ranges 3–30 min for Irganox 168, 10–71 min for Irganox DLTP, and 330–750 min for Irganox 242; these values were much higher than those of the systems with 1.5 phr DCP as a crosslinking agent. The binary combined systems of antioxidants decreased  $G'_\infty$  obviously except for the Irganox 300/168 pair. Nevertheless, the reduction in  $G'_\infty$  was smaller than that in the systems with only DCP as the crosslinking agent. The higher the mobility and the lower the  $T_m$  of the primary antioxidant were, the smaller  $G'_\infty$  was. However, little influence of the secondary antioxidants was observed when Irganox 1035 and 1076 were used as primary antioxidants. During the crosslinking reaction, DCP acted as an initiator, and the coagent TAIC bridged LDPE chains by polymerization.<sup>22,23</sup> Primary antioxidants designed to capture free radicals have a great influence on the initial radical concentration. On the other hand, secondary antioxidants can capture the initial radicals; this leads to the formation of 2-phenyl isopropyl radicals [as shown by eqs. (6) and (7) in Scheme 2], which may still initiate the polymerization of TAIC. Therefore,  $G'_\infty$  was less affected by the secondary antioxidants.

The depression of antioxidants on the crosslinking reaction depends greatly on their structures. Irganox 1076, which was very efficient in processing stability due to its low  $T_m$  and good compatibility, showed low performance under an oxygen atmosphere because of its high volatility at high temperatures. On the other hand, Irganox 1010 performed perfectly under an oxygen atmosphere but exhibited poor processing stability.<sup>24</sup> Sulfur-phenol antioxidants, such as Irganox 300 and 1035, acted as radical scavengers and hydroperoxide decomposers because they combined the functions of both phenolic and activated-sulfur-type antioxidants.<sup>17,18</sup> Irganox 300 performed poorly at low temperatures because of its high  $T_m$  of 160°C, in contrast to reported results.<sup>1</sup> Sulfur- or phosphorous-type antioxidants reacted preferentially with cumyloxy radicals yielded by decomposed DCP to produce a 2-phenyl isopropyl radicals<sup>9</sup> so that the antioxidants may have decreased the alkyl and allyl radical concentrations

and reduced the crosslinking level. Trivalent phosphorous compounds reacted with different peroxides by insertion of the peroxide bond.<sup>25</sup> Both Irganox 168 and 242 were phosphates, but they had different effects on the crosslinking reaction. Walling and Pearson<sup>19</sup> found that alkyl phosphites were more reactive than aryl phosphites; this may have been due to the small steric hindrance of alkyl phosphites, so alkyl phosphite Irganox 242 had a stronger depressing effect on the crosslinking reaction than the aryl phosphite Irganox 168. This differed from the previous finding that the aryl phosphite Irganox 329K decreased the radical concentration extremely and that alkyl phosphite Irganox PEP-8 had little effect on the crosslinking reaction of LDPE.<sup>9</sup> The sulfur-type antioxidant DLTP, with a  $T_m$  as low as 40°C, was in the melted state at 135°C so that it could be distributed in LDPE homogeneously and improve the resistance to scorching effectively.

### Influence of antioxidants on mechanical properties

The antioxidants interfered with crosslinking reaction and decreased  $f_{\text{gel}}$  so that they had a great influence on the mechanical properties of XLPE. Table III shows the influence of the binary combined systems of antioxidants on the mechanical properties of XLPE before and after the aging test. The tensile strength ( $\sigma_b$ ) and elongation at break ( $\varepsilon_b$ ) of the control sample with DCP as the crosslinking agent were 22 MPa and 519%, respectively. The use of the crosslinking agent TAIC together with DCP decreased  $\sigma_b$  and increased  $\varepsilon_b$  slightly because of the decrease in  $f_{\text{gel}}$ . The hindered phenol antioxidants used did not influence the initial mechanical properties markedly in the DCP/TAIC-crosslinked systems; this may have been due to the fact that TAIC could stabilize the processability and resist scorching. In the DCP-crosslinked systems, Irganox 300 decreased  $\sigma_b$  and  $\varepsilon_b$  compared with the control sample, whereas the other primary antioxidants improved the mechanical properties obviously by improving the scorching resistance. The systems with Irganox 168 and DLTP retained ideal mechanical properties, whereas Irganox 242 caused marked reductions in  $\sigma_b$  and  $\varepsilon_b$ . Figure 4 shows typical images for the drawn

TABLE III  
Mechanical Properties before (1) and after (2) Aging of XLPE Containing Different Binary Combined Systems of Antioxidants

Recipe	$\sigma_b$	$\varepsilon_b$	Irganox 300			Irganox 1010			Irganox 1035			Irganox 1076		
			Irganox 168	Irganox 242	Control	Irganox 168	Irganox 242	DLTP	Irganox 168	Irganox 242	DLTP	Irganox 168	Irganox 242	DLTP
DCP	1	22.0 ± 1.0	18.8 ± 1.3	16.9 ± 0.4	20.2 ± 1.8	21.2 ± 0.3	16.0 ± 0.2	23.5 ± 0.7	24.0 ± 0.8	14.8 ± 0.3	20.7 ± 0.8	23.6 ± 0.8	15.6 ± 0.6	22.2 ± 1.3
	2	17.2 ± 1.3	21.2 ± 1.3	12.7 ± 1.1	21 ± 0.5	21.3 ± 0.93	15.6 ± 0.2	24.2 ± 0.73	20.8 ± 0.5	15.3 ± 0.3	22.8 ± 0.5	24.8 ± 0.9	14.2 ± 0.8	23.1 ± 0.7
	%	-22.1	12.9	-24.9	4.1	0.5	-2.3	2.9	-13.2	3.2	10.1	5.1	-9.3	4.0
DCP/ TAIC	1	519 ± 7	467 ± 21	500 ± 9	550 ± 26	509 ± 9	488 ± 6	547 ± 13	538 ± 11	508 ± 12	551 ± 11	563 ± 8	486 ± 17	578 ± 19
	2	429 ± 19	441 ± 37	436 ± 22	554 ± 9	516 ± 13	471 ± 9	545 ± 5	526 ± 7	482 ± 9	551 ± 9	560 ± 10	438 ± 18	569 ± 6
	%	-17.3	-5.55	-12.7	0.75	1.4	-3.48	-0.4	-2.27	-5.18	0.15	-0.39	-9.91 ± 0.6	-1.52
DCP/ TAIC	1	18.9 ± 0.3	18.1 ± 0.3	16.2 ± 0.5	18.1 ± 0.3	17.5 ± 0.6	16.0 ± 0.4	17.7 ± 0.5	18.5 ± 0.3	12.6 ± 0.8	18.2 ± 0.3	18.4 ± 0.5	16.7 ± 0.1	18.9 ± 0.4
	2	16.5 ± 1.0	13.9 ± 1.1	15.5 ± 0.9	16.2 ± 0.7	15.3 ± 0.46	15.3 ± 0.4	16.3 ± 0.6	14.7 ± 0.8	14.4 ± 0.7	17.5 ± 0.4	16.7 ± 0.6	15.8 ± 0.8	16.6 ± 0.43
	%	-12.9	-23.2	-4.6	-10.3	-12.2	-4.4	-8.3	-20.4	13.8	-4	-9.5	-5.4	-12
DCP/ TAIC	1	538 ± 3	511 ± 2	547 ± 12	538 ± 9	513 ± 17	554 ± 14	545 ± 7	563 ± 6	441 ± 16	552 ± 6	543 ± 6	594 ± 9	573 ± 6
	2	434 ± 32	387 ± 34	525 ± 16	517 ± 10	434 ± 21	519 ± 21	527 ± 13	492 ± 23	516 ± 17	534 ± 10	527 ± 9	546 ± 12	507 ± 16
	%	-19.3	-24.4	-3.9	-3.9	-15.3	-6.3	-3.3	-12.6	17.2	-3.2	-3.1	-8	-11.4

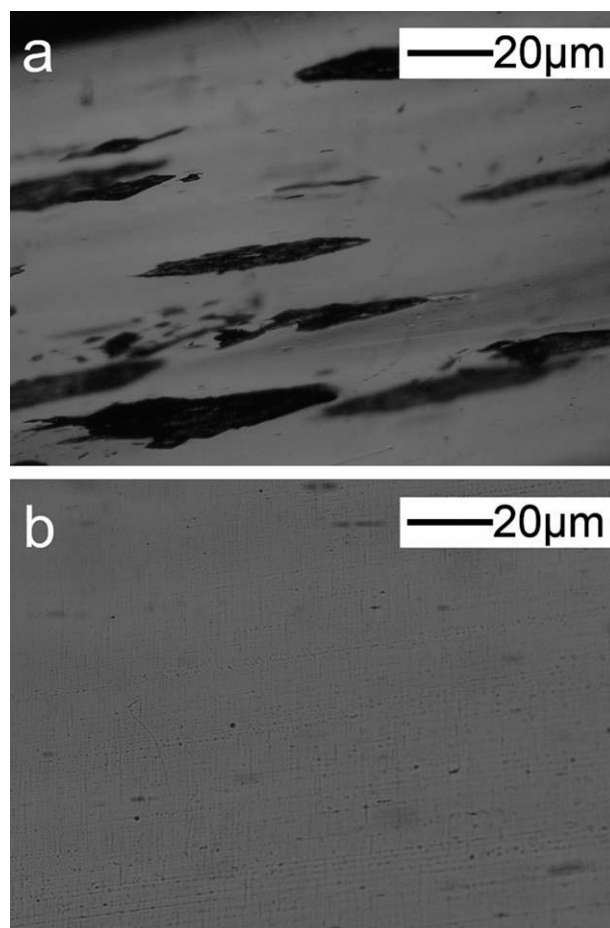


Figure 4 Typical images of drawn XLPE (a) with and (b) without antioxidant 242.

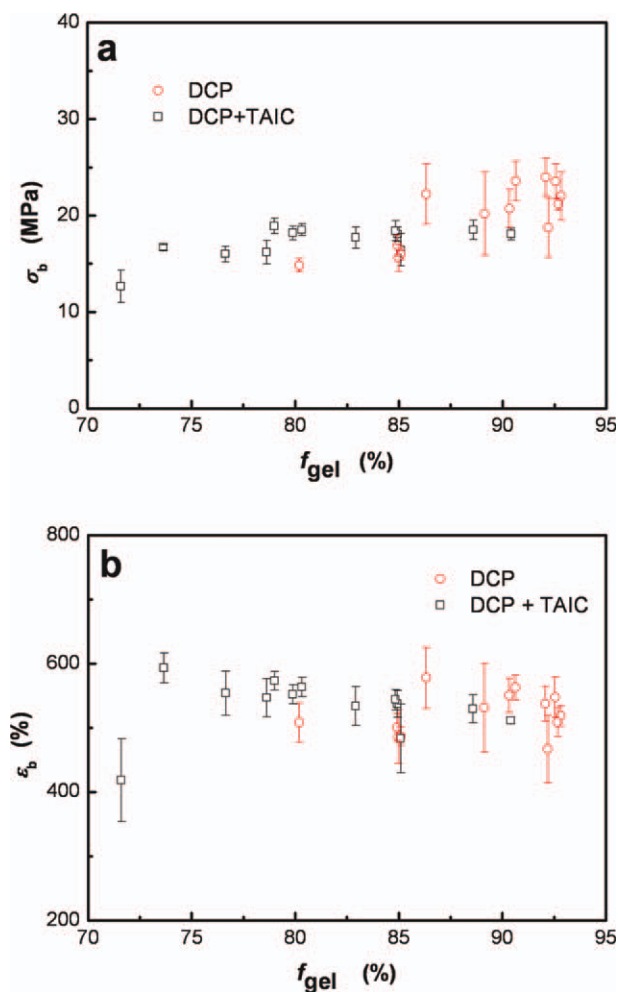
samples with and without Irganox 242 with DCP as the crosslinking agent. A large number of elliptical gaseous holes were observed in XLPE containing Irganox 242; this may have resulted from the reaction of DCP with Irganox 242. Heat treatment at high temperatures facilitated the removal of the byproduct generated in the crosslinking reaction in XLPE and modified the microcavities<sup>1</sup> so that most microcavities disappeared after the aging test. Microcavities were not observed when TAIC was used as the crosslinking agent together with DCP.

Figure 5 shows  $\sigma_b$  and  $\varepsilon_b$  as a function of  $f_{gel}$  for two kinds of crosslinking systems.  $\sigma_b$  of DCP-XLPE with a high crosslinking level was higher than that of DCP/TAIC-XLPE.  $\sigma_b$  and  $\varepsilon_b$  exhibited positive and negative corrections with  $f_{gel}$ , respectively, regardless of the crosslinking agents and the binary combined systems of antioxidants used.

#### Influence of the antioxidants on the aging behavior

A long-term aging test was performed in an air oven at 135°C for 168 h without forced air, and the results





**Figure 5** (a)  $\sigma_b$  and (b)  $\epsilon_b$  as a function of  $f_{gel}$  for XLPE crosslinked with DCP or DCP/TAIC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

are shown in Table III. The binary combined systems of antioxidants influenced the aging behaviors differently. The retained mechanical properties of the aged XLPE depended greatly on the primary and secondary antioxidants.<sup>26</sup> For the control DCP-crosslinked sample, thermal aging caused reductions in  $\sigma_b$  and  $\epsilon_b$  of 22 and 17%, respectively. In the absence of antioxidants, DCP/TAIC-XLPE showed relative changes of  $\sigma_b$  and  $\epsilon_b$  larger than the DCP-crosslinked system. DCP-XLPE had a higher crosslinking density and a homogeneous network that endowed it with resistance to thermal aging.<sup>27</sup> The sulfur-phenol primary antioxidants Irganox 300 and 1035 in combination with the phosphorous-type secondary antioxidants Irganox 168 and 242 exhibited poor resistance to thermal aging but performed well with Irganox DLTP. Both Irganox DLTP and the sulfur-type primary antioxidants contained activated sulfur atoms so that a better synergistic effect was achieved; nevertheless, the contradictory effects

between activated phosphorous and sulfur atoms may have decreased the efficiency of oxidation resistance.<sup>19</sup> Irganox 1010 performed nearly perfect, regardless of secondary antioxidants. The relative changes in  $\sigma_b$  and  $\epsilon_b$  of XLPE containing Irganox 1076 were higher than those with Irganox 1010 because of the loss of Irganox 1076 at high temperatures.<sup>24</sup> The thermal aging resistance of XLPE containing Irganox 242 depended on the structure of the primary antioxidant. A combination of Irganox 242 with Irganox 300 led to bad thermal aging resistance. On the other hand, when Irganox 1010, 1035, and 1076 were used as the primary antioxidants, Irganox 242 could endow good thermal aging resistance, although the initial  $\sigma_b$  and  $\epsilon_b$  values were lower than those of the control sample. Irganox DLTP provided good resistance to thermal aging except when it was combined with Irganox 1076 when DCP/TAIC was used as a crosslinking agent because of the low  $T_m$ 's of both Irganox 1076 and DLTP.

The crosslinking reaction and thermal oxidation are all based on a free-radical reaction. During the peroxide crosslinking reaction, peroxy and macromolecular radicals are formed. In the oxidation procedure, chain scission generates alkyl radicals that couple with  $O_2$  to form hydroperoxides. Primary antioxidants can scavenge radicals formed in crosslinking or oxidation reactions, whereas secondary antioxidants play a different role. Sulfur- or phosphorous-type antioxidants decompose hydroperoxides in an oxidation procedure but capture initial radicals in the peroxide crosslinking reaction; this leads to the reduction of crosslinking level. In all, the secondary antioxidant Irganox DLTP could not only provide good resistance to scorching but also endowed XLPE with long-term thermal aging stability. Irganox 168 provided good  $\sigma_b$  and heat stability but poor scorching resistance. As Irganox 242 produced much byproduct in the peroxide curing reaction, it is not suitable for use in insulation cables.

## CONCLUSIONS

Binary combined systems of antioxidants influenced the peroxide curing reaction of LDPE greatly. Low- $T_m$  primary phenol antioxidants in combination with secondary antioxidants had better synergistic effects on scorching at low temperature. For long-term stability, different synergistic effects were observed for different binary combined systems of antioxidants. The sulfur-phenol antioxidants Irganox 300 and 1035 performed poorly when combined with secondary antioxidants. Irganox 1010 performed nearly perfect in long-term aging tests, whereas Irganox 1076 behaved moderately. On the other hand, Irganox 242 decreased the mechanical properties of XLPE greatly.

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