

The β -Crystalline Form of Wollastonite-Filled Polypropylene

LIU JINGJIANG, WEI XIUFEN, and GUO QIPENG,*
*Changchun Institute of Applied Chemistry, Academia Sinica,
Changchun 130022, People's Republic of China*

Synopsis

A study has been made of the thermal, X-ray diffraction, and dynamic mechanical characteristics of polypropylene (PP1330, a copolymer containing 22% ethylene) filled with wollastonite. Various levels of β -form crystallinity were produced in the PP by mixing in varying amount of wollastonite. It has been found that all the wollastonite-filled samples contain both the α - and the β -forms, and four melting transitions were observed instead of only two of the unfilled PP on the DSC scan. The conversion of the β - to the α -form on heating has been observed. The relative amount of the β -form in the samples was measured from WAXS data by the K value. The K value obtained increases with increasing wollastonite content. Dynamic mechanical measurements showed an increase in the magnitude of the damping in the high-temperature region for the wollastonite-filled PP and the contribution from the filler-matrix boundary. Wollastonite acted as both a reinforcement and a β -nucleator for PP.

INTRODUCTION

Isotactic polypropylene (PP) is capable of crystallizing in three polymorphic forms.¹ They are the monoclinic α -form, the hexagonal β -form, and the triclinic γ -form. In the melt-crystallized material the predominant polymorph is the α -form. The β -form generally occurs at levels of only a few percent. The γ -form is only observed in low-molecular-weight or stereoblock fractions that have been crystallized at elevated pressures.^{1,2} It has been shown that the β -form could be formed in larger amounts under specific conditions, e.g., in the presence of a special β -nucleator,^{3,4} in a temperature gradient,⁵ or in the presence of shearing forces.^{6,7} However, to our knowledge, no study has been made concerning the crystalline forms of isotactic polypropylene containing inorganic fillers and the properties of the related composites. Inorganic fillers might act as β -nucleators formed larger amounts of the β -form. As a result, the properties of the related composites should be influenced. In this paper, a study on PP-wollastonite composites are presented. The techniques used include differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXS), and dynamic mechanical analysis (DMA). Indeed, it has been found that the β -form is formed in the composites as expected.

EXPERIMENTAL

Materials and Preparation of Samples

The sample of PP, PP1330, was commercially obtained from Yanshan Petrochemical Co., Beijing, China. PP1330 is a copolymer containing 22 wt %

* To whom correspondence should be addressed.

ethylene. The sample was synthesized following a procedure for preparing block copolymer; however, a detailed study at this institute⁸ showed that PP1330 contains random sequences. It has a melt index of 1.5 g/10 min and a density of 0.905 g/cm³ at 25°C. The wollastonite with a density of 1.889 g/cm³ at 25°C was ground to 400-mesh size; the wollastone particles then obtained were needle-shaped and were dried at 120°C for 8 h before use. The composites of PP and wollastonite were prepared by a Brabender at 180°C. The samples were further pressed at 180°C into sheets of thickness of ca. 0.3 mm.

Differential Scanning Calorimetry

A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) was employed to obtain the melting behavior of the samples. The sample weight used in the DSC cell was kept in the 8–12 mg range. The samples were first heated to 200°C to remove prior thermal histories. They were then cooled to 50°C at a rate of 10°C/min to trace the crystallization process, followed by heating to 200°C again to observe the melting behavior. A heating rate of 10°C/min was used in all cases. The heat of fusion was calculated from the melting peak area; and the maximum of the endotherm and the minimum of the exotherm were taken as the melting temperature (T_m) and the crystallization temperature (T_c), respectively.

WAXS Measurement

The WAXS patterns were taken on a Rigaku diffractometer with Cu K α radiation at room temperature. The angular scale and recorder reading (2θ) were calibrated to an accuracy of 0.01°. The samples were pressed at 180°C into sheets with thickness of ca. 1.5 mm.

Dynamic Mechanical Measurements

Dynamic mechanical measurements were carried out on a Rheovibron Model DDV-II-EA dynamic viscoelastometer (Toyo Baldwin Co., Japan). The frequency used was 3.5 Hz and heating rate 3.0°C/min. Dimensions of a typical sample were 4.0 × 0.4 × 0.03 cm.

RESULTS AND DISCUSSION

Cooling Crystallization and Melting Behavior

Cooling crystallization behavior of block copolymers of ethylene and propylene (PP-PE) has been studied by Wang et al.⁹ Figure 1 shows the DSC traces of PP1330 and a composite sample at a cooling rate of 10°C/min. For the pure PP1330, sample 1, two exothermic peaks occur at $T_{c1} = 116^\circ\text{C}$ and at $T_{c2} = 113.8^\circ\text{C}$ corresponding to crystallization of PP and PE sequences, respectively. For the wollastonite composite, sample 2, T_{c1} is raised to 123°C, which is 7°C higher than that of sample 1, but T_{c2} remains invariant. This result implies that wollastonite can act as a nucleator for PP. Table I lists the crystallization temperatures and exothermic heats of PP1330 and the composites with various wollastonite-content. It can be seen that the T_{c1} value of the composite remains almost constant up to 17.7 vol % wollastonite content.

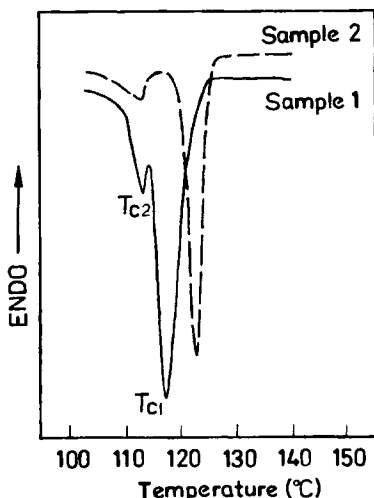


Fig. 1. Cooling crystallization curves at $-10^{\circ}\text{C}/\text{min}$ for sample 1, PP1330, and sample 2, a composite containing 3.2 vol % wollastonite.

Rybnikar¹⁰ found that the crystallization of PE sequences in PP-PE block copolymers depended on thermal history and crystalline phase. The crystallization rate of PE sequences is related to the nucleators in the sample. The first formed crystalline phase of PP sequences can also act as a nucleator of PE sequences in the copolymers. However, it can be seen from Table I that neither the crystallization temperature T_{c2} nor the overall crystallization heat ($\Delta H_{fc1,2}$) for PP1330 in the composite is markedly influenced by the addition of wollastonite, although the $\Delta H_{fc1,2}$ based on the total sample weight, i.e., the crystallization heat per gram sample, decreases with increasing wollastonite content due to relatively decreasing PP1330 content.

The melting behaviour after the cooling from the melt for the PP1330, sample 1, and the composites, samples 2 and 3, is presented in Figure 2. It can be seen that the sample 1 exhibits two melting endothermic peaks, T_{m1} and T_{m3} , referred to the melting of crystallites of PE and of PP sequences, respectively. For samples 2 and 3, two new endothermic peaks, $T_{m2} = 150^{\circ}\text{C}$ and $T_{m4} = 169^{\circ}\text{C}$, appear. Jacoby et al.¹¹ have measured the melting temperatures of all crystalline forms of PP. For the α -form, $T_m = 168$ and 162°C , whereas the values of T_m

TABLE I
Cooling Crystallization Data of PP1330 and the Composites

Sample	Wollastonite/PP (v/v)	T_{c1} ($^{\circ}\text{C}$)	$\Delta H_{c1,2}$		T_{c2} ($^{\circ}\text{C}$)
			(J/g)	(J/gPP1330)	
1	0/100	116.7	-94.8	-94.8	113.8
2	3.2/96.8	123	-78.0	-83.6	113.7
3	8.8/91.2	123	-78.7	-96.4	114.0
4	13.2/86.8	122	-66.4	-91.6	113.4
5	17.7/82.3	122	-61.2	-97.1	113.5

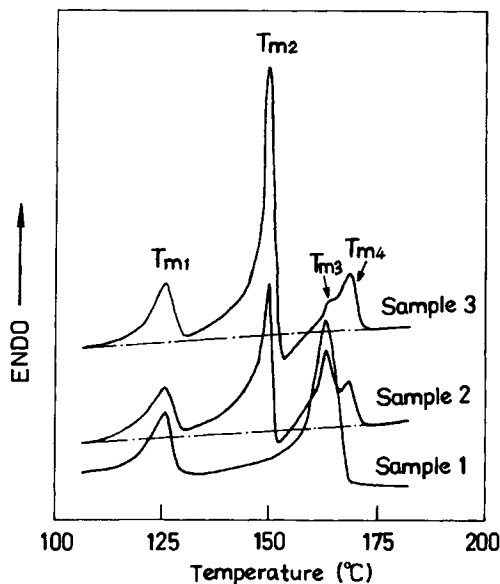


Fig. 2. DSC scanning curves of PP13300 and the composites after the cooling crystallization. The heating rate is $10^{\circ}\text{C}/\text{min}$.

obtained were 152 and 132°C for the β - and the γ -forms, respectively. Fujiwara¹² and Shi et al.¹³ observed the double melting phenomenon of the β -phase itself during DSC measurements for the predominantly β -form samples. It was implied that the double melting was caused by melting of the original β -phase and subsequent recrystallization to a stabler structure (β') and its melting during scanning. However, such double melting phenomenon of the β -phase is not observed in Figure 2. It can be seen that only one kind of the β -phase structure was formed in wollastonite-filled sample. Figure 2 also shows that the samples 2 and 3 exhibit two melting peaks of α -phase, T_{m3} at 162°C and T_{m4} at 169°C . It has been shown that the presence of two peaks of the α -phase was induced in some cases^{14,15} by high temperature ($> 155^{\circ}\text{C}$) conditioning, in other cases¹⁶⁻¹⁸ by appropriate choice of the temperature of crystallization ($130^{\circ}\text{C} < T_c < 150^{\circ}\text{C}$), and in still other cases by the particular conditions under which the differential thermal analysis was performed: at a low scanning rate¹² (heating rate $< 5^{\circ}\text{C}/\text{min}$) or on drawn samples restrained during the measurement.^{18,19} In the present case, the splitting of α -melting peak is due to the recrystallization of the β -form to a stabler structure (α_2) and its melting during the heating. In the figure, a crystallization exothermic peak is observed to locate between the melting endothermic peaks of the β - and the α -phases, and the crystallization heat and the intensity of peak T_{m4} increase with increasing the heat of fusion of the β -phase. This suggests that the β -phase first become molton and subsequently recrystallized to the stabler α -form of peak T_{m4} with increasing temperature during scanning. However, the melting temperatures of the composite are little influenced by the wollastonite-content from 3.2 vol % up to 17.7 vol % filler content.

X-Ray Diffraction

WAXS patterns of PP-PE block copolymers have been studied by Mo et al.²⁰ The WAXS measurement shows that the PP1330 exhibits the diffraction

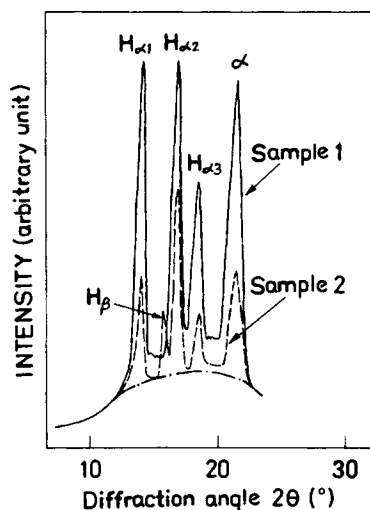


Fig. 3. WAXS patterns of sample 1, PP1330, and sample 2, the composite containing 3.2 vol % wollastonite.

peaks of PE crystal planes (110) and (200) as well as three strong equatorial α -peaks of PP, (110), (040), and (130). The patterns of the composites give three new peaks located at $2\theta = 11.8^\circ$, 23.8° , and 16° . The first two at $2\theta = 11.8^\circ$ and 23.8° are referred to diffractions of wollastonite but $2\theta = 16^\circ$ is the characteristic single β -peak (300). No diffraction peak is located between $2\theta = 12^\circ$ and 23° for the plain wollastonite. The relative amount of the β -form is usually described in terms of the K value, which is defined as follows¹²:

$$K = H_{\beta} / [H_{\beta} + (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3})]$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ are the heights of the three strong equatorial α -form peaks (110), (040), and (130) and H_{β} the height of the strong single β -form peak (300). The baseline is set as shown in Figure 3. Table II presents the K values so obtained, which show an increase in the relative amount of the β -form with increasing wollastonite-content. The K value remains constant at 0.37 for wollastonite content up to 17.7 vol %. It reached as high as 0.95 for the samples prepared by using β -nucleators as reported by Shi et al.¹³ This can be due to the larger particle size of wollastonite and then relatively smaller

TABLE II
Melting Behavior and β -Form Content of PP1330 and the Composites

Sample	T_{m1} (°C)	ΔH_{f1} (J/g)	T_{m2} (°C)	ΔH_{f2} (J/g)	T_{m3}/T_{m4} (°C)	$\Delta H_{f3,4}$ (J/g)	K value
1	126	20.3			162/—	65.0	0
2	126	15.9	151	60.6	162/169	21.4	0.14
3	126	14.8	150	40.3	163/169	24.6	
4	127	13.1	149	28.1	163/169	24.6	
5	127	12.2	150	26.5	163/169	21.7	0.37

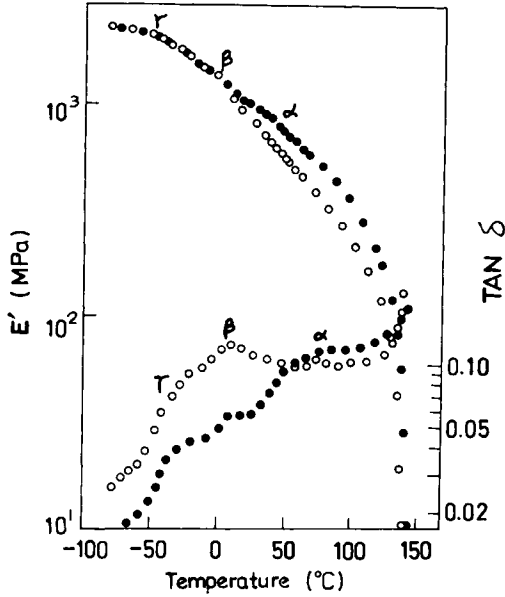


Fig. 4. Storage modulus E' and $\tan \delta$ vs. temperature for sample 1 (O), PP1330, and sample 5 (●), a composite containing 17.7 vol % wollastonite.

specific surface area since only the surface of the wollastonite particles can induce the formation of the β -form.

Dynamic Mechanical Properties

Figures 4 and 5 show the dynamic mechanical spectra of the pure PP1330, sample 1, and the composite with 17.7 vol % wollastonite, sample 5. The sharp

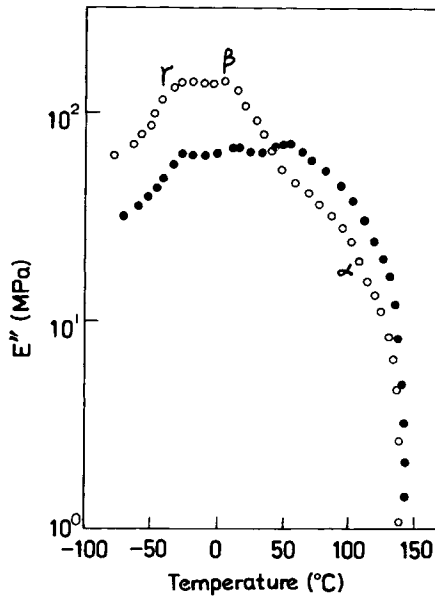


Fig. 5. Loss modulus E'' vs. temperature for sample 1 (O), PP1330, and sample 5 (●), a composite containing 17.7 vol % wollastonite.

decreases of storage modulus E' around 125 and 170°C are attributable to the melting of the crystalline phases of the PE and PP sequences, respectively. The $\tan \delta$ - T curves show three relaxation peaks at 75, 10, and -40°C, denoted by α -, β -, and γ -relaxations. It is noted that the low-temperature γ -relaxation at -40°C approaches the glass transition temperature (about -60°C) of ethylene-propylene rubber (EPR). The γ -relaxation can be attributable to amorphous, rubbery, random sequences in PP1330.²¹ The β -relaxation peak around 10°C is due to the glass transition of the PP sequences in PP1330. The α -relaxation peak at 75°C is attributed to the overlapping of mechanical dampings in the crystalline phases of PP and PE sequences.²¹ At temperatures above 60°C, the values of $\tan \delta$ and loss modulus E'' of the composite are higher than those of PP1330. The higher intensity of the α -relaxation of the composite can be due to the contribution from the filler-matrix boundary.

References

1. A. Turner-Jones, J. M. Aizlewood, and D. R. Beckett, *Makromol. Chem.*, **75**, 134 (1964).
2. R. J. Samuels and R. Y. Yee, *J. Polym. Sci. A-2*, **10**, 385 (1972).
3. H. J. Leugering, *Makromol. Chem.*, **109**, 204 (1967).
4. G. Shi and J. Zhang, *K'o Hsueh T'ung Pao*, **27**, 290 (1982).
5. J. M. Crissman, *J. Polym. Sci. A-2*, **7**, 389 (1969).
6. H. Dragaum, H. Hubeny, and H. Muschik, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 1779 (1977).
7. H. J. Leugering, *Angew. Makromol. Chem.*, **33**, 17 (1973).
8. Z. Sun, M.Sc. thesis, Changchun Institute of Applied Chemistry, Academia Sinica, 1989.
9. L. Wang, Y. Qi, D. Chen, and B. Huang, *Acta Polym. Sinica*, **6**, 432 (1987).
10. F. Rybnikar, *J. Macromol. Sci. Phys.*, **27**, 125 (1988).
11. P. Jacoby, B. H. Bersted, W. J. Kissel, and C. E. Smith, *J. Polym. Sci. Polym. Phys. Ed.*, **24**, 461 (1986).
12. Y. Fujiwara, *Kolloid Z. Z. Polym.*, **253**, 273 (1975).
13. G. Shi, Y. Cao, B. Huang, and S. Huang, *Acta Polym. Sinica*, **5**, 359 (1987).
14. W. W. Cox and A. A. Duswalt, *Polym. Eng. Sci.*, **7**, 1 (1967).
15. K. D. Pae and J. A. Sauer, *J. Appl. Polym. Sci.*, **12**, 1901 (1968).
16. K. Kamide and K. Yamaguchi, *Makromol. Chem.*, **162**, 219 (1972).
17. C. L. Siegloff and K. J. O'Leary, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **10**, 57 (1969).
18. R. J. Samuels, *J. Polym. Sci. Polym. Phys. Ed.*, **13**, 1417 (1975).
19. D. T. F. Pals, P. Van der Zee, and J. H. M. Albers, *J. Macromol. Sci. Phys.*, **6**, 739 (1972).
20. Z. Mo, L. Wang, H. Zhang, P. Han, and B. Huang, *J. Polym. Sci. Polym. Phys. Ed.*, **25**, 1829 (1987).
21. J. Liu, in *Transition and Relaxation in Polymers*, B. Qian et al., Eds., Scientific Press, Beijing, 1986, Chap. 12.

Received December 20, 1989

Accepted February 16, 1990