

# Effects of Interfacial Adhesion on Properties of Polypropylene/Wollastonite Composites

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**ABSTRACT:** Wollastonite reinforced polypropylene (PP/CaSiO<sub>3</sub>) composites were prepared by melt extrusion. A silane coupling agent and a maleic anhydride grafted PP (PP-g-MA) were used to increase the interfacial adhesion between the filler and the matrix. The increased adhesion observed by scanning electron microscopy (SEM) resulted in improved mechanical properties. A model was applied to describe the relationship between the interfacial adhesion and tensile properties of PP/CaSiO<sub>3</sub> composites. There is stronger interfacial adhesion between silane-treated CaSiO<sub>3</sub> and polymer matrix containing PP-g-MA

as a modifier. Results of dynamic mechanical thermal analysis (DMTA) showed that stronger interfacial adhesion led to higher storage modulus. The influence of CaSiO<sub>3</sub> particles on the crystallization of PP was studied by using differential scanning calorimetry (DSC). The introduction of CaSiO<sub>3</sub> particles does not affect the crystallization temperature and crystallinity of PP matrix significantly. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1718–1723, 2008

**Key words:** polypropylene; composites; interfaces

## INTRODUCTION

Inorganic fillers are frequently used to improve the mechanical properties of polymers, such as heat distortion temperature and hardness.<sup>1–4</sup> Generally, interfacial adhesion between fillers and polymer matrix greatly affects the mechanical properties of filler-reinforced composites. Good interfacial adhesion results efficient stress transfer from the continuous polymer matrix to the dispersed fillers, leading to improved mechanical properties of composites.<sup>5–6</sup>

Interaction between polypropylene (PP) and inorganic fillers is usually weak because PP is a nonpolar polyolefin while inorganic fillers have a polar surface. Thus, PP and inorganic fillers should be modified to ensure a good adhesion.<sup>7–9</sup> Wollastonite (CaSiO<sub>3</sub>) has acicular (needle-like) form and is characterized by repeating, twisted, three silica tetrahedron unit. Because of its high aspect ratio and relatively high hardness (Mohs hardness: 5), CaSiO<sub>3</sub> can be used to reinforce polymers.<sup>10–12</sup> To improve the interfacial adhesion between PP and CaSiO<sub>3</sub>, an appropriate coating should be chosen, which is based on the physical and chemical interactions that are possibly generated between the filler coating and the surrounding matrix. Maleic anhydride grafted PP (PP-g-MA) is a commonly used modifier for PP.

In this work, PP-g-MA was added to PP/CaSiO<sub>3</sub> composites and one of the coatings considered was  $\gamma$ -aminopropyl-triethoxysilane (KH-550). The secondary amine group is expected to react with MA functional group.

The objective of this work was to investigate the efficiency of a silane coupling agent and PP-g-MA as adhesion promoters in PP/CaSiO<sub>3</sub> composites. To explore the effect of interfacial adhesion on the mechanical properties of composites, this work attempts to reveal effects of interfacial adhesion on microscopic morphology, tensile properties, and dynamic mechanical properties of PP/CaSiO<sub>3</sub> composites.

## EXPERIMENT

### Materials

PP copolymer (Moplen RP344R, injection grade) was purchased from Basell Polymirae (Korea) with melt flow index (MFI) of 30 g/10 min at 230°C (ASTM D1238). CaSiO<sub>3</sub> was provided by Shanghai Huda Investment (China) with an aspect ratio of 9.3. Its weight loss at 900°C is about 1%. In this paper, CaSiO<sub>3</sub> was treated with 3 wt % (based on the dosage of CaSiO<sub>3</sub>) NDZ-101 titanate or KH-550 silane coupling agent in a high-speed mixer before use. The titanate and silane coupling agents were made by Nanjing Shuguang Chemical (China). PP-g-MA was made by Shanghai Sunny New Technology Development (China).

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### Sample preparations

Binary PP/CaSiO<sub>3</sub> composites with weight content ratio 70/30 (88/12 volume ratio), as well as ternary PP/PP-g-MA/CaSiO<sub>3</sub> composites with weight content ratio 65/5/30 were prepared. All materials (PP, PP-g-MA, and CaSiO<sub>3</sub>) were mixed and then dried in ovens at 70°C for 24 h. The materials were blended in a twin screw extruder with the temperature profiles of 200, 200, 210, 210, 200°C (denoted from the inlet hopper to the end of screws), and the extruded strands were chopped into granules and dried at 100°C for 5 h. Samples were injection molded under an identical condition using an injection molding machine. The temperature profiles of the injection molding were 220, 220, 220, 210, and 200°C and the injection pressure was 50 MPa. Testing specimens were molded according to ASTM standards: tensile properties (ASTM D638 Type I), flexural properties (ASTM D790), notched Izod (ASTM D256) and heat deflection temperature (HDT) (ASTM D648-01).

### Mechanical properties testing

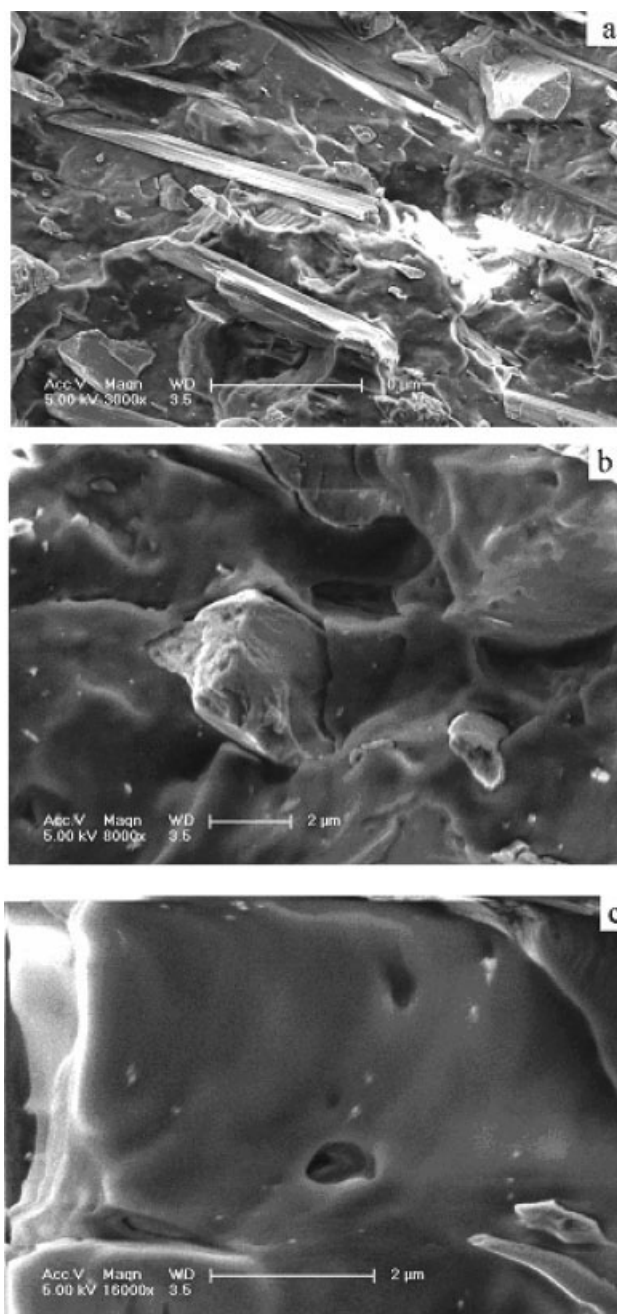
The mechanical properties were evaluated according to ASTM standards. Tensile properties (ASTM D638 Type I) and flexural properties (ASTM D790) were measured using a Instron 4465 universal test instrument at crosshead speed of 50 mm/min and 2 mm/min, respectively. Notched Izod impact tests (ASTM D256) were performed with 63.5 × 12.7 × 3.2 mm<sup>3</sup> specimens with a V-shape notch on a Ray-Ran universal pendulum impact tester. The hammer speed was 3.5 m/s, and the pendulum weight was 0.818 kg. The HDT was measured by using a Ray-Ran Vicat/HDT tester (ASTM D648-01).

### Scanning electron microscopy analysis

The fracture surfaces of the impact specimens were characterized by a scanning electron microscope (Hitachi S-2150, Tokyo, Japan). The fractured surfaces were coated with gold before scanning electron microscopy (SEM) observation.

### Differential scanning calorimetry

Differential scanning calorimetry (DSC) test was carried out on a Perkin–Elmer Paris 1 thermal analyzer under nitrogen atmosphere. A small piece of sample (about 7 mg) was used for each experiment. The sample was heated to 180°C and maintained at this temperature for 5 min to eliminate the effects of pre-conditions. The sample was cooled from 180 to 20°C at a rate of 10°C/min (cooling cycle), held for 5 min

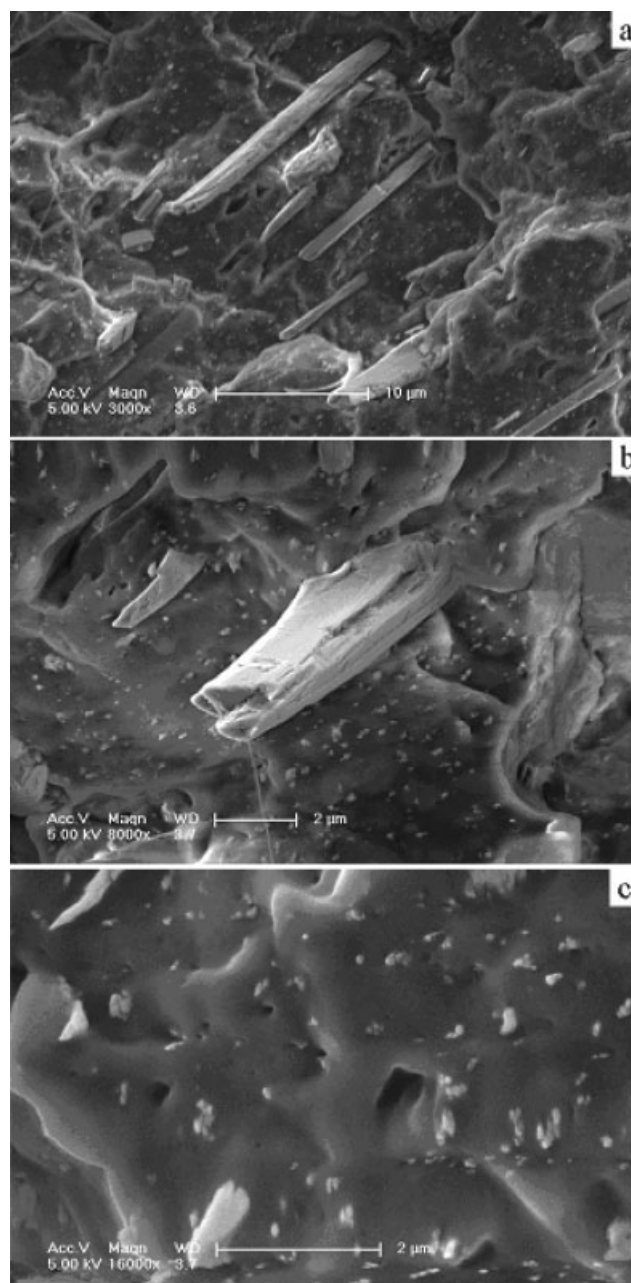


**Figure 1** SEM micrographs of impact fracture surface of PP/CaSiO<sub>3</sub> viewed under different magnifications.

at this temperature, and then heated again to 180°C at a rate 10°C/min (heating cycle).

### Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was carried out in a dynamic mechanical thermal analyzer (Rheometrics Scientific DMTA IV). Measurements were performed in the cantilever mode at a frequency of 1 Hz over a temperature range of –80 to 120°C, and at a heating rate of 3°C/min. The strain amplitude remained at 0.05%.



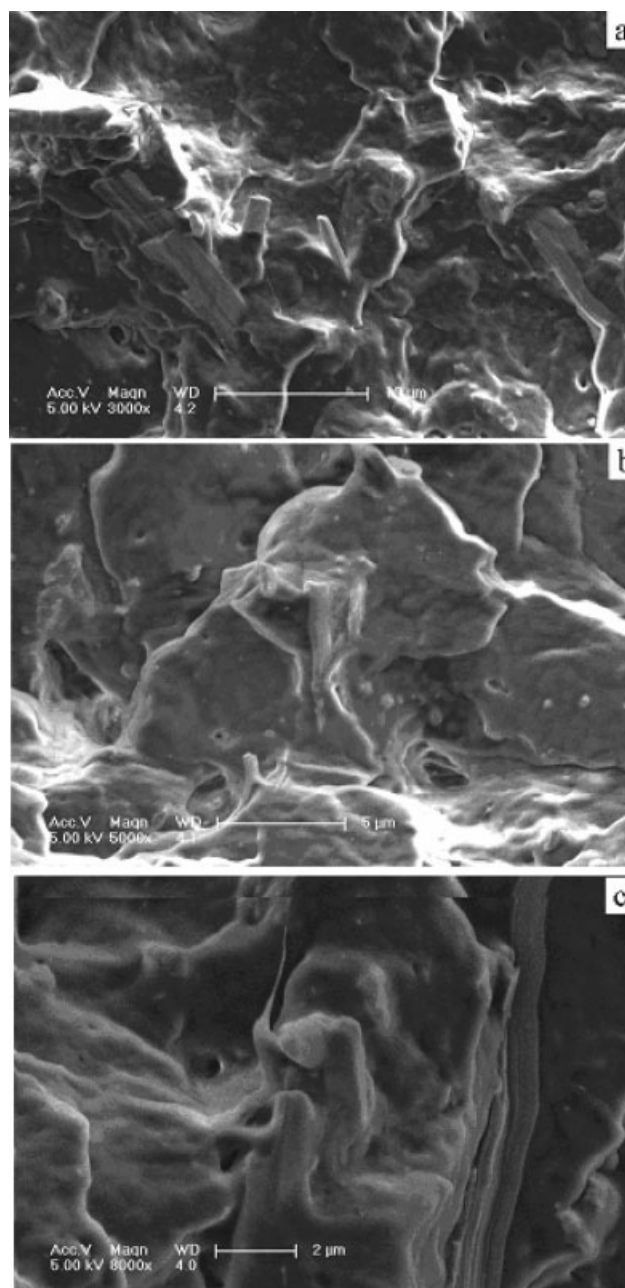
**Figure 2** SEM micrographs of impact fracture surface of PP/CaSiO<sub>3</sub>-titanate viewed under different magnifications.

## RESULTS AND DISCUSSION

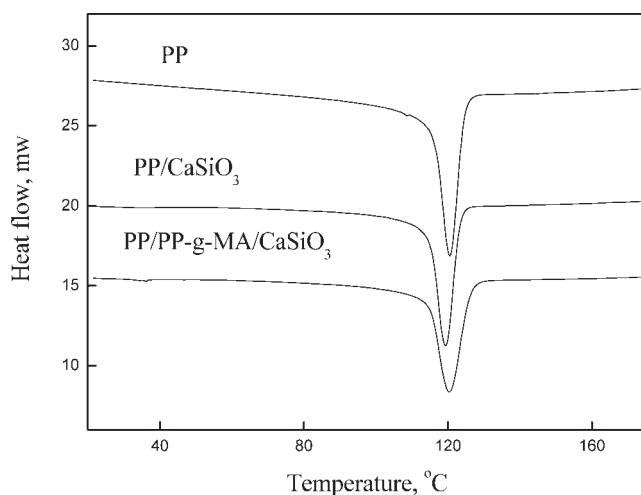
### Morphology of PP/CaSiO<sub>3</sub> composites

The morphology of fracture surfaces of PP/CaSiO<sub>3</sub> composites is presented in Figures 1–3, providing qualitative information on the composite interface. SEM micrograph of fractured PP/CaSiO<sub>3</sub> sample in Figure 1(a) shows that the fracture occurs at weaker PP-CaSiO<sub>3</sub> interface, for there are many exposed CaSiO<sub>3</sub> particles on the fracture surface of PP/CaSiO<sub>3</sub>. Moreover, higher magnification of this

micrograph [Fig. 1(b,c)] reveals that the interfacial adhesion between PP matrix and CaSiO<sub>3</sub> particles is poor, as evidenced by clean CaSiO<sub>3</sub> surfaces and CaSiO<sub>3</sub> pullout behavior. The fracture surface of PP/CaSiO<sub>3</sub>-titanate has similar micromorphology with PP/CaSiO<sub>3</sub> (Fig. 2), which indicates that titanate coupling agent did not effectively improve the interfacial adhesion. In contrast, many CaSiO<sub>3</sub> particles of PP/PP-g-MA/CaSiO<sub>3</sub> composite are embedded in the matrix and a large amount of matrix are bonded firmly to the CaSiO<sub>3</sub> surfaces (Fig. 3), indicating that



**Figure 3** SEM micrographs of impact fracture surface of PP/PP-g-MA /CaSiO<sub>3</sub> viewed under different magnifications.



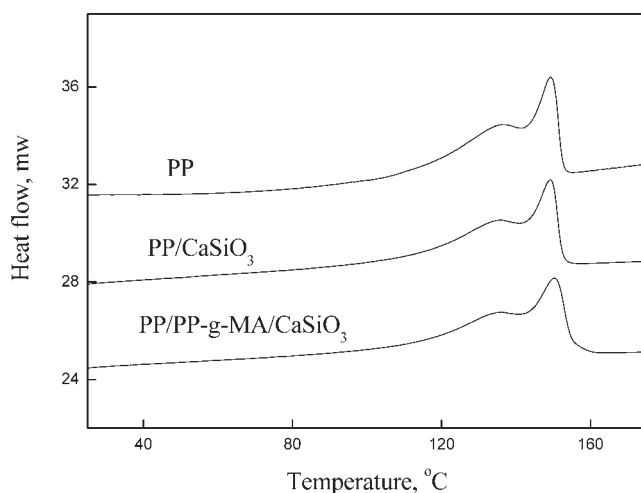
**Figure 4** DSC cooling flow curves for PP and composites.

a strong interfacial adhesion develops between PP and CaSiO<sub>3</sub>.

The CaSiO<sub>3</sub> was treated with an amino silane coupling agent, containing amino groups, which could react with maleic anhydride groups. Meanwhile, the silane coupling agent also contained hydroxyl groups and could bond to the CaSiO<sub>3</sub>. Because the silane layer formed at the CaSiO<sub>3</sub> surface, the CaSiO<sub>3</sub> particles in PP/PP-g-MA/CaSiO<sub>3</sub> composite should wet out more readily in the PP matrix, resulting in improved interfacial adhesion.

### Crystallization behavior

The mechanical properties of PP/CaSiO<sub>3</sub> composites are significantly dependant on the crystal form and crystallinity of PP.<sup>13–20</sup> The DSC curves of PP and PP/CaSiO<sub>3</sub> composites are shown in Figures 4 and 5, and the corresponding data are given in Table I. Inorganic fillers often have nucleating effects for PP



**Figure 5** DSC heating flow curves for PP and composites.

**TABLE I**  
Parameters Obtained from DSC Measurements for PP and Composites

Samples	$T_{p,m} = T_m$ (°C)	$T_{p,c} = T_c$ (°C)	$\Delta H_c$ (J/g)	$\Delta H_m$ (J/g)
PP	149.3	120.7	61.5	64.4
PP/CaSiO <sub>3</sub>	149.3	119.3	59.7	63.5
PP/PP-g-MA/ CaSiO <sub>3</sub>	150.5	120.5	60.1	63.1

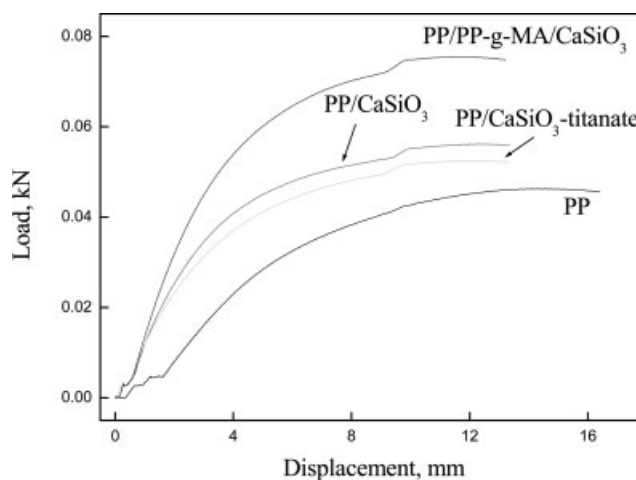
$T$ , temperature;  $H\Delta$ , specific enthalpy;  $m$ , melting;  $c$ , cooling;  $p$ , peak.

The  $H\Delta$  values (J/g) are recalculated on the basis of PP matrix.

and can increase crystallization temperature ( $T_c$ ) of PP.<sup>21,22</sup> However, CaSiO<sub>3</sub> does not act as an effective nucleating agent here and affects of the  $T_c$  of the PP matrix slightly. (Table I). Because the standard heat of crystallization of PP copolymer is not available, the crystallinity of PP composite cannot be calculated. Judged from the data of  $\Delta H_m$  (Table I), CaSiO<sub>3</sub> particles mildly decrease the crystallizability of PP.

### Mechanical properties

The flexural load-displacement curves for PP and PP/CaSiO<sub>3</sub> composites are shown in Figure 6. The incorporation of CaSiO<sub>3</sub> into PP leads to an effective increase in the flexural strength, because of its high hardness. The flexural strength of PP/CaSiO<sub>3</sub>-titanate is slightly lower than that of PP/CaSiO<sub>3</sub>. It is thought that the titanate coupling agent can act as a plasticizer, leading to decreased flexural strength. The PP/PP-g-MA/CaSiO<sub>3</sub> composite exhibits the highest flexural strength among all samples investigated. Because strong interfacial adhesion exists between CaSiO<sub>3</sub> and PP, it is thought that such inter-



**Figure 6** Flexural load-displacement curves of PP and PP/CaSiO<sub>3</sub> composites.

TABLE II  
Mechanical Properties of PP and PP/CaSiO<sub>3</sub> Composites

Samples	Yield strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Notched Izod impact strength (J/m)	Heat deflection temperature (°C)
PP	29.5	780	451.0	27.7	828	44.0	87.8
PP/CaSiO <sub>3</sub>	25.3	782	312.1	33.5	1564	27.8	95.6
PP/CaSiO <sub>3</sub> -titanate	23.3	1056	283.0	31.6	1345	24.6	94.8
PP/PP-g-MA/CaSiO <sub>3</sub>	31.8	810	357.2	44.3	1965	37.8	102.8

actions can promote stress transfer from the matrix to CaSiO<sub>3</sub> during flexural loading. The mechanical properties of PP and PP/CaSiO<sub>3</sub> composites are shown in Table II. HDT is an important parameter to evaluate the enforcing effect of inorganic filler. The HDT of PP/PP-g-MA/CaSiO<sub>3</sub> is 15°C higher than that of PP and 7.2°C of PP/CaSiO<sub>3</sub>, indicating that good interfacial adhesion can largely promote the enforcing effect of CaSiO<sub>3</sub>.

The extent of interfacial interaction could be quantitatively characterized by the followed equation:<sup>23</sup>

$$\sigma_{yc} = \sigma_{yp} \frac{1 - \phi_f}{1 + 2.5\phi_f} \exp(B\phi_f) \quad (1)$$

where  $\sigma_{yc}$  and  $\sigma_{yp}$  are yield strength of composite and polymer matrix, respectively.  $\phi_f$  is volume fraction of particles, and  $B$  is a parameter characterizing interfacial adhesion. Generally, a higher  $B$  value indicates a stronger interfacial adhesion.  $B$  value is 1.97 for PP/CaSiO<sub>3</sub>, 1.29 for PP/CaSiO<sub>3</sub>-titanate, and 3.88 for PP/PP-g-MA/CaSiO<sub>3</sub>. The titanate coupling agent results in a reduced polymer/filler interfacial adhesion (PP/CaSiO<sub>3</sub>-titanate), while the silane coupling and PP-g-MA result in an increased interfacial adhesion (PP/PP-g-MA/CaSiO<sub>3</sub>).

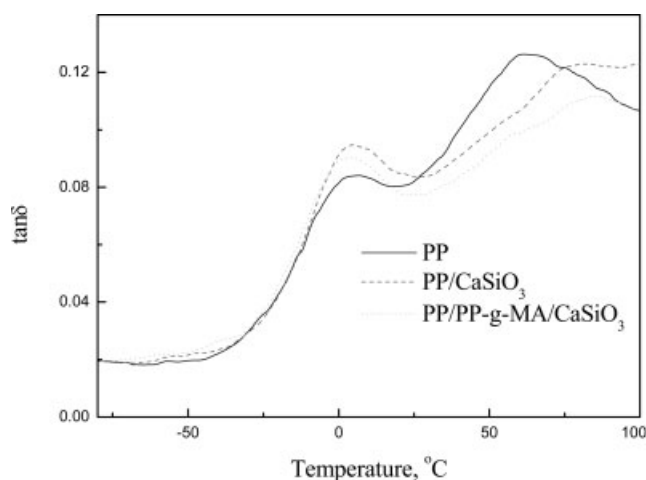


Figure 7 DMTA thermographs of PP and PP/CaSiO<sub>3</sub> composites: (a) the storage modulus, (b) tan  $\delta$ .

### DMTA measurements

Dynamic mechanical spectroscopy has long been used as a sensitive method for identifying interfacial interactions.<sup>24,25</sup> Figure 7 shows data for the tan  $\delta$  and  $E'$  of PP and PP/CaSiO<sub>3</sub> composites as a function of temperature. The tan  $\delta$  curve of PP [Fig. 7(a)] in the temperature range investigated in this study exhibits  $\beta$  relaxation located in the vicinity of 6°C. The  $\beta$  relaxation is the dominant relaxation, which corresponds to the glass-rubber transition of the amorphous portions. The temperature of the peak maximum is assigned to the glass-transition temperature ( $T_g$ ). Figure 7(a) shows that the position of  $\beta$  relaxation peak remains unchanged with CaSiO<sub>3</sub> incorporation. This would suggest that CaSiO<sub>3</sub> incorporation did not significantly influence the crystallization or percentage of PP crystallinity<sup>25,26</sup> as shown above.

The incorporation of CaSiO<sub>3</sub> particles in PP results a considerably enhanced stiffness and heat-form resistance of PP/CaSiO<sub>3</sub> composite [Fig. 7(b)]. Moreover, Figure 7(b) shows that the drop in modulus on passing through  $\beta$  relaxation temperature is comparatively less for reinforced material than for PP alone, and this drop is less as the temperature increases. In other words, the effect of the CaSiO<sub>3</sub> on the modulus is larger at higher temperature than at lower temperature. This is probably due to the fact that the incorporation of CaSiO<sub>3</sub> reduced the flexibility of the material by introducing constraints on the segmental mobility of the polymeric molecules or by retarding the lamellar movement at relaxation temperature,<sup>25,26</sup> which becomes more pronounced with increasing temperature.

The values of  $E'$  at selected temperatures are presented in Table III. The improvement of interfacial adhesion results in a further increased  $E'$  (PP/PP-g-MA/CaSiO<sub>3</sub>), which is in agreement with the mechanical property results and microscopic evidence. It appeared that the improvement of interfacial adhesion hindered the molecular motion, as well as the relative motion of the lamellae, leading to a stiffer, stronger, tougher material.<sup>25,27</sup> The ability of the MA groups to react with amino groups of KH-550 coated on CaSiO<sub>3</sub> particles translated to better composites properties.

**TABLE III**  
Storage Modulus of PP/CaSiO<sub>3</sub> Composites at Different Temperatures

Samples	Temperature (°C)			
	-50	25	50	100
Storage modulus (MPa)				
PP	3690	1135	554	123
PP/CaSiO <sub>3</sub>	4899	1539	925	250
PP/PP-g-MA/CaSiO <sub>3</sub>	4982	1602	1010	304

**CONCLUSIONS**

CaSiO<sub>3</sub> can be used to effectively reinforce PP if the interfacial adhesion between the filler and the matrix is promoted. CaSiO<sub>3</sub> was treated with a kind of amino-silane coupling agent and PP-g-MA was used as adhesion promoter. The interfacial adhesion was effectively increased, which can be attributed to the ability of the MA groups to react with the amino groups. Increased interfacial adhesion resulted in a material with increased mechanical properties. A model was applied to analyze the relationship between the interfacial adhesion and tensile properties. It was found that stronger interfacial adhesion existed in treated-CaSiO<sub>3</sub>-filled composite containing PP-g-MA as matrix modifier. Stronger interfacial adhesion led to higher HDT and storage modulus. The introduction of CaSiO<sub>3</sub> particles did not influence the crystallization temperature and crystallinity of PP matrix significantly.

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