

Silane Grafting Reactions of LDPE, HDPE, and LLDPE

YEONG-TARNG SHIEH, CHIH-MING LIU

Department of Chemical Engineering, National Yunlin University of Science and Technology, Touliu, Yunlin, Taiwan 640, R.O.C.

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ABSTRACT: Vinyl trimethoxysilane and vinyl triethoxysilane grafting reactions, induced by dicumyl peroxide, of LDPE, HDPE, and LLDPE were investigated. The apparent activation energy of vinyl trimethoxysilane grafting reactions was positive when the reactions were induced by 0.2 phr of the peroxide. The apparent activation energies were negative when 0.05, 0.1, 0.15, and 0.25 phr of peroxide were used. The extents of vinyl trimethoxysilane grafting reactions of polyethylenes were in the order of LLDPE > LDPE > HDPE, although the extents of peroxide cross-linking were in the order of LDPE > LLDPE > HDPE. As compared with vinyl trimethoxysilane, vinyl triethoxysilane produced a relatively high extent of grafting reactions of LDPE but showed a relatively low rate of water cross-linking reactions of the silane-grafted LDPE. The investigation of effects of the amount of peroxide on the vinyl trimethoxysilane grafting reaction heats demonstrated that the extent of silane grafting reactions increased proportionally as peroxide was increased until a certain amount (the value was dependent on the amount of silane used). Beyond this amount of peroxide, the silane grafting did not increase, whereas the peroxide cross-linking appeared to increase significantly with increasing amounts of peroxide. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3404–3411, 1999

Key words: polyethylene; grafting reactions; silane; reaction heat; activation energy

INTRODUCTION

Polyethylene (PE) has long been known as an excellent dielectric for use as an insulation material in power cable constructions. It has the advantages of excellent electrical properties, excellent resistance to cold flow, ease of processing, adequate mechanical properties and, notably, excellent value (cost and performance). The major drawback of thermoplastic PE is its relatively low upper use temperature. By cross-linking the material, this temperature limitation is overcome and the upper use temperature is increased.

There are a variety of ways to achieve the cross-linking of PE.¹ PE has no functional groups that can provide cross-linking capability, such as the kind one finds in typical thermosetting resins. Hence, the cross-linking must be induced by the incorporation of another component. The use of silane grafting provides one of several ways of cross-linking. The way of making crosslinkable PE by silane grafting has gained much attention in recent years because of its various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials.

The most common silane used in the manufacture of silane crosslinkable PE is vinyl trimethoxysilane. This silane conventionally has been introduced into PE by melt grafting using a peroxide. In producing the crosslinkable silane-grafted PE, a peroxide is mixed with the silane and PE,

Correspondence to: Y.-T. Shieh.

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and all these components are compounded in an extruder at high temperature. The silane-grafted PE is then crosslinked through hydrolyzation of the methoxysilane groups with water, followed by condensation of the formed hydroxyl groups.

Polyethylenes include low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear-low-density polyethylene (LLDPE). These polyethylenes are distinguished by their densities resulting from different structures. LDPE has more branches than HDPE does. This discrepancy results from different manufacturing processes for these PEs. LLDPE is produced by copolymerizing ethylene monomer with a small amount of alkene comonomer, such as 1-butene, 1-hexene, or 1-octene. The three PEs are compared in terms of silane grafting reactions in this study.

There have been some articles²⁻⁸ published on the cross-linking of polyethylene. Sen and colleagues^{2,3} reported some kinetics data, studied by differential scanning calorimetry (DSC), X-ray diffractometer, and dynamic mechanical analysis, on silane grafting and moisture cross-linking of PE and ethylene propylene rubber. Kao and Phillips⁴ reported the crystallinity and other structural information, using DSC and X-ray diffractometer, of LDPE cross-linked by dicumyl peroxide. Hjertberg and colleagues⁹ and Bullen and colleagues⁵ studied the cross-linking reactions of ethylene-vinyl trimethoxysilane copolymers. The article by Bullen and coworkers,⁵ cross-linking of the copolymer during high-temperature melt processing, was investigated using melt rheological and infrared spectroscopic techniques, whereas in the articles by Hjertberg and colleagues⁹ and Palmlof and colleagues,⁶ the kinetics of cross-linking of the copolymer when reacted with water was followed by measuring gel content and by determination of the content of different groups ($-\text{Si}-\text{OCH}_3$, $-\text{Si}-\text{OH}$, and $-\text{Si}-\text{O}-\text{Si}-$), using Fourier transform infrared (FTIR) spectroscopy. Narkis and coworkers⁷ presented studies on the cross-linking progress in different environments at various temperatures. Some properties, including mechanical properties of the silane-grafted, moisture-crosslinked polyethylene, were followed as a function of cross-linking conditions. Turcsanyi and coworkers⁸ studied structure/property relationships of silane-modified and cross-linked linear polyethylene, using DSC and a thermomechanical analyzer.

The aim of this work was to study the silane grafting reactions of various polyethylenes, in-

cluding LDPE, HDPE, and LLDPE. The silanes used included vinyl trimethoxysilane and vinyl triethoxysilane. The peroxide used was dicumyl peroxide. Based on data of reaction heats and activation energies of grafting reactions, the mechanisms of these reactions, as a function of the amount of silane used, the amount of peroxide used, the type of polyethylene, and the type of silane can be understood incrementally.

EXPERIMENTAL

Materials

All materials were used as received. LDPE (H0100) was received from Asia Polymer Corporation (Taipei, Taiwan) with a melt index (ASTM D1238) of 0.5 and a density (ASTM D1505) of 0.922 g/cm³. HDPE (LH606) was received from USI Far East Corporation (Taipei, Taiwan) with a melt index of 1.0 and a density of 0.961 g/cm³. LLDPE (AL3108ZD) was received from Exxon Corporation with 3.5 mol % of 1-hexene in the copolymer, a melt index of 0.8, and a density of 0.921 g/cm³. The peroxide used was dicumyl peroxide supplied by Aldrich Chemical Company (Milwaukee, WI). The silanes used included vinyl trimethoxysilane and vinyl triethoxysilane, both supplied by Tokyo Kasei Kogyo Co (Tokyo, Japan).

Sample Preparation

Polyethylene pellets of three kinds were individually crushed to powder, with a particle size between 30 and 60 mesh. These powders were then individually mixed with a previously prepared acetone solution of silane and peroxide. The amount of peroxide was varied from 0 to 0.3 phr (part of reagent per hundred parts of PE), whereas the amount of silane was 0 to 25 phr, depending on the experiment. Acetone in the uniform slurry was removed by evaporating the slurry in an oven at 75°C for 30 min. The content of silane and peroxide in a PE powder thus was able to be determined by weighing the dried PE powder sample. This process has been determined to be effective in providing uniform silane and peroxide dispersion on the surface of PE powder, with negligible residual acetone. Samples for FTIR measurements were prepared by making films of the dried PE powder in a hot press at a certain temperature for a certain time. Samples

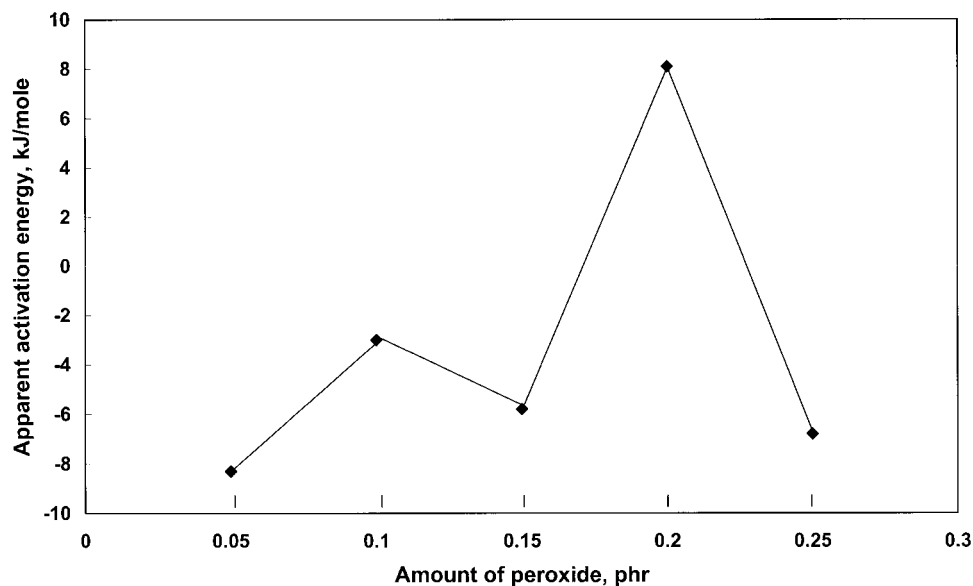


Figure 1 Apparent activation energies for grafting reactions of LDPE with 5 phr of vinyl trimethoxysilane as a function of amount of dicumyl peroxide used.

for DSC measurements were prepared by encapsulating 5–10 mg of the dried PE powder in hermetically sealed aluminum pans.

Analysis

Grafting reactions of silanes onto PEs were performed isothermally (170, 190, and 210°C) for 2 min in a hot press and dynamically on DSC (TA Instruments, New Castle, DE, DSC 2010) at a heating rate of 20°C/min from room temperature to 260°C under nitrogen. The extent of grafting reactions was analyzed on FTIR (BIO-RAD FTS155) using film samples, made in the hot press, as a function of temperatures. The grafting reactions were monitored in situ on DSC, and the grafting reaction heats were thus obtained. The degrees of silane-grafted and water-crosslinked PE samples were determined by extractions of the uncrosslinked portion in samples, using decalin refluxing at about 190°C for 6 h.

RESULTS AND DISCUSSION

In our previous article,¹⁰ vinyl trimethoxysilane grafting reactions, induced by a fixed amount of dicumyl peroxide at 0.2 phr, onto LDPE, was demonstrated and quantitatively analyzed for the extent of the reactions, using FTIR. In the article,¹⁰ an apparent activation energy of the silane grafting reactions was obtained by performing the

grafting reactions at various temperatures and applying the Arrhenius equation for the plot of the extent of the reactions as a function of reciprocal absolute temperatures.

The effects of the amount of peroxide used on apparent activation energies of the grafting reactions were investigated in this study. The grafting reactions of LDPE were performed at 170, 190, and 210°C with 5 phr of silane and varying amounts of peroxide. Figure 1 shows the plot of apparent activation energies as a function of the amount of dicumyl peroxide used. From Figure 1, the apparent activation energies increase as the amount of peroxide used increases up to 0.2 phr but decrease as the amount of peroxide used increases over 0.2 phr. For 0.2 phr of peroxide used, an activation energy of 8.1 kJ/mol was observed. This positive apparent activation energy suggests that the extent of silane grafting reactions increases as temperatures increase. For 0.25, 0.15, 0.1, and 0.05 phr of peroxide used, however, the apparent activation energies of the grafting reactions were all negative, suggesting that the extent of silane grafting reactions decreases as temperatures increase.

The reason for causing such a dependence of the apparent activation energies on the amount of peroxide used was because the silane grafting reactions of LDPE included a series of reactions. These reactions included, first, reactions of peroxide with LDPE (or with the silane, which is not

likely because of a very low concentration of silane in the system compared with LDPE) to form polyethylene radicals, and, second, reactions of the formed polyethylene radicals with each other or with the silane molecules to form silane grafts on LDPE. These reactions appeared to be affected by the amount of peroxide used. In other words, the amount of radicals, which were formed by thermal decompositions of the peroxide, affected the reaction mechanisms and, thus, affected the overall (apparent) activation energy of the overall reaction investigated.

For a smaller amount of peroxide used, the reactions between the radicals and polyethylene molecules to produce polyethylene radicals were less significant. The reaction rates of peroxide with LDPE increased significantly when the temperature was increased. This led to significant cross-linking between the formed polyethylene radicals, whereas the increase in reaction rates between the formed polyethylene radicals and the silane was relatively insignificant. A negative apparent activation energy, thus, was observed for using a smaller amount of peroxide.

For a larger amount of peroxide used, e.g., 0.2 phr, the positive apparent activation energy for the overall silane grafting reactions suggests that the reactions of the formed polyethylene radicals with the silane are increased significantly by raising the temperature. A large amount of peroxide can produce a large amount of radicals that have an increasingly greater chance of reacting with each other to produce dead molecules and thus do not contribute to grafting reactions. By increasing the temperature, the chance of radicals attacking the silane was increased and led to an increase of the extent of silane grafting reactions. For an amount of peroxide used over 0.2 phr, e.g., 0.25 phr, a negative apparent activation energy was observed for the overall silane grafting reactions. This was perhaps due to significant peroxide cross-linking reactions between the peroxide and polyethylene, and the cross-linking reactions increased significantly as the temperature was increased. The increase, with increasing temperature, in the reactions between the formed radicals and the silane was relatively insignificant. The grafting reactions between polyethylene and the silane, thus, decreased as the temperature was increased, leading to a negative apparent activation energy for the grafting reactions.

The grafting reactions were monitored in situ using DSC at a heating rate of 20°C/min under nitrogen. In our previous article,¹⁰ vinyl trime-

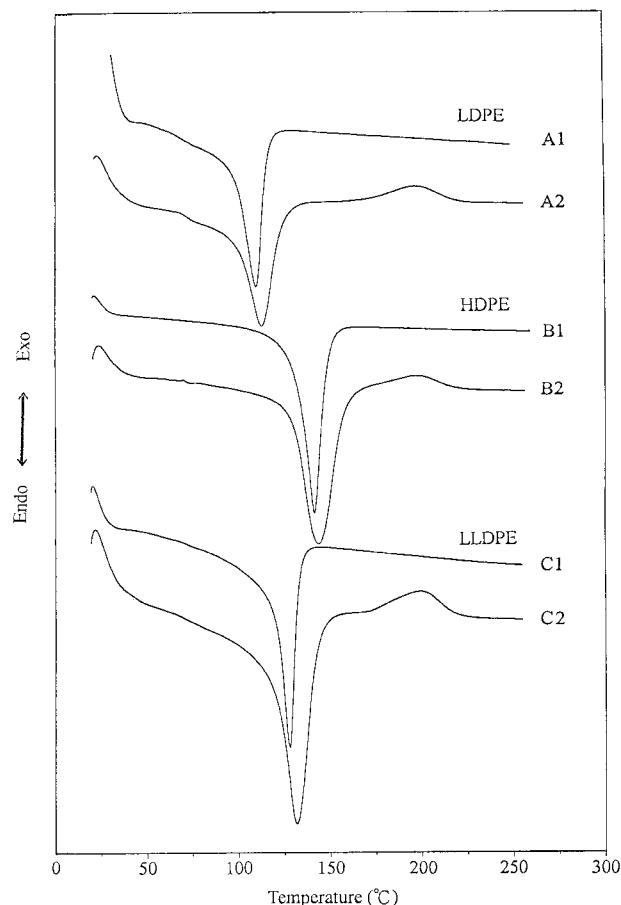


Figure 2 DSC traces at a heating rate of 20°C/min under nitrogen for samples without silane grafting reactions: (A1) LDPE, (B1) HDPE, (C1) LLDPE; for samples reacting with 0.2 phr of dicumyl peroxide and 17.5 phr of vinyl trimethoxysilane: (A2) LDPE, (B2) HDPE, (C2) LLDPE.

thoxysilane grafting reactions were demonstrated to be exothermic. An exothermic peak on the DSC thermogram between 150 and 230°C, with a peak value at about 190°C, was observed and was demonstrated to be due to the silane grafting reactions of LDPE, induced by 0.2 phr of peroxide. Figure 2 shows DSC traces at a heating rate of 20°C/min for samples LDPE, HDPE, and LLDPE for both before and after reactions with 0.2 phr of peroxide and 17.5 phr of silane. It should be noted that LDPE in this study was different from that in our previous article,¹⁰ in terms of melt index. The melt indices of LDPE, HDPE, and LLDPE were 0.5, 1.0, and 0.8, respectively, in this study. Similar melt indices were selected to exclude the effects of molecular weights of the materials on silane grafting reactions. Although melting tem-

peratures were different between the three materials, the exothermic peaks were similar in terms of the peak values, as shown in Figure 2. These exothermic peak values were all at about 190°C. The temperature to produce silane grafting reactions was independent of the types of polyethylenes and was determined mainly by the types of peroxides. Traces A2, B2, and C2 in Figure 2 demonstrate silane grafting reactions with 17.5 phr of silane used for LDPE, HDPE, and LLDPE, respectively. The integrating areas under the exothermic peaks (i.e., the grafting reaction heats) were varied for these materials.

According to ref. 11, the number of chains branching per 1000 carbon atoms on the polymer main chain falls in the range of 20–50 for LDPE and LLDPE and in the range of 2–7 for HDPE, based on the densities of these materials. The length of the chain branching for LDPE is believed to be larger than that for LLDPE, using 1-hexene as a comonomer. Thus, LLDPE has a higher number of chains branching than LDPE has, because both LDPE and LLDPE have similar densities. Also, in ref. 11, HDPE has more vinyl residue on the polymer chain, although this material has less chain branching than LDPE and LLDPE. As a result, HDPE has the most allyl hydrogens among the three materials, whereas LLDPE has more hydrogens attached to tertiary carbons than LDPE has. Homolytic bond dissociation energies¹² for hydrogens attached to primary, secondary, tertiary, and allyl carbons are 410, 397, 385, and 368 kJ/mol, respectively. Thus, the least energy needed for a free radical to abstract hydrogen is from an allyl carbon among the four kinds of carbons. In spite of different structures among the three polyethylenes, an enthalpy change was not observed for the reactions between any type of polyethylene and peroxide, with an amount of up to 1 phr. The exothermic peaks in traces of A2, B2, and C2 in Figure 2 all resulted from the silane grafting reactions that were induced by 0.2 phr of peroxide. The grafting reaction heats (i.e., the extent of grafting) for the three polyethylenes reacting with 17.5 phr of silane were in the order of LLDPE > LDPE > HDPE. This suggests that LLDPE gave rise to the highest extent of grafting reactions and HDPE the least.

Figure 3 shows degrees of cross-linking, performed in boiled water, of three vinyl trimethoxysilane-grafted polyethylenes, as a function of cross-linking time. LDPE gave rise to the highest extent of peroxide cross-linking (i.e., the cross-

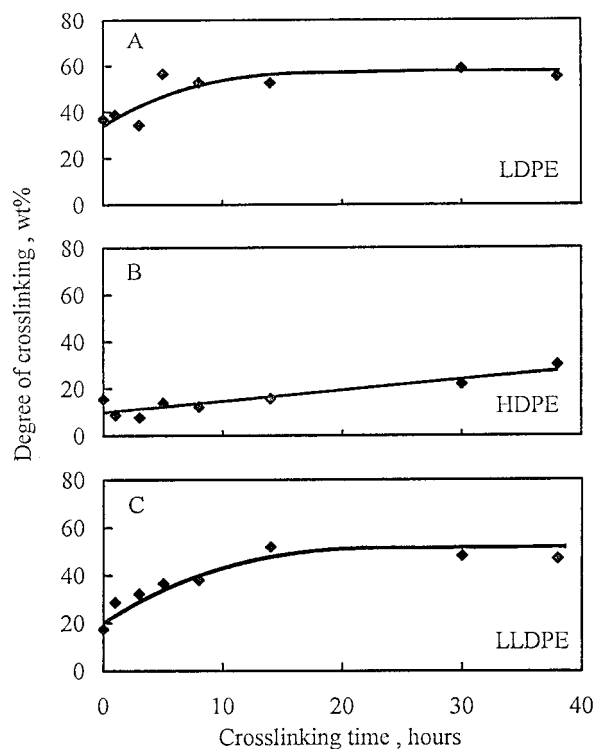


Figure 3 Degrees of cross-linking of the three polyethylenes that were grafted, induced by 0.2 phr of dicumyl peroxide, by 7 phr of vinyl trimethoxysilane at 170°C for 2 min, as a function of cross-linking time in boiled water: (A) LDPE, (B) HDPE, (C) LLDPE.

linking time in boiled water was 0 h) at about 40 wt %, whereas HDPE gave rise to the lowest extent at about 10 wt % and LLDPE at about 20 wt %. The extent of cross-linking of all three polyethylenes in boiled water increased as cross-linking time was increased. The increase in the extent of cross-linking in 14 h was the largest for LLDPE and the least for HDPE. This suggested that LLDPE had the highest extent of grafting and HDPE had the least. This was consistent with data in Figure 2, in which LLDPE showed the highest extent of silane grafting and HDPE showed the least. Figure 4 shows degrees of cross-linking of silane-grafted LDPE, induced by 0.2 and 0.05 phr, as a function of cross-linking time in boiled water. The lower amount of peroxide used gave rise to the lower extent of peroxide cross-linking.

Figure 5 demonstrates that the grafting reaction heats for the three materials studied increases as the amount of silane used increases. The data in plots of Figure 5 were fitted by straight lines, with slopes and intercepts for these

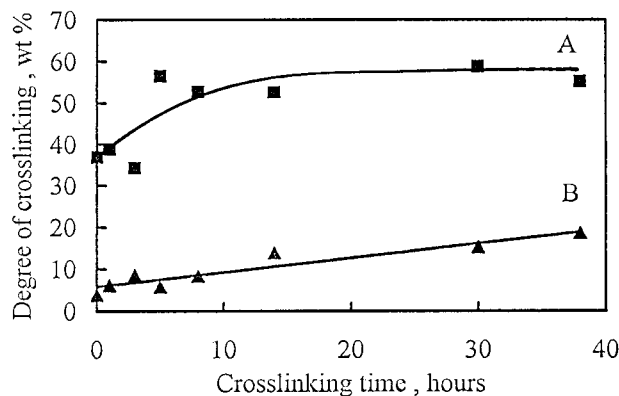


Figure 4 Degrees of cross-linking of LDPE that have been grafted by 7 phr of vinyl trimethoxysilane, induced by (A) 0.2 phr and (B) 0.05 phr of dicumyl peroxide at 170°C for 2 min, as a function of cross-linking time in boiled water.

lines being 0.65 and 3.69 for LDPE, 0.26 and 10.17 for HDPE, and 0.93 and 0.68 for LLDPE, respectively. The unit of the slopes is joules per 0.01 g of silane, whereas the intercept is joules per 0.002 g of peroxide. Thus, the reaction heats (kJ) of silane grafting induced by 0.2 phr of dicumyl peroxide, onto LDPE, HDPE, and LLDPE, were -9.63 , -3.85 , and -13.78 kJ per mole of silane used, respectively. The reaction heat of peroxide reacting with LDPE, HDPE, and LLDPE were -0.5 , -1.37 , and -0.09 kJ per millimole of peroxide used, respectively. In examining these exothermic reaction heats, however, no general correlation can be made between structures of polyethylenes and the reaction heats, apparently because of complicated reaction mechanisms in these reactions.

Vinyl triethoxysilane (VTES) was also used to study its grafting reactions induced by 0.2 phr of dicumyl peroxide onto LDPE and to investigate the effects of silane types on the grafting reactions in terms of reaction heats. Figure 6 shows a plot of grafting reaction heats as a function of amount of VTES used. The plot appears to be a fairly good fit, with a straight line that has a slope of 2.09 and an intercept of 5.98. Thus, the reaction heat of VTES grafting, induced by 0.2 phr of dicumyl peroxide onto LDPE per mole of VTES used, is -39.82 kJ, and the reaction heat per millimole of dicumyl peroxide used with LDPE is -0.81 kJ.

The reaction heat of peroxide reacting with LDPE was -0.5 kJ per millimole of dicumyl peroxide, as obtained previously in the presence of

VTMS (vinyl trimethoxysilane), which was close to -0.81 kJ, as obtained in the presence of VTES. Although different types of silanes were used, similar reaction heats of peroxide with LDPE were obtained. This suggested that the formed radicals from peroxide react mainly with polyethylene molecules. This finding was consistent with those in which a very low concentration of silane was used, compared with the concentration of LDPE in the system. The grafting reaction heats of LDPE with VTMS and VTES were -9.63 kJ (obtained previously) and -39.82 kJ, respectively, per mole of silane used. The difference in structure between two silanes was on the alkoxy groups. The formed radicals during grafting reactions of LDPE were believed to be reacting mainly with the reactive vinyl groups rather than with the alkoxy groups of the silanes. Grafting reaction

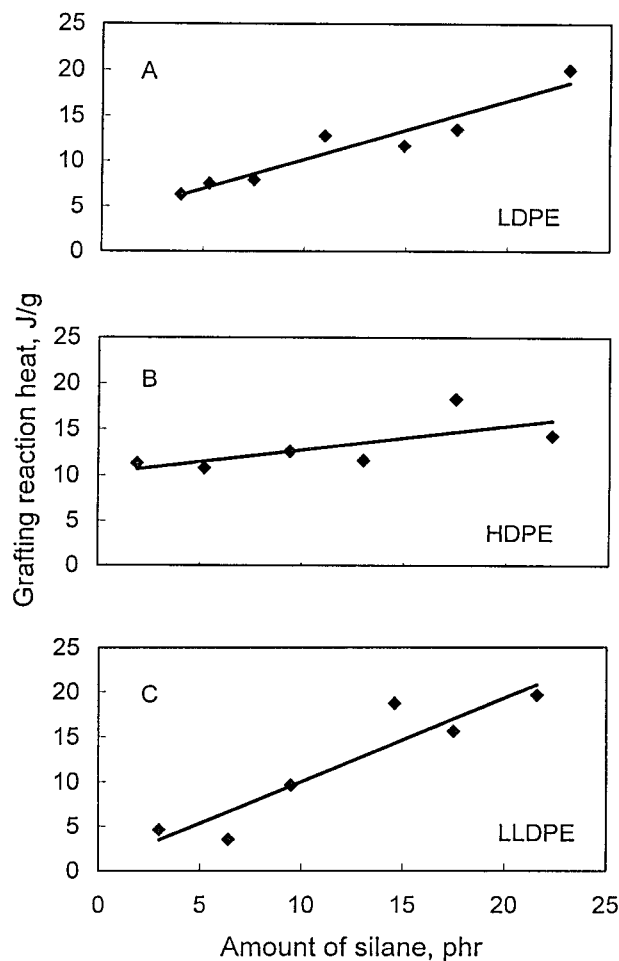


Figure 5 Vinyl trimethoxysilane grafting reaction heats of (A) LDPE, (B) HDPE, and (C) LLDPE, as a function of amount of silane used. The grafting reactions were induced by 0.2 phr of dicumyl peroxide.

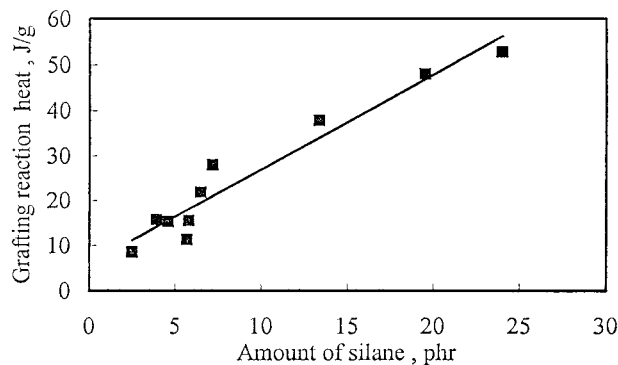


Figure 6 Vinyl triethoxysilane grafting reaction heats of LDPE, as a function of amount of silane used. The grafting reactions were induced by 0.2 phr of dicumyl peroxide.

heat which was four times greater for VTES than for VTMS, suggested that VTES gave rise to a higher extent of silane grafting than VTMS did. FTIR was used to analyze the extents of silane grafting reactions and demonstrated a higher extent from VTES. Figure 7 shows FTIR spectra of LDPE both for before and after silane grafting reactions with VTMS and VTES. From Figure 7, peaks at 1193 and 1092 cm^{-1} in spectra B were assigned to $\text{Si}-\text{O}-\text{CH}_3$, whereas peaks at 1167, 1082, 1105, and 958 cm^{-1} in spectra C were assigned to $\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$.¹³ The relative intensity of these assigned peaks to the intensity of the

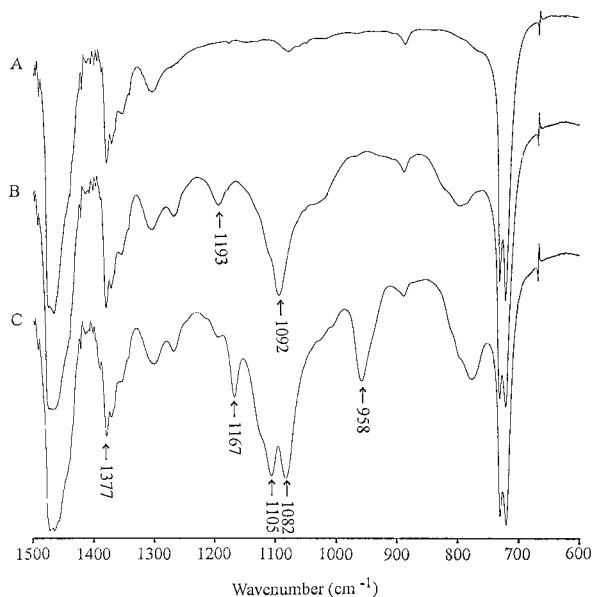


Figure 7 FTIR spectra of LDPE: (A) before grafting, (B) after grafting with vinyl trimethoxysilane, and (C) after grafting with vinyl triethoxysilane.

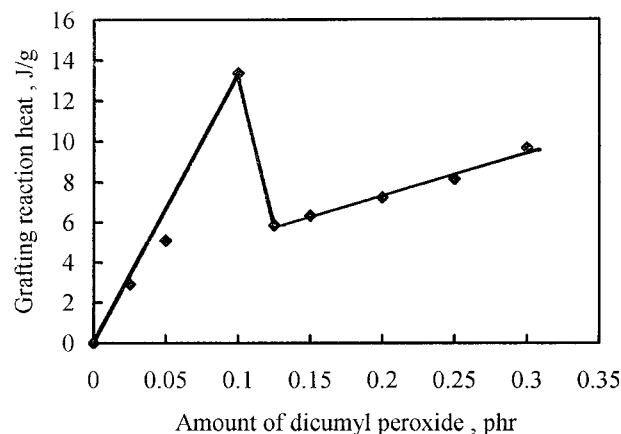


Figure 8 Silane grafting reaction heats of LDPE with 7 phr of vinyl trimethoxysilane, as a function of amount of dicumyl peroxide used.

peak at 1377 cm^{-1} can be used as an index of the extent of silane grafting reactions, if the peak at 1377 cm^{-1} , assigned to $-\text{CH}_3$, was used as an internal standard.¹⁰ The comparison between spectra B and C in Figure 7 demonstrates that VTES gave rise to a higher extent of silane grafting reactions of LDPE. This was consistent with the evidence from the grafting reaction heats. Degrees of cross-linking (not shown) of both VTES- and VTMS-grafted water-crosslinked LDPEs, however, were similar. It appeared that the ethoxy groups in VTES showed lower reactivity with water during cross-linking than did the methoxy groups in VTMS.

Silane grafting reactions of PE did not occur without the presence of peroxide. As discussed previously regarding apparent activation energies of silane grafting reactions of LDPE, the reactions included a series of reaction steps, and these reaction mechanisms were affected by the amount of peroxide used. To investigate the effects of the amount of peroxide on the grafting reaction heats of LDPE in this study, 7 phr of vinyl trimethoxysilane was used along with a varied amount of peroxide in the range of 0.025–0.3 phr, to produce the grafting reactions of LDPE. DSC was used to monitor in situ the reactions at a heating rate of 20°C/min. Figure 8 shows a plot of grafting reaction heats as a function of amount of peroxide used. The grafting reaction heat increased proportionally as the amount of peroxide used was increased up to 0.1 phr. This suggested that the extent of the silane grafting reactions increased proportionally with the increase of the amount of peroxide in the range of 0–0.1 phr.

Thus, 0.1 phr of peroxide can lead to a complete reaction of 7 phr of silane used in this study. For the amount of peroxide of higher than 0.1 phr, the extent of silane grafting reactions did not increase, because the overall reaction heat was no longer observed to be increasing. The endothermic hydrogen abstraction appeared to be increasing because of a decrease in the overall reaction heat, as shown in Figure 7, for the amount of peroxide greater than 0.1 phr. The overall reaction heat then increased with increasing amounts of peroxide used above 0.1 phr, because of increasingly significant exothermic chain formations (i.e., cross-linking reactions). Figure 4 provides evidence of significant peroxide cross-linking (about 40% for LDPE) with 0.2 phr peroxide.

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