Macromol. Symp. **2009**, 286, 125–134 DOI: 10.1002/masy.200951216

Effect of Initiator on the Over-Voltage Positive Temperature Coefficient of Linear Low Density Polyethylene/Carbon Black Nano Composites

Ching-Shan Tsai,[1] *Chia-I Liu,*[1] *Keng-Yu Tsao,*[1] *Kan-Nan Chen,*[2] *Jen-Taut Yeh,*[3]
*Chi-Yuan Huang**[1]

Summary: The composite of linear low density polyethylene (LLDPE) with carbon black (CB) and inorganic flame retardant (aluminum hydroxide, $Al(OH)_3$) was prepared by melt-blending method. The effect of cross-linking on the stability of positive temperature coefficient (PTC) of composite and the elimination of negative temperature coefficient (NTC) of composite were investigated. LLDPE was chemically cross-linking with different contents of initiator (dicumyl peroxide, DCP). The cross-linking effects of composite were analyzed by gel content analysis, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). By the effect of DCP, not only the composite appeared a high PTC intensity, but also the NTC effect of composite was eliminated. In this investigation, the optimum PTC intensity of composite reached 5.87 orders of magnitude for the composition of LLD0.10C33.7A28, and the PTC transitional temperature of composite decreased with increasing of DCP content. In addition, the good reproducibility of composites was proved by thermal cycling, and successfully passed the test of over-voltage resistance.

Keywords: carbon black; cross-linking; linear low density polyethylene; positive temperature coefficient

Introduction

Electrically conductive polymer composites consisted of conductive fillers and thermoplastic polymers. It exhibited a positive temperature coefficient (PTC) effect that was associated with a drastic increasing of resistivity in the melting point temperature of semi-crystalline polymer when the filler concentration was high enough.[1] The PTC phenomenon in polymer materials was originally discovered by Frydman in 1945.[2] No attention had been paid to the discovery until Kohler rediscovered the phenomenon in 1966,[3] he suggested that the PTC effect was caused by thermal expansion. However, the continuous heating reduced the resistivity of composites because of the negative temperature coefficient (NTC) effect. The NTC effect was related to the redistribution of CB in the molten polymer.[4] The presence of NTC effect had an adverse influence on the application of the PTC composites because of the instability of conductivity. To solve the NTC effect, cross-linking networks had been proven to reduce the mobility of CB in the polymer matrix effectively.[5] Therefore, the cross-linkings of chemical and irradiative were important strategy to eliminate the NTC effect that can result in more stable conductive behavior in those materials.[6] In this article, we investigated that the influence of chemical cross-linking by initiator

---

[1] Department of Materials Engineering, Tatung University, No.40, Chung-Shan N. Rd., 3rd Sec., Taipei 104, Taiwan
E-mail: cyhuang@ttu.edu.tw

[2] Department of Chemistry, Tamkang University, No.151, Yingzhuan Rd., Danshui Town, Taipei County 251, Taiwan

[3] Department of Polymer Engineering, National Taiwan University of Science and Technology, No.43, Sec.4, Keelung Rd., Taipei City 106, Taiwan

(dicumyl peroxide, DCP) on the PTC characteristics of composites. The gel content of composites was studied by solvent-extraction. Besides, the thermal properties of composites were studied by differential scanning calorimetery (DSC) and dynamic mechanical analysis (DMA). Finally, the structural stabilities of composites after over-voltage resistance test were also studied.

Experimental Part

Materials

Linear low density polyethylene (LLDPE) was used as the matrix polymer that was a commercial resin (LL110) from USI Co., Ltd. with melt index of 1 g/10 min and a density of 0.920 g/cm^3. The carbon black (CB) was the commercial name of Raven 430 from China Synthetic Rubber Corporation with an average particle size of 82 nm and a dibutyl phthalate (DBP) absorption value of 78 cm^3/100 g. Aluminum hydroxide [$Al(OH)_3$, SL-2926 K] with the average particle size of 1.4 μm was used as an inorganic flame retardant and was provided from Showa Chemical Co., Ltd., Japan. Initiator (dicumyl peroxide, DCP) was produced with chemically pure degree from Aldrich Chemical, Co., Inc. The antioxidant Irganox 1010 [pentaerthrityl-tetrakis-3-(3,5-di-ter-butyl-4-hydroxyphenyl)-propionate] with density of 1.15 g/cm^3 was purchased from Ciba-Geigy Co., Swizerland.

Composite Preparation

According to the experimental ingredients, the composites of cross-linked LLDPE, CB and other additives were prepared by melt-blending in a Brabender (PLE-330, Germany) for 10 min at 180 °C, respectively. The compounding process of composites were compressed into 2 mm thick sheet by hot-compression-molded at 180 °C under the pressure of 10 MPa for 6 min, and then the specimens were cooled down with cooling system of water. In order to reduce the contact resistance of specimens, the copper foil was served as electrode (SD 100 3 OZ (A); produced by Co-Tech Copper Foil Corporation) that was laminated to the melt-pressed slab under heat and pressure. The specimens were cut about $40 \times 40 \times 2\,mm^3$ in size. To reduce the residual stress of specimens, we went on the annealing treatment of specimens. The specimens put into oven at 130 °C for 1 h, and then natural cooling was from 130 °C to room temperature. The abbreviations of samples were denoted in the Table 1.

Electric Resistance Measurement

We connected a computerized system that comprising a computer, a multi-meter (KELTHLEY 7002 switch system and 2400 source meter), and a programmable oven (DELTA 9039). The resistance of composites along the thickness direction as a function of temperature was measured at a heating rate of 4 °C/min. To prepare the test specimens, the two sides of specimen

Table 1.
The abbreviations of samples.

Sample	CB (wt%)	$Al(OH)_3$ (wt%)	Initiator (DCP) (wt%)
LLC30A28	30.0	28.0	0.00
LLC33.7A28	33.7	28.0	0.00
LLC35A28	35.0	28.0	0.00
LLC37.1A28	37.1	28.0	0.00
LLC40A28	40.0	28.0	0.00
LLC43A28	43.0	28.0	0.00
LLC45A28	45.0	28.0	0.00
LLD0.03C33.7A28	33.7	28.0	0.03
LLD0.05C33.7A28	33.7	28.0	0.05
LLD0.10C33.7A28	33.7	28.0	0.10
LLD0.30C33.7A28	33.7	28.0	0.30
LLD0.50C33.7A28	33.7	28.0	0.50

were laminated with copper foil, and cut into a circular form which diameter of specimen was 5.0 mm and thickness of specimen was 2.0 mm. The volume resistivity of specimens was measured by testing standard of ASTM D 4496.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) observations of composites were performed on a JEQL JSM-6300 model. The fractured surface of composites was prepared in liquid nitrogen and then followed by coating with a thin layer of gold (coating time of 3 min). The morphology of composites was determined by accelerating voltage of 10 kV.

Gel Content Analysis

The percentage of insoluble material (gel) after chemical cross-linking was measured with a Soxhlet apparatus. Approximately 200 mg of sample wrapped in nickel mesh was exposed to refluxing xylene until the sample attained constant weight, which usually took 24 h. After that, the sample was dried overnight in a vacuum oven at 90 °C. The degree of cross-linking (DOC) was calculated by equation (1):

$$G\% = (W_1 - W_c)/(W - W_c) \tag{1}$$

where G % was the gel fraction, W_1 was the weight of the sample after refluxing, W was the weight of the sample before refluxing, and Wc was the weight of CB.

Thermal Analysis

The behaviors of melting and crystallizable in composites were carried out on a differential scanning calorimeter (TA DSC 2910 apparatus, TA Instruments, New Castle, DE) in N_2 atmosphere. The samples were heated from room temperature to 160 °C at a rate of 2 °C/min. The variation in heat capacity as a function of temperature was recorded. The sample weight of 5 mg was placed in circularly standard aluminum dish. The heat of fusion was obtained by integrating of the area under the endothermic peak.

Dynamic Mechanical Analysis

The dynamic mechanical properties of composites were investigated with a dynamic mechanical analyzer (DMA; DMA 2980, TA Instrument Company). Rectangular bar specimens in dimension of $15 \times 10 \times 2\,\text{mm}^3$ were used for this study. The temperature dependence of dynamic tensile modules were measured between room temperature and 160 °C at a constant frequency of 10 Hz and a heating rate of 3 °C/min.

Over Voltage Resistance Test

According to the testing standard (YD/T 741-95),[7] the composites were proceeded the over-voltage resistance test in the test conditions (electric voltage of 250 V, electric current of 3 A, frequency of 10 cycles).

Reproducibility

The composites that passed over voltage resistance test proceeded the reproducibility test. The testing condition was heating from room temperature to 140 °C and then natural cooling was from 140 °C to room temperature. The thermal cycles proceeded the frequency of 10 times continuously.

Results and Discussion

Effect of Carbon Black Content on Percolation and PTC Behavior

The relationship between room temperature volume resistivity and average PTC intensity for composites with different CB contents was showed in Figure 1. It could be found that the volume resistivity of composites decreased with increasing of CB content. With increasing of CB content, the average inter-CB gap became smaller, and there was an increase in the number of conductive pathways. It had been believed that filler particles passed through the polymer matrix at the critical volume fraction and then the conductive network was formed.[8] According to the percolation theory,[9] it could be described as the resistivity of PTC material that a sharp change in resistivity will happen when the

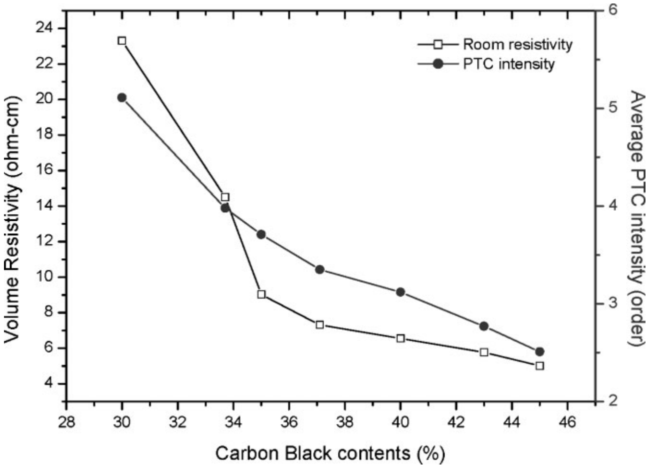

Figure 1.
The relationship between room temperature volume resistivity and average PTC intensity for composites with different CB contents.

CB content reaches a critical value, the so-called percolation threshold that had an advantage of high PTC intensity. In this study, the CB content of 33.7 wt% was the percolation threshold concentration.

The curve of volume resistivity and temperature in composites with CB content of 33.7 wt% was showed in Figure 2. The PTC behavior was referred to the breakage of CB conductive network, which induced by the volume expansion of LLDPE in T_m of LLDPE. The volume resistivity of composite reached a maximum in the vicinity of 116.1 °C, regardless of the CB contents. After the PTC transition, the volume resistivity of composites decreased with increasing of temperature, which was defined as the NTC effect. The NTC effect was explained to the formation of newly conductive pathways that induced by increasing of LLDPE mobility and the rearrangement of CB aggregates.[10] Concerning the occurrence of NTC effect, we thought that the CB particles could re-agglomerated easily in the molten matrix and then resulted in the formation of a new conductive network. The reason was that the viscosity of composite was decreased

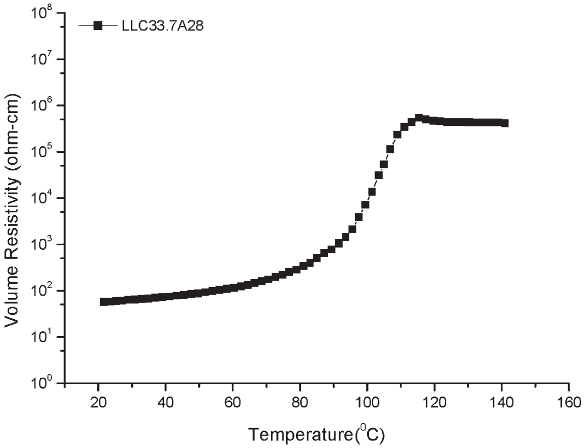

Figure 2.
The curve of volume resistivity and temperature in composites with CB content of 33.7 wt%.

with rising of temperature. The authors[11] had studied the NTC effect in CB-filled crystalline polymers above crystalline melting. Directing to this problem, we used the chemical cross-linking of LLDPE to limit the mobility of CBs in composites, and then the NTC effect was eliminated.

Effect of Cross-Linking by Initiator (DCP)

Cross-linking network of polymer had been proven to effectively reduce the mobility of CB in the polymer matrix, and to actually reduce the NTC effect.[5] In the research,[12] the chemical cross-linking method could be used to improve the structure property of PTC composites. In this work, the cross-linking of LLDPE with initiator (DCP) was discussed. The cross-linking of LLDPE with DCP was based on free radical mechanism. The free radicals generated on thermal decomposition of DCP that could attacked to the free chains of molten LLDPE, and cross-linking of the polymer chains occurred. The similar mechanism of cross-linking for PE with DCP was

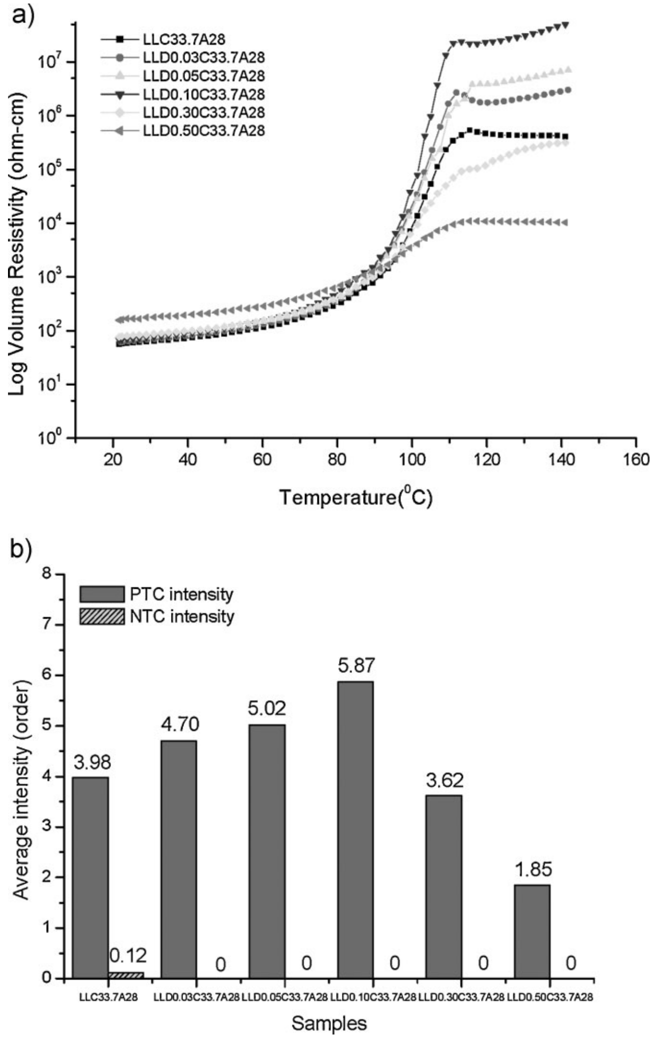

Figure 3.

The composites with different DCP contents. (a) The volume resistivity as a function of temperature; (b) The relationship between average PTC intensity and average NTC intensity.

proposed by Campus[13] and Lazar[14]. The temperature dependence of volume resistivity for composites with different DCP contents was showed in Figure 3(a). In the course of cross-linking, the degraded existence made the main chain of polymer to cut off that the amorphous part was slightly increased,[15] and the aggregation of CB particles was reduced relatively. Thus, the room temperature volume resistivity of composite was slightly increased. In addition, the cross-linking of composite limited the mobility of CB particles, and then CB particles of composite was not easy contacted again near the melting temperature of polymer. Thus, the composite with DCP

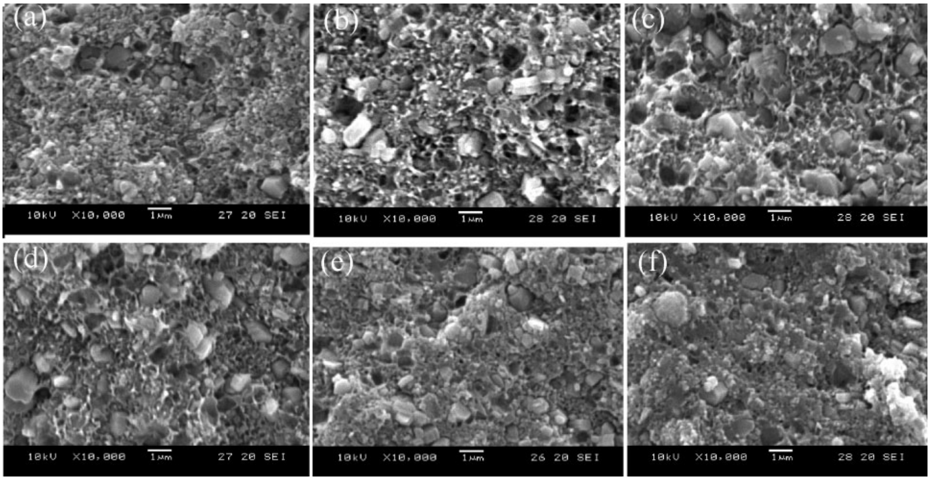

Figure 4.
SEM photographs of freeze-broken surfaces of composites with different DCP contents. (a) LLC33.7A28 10000x; (b) LLD0.03C33.7A28 10000x; (c) LLD0.05C33.7A28 10000x; (d) LLD0.10C33.7A28 10000x; (e) LLD0.30C33.7A28 10000x; (f) LLD0.50C33.7A28 10000x.

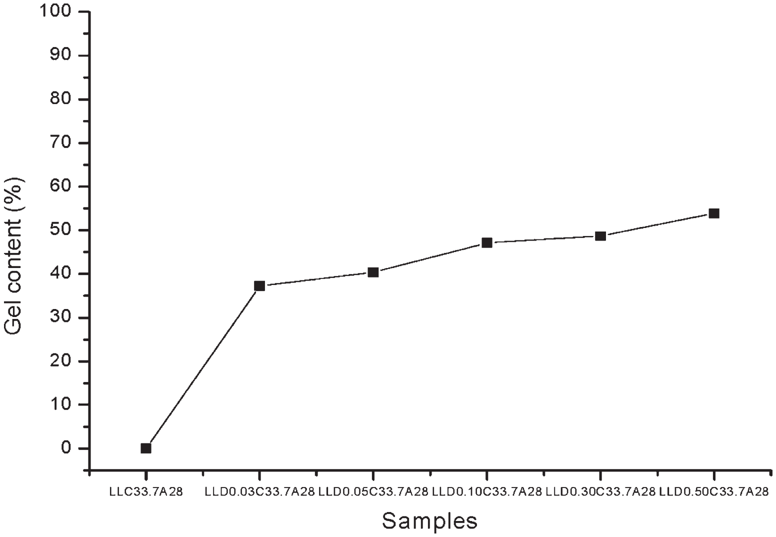

Figure 5.
The influence of different DCP contents on the gel content of composites.

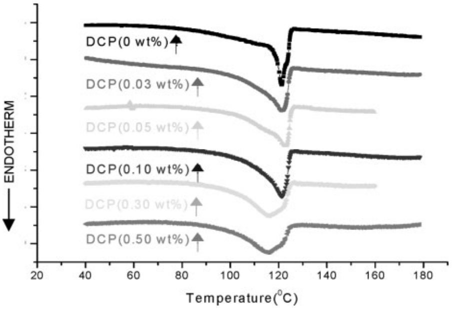

Figure 6.
The DSC diagram of composites with different DCP content.

had good PTC intensity, and the NTC effect could be eliminated. The early research[16] also got the same result. The relationship between average PTC intensity and average NTC intensity in composites with different DCP contents was showed in Figure 3(b). The PTC intensity of untreated composite was only 3.98 orders of magnitude, and had obvious NTC effect (0.1177 orders of magnitude). With increasing of DCP contents was up to 0.10 wt%, the PTC intensity (5.87 orders of magnitude) of composite was increased remarkably, and the NTC effect could be eliminated. After that increasing of DCP contents was up to 0.50 wt%, the PTC intensity (1.85 orders of magnitude) of composites was decreased. It was because that the higher cross-linking degree of composite not expanded suitably in PTC transition of composite. The CB particles were obviated outside the crystal zone,[4] and the cross-linking of polymer also occurred mainly in amorphous zone.[17] The CB particles of amorphous zone were bonded in network structure of cross-linking, and the sports of polymer chain were limited over the melting point of polymer. Thus, the NTC effect of composite was eliminated. In this work, the optimum composition of composite was LLD0.10C33.7A28.

The SEM photograph of composites with different DCP contents was showed in Figure 4. Figure 4(a) could be found that the distribution of surface structure of composite was random. However, the surface structure of composite with adding of DCP showed the silk-like structure in Figure 4(b) ~ Figure 4(f). In order to prove the existing of cross-linking in composite, the gel content analysis of composite was used. The gel content of composites with different DCP contents was showed in Figure 5. The gel content of cross-linking in composite increased with increasing of DCP content up to 53.87%. It could be seen that the increasing of DCP content induced the suitable cross-linking degree of composite, and then the mobility of CB particles in composite was effectively limited. Thus, the NTC effect of composites could be eliminated fully as the DCP content was above 0.03 wt%, demonstrating that the cross-linking structure of composite was fully formed at this time, and then the thermal expansion of composite could effectively increased in T_m of LLDPE. Consequently, the CB aggregates or agglomerates were bound to the three-dimensional cross-linking networks of composites.

Thermal Analysis

The effect of cross-linking on the regions of amorphous and crystalline in LLDPE was considered. The DSC diagram of composites

Table 2.
The results of temperatures of melting and crystallizable, heat of fusion (ΔH_m) and degree of crystallinity for the different DCP content of composites.

DCP content (wt%)	ΔH_m (J/g)	X_c (%)	Melting temperature (°C)	Crystallization temperature (°C)
0.00	102.70	35.67	121.28	117.50
0.03	100.70	34.97	120.94	111.90
0.05	94.90	32.95	120.13	111.29
0.10	94.32	32.75	119.53	110.54
0.30	93.34	32.41	116.29	100.61
0.50	84.20	29.24	115.40	99.81

with different DCP content was showed in Figure 6. It could be found that the temperatures of melting and crystallizable in LLDPE moved to the low temperature with increasing of DCP content. The temperatures of melting and crystallizable, heat of fusion (ΔH_m) and degree of crystallinity as determined from DSC was showed in Table 2, for LLDPE with different DCP content. The degree of crystallinity was calculated via the total enthalpy method, according to the equation $X_c = \Delta H_m/\Delta H_m^\circ$; where X_c was the degree of crystallinity, ΔH_m was the specific enthalpy of melting, andΔH_m° was the specific enthalpy of melting for 100% crystalline PE. TheΔHm value for 100% crystalline PE was taken as 287.93 kJ/kg as reported in the literature.[18] The temperatures of melting and crystallizable, heat of fusion (ΔH_m) and degree of crystallinity were observably decreased with increasing of DCP content. Cross-linking played the role of defect centers, which the folding of macromolecular chains was impeded, and the sizes of lamellar crystals were decreased.[15]

Dynamic Mechanical Analysis

The effect of cross-linking on the regions of amorphous and crystalline in composite was discussed by DMA. DMA of PE prior to melting revealed three peaks that termed as transitions of α, β and γ. The α transition occurred between the range of T_g to melting point. The temperature dependence of the storage modulus for composite in different DCP content was showed in Figure 7(a). It could be found that the storage modulus of composite increased with DCP content. The increase was attributed to the increasing of cross-linking. The temperature dependence of the loss modulus for composite in different DCP content was showed in Figure 7(b). The corresponding loss modulus of composite showed clearly maximum at 60 °C, corresponding to the α mechanism associated with crystal dispersion.[19] These increases in temperature of α transition was attributed to reduce in crystallinities with increasing of cross-linking, which enhanced the molecular motions of the amorphous phase, leading to increase in free volume. The free volume also increased as a result of restriction of the chain packing due to the cross-linking of

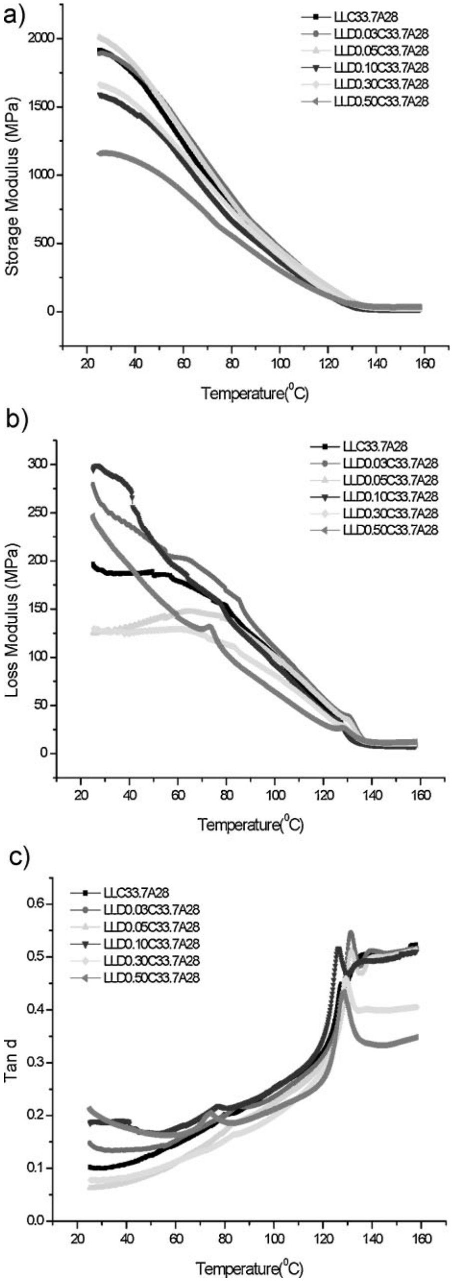

Figure 7.
The temperature dependence of dynamic mechanical properties for composite in different DCP content. (a) Storage modulus; (b) Loss modulus; (c) Tanδ.

polymer chains. The temperature dependence of the tanδ for composite in different DCP content was showed in Figure 7(c). It could be found that the tanδ decreased with increasing of DCP content. Because the tanδ was the emblem of cross-linking degree, so the decreasing of tanδ was with increasing of cross-linking and the range of tanδ became relatively wide.[20] The reason was usually supposed that the molecular weight distribution of cross-linking or network structure was not even.[21] There was an increase in storage modulus with increasing of cross-linking, which was attributed to reduce in crystallinity (Table 2) and to increase in free volume.

Over Voltage Resistance Test

The results of over-voltage resistance test for composites were showed in Table 3. It could be found that the chemical cross-linking of LLDPE effectively increased the structure stability of composite. The composition of LLD0.10C33.7A28 not only passed through the over voltage resistance test, but also had good structure stability simultaneously.

Reproducibility

The composites that passed over-voltage resistance test were proceeded the test of reproducibility. The electrical reproducibility of the passed over voltage resistance

Table 3.
The results of over-voltage resistance test for composites.

Sample	ρ_{RT}^* (ohm) (before)	ρ_{RT}^* (ohm) (after)	Pass	PTC intensity (order)	NTC intensity (order)
LLD0.03C33.7A28	20.10	21.91	○	5.90	0.19
LLD0.05C33.7A28	28.30	30.61	○	6.11	0.10
LLD0.10C33.7A28	30.24	33.75	○	6.35	0.00
LLD0.30C33.7A28	45.10	50.66	○	3.07	0.00

$^*\rho_{RT}$ was the room-temperature resistance value.

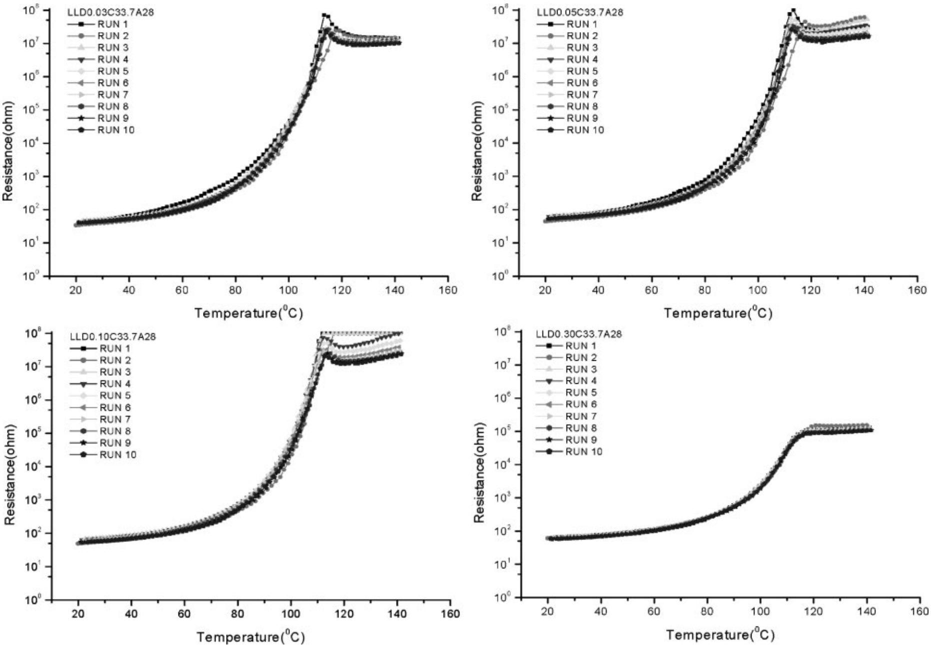

Figure 8.
The reproducibility of the passed over voltage resistance test of composites.

test of composites was showed in Figure 8. It could be found that the same reproducibility could be maintained when the frequency of thermal cycles increased up to 10 times. The trapping of CB within the cross-linking composite not only made the CB particles to redistribute during the expansion of composite at high temperature, but also took them back to their original positions when the composite was cooled. Thus, the good structure stability of composite was proved by thermal cycles of 10 times.

Conclusion

The effectively chemical cross-linking of composite with DCP was discovered. The gel content of composites was increased with increasing of DCP contents, and the composites could be got better PTC intensity and NTC effect was reduced effectively. In this study, the optimum amount of the DCP was 0.10 wt% in composite. The composites with DCP showed that the properties of temperatures of melting and crystallizable, heat of fusion, crystallinity were decreased with increasing of DCP content. Good reproducibility of composite (LLD0.10C33.7A28) was prepared, and successfully passed the over voltage resistance test.

[1] M. Zhang, G. Yu, H. Zeng, H. Zhang, Y. Hou, *Macromolecules* **1998**, *31*, 6724.
[2] E. Frydman, UK patent 604695 **1948**.
[3] F. Kohler, US patent 3243753 **1966**.
[4] J. Meyer, *Polym. Eng. Sci.* **1974**, *14*, 706.
[5] X. S. Yi, J. F. Zhang, Q. Zheng, Y. Pan, *J. Appl. Polym. Sci.* **2000**, *77*, 494.
[6] M. G. Lee, Y. C. Nho, *Radiat. Phys. Chem.* **2001**, *61*, 75.
[7] People's Republic of China communication behavior standard, YD/T 741-95, **1995**.
[8] I. Balberg, C. H. Anderson, S. Alexander, N. Wagner, *Phys. Review B, CondensMater* **1984**, *30*, 3933.
[9] D. Stauffer, A. Aharony, *Introduction to percolation theory*, 2nd ed. Taylor Francis, **1992**.
[10] G. Klason, J. Kubat, *J. Appl. Polym. Sci.* **1978**, *22*, 163.
[11] G. J. Lee, K. D. Suh, S. S. Im, *Polym. Eng. Sci.* **1998**, *38*, 471.
[12] A. Voet, F. R. Cook, *Rubber. Chem. Techonol.* **1968**, *41*, 1207.
[13] A. Campus, G. Matey, *PRI Conference 'Polymer in Cables'*, Manchester **1983**.
[14] M. Lazar, R. Rado, J. Rychly, *Adv. Polym. Sci.* **1990**, *95*, 151.
[15] H. A. Khonakdar, J. Morshedian, U. Wagenknecht, S. H. Jafari, *Polymer* **2003**, *44*, 4301.
[16] X. Yi, G. Wu, Y. Pan, *Polym. Inter.* **1997**, 44, 706.
[17] A. Keller, G. Ungar, *Radiat. Phys. Chem.* **1983**, *22*, 155.
[18] J. Brundrup, *Polymer Handbook*, 3rd edn. Wiley-Interscience, Wiley, New York **1989**.
[19] M. Takayanagi, M. J. Matsuo, *Macromol. Sci. Phys.* **1967**, *B1*, 407.
[20] A. S. Kenyon, L. E. Nielsen, *J. Macromol. Sci.* **1969**, *A3*, 275.
[21] K. Ueberreiter, G. Kanig, *J. Chem. Phys.* **1950**, *18*, 399.