Silane Grafting Reactions of Low-Density Polyethylene

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ABSTRACT: Reactions of vinyl trimethoxysilane grafting onto low-density polyethylene (LDPE) were investigated using Fourier transform infrared spectroscopy, differential scanning calorimetry, and thermal gravimetric analysis. The silane grafting reactions were induced by a fixed amount of dicumyl peroxide at 0.2 part of reagent per hundred parts with respect to LDPE. Fourier transform infrared data demonstrated that the extent of the silane grafting reaction was increased as the amount of silane used, the reaction time, or the reaction temperature was increased. The apparent activation energy of the silane grafting reaction was 9.7 kJ mol^{-1}. Differential scanning calorimetry was used to follow the silane grafting reactions *in situ* at a heating rate of 20°C per minute. The silane grafting reaction was exothermic starting at about 150°C and ending at about 230°C, indicating a completion of the reaction in 4 min. The grafting reaction heat has linear relations to the amount of silane used. The grafting reaction heat of about 1 J/g of sample was generated during reaction per part of reagent per hundred parts of silane used. The reaction heat of silane grafting onto LDPE per mol of silane used was 14.5 kJ mol^{-1} silane, and the reaction heat of peroxide that reacted with LDPE was -12 kJ mol^{-1} peroxide. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 255–261, 1998

Key words: polyethylene; grafting reactions; crosslinking reactions; kinetics

INTRODUCTION

The crosslinking of polyethylene is of considerable practical importance. It extends the range of use by raising the upper temperature limit of application and improves the mechanical properties of this polymer. The use of silane grafting provides one of several ways of crosslinkings.[1] The way of mak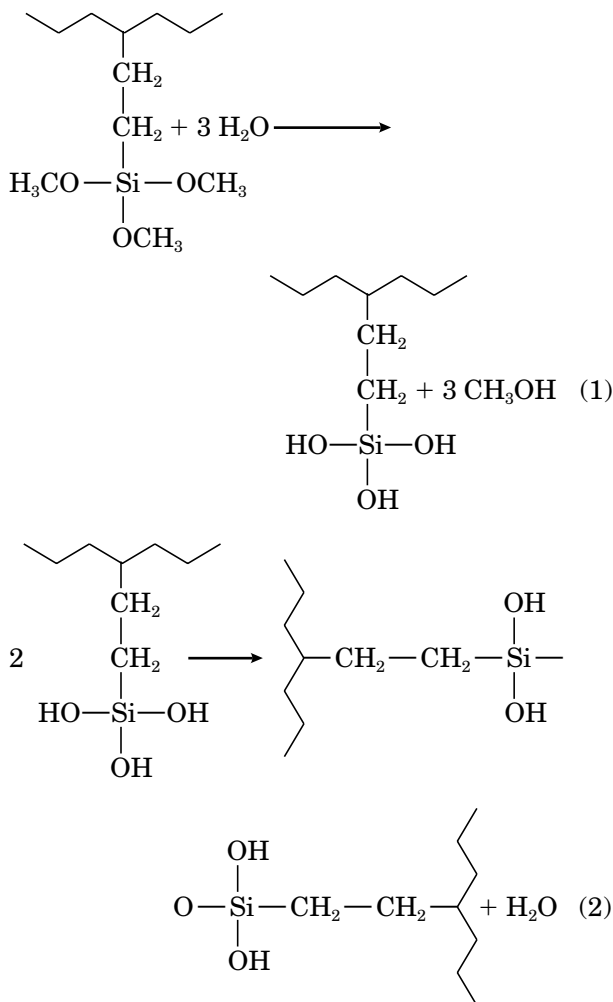ing crosslinkable polyethylene through silane grafting has gained much attention in recent years because of its various advantages, such as easy processing, low cost and capital investment, and favorable properties in the processed materials.

The most common silane used in the manufacture of silane crosslinkable polyethylene is vinyl trimethoxysilane. This silane has conventionally been introduced into polyethylene by melt grafting using a peroxide. The silane-grafted polyethylene is then crosslinked through hydrolyzation of the methoxysilane groups with water followed by condensation of the formed hydroxyl groups. The mechanisms leading to coupling between the methoxysilane groups in the silane-grafted polyethylene are believed to be as follows:[2]

$$
\begin{array}{c}
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} + 3\ \mathrm{H_2O} \longrightarrow \\
| \\
\mathrm{H_3CO-Si-OCH_3} \\
| \\
\mathrm{OCH_3}
\end{array}
$$

$$
\begin{array}{c}
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} + 3\ \mathrm{CH_3OH} \quad (1) \\
| \\
\mathrm{HO-Si-OH} \\
| \\
\mathrm{OH}
\end{array}
$$

$$
2\ \begin{array}{c}
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} \\
| \\
\mathrm{HO-Si-OH} \\
| \\
\mathrm{OH}
\end{array}
\longrightarrow
\begin{array}{c}
\mathrm{OH} \\
| \\
\mathrm{-CH_2-CH_2-Si-} \\
| \\
\mathrm{OH}
\end{array}
$$

$$
\begin{array}{c}
\mathrm{OH} \\
| \\
\mathrm{O-Si-CH_2-CH_2-} \\
| \\
\mathrm{OH}
\end{array} + \mathrm{H_2O} \quad (2)
$$

There have been some articles published on the crosslinking of polyethylene. Sen and colleagues[3,4] reported some kinetics data studied by differential scanning calorimetry (DSC), X-ray diffractometer, and dynamic mechanical analysis, on silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber. Kao and Phillips[5] reported crystallinity and other structural information, using DSC and X-ray diffractometer, of low-density polyethylene (LDPE) crosslinked by dicumyl peroxide. Hjertberg and colleagues[2] and Bullen and colleagues[6] studied the crosslinking reactions of ethylene-vinyl trimethoxysilane copolymers. The article by Bullen and coworkers,[6] crosslinking of the copolymer during high temperature melt processing was investigated using melt rheological and infrared spectroscopic techniques, whereas in the articles by Hjertberg and colleagues[2] and Palmlof and colleagues[7] the kinetics of crosslinking of the copoly-

mer when reacted with water was followed by measuring gel content and by determination of the content of different groups ($\mathrm{-Si-OCH_3}$, $\mathrm{-Si-OH}$, and $\mathrm{-Si-O-Si-}$) using Fourier transform infrared (FTIR) spectroscopy. Narkis and coworkers[8] represented studies on the crosslinking 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 crosslinking conditions. Turcsanyi and coworkers[9] studied structure/property relationships of silane modified and crosslinked linear polyethylene using DSC and thermomechanical analyzer.

The extent of crosslinking of polyethylene is closely dependent on the extent of silane grafting onto polyethylene. The silane grafting reaction with polyethylene has to be thoroughly understood and controlled to achieve a high degree of crosslinking. There are, however, very few articles studying the silane grafting reactions. In this article, the extent of silane grafting reaction with LDPE in the presence of a fixed amount of peroxide is followed as a function of the amount of silane used, the reaction temperature, and the reaction time. Infrared spectroscopic techniques, DSC, and thermogravimetry are used for this study.

EXPERIMENTAL

Materials

All materials were used as received. LDPE (C7100) was received from Asia Polymer Corporation (Taipei, Taiwan) with a melt index (ASTM D1238) of 7.3 and a density (ASTM D1505) of 0.9175 g cm^{-3}. The peroxide used was dicumyl peroxide supplied by Aldrich Chemical Company (Milwaukee, WI). The silane used was vinyl trimethoxysilane supplied by Tokyo Kasei Kogyo Co. (Tokyo, Japan).

Sample Preparation

LDPE pellets were crushed to powder with a particle size between 30 and 60 mesh. The LDPE powder was then mixed with a previously prepared acetone solution of silane and peroxide. The amount of peroxide was fixed at 0.2 phr (part of reagent per hundred parts of LDPE) for all experiments, whereas the amount of silane was varied in the range of 3 to 30 phr with respect to LDPE.

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 LDPE powder was thus able to determine by weighing the dried LDPE powder sample. This process has been determined to be effective in providing uniform silane and peroxide dispersion on the surface of LDPE powder with negligible residual acetone. Samples for FTIR measurements were prepared by making films of the dried LDPE powder in a hot press at a constant temperature for a certain time. The temperatures (i.e., the grafting reaction temperatures) of the hot press were 150, 170, 190, and 210°C, and the times (i.e., the grafting reaction times) were 2, 5, 8, and 11 min. Samples for DSC measurements were prepared by encapsulating the dried LDPE powder of 5–10 mg in hermetically sealed aluminum pans. Samples for thermal gravimetric analysis (TGA) measurements were from those film samples for FTIR measurements.

Analysis

Grafting reactions of silane onto LDPE were performed isothermally in a hot press and dynamically on DSC (TA Instruments, New Castle, Delaware, DSC 2010) at a heating rate of 20°C per minute under nitrogen. Samples were films after grafting reactions performed isothermally in the hot press. The extent of grafting in these films was analyzed on FTIR (Bio-Rad FTS155). The grafting reaction was monitored *in situ* on DSC and the grafting reaction heat was thus obtained. In addition, the effects of grafting on the morphology of LDPE was also observed by using DSC. TGA (TA Instruments, TGA 2050) was used to analyze the effects of the grafting reaction on the thermal decomposition of LDPE.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of LDPE before (spectrum A) and after (spectra B–E) reaction with various amounts of silane. Spectrum E in Figure 1 displayed that LDPE, which had reacted with 11 phr of silane, gave rise to at least three peaks at 789, 1092, and 1192 cm^{-1}. The silane grafting reactions thus occurred since the peaks at 1092 and 1192 cm^{-1} were assigned to the functional group Si—OCH$_3$.[2,3,10,11] Figure 1 clearly displayed that the extent of the silane grafting reaction at 170°C for 2 min increased as the
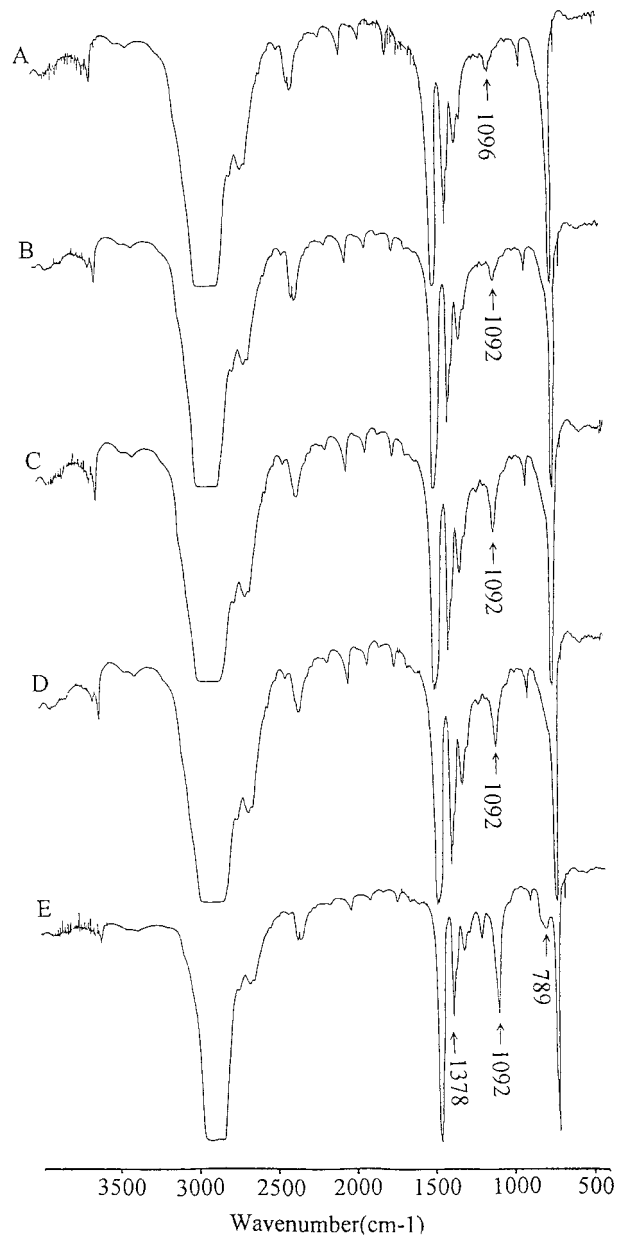
Figure 1 FTIR spectra of LDPE samples that have reacted with (A) 0 phr, (B) 3 phr, (C) 5 phr, (D) 7 phr, and (E) 11 phr of silane at 170°C for 2 min.

amount of silane used increased. Figure 2 shows FTIR spectra of LDPE after reaction with 5 phr of silane at 170°C for different reaction times. The extent of the silane grafting reaction at 170°C increased insignificantly as the reaction time increased. The insignificant effect of the reaction time on the extent of grafting suggested that the grafting reaction was complete at 170°C for 2 min. Figure 3 illustrates FTIR spectra of LDPE after grafting
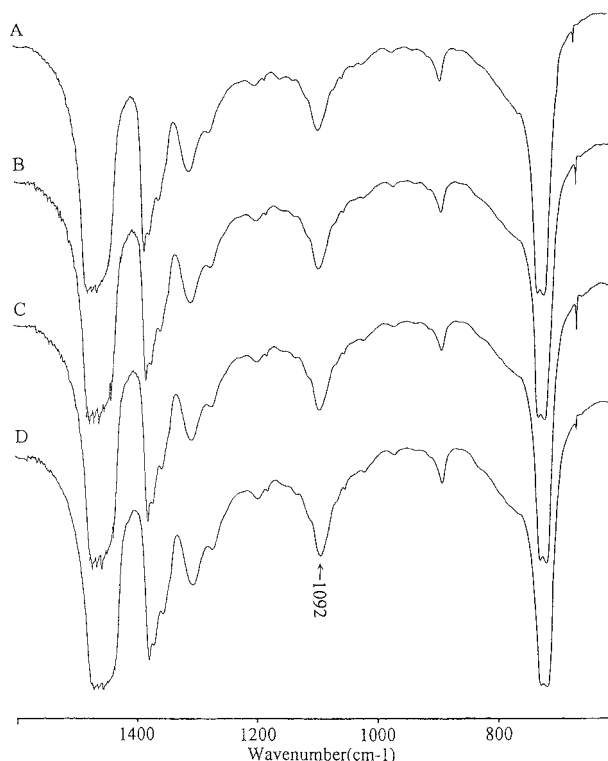
Figure 2   FTIR spectra of LDPE samples that have reacted with 5 phr of silane at 170°C for (A) 2 min, (B) 5 min, (C) 8 min, and (D) 11 min.
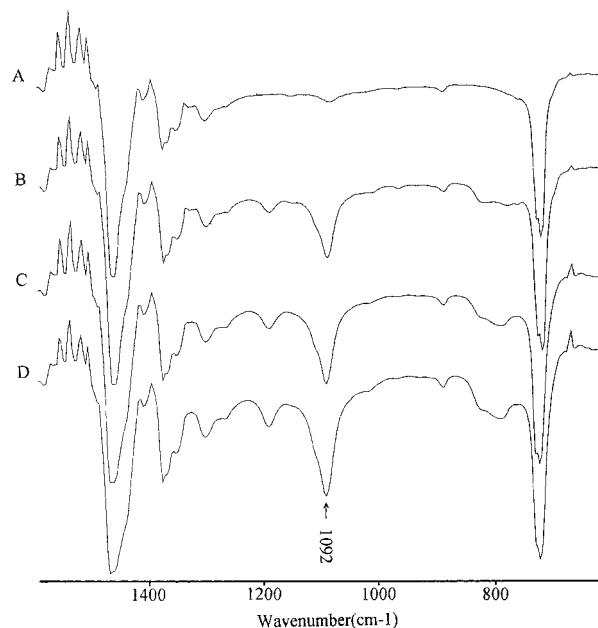
reactions with 5 phr of silane for 2 min at different reaction temperatures. The extent of the silane grafting reaction was found to increase significantly as the reaction temperature increased.

LDPE has a branched structure. The peak at 1378 cm^{-1} due to —CH$_3$ bending vibrations[11] in FTIR spectra (spectrum A in Fig. 1) provides evidence of the branched structure of LDPE. Because of the branched structure, there are hydrogens attached to tertiary carbons at the branched positions on the backbone of LDPE. These hydrogens are relatively easy to abstract during the silane grafting reactions, compared with those hydrogens attached to secondary and primary carbons. Moreover, the number of hydrogens attached to secondary carbons in a molecule of LDPE is much more than that of hydrogens attached to tertiary or primary carbons.[12] In the silane grafting reactions, therefore, the free radicals generated from dicumyl peroxide mostly attack and abstract the hydrogens at tertiary and secondary carbons rather than the hydrogens at primary carbons located at the ends of the backbone chains and branches. It is, thus, reasonably assumed that the

content of the —CH$_3$ groups in molecules of LDPE does not change throughout the grafting reaction. The absorption peak of the —CH$_3$ groups at 1378 cm^{-1} is thus used as an internal standard, and the extent of silane grafting (R) onto LDPE can be determined using the absorption peak of the —Si—O—CH$_3$ groups at 1092 cm^{-1} by calculating the ratio as follows:

$$R = \frac{A_{1092}}{A_{1378}} \tag{3}$$

where A_{1092} and A_{1378} represent absorbances at 1092 and 1378 cm^{-1}, respectively. Figure 4 displays R, the extent of grafting reactions, in natural logarithmic scale as a function of reciprocal absolute temperatures. A linear relationship was found for the two silane concentrations used. Apparent activation energies of 9.1 and 10.3 kJ mol^{-1} for the silane grafting reactions with 5 and 7 phr of silane used, respectively, were thus obtained by applying the Arrhenius equation for the linear relationship. The apparent activation energy of averaged 9.7 kJ mol^{-1} was obtained for the silane grafting reaction induced by 0.2 phr of dicumyl peroxide. The apparent activation energy of the silane grafting reaction was found to vary with the amount of dicumyl peroxide used.[13]
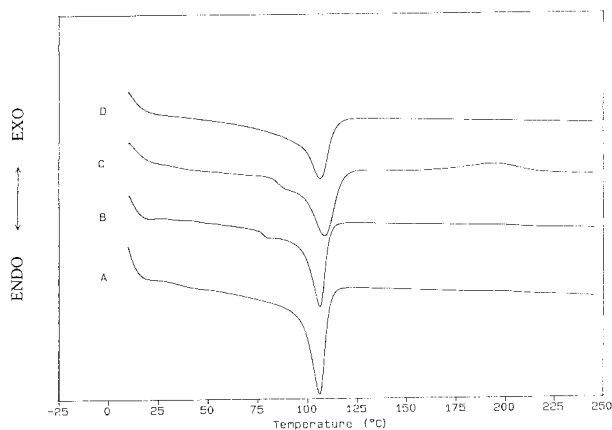

Figure 3   FTIR spectra of LDPE samples that have reacted with 5 phr of silane for 2 min at (A) 150°C, (B) 170°C, (C) 190°C, and (D) 210°C.
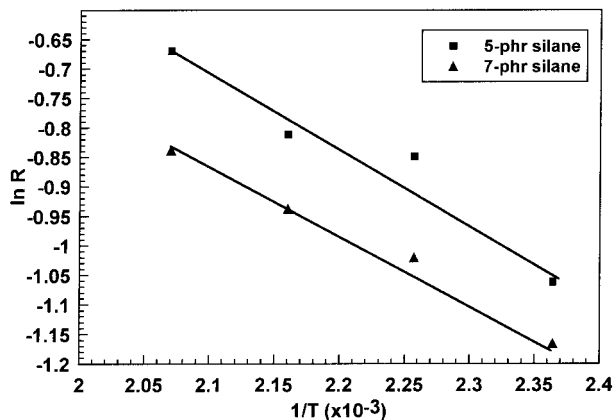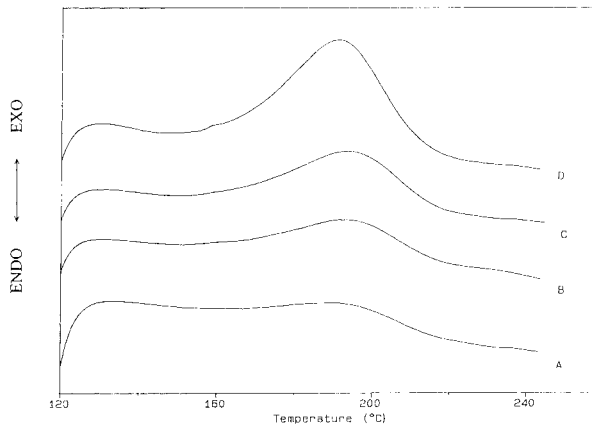
Figure 4 Extent of grafting reactions in natural logarithmic scale as a function of reciprocal absolute temperatures.

Figure 6 DSC traces of LDPE mixed with 0.2 phr of dicumyl peroxide and (A) 7 phr, (B) 15 phr, (C) 20 phr, and (D) 30 phr of silane at a heating rate of 20°C per minute in nitrogen.

The grafting reaction was monitored *in situ* using DSC at a heating rate of 20°C per minute under nitrogen. Figure 5 shows DSC traces for LDPE samples before (trace A) and after (traces B–D) reaction with peroxide and silane. An exothermic peak between 150° and 230°C was displayed in Figure 5 (trace C). This exothermic peak was due to the silane grafting reactions, because no apparent exothermic peak at the same location was observed (Fig. 5, trace B) for LDPE reacted with the peroxide. The exothermic peak disappeared during the second heating (Fig. 5,

trace D), indicating completion of the grafting reaction after the first heating. The exothermic peak in between 150° and 230°C suggests that the starting point of the silane grafting reactions is at about 150°C, and the silane grafting reaction can finish in 4 min when the LDPE sample is dynamically heated at 20°C per minute. A shoulder at around 80°C was found to the left of the melting peak of LDPE for traces B and C in Figure 5. These shoulders were confirmed[13] due to an annealing effect during the sample preparation at 75°C for 30 min. The integrating area under the exothermic peak (Fig. 6) (i.e., the grafting reaction heat) for the grafting reactions increases as the amount of silane used increases. Figure 7 demonstrates that the grafting reaction heats (ΔH, J g^{-1} sample) have linear relations to the amount of silane used (S, phr of silane). The lin-
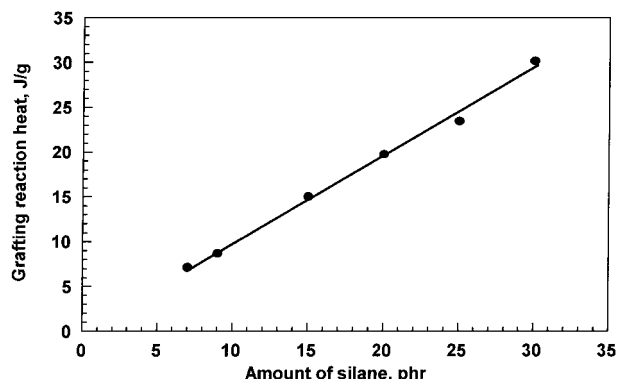

Figure 5 DSC traces of LDPE samples at a heating rate of 20°C per minute under nitrogen: (A) LDPE, the first heating; (B) LDPE mixed with 0.2 phr of dicumyl peroxide, the first heating; (C) LDPE mixed with 0.2 phr of dicumyl peroxide and 20 phr of silane, the first heating; and (D) LDPE mixed with 0.2 phr of dicumyl peroxide and 20 phr of silane, the second heating.
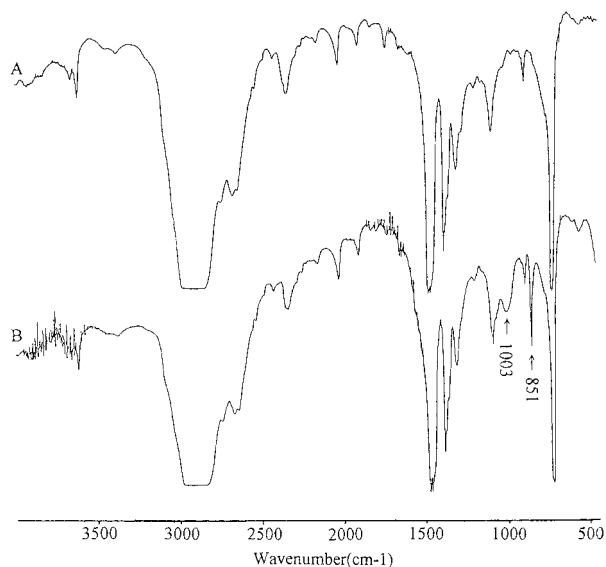

Figure 7 Grafting reaction heat as a function of the amount of silane used.
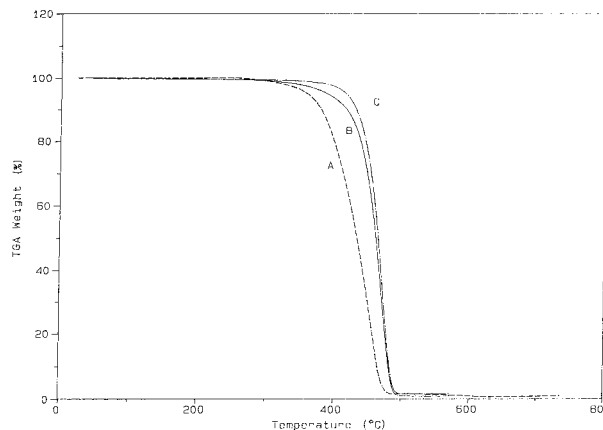
ear relation is simulated by a linear equation as follows:

$$\Delta H = 0.98S + 0.09 \qquad (4)$$

where 0.98 and 0.09 are the slope and the intercept of the line, respectively. The unit of the slope is J 0.01 g^{-1} silane, whereas the intercept is J 0.002 g^{-1} peroxide. Thus, the reaction heat (kJ) of silane grafting, induced by 0.2 phr of dicumyl peroxide, onto LDPE per mol of silane used, is -14.5 kJ mol^{-1} silane, and the reaction heat of peroxide reacted with LDPE is -12 kJ mol^{-1} peroxide. On the other hand, eq. (4) describes that about 1 J of heat per gram of sample is generated per 1 phr of silane used.

Figure 8 shows FTIR spectra of silane-grafted LDPE before (spectrum A) and after (spectrum B) crosslinking with boiled water for 8 h. In comparison with spectrum A, spectrum B displays at least two more peaks at 1003 and 851 cm^{-1}. The absorption peak at 1003 cm^{-1} is assigned to the Si—O—Si group,[2,10] suggesting the occurrence of crosslinking reactions according to eq. (2). The evidence of crosslinking supports the grafting reaction of silane onto LDPE. Figure 9 shows TGA traces of LDPE before (trace A) and after treatment with silane (trace B), and subsequently with water (trace C). The degradation tempera-

Figure 9 TGA traces of LDPE samples heated at a rate of 20°C per minute under nitrogen. (A) LDPE, (B) LDPE grafted with 7 phr of silane at 170°C for 2 min, and (C) LDPE grafted with 7 phr of silane at 170°C for 2 min and followed by crosslinking with boiled water for 8 h.

tures were found to increase after silane grafting reactions and crosslinking reactions. The degradation temperature of the crosslinked LDPE is higher than that of either the grafted LDPE or the ungrafted LDPE, suggesting that the crosslinking reactions of LDPE can raise its upper temperature limit of application.

CONCLUSIONS

The aims of this work were investigating the activation energy and reaction heat of vinyl trimethoxysilane grafting reaction onto LDPE induced by dicumyl peroxide. The apparent activation energy obtained based on quantitative analyses of FTIR spectra was 9.7 kJ mol^{-1}. The silane grafting reaction of LDPE was exothermic, occurred between 150° and 230°C, and finished in 4 min by *in situ* monitoring the reaction using DSC. The reaction heat of silane grafting onto LDPE per mol of silane used was -14.5 kJ mol^{-1} silane, and the reaction heat of peroxide reacted with LDPE was -12 kJ mol^{-1} peroxide.

Figure 8 FTIR spectra of LDPE samples that have grafted with 7 phr of silane at 170°C for 2 min. (A) Before crosslinking with boiled water and (B) after crosslinking with boiled water for 54 h.

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