

RECENT DEVELOPMENTS IN PHOTOINITIATED CROSSLINKING OF POLYETHYLENE AND ITS INDUSTRIAL APPLICATIONS*

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Abstract The recent developments in the photoinitiated cross-linking of polyethylene and the significant breakthrough of its industrial application are reviewed. The enhanced photo-initiation system, the dynamics of photoinitiated crosslinking, the optimum conditions, the crystal morphological structures and related properties, and the photo- and thermo-oxidation stability of photocrosslinked polyethylene (XLPE) materials have been elucidated systematically. A new technique for producing photocrosslinked XLPE-insulated wire and cable is described in detail. It can be expected that the future applications of photocrosslinking technique of polyolefins will be very promising.

Keywords Polyethylene, Enhanced photocrosslinking systems, Morphological structures and properties, Photo- and thermo-oxidation stability, Photocrosslinked XLPE insulated wire and cable

INTRODUCTION

Photoinitiated crosslinking of polyethylene (PE) by ultraviolet (UV) irradiation has been known since the 1950s when Oster and his co-workers^[1] first reported their studies. Using UV light in the 200~300 nm range, they found that the irradiation time could be decreased by a factor of 1000 when benzophenone was added as a photoinitiator. This simple method of UV light crosslinking has attracted considerable attention. Many attempts have been made to crosslink PE by UV irradiation^[2], but there was no significant breakthrough in the commercial application of UV crosslinking before 1990^[3]. It is difficult to crosslink thick solid PE samples homogeneously because there are two main problems: poor penetration of UV light in the bulk PE and the slow reaction rate of photocrosslinking of PE. Usually it takes at least several minutes of UV irradiation to obtain the necessary degree of crosslinking for practical application. Therefore, UV light crosslinking has been limited to the applications of photocuring and other surface modifications for films less than 0.3 mm thick. There has some comment^[4] that the practical importance of UV crosslinking of PE could be in surface grafting and that it was impossible to apply the technique to wire coating as insulation. The photocrosslinking of PE has several inherent advantages in comparison with the two commercially available methods i.e., high-energy electron beam and chemical reactions (with aromatic peroxides or vinylsilane). For example, UV photocrosslinking is a one-stage process using inexpensive and simple equipment and producing little degradation or oxidation of the polymer under the conditions of the UV crosslinking process; UV light sources are readily available and easy to handle. Therefore, the investment and the product cost are very low. Therefore, to date the photoinitiated crosslinking of PE and its industrial application still receive the attention of some researchers^[5, 6].

Comprehensive and systematic studies on the subject of photoinitiated crosslinking of PE have been conducted in Rånby's laboratories since the early 1980s. His first publication appeared in 1985^[7] and other

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related papers^[8–29] on photocrosslinking of PE have dominated the literatures in recent years. In more advanced studies, Rånby and his co-workers have developed a continuous laboratory method^[16, 30], synthesized new initiators^[16, 29] and exploited a new technique of photocrosslinking of PE in the melt for industrial manufacture of XLPE insulated wires and cables^[24, 31–33]. The great contributions of Rånby's group are the development of highly efficient enhanced photoinitiated systems for photocrosslinking PE in bulk and exploiting an industrial technology of photocrosslinking.

The objective of this article is mainly to summarize our work in Rånby's group, providing a comprehensive description of the basic reaction principles, describing the state-of-the-art and presenting the recent applications of the photocrosslinking of polyethylene. Therefore, the following fundamental aspects of photocrosslinking of polyethylene are covered: the enhanced photoinitiating systems, the reaction conditions, the dynamics of photoinitiated crosslinking, crystal morphological structures and properties, photo- and thermo-oxidation stability of the XLPE materials, and the new breakthrough of photocrosslinking technology for industrial application of wire and cable as insulated materials. Finally, advantages, limitations, and potential future applications of the photocrosslinking technology of polyolefin are discussed.

ENHANCED PHOTOCROSSLINKING OF POLYETHYLENE IN THE MELT

The main problems mentioned above in photocrosslinking of PE in bulk have been overcome by using the enhanced photoinitiating systems of photoinitiator and multifunctional crosslinker, by screening the product formation and optimizing reaction conditions, such as initiator and crosslinker and their concentrations, irradiation temperature, light intensity, and so on. The kinetic characteristics, the increasing penetration depth of UV light, the promoting initial rate, and the improving homogeneity of crosslinking density for the enhanced photoinitiated crosslinking systems of PE in the melt have been elucidated in detail. A mechanism of enhanced photoinitiated reactions has been proposed.

Photoinitiator

Photocrosslinking of PE requires UV light irradiation. The most common light source for commercial applications of photocrosslinking is the low-pressure, medium-pressure, or high-pressure mercury lamps that emit UV light in the range of 200–400 nm. The choice of light source depends upon the absorption spectrum of the photoinitiating systems used, the crosslinking process, and the requirements of the industrial applications. It is important that the absorption spectrum of the photoinitiator must overlap with the emission spectrum of the light source used^[34]. PE itself usually contains no light-absorption groups. It is necessary to initiate the crosslinking of PE by the addition of a photoinitiator.

Radical photoinitiators used for the photocrosslinking of PE can be classified into two groups: the cleavable photoinitiators, such as aryl ketone $R_1\text{-Ph-CO-R}_2$ acting mainly through α -cleavage (Norris type I), and uncleavable photoinitiators, such as benzophenone or xanthone functioning through hydrogen abstraction or electron transfer processes. Chen *et al.*^[10] has studied 18 kinds of radical photoinitiators in the photocrosslinking of HDPE and found that the H-abstraction type photoinitiators are much more efficient than the cleavable type. We also found^[32] that complex photoinitiators consisting of these two types of photoinitiators at a suitable ratio can greatly increase the photoinitiating rate at the first stage of crosslinking of PE. However, photoinitiators alone still can not satisfy the requirements of industrial production. It is necessary to use the enhanced photoinitiation system.

Enhanced Photoinitiation System

In the enhanced photoinitiation system, at least one kind of di- or polyfunctional monomers acting as the crosslinkers is needed. The photoinitiating system of a suitable initiator combined with a multifunctional crosslinker can enhance the photocrosslinking reactions^[5, 7–10, 14, 21]. Figure 1 illustrates the enhanced crosslinking of the 4-chlorobenzophenone/triallyl cyanurate (4-CBP/TAC) system^[3]. It can be seen that TAC is very efficient in promoting the crosslinking of polymer, especially in increasing the photoinitiating rate. It can also be seen that the rate of crosslinking at the first stage for a sample (Curve a) with TAC 1% only is very low. However, TAC

does considerably increase the photoinitiating efficiency in combination with a photoinitiator (4-CBP). As shown from the dotted lines, it takes 2 min for Curve b to reach 70 % gel content, while Curve c only needs less than 15 s.

Kinetic Characteristics of Photocrosslinking

Figure 2 shows the gel formation as a function of irradiation time for samples of LDPE, LLDPE and HDPE^[21]. It is evident that no crosslinking occurred for the PE resins without the additives because no measurable gel was formed after irradiating of 160 s. But in the presence of 4-CBP and TAC (1 wt% each) there was a rapid increase in gel content with increasing irradiation time. Gel contents of about 70%, 80% and 90% were obtained within an irradiation time of 15 s for the above three samples, respectively.

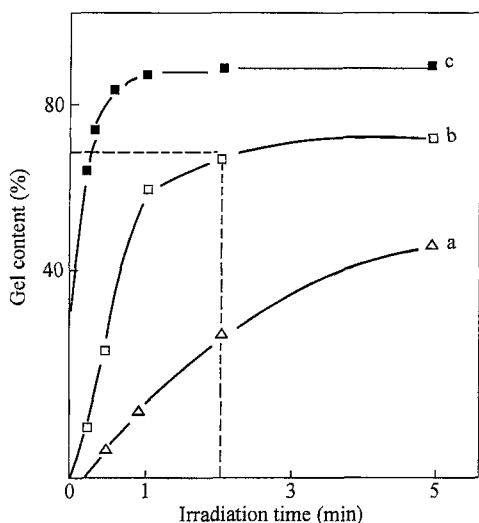


Fig. 1 Enhanced photocrosslinking of LDPE

- a) TAC 1 %
- b) 4-CBP 1 %
- c) 4-CBP 1 % + TAC 1 %

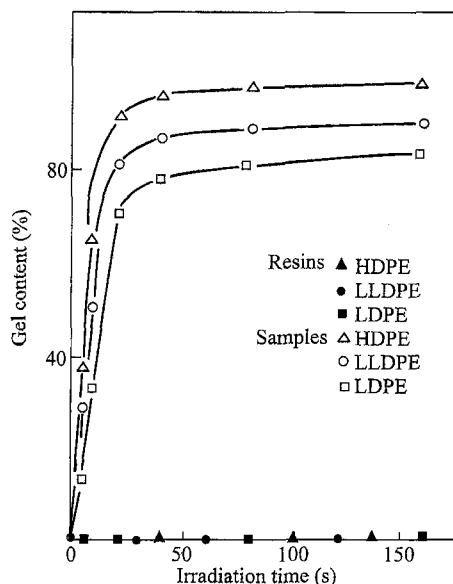


Fig. 2 Kinetics of gel formation during photocrosslinking of LDPE, LLDPE and HDPE in the melt

4-CBP: 1 wt %; TAC: 1 wt %

The kinetic characteristics of crosslinking of the three PE samples show differences in the initial rates of crosslinking which can be arranged in the following order:

$$\text{HDPE} > \text{LLDPE} > \text{LDPE}$$

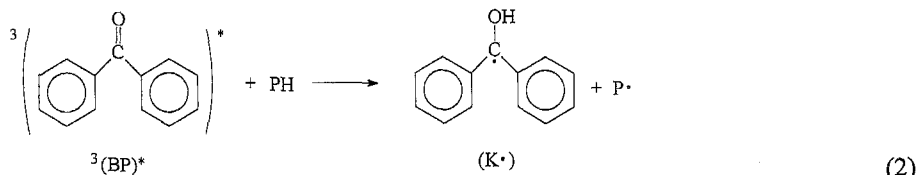
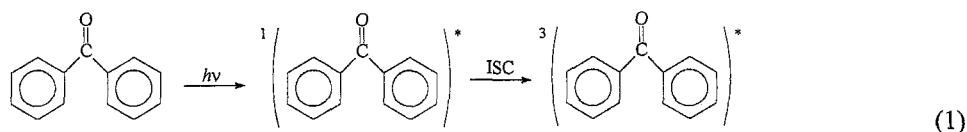
This difference is interpreted as being due mainly to the different structures of the polymers. The radicals formed by irradiation decay considerably faster in the branched LDPE than in the linear HDPE. According to the de Gennes' theory of diffusion^[35], the repetition motion of polymer chains is strongly suppressed by branching of the chains. This would explain why HDPE crosslinks at a higher rate and to a higher gel content than branched LDPE and LLDPE.

Mechanism of Enhanced Photoinitiated Crosslinking

According to the above experimental data^[9, 10, 14, 21] and literature^[36-39], the mechanism of enhanced crosslinking of TAC may be proposed as follows.

Initiation reactions

Hydrogen abstraction by excited triplet state of 4-CBP (abbreviated as BP) occurs:



where PH is the PE molecule, $\text{P}^\bullet$ represents both the alkyl and allyl radicals on the PE chain, $\text{T}^\bullet$ represents the TAC allyl radical and PT is an intermediate formed by combination of $\text{P}^\bullet$ (formula 2) and $\text{T}^\bullet$ (formula 3).

Propagation reactions

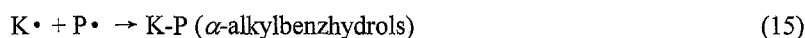
Radicals $\text{P}^\bullet$ and $\text{T}^\bullet$ react with TAC:



where $\text{PT}^\bullet$ is an allyl radical and $\text{PTn}^\bullet$ is a propagating radical.

Crosslinking and termination reactions

The macromolecule radicals in the Eq. (2) to (7) combine with each other to produce crosslinks and the termination reactions for the ketyl radical ($\text{K}^\bullet$) take place^[3, 28].



Without the participation of TAC, photocrosslinking of PE can only take place between the macromolecule radicals $\text{P}^\bullet$ (Eq. 8). It is very clear that TAC enhances the crosslinking reactions, indicating that TAC takes part in forming links between PE chains. The studies^[19, 20, 37-39] have confirmed that the allylic hydrogen of TAC is easily abstracted.

OPTIMIZING CONDITIONS FOR PHOTOCROSSLINKING

In addition to the structures of polymer chains and the concentrations of photoinitiator and crosslinker, other factors such as the physical state of polymer (irradiation temperature), light intensity, and irradiation atmosphere have important effects on the photocrosslinking processes of PE^[21].

Irradiation Temperature

The crosslinking of polyethylene in the melt is more efficient than in the solid state^[9, 10, 14, 21]. This is not surprising since photocrosslinking is a bimolecular reaction which is susceptible to the mobility of molecular

segments. The reacting groups have to meet each other during the life-time of the excited state of the active species unless the reacting groups are already at the proper distance with a favorable orientation. Irradiation temperature is crucially important for the photocrosslinking of thick PE sheets. Therefore, photocrosslinking of PE should be carried out in the melt. Figure 3 shows the effect of irradiation temperature on the gel formation of the LDPE and HDPE samples. The LDPE exhibits a gradual change in gel content when it is irradiated near its melting point ($T_m = 115^\circ\text{C}$), whereas the HDPE exhibits a abrupt change in gel content near its T_m (135°C)^[10]. This difference is interpreted as being due to the higher crystallinity of HDPE than that of LDPE. Crosslinking of PE below its melting point is assumed to take place mainly in the amorphous regions.

Light Intensity

The effect of the intensity of UV radiation on the rate of gel formation with increasing initiator concentration is shown in Fig. 4. If we select 30% as a gel content in the initial step, it needs 2% initiator concentration for the 1 kW lamp, but it only needs 0.5% initiator for the 2 kW lamp at the same irradiation time for the LDPE sample containing 0.2% antioxidant (Santoxex). This means that the photoinitiating efficiency of the 2 kW lamp is four times as powerful as that of the 1 kW lamp. Apparently, there is no severe screening effect at 2% initiator concentration, i.e., the crosslinking rate of PE is proportional to the square of the light intensity. It has been found^[9, 10, 21] that the photoinitiated crosslinking rate was proportional to the square of the light intensity for LDPE and HDPE in the same crosslinking process. The use of a high power output lamp is of practical importance in order to increase the reaction rate of crosslinking in industrial applications.

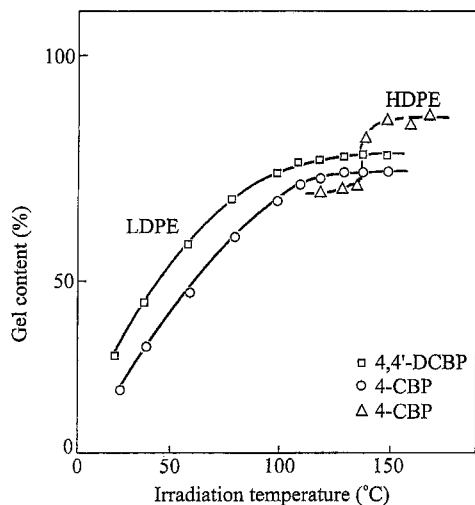


Fig. 3 Influence of irradiation temperature on crosslinking rate for LDPE and HDPE
Initiator: 1 wt%; TAC: 1 wt%

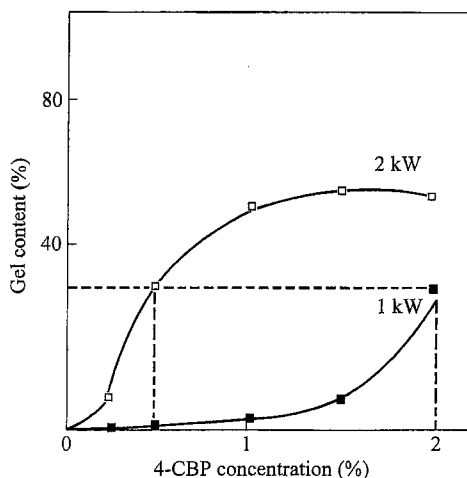


Fig. 4 Effect of light intensity on the gel formation at different initiator concentrations in LDPE
TAC: 1 wt%; Irradiation time 30 s

Irradiation Atmosphere

The effect of oxygen on photocrosslinking is an important practical problem because oxygen competes with the radical combination and the radical chain propagation process. Consequently, the stationary oxygen concentration and the diffusion rate of oxygen affect the radical reactions. When photocrosslinking is carried out in solid thick polymeric substrates, the inhibiting effect of oxygen is much less pronounced than in thin films^[5, 10, 40, 41]. There are two ways to overcome the oxygen inhibition, one is to carry out the crosslinking process under inert conditions^[21] and another is to carry out the crosslinking process in air by adjusting the crosslinking conditions^[27].

Figure 5 gives evidence that oxygen suppresses the crosslinking process. The gel content of the sample irradiated in air is decreased by about 10% and in O_2 by about 20% as compared with the sample irradiated in N_2 .

Because the solubility of oxygen in the PE sample is low, the photochemical reaction of oxygen is controlled by its diffusion rate^[42] and the effect of oxygen is mainly an oxidation at the surface^[27]. In the case of photocrosslinking of PE in bulk, thick samples and short irradiation times limit the penetration of oxygen into the inner part of the sample.

DENSITY AND HOMOGENEITY OF CROSSLINKS

The dependence of the degree of swelling (*q*), network chain density (*ν**), and the molecular weight between crosslinks (*M_c*) on the gel content of photocrosslinked LDPE networks is shown in Table 1^[22], together with the UV-irradiation time and corresponding gel content of XLPE samples. Samples with a higher gel content have a higher network chain density, a lower degree of swelling and a lower molecular weight between crosslinks *M_c*. The results of the swelling measurements in Table 1 are in line with those obtained for polyethylene crosslinked in solution^[43].

Table 1. Swelling data of LDPE photocrosslinked in the melt in xylene at 120 °C

Irrad Time (s)	Gel Content (%)	Swelling degree (<i>q</i>)	<i>ν*</i> × 10 ⁴ (mol · cm ⁻³)	<i>M_c</i> × 10 ⁻³ (g · mol ⁻¹)
5	35.1	50.2	0.40	23.0
10	55.6	25.5	0.83	11.2
20	67.7	16.9	1.31	7.02
40	75.2	12.1	1.95	4.74
80	80.2	10.6	2.26	4.07
160	82.0	9.39	2.64	3.60
360	83.5	8.43	3.02	3.04

A plot of *M_c* versus gel content for LDPE sample^[22] is shown in Fig. 6, together with the result obtained from HDPE photocrosslinked in the melt using 4-CBP as the initiator. It is interesting to note that the *M_c* values for LDPE are noticeably smaller, which means that compared with HDPE, more crosslinks are required in LDPE to obtain the same gel content. The difference might be due to the branched structure of LDPE and the higher MW of HDPE.

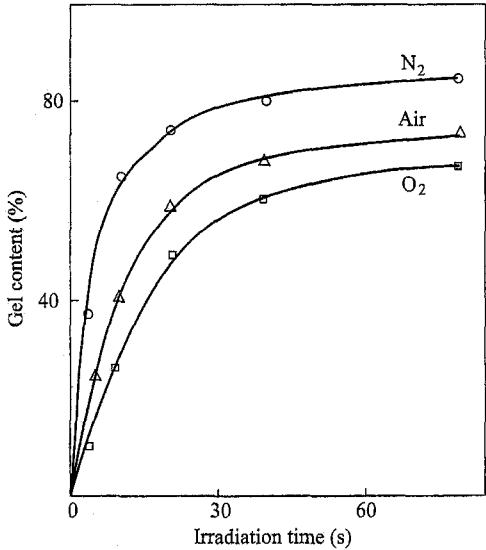


Fig. 5 Influence of irradiation atmosphere on crosslinking rate of LDPE
4-CBP: 1 wt %; TAC: 1 wt %

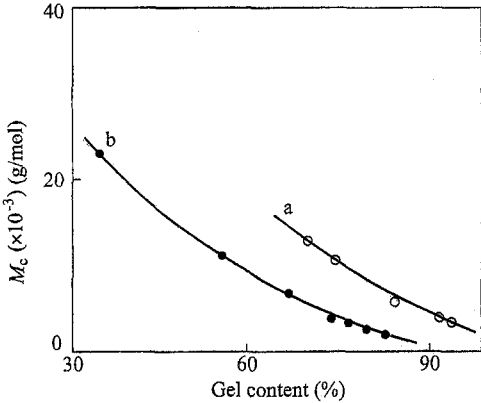


Fig. 6 The molecular weight between crosslinks, *M_c* versus gel content for HDPE (a) and LDPE (b)

In photocrosslinking of PE in bulk, the homogeneity of crosslinks is of great importance for industrial application. The homogeneity was studied by cutting a thick sample (5 mm) taken from the top surface into layers, and the gel content of every layer was then measured. The results for LDPE (curves c and d)^[5] and HDPE (curves a and b)^[11] are shown in Fig. 7. It can be seen that considerable inhomogeneity is produced if only 4-CBP is used (curves b and d) whereas the homogeneity of samples with TAC added (curves a and c) is remarkably improved. Gel contents of more than 70% are obtained within the range of 3 mm thickness. It is obvious that TAC not only plays an important role in enhanced crosslinking to increase the initiation rate, but also remarkably improves the homogeneity of crosslinks in the thick samples.

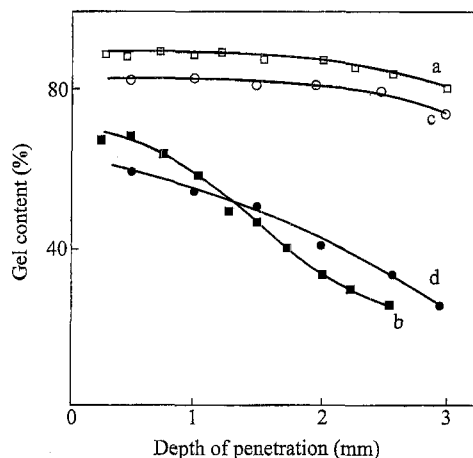


Fig. 7 Homogeneity of photocrosslinked PE
 HDPE: a) 1 % 4-CBP + 1 % TAC; b) 1 % 4-CBP
 LDPE : c) 1 % 4-CBP + 1 % TAC; d) 1 % 4-CBP

MORPHOLOGICAL STRUCTURES OF THE CRYSTAL

Before the XLPE materials are used for industrial applications, we have examined their morphological structures and related properties. Essentially, all physical properties are controlled by the molecular morphological structure of XLPE materials. The effects of chain structure changes caused by photocrosslinking on thermal behavior, crystallinity, crystal morphology, surface thermo- and photo-oxidation stability of XLPE materials have, therefore, been further studied^[11, 12, 15, 22, 23, 26, 27].

Phase Segregation

A significant result obtained from the DSC thermograms is the appearance of double melting peaks showing with increasing irradiation times at about 100°C, i.e., below the melting point of uncrosslinked LDPE, as shown in Fig. 8. The melting peak of the LDPE sample before photocrosslinking appears at 383 K, but after an irradiation time of only 5 s a new endothermal peak 2 emerges from the original melting peak 1 at the lower temperature side. With increasing irradiation time, peak 2 moves gradually toward lower temperatures and becomes broader, and its intensity increases. At the same time, the intensity and width of peak 1 decrease with increasing irradiation time, and the peak moves slowly toward higher temperatures.

The double melting peaks brought about by photocrosslinking of PE below the melting point (100°C) are interpreted as being due to the fact that the crosslinking of a semicrystalline polymer such as polyethylene preferentially occurs in the amorphous and interfacial regions, forming the crosslinked polymer as a second component. Crystallites formed when the crosslinked amorphous material is cooled from 100°C to room temperature are smaller and have a lower melting point than those which were originally in crystalline regions.

Crystallinity and Crystal Structure

The physical properties of bulk crystallized polymer, e.g., the level of crystallinity, the morphological structure of

the lamellar crystallites and the associated interfacial and amorphous regions are well interconnected. These parameters are affected by the extent of chain branching and crosslinking, and are also influenced by the rate of crystallization from the molten state.

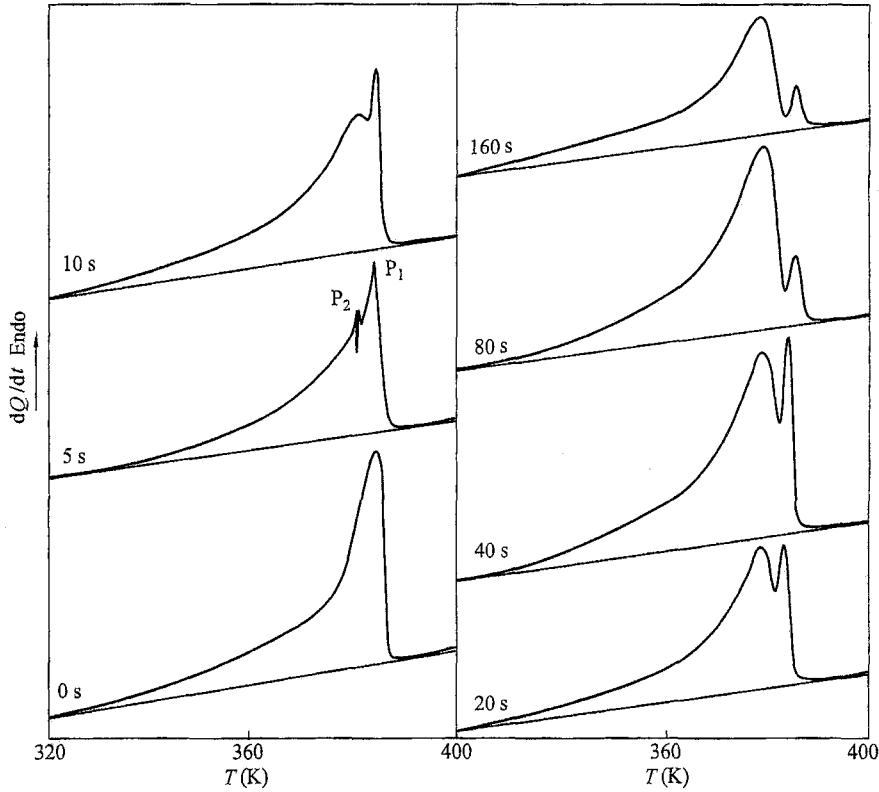


Fig. 8 DSC thermograms for LDPE photocrosslinked at 100°C with increasing irradiation times

Table 2. Variation of the degree of crystallinity with gel content

Sample type	Gel content (%)	Crystallinity (%)	
		X-ray	Density
LDPE	—	53.2	53.3
	45.1	52.6	52.7
	50.2	51.8	52.6
	53.5	51.4	52.4
	61.1	49.8	52.3
	63.9	49.5	52.2
	65.0	49.0	51.9
	71.1	45.1	51.7
	82.5	43.2	49.6
HDPE	—	77.0	76.9
	80.4	64.5	68.9
	86.2	60.0	62.6
	91.3	58.6	62.2

Wide angle X-ray diffraction (WAXD) was used to determine the crystallinity of PE photocrosslinked in the melt. The results are given in Table 2. The data in the table show to what extent the degree of crystallinity decreases with increasing gel content of XLPE. The crystallinity of LDPE drops from 53.2% before crosslinking

to 43.2% after a high degree of crosslinking (82.5%). The crystallinity of HDPE decreases from 77.0% before crosslinking to 58.6% at a gel content of 91.3%. The decrease of crystallinity with increasing degree of crosslinking is reasonable. The crosslinked polymer chains do not pack easily into a crystal lattice as uncrosslinked chains do. When polyethylene crystallizes from the melt, it produce smaller crystals because the crosslinks are excluded from crystals^[44], or act as defects within a crystal.

At low degree of crosslinking, the crystallinity data estimated from density measurements^[22, 45] are in good agreement with those given by the WAXD method. At high degree of crosslinking, however, the crystallinities given by the density method are appreciably higher than those given by the WAXD method. This difference is probably associated with the density of amorphous and interfacial regions where formation of crosslinks will increase the density and affect the crystallinity values derived. However, crosslinking of the amorphous and interfacial regions could reduce the size of the crystalline regions as indicated by the decrease in X-ray diffraction from the crystals.

Spherulitic Structures

The morphological structure of semicrystalline polyethylene is related to the spherulite formation^[46–49]. Small angle light scattering (SALS) patterns can be used to characterize the size and the degree of order of the spherulites and other morphologies formed in bulk.

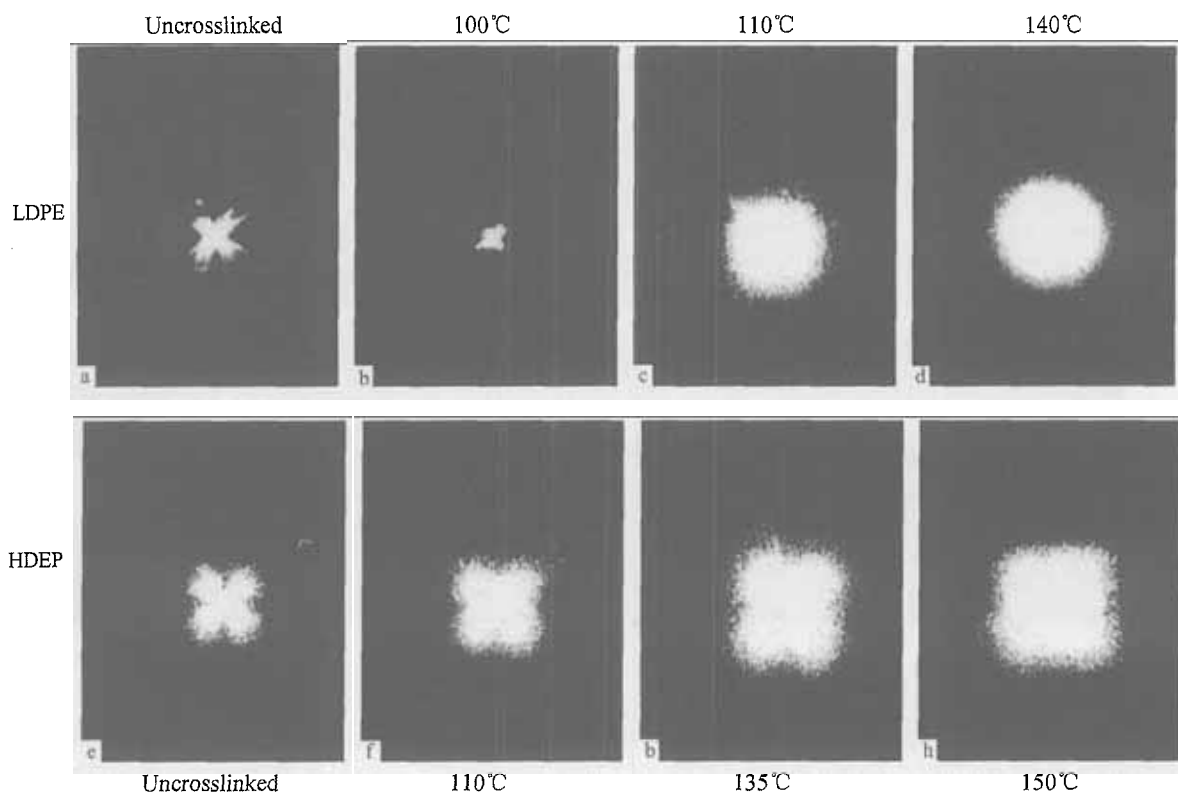


Fig. 9 The effects of irradiation temperature on the H_V SALS patterns of DFDS 6600 and HDPE samples
Irradiation time: 15 s

The H_V patterns from small angle light scattering (SALS) of DFDS 6600 and HDPE samples photocrosslinked by 15 s irradiation at different irradiation temperatures (below, at and above the melting temperature T_m) are shown in Fig. 9^[23]. The spherulite radius became smaller with increasing irradiation temperature as seen in Table 3, together with the increasing gel content and decreasing crystallinity. As can be

noted, an increase in irradiation temperature and gel content will cause a progressive deterioration of the initial spherulitic morphology characteristic of the uncrosslinked samples. This gradual deterioration of the spherulitic structure occurs with a simultaneous decrease in the level of crystallinity.

Table 3. SALS data correlated with gel content and crystallinity in Fig. 9

Samples	Irrad. temp. (°C)	$\theta_{\max}$ (Degree)	Radius (mm)	Gel (%)	Crystallinity (%)
DFDS 6600					
a		1.99	8.0		53.2
b	100	2.18	7.2	45.5	52.7
c	110			53.4	51.3
d	140			65.1	49.1
HDPE					
e		4.33	3.6		77.0
f	110	5.08	3.1	58.1	71.0
g	135	6.97	2.3	75.1	64.8
h	150	7.80	2.0	85.0	60.2

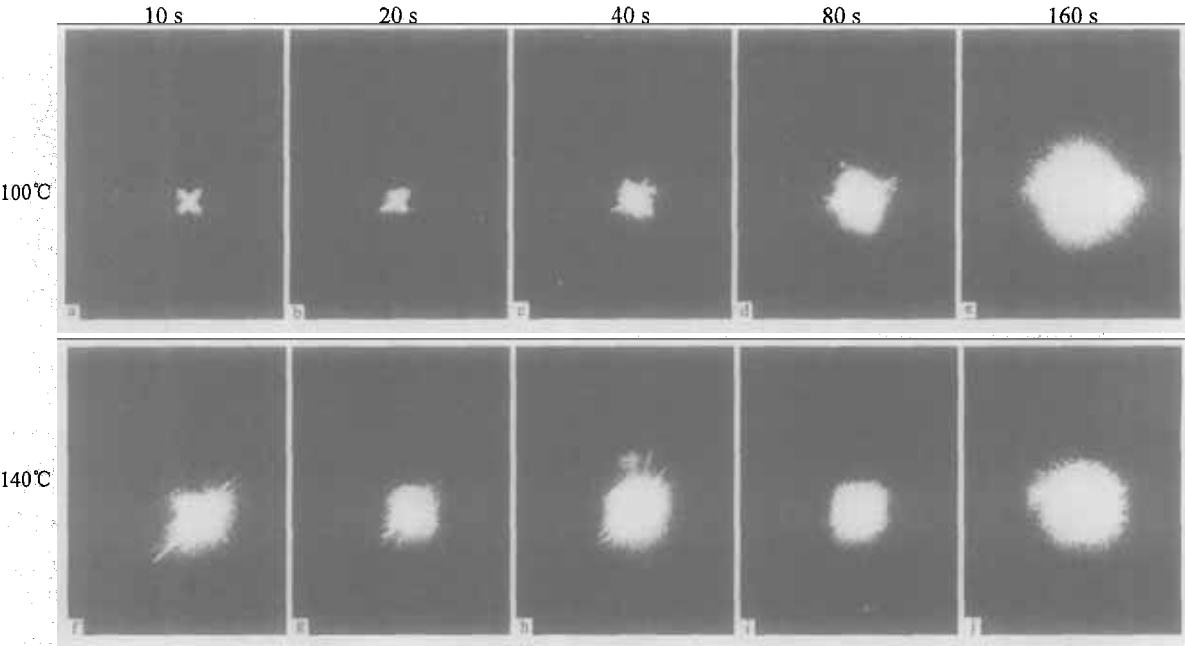


Fig. 10 The effects of irradiation time on the H_V SALS patterns of photocrosslinked DFDS 6600 samples

The effects of the degree of crosslinking on the spherulitic structures of samples crosslinked below or above the melting point are further shown in Fig. 10 for the LDPE sample. The H_V SALS patterns in Fig. 10 show the typical changes of morphology whose spherulitic structure and perfection progressively deteriorate as the degree of crosslinking increases. The upper-row H_V patterns in Fig. 10 obtained for irradiation times of 10 to 160 s at 100°C (below T_m) show a gradual deterioration from spherulitic morphology characteristic of a fourfold “X” to rod-like morphological form (“+” shaped) with increasing irradiation time, *i.e.*, rod-like aggregates of lamellar structure according to the literature^[46–49].

On the other hand, the bottom-row H_V patterns obtained from the corresponding irradiation times of 10 to 160 s at 140°C (above T_m) show dramatic changes of the morphological structure of XLPE with increasing irradiation time. The pattern (f) after only 10 s irradiation shows a nondistinct “X” type appearance (a

deteriorated spherulite type). The morphology in the crosslinked sample after 20 s irradiation has completely lost the spherulitic structure as seen in the pattern (g) similar to that in Fig. 10(c), an azimuth-dependent “+” appearance. The patterns (h) to (j) have circularly symmetric appearance due to the disordered lamellar structure^[46–49]. This can be attributed to the lower levels of crystallinity in the highly crosslinked samples (Table 4). Stein *et al.*^[46] suggested that a causal relation exists between the levels of crystallinity and the formation of spherulites for linear polyethylene. For high molecular weights and relatively low levels of crystallinity, spherulites are absent. For low molecular weights and high levels of crystallinity well-developed spherulites are observed. The patterns in Fig. 10 and the data of crystallinity in Table 4 are in good agreement with these conclusions. We can conclude that the overall effect of crosslinking on morphology is similar to that of an increase in the molecular weight of the polymer^[46–49].

Table 4. SALS data correlated with gel content and crystallinity in Fig. 10

Samples	Irrad. conditions	$\theta_{\max}$ (Degree)	Radius (mm)	Gel (%)	Crystallinity (%)
DFDS 6600	100°C				
a	10 s	2.45	6.5	34.9	53.0
b	20	2.73	5.7	48.6	52.2
c	40			63.5	49.5
d	80			72.9	45.6
e	160			79.2	44.5
DFDS 6600	140°C				
f	10 s	2.73	5.7	48.5	51.9
g	20			65.2	49.1
h	40			73.2	45.0
i	80			80.3	44.1
j	160			83.1	43.2

SOME PROPERTIES

Density and Melting Behavior

Density (ρ), melting point (T_m), and heat of fusion (H_f) are important thermodynamic parameters of polymers since they are closely related to the crystal morphological structures and physical properties such as crystallinity, permeability, mechanical strength, etc. The effects of the structure of crosslinked polyethylene on its physical properties can be seen from the changes of thermodynamic parameter^[22].

Table 5 lists the melting point (T_m), density (ρ) and heat of fusion (H_f) data obtained by DSC measurements. It can be seen that monotonic decreases are observed as the gel content increases, which agrees with results reported in the literature^[11, 50–52]. The density of LDPE drops from 0.924 g/cm³ before crosslinking to 0.920 g/cm³ after crosslinking to a gel content of 83.5%, while the melting point decreases from 383.0 K to 378.5 K. The decrease in density can be attributed to the decrease of crystallinity and the crystal lattice expansion of PE photocrosslinked in the melt. The change in heat of fusion due to photocrosslinking is quite large. H_f decreases from 26.7 to 15.5 cal/g when the gel content of crosslinked LDPE increases from 0 to about 82 %. The decrease in heat of fusion of XLPE has been reported in the literature^[50–52].

Table 5. Thermodynamic parameters of photocrosslinked LDPE

Irrad time (s)	T_m (K)	H_f (cal • g ⁻¹)	ρ (g • cm ⁻³)
0	383.0	26.7	0.9241
5	382.5	26.2	0.9236
10	381.8	25.4	0.9232
20	381.2	23.2	0.9225
40	380.5	18.2	0.9219
80	379.7	16.6	0.9210
160	378.5	15.5	0.9205

Flory^[50] assumed that the melting point depression associated with crosslinking was due to the reduction in concentration of segments of a length suitable for crystallization. On the basis of Flory's theory, Akana and Stein^[51] obtained an expression for the melting point depression of a crosslinked polymer system.

$$\frac{T_m^0 - T_m}{T_m^0 T_m} = \frac{R}{H_f} K M_0 \frac{1}{M_c}$$

where T_m^0 and T_m denote the melting temperatures of the uncrosslinked and crosslinked polymer respectively, R is the gas constant, H_f is the heat of fusion per monomer unit, K is the number of monomer units excluded from the crystals, M_0 and M_c are the molecular weight of the monomer unit and the molecular weight between crosslinks, respectively. Consequently, a plot of $(T_m^0 - T_m)/(T_m^0 T_m)$ against $1/M_c$ should give a straight line. Such a plot is given in Fig. 11. As we can see, good linearity is obtained in the case of low crosslink density, but the data points at the higher crosslink density deviate from the straight line. This can be interpreted as being due to the large decrease in the heat of fusion at increased degree of crosslinking and the lattice expansion caused by the higher crosslink density^[22].

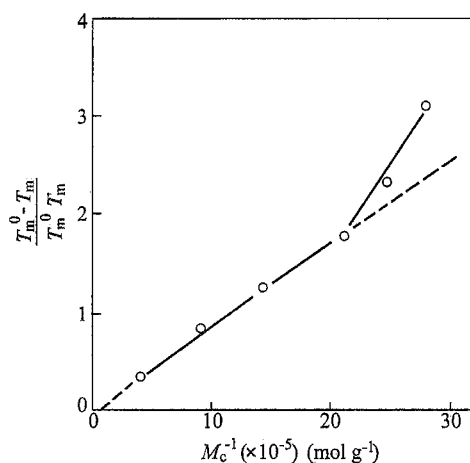


Fig. 11 Plot of $(T_m^0 - T_m)/(T_m^0 T_m)$ versus $1/M_c$ for LDPE sample according to the Flory-Rehner equation

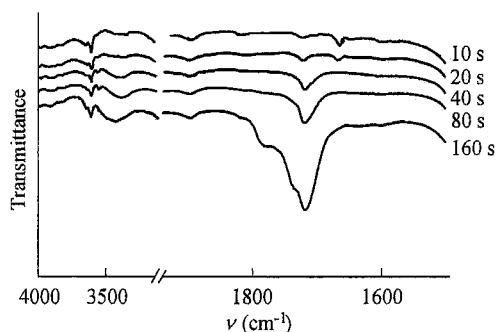


Fig. 12 FTIR spectra of the XLPE samples irradiated with a Philips HPM-15 lamp for different times

Surface Photo- and Thermo-Oxidation Stability of XLPE Materials

The surface photo-oxidation and photostabilization of photocrosslinked XLPE has been studied by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS)^[27]. The FTIR and XPS data gave evidence that the surface photo-oxidation of XLPE increases apparently with increasing UV-irradiation time. The main photo-oxidation products have been identified as hydroperoxides and various carbonyl compounds. The photostabilization of XLPE can be carried out by suitable pre-irradiation with low-pressure mercury (LPM) lamp or by the addition of hindered amine light stabilizers (HALS). The FTIR and XPS data also show that the optimum time of pre-irradiation with LPM lamp is 10 s under the conditions described in the literature^[27]. The addition of HALS to PE resin can protect the XLPE efficiently from surface photo-oxidation in the photocrosslinking process of PE.

Figure 12 shows the FTIR spectra of samples UV-irradiated with a HPM-15 lamp for different times. The main changes in the spectra appear in the 3400 cm^{-1} and 1700 cm^{-1} regions corresponding to the hydroxyl and carbonyl groups, respectively. The broad absorption band in the 3400 cm^{-1} region is ascribed to the hydrogen-bonded hydroxyl groups (alcohols, hydroperoxides and carboxylic acids). The two narrow and weak absorption peaks at 3605 cm^{-1} and 3550 cm^{-1} can be attributed to the nonhydrogen-bonded alcohols and hydroperoxides^[53], respectively. The small peak at 1666 cm^{-1} belongs to the carbonyl absorption of photoinitiator benzophenone and

its intensity decreases rapidly with increasing irradiation time. The absorption peak of the oxidation products of the 10 s sample appeared at 1722 cm^{-1} , which is mainly due to the ketone group. Its absorption intensity increased rapidly with increasing irradiation time, as shown in the 20–80 s samples of Fig. 12. At the same time, the absorption peak of the ketone group was shifted to 1716 cm^{-1} because of the overlapping of the peak (1710 cm^{-1}) from the growing carboxylic acid groups. For the 160 s sample, two new shoulder peaks at 1780 cm^{-1} and 1730 cm^{-1} appeared in the absorption region for carbonyl groups, which have been assigned to the lactone^[54] and aldehyde compounds, respectively. The 1176 cm^{-1} peak of the lactone groups was also observed from the 160 s sample. On the other hand, the appearance of unsaturated group also reflects the occurrence of photo-oxidation degradation in the XLPE samples. The increase of absorption intensities of 1645 cm^{-1} and 909 cm^{-1} peaks in the FTIR spectra indicate the formation of unsaturated vinyl groups^[55].

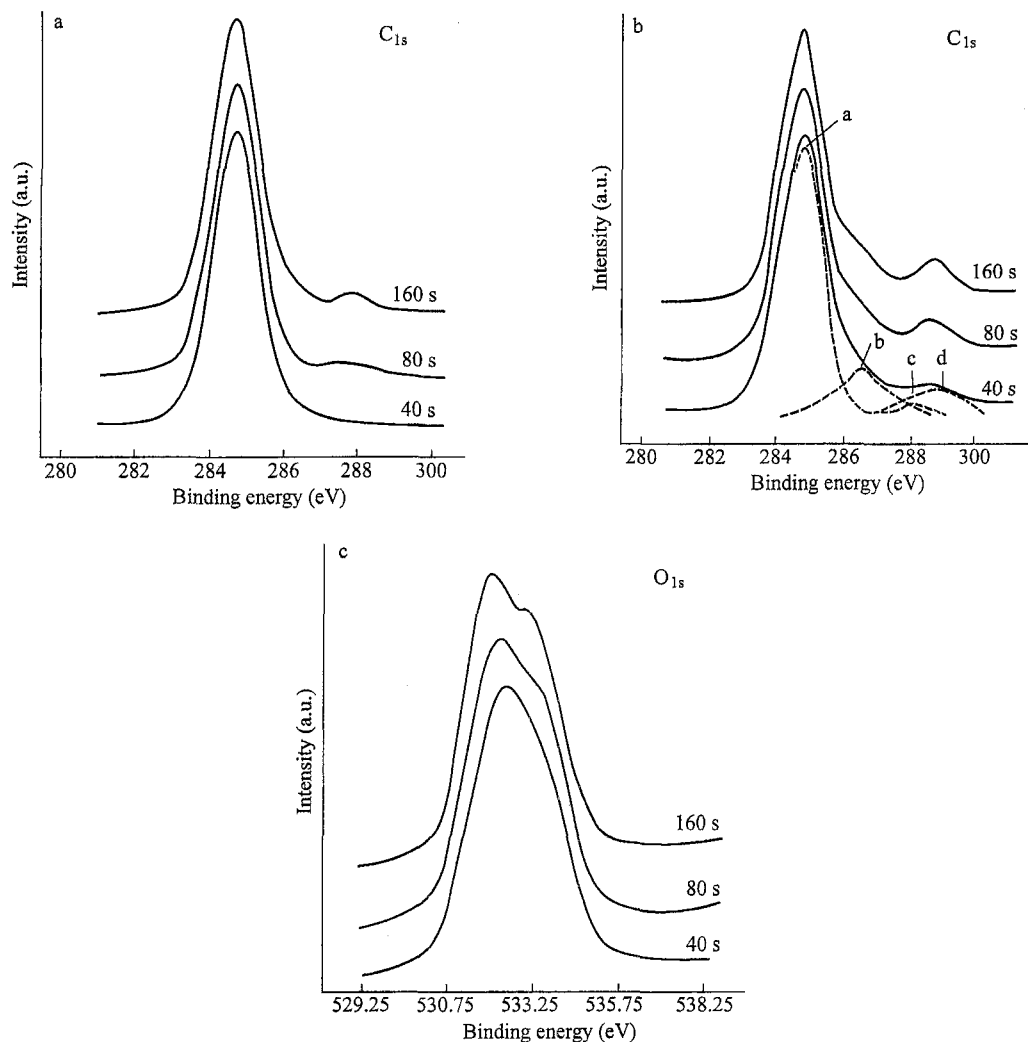


Fig. 13 (a) C_{1s} XPS spectra of the XLPE samples irradiated with a Philips HPM-15 lamp for different times; (b) and (c) C_{1s} and O_{1s} XPS spectra of the XLPE samples after the thermal aging at 135°C for 168 h, respectively

Figure 13(a) shows the C_{1s} XPS spectra of the XLPE samples UV-irradiated with a Philips HPM 15 lamp for different irradiation times. The strong peak at 285.0 eV is due to the C_{1s} electron from the C—C and C—H bonds of PE. The intensity of the small peak appearing at $286\text{--}290\text{ eV}$ in the C_{1s} band increases with increasing

irradiation time, which indicates the formation of surface photo-oxidation products, such as $-\underline{\text{C}}\text{H}_2-\text{O}-$, $-\underline{\text{C}}(=\text{O})-$, and $-\underline{\text{C}}(=\text{O})-\text{O}-$ groups.

The surface photo-oxidation occurring during the photocross-linking of PE has a significant effect on the thermo-oxidative aging property of XLPE. The XPS spectra of the XLPE samples with different irradiation times after thermal-oxidation aging for 168 h at 135°C are shown in Fig. 13(b) and (c), respectively. It can be seen from the C_{1s} peaks that the oxidation products after thermal aging increase apparently with increasing UV-irradiation time. The oxidation products b, c and d marked by broken lines obtained by computer separating peaks of C_{1s} bands appear at 286.5 eV, 288.0 eV, and 289.0 eV, which have been assigned to the $-\underline{\text{C}}\text{H}_2-\text{O}-$, $-\underline{\text{C}}(=\text{O})-$, and $-\underline{\text{C}}(=\text{O})-\text{O}-$ groups, respectively. From the O_{1s} peaks it also show that the oxidation products increase quickly with the irradiation time of XLPE samples. The O_{1s} peak of the $-\underline{\text{C}}(=\text{O})-$ and $-\underline{\text{C}}\text{H}_2-\text{O}-$ groups for 40 s sample mainly appeared at 532.5 eV. The O_{1s} shoulder peaks of the $-\underline{\text{C}}(=\text{O})-\text{O}-$ groups appeared at 534.2 eV for the 80 s and 160 s samples.

The surface photostabilization of XLPE materials can be carried out by the addition of hindered amine light stabilizers (HALS) or the suitable pre-irradiation deoxidation of the low-pressure mercury lamp, as described in the literature^[27].

Properties of Photocrosslinked XLPE Materials

The properties of photocrosslinked XLPE material applied as high voltage insulation are summarized in Table 6^[24]. The results demonstrate that the photocrosslinked XLPE materials not only possess excellent electrical properties, such as volume resistivity, discharge breakdown and dielectric properties, but also have excellent mechanical properties, measured as tensile, elongation, heat aging and brittleness at low temperature. The heat aging test was carried out at 150°C. All these properties meet the requirements of XLPE insulation materials for both low voltage and high voltage (35 kV) power cables.

Table 6. Properties of photocrosslinked XLPE materials ^a

Items of test	Results
(1) Mechanical properties	
Original tensile strength (Mpa)	22.4
Original elongation at break (%)	550
(2) Heat aging test, 150°C × 7 days	
Tensile strength (T. S.) (Mpa)	24.2
Retention of T. S. (%)	108
Elongation (EL) at break (%)	490
Retention of EL (%)	90
(3) Heat Extension Test, 200°C × 15 min	
Extension under load test (%)	32.5
Permanent extension (%)	0
(4) Gel content (%)	82
(5) Low temperature test, -76°C	Pass
(6) Volume resistivity, Ω·cm	
20°C	2.4×10^{16}
90°C	3.0×10^{16}
(7) Discharge breakdown (kV/mm)	41.6
(8) Dielectric dissipation angle, $\tan\delta$	3.26×10^4
(9) Dielectric constant, ϵ	2.2

^a The results were reported by Shanghai Institute of Cables, the Ministry of Mechanics and Electronics Industry of China.

PROSPECTS OF INDUSTRIAL APPLICATIONS

A photocrosslinking process for polyethylene and its industrial irradiation apparatus have been developed recently and applied successfully for the manufacture of thin wall crosslinked high voltage television (TV) XLPE wires^[24, 31] and power cables^[32, 33]. Polyethylene resin with the desired amounts of additives, such as

photoinitiator, multifunctional crosslinker, antioxidant etc., is mixed homogeneously. The resulting PE is granulated and then extruded on a conductive wire. The coated PE layer in the melt is subsequently irradiated in a specially designed UV irradiation apparatus for 5~10 s. The studies show that the photocrosslinked XLPE-insulated high voltage wires produced by this new technique possess excellent electrical and mechanical properties and much lower production costs compared with the electron beam crosslinking technique.

UV Irradiation Apparatus and Industrial Production Line

We have developed different kinds of photocrosslinked XLPE-insulated power cables^[32, 33] and high voltage TV wires^[24, 31] of 20, 30, 40, and 50 kV DC ratings at 105°C. A block diagram of the industrial production line of photocrosslinked XLPE-wires and cables is shown in Fig. 14. The TV wires are used as the examples to illustrate the photocrosslinking process applied for the manufacture of thin wall crosslinked PE-insulated wires. The photocrosslinking processes of TV high voltage wires with polyvinyl chloride (PVC) jacket were as follows:

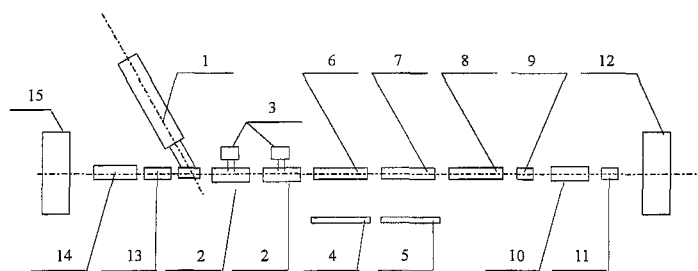


Fig. 14 Block diagram of production line for photocrosslinked XLPE wires and cables
1) Extruder; 2) UV irradiation unit; 3) exhaust fan; 4) cabinet of electric controller; 5) cabinet of electrical system; 6) hot water tank; 7) warm water tank; 8) cool water tank
9) length counter; 10) down-drawing; 11) test machine of breakdown; 12) take up; 13) preheater; 14) up-drawing; 15) pay-off

Mixing and granulating

PE resin with the desired additives, such as BP, TAC, different stabilizers etc., is mixed homogeneously for 10 min in a molten condition using a plasticator. The compound is granulated to a size of about 15 mm³.

Extruding PE compound on wires

The compound granules are coated on conductive wires at the suitable temperature by extrusion to form the insulation layers. The conductor is composed of $7 \times \phi 0.26$ mm twisted tinned copper wires. There are four kinds of specifications according to the coated PE wall thickness: (1) 0.5 mm; (2) 0.6 mm; (3) 0.7 mm; (4) 1.0 mm.

Photocrosslinking process

The above layers coated on the wires are subsequently crosslinked by UV irradiation in a specially designed apparatus (see the following section). The high pressure mercury UV lamps used in this study of the type GGZ 6000 with the characteristic main wavelength range of 300~400 nm and power density of 85 W/cm. The pulling speed of the wire usually is controlled at about 50 meters per minute dependent on the lamp power density and irradiation time needed. The irradiation temperature around the wire is controlled in the range of 110~150°C by regulating the cooling air flow passed through the UV irradiation apparatus.

XLPE-insulation baseline coated with a PVC jacket

According to the usual process for coating a jacket, the above photocrosslinked XLPE insulated wires are coated by the flame-retardant PVC jacket materials. The PVC thickness is (1) 0.6 mm, (2) 0.7 mm, (3) 0.95 mm, (4) 1.1 mm corresponding to the SJ 2933-88 standards, respectively. Thus, four different types of flame resistant TV high voltage wires are produced.

Properties of the XLPE-Insulated TV Wire Products

The properties of the XLPE-insulation coated on the 40 kV DC TV high voltage wires without PVC jacket are listed in Table 7. The data show that photocrosslinked XLPE-insulation has excellent heat-resistant, mechanical and electrical properties, which completely meet the requirements specified in the SJ 2999-88 standards. Some properties of the TV wires with PVC jackets, such as breakdown voltage in water and insulation resistance, are presented in Table 7.

Table 7. Properties of photocrosslinked XLPE insulation of TV wire without PVC jacket ^a

Items of Test	Results
(1) Mechanical properties	
Original tensile strength (Mpa)	19.0
Original elongation at break (%)	610
(2) Heat aging test, 150 °C × 7 days	
Tensile strength (T. S.) (Mpa)	18.9
Retention of T. S. (%)	99.5
Elongation (EL) at break (%)	600
Retention of EL (%)	98.4
(3) Chap-resistant test, 136 °C × 1 h	No chap
(4) Heat deformation, 136 °C × 1 h	32.5
Variation in thickness (%)	19
(5) Heat extension test, 200 °C × 15 min	
Extension under load test (%)	55
Permanent extension (%)	0
(6) Low temperature mandrel test, -20 °C	No chap
(7) Breakdown voltage test	
50 Hz, 15 000 V × 1 min	No breakdown

Note: The outer diameter of high voltage TV wire sample is 3.79 mm and the average thickness of insulation layer of XLPE is 0.82 mm.

^a The results were reported by Shanghai Institute of Cables, the Ministry of Mechanics and Electronics Industry of China.

Unique Advantages of Photocrosslinking Technology

In comparison with the electron beam (EB) irradiation and the chemical crosslinking processes, the photocrosslinking technology in the manufacture of thin wall crosslinked PE insulation wires and low voltage power cable has some unique advantages: (1) much lower primary investment cost about 1/20~1/10 of that of EB and chemical processes; (2) simple control conditions, easy operation and maintenance; (3) occupied smaller space by the apparatus, which is easy to incorporate into the normal production line for wire and cable; (4) lower operating costs for excellent electrical and mechanical properties of XLPE wire and products. According to the detailed cost accounting, the estimated operating costs of 40 kV DC high voltage TV wire and 1 kV low voltage power cables produced by photocrosslinking technique were as low as 35%~50% of those produced by the EB accelerator or chemical crosslinking methods.

A simplified flow diagram of the photocrosslinking process compared with the electron beam (EB) and the chemical processes is shown in Fig. 15^[24]. In the chemical process, the steps of extrusion and heating in the CV tube are continuous. The throughput speed in the extruding step is therefore controlled by the relatively lower speed in the heating step, thereby reducing the operating efficiency of the entire process. What is more, the chemical process causes a marked increase in the loss due to start-up time and in the waste when the wire to be produced is changed from one type to another. In contrast, the EB irradiation process is possible to separate the extruding and irradiation crosslinking steps from each other and these two steps can therefore be controlled for the most efficient operation. However, the two-step operation also requires additional time and costs for transportation and storage space, etc. In the photocrosslinking process, the steps of extrusion and UV crosslinking are continuous and on line and the UV-irradiation time required is only a few seconds. The

irradiation time can be further decreased if the numbers of UV lamps increase. Moreover, the UV-process does not cause increase in loss and waste materials due to start-up time when the wire to be produced is changed from one type to another.

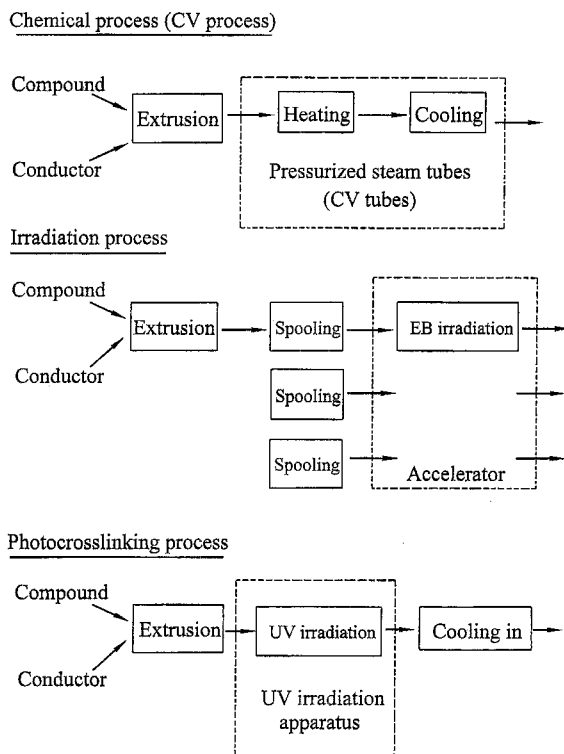


Fig. 15 Comparison of photocrosslinking process with EB and chemical processes

Future Development and Applications

General advantages of photocrosslinking method

Compared with the tradition crosslinking methods, photocrosslinking has the following general advantages: (1) rapid crosslinking in a one-step process forms the basis for on-line production units; (2) crosslinking can be carried out at room temperature for thin coatings and for thicker samples in the melt; (3) without environmental pollution problems because the use of organic solvents can often be avoided; (4) inexpensive and simple equipment, readily available UV light sources, and easy operation and maintenance; (5) low energy consumption.

Some limitations of photocrosslinking

However, photocrosslinking method itself has some limitations, for instance: (1) limited thickness (about 3 mm) of the layers which can be photocrosslinked at one time; (2) problems with pigmented layers which scatter and absorb light; and (3) oxygen inhibition or rate decrease may occur with radical initiating systems.

Future development and applications

The crosslinking of wire and cable insulation has been applied on a large industrial scale all over the world. The XLPE-insulated materials used for wires and cables have been rapidly growing in recent years, especially for small diameters and thin insulations of less than 3 mm used for low voltage applications, such as in household electrical appliances, communication devices, parts in automobile and aerospace, and power cables to replace PVC power cables. Although the thickness of photocrosslinked XLPE sheet is limited to 3 mm with one time UV-irradiation, the photocrosslinking technique has full scope in the manufacture of thin wall crosslinked XLPE-insulation wires.

A part from electrical insulation of wires and cables at elevated temperatures, the photocrosslinked XLPE materials can be also used for hot water piping, heat-shrinkable tubing, film, and foam because they have excellent performance-to-cost ratios, as described above.

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