

# Crystallization Behavior of Polypropylene Filled with Surface-Modified Talc

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## SYNOPSIS

Talc-filled polypropylene (PP) composites were prepared by extrusion in a wide composition range (0–40 wt %). To improve the affinity relation between talc and the PP matrix, we modified the talc surface with silane coupling agents. Differential scanning calorimetry investigations on test samples, prepared by injection moulding, revealed that the talc content and its surface modification had a pronounced effect on the crystallization behavior of the filled PP composites. The experimental results indicate that a talc concentration of 2 wt % strongly affects the nonisothermal crystallization process of the PP, especially when talc is silane treated. Isothermal crystallization experiments on samples with minimum amounts of talc (2 wt %) revealed an improved nucleation activity with silane-treated talc.

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## INTRODUCTION

Talc-filled polypropylene (PP) is now commonly used in many applications, and its manufacture volume is one of the highest in the plastic market. The surface of the talc particles acts as nucleation points for PP<sup>1</sup> and may by that alter the amount or type of crystallinity and so influence the macroscopical properties of the composite. In general, the fine spherulitic microstructure produced in PP by adding nucleating agents gives rise to greatly enhanced ductility and strength.

To optimize the reinforcing properties of minerals in plastics, it is necessary to render the surfaces of the mineral and polymer compatible. To achieve this, several types of surface coatings, coupling agents, or similar additives are usually used, and practical systems have been developed for nearly all plastics with common mineral fillers and reinforcements.<sup>2</sup> These agents act by modifying the interfacial region between the inorganic filler and the organic polymer to provide an improved bonding between them. The surface modification of the filler

particles by silanes also affects the rheology of the melt-filled polymer by improving the dispersion of the particles<sup>3</sup> and reducing the melt viscosity by acting as a lubricant or surfactant.<sup>4,5</sup> The improvement of some properties of filled PP with surface-modified minerals can be due to these effects or even to modifications in the crystalline fraction of the matrix.<sup>6–8</sup> Any modification of the filler surface may lead to a change of the nucleation kinetics of PP, because the filler surface interacts with the polymer through catalytic activity and orientation of molecular segments. In this sense, one important function of filler treatments by silanes is to promote alignment of molecular segments of thermoplastic polymers.

The purpose of this study was to examine, by differential scanning calorimetry (DSC), the effect of a surface treatment of talc with silanes on the crystallization behavior of talc-filled PP composites.

## EXPERIMENTAL DETAILS

### Materials and Compounding

Commercial isotactic polypropylene, Isplen-051 (Rep-sol Química S.A., Puertollano, Spain), was used as a matrix. Its molecular characteristics are as follows:

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**Table I** Characteristics of the Talc Used

Laminar Particles (%)	Average Platelet Diameter ( $\mu\text{m}$ )	Specific Surface ( $\text{m}^2\text{g}^{-1}$ )	Density ( $\text{gcm}^{-3}$ )
92	22	3.8	2.7

$M_w = 248,297$ ,  $M_w/M_n = 6.24$ , isotacticity = 97% (from  $^{13}\text{C}$ -NMR data), MFI = 5.4 g/10 min (230°C and 2160 gf). Talc LU-1445 (Luzenac, Toulouse, France) was used as filler in our investigation. Its most important physicochemical properties are described in Table I.

Conventional organosilane coupling agents, Ucarsil PC-1A and PC-1B (Union Carbide Co.), were used for surface treatment of the mineral to study the eventual improvements obtained in the composites properties. For complete surface wetting, the following amounts were required per kg of talc: 240 mL of methanol, 60 mL of water, and 20 mL of silane mixture (3 : 1 in volume of PC-1A and PC-1B). After the wetting process, the mineral was dried in an oven for 24 h at 60°C. All materials were courteously supplied by Repsol Química S.A.

Polypropylene was initially mixed with fixed amounts of talc (nominal 40 wt %), untreated and silane-treated, and extruded by a twin-screw APV-2030 extruder. The composite with untreated talc is called PP40-N and similarly the composite prepared with silane-treated talc is called PP40-S. By dilution of these materials with the original PP, in a single-

**Table II** Initial Characterization of Materials

Material	Talc Weight Fraction, $W_p$ (%)	Measured Density ( $\text{gcm}^{-3}$ )	MFI* (g/10 min)
PP	0.00	0.9149	5.4
PP2-N	1.70	0.9278	5.9
PP10-N	10.40	0.9899	5.2
PP40-N	40.44	1.2636	1.8
PP2-S	1.47	0.9240	4.4
PP10-S	8.44	0.9789	5.8
PP40-S	35.05	1.1917	7.4

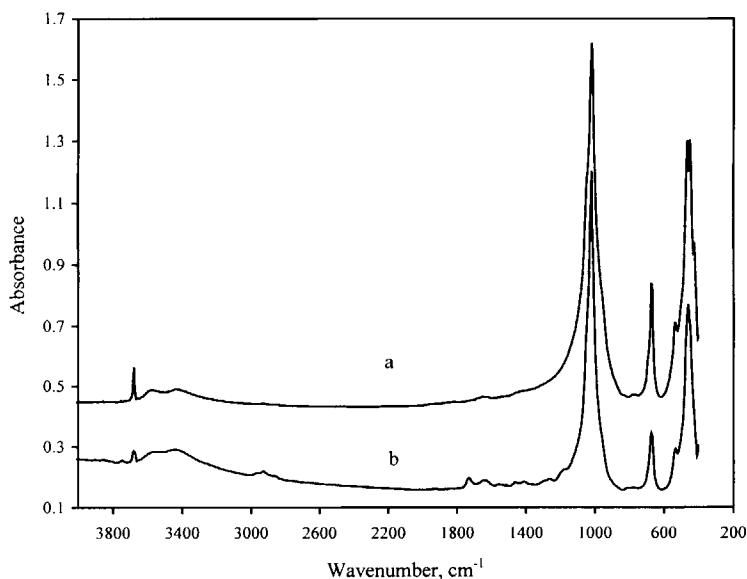
\* Measured at 230°C and 2.16 kg.

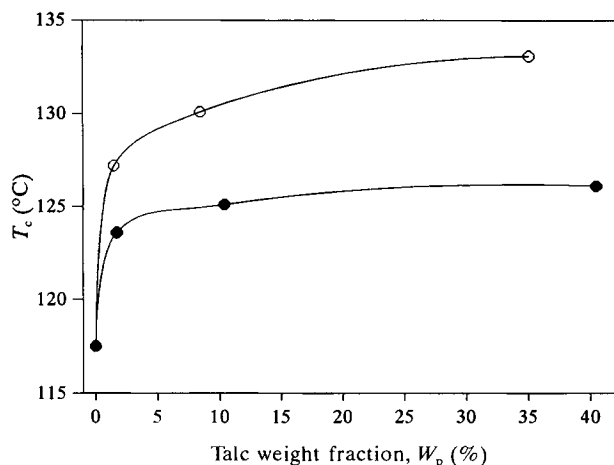
screw extruder, composites were prepared with nominal talc contents of 2, 10, and 20 wt % (N-series and S-series, respectively).

An initial characterization of the composites, based on density and melt flow index measurements, was carried out. Moreover, the true ponderal compositions of the prepared materials were calculated by the calcination method. These initial characteristics of the samples are shown in Table II.

### Samples

Samples for DSC experiments (typical weight, 12–14 mg) were always taken from a concrete region in standard tensile specimens, which were injection molded in a U-40/30 injection machine (Margarit SL., Barcelona, Spain). The temperature profile of

**Figure 1** FT-IR spectra of (a) untreated talc and (b) silane-treated talc.



**Figure 2** Temperature of nonisothermal crystallization ( $T_c$ ) versus talc weight fraction ( $W_p$ ). Untreated talc (●) and silane-treated talc (○).

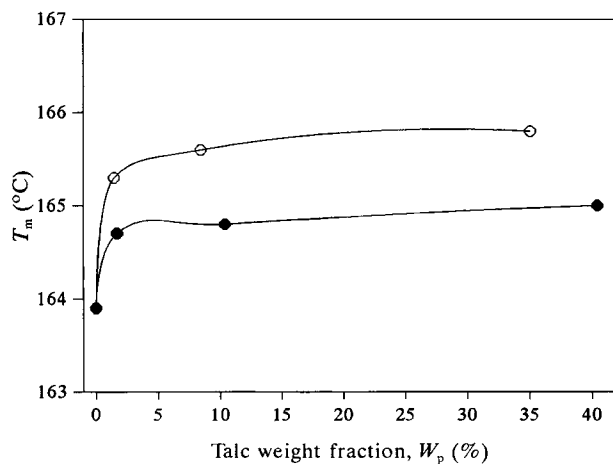
injection was 150, 210, and 230°C and the injection pressure was 20 MPa.

### IR Spectroscopy

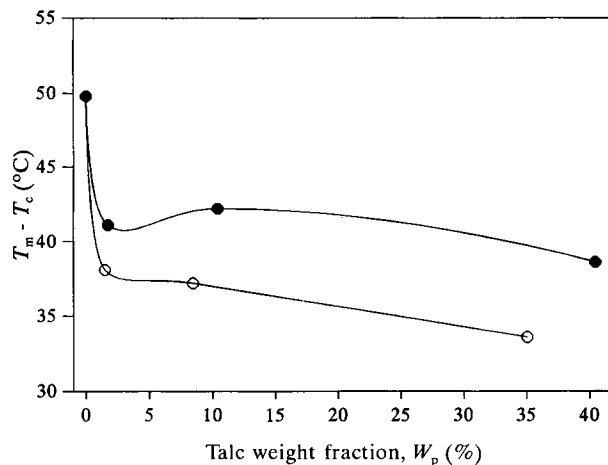
To observe the effect of the silane treatment on the talc surface, IR spectra of both untreated and silane-treated talc were obtained, using a Nicolet 510 Fourier transform (FT-IR) spectrometer.

### DSC Measurements

DSC measurements were performed with the DSC-20 (Mettler) apparatus. First, to characterize the thermal behavior of the composites, nonisothermal

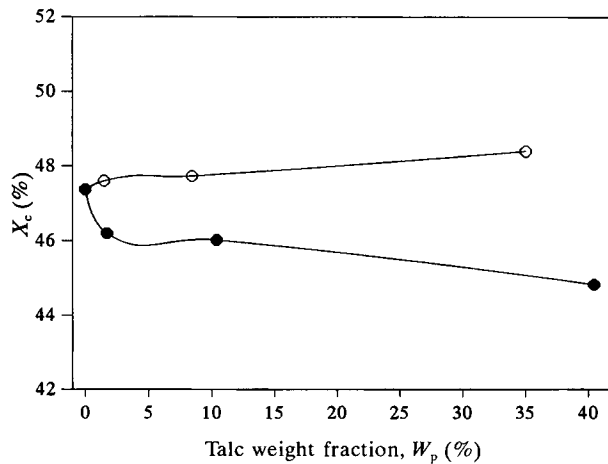


**Figure 3** Melting temperature ( $T_m$ ) versus talc weight fraction ( $W_p$ ). Untreated talc (●) and silane-treated talc (○).

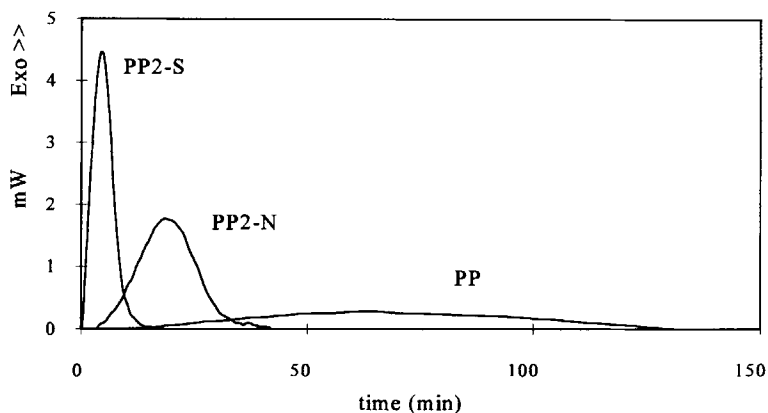


**Figure 4** Degree of supercooling ( $T_m - T_c$ ) versus talc weight fraction ( $W_p$ ). Untreated talc (●) and silane-treated talc (○).

experiments were carried out. The samples were heated up to 230°C, kept at this temperature for 3 min to erase the thermal history, and then cooled down 10°C/min to 90°C in nitrogen gas. Next, the samples were heated at 10°C/min up to 200°C. During the cooling and heating processes, the crystallization and melting patterns were recorded; crystallization and melting temperatures ( $T_c$  and  $T_m$  peak temperatures of crystallization and melting) and crystallization and melting enthalpies [ $\Delta H_c$  and  $\Delta H_m$  (mJ/mg)] were measured for the talc-filled PP composites. From the values of  $\Delta H_m$ , it was possible to estimate a crystallinity index ( $X_c$ ) for the PP in each composite, by referral to the theoretical value of enthalpy of 100% crystalline polypropylene (207.15 J/g).<sup>9</sup>



**Figure 5** Degree of crystallinity ( $X_c$ ) versus talc weight fraction ( $W_p$ ). Untreated talc (●) and silane-treated talc (○).



**Figure 6** Comparative DSC patterns of isothermal crystallization at 140°C.

Second, the nucleation activity on the PP by both untreated and silane-treated talcs was studied by means of isothermal crystallization experiments. Samples (PP, PP2-N, PP2-S) were melted at 230°C for 5 min and then cooled down at the maximum cooling rate of the apparatus to the isothermal crystallization temperature ( $T_{ic}$ ) using methanol as a refrigerant. The total crystallization rate was characterized by the value of the crystallization half-time ( $\tau_{1/2}$ ). The exponent ( $n$ ) and the rate constant of crystallization ( $K$ ) of the Avrami equation (below) were also obtained,

$$\alpha_t = \alpha_\infty [1 - \exp(-Kt^n)]$$

where  $\alpha_t$  is the crystallinity at time  $t$  and  $\alpha_\infty$  is the crystallinity at infinite time.

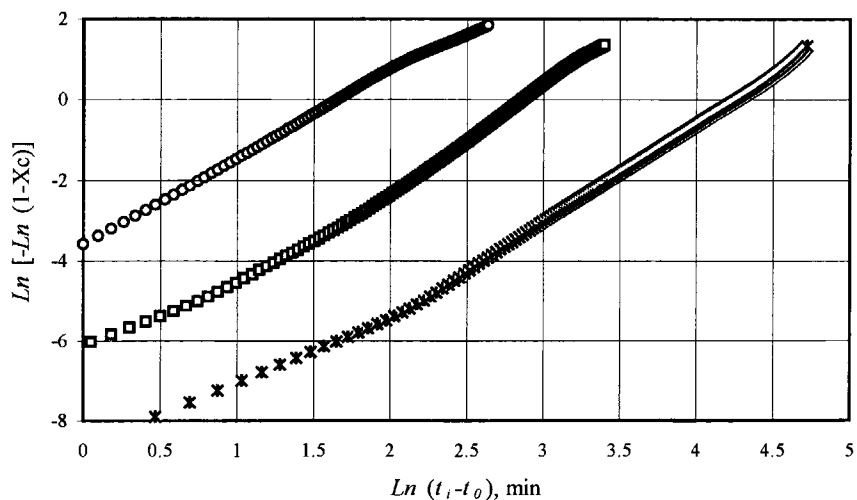
After each process of isothermal crystallization, the samples were heated at 10°C/min up to 230°C,

recording the corresponding pattern to obtain the melting temperature after isothermal crystallization ( $T_{im}$ ). From this value, an estimation of the melting temperature of PP at equilibrium ( $T_m^0$ ) was made.

## RESULTS AND DISCUSSION

### FT-IR Evidence of Talc Surface Modification

Concerning the role of the organosilane compound, we suppose that it is bonded by the polar part of the molecule, through weak intermolecular forces, to the OH groups of octahedral layers of the talc surface. This would lead to slight changes in both the OH stretching ( $3678\text{ cm}^{-1}$ ) and OH libration ( $673\text{ cm}^{-1}$ ) bands, apart from the observation of the fundamental vibrations of silane in the  $1250$  to  $1750\text{-cm}^{-1}$  and



**Figure 7** Comparative linearization of points according to Avrami's equation for PP (\*), PP2-N (□), and PP2-S (○).

**Table III Crystallization Kinetics of Talc-Filled PP Composites**

Sample	$T_{ic}$ (°C)	$n$	$K \times 10^2$ ( $\text{min}^{-n}$ )	$\tau_{1/2}$ (min)
PP	128	2.1	3.0	4.4
	130	2.0	1.8	6.6
	132	2.1	0.48	10.9
	134	2.3	0.055	19.0
	136	2.2	0.048	29.3
	140	2.5	0.0029	60.4
PP2-N	132	2.5	6.5	2.6
	134	2.1	4.0	3.7
	136	2.5	0.75	6.2
	138	2.6	0.17	9.8
	140	2.1	0.12	15.3
	142	2.3	0.03	23.6
PP2-S	144	2.5	0.015	29.3
	138	2.3	6.1	2.9
	140	2.2	2.8	4.4
	142	2.4	0.78	6.6
	144	2.4	0.28	9.7
146	2.4	0.091	14.7	

2850 to 2950- $\text{cm}^{-1}$  regions (Fig. 1). This implies the presence of a layer adhering to the talc surface.

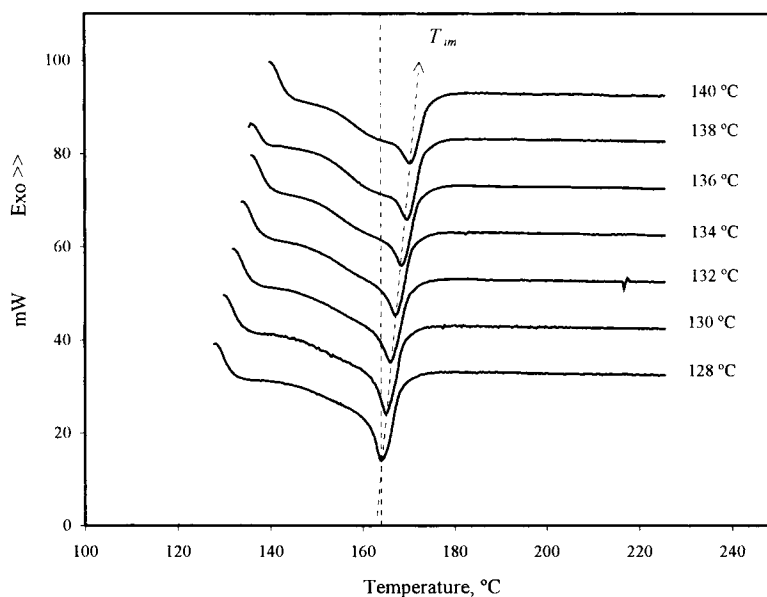
### DSC Nonisothermal Behavior

Figure 2 shows the relation between the  $T_c$  of the talc/PP composites and the talc weight fraction

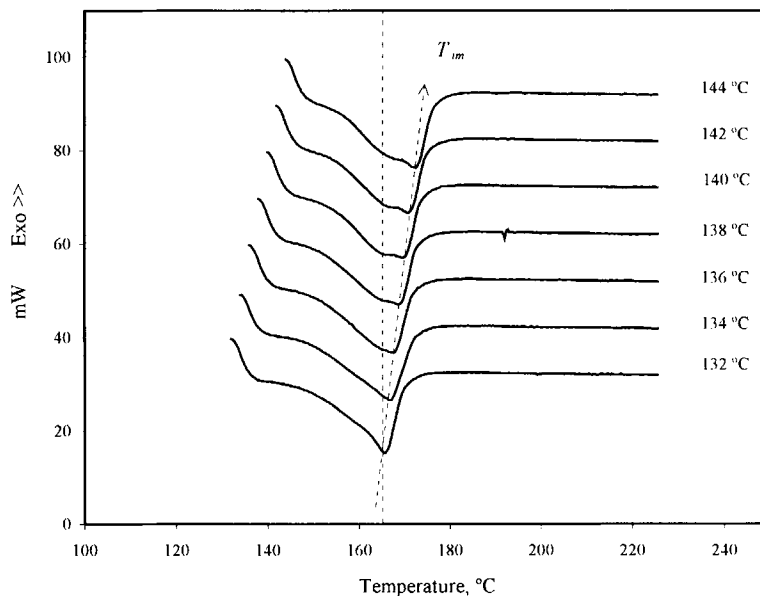
( $W_p$ ). The value of  $T_c$  increases with  $W_p$ , particularly at low talc concentrations, and the increase is shown more acutely in the samples containing silane-treated talc, which may be due to an increase in the interactions between the talc particles and the PP matrix, promoting faster crystallization during the cooling down process.

The value of  $T_m$  remains almost constant with  $W_p$  and with the silane-treatment of the talc (Fig. 3), and therefore the degree of supercooling of the composite decreases as it is shown in the Figure 4. This behavior is not related to higher stability of the crystalline entities but rather is the result of an improved activity of the silane-treated talc as a nucleating agent for the PP. As is explained later, our results from isothermal crystallization experiments confirm this hypothesis.

It has been reported<sup>10</sup> that higher talc concentrations do not result in a further increase of the crystallization rate of PP and that a limiting concentration of crystallization nuclei is reached. Our results are in good agreement with this observation and indicate a limiting talc concentration of  $W_p \approx 2\%$  over which the increase of  $T_c$  in the composite almost stop. At this talc concentration, a limiting nucleation rate is reached in the talc/PP composites. Additionally, studies by diffraction techniques on talc/PP composites show that the preferential orientation of PP on the talc particles has a maximum value at a concentration of 10 wt % and decreases as the talc concentration is raised from 10 wt % to



**Figure 8** Comparative DSC patterns of PP melting after isothermal crystallization. The numbers listed on the right indicate the temperature of isothermal crystallization ( $T_{ic}$ ).



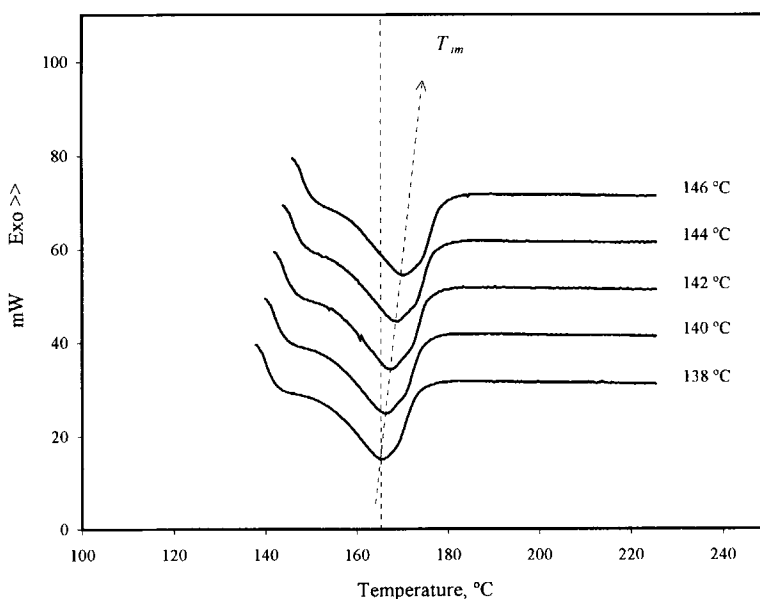
**Figure 9** Comparative DSC patterns of PP2-N melting after isothermal crystallization. The numbers listed on the right indicate the temperature of isothermal crystallization ( $T_{ic}$ ).

the highest concentration of 40 wt %.<sup>11</sup> Likewise, previous experiments by micro-Raman spectroscopy revealed a higher degree of molecular orientation at the interface in the PP2-S sample than in the PP2-N sample.

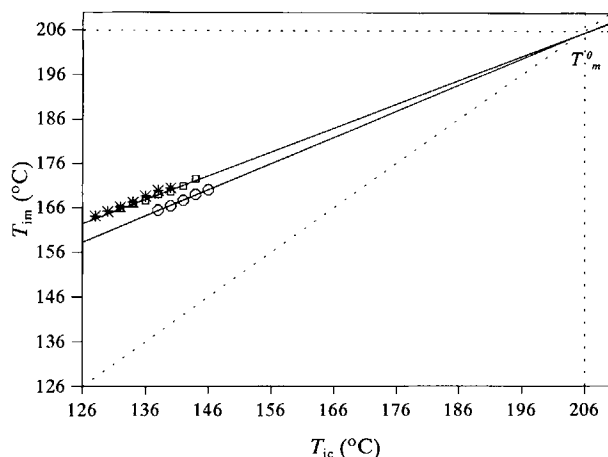
In light of the above observations, a relation between  $T_c$ , concentration of crystallization nuclei, and increased molecular orientation promoted by modification of the talc surface with silanes seems to be

coherent. Additional investigations in this area must still be carried out.

Although the values of the crystallinity obtained by DSC must be viewed with caution, Figure 5 indicates that the degree of crystallinity of the S-series composites seems to be greater than that of N-series. Silane coupling agents improve talc dispersion and wetting, and they act as internal lubricants for filled PP by reducing the melt viscosity. All these factors



**Figure 10** Comparative DSC patterns of PP2-S melting after isothermal crystallization. The numbers listed on the right indicate the temperature of isothermal crystallization ( $T_{ic}$ ).



**Figure 11** Estimation of the melting temperature at the equilibrium ( $T_m^0$ ). PP (\*), PP2-N ( $\square$ ), and PP2-S ( $\circ$ ).

could slightly raise the crystallinity of the PP matrix when it is filled with silane-treated talc.

### Isothermal Crystallization

Figure 6 shows the isothermal crystallization patterns at 140°C for the studied samples (PP, PP2-N, PP2-S). PP composites crystallize much faster than PP alone, especially when the talc is silane treated (PP2-S).

The parameters of the Avrami equation were obtained from plots of  $\ln[-\ln(1 - X_c)]$  versus  $\ln(t_i - t_0)$  as shown in Figure 7, where  $X_c$  is the fraction of crystallinity developed at time  $t_i$ , obtained as the area under the crystallization pattern, and  $t_0$  is the time of initiation. The rate constant of crystallization ( $K$ ) is given by the intersection of the fit data line with the  $y$ -axis, and the exponent ( $n$ ) is given by the slope. Although  $n$  would ideally be three for heterogeneous nucleation, it frequently has nonintegral values, which have been attributed to simultaneous development of lamellar and spherulitic entities by several authors.<sup>12,13</sup> In our case, the experimental values of  $n$  were 2–2.6.

All results are listed in Table III. The crystallization half-time decreases when PP is talc filled, when the talc is silane treated, and obviously when  $T_{ic}$  decreases. Comparison of the total crystallization rate of the PP and its composites, under identical conditions, shows the difference in the heterogeneous nuclei number, as the crystalline growth rate does not depend on this value. Therefore, differences in the crystallization half-time indicate the nucleation activity of the talc particles.

From the results it is clear that modifying the talc surface with silane coupling agents increases the nucleation activity of the mineral. A similar conclusion is also drawn from the values determined for the rate constant of crystallization,  $K$ . In relation with these results, it has been shown<sup>6</sup> that improved wetting of glass beads surfaces changes the initially inert filler into a nucleation-active one.

### Melting Behavior After Isothermal Crystallization

After each isothermal crystallization process, the sample temperature was increased from  $T_{ic}$  up to 230°C at 10°C/min. The melting patterns are compiled in Figures 8–10. PP and PP2-N samples demonstrate similar behavior. At the lower values of  $T_{ic}$ , the melting patterns show common single peaks, but as  $T_{ic}$  increases, a shoulder appears at low temperature with respect to the principal peak. This could be assigned to the melting of a secondary crystalline fraction of lesser stability and size, formed during slow isothermal crystallization. Generally, multiple peaks or shoulders are present in the DSC patterns due to annealing effects. The shoulder peaks are shown more acutely in the PP2-N patterns because the talc particles promote smaller crystalline sizes during the isothermal crystallization due to its nucleating capacity. The patterns recorded for the PP2-S sample also show a shoulder, but in this case the shoulder appears at higher temperatures with respect to the principal peak. This indicates significant formation of smaller crystalline entities during the isothermal process, caused by the improved nucleation activity of the silane-treated talc.

As it is expected, from the nucleation behavior shown by the samples, both principal and shoulder peak temperatures of melting increased with  $T_{ic}$  because the crystalline entities, which are formed during slow isothermal crystallization, melt at higher temperatures than those formed during fast crystallization. The temperature of the principal peak ( $T_{im}$ ) must be assumed as the melting temperature of the major, and therefore representative, crystalline fraction.

Figure 11 shows the linear fit of the  $T_{im}$  versus  $T_{ic}$  values. The intersection of the fit lines with the  $T_{im} = T_{ic}$  line gives  $206 \pm 2^\circ\text{C}$  as an approximated value of the PP melting temperature at equilibrium. This value matches well with the generally accepted one in the literature ( $T_m^0 = 208^\circ\text{C}$ )<sup>14</sup> and indicates no influence of small amounts of talc, and its surface-modification, on the stability of the major crystallized fraction of PP.

## CONCLUSIONS

The modification of talc surface on the crystallization behavior of talc-filled polypropylene was investigated. The obtained results are as follows. First, the crystallization temperature in nonisothermal crystallization increased with the talc content and with the talc surface-modification, particularly at low talc concentrations. However, the melting temperature of the composite are influenced little by these factors. Second, the talc nucleation activity on PP was increased by surface modification with silane coupling agents. Finally, few amounts of unmodified and surface-modified talc do not influence the stability of the principal crystalline fraction of PP.

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