Thermal, Mechanical, and Dielectric Behaviors of Crosslinked Linear Low density Polyethylene/Polyolefin Elastomers Blends

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ABSTRACT: Crosslinked linear low density polyethylene (XLPE) containing polyolefin elastomers (POE) has been evaluated. The blends with different dicumyl peroxide (DCP) and POE contents have been prepared and processed by compression molding. A series of the samples obtained have been investigated by gel content determination, scanning electron microscopy (SEM), different scanning calorimetry (DSC), mechanical, and dielectric behaviors measurements. The results obtained clearly show the relevant influence of the POE content, as well as of the DCP content, which tends to enhance crosslinking. As expected, the toughness of XLPE is improved by using adequate content of POE, and the blends exhibit a much more similar tensile behavior to that of elastomer. In addition, the results indicate that the blends possess the excellent dielectric behaviors, such as dielectric constant and dissipation factor. The crystallinity of the blends decreases as the DCP and POE contents increase. The melting temperature of the blends also decreases with the increase of DCP content, while POE content has few influences on the melting temperature of the blends. The SEM images strongly reveal that the blends are partially compatible, and the POE can be dispersed well in the matrix. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1920–1927, 2007

Key words: polyethylene; polyolefin elastomers; crosslinking; blends

INTRODUCTION

Polyethylene is the most widely used thermoplastic polymer in a range of fields, yet its use is restricted in certain applications because of its relatively low upper use temperature.[1–4] Thus, polyethylene is often extended its uses by introducing crosslinks between the polymer chains to form networks, which raise the upper temperature limit of application and improve the mechanical properties at high temperature. There are presently three main crosslinking methods, such as radiation crosslinking, silane crosslinking, and peroxide crosslinking.[2,5]

Among the crosslinking methods of polyethylene, silane crosslinking and peroxide crosslinking are the most important methods in commercial use today. Furthermore, the most significant field of application of crosslinked polyethylene (XLPE) is as insulation materials in power cables. Over the last 30 years or so, XLPE has been widely used as insulating materials and largely replaced by paper/oil insulation in me-dium and high voltage cables because of its excellent mechanical properties and dielectric properties.[6,7]

However, electrical aging of insulation in power cables is inevitable and may give rise to costly cable failure in service. Therefore, many researchers have been focused on improving the properties of XLPE for prolong the life of power cables. And there are many methods, such as blending, filling additives, copolymerization, and other techniques, for improving the mechanical or electrical properties of insulating materials.[1,8–12] According to the previous researches, two kind of compounds are often used in the chemical and physical modification of polyethylene for improving its properties, including polar and nonpolar additives. Ethylene vinyl acetate (EVA), acrylic acid (AA), and ethylene ionomer were used to improve the electrical properties of polyethylene by blending and copolymerization.[10,12–14] Although they can improve the water tree resistance, breakdown strength, and space charges, the polar additives increase the dissipation factor of matrix and deteriorate other properties of matrix because of the poor compatibility with polyethylene. Nevertheless, as a nonpolar polymer, polybutadiene (PB) not only enhance the crosslinking of polyethylene as a coagent, but also improve the impact strength and water tree resistance of XLPE.[1,15] Thus, the nonpolar polymers possessing adequate compatibility with polyethylene should be better choice as the modification of XLPE insulation in power cables.

Polyolefin elastomer (POE), as a nonpolar polymer, is compatible with polyethylene. Yet few studies of XLPE modified by POE can be found in the literature to our knowledge.[16] Hence, the purpose of present work is to study the influences of POE on the cross-linking and properties of XLPE. The effects of POE and DCP contents on the gel content, mechanical and dielectric behaviors of XLPE were investigated. Moreover, the thermal behaviors of XLPE/POE blends were also explored by DSC measurements and their morphology was observed through SEM.

EXPERIMENTAL

Materials

The polyethylene used in this study is LLDPE (LL4004) from ExxonMobil in Saudi Arabia, which has a melt flow index (MFI) of 3.6 g/min and a density of 0.924 g/cm^3. And it is obtained using Ziegler Natta as catalyst. The polyolefin elastomer (POE) is Engage 8150 from DOW-DuPont which has an octene comonomer content of 25 wt %, a MFI of 0.5 g/min, and a density of 0.868 g/cm^3. The organic peroxide used is dicumyl peroxide (DCP) (Chemical Reagent) with an assay higher than 99.5%, which is supplied from Shanghai Gaoqiao Petroleum, China.

Sample preparation

Different LLDPE/POE/DCP ratios were mixed in a HAAKE Rheometer RC90 at a temperature of 130°C and a rotor speed of 40 rpm for 8 min. After, all samples were compressed at 170°C and 10 MPa for 15 min, the crosslinked LLDPE/POE blends were obtained for following measurements.

Characterization

Gel content

The gel content was determined on thin films of around 1 mm-thickness, which were pressed at 170°C and 10 MPa for 15 min. Approximately 0.2 g of the crosslinked films were exactly weighed and placed in a 120 mesh copper net. Then, they were extracted in a Soxhlet extractor for 36 h using *p*-xylene as extractant. After extraction, the copper nets were dried in a vacuum oven at 80°C until constant weight. Finally, the remaining gel was weighed and calculated as follows:

$$\text{Gel content (\%)} = W_t/W_0 \times 100$$

Where, W_0 and W_t are the sample masses before and after extraction, respectively.

Scanning electron microscopy

A Hitachi S520 scanning electron microscope (SEM) was used to observe the morphology of the fractured surfaces of samples. All samples were prepared by immersing the test pieces in liquid nitrogen before breaking. The fractured surfaces of the test pieces were etched with toluene at 50°C to remove the unreacted POE. And they were coated with gold before examination.

Differential scanning calorimetry

A Perkin–Elmer Pyris 1 DSC Calorimeter was used to perform Differential scanning calorimetry analysis on the samples in a flowing nitrogen atmosphere. Samples ranging from 2.5 to 3.0 mg were initially heated from 20 to 150°C at 20°C/min, held at 150°C for 3 min to eliminate thermal history effects, and then cooled to 20°C at 20°C/min. A value of 290 J/g has been taken as the melting enthalpy of 100% crystalline polyethylene to calculate the crystallinity of polyethylene from the melting enthalpies.[17] The peak temperature of DSC curves is taken as the melting or crystallization temperature.

Mechanical measurements

The tensile tests were performed according to ASTM D 638-2003 in an Instron series IX 4465 materials tester, with a crosshead speed of 250 mm/min. Dumbbell shaped specimens with cross-sectional area of 4×1 mm^2 and gauge length of 20.0 mm were used for the measurements. Five specimens for each sample were used for the tests and the arithmetic mean of all values obtained was reported as the average value for the particular properties of each sample. In addition, the standard deviation was also calculated according to ASTM D 638-2003.

The Notched Izod impact tests were performed according to ASTM D 256-2005 in a Rayran impact tester. Notched specimens of $8 \times 10 \times 3$ mm^3 with a V-shape notch (the depth of notch is 2.7 mm and the radius of notch tip is 0.25 mm) were tested at a hammer speed of 3.5 m/s and pendulum weight of 3.462 kg.

Dielectric constant and dissipation factor

All specimens were pressed into thin sheet at 170°C and 10 MPa for 15 min, with a thickness of 1.0 mm. The dielectric constant and the dissipation factor were measured on a QS30 high-voltage Bridge (Shanghai huguang, Shanghai, China) according to ASTM D 150-2004.
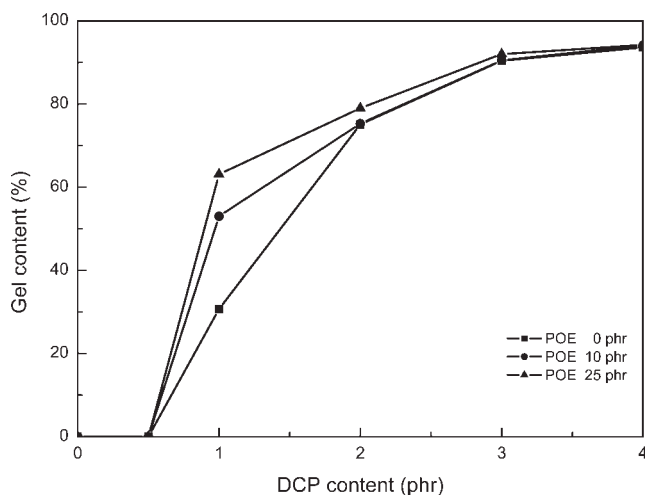
Figure 1 Gel content of the samples with different DCP and POE content.

RESULTS AND DISCUSSION

Gel content

It is well known that gel content is used to evaluate the crosslinking extent of crosslinked polymers. So it is worth mentioning the influences of the DCP and POE contents on gel content of XLPE/POE blends, which is shown in Figure 1. It can be observed that gel content increases with DCP contents; in the absence of POE, the gel content is low when the DCP content is below 1 phr (part of reagent per hundred parts of

LLDPE), and it will exceed 70% until the DCP content is around 2 phr. The most interesting aspect shown in Figure 1 is the influence of POE, which at 10 phr and 25 phr combined with 1 phr DCP yields gel content of around 60%. And the gel content in the presence of POE is higher than that in the absence of POE when the DCP content is from 0.5 to 2 phr, strongly indicating that POE enhances the crosslinking of blends. This should be attributed to POE crosslinking and the formation of a cocrosslinked network of POE and PE because POE has more (compared with LDPE) evenly distributed long and short chain branches and results in higher crosslinking efficiency.[18]

Morphology

As stated earlier, POE can enhance the crosslinking of XLPE/POE blends by its crosslinking and cocrosslinking with PE, which can be exhibited through the morphology observation of their blends. Figure 2 depicts the morphology of crosslinked and uncrosslinked blends of PE with POE, respectively. It can be seen that the uncrosslinked blends display a fine and two-phase morphology [Fig. 2(a,c)], which is due to the POE portions of the blends were etched out with a suitable solvent. Yet, the two-phase morphology can not be found remarkably in the crosslinked blends [Fig. 2(b,d)] because the POE portions were not etched out. The morphological change reveals that POE easily reacts with radicals created by DCP and is cross-
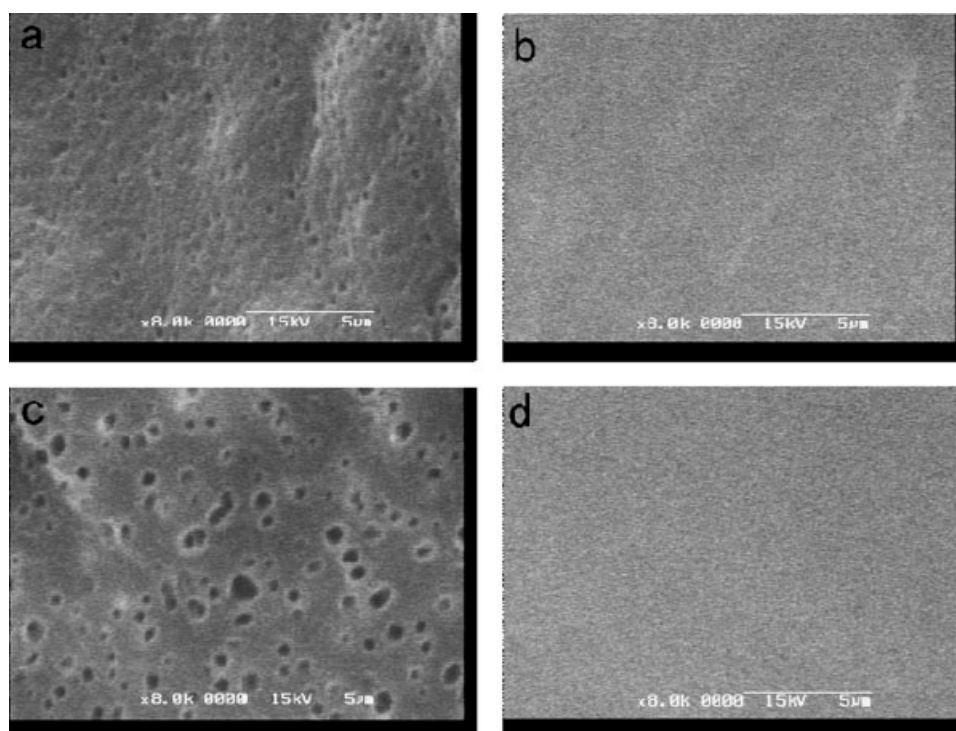
Figure 2 SEM images of the samples with different DCP content and POE content: (a) LLDPE/POE/DCP (100/10/0), (b) LLDPE/POE/DCP (100/10/2.0), (c) LLDPE/POE/DCP (100/25/0), and (d) LLDPE/POE/DCP (100/25/2.0).
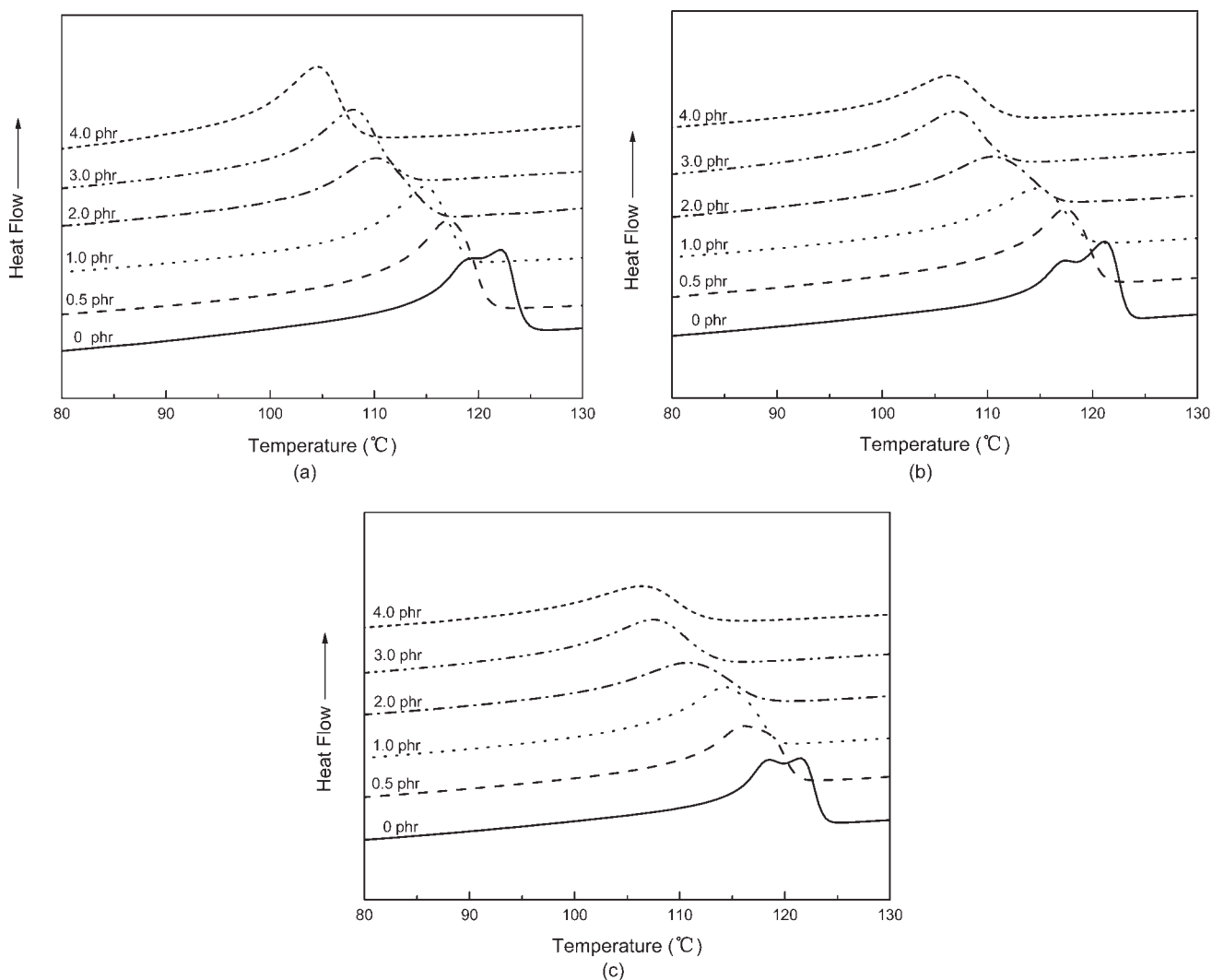
Figure 3 DSC melting curves of the samples with different DCP and POE contents: (a) 0 phr POE, (b) 10 phr POE, and (c) 25 phr POE.

linked. In addition, although the size of dispersed phase increased with the increase of POE content [Fig. 2(a,c)], the POE is dispersed evenly in the matrix and gives rise to fine and two-phase morphology. The results obtained suggest that POE is partially compatible with PE and form blends of excellent dispersed phase.

Thermal analysis

The DSC melting curves of XLPE with different DCP content, as well as of crosslinked LLDPE/POE blends with different DCP and POE content, are exhibited in Figure 3(a–c). The details of the melting temperature, crystallization temperature, crystallinity, and melting peak area or the melting enthalpies of all samples are listed in Table I. Figure 3(a–c) clearly show that a slight modification in the shape of the melting peak, even at a low DCP content. Moreover, the changes in the presence of POE are more obvious. Thus, it can be

concluded that crosslinking has occurred and crystallization process in samples has been modified in a certain way. Especially, POE has a slight enhancement on the modification. However, the crosslinks result in almost no gel content, which is due to the fact that the molecular weight of polyethylene is adequate low so that it is easily dissolved by *p*-xyelene.

The general trend in each graph in Figure 3(a–c) is a decrease in the peak area and a shift to low temperature as the DCP content increases. The variation of melting temperature may be correlated with the crystal perfection of polyethylene, yet the melting peak area is directly proportional to the crystallinity.[19] Therefore, the changes in Figure 3(a–c) strongly reveal that crosslinking decreases the ability of the polyethylene molecules to be arranged in crystalline structures of lamellas. This is attributed to the formation of a three-dimensional network, which prevents obviously lamellar thickening during crystallization and results in the decrease of melting temperature of samples.[20,21]

TABLE I
Summary of DSC Data of the Samples with Different DCP and POE Contents

LLDPE/ POE/DCP	T_m (°C)	T_c (°C)	ΔH_m (J/g)	X_c (%)
100/0/0	121.9	106.6	126.7	43.7
100/0/0.5	117.2	104.6	106.1	36.6
100/0/1.0	114.9	102.9	94.8	32.7
100/0/2.0	110.4	97.1	82.4	28.4
100/0/3.0	107.9	94.2	77.7	26.8
100/0/4.0	104.6	91.9	68.5	23.6
100/10/0	121.2	105.5	109.3	37.7
100/10/0.5	117.3	102.3	101.6	35.0
100/10/1.0	114.5	101.8	87.8	30.3
100/10/2.0	110.5	97.8	72.9	25.1
100/10/3.0	106.9	92.5	66.5	22.9
100/10/4.0	106.5	91.5	52.7	18.2
100/25/0	121.5	104.5	78.1	26.9
100/25/0.5	116.2	102.8	76.0	26.2
100/25/1.0	114.2	101.2	68.2	23.5
100/25/2.0	110.8	97.5	62.4	21.5
100/25/3.0	107.5	93.5	55.3	19.1
100/25/4.0	106.5	90.5	50.7	17.5

Moreover, the formation of three-dimensional network also makes crystallization difficult and lowers the crystallinity of polyethylene.[1]

To illustrate the influences of POE on the melting behavior of samples, the curves corresponding to the samples with the same DCP content are paid special attention (Fig. 4). It is obvious that POE has few influences on the melting temperatures of samples, whereas the peak area decreases with the increase of POE content whether DCP is present or not. The results obtained indicate that POE does not prevent the lamellar thickening of polyethylene during crystallization possibly because of the excellent compatibility of POE and PE. But POE lowers the crystallinity,

which is depicted clearly in Figure 5 and Table I. This is maybe due to the fact that the existence of intermingled POE and PE molecules makes crystallization difficult.[1]

Mechanical behaviors

Mechanical resistance is one of the many polymer properties to be considered in choosing a material for cable insulation; therefore, the mechanical behaviors of XLPE/POE blends containing different DCP and POE contents are worthy to be discussed. Figures 6 and 7 show the tensile stress-strain curves of samples with different DCP and POE contents, respectively. Furthermore, the tensile strength and elongation at break of samples are also presented in Figure 8.

In Figure 6(a–c), it can be seen that the change of stress-strain curves in each graph is similar as the DCP content increases. The yield points will be not obvious and be shifted to higher strains with the increase of DCP content. The results obtained reveal that the samples undergo a transition to a rubber like state with their crosslinking, because the formation of three-dimensional network will maintain the structure of polyethylene and prevent it from flowing, which follows a behavior similar to that of an elastomer.[1,20] Figure 7 reveals that the tensile behaviors of LLDPE/ POE blends in the absence of DCP still show the typical characteristics for pure LLDPE although the yield strength decreases, yet crosslinked LLDPE/POE blends with 2 phr DCP show a similar behavior to that of POE. Furthermore, the tensile behaviors are much more close to that of elastomer with the increase of POE content in the samples. This is possibly due to the enhancement on the crosslinking of polyethylene in the presence of DCP.
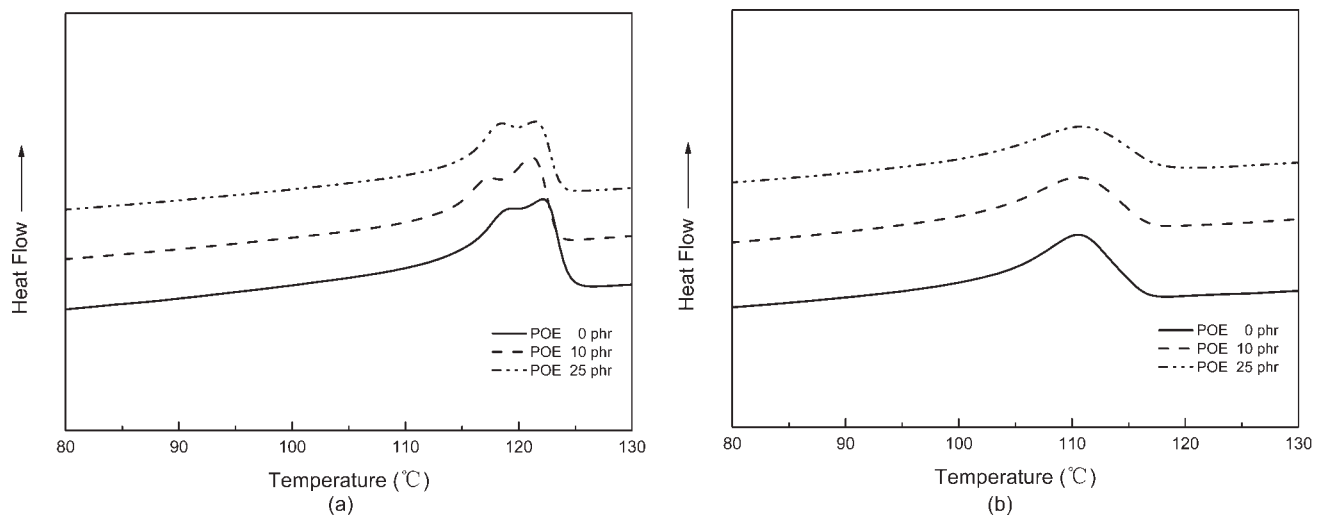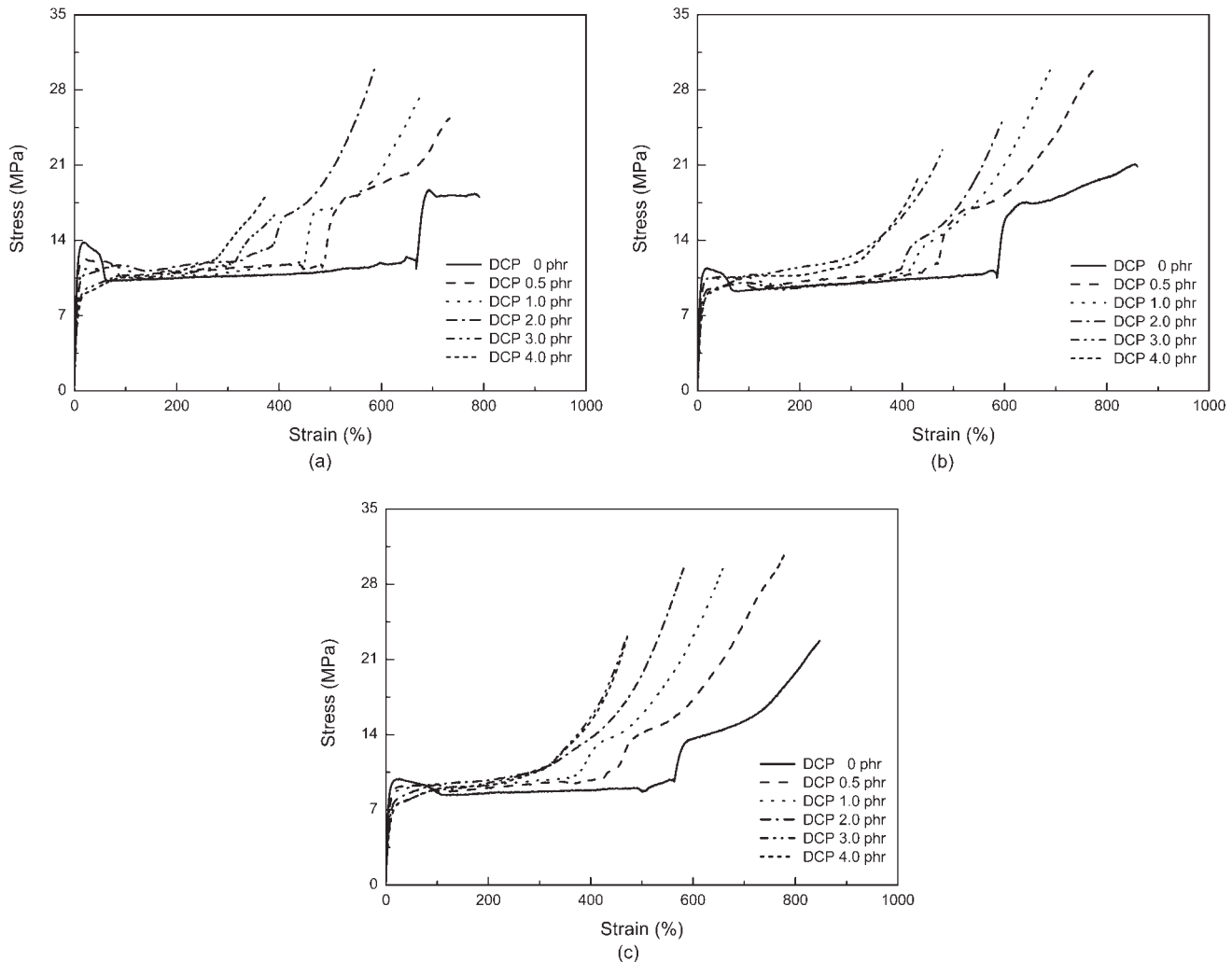

Figure 4 DSC melting curves of the samples with different POE content: (a) 0 phr DCP and (b) 2.0 phr DCP.
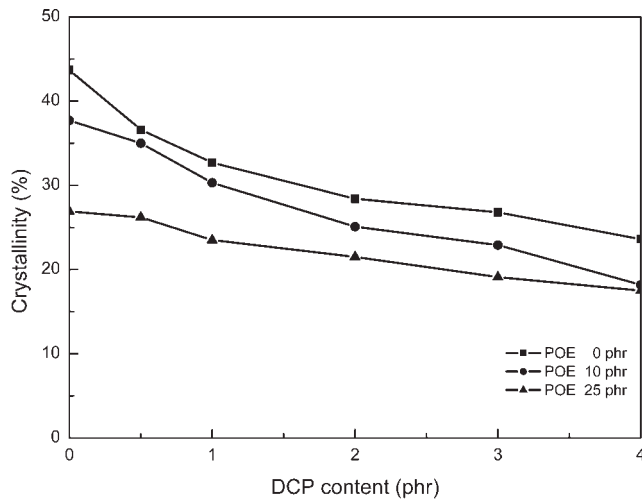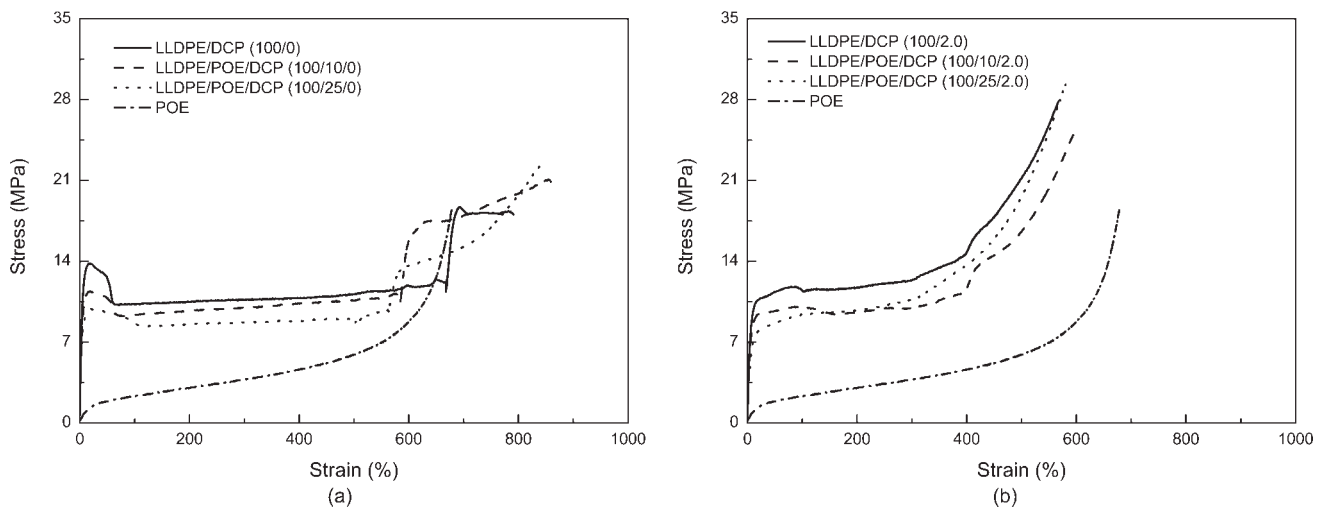
Figure 5 Crystallinity of samples with different DCP and POE contents.

Figure 8 shows that the tensile strength of the samples increases with the increase of DCP content, and then it will decrease markedly when the DCP content exceeds 2 phr. In addition, it is interesting to find that the tensile strength of the samples containing POE reaches the maximum value at a DCP content of 0.5 phr, and then it has few variations until the DCP content reached 2 phr. While in the absence of POE, the tensile strength of the samples increases with the increase of DCP content, and it reaches the maximum value at a DCP content of 2.0 phr. The results point out that POE improves the tensile strength of XLPE even at a low DCP level, owing to the enhancement of POE on the crosslinking of XLPE. As the DCP content exceeds 2.0 phr, the decrease of tensile strength in all samples may be due mainly to the excessive DCP and by-products of DCP decomposition, which acts as a plasticizing reagent. The elongation at break of the samples decreases consistently with an increase of DCP content, because of the formation of a three-dimensional network, which restrains the mobility and elongation of polymer chains. Yet POE has a slight improvement on the elongation of XLPE, which is attributed to the rubber elastic properties of POE.

Figure 6 Tensile stress-strain curves of the samples with different DCP and POE contents: (a) 0 phr POE, (b) 10 phr POE, and (c) 25 phr POE.
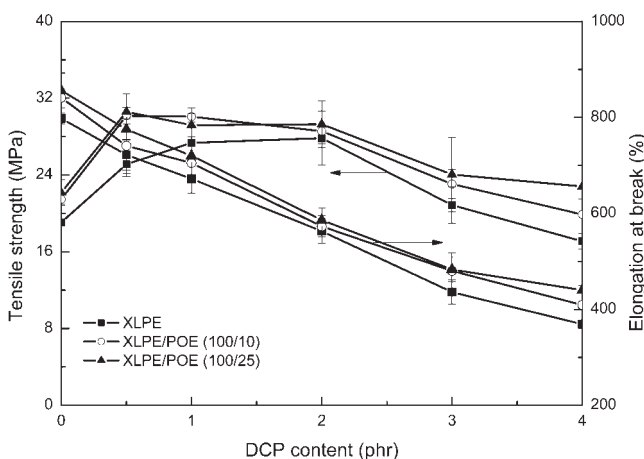
Figure 7 Tensile stress-strain curves of the samples with different POE contents: (a) 0 phr DCP and (b) 2.0 phr DCP.

The impact strength is often taken as a characteristic method of the toughness of materials. For the influences of POE on the toughness of XLPE, the impact strength of the samples containing different DCP and POE contents is depicted in Figure 9. As expected, the impact strength of the samples reaches the maximum value at a DCP content of 0.5 phr, and then it will decrease with an increase of DCP content. Compared with that of XLPE, the impact strength of samples containing POE is improved definitely. Especially, as the POE content increases from 0 to 25 phr, the impact strength of samples increases from 138.4 to 154.3 kJ/m^2 at a DCP content of 2.0 phr. The results strongly suggest that POE can improve the toughness of XLPE because POE is rubber elastic in nature.

Dielectric constant and dissipation factor

The dielectric behaviors of XLPE/POE blends containing various amounts of DCP and POE were measured, and the results are exhibited in Figure 10. It can be observed clearly that POE has few influences on the dielectric constant of the samples, owing to the close dielectric constant of them because the molecular chains of POE are similar to those of polyethylene. Yet the dissipation factor of the samples decreases slightly with the increase of POE content, indicating that POE enhances the crosslinking of LLDPE. It is worth notice that the formation of a three-dimensional network restrains the mobility of polyethylene molecular chains and lowers their polarized rates, which leads to the decrease of dissipation factor and dielectric constant of polyethylene.[22] Because of the facts, the dissipation factor and dielectric constant of the samples also decreases slowly as the DCP content increases. The results obtained reveal that the XLPE/POE blends still possess the same excellent dielectric constant and dissipation factor as XLPE.

Figure 8 Tensile properties of the samples with different DCP and POE contents.
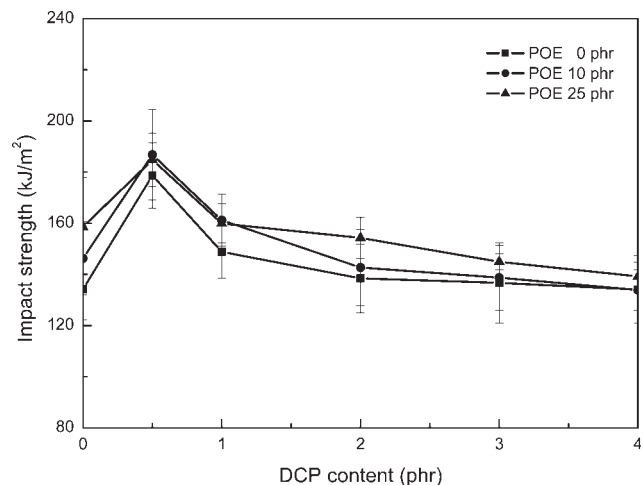
Figure 9 Impact strength of the samples with different DCP and POE contents.
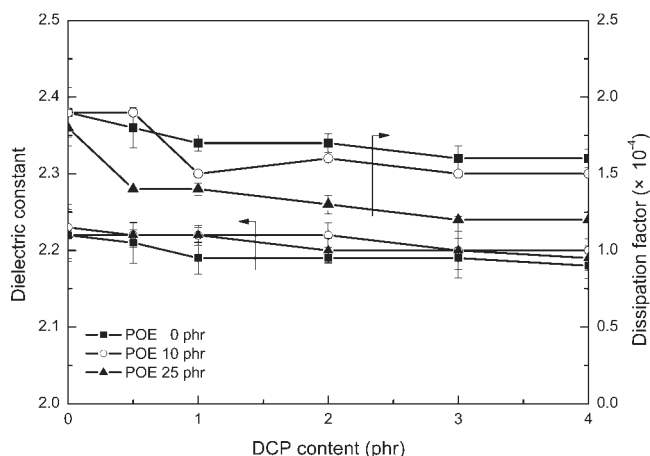
Figure 10 Dielectric behaviors of the samples with different DCP and POE contents.

CONCLUSIONS

The results obtained show that the polyolefin elastomers (POE) can enhance the crosslinking of linear low density polyethylene (LLDPE). Especially, the gel content in the presence of POE is much higher than that in the absence of POE when the DCP content is from 0.5 to 2 phr. In addition, the morphology observation of the samples reveals that POE is partially compatible with PE, and POE is crosslinked with the adding of DCP. Because of the fact that the existence of intermingled POE and PE molecules makes crystallization difficult, the crystallinity of the samples decreases with the increase of POE content. Moreover, the crosslinking of blends makes crystallization difficult and lowers the crystallinity of polyethylene as the DCP content increases. Because the crosslinking prevents lamellar thickening during crystallization, the melting temperature of samples also decreases with the increase of DCP content.

The mechanical behaviors of the samples reveal that POE can improve the toughness of XLPE because of its rubber elastic in nature. And the tensile behaviors of the crosslinked LLDPE/POE blends with 2 phr DCP are much more close to that of elastomer with the increase of POE content. In addition, POE has a slight improvement on the tensile strength and elongation at break of the samples, owing to its rubber elastic in nature and enhancement on the crosslinking of LLDPE. However, the XLPE/POE blends still possess the same excellent dielectric constant and dissipation factor as XLPE, which is mainly attributed to the facts that POE is also nonpolar polymer, and its molecular chain structures are similar to those of polyethylene.

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