Thermal and Mechanical Properties of Silane- Grafted Water Crosslinked Polyethylene

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ABSTRACT: The effects of linear low density polyethylene (LLDPE) grafting with vinyltrimethoxysilane by different types and contents of peroxide were studied. When grafting silane onto LLDPE, with 0.10 phr of Dicumyl peroxide (DCP) or 0.05 phr content of 2,5-Dimethyl-2,5-di (tert-butyl-peroxy)-hexane (DHBP), it was found that the grafting effect was improved; however, as Di(2-tert-butylperoxypropyl -(2))-benzene (DIPP) or excess DHBP was used, LLDPE was supposed to cause self-crosslinking, which reduced the grafting effect of silane and was invalid in the processing of extrusion. In this study, vinyl trimethoxysilane (VTMS) was grafted onto various polyethylenes (HDPE, LLDPE, and LDPE) using DCP as an initiator in a twin screw extruder. The grafted polyethylenes were able to crosslink utilizing water as the crosslinking agent. The effects of varied crosslinking time on the mechanical properties of the crosslinked polyethylenes were studied. It was found that the HDPE and LLDPE were apt to crosslink during the grafting process and thus decreased the grafting ratio. Multiple melting behavior was observed for crosslinked LDPE and LLDPE. Mechanical and thermal properties of the crosslinked PE are much better than that of uncrosslinked PE. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2383–2391, 2005

Key words: water-crosslinking; peroxide; polyethylene; mechanical property

INTRODUCTION

Scott et al first proposed water crosslinking of PE in 1972.[1] The advantages of this process are energy saving, low cost, and higher productivity. Crosslinked polyethylene possesses better physical properties than general polyethylene, and also has become widely adapted for a number of industrial applications. Currently, there are three main approaches to crosslink polyethylene: (1) using high-energy radiation (gamma or UV) or electrons, (2) utilizing a thermochemical method (e.g., heating in the presence of peroxides), and (3) using water to crosslink certain polyethylene that has been "grafted" with reactive groups.[2–4]

Crosslinked PE is superior to uncrosslinked PE in many aspects, such as excellent electrical properties, good abrasion resistance, and improved heat performance and chemical resistance. It is widely used in the applications of primary wire and cable insulation, tubes and pipes, and cable jackets. There are three methods for preparing crosslinked PE industrially: crosslinking with radiation, crosslinking with peroxide, and crosslinking with water.[5–8] Crosslinking with radiation is only suitable for thin wall parts and is limited by its high-energy cost and safety. Peroxide induced crosslinking has to be operated at high vacuum, and it is difficult to control the thickness of the products. Crosslinking with water is achieved by grafting with silane, followed by hydrolysis to Si-OHgroups and subsequently condensation to form Si-O-Si bonds.[9–15] The mechanism is believed to be as follows[8,16]:

$$ (1) $$

$$ (2) $$

$$ CH_3\cdot \; + \; \text{wwwC-H} \longrightarrow \text{wwwC}\cdot \; + \; CH_4 \qquad (3) $$

$$ (4) $$

$$ (5) $$

$$ (6) $$
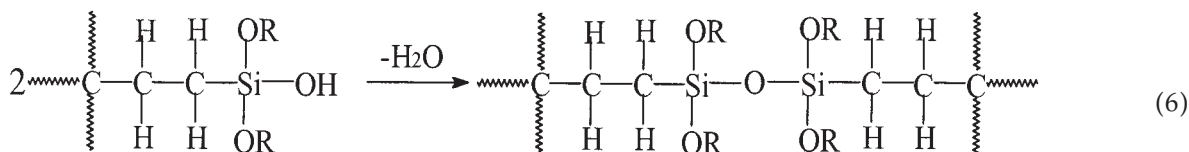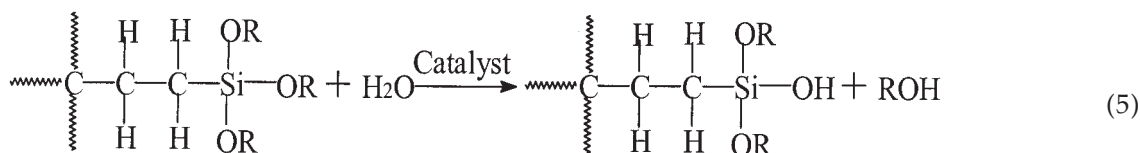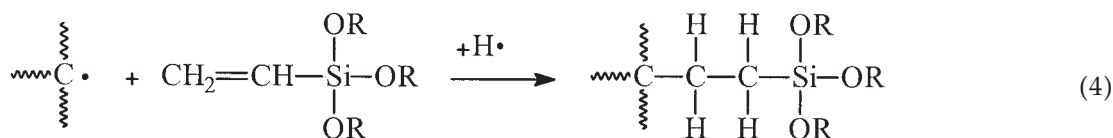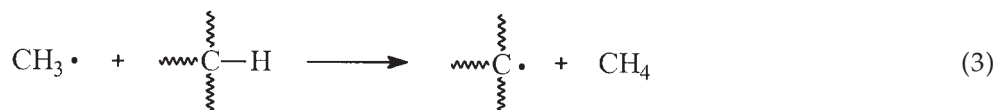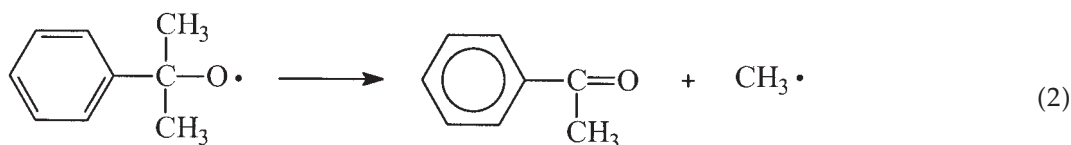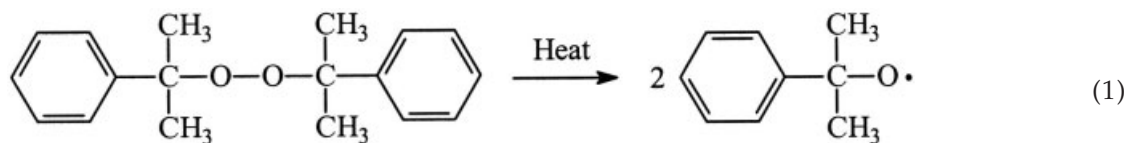
The grafting of vinyltrimethoxysilane onto the polyethylene polymer chain is becoming more popular due to the low investment cost and high production rate of such a process. This process is through free radical initiators and can subsequently condense through water, leading to the formation of crosslinking.

The first part of the present work is to investigate the effects of silane grafting onto LLDPE. Three types of peroxide (DCP, DHBP, and DIPP) and various peroxide contents are added. In these systems, the self-crosslinking reaction competed with the water-crosslinking reaction. In the second part, vinyl trimethoxysilane (VTMS) was grafted onto various polyethylenes (HDPE, LLDPE, and LDPE), and the effects of varied crosslinking time on the mechanical properties of the crosslinked polyethylene are discussed.

EXPERIMENTAL

Material

The materials used were:

1. (a) Linear Low Density Polyethylene (LLDPE): No. LL120 with a melt index of 2.0, produced by Taiwan Polymer Corporation, Taiwan. (b) High density polyethylene (HDPE) : No. LH901, with a melt index of 0.95, and (c) Low density polyethylene (LDPE) : No. F2201 with a melt index of 2.0, were purchased from Asia Polymer Corporation.
2. Vinyltrimethoxysilane (VTMS), No. Q9-6300, was supplied by Dow Corning Co., USA.
3. Dicumyl Peroxide (DCP), No. PEROXIMON DC, was produced by ELF ATOCHOEM, France.
4. 2,5-Dimethyl-2,5-di(tert-butyl-peroxy)-hexane (DHBP), No. LUPEROX 101, was produced by ELF ATOCHOEM, France.
5. Di(2-tert-butylperoxypropyl-(2))-benzene (DIPP), No. PEROXIMON F40, was produced by ELF ATOCHOEM, France.
6. Di-n-butyltin dilaurate (DBTDL), No. T12, was supplied by AIR PRODUCTS, USA.

TABLE I
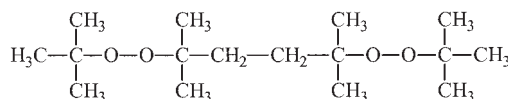**Recipes for Sample Preparation in This Study**

Sample code	LLDPE (parts)	Peroxide type*			Silane (phr)
		DCP (phr)	DHBP (phr)	DIPP (phr)	
A	100	0.05	—	—	—
B	100	—	0.05	—	—
C	100	—	—	0.05	—
D	100	0.1	—	—	—
E	100	—	0.1	—	—
E	100	—	0.1	—	—
G	100	0.05	—	—	1.50
H	100	—	0.05	—	1.50
I	100	—	—	0.05	1.50
J	100	0.1	—	—	1.50
K	100	—	0.1	—	1.50
L	100	—	—	0.1	1.50

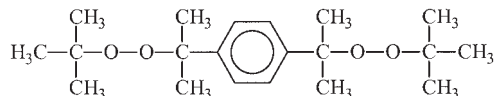* Chemical Structure of Peroxides:

1. Dicumyl Peroxide (DCP)
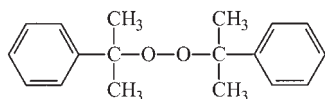
2. 2,5-Dimethyl-2,5-di(tert-butyl-peroxy)-hexane(DHBP)

3. Di(2-tert-butylperoxypropyl-(2))-benzene(DIPP)

7. Anti-oxidant agent, No. 1010, was produced by Ciba Geigy Corp., Switzerland.

Sample preparation

Sample preparation was conducted according to the recipes listed in Table I (three types of peroxide and various peroxide contents). Samples were compounded by single screw extruders. Processing temperatures were selected from 140°C to 160°C (samples A–F). The silane grafting reaction was performed at a fixed silane content (1.50 phr part per hundred parts of resin) and the grafted master batches were prepared (samples G–L). The master batches with catalyst were prepared from LLDPE and DBTDL catalysts and anti-oxidant agents (for the samples with silane treatment, and the content is 5 phr). All testing specimens were injection molded following the ASTM method. The specimens with silane treatment were placed in an isothermal water bath at 85°C for 4 h to proceed to the water-crosslinking reaction.

Various PE pellets (HDPE, LDPE, and LDPE) were premixed with silane and DCP and then fed to a twin screw extruder with barrel temperature ranging from 110 to 180°C. The amounts of DCP and silane were 0.1 phr and 1 phr, respectively. The compounded pellets were injection molded to standard testing specimens. Some of the specimens were subsequently subjected to water-crosslinking with different crosslinking time.

Properties tests

Processability measurement was tested using a rheometer (PLASTI-CORDER PL 2000, Brabender Co.) to observe the chemical reaction and process ability of the polymer melt, and the rotor speed was 50rpm. The mechanical properties of dumbbell shaped specimens were measured on an Instron Model 4468 machine. Tensile test procedures followed the ASTM D638-82 method with a crosshead speed of 20 mm/min. The dimensions of the samples were 25.0 × 10.0 × 1.4 mm (length × width × thickness). Six specimens were tested in each case. Flexural tests followed the ASTM D790 method with a span-to-depth ratio of 40 and crosshead speed of 1.0 mm/min. Notched impact strength was tested according to ASTM D256, and a TMI Testing Machine (TMI Co. U.S.A.) was used (the dimensions of these samples were 63.0 × 12.7 × 3.2 mm (length × width × thickness)). All tests were performed at ambient temperature of 25 ± 2°C. The differential scanning calorimeter (DSC) analysis of the samples was carried out under aN_2 atmosphere with a Perkin–Elmer DSC Pyris 1. These amorphous samples were then heated again to 100°C at a heating rate of 10°C/min. Heat deflection temperature (HDT) was measured by a TOYOSEIKI S-6M HDT tester, and followed the ASTM D648 method. The loading pressure was 4.6 kgf/cm^2, and the heating rate was 120°C/h.

RESULTS AND DISCUSSION

Effects of peroxide concentration on moisture-crosslinking of LLDPE

Figure 1a shows that with LLDPE with 0.05 phr DCP and with silane (curves A–G), the torque value approaches that of pristine LLDPE, it represents that the effect of self-crosslinking and silane grafting on LLDPE is insignificant. However, when 0.1 phr DCP is added (curve D), the torque value increased slightly. If the silane content increases, torque value increased obviously (curve J), showing that free radicals are released by
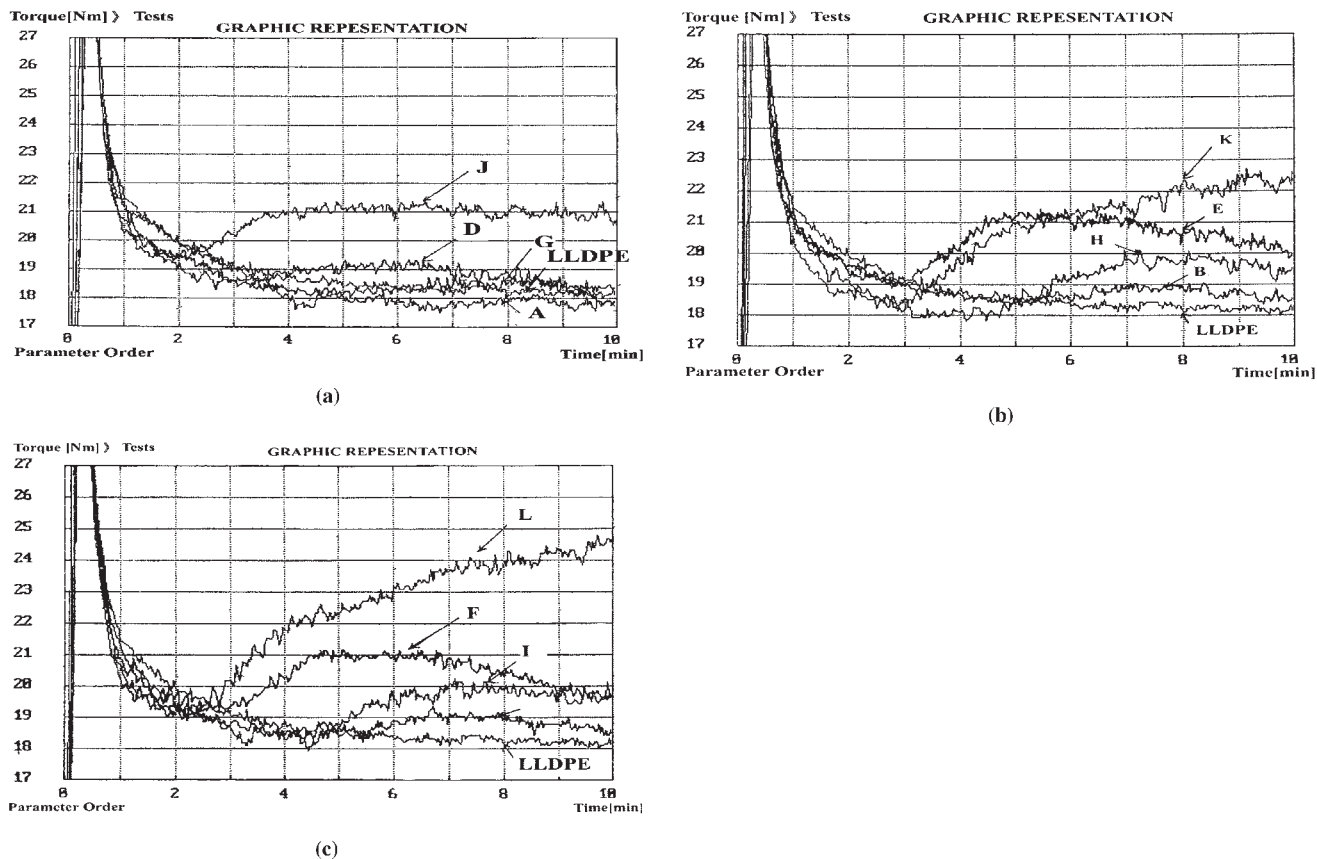
(a)

(b)

(c)

Figure 1 The Brabender Plot (the relationships between Torque Value and Reaction Time, t) of silane-grafted water-crosslinked LLDPE with (a) different DCP contents, (b) different DHBP contents, and (c) different DIPP contents.

peroxide and induce the slight self-crosslinking. Consequently, silane grafting reacts with LLDPE.

The peroxide used in Figure 1b is DHBP. When 0.05 phr DHBP is added into LLDPE, the torque value increases slightly (curve B), and it increases more if silane is added (curve H), indicating that 0.05 phr DHBP content can induce slight self-crosslinking and silane was grafted to LLDPE. When 0.10 phr DHBP is

TABLE II
Tensile Strength of Silane-Grafted Water-Crosslinked LLDPE When Three Types and Various Contents Peroxides Are Added

Sample codes	Peroxide content (phr)	Silane content (phr)	Tensile strength (Kgf/cm^2)	Tensile strength after water-crosslinking 4hr(Kgf/cm^2)	Increased percentage after water-crosslinking (%)
LLDPE	—	—	148.4	—	—
A	DCP 0.05	—	161.8	—	—
G	DCP 0.05	1.5	160.4	166.8	4.0
B	DHBP 0.05	—	164.0	—	—
H	DHBP 0.05	1.5	180.8	198.5	9.8
C	DIPP 0.05	—	162.0	—	—
I	DIPP 0.05	1.5	168.3	173.8	3.3
D	DCP 1.0	—	166.0	—	—
J	DCP 1.0	1.5	164.1	193.2	17.7
E	DHBP1.0	—	170.4	—	—
K	DHBP 1.0	1.5	198.0	204.8	3.4
F	DIPP1.0	—	183.0	—	—
L	DIPP 1.0	1.5	189.7	192.6	1.5

TABLE III
Tensile Elongation of Silane-Grafted Water- Crosslinked LLDPE When Three Types and Various Contents Peroxides Are Added

Sample codes	Peroxide content (phr)	Silane content (phr)	Elongation (%)	Elongation after water-crosslinking 4hr(%)	Increased percentage after water-crosslinking (%)
LLDPE	—	—	448.8	—	—
A	DCP 0.05	—	407.9	—	—
G	DCP 0.05	1.5	108.3	107.3	−0.9
B	DHBP 0.05	—	262.3	—	—
H	DHBP 0.05	1.5	82.9	74.5	−10.1
C	DIPP 0.05	—	367.5	—	—
I	DIPP 0.05	1.5	106.3	101.5	−4.5
D	DCP1.0	—	122.9	—	—
J	DCP1.0	1.5	105.5	63.0	−40.2
E	DHBP1.0	—	109.5	—	—
K	DHBP1.0	1.5	79.2	74.9	−5.4
F	DIPP1.0	—	106.7	—	—
L	DIPP1.0	1.5	88.1	86.6	−5.1

TABLE IV
Flexural Strength of Silane-Grafted Water-Crosslinked LLDPE When Three Types and Various Contents Peroxides Are Added

Sample code	Peroxide content (phr)	Silane content (phr)	Flexural strength (Kgf/cm^2)	Flexural strength after water-crosslinking 4hr (Kgf/cm^2)	Increased percentage after water-crosslinking (%)
LLDPE	—	—	109.7	—	—
A	DCP 0.05	—	111.5	—	—
G	DCP 0.05	1.5	118.7	125.9	6.1
B	DHBP 0.05	—	112.8	—	—
H	DHBP 0.05	1.5	119.9	131.8	9.9
C	DIPP 0.05	—	110.5	—	—
I	DIPP 0.05	1.5	121.4	126.5	4.2
D	DCP1.0	—	115.9	—	—
J	DCP 1.0	1.5	120.5	135.3	10.9
E	DHBP 1.0	—	121.8	—	—
K	DHBP 1.0	1.5	130.3	134.7	3.4
F	DIPP1.0	—	121.9	—	—
L	DIPP 1.0	1.5	130.4	132.2	1.4

TABLE V
Impact Strength of Silane-Grafted Water-Crosslinked LLDPE When Three Types and Various Contents Peroxides Are Added

Sample code	Peroxide content (phr)	Silane content (phr)	Impact strength (J/M)	Impact strength after water-crosslinking 4hr(J/M)	Increased percentage after water-crosslinking (%)
LLDPE	—	—	433.3	—	—
A	DCP 0.05	—	447.1	—	—
G	DCP 0.05	1.5	453.2	484.0	6.8
B	DHBP 0.05	—	456.7	—	—
H	DHBP 0.05	1.5	463.5	533.0	15.0
C	DIPP 0.05	—	446.4	—	—
I	DIPP 0.05	1.5	472.7	507.2	7.3
D	DCP 1.0	—	454.3	—	—
J	DCP1.0	1.5	461.5	541.5	17.3
E	DHBP 1.0	—	481.8	—	—
K	DHBP 1.0	1.5	490.6	523.0	6.6
F	DIPP 1.0	—	482.9	—	—
L	DIPP1.0	1.5	503.3	522.5	3.8

TABLE VI
The Characteristics of Pure HDPE and Silane-Grafted Water Crosslinked With Varying Crosslinking Time

Time of exposure Test item	HDPE	HDPE-g-VTMS				
		0 hr	0.5 hr	1 hr	3 hr	6 hr
Tensile strength (Kgf/cm^2)	247.9	326.3	344.4	346.1	346.3	348.0
Elongation (%)	239.7	48.4	46.9	39.2	35.9	35.1
Flexural strength (Kgf/cm^2)	310.2	357.1	382.0	382.7	391.0	391.7
Flexural modulus (Kgf/cm^2)	9240	9512	10170	10613	10893	10975
Notched Izod impact strength (J/M)	783.2	404.8	388.3	371.5	364.3	310.8
HDT (°C)	78.1	84.1	96.1	97.3	100.7	101.2

added, the torque value is higher than that of pristine LLDPE (curve E). The self-crosslinking reaction of LL-DPE occurs significantly when 0.10 phr DHBP is added, and the processability was deducted. When silane is added, the torque value increases even higher (curve K). The effects of the DIPP series of peroxide on processability are shown in Figure 1c. These results are similar to that of DHBP peroxide. When 0.10 phr DIPP is added to the system (curve L), the torque value is higher than that of DHBP peroxide (curve K), indicating that the silane grafting effect of DIPP peroxide on LLDPE is higher than that of DHBP peroxide; however, its processability becomes worse.

From the changes of mechanical properties, one may realize the effect of peroxide on the self-crosslinking reaction of LLDPE and the effective degree of silane grafting. From Table II, one can find the tensile strength of neat LLDPE is 148.8 kgf/cm^2. Tensile strength increases as peroxides and silane are added, especially when DHBP and DIPP peroxide content are more than 0.1 phr (samples E, K, F, and L). But the tensile strength only increases 3.4% after water-crosslinking for 4 h. From these results, one can find that the torque values of curves K and L in a Bra-bender plot are increased (Figs. 1a and b), which is caused by the self-crosslinking reaction of LLDPE, not from the silane grafting reaction. The effective degree of grafting in the same time was reduced.

From Table III, the tensile elongation of LLDPE is 448%. When three types of 0.05 phr peroxides are added (samples A, B, and C), the tensile elongations are still acceptable (260–400%), indicating the degree of crosslinking is small as 0.05 phr peroxide content is added. When silane is added, the tensile elongation decreases obviously (samples G, H, and I), representing that peroxide can promote the self-crosslinking reaction of LLDPE. The tensile elongation of sample J decreases 40% after water-crosslinking, caused by the effect of silane grafting and the water-crosslinking reaction of LLDPE.

Table IV summarizes the results of flexural strength testing. Table V summarizes the results of impact strength. The trends are similar to the results of tensile property. From these mechanical properties tests, it can be concluded that the better degree of water-crosslinking can be achieved with 0.10 phr DCP content than with 0.05phr DCP content (samples J and G). LLDPE utilizing 0.1 phr DHBP possesses a higher degree of water-crosslinking than
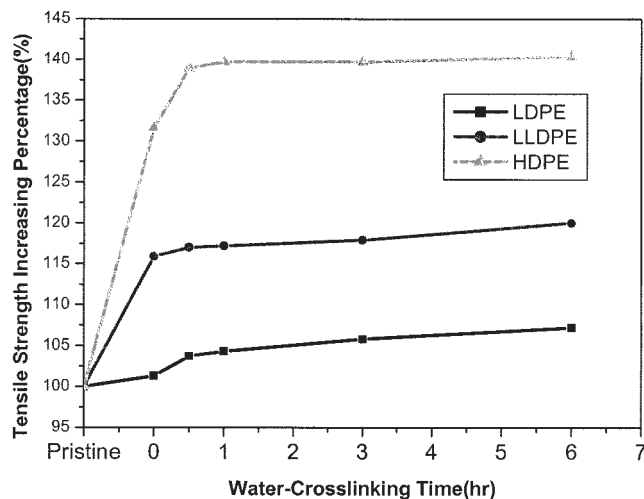

Figure 2 Effect of various water-crosslinking time on tensile strength of pristine and silane-grafted polyolefin.
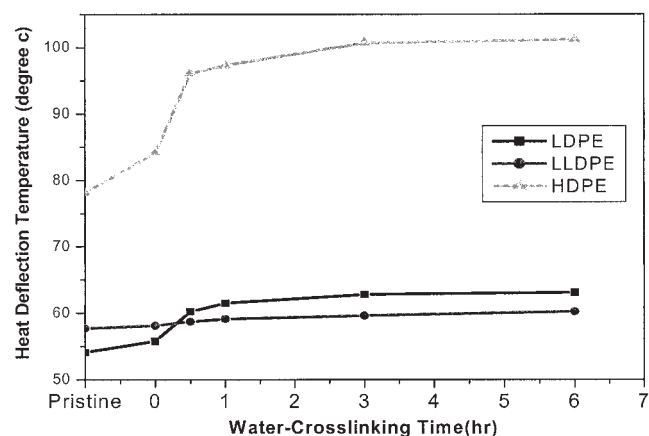

Figure 3 Effect of various water-crosslinking time on heat deflection temperature of pristine and silane-grafted polyolefin.

TABLE VII
The Characteristics of Pure LLDPE and Silane-Grafted Water Crosslinked With Varying Crosslinking Time

Time of exposure		LLDPE-g-VTMS				
Test item	LLDPE	0 hr	0.5 hr	1 hr	3 hr	6 hr
Tensile strength (Kgf/cm^2)	140.0	162.2	163.8	164.1	165.0	167.8
Elongation (%)	403.5	57.5	57.2	56.3	55.7	54.9
Flexural strength (Kgf/cm^2)	104.3	132.3	134.8	135.2	135.6	137.1
Flexural modulus (Kgf/cm^2)	2367	2513	2514	2588	2594	2632
Notched Izod impact strength (J/M)	453.0	553.5	544.3	533.8	532.5	522.6
HDT (°C)	57.7	58.1	58.7	59.1	59.6	60.2

that of 0.01 phr DHBP content (samples H and K). Results show that LLDPE possesses a higher degree of silane grafting when peroxide contents are 0.10 phr DCP and 0.05 phr DHBP. The using of DIPP peroxide obtains a less degree of water-crosslinking when the peroxide content is the same, and the processability is also worse.

Thermal and mechanical properties of silane-grafted moisture-crosslinked polyethylene

Table VI shows the characteristics of pristine HDPE and silane grafted water crosslinked with varying crosslinking time. It is found that the tensile strength of the silane grafted HDPE increases 31.6%, compared to pristine HDPE (increasing percentage is greater than LLDPE and LDPE, as shown in Fig. 2). After water-crosslinking for 4 h at 85°C, the tensile strength increased only 5.5 to 6.7%, compared to the silane grafted HDPE. This implies that the increase of the tensile strength of the silane grafted HDPE is due to the crosslinking of HDPE during the grafting process. The elongation of the crosslinked HDPE is decreased because the crystallinity of HDPE is destroyed. HDPE

is a polymer with a high degree of crystallinity, and its physical properties are deeply affected by the degree of crystallinity. As can be seen from Table 6, the impact strength of the silane grafted water crosslinked HDPE was decreased, which was probably caused by the decreasing of the degree of crystallinity of HDPE. The HDT of the crosslinked HDPE is increased with increasing crosslinking time. After being crosslinked for 6 h, the HDT can be increased from 78.1°C to 101.2°C (greater than that of LDPE and LLDPE, as shown in Fig. 3).
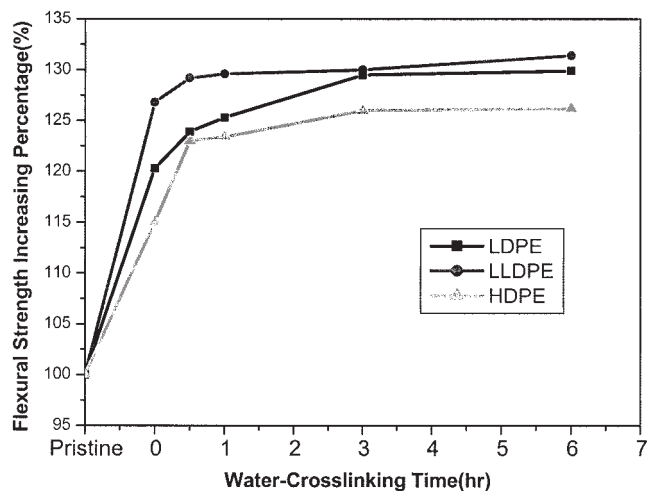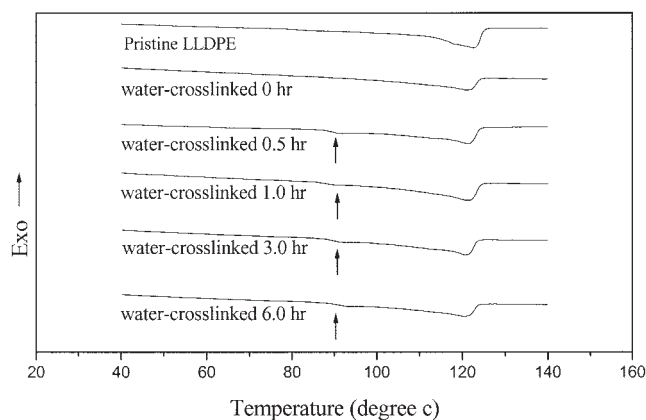
Figure 5 Differential thermal analysis traces for LLDPE and crosslinked LLDPE.
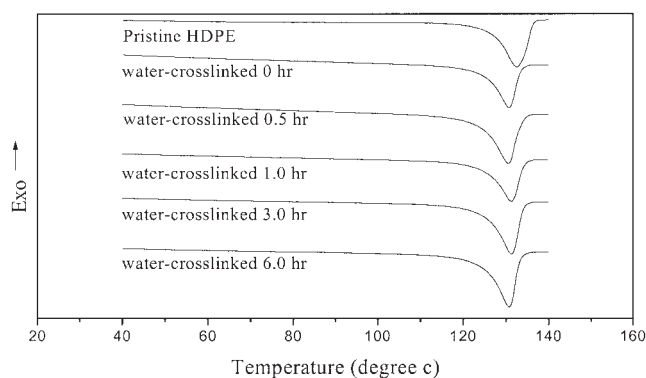
Figure 6 Differential thermal analysis traces for HDPE and crosslinked HDPE.

Figure 4 Effect of various water-crosslinking time on flexural strength of pristine and silane-grafted polyolefin.

TABLE VIII
The Characteristics of Pure LDPE and Silane-Grafted Water Crosslinked With Varying Crosslinking Time

Time of exposure		LDPE-g-VTMS				
Test item	LDPE	0 hr	0.5 hr	1 hr	3 hr	6 hr
Tensile strength (Kgf/cm^2)	133.8	135.6	138.8	139.5	141.6	143.4
Elongation (%)	119.5	114.8	110.6	107.9	101.9	100.6
Flexural strength (Kgf/cm^2)	92.5	111.3	114.6	115.9	119.8	120.2
Flexural modulus (Kgf/cm^2)	1589	1988	1912	1947	2044	2105
Notched Izod impact strength (J/M)	523.3	511.9	505.5	470.5	483.8	445.0
HDT (°C)	54.1	55.8	60.2	61.5	62.8	63.1

Table VII lists the mechanical properties of pure LLDPE and silane grafted water crosslinked LLDPE subjected to different curing times. The tensile strength, flexural strength, and impact strength are all increased (the percentage of increasing of flexural strength is greater than that of HDPE and LDPE, as shown in Fig. 4), while the elongation is decreased. From these data it is also found that crosslinking of LLDPE during silane grafting shows more significant effects on the increase of mechanical properties than that of water induced crosslinking. Unlike HDPE, the impact strength of crosslinked LLDPE is increased with increasing crosslinking time. The reason could be due to the crystallinity of LLDPE, which is much lower than that of HDPE, and therefore upon crosslinking, the degree of crystallinity was not decreased as drastically as HDPE. In addition, from the DSC data in Figure 5, multiple melting behaviors were observed for the cross-linked LLDPE (it cannot be seen in the system of HDPE, as shown in Fig. 6). It is the result of the phase separation of the two different crystallines, the PE crystalline and the newly formed Si-O-Si crystalline.

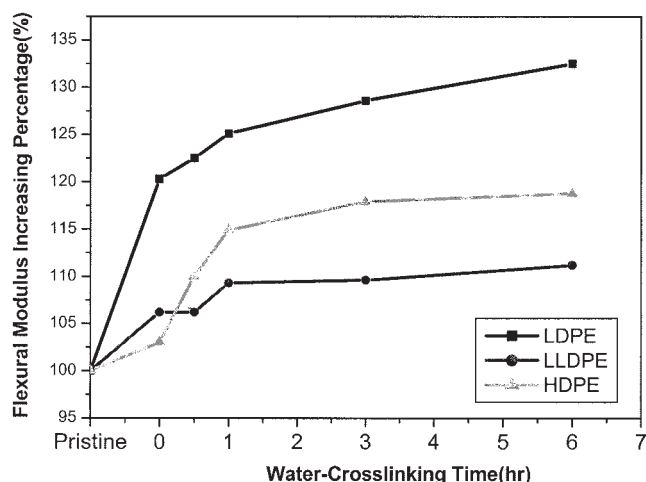The mechanical properties of pure LDPE and silane grafted water crosslinked LDPE are presented in Table VIII. Contrary to silane grafted HDPE and LLDPE, the tensile strength and elongation of the silane grafted LDPE are not affected, implying that the crosslinking of LDPE is not favored during the silane grafting process. The nature of the long chain branch of LDPE is responsible for the more effective silane grafting. Upon crosslinking, the tensile strength, flexural strength, and flexural modulus were increased with increasing crosslinking time (percentage of increasing of flexural modulus is greater than that of HDPE and LLDPE, as shown in Fig. 7). The reasons causing the increase of these properties resemble those of LDPE. Multiple melting behaviors were observed for crosslinked LDPE, as well in Figure 8.

CONCLUSIONS

1. Suitable peroxide and the optimal peroxide content can enhance effective silane grafting on LLDPE, and the mechanical properties can be increased after water- crosslinking.
2. Silane can prompt the peroxide to proceed to the self-crosslinking reaction of LLDPE.
3. The effective silane grafting on LLDPE decreases when the self-crosslinking reaction of LLDPE occurs, and the processability might be reduced.
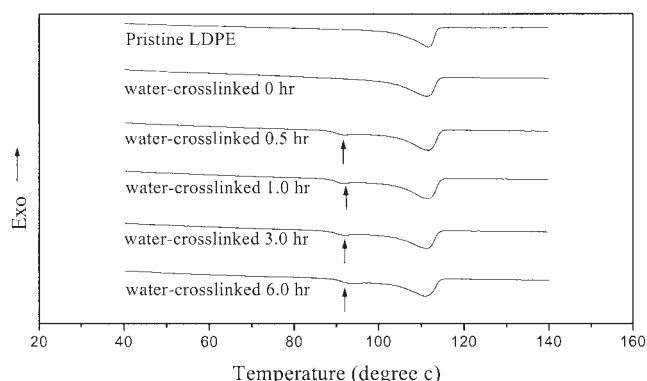

Figure 7 Effect of various water-crosslinking time on flexural modulus of pristine and silane-grafted polyolefin.

Figure 8 Differential thermal analysis traces for LDPE and crosslinked LDPE.

4. During the silane grafting process using DCP as an initiator, polyethylene tends to crosslink and thus lowers the degree of grafting. LDPE has the lowest tendency to crosslink during grafting.

5. Multiple melting behaviors were observed for crosslinked LDPE and LLDPE, which is the result of the phase separation of the two different crystals, the PE crystalline and the newly formed Si-O-Si crystalline.

6. The mechanical and thermal properties of the crosslinked PE are better than those of the un-crosslinked PE.

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