Crystallization and Melting of Highly Filled Polypropylene Composites Prepared with Surface-Treated Fillers

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ABSTRACT: Polypropylene (PP) composites with high filler content have been prepared with surface-treated fillers. The effect of the filler is twofold; nucleation of crystallization occurs, though the PP is also adsorbed onto the filler thereby retarding its motion. Differential scanning calorimetry has been used to study the crystallization of the PP. Melting and recrystallization during melting has been characterized by differential scanning calorimetry. The properties of the composites are more than an additive combination of the filler and polymer. In the case of highly filled composites, the morphology of the PP is important in limiting brittleness and for the strength of the interface between filler and polymer. Surface treatment of the filler has been found to have a significant control over the morphology and properties of the composites. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1942–1948, 2001

Key words: polypropylene; composite; crystallization; melting; surface modification; modified filler

INTRODUCTION

The properties of highly filled composites are determined by their crystalline structure and the relative amounts of amorphous and crystalline phases. Introduction of a second component—a filler—into the polymer can provide a nucleating agent to effect both crystalline and amorphous structure.[1,2] The addition of talc into polypropylene (PP) can lead to a complete change of crystalline structure: a higher crystallization temperature of the α modification has been found to prevent formation of the β form.[3,4]

On the contrary, many fillers have shown a weak nucleation effect.[5–7] Some of them have nearly no influence on the crystalline structure.[8,9] Fillers have also been classified as active or inactive depending on their nucleation performance. The classification of talc is active and $CaCO_3$ is inactive, although contradictory observations[10] have found a very strong nucleation effect of $CaCO_3$. This results in the appearance of a second crystallization peak, then in the shift of the complete crystallization exotherm to higher temperatures. The nucleating effect of many fillers has been unambiguously proven.

Changes in surface chemistry have significantly influenced the behavior of the crystallization and amorphous phases.[6] Surface treatment of a filler with an organic compound led to a drastic decrease in surface tension, but did not influence nucleation.[11,12] A wide range of organic compounds can be used for surface modification, such as silane,[13,14] titanate,[15,16] dicarboxylic anhydride,[13] bismaleimide derivatives,[17] phosphate ester,[18] latexes,[19] zirconate,[16] fatty acid, and fatty acid derivatives.[20]

The *trans*-crystallization phenomenon has been indicated as a proof of the importance of
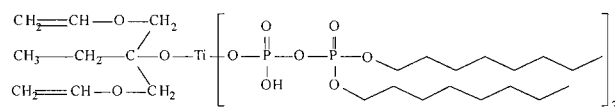
Scheme 1

topological effects. Row nuclei can form on anisotropic filler particles or reinforcements, and in such cases, spherulites can grow epitaxially from the surface of the particle.[6,11,12,21,22] Properties of the *trans*-crystalline layer differ from those of the spherulitic form of PP; it possesses higher rigidity and lower deformability, which lead to easier crack initiation and propagation.[22]

The correlation between tensile properties and the strength of the filler–matrix interaction in both amorphous and crystalline polymers has been reported in many articles. The determining factor in changes of mechanical properties is the strength of the matrix—filler interaction in both amorphous and crystalline regions or the matrix structure. In some cases, the effect of matrix structure was neglected. Changes in matrix structure did not influence impact properties of particulate-filled composites.[23] In other cases, a close and linear correlation was found between the crystallinity or other crystallization characteristics of PP and composite properties.

In this study, the effect of two different agents, titanate as a reactive, and silicone as nonreactive coupling agent were investigated as a function of their chemical composition. The thermal behavior, crystallization, and tensile characteristics of the composites were determined with various shaped, sized, and nucleation action of fillers at different concentrations. The results are discussed in three ways: the changes in the extent of crystallization, the difference of interfacial behavior, and the nucleation action in influencing the composite morphology and tensile properties.

EXPERIMENTAL

Materials

Isotactic PP (melt flow index 2.8 dg/min, density 0.905 g/cm^3) was obtained from Orica Australia Pty Ltd. Talc (density 2.71 g/cm^3, mean particle diameter 17.02 μm) was from Commercial Minerals Ltd. Barium sulfate was obtained from BDH Laboratory Supplies (density 4.49 g/cm^3, mean particle diameter 4.08 μm). Calcium carbonate

(density 2.93 g/cm^3, mean particle diameter 1.55 μm) was obtained from APS Ajax Finechem. The coupling agent, used to treat the surface of the filler of talc, calcium carbonate, and barium sulfate, was neopentyl(diallyl)oxy-tri-(dioctyl pyrophosphato)titanate, LICA-38, which was supplied by Kenrich Petrochemical Inc. (Scheme 1).

Silicone, polydimethylsiloxane, Dow Corning 200/350cS fluid, was obtained from Dow Corning Corporation. This polysiloxane is used commercially to coat filler particles and functions as a processing aid.

Surface Modification of Fillers

A very low proportion of titanate (LICA-38), (0.3 wt %) and of silicone (0.4 wt %) on the basis of talc, CaCO$_3$, and BaSO$_4$ particles, respectively, was diluted in 1000 mL of hexane and then mixed with filler particles in a high-speed mixer. The treatment conditions for variant fillers are listed in Table I. The slurry was filtered, and the modified filler was dried in a vacuum oven at 100°C for 12 h.

Preparation of Composites

A single-screw extruder (Axon-B12, 12.5-mm diameter, length/diameter ratio 26:1) with a gateway screw was used to prepare the composites at a screw speed of 80 rpm. The temperatures of the four zones in the extruder were 150, 200, 200, and 165°C for PP composites, 150, 200, 200, and

Table I   Treatment Conditions for Various Fillers Modified with the Different Coupling Agents

Polymer	Organofunctional Modifier	Fillers	vol %
PP	—	Unfilled	—
PP	Untreated	BaSO$_4$	11.8
PP	Silicone	BaSO$_4$	8.00
PP	Silicone	BaSO$_4$	11.8
PP	Silicone	BaSO$_4$	16.8
PP	Silicone	BaSO$_4$	23.5
PP	Silicone	BaSO$_4$	32.0
PP	Titanate	BaSO$_4$	11.8
PP	Untreated	CaCO$_3$	11.7
PP	Silicone	CaCO$_3$	11.7
PP	Titanate	CaCO$_3$	11.7
PP	Untreated	Talc	18.2
PP	Silicone	Talc	18.2
PP	Titanate	Talc	18.2

Table II   Proportions of Crystalline and Amorphous Phases in the Composites with Various Volume Fractions of Filler

Composites	ΔHm (J/g[a] °C)	Crystallinity (vol %)	Filler (vol %)
PP	101	100.0	0.0
PP Si Ba 8[a]	76.3	69.9	8.0
PP Si Ba 11.8	67.5	59.8	11.8
PP Si Ba 16.8	61.2	51.9	16.8
PP Si Ba 23.5	42.0	33.7	23.5
PP Si Ba 32.0	32.5	24.4	32.0

[a] Ba, $BaSO_4$; Ca, $CaCO_3$; Ta, talc; Si, silicone; Ti, titanate; 8, 8 vol % of filler.

185°C for ethylene copolymer–PP composites, respectively. The treated fillers and untreated fillers were introduced into the polymer. The extrudate was cooled in water at room temperature, cut into pellets, and then dried at 120°C for 15 min and finally extruded into a tape through slit die, then passed through a cold roll press. Circular flat samples were then cut from the tape for differential scanning calorimetry (DSC).

Thermal Properties

Thermal properties, such as crystallization temperature, crystallization enthalpy, melting temperature, and melting enthalpy were measured with a Perkin-Elmer DSC7 using a heating rate of $10°C$ min^{-1}. Before measurement, the samples were heated to 180°C and held 3 min, then cooled to 30°C for measurement of crystallization. After another 3-min holding, samples were heated again to 180°C by $10°C$ min^{-1} for measurement of melting.

RESULTS AND DISCUSSION

Effect of Addition of High Volume Fraction of Filler on Morphology

Table II and Figures 1 and 2 show that the enthalpy of melting of composites decreases drastically with increasing filler volume fraction, which means a decrease of crystallinity with increasing filler volume fraction. In composites of higher filler volume fraction, the amorphous phase became larger than the crystalline phase. A reason for this is that motion of polymer chains is limited in a highly filled composite. The amorphous phase
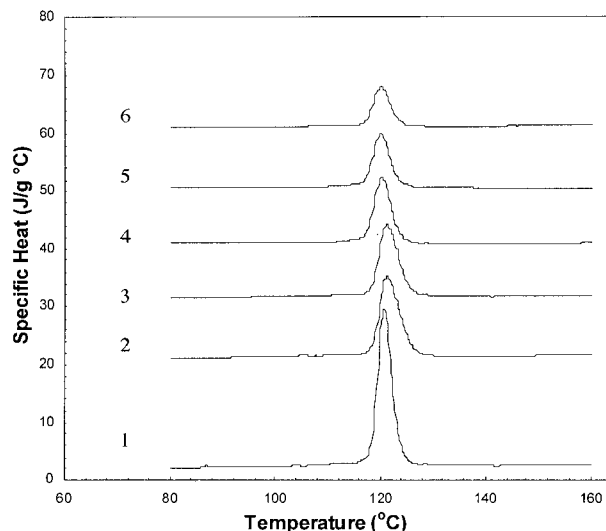

Figure 1   DSC traces of $BaSO_4$-filled PP composite with silicone treated at a cooling rate of $10°C$ min^{-1}: (1) unfilled PP; (2) 8.0 vol % $BaSO_4$; (3) 11.8 vol % $BaSO_4$; (4) 16.8 vol % $BaSO_4$; (5) 23.5 vol % $BaSO_4$; (6) 32.0 vol % $BaSO_4$.

will become a more important factor in influencing the composite properties.

Figure 3 shows that crystallization temperatures for $BaSO_4$-filled composites decreased slightly with increasing filler volume fraction. In Table III and Figure 1, crystallization tempera-
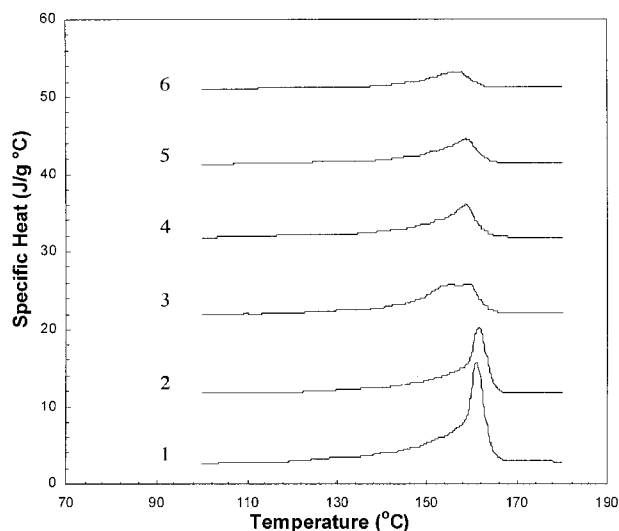

Figure 2   DSC traces of $BaSO_4$-filled PP composite with silicone treated at a cooling rate of $10°C$ min^{-1}: (1) unfilled PP; (2) 8.0 vol % $BaSO_4$; (3) 11.8 vol % $BaSO_4$; (4) 16.8 vol % $BaSO_4$; (5) 23.5 vol % $BaSO_4$; (6) 32.0 vol % $BaSO_4$.
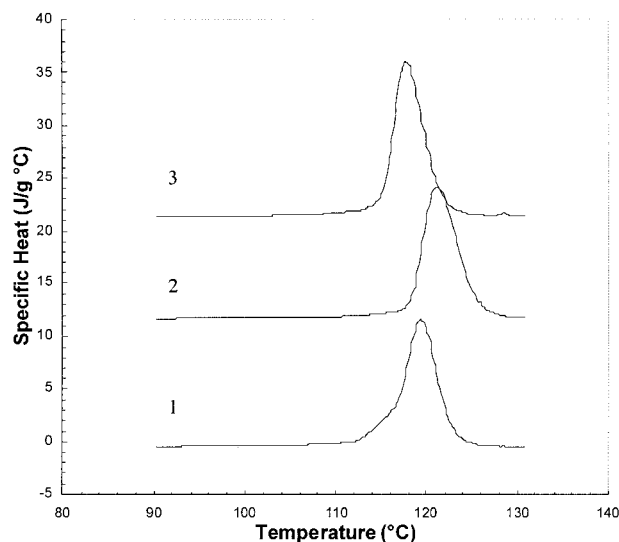
Figure 3 DSC traces of 11.8 vol % $BaSO_4$-filled PP composite at a cooling rate of 10°C min^{-1}: (1) untreated; (2) silicone-treated; (3) titanate-treated.

tures for composites with $BaSO_4$-filled composites show no significant change with increasing filler volume fraction. This indicates that $BaSO_4$ and $CaCO_3$ acted as weak nucleating agents and were unable to shift the peak of crystallization exotherm to higher temperatures.

Differences of Nucleating Action of Talc, $BaSO_4$, and $CaCO_3$

As a comparison, Table III shows that crystallization temperatures of talc-filled composites are much higher than that of pure PP. Crystallization temperatures of calcium carbonate and barium sulfate-filled composites are lower than that of pure PP.

This change of thermal properties is attributable to a nucleation effect and an adsorption effect. The performance of nucleating agents was determined by three factors: 1. surface activity of filler; 2. topology of filler; and 3. surface modification.

Talc usually has been classified as an active filler and a strong nucleating agent because talc has a lower surface free energy (140 mJ/m^2) than the other fillers. Strong nucleation can lead to a change in crystallization.

Mostly physical, and especially topological factors, determine the nucleation effect of fillers. In some cases,[6] it has been shown that the significant increase of the nucleation effect in the case of $CaCO_3$ was connected to aggregation, which increases with decreasing particle size. On the contrary, Varga[3] and Varga and Schulek–Tóth[4] classified talc as an active filler, and $CaCO_3$, carbon black, and dolomite as inactive ones. In this study, calcium carbonate shows a weak nucleation effect. Calcium carbonate and barium sulfate have been proven to be inactive fillers. Inactive fillers do not increase nucleation.

It is quite interesting to note that Table III shows that enthalpies of melting and crystallization of both calcium carbonate and barium sulfate-filled composites are higher than those of talc-filled composites. This indicates that crystal-

Table III   Crystallization and Melting Data for Nucleated Polypropylene-Filled Composites Measured by DSC

Composites	Tm2 (°C)	Tmp (°C)	ΔHm (J/g^a °C)	Tc °C Onset	Tc2 (°C)	Tcp (°C)	ΔHc (J/g^a °C)
PP	116.1	161.0	101.0	123.6	130.5	120.7	100.7
PP Ba 11.8^a	76.7	159.4	64.8	122.3	128.3	119.2	57.1
PP Si Ba 8	97.1	161.5	76.3	126.1	134.2	121.2	72.1
PP Si Ba 11.8	85.6	161.3	67.5	125.4	132.6	121.1	61.6
PP Si Ba 16.8	89.9	158.6	61.2	123.2	12.6	120.1	49.5
PP Si Ba 23.5	93.8	158.6	42.0	123.0	131.5	120.0	40.3
PP Si Ba 32	76.1	156.7	32.5	123.2	132.8	119.9	29.6
PP Ti Ba 11.8	105.5	156.7	62.2	126.5	121.0	117.8	60.5
PP Ca 17.1	97.2	160.1	62.0	123.5	130.5	120.3	58.3
PP Si Ca 17.1	107.2	159.2	61.0	123.1	12.5	119.9	59.1
PP Ti Ca 17.1	72.2	160.1	64.6	121.5	126.1	118.1	58.4
PP Ta 18.2	112.8	164.2	55.2	132.7	139.7	128.7	57.0
PP Si Ta 18.2	106.6	163.9	62.7	132.9	138.9	123.0	62.0
PP Ti Ta 18.1	110.6	163.3	55.9	130.2	135.6	126.5	52.2

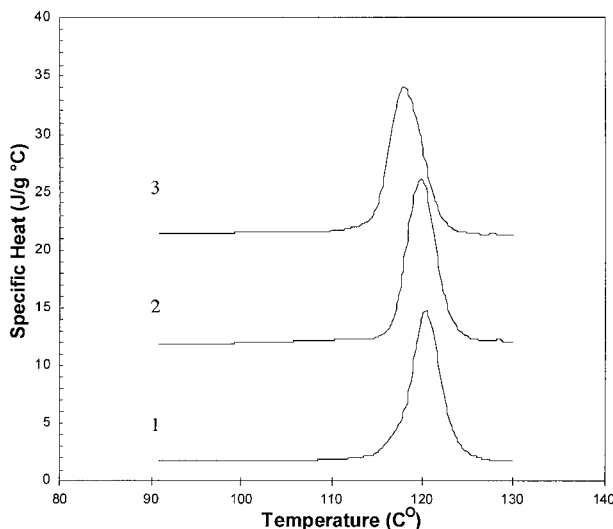^{a} Ba, $BaSO_4$; Ca, $CaCO_3$; Ta, talc; Si, silicone; Ti, titanate; 11.8, 11.8 vol % of filler.

Figure 4   DSC traces of 17.1 vol % $CaCO_3$-filled PP composite at a cooling rate of $10°C\ min^{-1}$: (1) untreated; (2) silicone-treated; (3) titanate-treated.

linities in the former composites are larger than those of the latter. An explanation for this difference is that adsorption onto the PP is weak, therefore the PP molecules remain sufficiently mobile to undergo a greater extent of crystallization, though less than in pure PP.

Interfacial Modification

Figure 3 and Table III show that crystallization temperatures of $BaSO_4$-filled composites with silicone modification are the highest. The middle compositions are untreated composites, whereas the lowest ones are titanate-treated composites.

Figure 4 and Table III show different trends. Crystallization temperatures of both calcium carbonate-filled composites with silicone and titanate treatment are lower than those of the untreated composite.

Figure 5 and Table III show crystallization temperatures of talc-filled composites with no surface treatment are the highest, followed by titanate-treated composites and then silicone-treated composites. Figure 5 and Table III show a similar trend to Figure 4. Both treated composites decreased their crystallization temperatures.

It has been indicated that treatment of the surface of a filler with different additives leads to changes in the nucleation effect.[7] A change of surface properties and energetics might be reasons for these differences. However, the literature also indicated that surface treatment of a filler

with an organic compound results in a large decrease of surface energy, which is very often not accompanied by a change in nucleation efficiency. Examples have been given in the literature in which surface treatment did not influence nucleation.[12,13] In this case, the experimental data proved that treatment of the surface of the filler led to slight changes in the nucleation effect. Topological factors also significantly effect nucleation.

In comparison, Table III shows that values of the crystallization enthalpy of silicone-treated composites are the highest, followed by titanate-treated composites (except for talc-filled composites) and then untreated composites. These results indicate that silicone, a nonactive coupling agent, is a more effective modifier than titanate, an active coupling agent, in enhancement of crystallinity. The reason for the enhancement can be explained by better dispersion of the filler, resulting in better growth of crystals.

Homogenization and Structure of Composites

In Table III and Figures 6 and 7, an increase of melting enthalpies of both barium sulfate- and talc-filled composites with silicone treatment has been found in comparison with those of untreated composites. This implies that crystallization of composites has been improved by surface treatment.
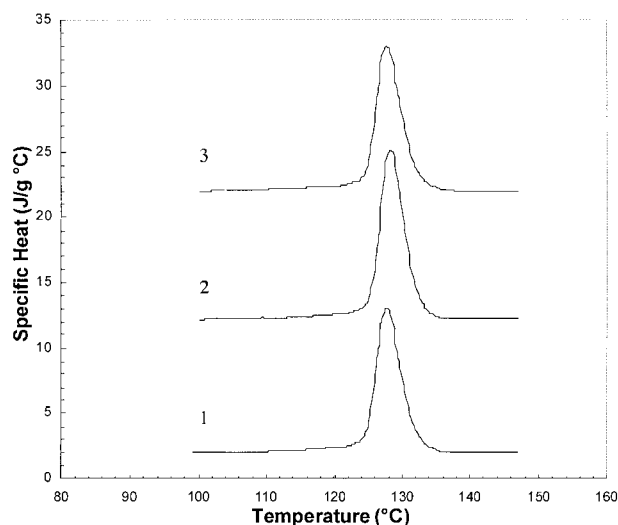

Figure 5   DSC traces of 18.2 vol % talc-filled PP composite at a cooling rate of $10°C\ min^{-1}$: (1) untreated; (2) silicone-treated; (3) titanate-treated.

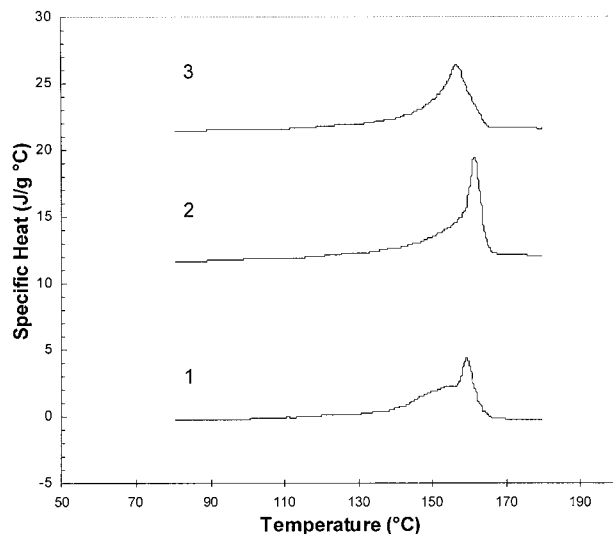**Figure 6** DSC traces of 11.8 vol % $BaSO_4$-filled PP composite at a heating rate of 10°C min^{-1}: (1) untreated; (2) silicone-treated; (3) titanate-treated.

Figure 8 DSC traces of 17.1 vol % $CaCO_3$-filled PP composite at a heating rate of 10°C min^{-1}: (1) untreated; (2) silicone treated; (3) titanate-treated.

In comparison, a decreasing tendency of melting enthalpies of calcium carbonate-filled composites has been observed compared with those of barium sulfate-filled composites, as shown in Table III and Figures 6 and 8. This decrease of crystallinity could be attributed to the decreasing particle size, which leads to an increase of specific surface area. The large specific surface area of the fillers indicates a significant fraction of small particles and strong aggregation. The aggregation of
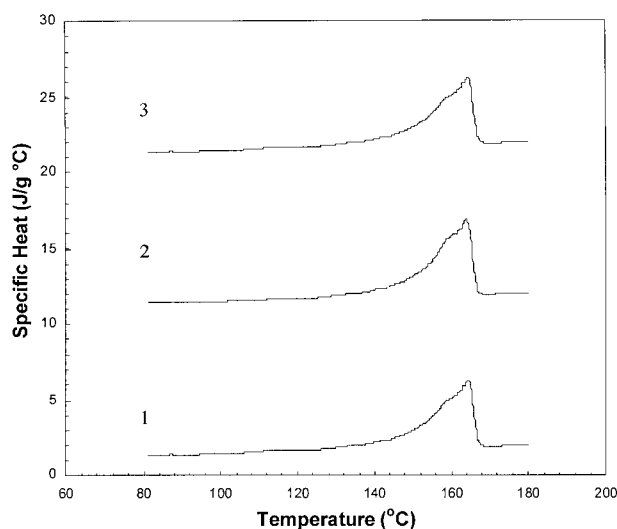

Figure 7 DSC traces of 18.2 vol % talc-filled PP composite at a heating rate of 10°C min^{-1}: (1) untreated; (2) silicone-treated; (3) titanate-treated.
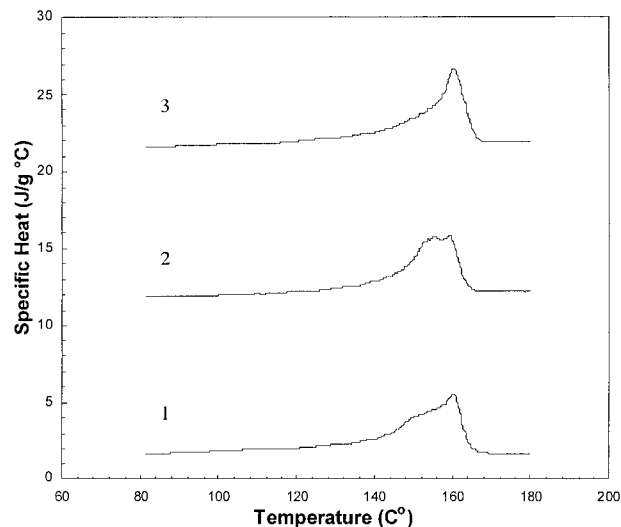
filler particles leads to insufficient homogeneity and rigidity.

Figure 2 and Table II show that the melting enthalpies of barium sulfate-filled composites decrease with decreasing volume fraction. This indicates that an increase of filler will adsorb more of the PP and reduce crystallization.

In talc-filled composites, the crystallization temperature was increased (see Table III). The reason for the increase is the nucleation action of talc.

In particulate-filled polymers, the structure of composites is determined by the component properties, especially by the particle characteristics and anisotropy, as well as by the processing technique and conditions. The most important structure-related factors are: 1. aggregation and interfacial interaction and distribution; 2. the structure of the composites; and 3. the nucleation characteristic of the filler.

In particulate-filled polymers the structure of the composites is determined by the component properties, especially by particle characteristics and nucleation, as well as by processing techniques and conditions. The most important structure-related factors are aggregation, distribution of filler throughout the product, and orientation of anisotropic particles. All three influence the properties of PP composites and must be controlled to prepare products of high quality.

CONCLUSIONS

Results showed that crystallinity of the composites decreased drastically with increasing filler volume fraction. In the range of higher filler volume fraction, the amorphous phase became larger than the crystalline phase. Consequently, the influence of amorphous properties should be taken into consideration when considering the properties of highly filled composites.

In highly filled composites, talc, an active nucleating agent, depended on its topological properties. Both calcium carbonate and barium sulfate were found to have a weak crystallization nucleating effect. In this case, the data proved that treatment of the surface of the fillers led to slight changes in the nucleation effect. For talc composites, with a high filler content, the topological properties of the talc were the primary influences on the composite properties.

The results indicate that silicone, an inactive coupling agent, is a more effective modifier than titanate, an active coupling agent, in enhancing crystallinity.

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