Silane-crosslinked HDPE

Gel and extraction results

In this part, a silane-grafted sample was immersed in hot water for various durations. The silane-crosslinked products were then analyzed. Figure 6 shows the results of gel content and swelling factor of various silane-cured HDPE. The amount of gel in the crosslinked samples increases rapidly in the initial stage of crosslinking. For example, a gel content of 70 % was gained after 120 h of crosslinking in the absence of catalyst. The initial slope of the graph is very steep, inferring a high rate of crosslink formation. In our previous work on silane-crosslinked ethylene-octene copolymer, we found that the rate of crosslinking of the polymer depends strongly on the relative amounts of crystalline and amorphous material. The copolymer with higher octene content and lower crystallinity showed higher rate of crosslinking than that with lower content of octene comonomer [25]. After this initiation period, the rate of crosslinking slows and a slight increase in the gel content is observed. A gel content of approximately 90 % is gained after 600 h of the curing process. With increasing the time of curing further, the percentage of gel in the crosslinked products is hardly changed and the maximum gel of 93 % is reached for HDPE crosslinked for 1200 h.

Apart from gel content, the swelling factor is a good indicator of crosslinking in the gel phase. From Figure 6, the values of swelling factor also increase sharply in the initial stage and reach a maximum at the crosslinking time of 120 h. The time to reach maximum swelling may vary among various types of PE [26]. In the case of ethylene copolymer, a maximum swelling factor was observed at the crosslinking time of 48 h, owing to the much higher rate of crosslinking of ethylene copolymer compared to that of HDPE [27]. On increasing the crosslinking time beyond this duration, the network structure becomes denser and the diffusion

of water is limited by this network structure formed. This results in a lower swelling factor together with a continued increase in gel content. This is indicative of a development in network strength associated with the longer crosslinking time. The results of gel and swelling factor agree well with the results from rheological measurement as shown in Fig. 7. Chain branching and crosslinking in the samples lead to difficulty in the movement of polymer chains [2]. As a result, the polymer viscosity increases and more energy is needed for the mobility of chains. By plotting complex modulus (G*) of silane-crosslinked HDPE as a function of crosslinking time, the graph of Figure 7 shows the increase in G* of all crosslinked samples with increasing time, just as observed in the solvent extraction results.

Thermal Properties

The results from DSC, HDT, and TGA experiments are summarized in Table 1. These include the melting (T_m) and crystallization (T_c) temperatures, heat distortion temperature (HDT), and decomposition temperature (T_d). HDPE shows a melting temperature at 133 °C. DSC analysis clearly reveals that the presence of silane crosslink network in the HDPE has insignificant effect on the T_m and T_c of the polymer. This is due to the fact that the crosslink process is performed after the polymer has been crystallized during the shaping stage. It is believed that silane crosslink occurs mainly in the amorphous portion of the polymer [3, 28]. Similar findings were found on the effects of silane crosslink on thermal behaviors of polypropylene (PP) [29], low-density PE [30], and ethylene-octene copolymer [31]. HDT tests demonstrate the effect of silane crosslinks on the thermal stability of HDPE. The HDT of pure HDPE increases markedly from 66 to 93 °C after silane crosslinking. A similar observation was reported by Kuan et al. [17] where an HDT of HDPE was increased from 78 to 101 °C after the introduction of a silane crosslink network. In the case of PP, our previous work showed a HDT

value of silane-crosslinked sample as high as 180 °C [32]. Apart from HDT, the improvement in thermal stability of HDPE by silane crosslinking can be seen from the results of TGA performed under an oxygen atmosphere. Pure HDPE shows a T_d at 413 °C. The T_d value of HDPE after crosslinking increases from 413 for virgin resin to 449 °C for the crosslinked product with 90 % gel. These results clearly show that the crosslinked samples are thermally more stable than the unmodified samples.

Tensile properties

Figure 8 shows the relationships between the content of gel in the silane-crosslinked samples and the tensile properties, including Young's modulus, elongation at break, and tensile strength. Interestingly, there is a sudden change in tensile properties with the content of gel in the crosslinked products. Significant increase in modulus with a drastic drop in elongation and strength are clearly observed at around 70 % gel. For the HDPE samples being crosslinked for a time period shorter than the time for maximum swelling to be reached ($t < 120$ h), the variation of gel amounts (from 0 to 70 %) does not show a significant effect on the tensile properties. In those samples, a loose network structure is formed and this allows polymer chain movement when the tensile stress is applied. As the time of crosslinking increases, the network structure becomes tighter and the polymer chains in the tight network have less movement or orientation during extension. Thus less force is needed for the material to break on exposure to stress [33]. As a result, elongation at break and strength decrease sharply. In contrast to the failure properties, the modulus is increased by crosslinking. A sharp increase in modulus is clearly observed from the plot of Fig. 8.

Thermal aging property

In many applications, a material with good heat deformation resistance and thermal endurance properties is needed. In cable jacketing, especially for low-voltage application (< 10 kV), the mechanical properties and thermal stability are very important. In this study, the thermal aging test was performed according to ASTM D 2655-00. This is the method for the characterization of the thermal aging properties of insulation for electrical wires and cables. The samples were heated at 121 ºC for 168 h. To pass the test, a drop in tensile properties of aged samples should not exceed 25 %, compared to the unaged samples.

The HDPE used in this study, with a T_m of 133 °C, shows an inevitable change in sample appearance during the aging experiment performed at 121 °C. However, the test results show 33 and 19 % reduction in modulus and elongation at break, respectively. In the other words, the HDPE sample without any modification fails the aging test. The grafted and crosslinked HDPE retain their specimen shape and size after thermal aging but a deterioration of tensile modulus, elongation at break, and strength results. However, a drop in tensile properties of the silane-crosslinked polymers after aging does not exceed 25 % and, therefore, it could be said that all silane-crosslinked polymers prepared in this study pass the test specification of the ASTM D 2655-00. The effect of network structure, either a loose or a tight network, on thermal stability of the HDPE is clearly seen from the aging results. The drop in tensile properties is more severe for the samples crosslinked for time periods lower than 120 h (or lower than the point of maximum swelling factor) where loose networks are formed and gel content of approximately 70 % or lower is gained.

Increasing the experimental temperature to 132 °C, which is closer to the melting temperature of HDPE, unmodified HDPE and the loosely crosslinked samples (crosslinking time < 120 h) cannot withstand the high aging heat of 132 °C. The specimens deformed and distorted

after only 4 min of the aging experiment. Therefore, no results on their tensile properties are shown in Fig. 9. Chain slippage is believed to occur under these circumstances [34]. Better thermal aging resistance is obtained by curing the samples for longer duration beyond 120 h or beyond the point of maximum swelling factor. The samples with tight networks are able to withstand the high heat of 132 °C. The sample with 90 % gel shows only 5 % reduction in tensile properties after aging at 121 ºC for 168 h and 10 % reduction in properties after aging at 132 ºC.

CONCLUSIONS

Melt grafting of VTMS onto the HDPE was performed in a twin-screw extruder. The appearance of IR peaks of methoxysilane (Si-OCH_3) groups at 798, 1092, and 1192 cm^{-1} in the reacted PE confirmed the presence of silane grafting.

The grafting level depended on the VTMS concentration, initiator type and contents, and extrusion temperature. Using of a binary BPO/DCP initiator was effective in improving the silane grafting yield while minimizing the formation of premature gel.

Analysis of gel content and swelling factor provided an insight into understanding the structure of the silane crosslink network formed in the desired crosslinking reaction. A sharp increase in the content of gel and swelling factor was observed in the early stage of curing process, revealing the formation of a loose network structure. A tighter network was achieved after the maximum swelling factor was reached.

There was a sudden change of tensile properties with the gel content. Elongation at break and strength decreased and modulus increased sharply after the tight network was formed. All silane-crosslinked polymers prepared in this study passed the aging test specification for low-voltage applications. The structure of the network, either loose or tight, showed a strong role in the heat aging properties of the crosslinked products.

The melting and crystallization behavior of silane-crosslinked samples was insignificantly affected by the crosslink structure. TGA and HDT tests showed an increase in the values of T_d and HDT, inferring an improvement in thermal stability of the materials after crosslinking.

REFERENCES

[1] A. Smedberg, T. Hjertberg, B. Gustafsson, *Polymer*, 38, 4127 (1997).

[2] S. Dadbin, M. Frounchi, M.H. Saeid, F. Gangi, *J. Appl. Polym. Sci*., 86, 1959 (2002).

[3] G.L. Oliveira, M.F. Costa, *Mater. Sci. Eng. A*, 527, 4593 (2010).

[4] Y. Zhu, H.G. Yoon, K.S. Suh, IEEE Trans. Electr. Insul., 6, 164 (1999).

[5] R. Anbarasan, O. Babot, B. Maillard, *J. Appl. Polym. Sci*., 93, 75 (2004).

[6] M. Celina, G.A. George, *J. Appl. Polym. Sci.*, 48, 297 (1995).

[7] B. Jalal, A. Hamed, M. Jalil, *Polym.-Plast. Technol. Eng*., 45, 979 (2006).

[8] S. Tokuda, S. Horikawa, *Furukawa Review*, 23, 88 (2003).

[9] C. Jiao, Z. Wang, Z. Gui, Y. Hu, *Eur. Polym. J.*, 41, 1204 (2005).

[10] H. Huang, H.H. Lu, N.C. Liu, *J Appl Polym Sci*., 78, 1233 (2000).

[11] S.S. Pesetskii, B. Jurkowski, Y.M. Krivoguz, K. Kelar, *Polymer*, 42, 469 (2001).

[12] Y.T. Shieh, C.M. Liu, *J. Appl. Polym. Sci*., 74, 3404 (1999).

[13] Y.J. Sun, G.H. Hu, M. Lambla, *J. Appl. Polym. Sci*., 57, 1043 (1995).

[14] K.J. Ganzeveld, L.P.B.M. Janssen, *Polym. Eng. Sci*., 32, 467 (1992).

[15] T. Bremner, A. Rudin, *J. Appl. Polym. Sci*., 49, 785 (1993).

[16] M.K. Naqvi, R. Reddy, *Polym. Plast. Technol. Eng*., 36, 585 (1997).

[17] H.C. Kuan, J.F. Kuan, C.C.M. Ma, J.M. Huang, *J. Appl. Polym. Sci*., 96, 2383 (2005).

[18] Y.T. Shieh, K.-I. Hsiao, *J. Appl. Polym. Sci.*, 70, 1075 (1998).

[19] J. Morshedian, P.M. Hoseinpour, H. Azizi, R. Parvizzad, *Express Polym. Lett*., 3, 105 (2009).

[20] K. Sirisinha, M. Boonkongkaew, S. Kositchaiyong, *Polym. Test*., 29, 958 (2010).

[21] K. Adachi, T. Hirano, *J. Sol-Gel Sci. Technol*., 49, 186 (2009).

[22] R. Qi, J. Qian, C. Zhou, *J. Appl. Polym. Sci*., 90, 1249 (2003)

[23] T.H. Kim, H.K Kim, D.R. Oh, M.S. Lee, K.H. Chae, S.Y. Kaang, *J. Appl. Polym. Sci*., 77, 2968 (2000).

[24] K.Y. Cho, J.-Y. Eom, C.-H. Kim, J.-K. Park, *J. Appl. Polym. Sci*., 108, 1093 (2008).

[25] K. Sirisinha, S. Chimdist, *J. Appl. Polym. Sci*., 109, 2522 (2008).

[26] S. Kositchaiyong, "Influence of various ethylene copolymers on the silane-water crosslinking of high-density polyethylene," M.Sc. Thesis, Dissertation, Mahidol University, Bangkok (2007).

[27] W. Kamphunthong, "A study on ethylene-octene copolymer composite crosslinked through siloxane linkage," M.Sc. Thesis, Dissertation, Mahidol University, Bangkok (2006).

[28] W. Kamphunthong, K. Sirisinha, *J. Appl. Polym. Sci*., 109, 2347 (2008).

[29] M. Beltran, C. Mijangos, *Polym. Eng. Sci*., 40, 1534 (2000)

[30] Y.T. Shieh, J.S. Liau, T.K. Chen, *J. Appl. Polym. Sci.*, 81, 186 (2001).

[31] K. Sirisinha, D. Meksawat, *J. Appl. Polym. Sci.*, 93, 1179 (2004).

[32] K. Sirisinha, K. Kawko, *Macromol. Mater. Eng*., 290, 128 (2005).

[33] G.B. Shah, M. Fuzail, J. Anwar, *J. Appl. Polym. Sci*., 92, 3796 (2004)

[34] P. Eyerer, *Polymer-Opportunities and risks I*, Springer Heidelberg Dordrecht, London (2010).

TABLE 1. Melting temperature (T_m), crystallization temperature (T_c), heat distortion temperature (HDT), and decomposition temperature (T_d) of unmodified HDPE and silane-crosslinked HDPE (90 % gel)

Properties	Unmodified HDPE	Crosslinked HDPE
T_m (°C)	133	131
T_c (°C)	117	116
HDT (°C)	66	93
T_d (°C)	413	449

T1 profile	170	170	170	160	160	°C
T2 profile	170	170	170	200	160	°C

FIG. 1. Schematic of screw configuration and temperature profiles used in silane grafting experiments.

K. Sirisinha* and M. Boonkongkaew

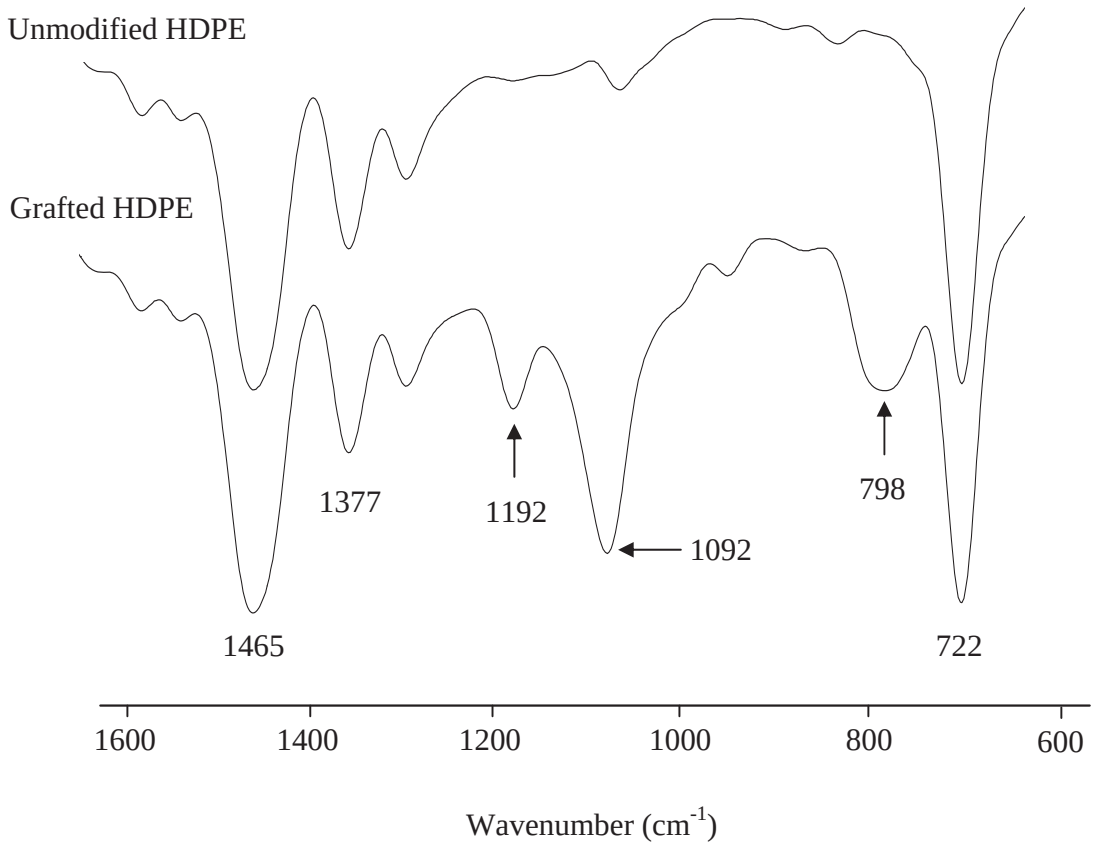


FIG. 2. FTIR spectra of unmodified HDPE and HDPE grafted with 5 % silane.

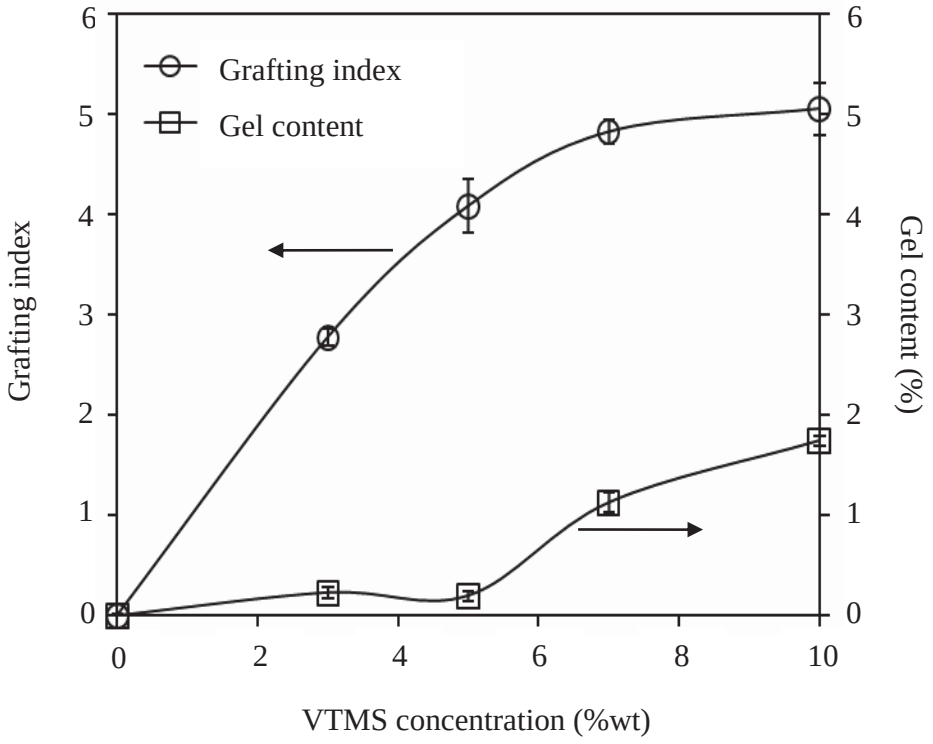


FIG. 3. Effect of VTMS concentration on grafting index and premature gel of silane-grafted HDPE. DCP loading was constant at 0.1 %.

K. Sirisinha* and M. Boonkongkaew

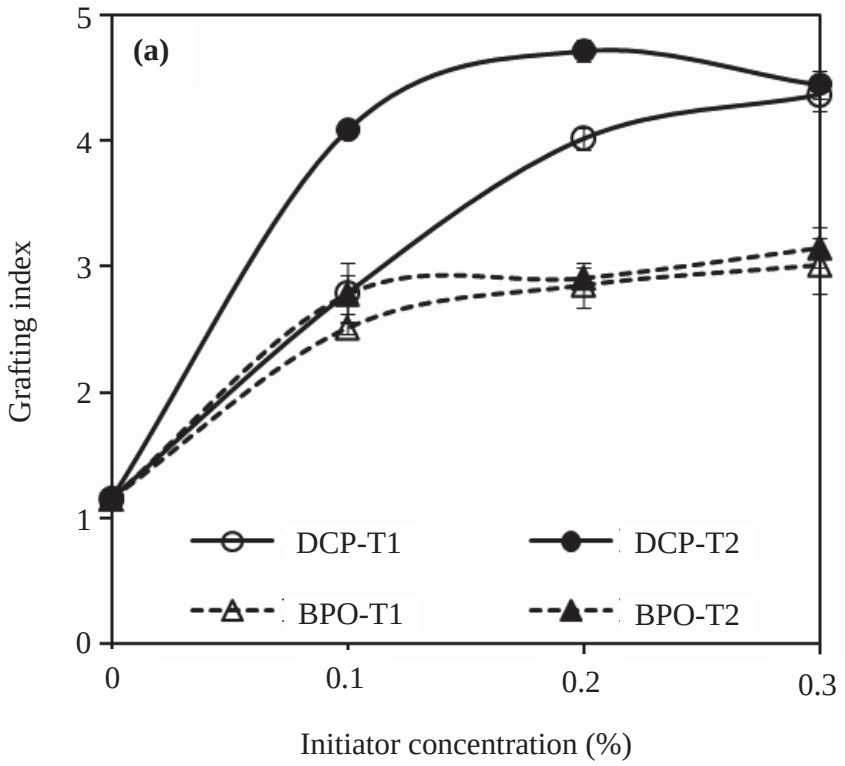


FIG. 4a. Effect of initiator type and concentration, and extrusion temperature on grafting index of grafted HDPE. VTMS loading was constant at 5 %.

K. Sirisinha* and M. Boonkongkaew

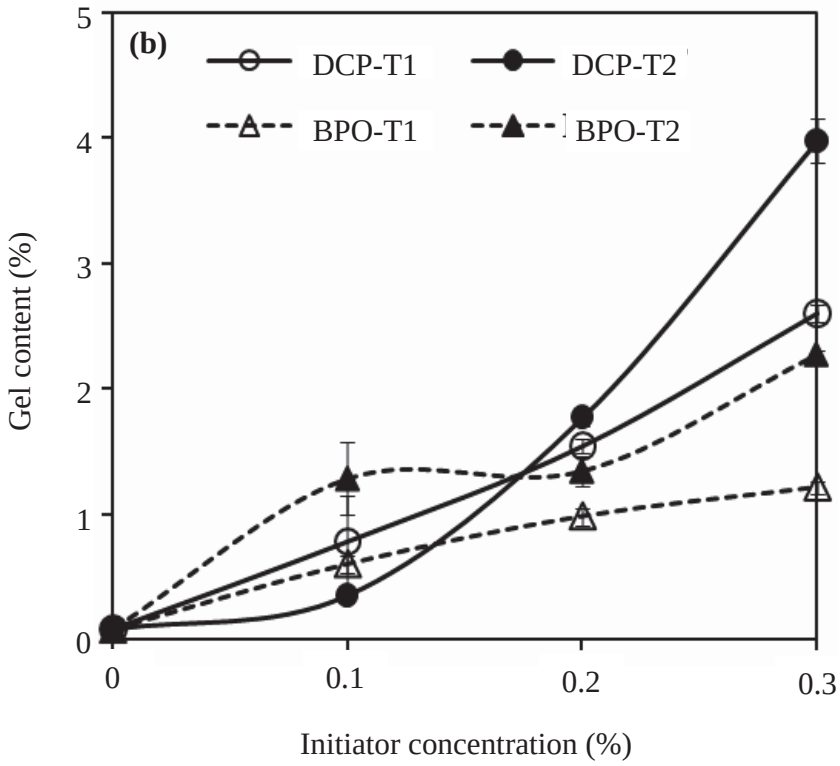


FIG. 4b. Effect of initiator type and concentration, and extrusion temperature on premature gel of grafted HDPE. VTMS loading was constant at 5 %.

K. Sirisinha* and M. Boonkongkaew

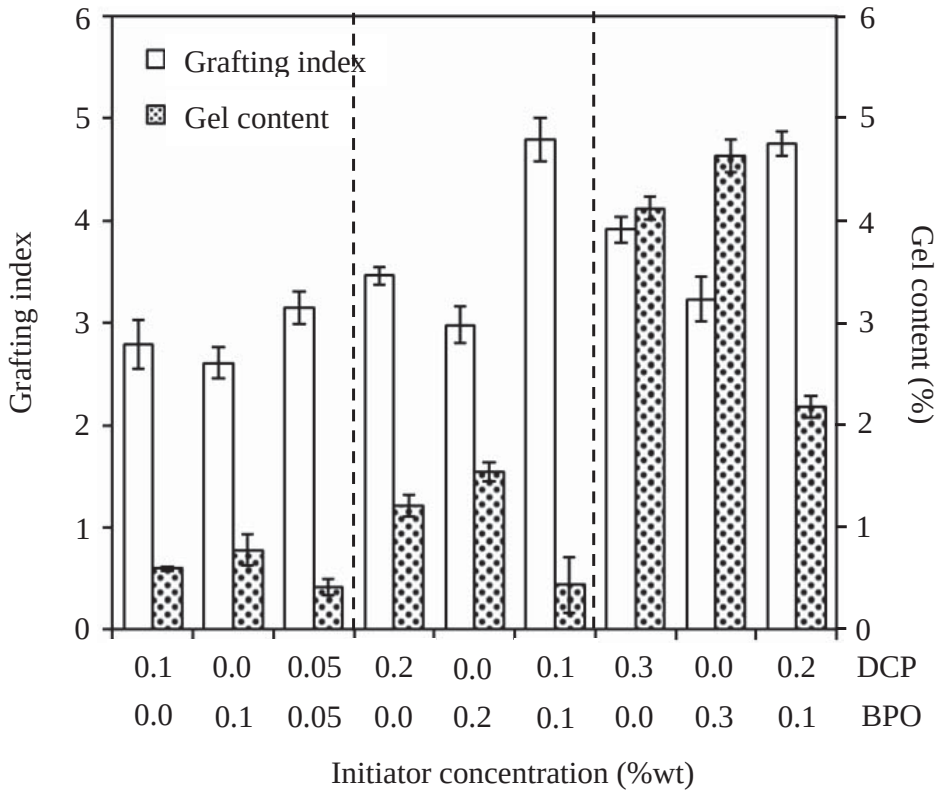


FIG. 5. Effect of single and binary peroxides on grafting index and premature gel of grafted HDPE. VTMS loading was constant at 5 %.

K. Sirisinha* and M. Boonkongkaew

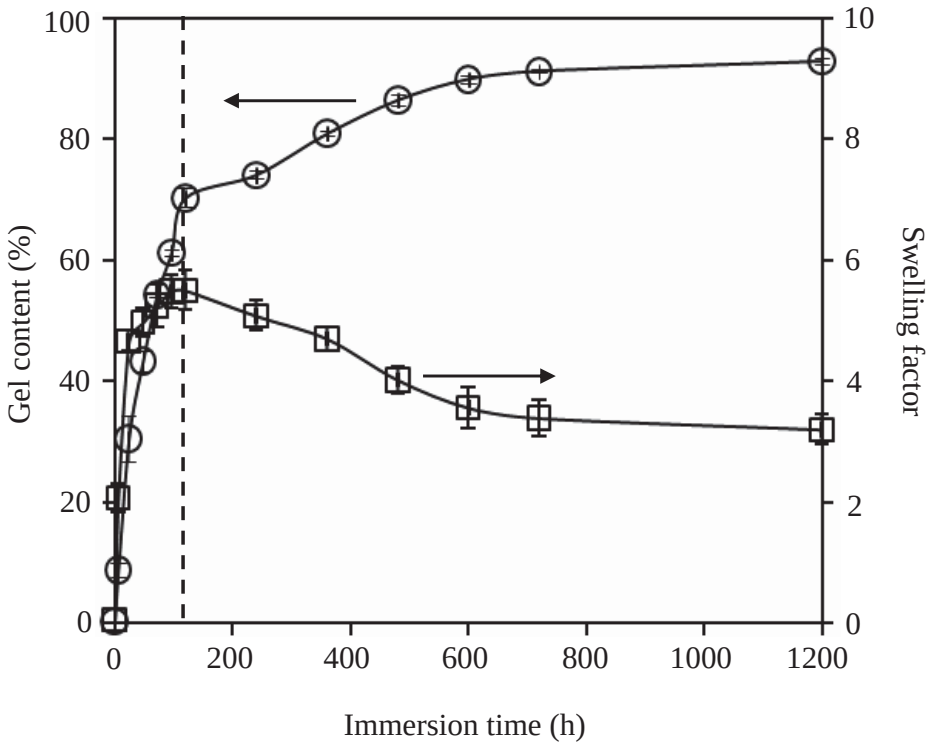


FIG. 6. Gel content and swelling factor as a function of crosslinking time.

K. Sirisinha* and M. Boonkongkaew

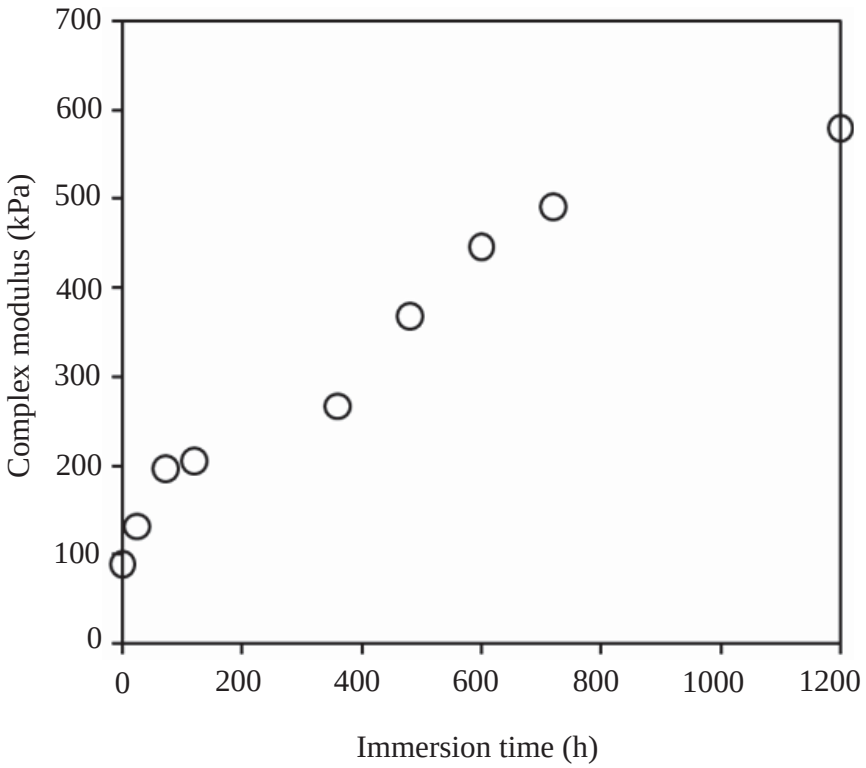


FIG. 7. Complex modulus as a function of crosslinking time.

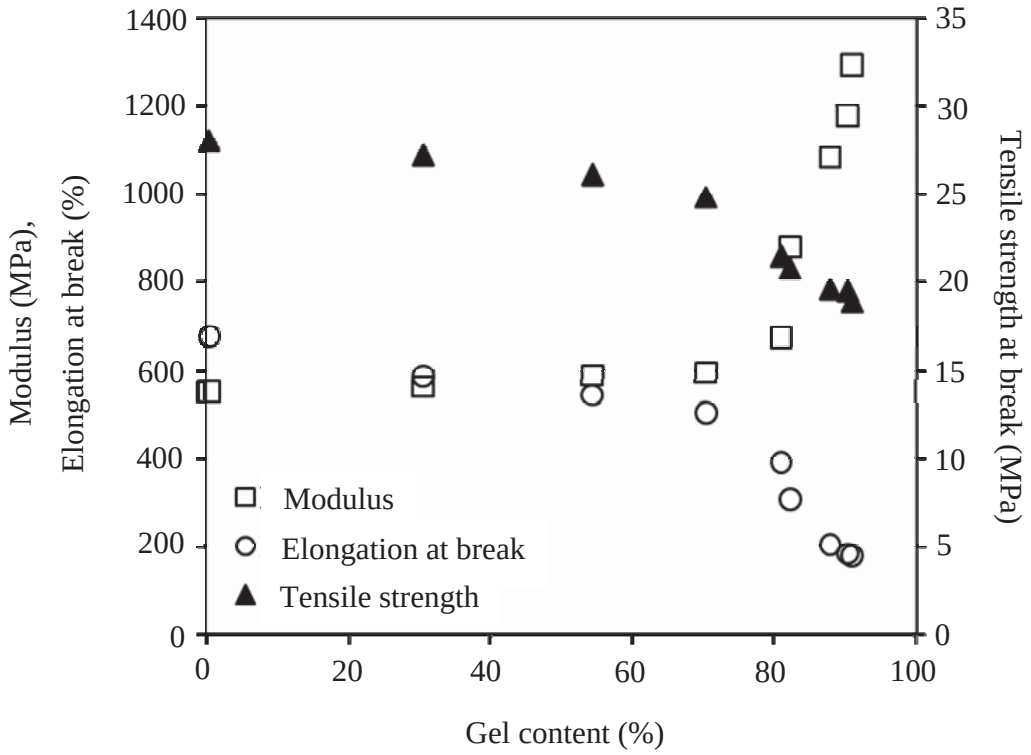


FIG. 8. Relationship between gel content and mechanical properties of silane-crosslinked HDPE.

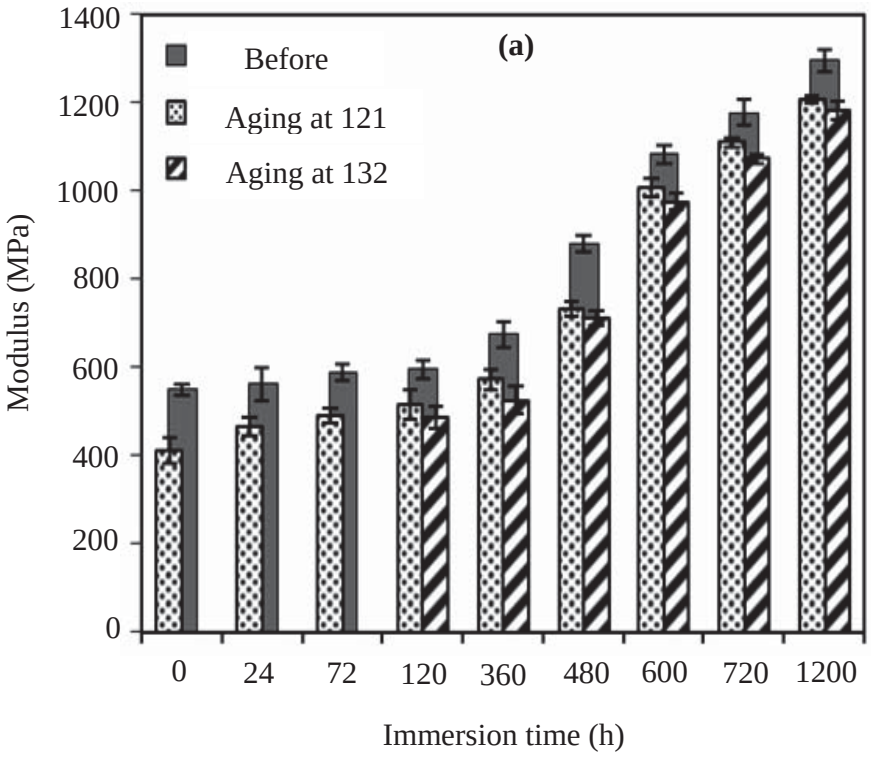


FIG. 9a. Young's modulus of crosslinked products before and after thermal aging at 121 ºC for 168 h and 132 ºC for 24 h.

K. Sirisinha* and M. Boonkongkaew

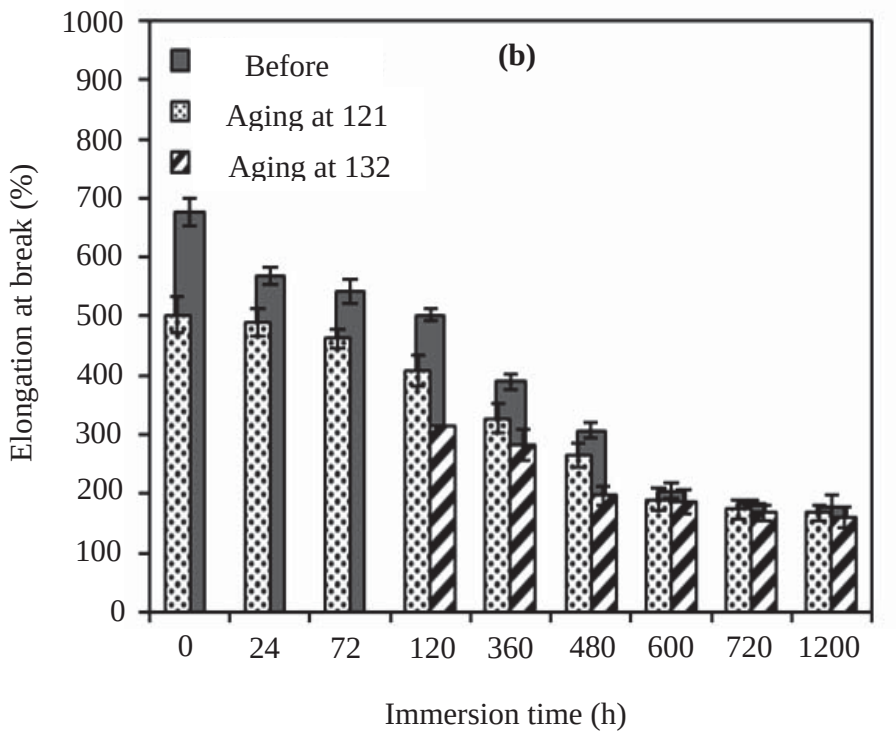


FIG. 9b. Elongation at break of crosslinked products before and after thermal aging at 121 ºC for 168 h and 132 ºC for 24 h.

K. Sirisinha* and M. Boonkongkaew

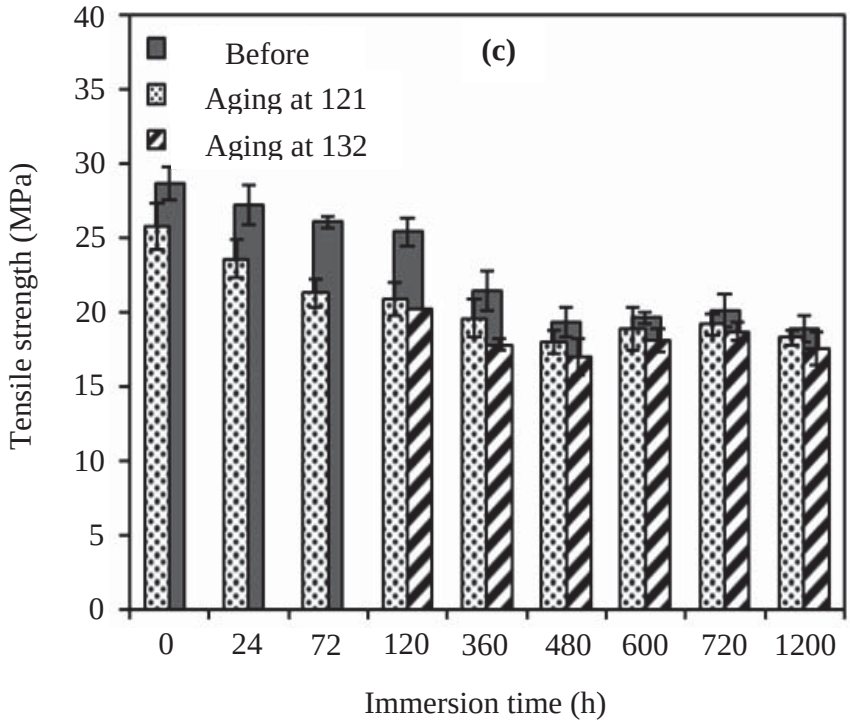


FIG. 9c. Tensile strength at break of crosslinked products before and after thermal aging at 121 ºC for 168 h and 132 ºC for 24 h.

K. Sirisinha* and M. Boonkongkaew

ภาคผนวก ข

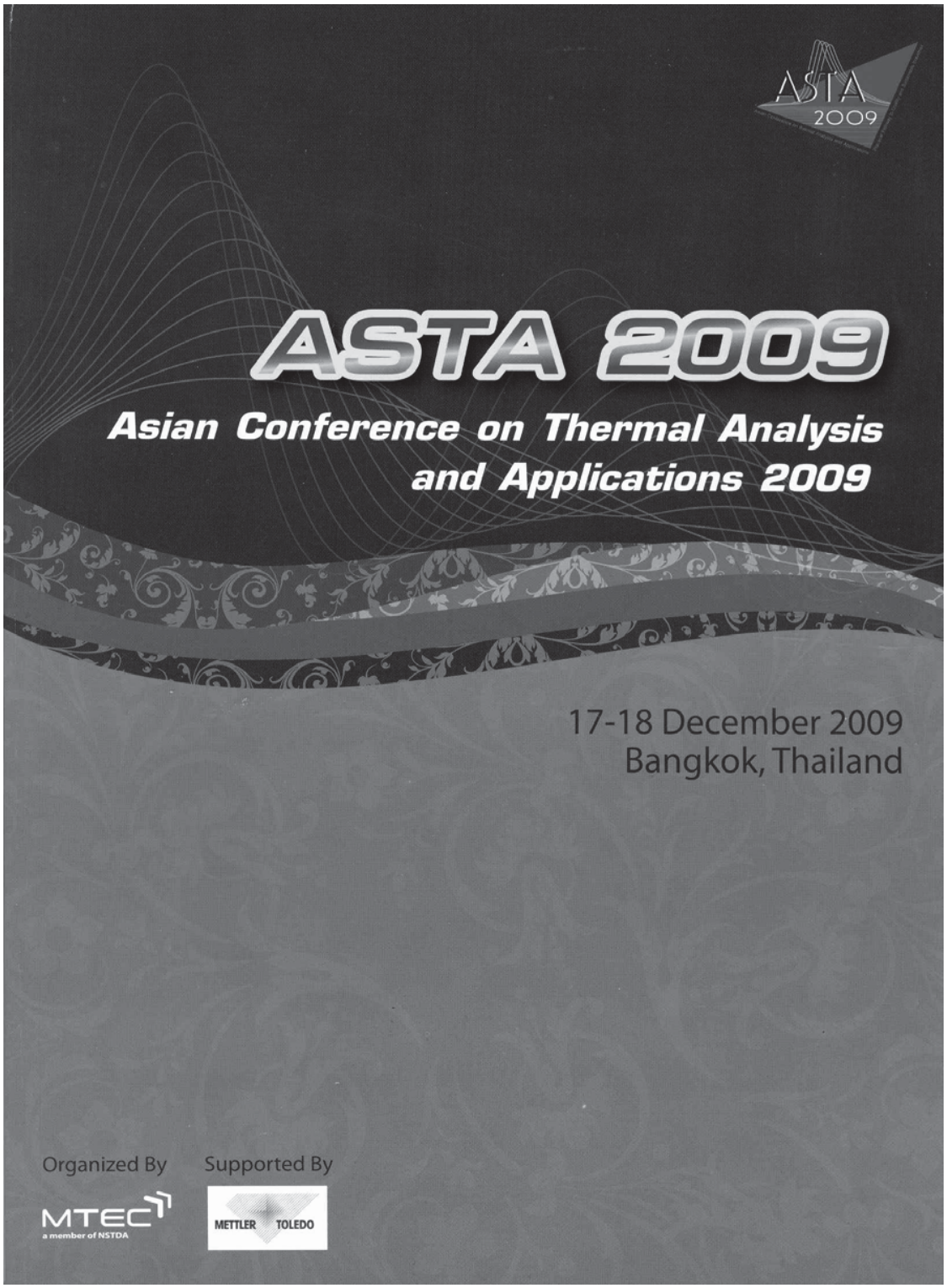
การเสนอผลงานวิจัยในที่ประชุมวิชาการ


BURAPHA UNIVERSITY
15-17 October 2009
วทท STT 35th
FACULTY OF SCIENCE
Abstracts
THE 35th CONGRESS
on SCIENCE and TECHNOLOGY
of THAILAND (STT 35)
การประชุมวิชาการวิทยาศาสตร์และเทคโนโลยีแห่งประเทศไทย
ครั้งที่ 35 (วทท 35)
วิทยาศาสตร์และเทคโนโลยีเพื่ออนาคตที่ดีขึ้น
SCIENCE AND TECHNOLOGY FOR A BETTER FUTURE
To Celebrate the 35th Anniversary of Faculty of Science, Burapha University
To Celebrate the 30th Anniversary of Ministry of Science and Technology
October 15 - 17, 2009
Venue : The Tide Resort (Bangsaen Beach), Chonburi, Thailand.
15-17 ตุลาคม 2552 ณ เดอะ ไทด์ รีสอร์ท (หาดบางแสน) จังหวัดชลบุรี
WWW.STT35.SCISOC.OR.TH

E_E0127 PREPARATION AND PROPERTIES OF SILANE-WATER CROSSLINKED HIGH-DENSITY POLYETHYLENE

Marnviga Boonkongkaew[1], Kalyanee Sirisinha[2]
Department of Chemistry, Faculty of Science, Mahidol University, Phuttamonthon 4 Road, Salaya, Nakhon Pathom 73170, Thailand
E-mail: mavy_chem@hotmail.com[1], sckpr@mahidol.ac.th[2]

Abstract: Crosslinking is an important method to improve tensile properties, thermal stability and high temperature properties of polymer. In this work, the silane-water crosslinking of polyethylene was investigated. The studied materials include high-density polyethylene (HDPE), ethylene-octene copolymer (EOC), and their blends. The polymers were first grafted with vinyl trimethoxysilane (VTMS) in a twin-screw extruder using peroxide as an initiator. The grafted polymers were subsequently crosslinked in the presence of water. The effects of the incorporation of carrier polymers and physical form of polymer on the degree of grafting and rate of crosslinking are reported. The properties of grafted and crosslinked products are also included.


ASTA 2009
ASTA 2009
Asian Conference on Thermal Analysis and Applications 2009
17-18 December 2009
Bangkok, Thailand
Organized By
MTEC
a member of NSTDA
Supported By
METTLER TOLEDO

DSC AND TGA ANALYSIS OF SILANE-WATER CROSSLINKED HIGH-DENSITY POLYETHYLENE

ASTA2009 Conference

Marnviga Boonkongkaew[1], Kalyanee Sirisinha[2]

Department of Chemistry, Faculty of Science, Mahidol University, Phuttamonthon 4 Road, Salaya,

Nakhon Pathom 73170, Thailand

Phone: 0-2441-9816 ext 1148, Fax. 0-2441-0511, E-mail: mavy_chem@hotmail.com[1], sckpr@mahidol.ac.th[2]

Abstract

Crosslinking is an important method to improve mechanical property, thermal stability and high temperature property of polymer. In this work, the silane-water crosslinking of high-density polyethylene (HDPE) and its blends with ethylene-octene copolymer (EOC) was performed. The effects of silane crosslink on melting, crystallisation and thermal stability of the materials were investigated using Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA). The results show that the incorporation of copolymer in the blends and the presence of silane crosslink network hardly change the crystallisation and melting behaviours of HDPE. Strong effect of silane crosslink is observed on improving the thermal oxidative property of HDPE and its blends.

Keywords: silane-water crosslinking, thermal properties

1. Introduction

High-density polyethylene (HDPE) is one of the most widely used polymers in many fields of industry. Having good chemical resistance and insulation property, HDPE is desirable for using in the applications of hot-water pipe and crude-oil pipe [1]. However, one of its major drawbacks for those applications is a relatively low upper uses temperature. Crosslinking can extend the uses of PE by raising the upper temperature limits of application and improving the mechanical properties of the polymer [2]. Three main methods for preparing crosslinked PE are peroxide crosslinking, radiation crosslinking, and silane-water crosslinking. It was reported earlier that the mechanical properties of ethylene copolymers crosslinked by peroxide are different to those crosslinked using silane reaction [3]. Silane-crosslinked PE can be achieved by grafting vinyl silane to the polymer backbone and subsequent crosslinking of the grafted products by forming siloxane linkage, in the presence of water [4]. Silane-crosslinking of HDPE is rather difficult, comparing to the low-density or linear low-density PE. A high degree of crystallinity of HDPE causes low silane absorption of this polymer and as a consequence, low silane grafting degree. Also, the presence of crystals in the polymer leads to a difficulty in water diffusion, causing a slow crosslinking rate.

In this study, a silane crosslinked HDPE was prepared. Ethylene-octene copolymer (EOC) was used as a silane carrier. The silane grafting was carried out in a twin-screw extruder where HDPE was in the melt state. The crosslinking reaction was performed in hot water, after the shaping process. The crosslinked products were then analysed for their melting and crystallisation behaviours using Differential Scanning Calorimeter (DSC). The thermal stability and decomposition temperature of the materials were characterised using Thermogravimetric Analysis (TGA).

2. Experimental

Materials

The main materials used in this study are HDPE (5000S), supplied from Bangkok Polyethylene Co. Ltd., and EOC (E8003) from DuPont Dow Elastomer Co. Ltd., with an octene content of 7.6% mole. Dicumyl peroxide (DCP) was used as initiator and vinyl trimethoxysilane (VTMS) was used as monomer for the grafting reaction. They were purchased from Aldrich Chemical Company, Inc.

Preparation of silane-water crosslinked polymers

The HDPE/EOC blends in the weight ratio of 50/50 were prepared in a co-rotating twin-screw extruder (Prism TSE16). The mixing temperature was kept at 170°C and screw speed of 120 rpm was used. The blends prepared were then pre-mixed with 5% VTMS and 0.1 % DCP in a container. The mixture was kept immediately under N_2 gas and allowed to stand overnight. The grafting reaction was carried out at around 200°C in an extruder. The screw speed of 30 rpm was used. The total reaction was finished within 5 min. The grafted products were then compression molded into a 1 mm thick sheet. The grafted samples were immersed in hot water at 70 °C for 120, 360 and 600 hrs to conduct a crosslink reaction.

Characterisations

Crosslink determination

Solvent extraction technique is used in evaluating the crosslinking degree in crosslinked products by determining the content of gel or insoluble fraction after extraction process. The solvent extraction was performed at 250°C using xylene as a solvent [2]. The content of crosslinked part or gel was calculated from the weight of gel after being dried in a vacuum oven with respect to the initial weight of sample.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC-7 was used for the characterisation of melting and crystallisation behaviours of HDPE, EOC and its blends, before and after crosslink reaction. The samples of about 7±1 mg were heated from 50 to 170°C at a scan rate of 20°C.min^{-1}. The temperature was then held at 170°C for 5 min before cooling to 50°C at the same rate. The melting and crystallisation temperature as well as crystallinity of the crosslinked samples were examined. The degree of crystallinity (%χ_c) was calculated by taking the values of heat of fusion (ΔH_f), which is the area of the melting peak, using equation (1)

$$\text{Percentage crystallinity, } \%\chi_c = \frac{\Delta H_f}{\Delta H_{f100}} \times 100 \quad (1)$$

where ΔH_f is enthalpy of fusion of the samples and ΔH_{f100} is enthalpy of fusion of a perfectly crystalline PE which is equal to 290 J.g^{-1} [5].

Thermogravimetric analysis (TGA)

The thermogravimetric analysis was performed using a Mettler Toledo SDTA 851. The samples were heated in the temperature range from 40 to 600 °C using a heating rate of 20 °C.min^{-1}. Weights of the samples tested were about 8±1 mg. The maximum decomposition temperature (T_d) is evaluated to indicate the temperature of maximum decomposition rate.

3. Results and Discussion

Melting and crystallisation behaviours

Figure 1 shows the DSC heating thermograms of unmodified HDPE, EOC, and its (50/50) blend. HDPE shows a sharp melting peak at 133°C, while EOC exhibits a broad melting endotherm in the range of 60 to 100°C. The broad endotherm observed in this sample is due to the distribution in length of crystallisable ethylene sequence imposed by the placement of noncrystallisable comonomer units along the chain, leading to a broad distribution of crystal sizes in this polymer. In the case of the blend, a sharp peak at 129°C is corresponding to the melting of the HDPE crystals whereas the shoulder around 84°C belongs to the EOC component. The %χ_c values of HDPE, EOC, and its blend are 61, 8, and 29, respectively. By calculating the percentage of normalised crystallinity based solely on the weight of HDPE component, the value of 30 is found. This result indicates that ethylene copolymer has no effect on the crystallisation of HDPE component.

The DSC results of HDPE, EOC, and its blend both before and after silane-grafting and crosslinking process are summarised in Table 1. The contents of gel or crosslink portions in the samples are also included in the table, showing a progressive increase in crosslinking degree after increasing the time of crosslink reaction. After silane grafting reaction, T_m and % χ_c of HDPE, EOC, and its (50/50) blend decrease slightly. This may be due to a reduction in the structure regularity of polymer

brought about by the presence of the silane grafts. The interesting results are found for the crosslinked samples where insignificant changes in the T_m and % χ_c are observed. Similar trend is found for the T_c. Also, a small melting peak of EOC at 86°C clearly appears after performing a crosslink reaction for 120 hrs as shown in Figure 2. In such system, the gel content of about 75 % is gained. It is believed that after a long crosslinking time at 70°C, the recrystallisation of polymer chains that are long enough to crystallise occurs during the crosslinking process (annealing effect). This points out that the silane crosslink, unlike to the common peroxide crosslink, mainly occurs in the amorphous phase of polymer. Therefore, the silane-crosslinked materials are able to maintain their crystal structure in the system. The crystalline arrangement still carries on during the proceeding of crosslink reaction.

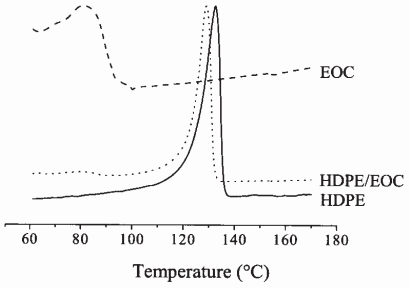


Figure 1 DSC 1st heating thermograms of unmodified HDPE, EOC and its blends

Table 1 Gel content, melting temperature (T_m), percentage of crystallinity (%χ_c), and crystallization temperature (T_c) of pure and modified HDPE, EOC and its blends

Systems	Time of crosslink reaction (hrs)	Samples	Gel content (%)	1st heating		Cooling
				T_m (°C)	χ_c (%)	T_c (°C)
Unmodified	0	HDPE	0	133	61	112
		HDPE/EOC	0	84, 129	29	112
		EOC	0	60-100	8	59
Grafted	0	HDPE	0	130	56	111
		HDPE/EOC	0	126	25	109
		EOC	0	60-97	5	59
Crosslinked	120	HDPE	70	130	56	111
		HDPE/EOC	74	87, 126	24	107
		EOC	75	86	8	58
	360	HDPE	81	130	56	110
		HDPE/EOC	81	89, 128	23	105
		EOC	85	86	9	57
	600	HDPE	88	130	63	111
		HDPE/EOC	89	88, 127	25	106
		EOC	91	88	9	55

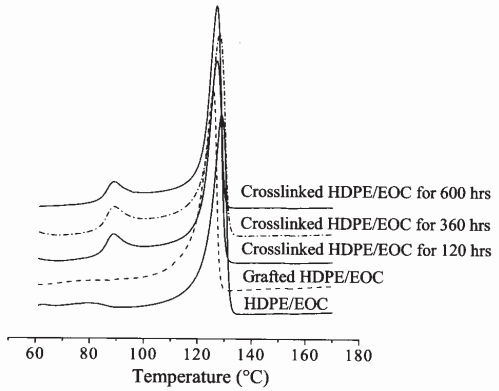


Figure 2 DSC thermograms of unmodified, grafted, and crosslinked HDPE/EOC

Thermal stability

One of the main aims of crosslinking polymer is to improve the polymer properties, in particular, high temperature properties. In this study, the thermal stability of various crosslinked samples was investigated and reported in a term of maximum decomposition temperatures (T_d). Figure 3 shows TGA thermograms of HDPE obtained under various environmental conditions at a heating rate of 20°C.min^{-1}. It can be seen that the T_d of HDPE has occurred at a temperature of 484°C in a nitrogen environment The T_d values are much lower in air (469°C) and oxygen (413°C) environments. This is owing to the well-known action of oxygen in reducing the stability of polymer bonds when temperature increases.

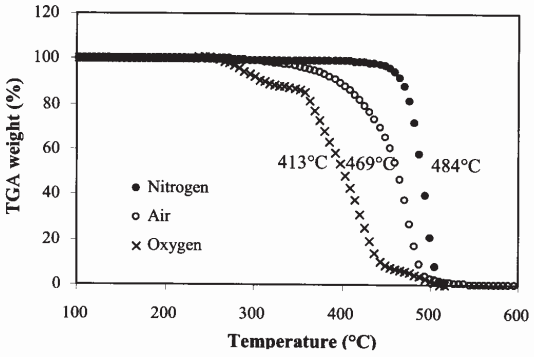


Figure 3 TGA thermograms of unmodified HDPE under various ambient gases

Table 2 The maximum decomposition temperatures (T_d) of unmodified, grafted, and crosslinked HDPE and HDPE/EOC samples under oxygen and nitrogen atmosphere

Table 2 summarises the effect of silane crosslink on thermal decomposition temperature of HDPE and its blends. Significant improvement in thermal stability of HDPE by silane crosslinking can be clearly observed from the TGA experiments in oxygen atmosphere. In the other words, the thermal oxidative stability of HDPE can be improved by silane crosslinking. For example, the silane crosslinked HDPE containing around 80% gel has the T_d value of 449°C which is 30°C higher than the unmodified one. Similar trend is found for the blend systems but the incorporation of EOC gives the blends with slightly lower T_d than the unblended samples. No effect of silane crosslink on T_d of HDPE can be observed when performing the TGA analysis in nitrogen atmosphere. However, in the case of crosslinked HDPE/EOC blends, slight enhancement in thermal stability is observed.

System	Time of crosslink reaction (hrs)	Samples	T_d (°C)	
			Oxygen atmosphere	Nitrogen atmosphere
Unmodified	0	HDPE	413	484
		HDPE/EOC	412	477
Grafted	0	HDPE	414	484
		HDPE/EOC	414	478
Crosslinked	120	HDPE	440	489
		HDPE/EOC	441	482
	360	HDPE	448	488
		HDPE/EOC	441	484
	600	HDPE	449	488
		HDPE/EOC	446	484

4. Conclusions

The effects of silane-grafting and water-crosslinking on the thermal properties of HDPE, EOC, and its blends were studied using DSC and TGA techniques. DSC results indicate that ethylene copolymer does not affect the crystallisation and melting behaviours of HDPE. T_m and % χ_C hardly change upon crosslinking. The silane-crosslinked materials are able to maintain their crystal structure in the system. TGA analysis shows that the thermal oxidative stability of HDPE and its blends can be improved by introducing a silane crosslink network to the systems.

References

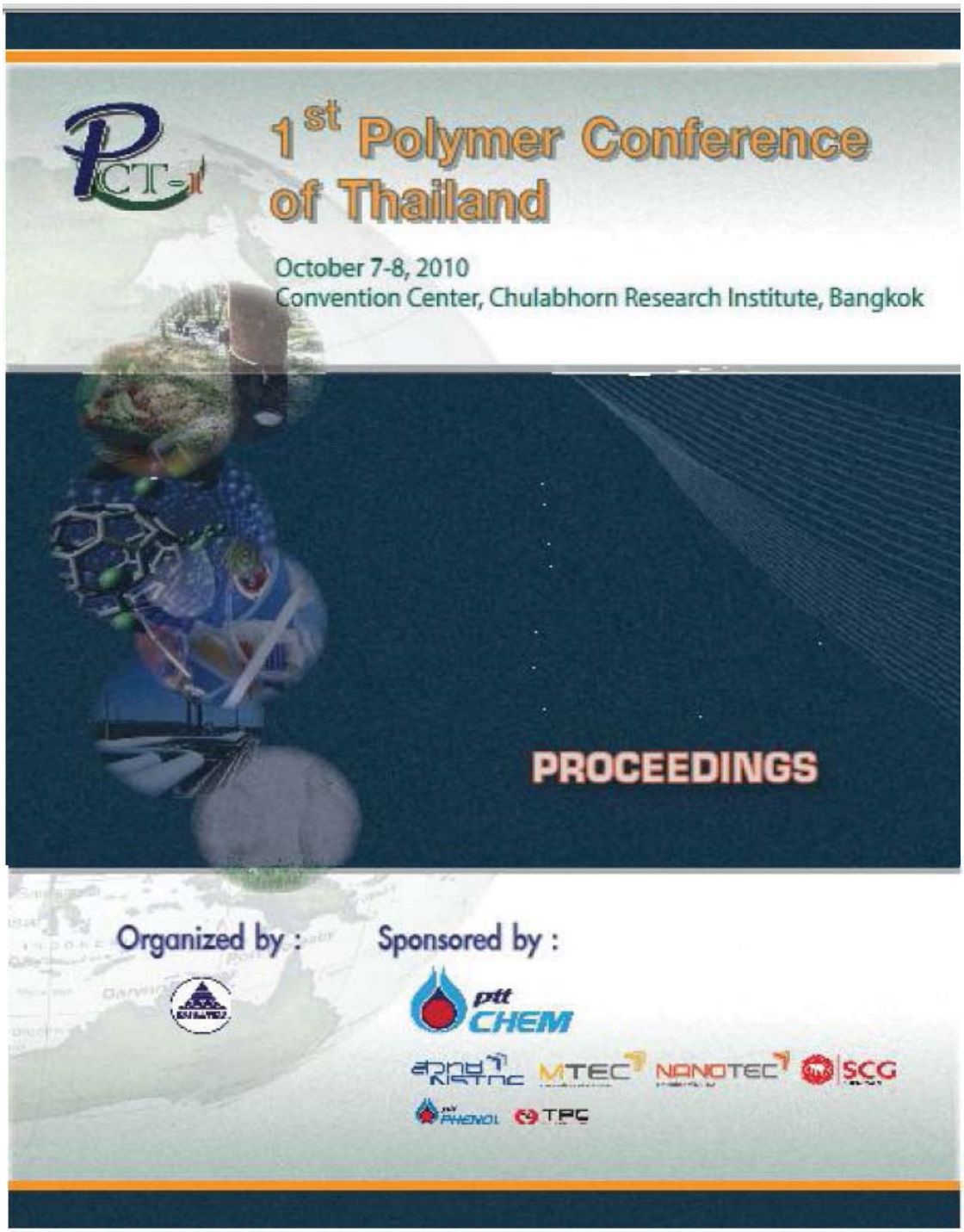
1. Ritums JE, Mattozzi A, Gedde UW, Hedenqvist MS, Bergman G, Palmlof M. *J Polym Sci Part B: Polym Phys* 2006; **44**: 641–648.

2. Kamphunthong W, Sirisinha K. *J Appl Polym Sci* 2008; **109**:2347-2353.

3. Sirisinha K, Chimdist S. *Polym Test* 2006; **25**: 518–526.

4. Sirisinha K, Mekasawat D. *J Appl Polym Sci* 2004; **93**:1179-1185.

5. Bensason S, Minick J, Moet A, Chum S, Hiltner A, Baer E. *J Polym Sci, Part B: Polym Phys* 1996; **34**: 1301-1315.


1st Polymer Conference of Thailand
October 7-8, 2010
Convention Center, Chulabhorn Research Institute, Bangkok
PROCEEDINGS
Organized by :
Sponsored by :
ptt CHEM
MTEC
NANOTEC
SCG
TPC

PS-OP-03

Utilization of Silane-crosslinked Polymer Waste as Additive for High-Density Polyethylene

Phawitporn Chuaythong[1] and Kalyanee Sirisinha[2]

Department of Chemistry, Faculty of Science, Mahidol University, Phuttamonthon 4 Road

Salaya, Nakhon Pathom 73170, Thailand

Phone 0-2441-9816 ext 1148, Fax. 0-2441-0511 E-Mail: [1] au_psu766@hotmail.com, [2] sckpr@mahidol.ac.th

Abstract

Management of solid waste is an important worldwide problem. Crosslinked polymers are particularly problematic for recycling. Silane-crosslinked polyethylenes are widely used in the production of insulation materials, crude-oil pipes and hot-water pipes. The production process involves melt-grafting of polymers with an alkoxysilane, followed by crosslinking of the polymer products with water or moisture. During the production, silane crosslinked wastes cannot be totally eliminated. In this study, efforts have been made in utilizing the polymer wastes from the silane-crosslink process as additive for enhancing the properties of high-density polyethylene (HDPE). The silane-crosslinked materials with different degree of crosslinking were prepared. The partially crosslinked materials were then melt-mixing with HDPE in a twin-screw extruder. The crosslink content (from 0-70%gel) in the crosslinked materials and their loading (from 0-50 % wt) in HDPE were investigated for their effects on tensile and thermal properties of the blends.

The results showed that the crosslinked materials with a gel content of up to 60% were successfully melt-blended with HDPE in a conventional extruder. A systematic improvement in tensile modulus and an increasement in heat distortion temperature (HDT) of the blends were observed as the content of the crosslinked materials in the blends increased. The effect of crosslinked materials on those aspects was more pronounced when the content of gel in the crosslinked materials was higher than 50 %.

Keywords: Silane, Crosslink, Recycling, Blend, Polyethylene, Property

1. Introduction

The primary reason to crosslink polyethylene (PE) is to raise the thermal stability of the material under load. Crosslinked PE is produced by different techniques, i.e. chemical crosslinking, electron beam radiation and silane - water crosslinking. Silane-water crosslinking is a widely used technique in crosslinking PE because of its several advantages, such as easy processing, low capital investment, favorable properties in the processed materials and low cost [1]. Silane-crosslinked PEs are used in the production of insulation materials, crude-oil pipes and hot-water pipes [2]. The production process involves melt-grafting of polymers with an alkoxysilane, followed by crosslinking of the polymer products with water or moisture. Recycling of crosslinked materials, including HDPE, are generally thought to be difficult using a simple heating procedure, because of the presence of three-dimensional network structure which restricts the material from melting [3].

In this study, efforts have been made in utilizing the polymer wastes from the silane-crosslink process as additive for enhancing the properties of high-density polyethylene (HDPE). The silane-crosslinked materials with different crosslink contents were prepared. The partially crosslinked materials were then melt-mixing with HDPE in a twin-screw extruder. The tensile properties, thermal properties and morphology of the blends were investigated.

2. Experimental

2.1 Materials

High-density polyethylene (HDPE) with a MFI of 0.8 g.10 min^{-1}, is a main material used in this study. Vinyl trimethoxysilane (VTMS) is used as a grafting agent and dicumyl peroxide (DCP) is used as an initiator.

2.2 Preparation of crosslinked HDPE

The preparation of silane-water crosslinked HDPE was performed through two steps, consisting of the alkoxysilane grafting reaction of the HDPE and the crosslink reaction of the grafted polymer via hydrolysation and condensation of alkoxysilane groups. The first step was carried out in a twin-screw extruder. The HDPE pellets were tumble-mixed with 5 wt% VTMS and of 0.1 wt% DCP in a sealed container. The mixture was kept immediately under N_2 atmosphere and left standing overnight before the grafting process. The prepared mixture was then taken into the extruder for conducting the grafting reaction. The temperature profile from feed zone to die was set at 160, 200, 170, 170 and 170 °C, respectively. The screw speed of 30 rpm was controlled and the total residence time in the extruder was approximately 3 min.

To conduct a crosslink reaction, the grafted product was immersed into a hot water at 70°C for a specified time in order to produce partially crosslinked products (X-HDPE) with gel content in the range of 0-70%.

2.3 Preparation of HDPE/X-HDPE blend

The partially silane crosslinked HDPE (X-HDPE) was melt-mixing with a virgin HDPE in a twin-screw extruder. Their loadings were varied from 0-50 % wt. The temperature profile from feed zone to die was set at 160, 190, 200, 200 and 200°C, respectively. The screw speed was kept constant at 30 rpm.

2.4 Gel content determination

The gel content or insoluble fraction of crosslinked HDPE was determined according to ASTM D2765-95a by mass of polymer insoluble after extraction. The sample of about 0.3 g was wrapped in a 120-mesh stainless steel cage and extracted in boiled xylene containing 1% of antioxidant (Irganox 1010) for 6 hrs. After extraction, the cage was dried in a vacuum oven. The gel content was calculated using equation 1. At least three samples of each crosslinked polymer were used to yield three values and the averages of which were then reported.

$$\text{Gel content (\%)} = \frac{\text{final weight of dried gel}}{\text{initial weight of sample}} \times 100 \qquad (1)$$

2.5 Tensile testing

A 1 mm thick sheet was prepared using a compression moulding machine. The blend samples were heated at 190°C under the pressure of 15 MPa for 3 min. The compression moulded sheets were then cut into a dumbbell specimen. The test was performed using an Instron 5566 tensile testing machine at a crosshead speed of 50 $mm.min^{-1}$ with a load cell of 1 kN. At least 5 test specimens were used for each measurement.

2.6 Heat distortion temperature (HDT)

The heat distortion temperature (HDT) test was conducted using Ceast 6510 following ASTM D 648. A 3 mm thick rectangular bar was tested in the edgewise position with a load applied at its center to give a maximum fiber stress of 0.455 MPa. The specimen was immersed under load in a heat transfer medium (silicone oil) provided a heating rate of 2 $°C.min^{-1}$. The temperature of the medium is measured when the test bar has deflected 0.25 mm. This temperature was recorded as the deflection temperature under flexural load of the test specimen.

3. Results and discussion

3.1 Gel results

The relationship between the content of gel and the time of crosslinking is shown in Figure 1. The gel content in the silane-grafted sample is negligible. In the early stage of crosslinking process (0-24 h), the rate of crosslinking is

rather high. With increasing the time of crosslink, the gel content increases systematically and reaches the values of 81% after 600 hrs of crosslinking time. Increasing the crosslinking time further (beyond 600 hrs), the increase in the content of gel is very slight. After 1200 hrs of crosslinking time, the gel content of 82% is gained.

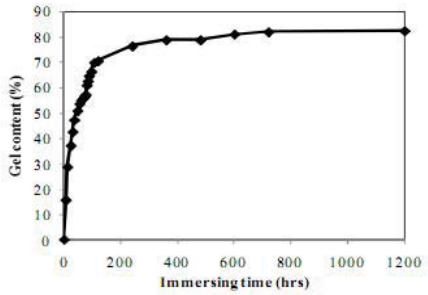


Figure 1. Effect of immersing time on gel content of silane- grafted HDPE

3.2 Tensile results

Figure 2 shows the tensile results of various HDPE/X-HDPE (80/20) blends. HDPE exhibits the % elongation at break of 965, tensile strength of 33.7 MPa, and modulus of 650 MPa. The incorporation of X-HDPE causes an increasing in modulus with a reduction of stress and strain at break. These effects are more pronounced when X-HDPE has gel contents higher than 60%. This indicates that the rigidity of X-HDPE affect strongly to the tensile properties of the blends, which serve to induce inter-lamellar linking of the amorphous domains via tie molecules [4]. It also results a reduction of strain at break.

The effects of blend composition on tensile properties of HDPE/X-HDPE blends are given in Figure 3. The blend compositions show a strong impact on tensile modulus but a slight effect on tensile strength and strain at break. An increase in the amount of X-HDPE in the blends results in a systematic increase in tensile modulus. The magnitude of property changes depends strongly on the content of crosslink portion or gel in the X-HDPE component. The incorporation of 30 wt% of X-HDPE with 70% gel, for example, results in a blend of 62 % increase in modulus with 89% reduction in elongation compared with virgin HDPE.

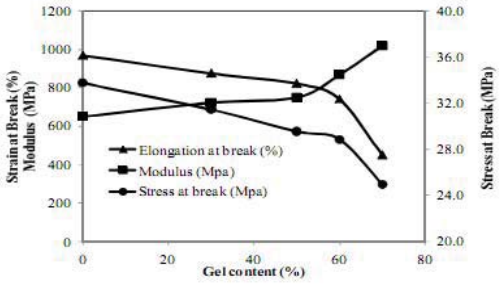


Figure 2. Effect of gel content in X-HDPE on tensile properties of HDPE/X-HDPE (80/20) blend

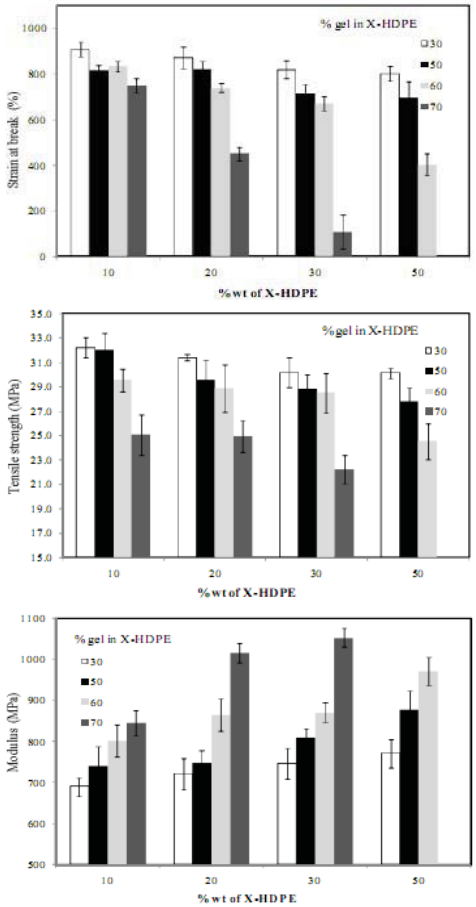


Figure 3. Tensile strength, strain at break and modulus of HDPE/X-HDPE

3.3 Heat distortion temperature (HDT)

The heat distortion temperature (HDT) results of HDPE/X-HDPE are presented in Figure 4 and 5. The HDT value of virgin HDPE is 67 °C. The addition of crosslinked materials causes an increase in HDT by 4.0, 10.0, 16.7 and 24.9% when using the X-HDPE which contains the content of gel of 30, 50, 60 and 70% respectively. The increase in HDT values of blends after the incorporation of X-HDPEs is primarily due to the presence of a high HDT component in the systems.

Figure 5 shows the effect of blend composition on the HDT of HDT/X-HDPE (with 60% gel). A systematic increase in the HDT values is observed as the content of X-HDPE in the blends increases. The addition of 10, 20, 30 and 50% of X-HDPE leads to an increase in the HDT by 8, 17, 25, 29 and 44% respectively compared to virgin HDPE.

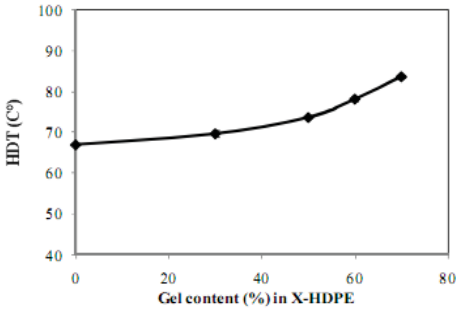


Figure 4. HDT of HDPE/X-HDPE (80/20) blend of various crosslink contents

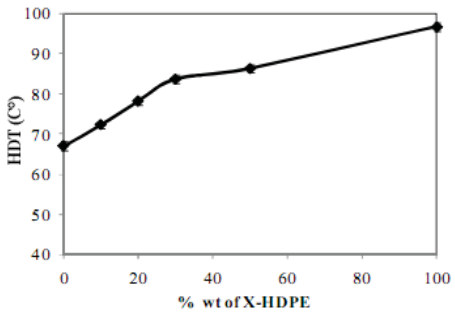


Figure 5. HDT of HDPE/X-HDPE (with 60% gel) blends of various compositions

4. Conclusions

The various HDPE blends containing silane crossinked materials were successfully prepared. Improvement in polymer modulus and thermal stability was achieved by incorporation of silane crosslinked polymer, while reduction in elongation at break and stress at break were observed. Crosslinked content plays major roles on blend properties whereas composition shows minor effects.

Acknowledgement

The Thailand Research Fund and the Research and Development Centre for Thai Rubber Industry (RDCTRI) are gratefully acknowledgement.

References

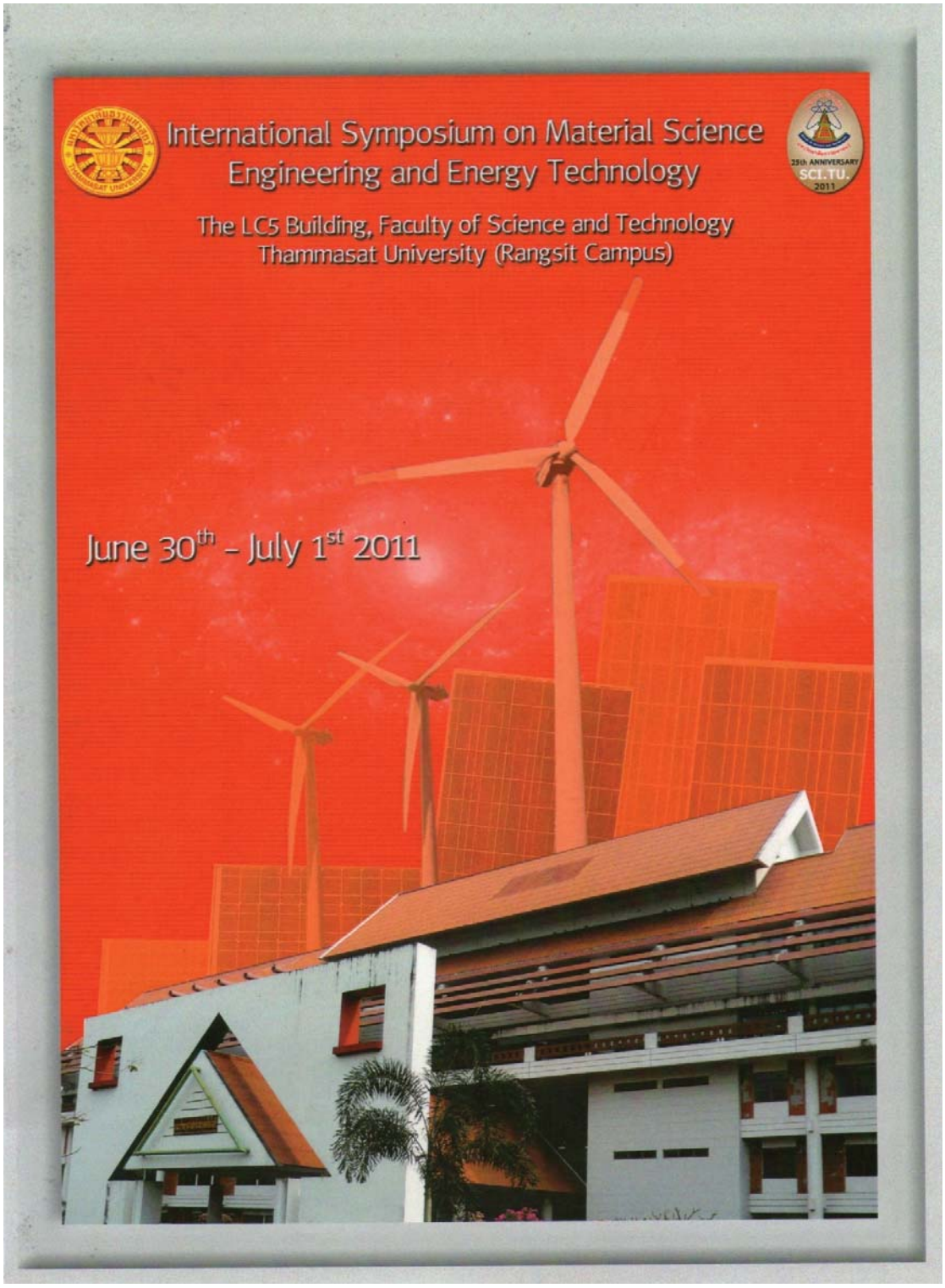
[1] Z. Guoqiang, W. Genlin, Z. Jun, W. Ping, and J. Pingkai, *J Appl Poly Sci* 2006, **102**, 5057–5061.

[2] H. Azizi, J. Morshedian, *J Vinyl Addit Technol* 2009, **15**, 184-190.

[3] S. Tokuda, S. Horikawa, *Furukawa Rev* 2003, **23**, 88-93.

[4] S.M. Kurtz, L.A. Pruitt, *Biomaterials* 1999, **20,** 1449–1462.

(เอกสารแนบ 6)


International Symposium on Material Science
Engineering and Energy Technology
The LC5 Building, Faculty of Science and Technology
Thammasat University (Rangsit Campus)
June 30th - July 1st 2011
25th ANNIVERSARY
SCI.TU.
2011

O04-016

Effect of silane-crosslinked polymer waste on thermal and impact properties of high-density polyethylene

Phawitporn Chuaythong[1] and Kalyanee Sirisinha[2*]

Department of Chemistry, Faculty of Science, Mahidol University
Phuttamonthon 4, Salaya, Nakhon Pathom 73170, Thailand

Abstract

Nowadays, silane-crosslinked polyethylenes are widely used in various applications. As a result, a large amount of crosslinked polymer waste is produced. This study focused on the utilisation of silane-crosslinked polymers in the production of high-density polyethylene (HDPE) blends. The effects of silane- crosslinked materials on the thermal and impact properties of HDPE are reported. FTIR revealed the presence of silane in the grafted HDPE. Blend composition played strong role in those properties.

1. Introduction

Crosslinked polymers are widely used in various applications such as cable insulation, crude oil pipe and hot-water pipe. Crosslinked polyethylene (PE) can be produced by a number of techniques, such as chemical crosslinking, electron beam radiation and silane-water crosslinking [1]. Nowadays, silane-water crosslinking is a widely used technique in crosslinking PE because of its several advantages, such as easy processing, and low capital investment. The production process involves melt-grafting of polymers with an alkoxysilane, followed by crosslinking of the polymer products with water or moisture [2]. The mechanisms of silane-grafting and crosslink reaction of PE are shown in figure 1. The grafting reaction is initiated by the use of organic peroxide. The silane-grafted polymers obtained are crosslinked through hydrolysation of alkoxysilane group. The crosslinking reaction takes place when the hydroxyl groups on the chains recombine through a condensation step, providing siloxane (Si-O-Si) linkages. During the production, silane crosslinked wastes cannot be totally eliminated. In this study, the polymer wastes from silane crosslinking process were recycled by blending them with virgin high-density polyethylene (HDPE). The aim of the work was to study the effects of partially silane- crosslinked materials on the thermal and impact properties of high-density polyethylene (HDPE).

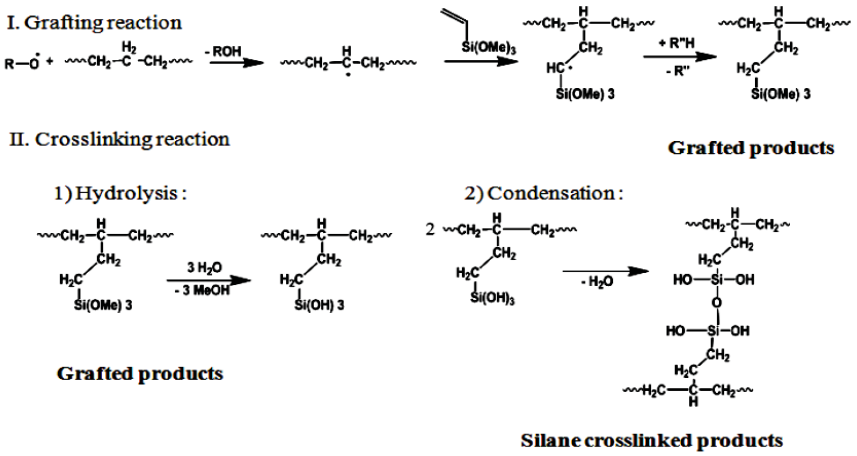


Figure 1 Silane-water crosslink reactions of PE

2. Experimental

2.1 Materials

High-density polyethylene (HDPE) with a MFI of 0.8 g.10 min^{-1}, was the main material used in this study. Vinyl trimethoxysilane (VTMS) was used as a monomer and dicumyl peroxide (DCP) was used as an initiator for the silane grafting reaction

2.2 Preparation of silane-crosslinked HDPE

The preparation of silane-water crosslinked HDPE was performed through two steps, i.e. silane grafting reaction of the HDPE and the crosslink reaction of the grafted products. The first step was carried out in a twin-screw extruder. The HDPE pellets were tumble-mixed with 5 wt% VTMS and of 0.1 wt% DCP in a sealed container. The mixture was kept immediately under N_2 atmosphere and left standing overnight before the grafting process. The prepared mixture was then taken into the extruder for conducting the grafting reaction. The grafting temperatures were in the range of 160-200°C. The screw speed of 30 rpm was controlled and the total residence time in the extruder was approximately 3 min. To conduct a crosslink reaction, the grafted product was immersed into a hot water at 70°C for a specified time in order to produce partially crosslinked polymers (XE) with gel content in the range of 0-70%.

2.3 Preparation of HDPE/XE blends

The silane crosslinked HDPE (XE) was melt-mixing with a virgin HDPE in a twin-screw extruder. The contents of XE in the blends were varied from 0-50 % wt. The temperature profile from feed zone to die was set at 160, 190, 200, 200 and 200°C, respectively.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of silane-grafted HDPE and silane crosslinked HDPE were recorded in the transmission mode at a resolution of 4 cm^{-1} for 16 scan over the range of 4000 to 600 cm^{-1} wave number. Film samples of approximately 50 μm thick were prepared by hot pressing the polymers at 190 °C. The films were washed with an excess amount of acetone to remove any unreacted silane and peroxide residuals. The degree of grafting was reported in a term of

grafting index (GI), calculated from the relative intensity of absorption peak of methoxysilane (Si-OCH_3) groups at 1092 cm^{-1} to that of the reference peak of methyl (-CH_3) groups at 1377 cm^{-1}.

2.5 Different scanning calorimetry (DSC)

The thermal behaviours of samples were studied by a Perkin-Elmer DSC-7. The samples were heated under nitrogen atmosphere from 50 to 170 °C at a scan rate of 20 °C.min^{-1}. The temperature was then maintained at 170 °C for 5 min before cooling to 50 °C at the same rate. The melting and crystallisation temperatures were examined. The percentage of crystallinity (%χ_c) was then calculated using equation 1.

$$\%\chi_c = \frac{\Delta H_f}{\Delta H_{f100}} \times 100 \quad (1)$$

where: ΔH_f is the enthalpy of fusion of the samples ($J.g^{-1}$)

ΔH_{f100} is the enthalpy of fusion of a perfectly crystalline polyethylene (100% crystallinity polyethylene) which is equal to 290 $J.g^{-1}$ [3].

2.6 Heat distortion temperature (HDT)

The HDT test was conducted using Ceast 6510, following ASTM D 648. A 3 mm thick rectangular bar was tested in the edgewise position with a load applied at its center to give a maximum fiber stress of 0.455 MPa. The specimen was immersed under load in a heat transfer medium (silicone oil) provided a heating rate of 2 °C.min^{-1}. The temperature of the medium was measured when the test bar has deflected 0.25 mm. This temperature was recorded as the deflection temperature under flexural load of the test specimen.

2.7 Impact testing

The notched Izod impact test is a method for evaluating the relative toughness of engineering materials. The impact strengths of various HDPE/XE blends were investigated. At least six specimens were stamped cut from a 3 mm thick compression-mold sheet. The dimension of test specimens used was according to ASTM D256. The rule of mixture was applied to calculate the impact strength values of polymer blends as shown in equation 2.

$$P_b = f_1P_1 + f_2P_2 \quad (2)$$

where: P is impact strength of polymer, f is volume fraction, b is the blend and subscripts 1 and 2 refer to component 1 (HDPE) and component 2 (XE), respectively.

3. Results and discussion

3.1 Evidence of silane graft and crosslink information

Figure 2 shows the FTIR spectra of HDPE before and after grafting reaction. Pure HDPE shows characteristic peaks at 722, 1377 and 1465 cm^{-1} which assign to the CH_2 rocking, and CH bending of methyl and methylene groups, respectively. The introduction of VTMS into HDPE leads to the appearance of absorption bands at 798, 1092 and 1192 cm^{-1} which correspond to the absorption peaks of methoxysilane (Si-OCH_3) groups. After conducting a crosslink reaction, the crosslink network was formed. The relationship between the content of gel and the time of crosslinking is shown in Figure 3. The result shows the increasing of the content of gel when the crosslinking time is increased. The samples with crosslink content ranged from 0-70%gel were used in the preparation of HDPE blends. The sample code and base characteristics of crosslinked materials are shown in Table 1.

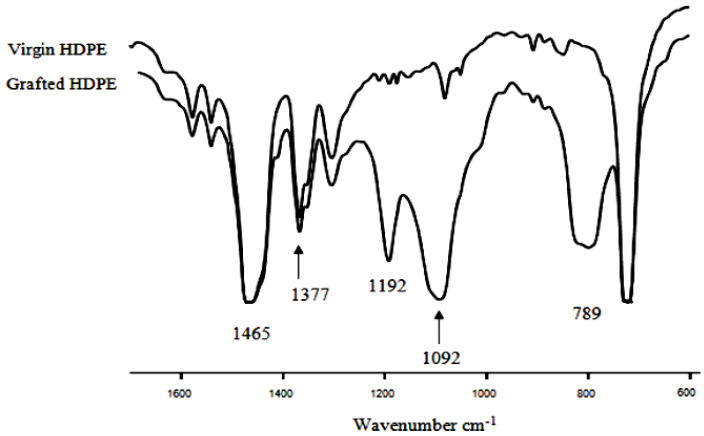


Figure 2 FTIR spectra of HDPE and silane-grafted HDPE

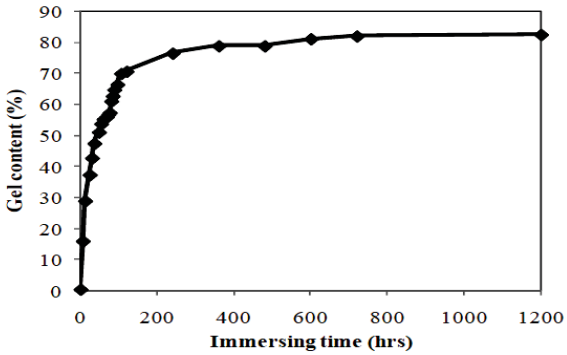


Figure 3 Effect of crosslinking time on gel content of crosslinked HDPE

Table 1 Sample code and characteristics of crosslinked samples (XE)

Sample code	% gel in XE	T_m (°C)	T_c (°C)	$T_{c\ onset}$ (°C)
HDPE	0	133	112	116
XE30	30	132	111	117
XE50	50	130	114	118
XE60	60	131	114	119
XE70	70	132	112	118

3.2 Effect of the content of crosslink in HDPE on the properties of HDPE/XE blend

Table 2 summarises the effects of the content of crosslink in XE on the melting and crystallisation behaviours, and HDT of HDPE/XE (80/20) blends. The melting temperature (T_m), crystallisation temperature (T_c) and onset temperature of crystallisation ($T_{c\ onset}$) of HDPE hardly change with the addition of XE, while the crystallinity slightly deceases. The HDT value of virgin HDPE is observed at 67 ◦C. The addition of XE leads to an increase in HDT by 4.0, 10.0, 16.7 and 24.9% when using the XE which contains the content of gel of 30, 50, 60 and 70% respectively. The increase in HDT values of blends after the incorporation of XE is primarily due to the presence of a high HDT component in the systems.

Table 2 Thermal properties of various HDPE/XE (80/20) blend

Sample code	% gel in XE	T_m (°C)	T_c (°C)	$T_{c\ onset}$ (°C)	% χc	HDT (°C)
Virgin HDPE	0	133	112	116	63	67 ± 0.2
HDPE /XE30	30	133	113	116	53	69 ± 0.4
HDPE /XE50	50	133	113	116	58	73 ± 0.5
HDPE /XE60	60	133	112	116	57	76 ± 0.5
HDPE /XE70	70	133	112	116	61	78 ± 0.2

Figure 4 demonstrates the effect of XE on the impact strength of various HDPE/XE (80/20) blends. Virgin HDPE exhibits the impact strength of 36.02 KJ/m^2. The incorporation of XE results in an improvement in impact strength of the blends. The effect of XE is more pronounced when XE has gel contents higher than 40%. The impact strength becomes unchanged when the gel content of XE is higher than 60 %.

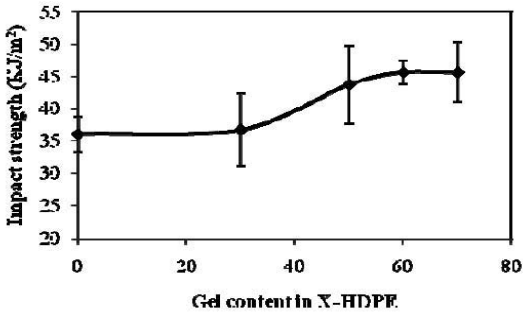


Figure 4 Impact strength of HDPE/XE (80/20) blends of various crosslink contents

3.3 Effect of blend composition on the thermal properties of HDPE/XE60 blends

Effects of blend composition on the melting and crystallisation behaviours and HDT of HDPE/XE60 blend are summarized in Table 3. The T_m, T_c, $T_{c\ onset}$ and % crystallinity seem to be relatively unchanged for all composition. In contrast, a systematic increase in the HDT values is clearly observed as the content of XE60 in the blends increases. The addition of 10, 20, 30 and 50% of XE leads to an increase in the HDT by 8, 17, 25, 29 and 44%, respectively compared to virgin HDPE.

Table 3 Effect of blend composition on the thermal properties of HDPE/XE60 blend

HDPE/XE60	% gel in XE	T_m (°C)	T_c (°C)	$T_{c\ onset}$ (°C)	% χ_c	HDT (°C)
100/0	60	133	112	116	63	67 ± 0.2
90/10	60	133	113	116	60	72 ± 0.4
80/20	60	133	113	117	58	78 ± 0.2
70/30	60	132	112	116	57	83 ± 1.2
50/50	60	133	112	116	63	86 ± 0.5
0/100	60	132	112	118	63	97 ± 0.5

Figure 5 shows the plot of impact strength as a function of the amount of XE60 in the blends. The experimental data are also compared to those calculated from the rule of mixture. A significant increase in impact strength is clearly observed as the amount of XE in the blends increases. The experimental data seems to be higher than the predicted ones.

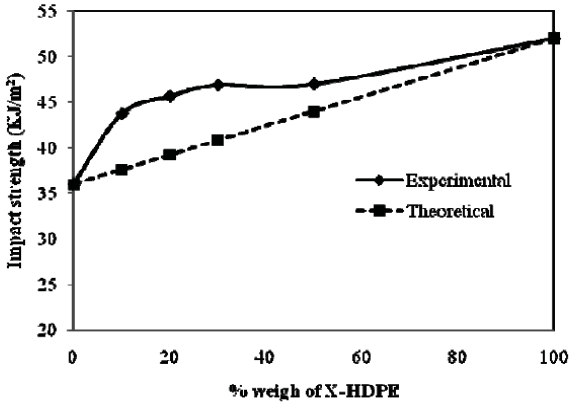


Figure 5 Experimental and theoretical impact strength of various HDPE/XE60 blends

4. Conclusions

The silane-grafted and crosslinked HDPE were prepared. The silane-crosslinked materials were then blended with virgin HDPE. The results showed a significant improvement in impact strength and HDT of the blends by the incorporation of silane-crosslinked polymers. The crosslinked materials, however, showed inevitable effect on the crystallization behaviours of HDPE.

Acknowledgements

The Thailand Research Fund (TRF) and the Research and Development Centre for Thai Rubber Industry (RDCTRI) are gratefully acknowledged.

References

[1] S. M. Tamboli, S. T. Mhaske, D. D. Kale, Crosslinked polyethylene, Indian J Chem Technol, 2004, 11, 853-864.

[2] K. Sirisinha, S.Chimdist, Comparison of techniques for dictating crosslinking in silane-water crosslinked materials, Polym. Testing, 2006, 25, 518-526.

[3] M. Lazar, R. Rado, J. Rychly, Crosslinking of polyolefins, Adv Polm Sci, 1990, 95, 149-197.