

Crosslinkable Polypropylene Composites Made by the Introduction of Silane Moieties

Kalyanee Sirisinha, Keskanok Kawko

Department of Chemistry, Mahidol University, Rama VI Road, Bangkok 10400, Thailand

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ABSTRACT: Silane-crosslinkable polypropylene (PP) composites containing calcium carbonate (CaCO_3) as a filler have been investigated. The melt grafting of vinyl trimethoxysilane to PP with dicumyl peroxide (DCP) as a radical initiator is demonstrated. The thermal and mechanical properties of the crosslinkable products are also discussed. The results show that two reactions, that is, silane grafting and PP degradation, take place in parallel. The extents of silane grafting and PP degradation strongly depend on the reaction temperature, grafting formulation, and amount of the filler in the systems. Increasing the DCP concentration (up to 0.05 wt %) leads to an increase in the grafting degree. However, when the concentration of radicals is over a certain degree, the dominant reaction is PP chain scission. This results in a drastic decrease in the polymer viscosity. In systems containing both silane and

CaCO_3 , the viscosity of the polymer is higher than that of a grafted sample without CaCO_3 addition; in other words, the effect of the filler on the polymer viscosity compensates for the effect caused by PP degradation. Differential scanning calorimetry results show that the crystallization starts earlier for grafted samples. The percentage of the crystallinity of grafted PP is higher than that of the pure polymer. The incorporated silane does not have a strong effect on the mobility of the PP chains, as revealed by dynamic mechanical analysis. In comparison with ungrafted composites, the silane-crosslinkable products show higher tensile stress and modulus. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1476–1483, 2005

Key words: composites; crosslinking; poly(propylene) (PP)

INTRODUCTION

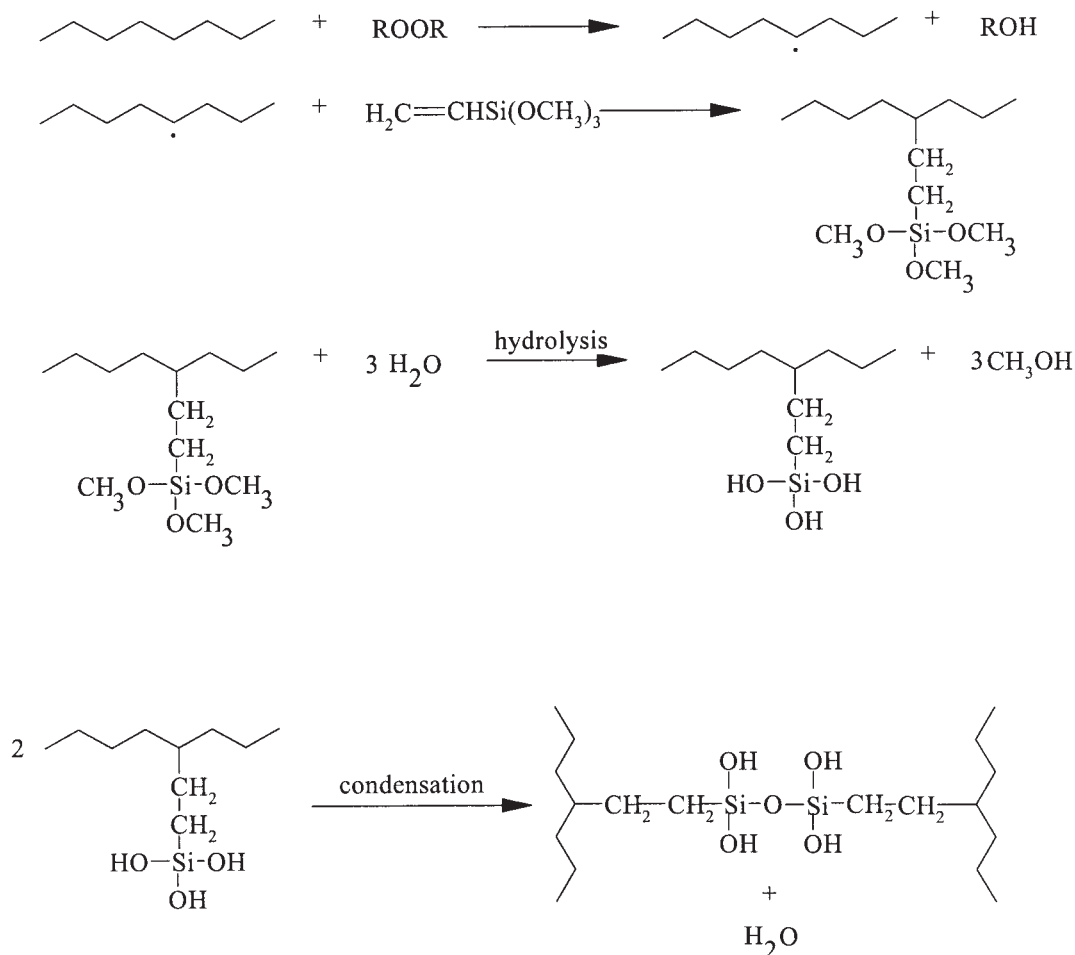
Polypropylene (PP) composites with mineral fillers are of great practical importance because it is possible to modify the physical properties of PP with low-cost fillers. The properties of these composites depend on several factors, including the composition, size and shape of the fillers, and adhesion between the polymer and fillers. Effective ways of improving adhesion between hydrophobic polymers and hydrophilic fillers include the chemical modification of polymers and the introduction of a coupling agent to the filler surface. The use of compounds such as alkoxy silanes in the chemical modification of polymers has greatly increased over the last 20 years. The main objectives are either producing new materials of specific properties or crosslinking commercial polymers by moisture to improve their physical and mechanical properties. Among the different possibilities for crosslinking polymers, silane–moisture crosslinking has received much attention in recent years because of the easy processing, low capital investment, and favorable

properties of the processed materials. This is in contrast to radiation and peroxide crosslinking techniques, which suffer some disadvantages such as high investment cost and thickness limitations in radiation crosslinking, as well as the risk of precurcuring and the high production cost in peroxide crosslinking.

The silane-crosslinking process involves at least two stages, which may be performed together (Scheme 1). In the first stage, a silane-crosslinkable polymer is prepared by the free-radical grafting of vinyl alkoxy silanes onto the polymer chains with peroxides as initiators, and in the second stage, the silane-grafted polymer is crosslinked by exposure to a humid environment. The crosslinking reaction involves the hydrolysis of the alkoxy groups with moisture, followed by the condensation of the formed hydroxyl groups to form stable siloxane linkages. The grafting step may be performed while the polymer is in a solution or molten state, whereas the crosslinking step is normally carried out after the polymer has been shaped into products while the polymer is in a solid state. The most commonly used silanes are vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane. The vast majority of the studies on silane-grafting and water-crosslinking techniques are concerned with polyethylene and ethylene copolymers.^{1–12} Not many studies concerning the grafting and crosslinking of PP have been reported.^{13–18} This is most likely a result of the

Correspondence to: K. Sirisinha (sckpr@mahidol.ac.th).

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Scheme 1

nature of the PP chain structure. It has been well established that PP mainly experiences chain scission during radiation and peroxide modification, and this leads to a decrease in the molecular weight and molecular weight distribution.¹⁹ Because of the high instability of tertiary macroradicals, the degradation process is extremely fast at a high temperature [above the melting temperature (T_m)], especially during melt mixing. Consequently, the silane grafting of PP has to be carefully controlled to achieve a high degree of grafting without the expense of PP degradation.

The aim of this work is to study the silane grafting of PP and its filled composites with calcium carbonate (CaCO_3). Attention is focused on the effects of the grafting process temperature, the concentrations of dicumyl peroxide (DCP) and VTMS, and the filler content upon grafting and melt flow index (MFI) of modified PP. Changes in the crystallization and melting behavior of PP upon grafting are also investigated. The mechanical properties of unmodified PP, grafted PP, and their corresponding composites are studied.

EXPERIMENTAL

Materials

Composites were prepared from a PP homopolymer (P400S, Thai Polyethylene Co., Ltd., Bangkok, Thailand), with an MFI of 3.64 g/10 min and a density of 0.903 g cm^{-3} , filled with CaCO_3 (Turboplex, Lime Quality Co., Ltd., Bangkok, Thailand). The filler surface was coated with 2 wt % stearic acid. The filler had a specific gravity of 2.7 g cm^{-3} , a median particle diameter of 3–6 μm , and a specific surface area of $22 \text{ m}^2/\text{g}$. According to the literature,^{20,21} 1 g of stearic acid would cover around 445 m^2 of the available mineral surface. A 2 wt % stearic acid treatment, therefore, would ensure 100% surface coverage of the CaCO_3 used in this study. For the grafting reaction, the initiator was DCP, and the silane was VTMS. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without purification.

Preparation of the PP composites

PP and CaCO_3 master batch (50/50 wt %) was prepared in a corotating twin-screw extruder (Prism

TSE16, Staffordshire, UK). Before the mixing, CaCO_3 was dried in an oven to remove moisture for 8 h. The master batch was diluted with PP to a required concentration. The barrel temperature profile from the feed zone to the die was set between 160 and 190°C. A screw speed of 220 rpm was used.

Preparation of silane-crosslinkable PP

The silane-grafting process was carried out in a Prism TSE16 corotating twin-screw extruder with a length/diameter ratio of 25/1 and a diameter of 16 mm. The screw configuration was designed to provide good dispersive and distributive mixing. The PP pellets were tumble-mixed with a solution of VTMS and DCP in a sealed container. The mixture was kept immediately under N_2 gas and allowed to stand overnight. To study the effect of the processing temperature on the grafting and degradation of PP, three barrel temperature profiles were investigated. They are designated as the normal-temperature (NT) profile, the high-temperature (HT) profile, and the reverse-temperature (RT) profile. The barrel temperatures from the feed zone to the die zone were set as follows: 150, 190, 190, 190, and 190°C for the NT profile; 150, 210, 210, 210, and 210°C for the HT profile; and 150, 210, 170, 170, and 170°C for the RT profile. The screw speed was kept constant at 30 rpm, and this gave a total residence time of approximately 5 min. After the reaction, the grafted products were shaped into 1-mm-thick compression-molded sheets as follows: the polymers were preheated at 200°C for 5 min and then pressed for 5 min under 15 MPa of pressure. After cooling, a sheet was cut into tensile bars. The specimens were stored under dried conditions before testing. For the CaCO_3 -filled PP composites, the weight percentages of CaCO_3 were 5 and 50, representing low and high filler loading contents, respectively. The silane-grafting reaction was carried out with an RT profile. A screw speed of 30 rpm was used. The samples were collected and stored in a similar manner to that for the unfilled polymers.

Characterization and testing

Fourier transform infrared (FTIR) spectroscopy was used to analyze the presence of silane in the grafted products. Films (50 μm thick) were prepared by hot pressing at 200°C. Before the FTIR measurements, the films were washed with an excess volume of acetone to remove unreacted silane or residual peroxide. The IR spectra were then recorded with a FTIR spectrometer (PerkinElmer system 2000, Boston, MA) in the range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1} . The peak of the methyl group at 899 cm^{-1} was used as an internal reference. In the analysis of the experimental results, the relative absorption peak intensity of the Si—O—C stretching of the silane-grafted polymer at

1102 cm^{-1} to that of the methyl group at 899 cm^{-1} was evaluated and reported in terms of the grafting index.

MFI was used here as a tool for investigating the degree of degradation of PP by chain scission. The experiments were carried out with a Kayaness D-7053 instrument (Morgan Town, PA) according to ASTM D 1238-90b. The samples were melted at 230°C and driven through the capillary die with a 2.16-kg piston. The weight of the extrudate in gram units at 10-min intervals was measured.

The tensile properties were measured in accordance with ASTM D 638-99 with a tensile testing (Instron 4301, Canton, MA) at a crosshead speed of 50 mm/min and with a 1-kN load cell. Dumbbell specimens of type IV were stamped from a compression-molded sheet.

The melting and crystallization behavior of selected samples was studied with a PerkinElmer DSC7 differential scanning calorimeter. The samples were first heated from 50 to 230°C at a scanning rate of 20°C/min and then maintained at 230°C for 5 min before cooling to 50°C at the same rate. The percentage of crystallinity was calculated from the heat of fusion with a heat of fusion of 100% crystalline PP (ΔH_0) value of 189 J/g.²²

The dynamic mechanical properties of selected samples were determined with a Gabo dynamic mechanical analyzer (Ahliden, Germany). Testing was carried out in the tension mode over a temperature range of –50 to 50°C at a frequency of 6.28 rad/s (1 Hz).

RESULTS AND DISCUSSION

A comparison of the FTIR spectra of the unmodified PP and a typical silane-grafted PP is presented in Figure 1. Pure PP shows characteristic peaks at 899, 1380, and 1465 cm^{-1} that correspond to the C—H bending, asymmetric C—H stretching, and symmetric C—H stretching vibrations of the methyl groups, respectively.²³ The introduction of VTMS into PP leads to the appearance of absorption bands at 803, 1102, and 1215 cm^{-1} that correspond to the functional methoxysilane groups (Si—OCH₃). The structure of silane grafts is believed to occur as alkoxy silane units on the PP chains. Because of the bulky and rigidity of the side group, it is difficult for VTMS to homopolymerize. From our experiments, we found no change in the intensity of the absorption peak at 1600 cm^{-1} corresponding to the C=C bond in VTMS after the reaction of VTMS and DCP was conducted in a glass vessel at 200°C for more than 30 min (the FTIR results are not shown here). This implies that the homopolymerization of VTMS could not occur under the process conditions. Similar results were reported earlier by Kim and Jang.²⁴ To facilitate our understanding of the factors affecting the silane-grafting reaction, we analyzed the extent of the reactions quantitatively from the

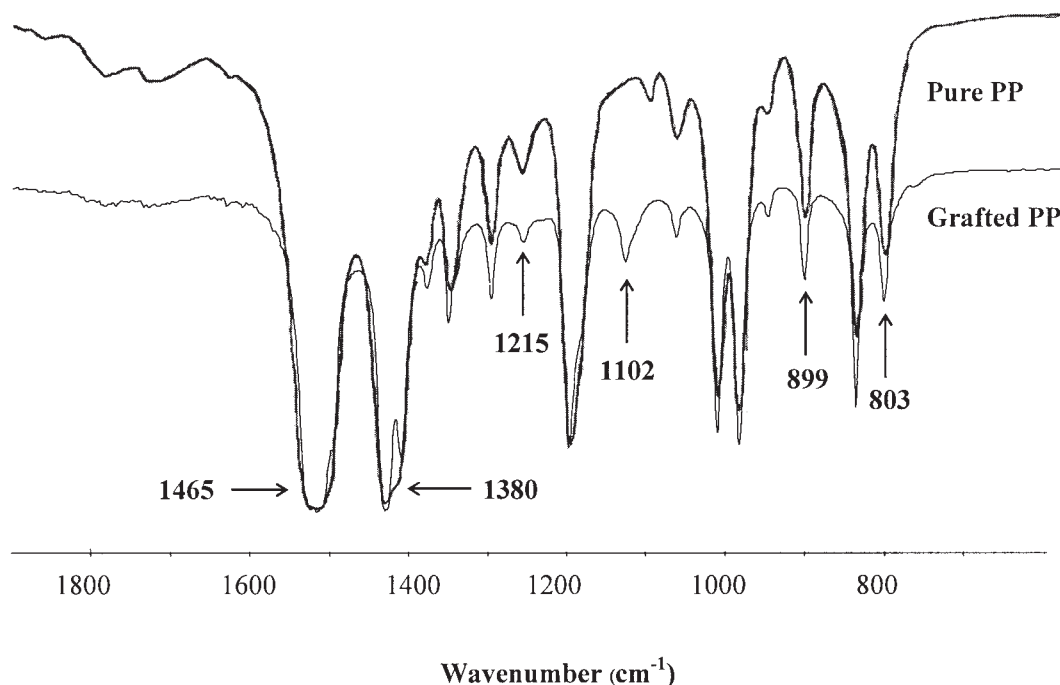


Figure 1 FTIR spectra of unmodified PP and silane-grafted PP.

FTIR spectra by calculating the ratio of the intensity of the absorption peak of the Si—OCH₃ group at 1102 cm⁻¹ to that of a reference peak at 899 cm⁻¹. The results from the peak intensity analysis show good reproducibility of the experimental results, with the standard deviation in the range of 0.02–0.06. Table I shows the values of the grafting index averaged from five experiments.

A comparison of the three investigated temperature profiles shows that the use of the RT profile seems to give the product of highest grafting. For the system with 5% VTMS, the grafting degree increases by 15 and 33% when the temperature profiles are changed from NT to RT and from HT to RT, respectively. During the grafting process, the degradation of PP

chains occurs as a side reaction. Evidence of PP chain scission can be clearly seen in the MFI results of Table I. The MFI values of processed PP (without DCP and VTMS) are considerably higher than those of the parent material (pellet), reflecting a reduction in the polymer viscosity brought about by PP macroradical fragmentation. The reduction of the polymer viscosity is more pronounced with increases in both the process temperature and initiator concentration (Tables I and II). The competition between the grafting and degradation reaction depends markedly on the temperature during the grafting process (Table I). The use of the RT profile gives a product of highest grafting with the

TABLE I
Effect of the Process Temperature on the Grafting and MFI Values

PP (parts)	DCP (%)	VTMS (%)	Temperature profile	Grafting index	MFI (g/10 min)
Pellet	—	—	—	—	3.64
100	—	—	NT	—	4.06
100	—	—	HT	—	4.66
100	—	—	RT	—	3.81
100	0.05	3	NT	0.87	9.70
100	0.05	3	HT	0.80	11.02
100	0.05	3	RT	0.95	9.78
100	0.05	5	NT	1.06	15.53
100	0.05	5	HT	0.91	17.22
100	0.05	5	RT	1.21	12.37

TABLE II
Effects of DCP and VTMS Concentrations on Grafting and MFI Values (with RT Profile)

DCP (%)	VTMS (%)	Grafting index	MFI (g/10 min)
0	1	0.13	4.54
0.05	1	0.38	11.12
0.10	1	0.21	17.38
0	3	0.31	6.10
0.05	3	0.95	9.78
0.10	3	0.72	19.24
0	5	0.56	6.69
0.05	5	1.21	12.37
0.10	5	0.90	21.74
0	7	0.89	7.27
0.05	7	1.53	13.25
0.10	7	1.01	22.03

TABLE III
Effect of CaCO₃ on Grafting and MFI Values

CaCO ₃ (wt %)	Grafting index	MFI (g/10 min)	
		Grafted system	Ungrafted system
0	1.21	12.37	3.81
5	1.09	11.37	3.16
50	0.98	9.46	2.85

lowest degree of degradation. Under this particular condition, the barrel temperature next to the feed zone was set high at 210°C to facilitate the thermal decomposition of the peroxide initiator. In the following zones, a flat temperature of 170°C was used across the extrusion barrel to minimize extensive degradation of PP resins due to radicals produced by peroxide decomposition and/or by mechanical shear and temperature. Under the HT condition, the higher concentration of free radicals promotes chain scission and therefore leads to a lower grafting degree.

The effects of the DCP and VTMS concentrations on silane grafting and PP degradation are shown in Table II. Under conditions in which no peroxide is present, silane grafting is possible. Under such circumstances, macroradicals are produced, probably by high mechanical shear in the extruder, a high process temperature, or both. In the presence of DCP, increasing the VTMS concentration results in an increasing grafting degree for a constant DCP level. Maximum grafting seems to occur at 0.05 wt % DCP for all the experimental systems. The initial increase of the grafting degree when the DCP concentration increases from 0 to 0.05 wt % is believed to be due to the increasing number of free radicals produced by peroxide decomposition, which promote the formation of radical sites on the PP chains. Increasing the DCP concentration beyond 0.05 wt % unfortunately results in less grafting and more chain scission. This implies that PP chain fragmentation dominates at a high concentration of free radicals, leading to a great reduction in the polymer molecular weight and consequently an increase in the MFI values. An increase in the MFI values of the grafted products is a result not only of the degradation

process of PP but also of the lubricating effect that VTMS may have on the PP melt. Table II shows that in the systems containing VTMS alone (DCP is absent), the MFI values of the grafted products increase systematically with increasing VTMS concentration.

The effect of the filler on the silane-grafted products is presented in Table III. The concentrations of CaCO₃ were 5 and 50 wt %, representing low and high filler loadings, respectively. The grafted polymer composites were prepared with 5 wt % VTMS and 0.05 wt % DCP. The reaction was carried out under RT conditions. The results show a slight decrease in the degree of grafting brought about by filler addition. The incorporation of the filler also causes a reduction in the MFI value, that is, an increase in the polymer viscosity. In the systems containing both silane and CaCO₃, the viscosity of the polymer is lower than that of the grafted sample without CaCO₃ addition; in other words, the effect of the filler on the polymer viscosity compensates for the effect caused by PP degradation.

Table IV summarizes the differential scanning calorimetry (DSC) results for unmodified PP, CaCO₃-filled PP, and their silane-crosslinkable products. For the ungrafted system, the incorporation of the filler leads to an increase in the onset temperature of crystallization ($T_{c,onset}$) and crystallization temperature (T_c) of PP, with a slight reduction in T_m . These results point out that the CaCO₃ filler presumably acts as a nucleating agent promoting the crystallization of PP, leading to a composite with a higher number of spherulites of smaller sizes. A similar finding was reported earlier: CaCO₃ acted as a nucleating agent in the crystallization of PP, and this effect was more pronounced with untreated CaCO₃ than a stearic acid coated type.^{25,26} The percentage of crystallinity observed in the filled composites is lower than that of unfilled PP, and this can be explained by the substitution of PP by the rigid filler. To compare the crystallinity of only the crystallizable component in each sample, the percentage of crystallinity per unit weight of the crystallizable component was calculated and reported as a percentage of the normalized crystallinity. Table IV shows that the percentage of normalized crystallinity in-

TABLE IV
 $T_{c,onset}$, T_c , T_m , Crystallinity, and Normalized Crystallinity Values of Various Composites

System	CaCO ₃ (wt %)	$T_{c,onset}$ (°C)	T_c (°C)	T_m (°C)	Crystallinity (%)	Normalized crystallinity (%)
Ungrafted	0	117.5	113.5	163.5	48.1	48.1
	5	120.2	116.8	162.2	46.0	48.4
	50	119.3	115.9	161.2	26.9	53.8
Grafted	0	119.9	116.1	162.9	51.6	51.6
	5	121.1	117.3	161.7	49.4	52.0
	50	121.0	117.2	161.1	28.8	57.6

TABLE V
Modulus, Tensile Yield Stress, and Elongations at Yield and at Break of Various PP Composites

System	CaCO ₃ (wt %)	Modulus (GPa)	Yield stress (MPa)	Elongation at yield (%)	Elongation at break (%)
Ungrafted	0	1.31 ± 0.03	39.83 ± 0.75	8.56 ± 0.13	331.04 ± 0.72
	5	1.38 ± 0.05	38.42 ± 0.64	8.60 ± 0.51	104.93 ± 0.67
	50	1.89 ± 0.05	28.36 ± 0.60	8.10 ± 0.34	20.84 ± 0.77
Grafted	0	1.31 ± 0.04	41.23 ± 0.85	8.60 ± 0.51	94.93 ± 0.90
	5	1.45 ± 0.06	40.02 ± 0.65	8.18 ± 0.42	82.16 ± 0.65
	50	2.17 ± 0.06	30.10 ± 0.73	4.98 ± 0.29	21.91 ± 0.91

creases systematically with an increase in the filler concentration.

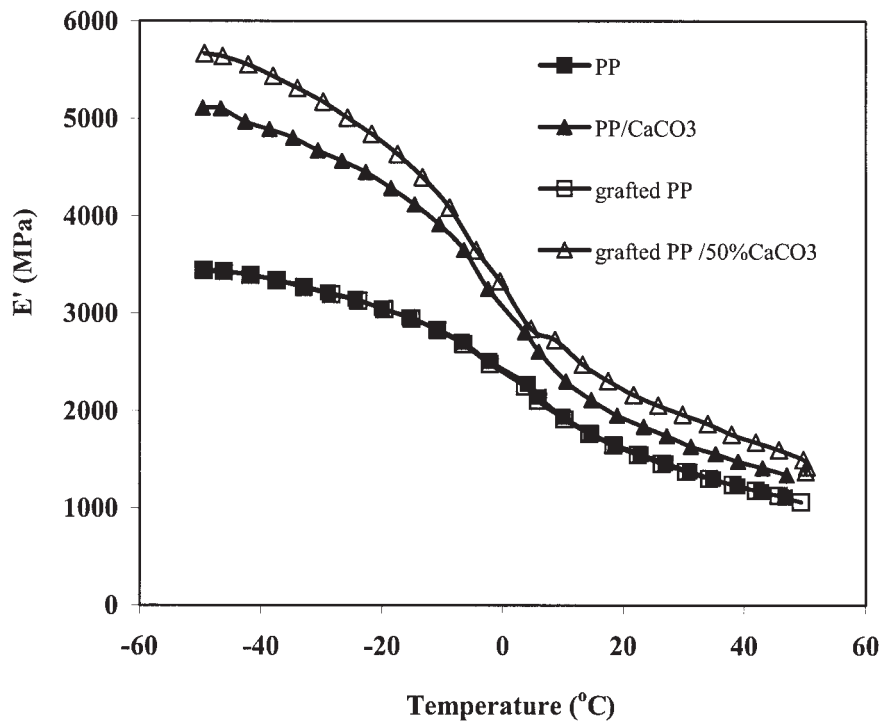
In comparison with pure PP, the silane-grafted PP shows evidently higher $T_{c,onset}$ and T_c values, and this means that the crystallization starts earlier for the grafted samples. The changes in the crystallization behavior observed in the grafted PP are believed to be partly due to a reduction in the polymer viscosity after the grafting reaction is conducted. A lowering of the viscosity of the polymer makes polymer chains move more easily and enables the formation of crystals at a relatively higher temperature. Apart from $T_{c,onset}$ and T_c , the percentage of normalized crystallinity of grafted PP is higher than that of pure PP, whereas T_m shifts to a lower value; this implies that the silane-grafted PP has a large number of spherulite of smaller sizes than those of the unmodified PP. In the filled composites, the filler shows similar effects on the melting and crystallization of the ungrafted and grafted systems.

The tensile properties of silane-crosslinkable PP and PP composites are shown in Table V. As expected, the incorporation of the filler into PP results in an increase in the composite modulus but leads to a decrease in the tensile yield stress, the elongation at yield, and, in particular, the elongation at break. The marked fall in the elongation at break in the filled composites was reported to be due to the presence of a filler acting as a stress precursor.²⁷ The effect of the CaCO₃ filler on the properties of the silane-grafted polymers is similar to that observed in the ungrafted systems. In comparison with the ungrafted PP, the silane-crosslinkable PP shows slightly higher tensile stress and a comparable modulus. The higher tensile stress of the grafted PP could be due to a higher crystallinity of this material (from the DSC results of Table IV) or a slightly higher rigidity of the polymer brought about by the incorporated silane. To investigate the effect of the silane moieties on the mobility of PP chains, some selected samples were investigated with dynamic mechanical analysis (DMA). Figure 2 shows the temperature dependence of the storage modulus (E') and loss factor ($\tan \delta$) at 1 Hz for pure PP, grafted PP, and their corresponding composites with 50% CaCO₃. Pure PP

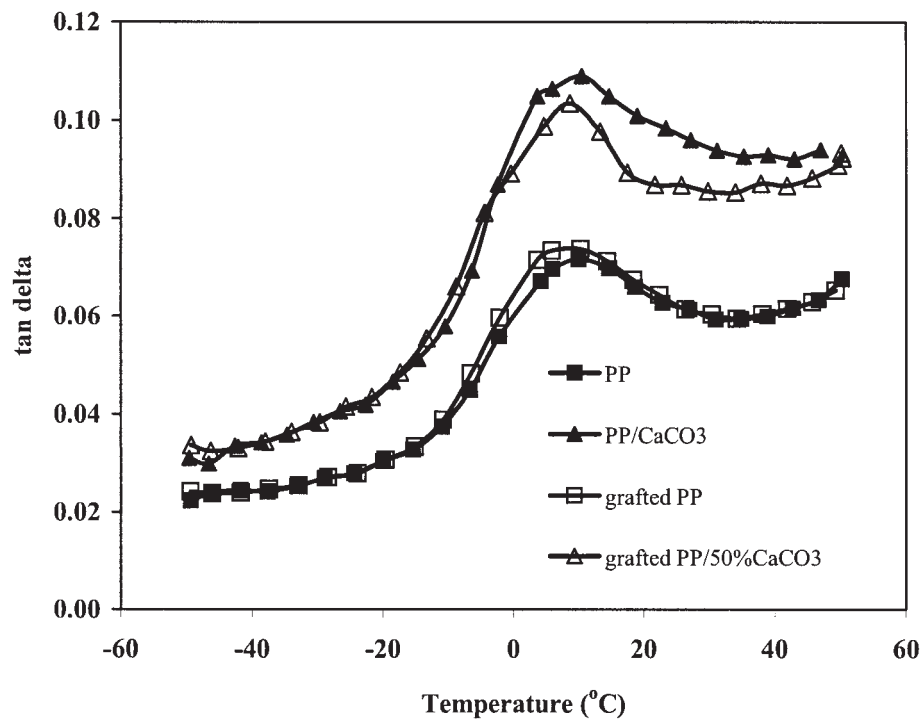
shows a $\tan \delta$ peak at 10.0°C corresponding to the glass-transition temperature (T_g) of the material. The incorporation of silane moieties into the PP chains has no influence on E' and $\tan \delta$ of PP. A T_g value for the silane-grafted PP was seen at 10.3°C, and this indicates that silane moieties have no effect on the mobility of the PP chains. The T_g value of the PP/CaCO₃ composite is similar to that observed for pure PP. No shift in the T_g peak was observed in the grafted composite. In the composite containing 50% CaCO₃, a marked increase in E' by filler addition can be clearly seen. The E' values of grafted PP filled with 50% CaCO₃ are higher than those of ungrafted composites with a similar concentration of the filler. These E' results agree reasonably well with the previous results from the tensile study. From all these results, it can be concluded that the incorporated silane does not affect the mobility of the PP chains or promote the interaction between the CaCO₃ filler and PP in the system.

CONCLUSIONS

Silane-crosslinkable PP composites filled with CaCO₃ have been investigated. During the silane-grafting process, the degradation of PP chains occurs as a side reaction. The extents of the silane grafting and PP degradation depend strongly on the reaction temperature, concentrations of DCP and VTMS, and amount of the filler in the composites. Without the presence of peroxide, silane grafting is possible. The extent of the grafting reaction increases with increasing DCP concentration (up to 0.05 wt %). When the concentration of free radicals is over a certain degree, the dominant reaction is PP chain scission. As a result, the polymer viscosity decreases drastically. In the systems containing both silane and CaCO₃, the viscosity of the polymer is higher than that of the grafted sample without CaCO₃ addition; in other words, the effect of the filler on the polymer viscosity compensates for the effect caused by PP degradation. In comparison with pure PP, crystallization starts earlier for the grafted samples. The percentage of crystallinity of grafted PP is also higher than that of the pure polymer. DMA



(a)



(b)

Figure 2 Temperature dependence of (a) E' and (b) $\tan \delta$ of PP, grafted PP, and their corresponding composites with 50% CaCO₃.

results reveal that the incorporated silane does not have a strong effect on the mobility of the PP chains. The tensile results show that the silane-grafted PP has slightly higher tensile stress and a comparable modu-

lus in comparison with pure PP. After filler addition, the silane-crosslinkable composites show higher tensile stress and modulus than the ungrafted composites.

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