

# Processing, Crystallization, and Dynamic Mechanical Analysis of High Molar Mass Polysiloxane-Modified PP/CaCO<sub>3</sub> Composites

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**ABSTRACT:** A ternary system polypropylene (PP)/calcium carbonate (CaCO<sub>3</sub>)/high molar mass polysiloxane has been investigated with respect to its processing, crystallization, and dynamic mechanical properties. The filling level of PP varied from 2.5 vol % to 6.5 vol % CaCO<sub>3</sub> and 0.6 vol % to 2.5 vol % polysiloxane, and the mixing was done in a single screw extruder. The polysiloxane molecules had different functionalities added (epoxy and methacrylate reactivity, respectively). However, the functionality did not influence processing, crystallinity, or mechanical properties. It was found that the polysiloxane molecules tended to surround the CaCO<sub>3</sub> particles, thus forming a core-shell structure. This structure was achieved without surface treatment of the filler. The polysiloxane also provided a lubrication effect in the melt and thus enabled an easier processing of the composite. A nucleating effect of the filler could be detected. The mechanical properties were similar to those found in other core-shell structured samples, where the structure was achieved by surface treatment. It was found that the polysiloxane exhibited a lubricant effect only if it was mixed with PP together with CaCO<sub>3</sub>. If polysiloxane was added to the PP matrix alone, screw slippage occurred and the polysiloxane molecules agglomerated. The mechanical properties of these composites were similar to those of pure PP. No influence on the matrix crystallisation could be detected in this case. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3091–3098, 2001

**Key words:** polypropylene; calcium carbonate; polysiloxane; composites; dynamic mechanical analysis

## INTRODUCTION

Polypropylene (PP) is often modified with fillers to provide mechanical strength and increased thermal resistance. Such polypropylene composites tend to lack sufficient toughness for many applications; particularly low-temperature impact resistance. A commonly used filler for PP is

Calcium Carbonate (CaCO<sub>3</sub>) because of its low cost and its ability to provide an increased modulus.<sup>1</sup> However, the filler content is usually about 10–20 wt %, because highly filled polymers are difficult to process and the composites may be too brittle. The mechanical properties of CaCO<sub>3</sub>-filled PP has widely been discussed with regard to filler content, particle shape, and matrix crystalline form.<sup>2–4</sup> Increased toughness in PP blends may be achieved using elastomers such as poly(ethylene-co-propylene) with the elastomer content in the range of 0–30 wt %.<sup>5</sup> A combination of toughness and strength has been found with both filler and elastomer in the composition.<sup>6</sup> For such a

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system, enhanced properties can be achieved for hybrids in which the filler has been encapsulated by the elastomer (core-shell structure).<sup>7-10</sup>

The key factor controlling the performance of composites is the polymer-filler interface. Strong interfacial adhesion is essential if high performance is to be achieved. Fillers are often modified to provide a hydrophobic surface to increase the adhesion of hydrophobic polymers such as polypropylene. Various reactive surface modifiers have been used including alkylalkoxysilanes, alkylsilyl chlorides, dialkyltitanates, and stearic acid. Other nonreactive filler coatings are calcium and magnesium stearates, silicone oils, waxes, and ionomers.<sup>11-14</sup> In addition, silicone oils have also been used as internal lubricants and mold release agents in polymer processing.<sup>15-17</sup> However, the short chain oil tended to migrate to the polymer surface after processing causing problems in surface finishing such as printing.<sup>18</sup> To stop the silicone migration, high molecular weight polysiloxanes (i.e., polydimethylsiloxane) were introduced. Using them in small amounts (0.5-2 wt %) resulted in easier processing and slightly enhanced mechanical properties, which has been studied elsewhere.<sup>19-24</sup> So far, no investigation has been conducted using high molar mass polysiloxane as a processing aid for calcium carbonate-filled PP composites.

Addition of surface modifiers usually involves an extra processing step. Prior to mixing with the polymer, the filler needs to be uniformly coated by the modifier. This step is time consuming. A further approach, therefore, is to combine the modifier with the polymer and filler during the processing stage. In the present investigation we focused on this approach. High molar mass polysiloxane elastomers were studied as processing aids for PP/CaCO<sub>3</sub> composites and as modifiers of the CaCO<sub>3</sub> particle surface. The surface energy of the polysiloxane and the high molar mass should cause it to preferentially coat the filler particles and thus act as a surface modifier without primary treatment. While solid and elastomeric are at ambient temperatures, it is expected that the polysiloxanes will have sufficient flow at processing temperatures to provide lubrication. At ambient temperatures the elastomeric properties could be similar to the encapsulated filler in a maleated poly(ethylene-co-propylene) elastomer, and so may provide a moderate toughening effect.

## EXPERIMENTAL

### Materials

A polypropylene (PP) homopolymer, melt flow index (MFI) 3.0 g/10 min, density 0.905 g/cm<sup>3</sup> obtained from Montell was used in this investigation. The fillers were calcium carbonate (CaCO<sub>3</sub>) with an average particle size <5 μm and density of 2.93 g/cm<sup>3</sup> as well as high molar mass polysiloxane supplied by Dow Corning (Resin Modifiers 4-7081 and 4-7051) with a density of 1.2 g/cm<sup>3</sup>. These resin modifiers had a functionality added, which allowed reactions with either the polymer or the filler. In the case of high molar mass polysiloxane 4-7081, this has a methacrylate reactivity, allowing reaction of the polysiloxane with double bonds in a polymer matrix. Resin modifier 4-7051 had an epoxy reactivity, allowing reactions with labile hydrogens such as in polyamide or carboxyl.

### Sample Preparation

The required amounts of filler and polymer were weighed. If two different fillers were added to PP, they were dry mixed thoroughly with each other prior to dispersion in the polymer matrix.

An Axon B12 single screw extruder was used to disperse the filler into the polymer matrix. The extruder was supplied with a Gateway slotted screw, which enabled reverse flow of parts of the polymer melt. Hence, the residence time of the polymer melt in the extruder was extended and a better mixing as well as an increased heat transfer was achieved. The screw length : diameter ratio (L : D ratio) was 26 : 1, and the temperatures of the four heating zones of the extruder were 150°C (feeding zone), 210°C, 210°C (melting and metering zones), and 190°C (die zone). The screw speed was varied between 80 to 100 rpm. Two different methods were used to prepare the composites: (a) one-step extrusion—all filler was introduced into the polymer matrix in one step. For a uniform dispersion of the filler, the composite was reextruded seven times; (b) stepwise extrusion—the filler was introduced into the polymer matrix in eight incremental steps. The amount of filler added was increased with each extrusion step.

As a reference, pure PP was also extruded eight times and DSC measurements were taken to check that thermal degradation had not occurred.

**Table I Filler Content Analysis Results**

Sample No.	Composition				Mixing
	CaCO <sub>3</sub> (wt %)	CaCO <sub>3</sub> (vol %)	Siloxane (wt %)	Siloxane (vol %)	
1	—	—	—	—	
2	18.4	6.5	—	—	one step
3	7.7	2.5	0.8 (4-7051)	0.6	one step
4	14.9	5.2	1.5 (4-7051)	1.3	stepwise
5	7.9	2.7	0.8 (4-7081)	0.7	one step
7	—	—	1.0 (4-7051)	0.8	one step
8	—	—	1.7 (4-7051)	1.3	stepwise
9	—	—	3.3 (4-7051)	2.5	one step
10	—	—	1.9 (4-7081)	1.4	one step
11	—	—	2.1 (4-7081)	1.6	stepwise

The sample compositions are given in wt % and vol %. The table also provides information about the type of extrusion (one step or stepwise), which high molecular weight polysiloxane was used (4-7051 or 4-7081) and a sample number as abbreviation.

Prior to their mechanical analysis, the prepared composites were extruded and calendered to polymer tapes of 0.25–0.30-mm thickness.

#### Thermogravimetry Analysis (TGA)

A Perkin-Elmer TGA7 instrument was used to analyze the filler content of the composites. Three different samples of each composition were prepared for multiple measurements. The samples were heated from 50 to 850°C at 10 K/min, and the purge gas (flow rate: 20 mL/min) was changed from nitrogen to air at 750°C.

#### Differential Scanning Calorimetry (DSC)

The crystallization and melting characteristics of the samples were measured using a DSC7 instrument supplied by Perkin-Elmer. In a first step, the samples were heated from 20 to 200°C to erase their thermal history. Afterwards, they were cooled to 20°C and heated again to 200°C. The cooling and heating rate, respectively, for all steps was 10 K/min. Nitrogen purge gas at a flow rate of 20 mL/min was applied.

#### Dynamic Mechanical Analysis (DMA)

Samples of approx. 15 × 6 mm size were cut from the extruded tapes parallel to the extrusion direction. The samples were placed in an oven at 150°C and left for at least 1.5 h. Subsequently, they were cooled to room temperature at ~2 K/min. A DMA7e instrument from Perkin-Elmer fitted with a dual cantilever geometry was used for the dynamic mechanical measurements. It was found

that the results were very sensitive to sample mounting: the cantilever clamps should only be tightened slightly, to avoid any transverse force induction into the samples. For measurement, the samples were cooled to –50°C in the instrument and subsequently heated to 150°C at 2 K/min. A dynamic force of 50 mN oscillating at 1 Hz was used with no static force applied. Nitrogen purge gas was used at a flow rate of 40 mL/min. At least three samples of each composition were prepared for multiple measurements.

#### Scanning Electron Microscopy (SEM)

A Philips XL-30 scanning electron microscope was used for morphological observation of freeze-fractured surfaces of the composites. The samples were carbon coated and different acceleration voltages used (10, 15, and 20 kV). Images were taken with a secondary electron as well as a backscatter detector. The microscope was connected to a energy disperse X-ray analysis (EDX) program, which was applied to identify and distinguish the filler particles.

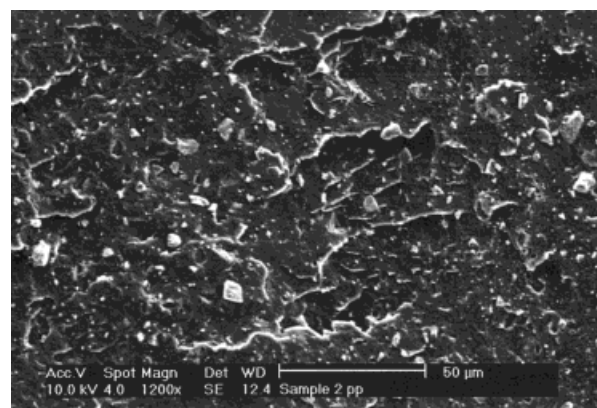
## RESULTS AND DISCUSSION

### Sample Preparation and Composition

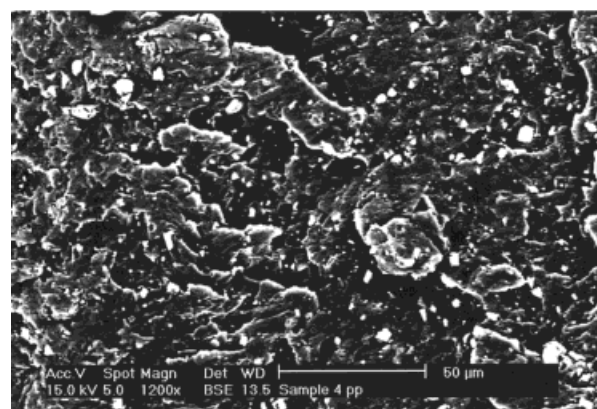
The results of the thermogravimetry analysis of filler content are listed in Table I. Table I also introduces numbers as abbreviations for the sample names and indicates whether the sample was produced in one step or stepwise. It was found

that the extrusion method influenced the final filler content. In the case where the material was added in a one step extrusion into the polymer (one step mixing) the filler particles tended to agglomerate and blocked the throat of the extruder. The extruder needed to be cleaned and, hence, filler was partly lost. Furthermore, the initial distribution of the filler in the matrix was poor. However, after reextrusion (seven times) of the composite, the calcium carbonate and/or polysiloxane agglomeration was broken and the particles were evenly distributed. If the filler was mixed stepwise into the polymer (as in sample 4), no blocking of the extruder occurred. Therefore, all of the initial added material remained in the matrix achieving a high filling level. Polysiloxane is widely used as an internal lubricant for polymer processing<sup>16,22</sup> and as a mold release agent,<sup>17</sup> therefore, easier processing should be expected when Si 4-7051 or Si 4-7081 was added to the composites. However, this could only be confirmed in this investigation, if the polysiloxane was added to PP together with calcium carbonate. If the polysiloxane was added to PP in a one-step mixing, without calcium carbonate present (samples 7, 9, and 10), screw slippage occurred and the processing of the composite took much longer. This effect could be reduced by adding the material stepwise (sample 11), but the processing was still not enhanced compared with the extrusion of pure PP. To ensure that no thermal degradation of the polymer had occurred, DSC measurements were performed on PP samples before mixing and after the final extrusion step. No evidence for thermal degradation could be found.

SEM images in Figure 1(a)–(c) display the morphology of samples 2, 4, and 11, respectively. It was observed that the filler particles of samples 2 and 4 were evenly distributed. The diameter of the largest particles was similar ( $\sim 5 \mu\text{m}$ ) in both samples. Using EDX analysis to identify the filler in sample 4, neither pure  $\text{CaCO}_3$  nor pure polysiloxane could be found. Instead, every  $\text{CaCO}_3$  particle also showed a Si peak in the EDX spectrum (Fig. 2). This suggests that the polysiloxane formed a layer on top of calcium carbonate. A reason for this may be the low surface energy of the polysiloxane and its high molar mass, which causes it to cover other particles. This could decrease the stiffening effect of the calcium carbonate and enable easier processing of the composite. However, we could not determine whether the  $\text{CaCO}_3$  was completely or partly surrounded by the polysiloxane.



(a)



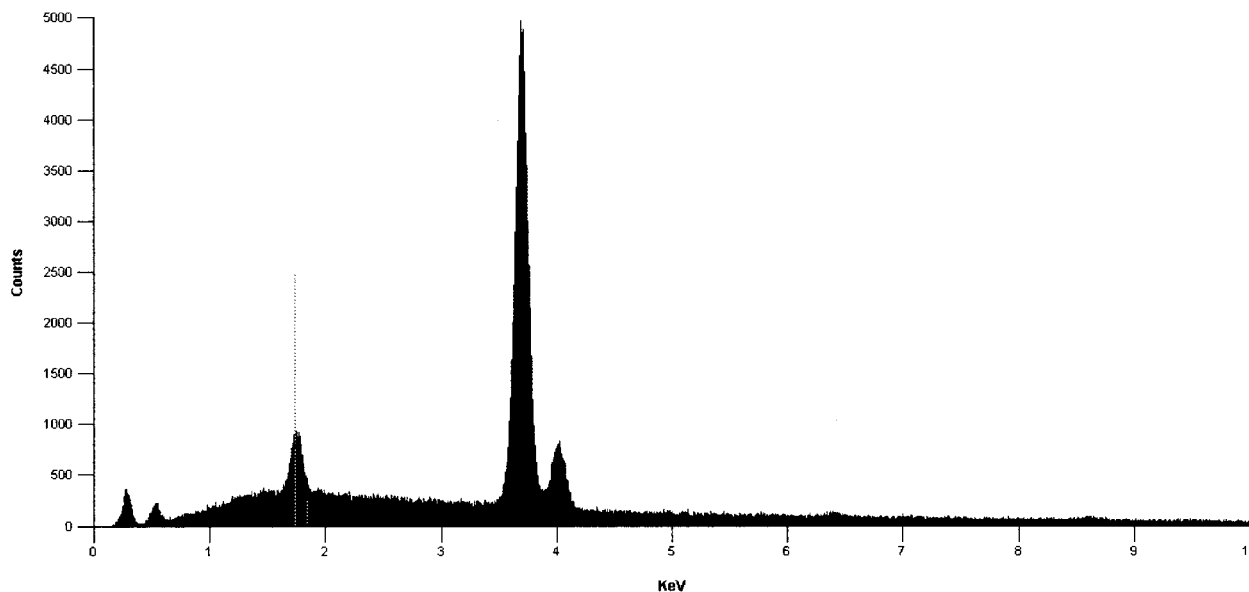
(b)



(c)

**Figure 1** SEM pictures taken from (a) sample 2 (PP + 6.5 vol %  $\text{CaCO}_3$ ), (b) sample 5 (PP + 2.7 vol %  $\text{CaCO}_3$  + 0.7 vol % Si 4-7051 – one step), and (c) sample 11 (PP 1.6 vol % Si 4-7051 – stepwise).

The SEM image of sample 11 [Fig. 1(c)] shows a poor distribution of the filler in the polymer matrix of this sample. In the middle of the micrograph a rather large agglomeration is clearly visible, which continues almost throughout the entire fracture surface. This agglomeration of the



**Figure 2** EDX spectrum, at 20 kV beam energy, of the surface of a CaCO<sub>3</sub> filler particle in PP composite (sample 4), Si peak is marked with a line.

polysiloxane may explain the poor processing of the composites found in samples 7–11. With no other particles in the matrix available, the polysiloxane tended to cover the metal surface of the extruder screw and thus caused slippage. The shear force eventually peeled the polysiloxane layer from the screw, but this obviously did not disrupt the agglomerated particles.

### Melting and Crystallization

The melting and crystallization properties of the prepared polymer composites were studied. Table II shows the onset crystallization temperature ( $T_{c\text{ onset}}$ ) and peak crystallization temperature ( $T_{c\text{ peak}}$ ) for some selected samples. For pure PP (sample 1) the peak crystallization temperature was found to be at 109.7°C, which corresponds to values found elsewhere (e.g., Bogoeva-Gaceva et

al. report for PP (MFI: 13 g/10 min)  $T_{c\text{ peak}} = 106.9^\circ\text{C}$  at a cooling rate of 10 K/min<sup>25</sup>). With CaCO<sub>3</sub> added to PP (sample 2), we detected an increase in the peak crystallization temperature of  $\Delta T_{c\text{ peak}} = 4.5$  K and in the onset crystallisation temperature  $\Delta T_{c\text{ onset}} = 2.3$  K. Tjong et al found a similar result ( $\Delta T_{c\text{ peak}} = 3.8$  K at a cooling rate of 10 K/min) for 20 wt % CaCO<sub>3</sub> in PP.<sup>26</sup> If polysiloxane only was added (samples 8 and 11), an increase of  $\Delta T_{c\text{ onset}} = 2.0$  K (sample 8) and  $\Delta T_{c\text{ onset}} = 1.4$  K (sample 11), respectively was measured. A change in  $T_{c\text{ onset}}$  indicates whether a filler is acting as a nucleating agent. Because the increase in  $T_{c\text{ onset}}$  is small for samples 2, 8, and 11, it can be concluded that neither polysiloxane nor CaCO<sub>3</sub> on their own nucleated the polymer. However, if both materials were added together to PP (samples 3 and 5) a clear increase in

**Table II** Peak Crystallization Temperature ( $T_{c\text{ peak}}$ ) and Onset Crystallization Temperature ( $T_{c\text{ onset}}$ ) for Some Representative Chosen Samples

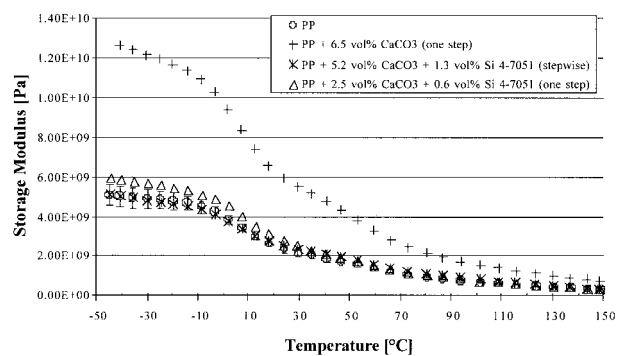
Sample No.	Composition	$T_{c\text{ onset}}$ (°C)	$T_{c\text{ peak}}$ (°C)	$T_{c\text{ onset}} - T_{c\text{ peak}}$ (K)
1	PP	115.9	109.7	6.2
2	PP + 6.5 vol % CaCO <sub>3</sub> (one step)	118.2	114.2	4.0
3	PP + 2.5 vol % CaCO <sub>3</sub> + 0.6 vol % Si 4-7051 (one step)	121.8	118.7	3.1
5	PP + 2.7 vol % CaCO <sub>3</sub> + 0.7 vol % Si 4-7081 (one step)	122.6	119.3	3.3
8	PP + 1.3 vol % Si 4-7051 (stepwise)	117.9	112.7	5.2
11	PP + 1.6 vol % Si 4-7081 (stepwise)	117.3	112.8	4.5

$T_{c \text{ onset}}$  ( $\Delta T_{c \text{ onset}} = 5.9 \text{ K}$  and  $\Delta T_{c \text{ onset}} = 6.7 \text{ K}$ , respectively) was detected, indicating that these samples were nucleated by the filler. Mitsuishi et al investigated the influence of  $\text{CaCO}_3$  in PP on  $T_{c \text{ peak}}$ .<sup>27</sup> They report a decrease of  $T_{c \text{ peak}}$  with increasing calcium carbonate particle size and an increase of  $T_{c \text{ peak}}$  with increasing  $\text{CaCO}_3$  content. In the present investigation, the micrographs discussed earlier showed for samples 2 and 5 a similar particle size distribution. Therefore, the particle size did not influence the  $T_{c \text{ peak}}$  values. Furthermore, sample 2 had a higher  $\text{CaCO}_3$  content than sample 5. According to Mitsuishi et al, this should have caused a decrease in the crystallization temperature of sample 5 compared with sample 2. However, a higher value was detected. The polysiloxane molecules must have caused this increase. As stated earlier, the polysiloxane particles were agglomerated and not uniformly distributed in samples 8 and 11 and did not influence the peak crystallization temperature. However, with  $\text{CaCO}_3$  particles present, the polysiloxane covered their surface and was evenly distributed in the matrix. As a result, the polysiloxane could nucleate the PP and the peak crystallization temperature was increased. These effects were not influenced by the functionality of the polysiloxane (Si 4-7051 and Si 4-7081) because no significant differences in  $T_{c \text{ peak}}$  and  $T_{c \text{ onset}}$  could be detected between samples 8/11 and 3/5, respectively. Caldas et al. report a silica/siloxane copolymer to act as a nucleating agent for PP under isothermal conditions.<sup>28</sup> In their investigation the copolymer was well distributed in the matrix which supports our conclusion.

The difference  $T_{c \text{ peak}} - T_{c \text{ onset}}$  corresponds to the half-width of the crystallization peak of the material. A narrow peak indicates a narrow spherulite size distribution (i.e., most spherulites have the same diameter) in the polymer. Because samples 3 and 5 crystallized via heterogenous nucleation, they show the narrowest peak ( $T_{c \text{ onset}} - T_{c \text{ peak}} = 3.1$  and  $3.3 \text{ K}$ , respectively). Pure PP (sample 1) crystallized with a very broad spherulite size distribution, which is indicated by the widest peak ( $T_{c \text{ onset}} - T_{c \text{ peak}} = 6.2 \text{ K}$ ).

### Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) was performed on three different samples of each composite. The standard deviation of the results was  $\pm 10\%$ . The DMA results for pure PP are shown as circles in Figure 3, with error bars indicating the

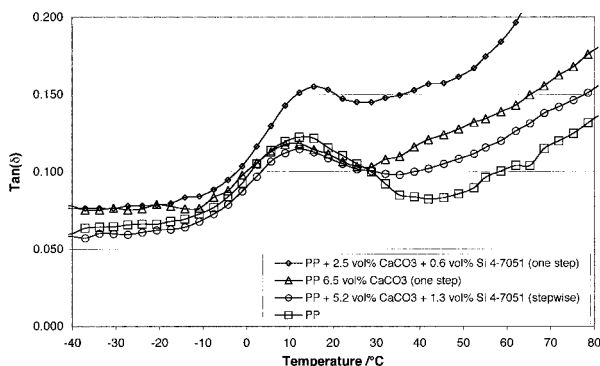


**Figure 3** Storage modulus as a function of sample temperature of pure PP, sample 2 (PP + 6.5 vol %  $\text{CaCO}_3$ ), 3 (PP + 2.5 vol %  $\text{CaCO}_3$  + 0.8 vol % Si 4-7051 – one step) and 4 (PP + 2.5 vol %  $\text{CaCO}_3$  + 0.8 vol % Si 4-7051 – stepwise). The error bars for pure PP data indicate the standard deviation for all measurements.

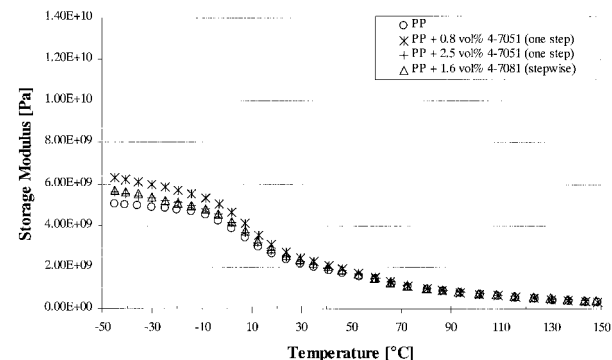
standard deviation for all results. Figure 3 also exhibits the results for sample 2 (PP + 6.5 vol %  $\text{CaCO}_3$ ), sample 3 (PP + 2.5 vol %  $\text{CaCO}_3$  + 0.8 vol % Si 4-7051 – one step) and sample 4 (PP + 2.5 vol %  $\text{CaCO}_3$  + 0.8 vol % Si 4-7051 – stepwise). As expected if  $\text{CaCO}_3$  only was added to PP, the flexural modulus was increased significantly ( $\sim 2.5$  times higher). The  $\text{CaCO}_3$  introduces a rigid phase in the polymer, and the bulk modulus of the composite is a function of the filler volume fraction. Further, the polymer chains surrounding the filler particles may have a reduced mobility, which also leads to a higher modulus. Similar results have been reported elsewhere.<sup>2</sup> However, if  $\text{CaCO}_3$  and polysiloxane were added together to PP (samples 3, 4, and 5) the flexural storage modulus of the composite is of the same magnitude as the one of pure PP (Fig. 3). Taking into account the standard deviation, no significant differences between sample 1, 3, and 4, respectively, could be detected. Additionally, sample 5 (PP + 2.5 vol %  $\text{CaCO}_3$  + 0.8 vol % Si 4-7081 – one step) had a similar modulus indicating that the functionality of the polysiloxane did not influence the modulus either. These results may also be explained by the earlier stated assumption that the polysiloxane built a layer surrounding the  $\text{CaCO}_3$  particles (core-shell structure). Jancar et al investigated the mechanical properties of  $\text{CaCO}_3$  filled PP (filled at 30 vol %) as a function of an elastomer volume fraction.<sup>8</sup> They found for core-shell structured filler that the elastic modulus of the composite was of the same value of pure PP if 7.5 vol % elastomer was added. Calculating this  $\text{CaCO}_3$  : elastomer ratio gives  $30/7.5 = 4$ , which corre-

sponds to the ratio used in our investigation ( $2.5/0.6 \approx 4$  sample 3 and  $2.7/0.7 \approx 4$  sample 5, as well as  $5.2/1.3 = 4$  sample 4). Jancar et al. also proved that the modulus would be higher, if CaCO<sub>3</sub> and the elastomer were dispersed separately in the PP matrix (separated structure). This confirms the assumption of a polysiloxane layer on the CaCO<sub>3</sub> filler in our investigation, and furthermore indicates that this layer completely surrounded the particles. Thus, a core-shell structure was achieved. Jancar et al. showed that in a core-shell system with elastomer contents of more than 2 vol %, a negligible amount of stress is transferred to the core. Here, the core-shell filler principally behaves like an elastomer with the volume extended by the CaCO<sub>3</sub> core. This could not be confirmed in our investigation, because we used elastomer contents well below 2 vol %. However, as it can be clearly seen in Figure 3, we could prove that the reinforcing properties of the CaCO<sub>3</sub> particles were reduced by the polysiloxane significantly. The functionality of the polysiloxane molecules did not influence this behavior.

Figure 4 exhibits the  $\tan \delta$  values of some composites as a function of the sample temperature. The maximum in the curve indicates the glass transition temperature ( $T_g$ ). The standard deviation of these results is  $\pm 0.7^\circ\text{C}$ . Pure PP showed  $T_g$  at about  $13^\circ\text{C}$ , which is higher than the value reported in literature ( $T_g \sim -10^\circ\text{C}$ ).<sup>29</sup> However, the literature value was measured by DSC and such results usually vary from the DMA results due to thermal lag or frequency dependence.<sup>30</sup> The glass transition temperature of sample 3 (PP + 2.5 vol % CaCO<sub>3</sub> + 0.8 vol % Si 4-7051 – one



**Figure 4**  $\tan \delta$  as a function of temperature for pure PP, sample 2 (PP + 6.5 vol % CaCO<sub>3</sub>), sample 3 (PP + 2.5 vol % CaCO<sub>3</sub> + 0.8 vol % Si 4-7051 – one step) and sample 4 (PP + 2.5 vol % CaCO<sub>3</sub> + 0.8 vol % Si 4-7051 – stepwise).



**Figure 5** Storage modulus vs. sample temperature of sample 7 (PP + 0.8 vol % Si 4-7051 – one step), sample 9 (PP + 2.5 vol % Si 4-7051 – one step), and sample 11 (PP + 1.6 vol % Si 4-7081 – stepwise).

step) was higher ( $\sim 14.7^\circ\text{C}$ ), whereas  $T_g$  of sample 2 (PP + 6.5 vol % CaCO<sub>3</sub>) and sample 4 (PP + 2.5 vol % CaCO<sub>3</sub> + 0.8 vol % Si 4-7051 – stepwise) were slightly lower ( $\sim 10^\circ\text{C}$ ). This is somewhat unexpected. For example, Díez-Gutiérrez et al. found for talc-filled PP a lower  $T_g$  than for the unfilled PP.<sup>31</sup> The talc acted as a nucleating agent in the PP matrix, and the increased crystallization rate caused an amorphous phase with bigger mobility, which resulted in lower  $T_g$  values. However, this is contradicted by our result for sample 3, which showed a higher  $T_g$ , thus indicating less mobility of the PP molecules. This could be due to a stronger adhesion between the filler and the matrix.

In Figure 5, the flexural storage modulus of sample 7 (PP + 0.8 vol % Si 4-7051 – one step), sample 9 (PP + 2.5 vol % Si 4-7051 – one step) and sample 11 (PP + 1.6 vol % Si 4-7081 – one step) are shown. The measured storage modulus of all these composites are higher than the one of pure PP (circles). However, taking into account the 10% standard deviations of the measurements, the differences are not significant. This confirms that the given functionality in the two different polysiloxane types did not influence the overall mechanical properties of the composites. However, because the polysiloxane molecules exhibit elastomeric properties, one might expect a decrease in the flexural modulus of PP in a PP/polysiloxane composite. For a polymer/rubber blend, Wu found that the mechanical properties of the blend depended on the surface to surface distance between the embedded rubber particles.<sup>32</sup> Therefore, if the particles are evenly distributed in the matrix, the surface to surface distance becomes small and the rubbery properties are stronger. If the particles, however, agglomer-

ate, the surface-to-surface distance increases, and the rubber influence is weaker. In this case, the blend may even become brittle. A similar result was found by Shanks et al.<sup>6</sup> As previously discussed, if polysiloxane was added only to PP, the molecules tended to agglomerate, leading to a large surface-to-surface distance of the molecules. This may explain values of the flexural modulus measured in this investigation.

## CONCLUSION

Polypropylene/calcium carbonate/polysiloxane composites were investigated with respect to processing, crystallization behavior, and mechanical properties. It was found that the method of mixing of filler and polymer (stepwise or one step and reextrusion) did not influence the final filler distribution in the matrix (particle sizes and distances). However, more material could be mixed with PP, and no blocking of the extruder occurred if the stepwise method was applied. Two polysiloxane types with different functionality were used. No influence of this functionality on any result could be detected.

In the case, where CaCO<sub>3</sub> and polysiloxane were mixed together with PP, the polysiloxane molecules surrounded the CaCO<sub>3</sub> particles, forming a core-shell filler structure. This structure was achieved without surface treatment of the filler particles prior to extrusion. The composites were easy to process, and a nucleating effect could be measured. The resulting mechanical properties are similar to results determined in other core-shell structured composites, where surface treatment had been applied.

In the case where polysiloxane was added to PP only, the molecules tended to agglomerate. The processing was difficult due to screw slippage. Neither the type of extrusion nor the amount of filler nor the functionality of the polysiloxane molecules influenced this. The flexural modulus of the PP matrix was not changed significantly by the polysiloxane molecules.

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