

INFLUENCE OF CROSSLINKING ON PHYSICAL PROPERTIES OF LOW DENSITY POLYETHYLENE*

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Abstract Influence of crosslinking on physical properties of low density polyethylene was studied. The results indicated that, at low degrees of crosslinking, the network hardly affects the crystallinity, elastic modulus (E) and yielding stress while it improves the tensile strength and strain at break simultaneously. Tensile strength reaches a maximum of about 24 MPa at 1.5 phr dicumyl peroxide (DCP) then decreases to a constant value of about 18 MPa due to decrease of crystallinity. E reaches its maximum at 0.5 phr DCP corresponding to gel fraction of about 75% without marked change in crystallinity. The crosslinked polyethylene exhibits two yielding processes, and both yielding stresses approximately linearly depend on crystallinity.

Keywords: XLPE; Crystallinity; Deformation behavior; Yielding.

INTRODUCTION

It is well known that physical properties of polymers greatly depend on their condensed state^[1–9]. Chemical crosslinking^[2, 10–13] is an effective way for improving physical properties especially thermal resistance of polymeric materials^[14]. The crosslinking network seriously restrains the movement of molecular chains in the melt state, preventing them from arranging into lamellar folds and affecting polymer crystallization finally^[15, 16]. A lot of researches have been focused on the relationship among crystallinity and mechanical properties of low density polyethylene (LDPE)^[2, 16–19] crosslinked using no more than 3% dicumyl peroxide (DCP). Deterioration in mechanical properties of crosslinked low-density polyethylene (XLPE) with high DCP dosages is mostly attributed to the degradation of LDPE with ignoring the impact of crystallinity^[2, 17, 20, 21].

Semicrystalline polymers upon drawing exhibit cold draw and yielding^[6, 7, 22–29]. Crystallinity plays an important role in yielding^[6, 8, 23, 25, 27, 28, 30]. Tresca yield criterion^[4, 8] has been proposed to describe yielding of polymers with a wide variation of crystallinity^[4, 7, 31]. Two mechanisms, the partial melting-recrystallization and chain slip mechanisms^[7, 8, 27–29], have been proposed for explaining the yielding. Nozue^[22] and Manzur^[32] *et al.* supported the partial melting-recrystallization during drawing, while results from wide and small angle X-ray scattering support the later mechanism^[24, 27–29, 33].

In this work, we prepared XLPE with a wide range of crosslinking density (as well as crystallinity formed under the same condition) by using DCP diffusion into solid LDPE granules before melt blending^[34]. Mechanical properties of XLPE were investigated for revealing the contributions of crosslinking network and crystallinity.

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EXPERIMENTAL

Materials

Low density polyethylene (LDPE) with $M_n = 13.3 \times 10^3$, $M_w = 77.5 \times 10^3$, density 0.921 g/cm^3 and melting index 2.12 g/10min was a product from Yanshan Co. SINOPEC, China. Dicumyl peroxide (DCP) as crosslinking agent and 3,5-bis(1,1-dimethylethyl)-4-hydroxyl-hydroxylbenzenepropanoic acid thiodi-2,1-ethanediyl ester (Irganox1035) as antioxidant were kindly provided by Virtulla Tianjin Tech. Co. Ltd., China. Xylene (AR) as solvent was obtained from Hangzhou Chem. Agent Co. Ltd., China. All the materials were used as received.

Sample Preparation

LDPE granules and antioxidant with a weight ratio of 100:1 were put into a 500 mL flask and were mixed through a rotary evaporator at 90°C to allow antioxidant to diffuse into LDPE granules for about 90 min. The mixture was cooled down to room temperature. Ten grams of the mixture were mixed with 40 g LDPE and certain amounts of DCP in the flask on a rotary evaporator at 80°C for about 1 h. The procedure allowed melted DCP to diffuse into the granule. The mixtures were further mixed using a torque rheometer (XSS-300) at 110°C and 50 r/min for 8 min.

The compounds were press moulded into sheets of 1.2 mm in thickness under 15 MPa and 175°C for 10 min and were then quenched to room temperature under pressure of 15 MPa for 10 min. Dumbbell-shaped samples for tensile test were punched out. The samples were kept for 24 h at 70°C in order to outgas by-products of crosslinking reaction. XLPE films for Fourier-transform infrared (FTIR) measurements were prepared at the same condition.

Analyses

Fourier-transform infrared (FTIR) spectra

FTIR spectra were recorded using a Vector 22 FTIR Spectrometer (Bruker, Germany) at a resolution of 2.0 cm^{-1} with 32 scans. Quantitative analysis was done using OMNIC 6.1a analysis software. Carbonyl index A_{1725}/A_{2019} and decomposition index A_{1690}/A_{2019} were chosen to characterize the thermal oxidation and decomposition, respectively, during the peroxide-cure procedure. Here A represents the area intensity of the selected peaks.

Gel fraction and crosslinking density

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

Apparent average molecular weight of effective chains between crosslinking sites, M_c^* , was calculated according to Flory-Rehner formula, $M_c^* = \rho_p V_0 \left(V_r^{1/3} - \frac{V_r}{2} \right) / \left[-\ln(1 - V_r) - V_r - \chi V_r^2 \right]$. Here, $\chi = 0.31$ is Huggins solvent-polymer interaction parameter, $V_0 = 139.3 \text{ cm}^3/\text{mol}$ is partial molar volume of the solvent^[15], ρ_p is density of polymer and V_r is volume fraction of polymer in the swollen gel, respectively. Average molecular weight of network chains was evaluated according to $1/M_c = 1/M_c^* + 2/M_n$ in order to take into account network imperfections such as chain segments terminated by a crosslink at only one end.

Differential scanning calorimetry (DSC)

Thermal properties of XLPE and the gels were examined using a Q100 differential scanning calorimeter (TA, USA) at 10 K/min under nitrogen atmosphere. Lamellar thickness l_c of both XLPE and the gels was estimated from melting point T_m according to the Gibbs-Thompson equation, $T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta H l_c} \right)$. Here, $T_m^0 = 418.7 \text{ K}$ is the equilibrium melting point of polyethylene crystal of infinite thickness, $\Delta H = 280 \text{ J/cm}^3$ is the enthalpy per unit volume, and $\sigma = 93.4 \times 10^{-7} \text{ J/cm}^2$ is the interfacial free energy associated with the basal plane of the mature crystallite.

Mechanical properties

Tensile tests were performed to dumbbell-shaped samples on a universal testing machine (CMT 4204, Shenzhen SANS Test Machine Co. Ltd., China) at 250 mm/min at room temperature ($(25 \pm 3)^\circ\text{C}$). Mechanical properties were determined from five replicates for each sample.

RESULTS AND DISCUSSIONS

Influence of DCP on Structure of XLPE

Crosslinking reaction in LDPE proceeds *via* radical coupling mechanism^[13, 35, 36], which might be accompanied with thermal oxidation of LDPE^[21, 37]. Chain scission reaction may become more important at high temperatures. Consequently, a greater proportion of antioxidant is necessary for restricting thermal degradation of LDPE during crosslinking^[21]. Figure 1 shows relative absorbances A_{1725}/A_{2019} and A_{1690}/A_{2019} as a function of DCP dosage for XLPE. A_{1725}/A_{2019} does not vary significantly after crosslinking LDPE using different DCP dosages. Degradation index A_{1690}/A_{2019} increases apparently with increasing DCP content, indicating that double bonds like $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ are generated from β -scission of chain branch^[21]. The more DCP is used, the much serious degradation is. Though thermal degradation takes place, crosslinking through coupling termination of radicals is still the main reaction^[36, 38].

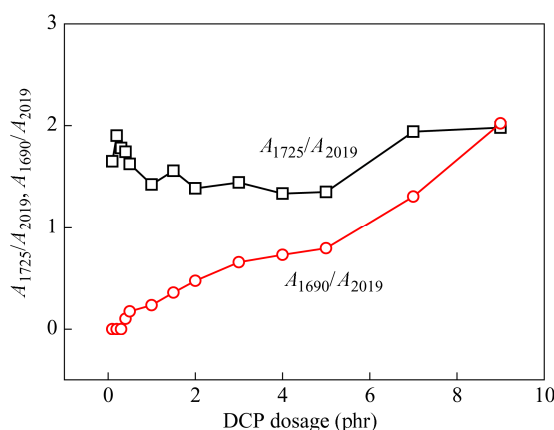


Fig. 1 A_{1725}/A_{2019} and A_{1690}/A_{2019} as a function of DCP dosage for XLPE

f_{gel} and M_c are used to characterize the degree of crosslinking^[39–41]. Figure 2 shows the influence of DCP content on f_{gel} , M_c and enthalpy of crosslinking reaction. Crosslinking enthalpy is almost linearly dependent on DCP content. At DCP content below 0.2 phr, f_{gel} remains zero and $M_c = 6.5 \times 10^3$ corresponds to the entanglement molecular weight. f_{gel} increases quickly with increasing DCP content and reaches 94% at 2 phr DCP. f_{gel} levels off at high DCP contents. In comparison with the rapid increment of f_{gel} , the decrease of M_c is rather slow. At 7–9 phr DCP contents, LDPE is almost completely crosslinked to form a network with $f_{\text{gel}} = 99\%$ and $M_c = 1.2 \times 10^3$, respectively.

Chain branches and chemical crosslinking have important influences on crystallization behavior^[15, 16, 42]. Crystallinity, T_m , l_c , and crystallization temperature (T_c) are used to evaluate the influence of crosslinking on structure of XLPE and the gels, and the data are listed in Table 1. It is seen that T_m and T_c decrease by about 17 K with increasing DCP content from 0 phr to 9 phr, which can be attributed to the branch or network formation preventing chains from regular arrangement into crystalline lamellae. The change in crystallinity and l_c below 0.5 phr DCP is rather small though f_{gel} increases sharply from 0 to 75%. A similar result is reported by other researchers^[16]. At DCP content below 0.3 phr, no gel forms after thermal crosslinking of the samples and crystallinity remains almost constant at about $(40.1 \pm 0.8)\%$. After the gel point (DCP content equal to or above 0.3 phr), crystallinity and l_c are proportional to each other (see inset in Fig. 4) and both decrease with increasing

DCP content (or crosslinking density characterized by $1/M_c$). Because all the samples underwent the same non-isothermal crystallization during preparation, the variations of crystallinity and l_c are involved in the restriction of the crosslinking network on the lamella formation. The size of network chains decreases with increasing crosslinking density, resulting in reduction in l_c of crystals together with reduction in crystallinity. Both T_m and T_c of gels with DCP from 0.3 phr to 3 phr (f_{gel} from 47.5% to 96.4%) are lower than those of XLPE, indicating the restriction of the crosslinking network on the nonisothermally crystallization of the network chains into lamellae slightly thinner than those formed in XLPE. At high crosslinking densities, the gels do not exhibit marked difference in crystallization and melting behaviors from XLPE.

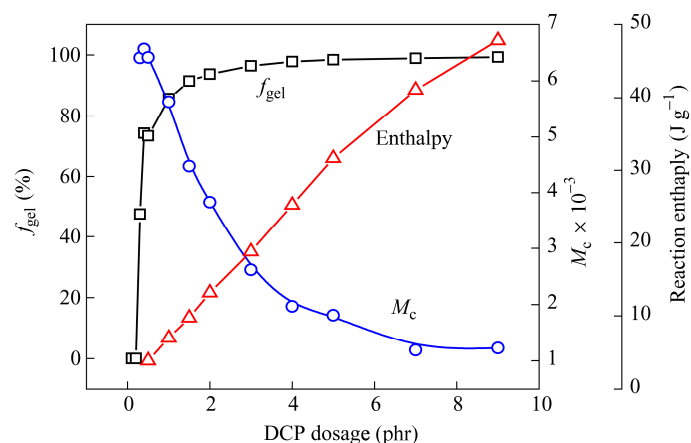


Fig. 2 Influence of DCP dosage on f_{gel} , M_c and enthalpy of crosslinking reaction

Table 1. Crystalline and melting behavior of XLPE and PE gel

XLPE					Gel		
DCP	T_m (°C)	T_c (°C)	l (nm)	Crystallinity (%)	T_m (°C)	T_c (°C)	l (nm)
0	109.6	—	7.8	41.1	—	—	—
0.1	108.2	97.1	7.5	39.8	—	—	—
0.2	107.9	96.6	7.4	39.5	—	—	—
0.3	107.1	96.2	7.3	40.0	105.8	95.5	7.0
0.4	106.9	96.0	7.2	39.2	104.9	94.4	6.9
0.5	106.4	95.5	7.1	38.4	105.2	92.6	6.9
1.0	104.6	94.0	6.8	35.5	104.3	91.9	6.8
1.5	103.8	92.5	6.7	35.3	103.6	91.2	6.7
2.0	102.6	91.4	6.5	34.1	102.0	90.4	6.4
3.0	100.4	89.2	6.2	32.6	100.6	88.8	6.2
4.0	98.0	87.3	5.9	30.9	98.5	86.8	5.9
5.0	96.8	85.0	5.7	29.9	96.8	84.9	5.7
7.0	94.3	82.8	5.4	28.2	96.2	81.5	5.7
9.0	92.6	80.6	5.3	26.8	92.0	79.6	5.2

Influence of Crosslinking on Tensile Behavior

Crosslinking network, morphology and chain entanglement are three important factors determining physical properties and deformation behavior of polymers^[43–46]. Crosslinking may greatly enhance tensile strength at the expense of elongation at break and crystallinity of XLPE^[15, 16, 42]. However, properties dominated by crystallinity, for example, yielding stress (σ_y) and elastic modulus (E), may deteriorate with increasing crosslinking density^[8, 24, 25, 30, 45]. After crosslinking, the tensile strength of the samples with high molecular weight decreases while that of the samples with low molecular weight increases^[42]. Moreover, long chains result in much more entanglements leading to strain hardening upon stretching^[8, 46].

Figure 3 shows the stress-strain (σ - ϵ) relationship for XLPE with different DCP contents indicated.

Uncrosslinked LDPE shows two yielding points at $\varepsilon = (20.2 \pm 0.3)\%$ and $\varepsilon = (69.4 \pm 1.8)\%$, respectively. The postyielding deformation is characterized by a strain softening up to $\varepsilon = (132 \pm 10)\%$, a cold drawing up to $\varepsilon = (500 \pm 5)\%$ and a strain hardening up to $\varepsilon = (530 \pm 7)\%$. The onset strain of hardening corresponds to the complete transformation of the original lamellar into microfibrillar structure^[47]. Drawing of the microfibrillar structure happens uniformly through displacement of adjacent fibrils containing a great many microfibrils of finite length. The samples break shortly during the hardening. In XLPE, the strain range for cold draw is shortened while that from the onset of hardening to the break strain is extended as DCP is added. The formation of crosslinking sites in the amorphous phase, as well as the anchored entanglements between crosslinking sites, strengthens strain hardening of XLPE^[39].

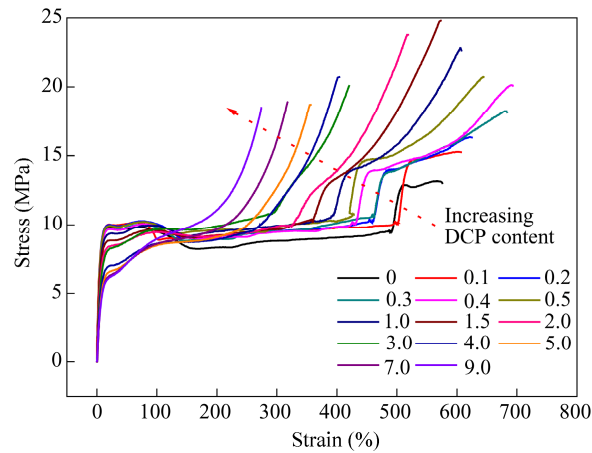


Fig. 3 Stress-strain curves of XLPE with different DCP contents in phr as indicated

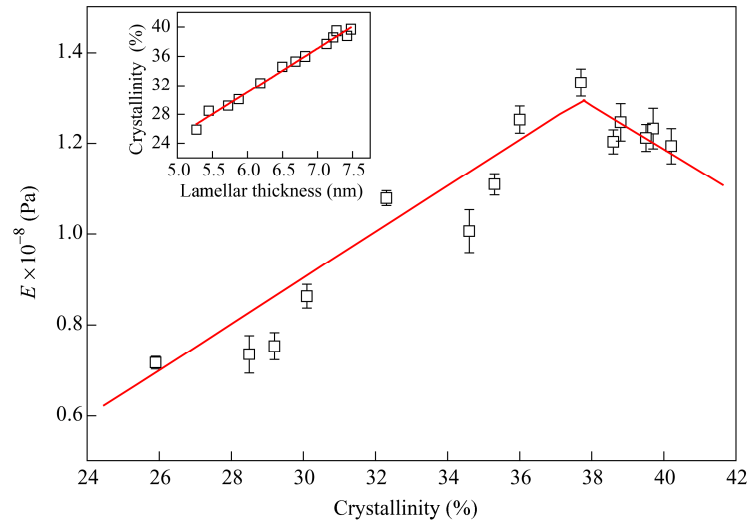


Fig. 4 E as a function of crystallinity for XLPE of different crosslinking densities. The inset shows crystallinity against l_c .

As is reported, E of semicrystalline polymers decreases with crosslinking^[2, 4, 16, 39]. Figure 4 shows the dependence of E on crystallinity. As the initial elastic deformation is mainly associated with the deformation of the amorphous region through slip, separation and rotation of lamellae, the interlamellar regions have important influence on E . As shown in Fig. 4, E exhibits a maximum at a crystallinity of 37.8% (0.5 DCP, $f_{\text{gel}} = 73.4\%$). At low degree of crosslinking, crosslinking sites interconnect the amorphous chains among lamellae but don't have

significant influences on crystallinity, which is responsible for the slight increment of E with increasing DCP from 0 phr to 0.5 phr (crystallinity decreasing from 41.1% to 38.4%). On the other hand, the reductions of l_c (from 6.8 nm to 5.3 nm) and crystallinity (from 35.5% to 26.8%) account for the E reduction at high degrees of crosslinking (DCP from 1.0 phr to 9.0 phr).

Double yielding is common in vinyl copolymers, which is assigned to a slip of crystal blocks passing each other in the mosaic crystalline structure and a homogenous shear of crystal block^[4, 8, 22, 27–29]. Figure 5 shows the first and the second yielding stresses, σ_{y1} and σ_{y2} , as a function of crystallinity. Both σ_{y1} and σ_{y2} are approximately linearly dependent on crystallinity^[4, 31] with different slopes.

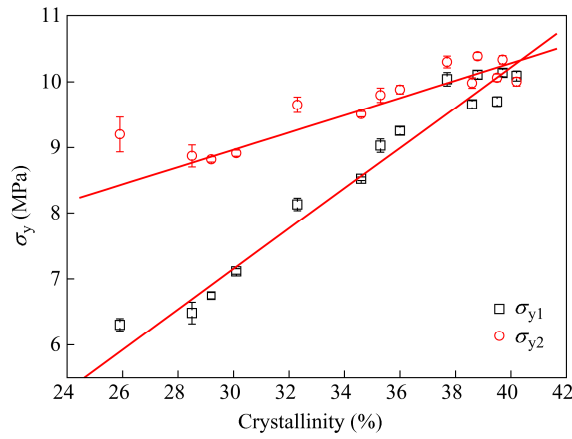


Fig. 5 Yielding stress as a function of crystallinity for XLPE of different crosslinking densities

Figure 6 shows the influence of DCP content on tensile strength (σ_b) and strain at break (ε_b). σ_b and ε_b increase with increasing DCP content below 1.5 phr and 0.4 phr, respectively, while they decrease at high DCP contents. The σ_b maximum occurs at the DCP content corresponding to $f_{gel} = 91.4\%$. On the other hand, the ε_b maximum occurs at the DCP content above which M_c starts to decrease. At low degrees of crosslinking, the increments in both σ_b and ε_b may be related to the formation of network that restrains the intercrystal slippage and microcrack of oriented crystals. At high degrees of crosslinking, on the other hand, the dense network with gradually reduced M_c restricts the deformability of the crystalline and the amorphous phases^[17]. Figure 7 shows the dependences of ε_b and hardening strain ε_h as a function of M_c . Both ε_b and ε_h are linearly dependent on M_c .

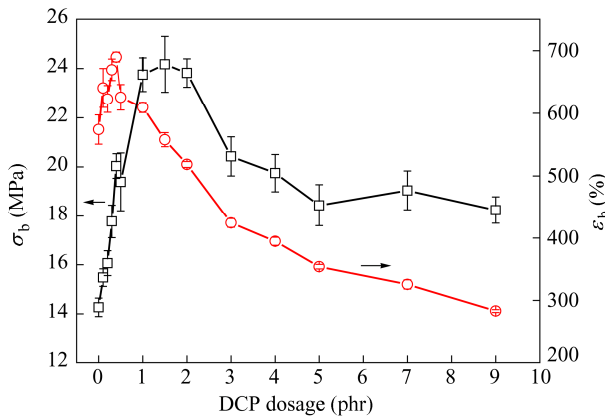


Fig. 6 σ_b and ε_b as a function of DCP content

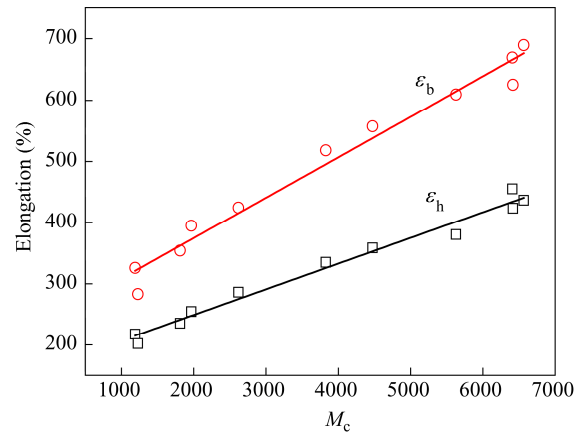


Fig. 7 ε_b and ε_h as a function of M_c for XLPE of different crosslinking densities

It is clear that both the ultimate deformability of XLPE and the limit draw ratio during necking are closely related to M_c .

CONCLUSIONS

Crosslinking density has a great influence on crystalline behavior and mechanical properties of LXPE. Below the gel point the crystallinity and lamellar thickness almost remain unvaried. Above the gel point, the crystallinity and lamellar thickness are proportional to each other and both decrease with increasing crosslinking density. Elastic modulus and strain at break reach a maximum in the vicinity of the gel point. Tensile strength reaches a maximum at 1.5 phr DCP corresponding to a gel fraction of 93%. Both the first and the second yielding stresses exhibit a linear dependence on crystallinity. On the other hand, the strain at break and hardening strain exhibit strong corrections to molecular weight of network chains between crosslinking sites.

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