

Morphology, Crystallization and Melting Properties of Isotactic Polypropylene Blended with Lignin

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ABSTRACT: The influence of lignin (L) on the thermal properties and kinetics of crystallization of isotactic polypropylene (PP) is reported in this article. PP blends containing 5 and 15 wt % of L were prepared by mixing the components in a screw mixer. An increase of the thermal degradation temperature of the blends was observed as a function of L content. The crystallization and thermal behavior of the pure PP and of the PP/L blends were analyzed by differential scanning calorimetry (DSC). Isothermal crystallization kinetics were described by means of the Avrami equation, which suggests a three-dimensional growth of crystalline units, developed by heterogeneous nucleation. The isothermal growth rate of PP spherulites was studied using a polarizing optical microscope. The enhancement of PP crystallization rate for the PP/L blends was observed and ascribed to the nucleating action of lignin particles. Non-iso-

thermal crystallization kinetics were applied, according to the results elaborated by Ziabicki and the method modified by Jeziorny. The kinetic crystallizability of the PP is not influenced by the L present in the blend. In the presence of L, PP can simultaneously crystallize in both the α and β crystalline forms, and the ratio between the α and β forms was determined by X-ray diffraction analysis. Two melting peaks relative to the two crystalline form of PP were observed for the PP/L blends, for all isothermal crystallization temperatures investigated by means of DSC. The equilibrium melting temperature for α -form of pure PP was obtained. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1435–1442, 2004

Key words: poly(propylene); flame retardance; nucleation; degradation

INTRODUCTION

Lignin (L) is an amorphous, polyphenolic, low molecular weight plant constituent, able to give a high char amount when heated at high temperatures in an inert atmosphere. The ability to form char during combustion is a basic aspect of flame retardant additives, since char reduces the combustion rate of polymeric materials. In previous papers, we have described this property of L and modified L in their use as flame retardant additives for polypropylene (PP).^{1,2}

It is known that the addition of fillers can produce changes in the rate of crystallization and the crystalline structure of PP.³ In melt crystallized PP, the predominant crystal structure is the α -form, which is eventually accompanied by the presence of the β -form. The relative amounts of α and β forms in the melt crystallized PP are determined by the crystallization temperature and/or the cooling rate due to the different nucleation and growth rates of the two crystalline forms.^{4–6} The formation of the β -form crystal structure can be promoted by the addition of foreign seed material to the PP.^{7–11} The presence of the β -form crystal structure can improve the mechanical proper-

ties of PP.^{12–14} Pure PP and a PP/L blend with a weight ratio of 95/5 showed no significant differences when tested by dynamic mechanical analysis over a large range of temperatures, while a small increase in storage modulus was observed for a PP/L blend with a weight ratio of 85/15.¹⁵

In this article, we report investigations on the effect of L on the thermal degradation, structure, melting properties and kinetics of crystallization of isotactic PP.

EXPERIMENTAL

Materials

Binary blends of isotactic PP (Moplen FLP 20, Himont, Ferrara, Italy, MFI of 12 g/10 min at 230°C) and hydrolytic L (Aldrich, Milan, Italy, CAS n. 8072-93-3) were prepared by melt-mixing the components at 190°C for 10 min in a Brabender electronic plasticorder AEV 153 mixer, with PP/L weight ratios of 100/0, 95/5 and 85/15.

Methods

Thermogravimetric analysis was carried out by means of a Perkin–Elmer TGS-2 thermogravimetric analyzer with platinum pans at a scanning rate of 20°C/min in air atmosphere with a flow rate of 30 mL/min. Ther-

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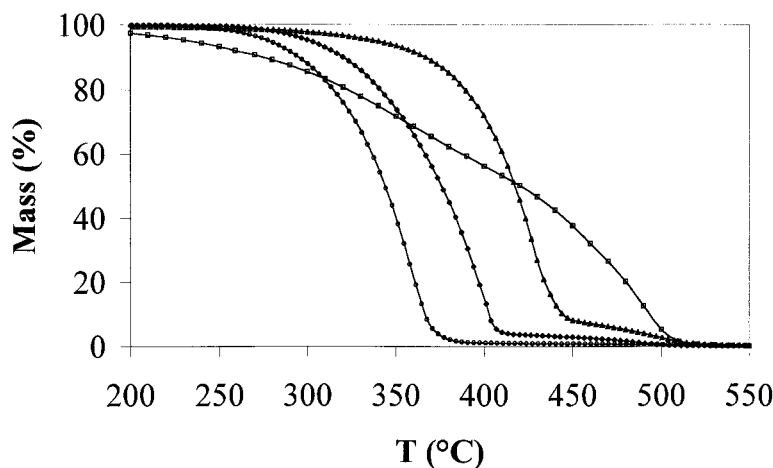


Figure 1 Comparison of thermogravimetric curves of mass loss versus temperature for PP, L and PP/L blends: (○) pure PP, (◆) PP/L 95/5, (▲) PP/L 85/15 and (□) pure L.

mogravimetric curves are reported as percent weight loss as a function of temperature. Sample sizes were about 5 mg.

The isothermal growth rate, Γ , of PP spherulites was studied on thin films using a polarizing optical microscope equipped with a Mettler FP82 hot stage (precision $\pm 0.2^\circ\text{C}$). The films of pure PP and PP/L blends were first melted at 200°C for 5 min and then rapidly cooled to the fixed crystallization temperature (T_c). The radii of the growing spherulites were measured as a function of time by taking photomicrographs at specified time intervals.

The thermal properties of the PP homopolymer and the PP/L blends were analyzed by differential scanning calorimetry (DSC) using a Perkin-Elmer Pyris 1 instrument equipped with a liquid subambient device. Non-isothermal melt crystallization kinetics were studied by melting the samples (about 5 mg) at 200°C for 5 min and then cooling them to 10°C at cooling rates of 5, 10 and $20^\circ\text{C}/\text{min}$. Exothermic crystallization peaks were recorded as a function of temperature.

Isothermal crystallization kinetics were studied by melting the samples (about 5 mg) at 200°C for 5 min and then rapidly cooling them to the desired T_c . The heat evolved during the isothermal crystallization was recorded as a function of time. After the isothermal crystallization process, the samples were heated to the melting point at a scanning rate of $20^\circ\text{C}/\text{min}$. The observed melting temperatures (T_m) were obtained from the maxima of the endothermic peaks.

The glass transition temperatures (T_g) were determined by heating the samples at a scanning rate of $20^\circ\text{C}/\text{min}$. The samples (about 10 mg) were previously quenched from the melt in liquid nitrogen. The T_g was taken at the temperature corresponding to the midpoint of the transition.

An indium standard sample was employed to calibrate the temperature scale and the heat of transition.

Wide angle X-ray diffraction data were obtained at 20°C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000W tube (Cu K_α radiation, $\lambda = 1.54 \text{ \AA}$). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from $5 2\theta^\circ$ to $40 2\theta^\circ$ at $0.02 2\theta^\circ$ intervals. The degrees of crystallinity and the ratios of the different crystalline forms present in the samples were calculated.

RESULTS AND DISCUSSION

Thermal Degradation

Figure 1 presents the thermogravimetric curves used to compare the performance of pure PP in air with that of the PP/L blends. The curves show that the thermal degradation temperature increases with an increase in the amount of L in the blend. The thermogravimetric curve of pure L is also reported to show the synergistic effect obtained by blending the components. The temperature at which 5% of the initial mass of the material has been lost (T_i), the temperature corresponding to the maximum rate of weight loss (T_{mr}), and the percentage of char obtained at a temperature of 450°C are reported for pure PP and PP/L blends in Table I, as calculated from thermogravimetric curves. It is interesting to note that only 15% L in the PP/L blend is able to increase the thermodegradation temperature, T_{mr} .

TABLE I
Thermogravimetric Results for Pure PP and PP/L Blends

PP/L	T_i ($^\circ\text{C}$)	T_{mr} ($^\circ\text{C}$)	Char Yield (wt %)
100/0	277	343	<0.5
95/5	300	375	2.9
85/15	341	415	8.0

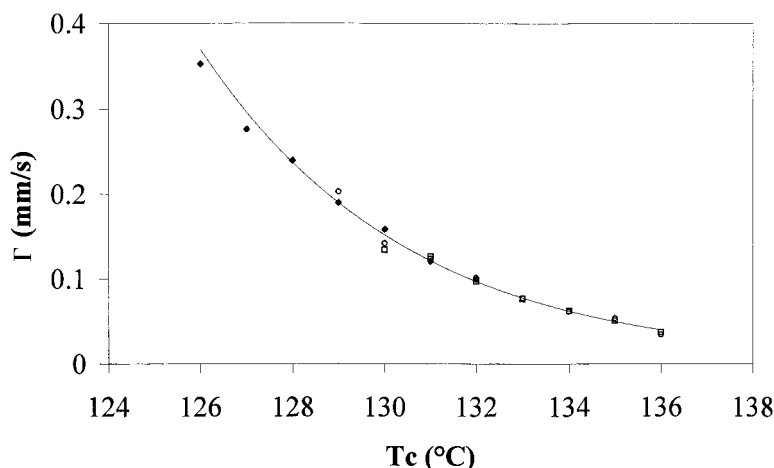


Figure 2 Radial growth rate of spherulites (Γ) versus crystallization temperature (T_c) for pure PP and PP/L blends: (◆) pure PP, (○) PP/L 95/5 and (□) PP/L 85/15.

in air from 343°C for pure PP to 415°C for the PP/L blend.

Morphology and Spherulite Radial Growth Rate

The dispersion degree of L in the blends has been visualized by optical microscopy by carrying out a morphological analysis on the samples melted at 200°C. The analysis showed that the L is observable as a dispersion of particles having an average diameter of 3 μm .

Thin films of pure PP and PP/L blends, when observed under the optical polarizing microscope during the isothermal crystallization process, show birefringent spherulitic structures. The spherulite radius, R , increases linearly with time, t , for all crystallization temperatures and compositions investigated. For all samples, the isothermal radial growth rate, Γ , was calculated at different T_c values, by:

$$\Gamma = dR/dt \quad (1)$$

The values of Γ calculated for pure PP and for PP blended with L are reported as a function of T_c in Figure 2 and Table II. It can be observed that, at a given T_c , Γ values of the PP/L blends were not influenced by the presence of L. A general depression of the PP spherulite growth rate with the increase of T_c values was observed.

Isothermal Crystallization Kinetics

The rate of crystallization, determined by DSC under isothermal conditions, of the PP and PP/L blends, is influenced by the crystallization temperature, T_c . The weight fraction of the material crystallized at time t (X_t) was calculated by the relation:

$$X_t = \int_0^t (dH/dt)dt / \int_0^\infty (dH/dt)dt \quad (2)$$

where the first integral is the heat generated between the beginning of crystallization and time t , and the second is the total heat generated at complete crystallization.

In Figure 3, the fraction, X_t , of the material crystallized as a function of the crystallization time, t , is reported for the PP/L 95/5 sample, at different T_c values. The PP crystallization rate decreases with increasing crystallization temperature as it increases from 126 to 136°C.

The isotherms of crystallization of pure PP and PP/L blends, compared at the same T_c value, show that the rate of crystallization increases with an increasing amount of L in the sample. In Figure 4, differential curves concerning the isothermal crystallization process at 130°C for pure PP and PP/L blends are reported. A strong effect, the enhancement of the PP crystallization rate, is observed. The isotherms of crystallization of pure PP and PP/L blends, compared at the same T_c value, evidenced that the rate of crystallization increases with an increasing amount of lignin in the sample.

In Table II, the half-time of crystallization, $t_{0.5}$, defined as the time required to reach 50% of the complete crystallization, is reported for different T_c values.

The isothermal crystallization of pure PP and of the PP in the PP/L blends has been described by means of the Avrami equation¹⁶ using the experimental data X_t and t coming from isothermal crystallization:

$$X_t = 1 - \exp(-K_n t^n) \quad (3)$$

where n and K_n are parameters depending on the type of nucleation and on the geometry of the growing

TABLE II
Avrami Exponent (n), Overall Kinetic Rate Constant (k_n), Radial Growth Rate of Spherulite (Γ), and Number of Nuclei Per Unit Volume (N), for Pure PP and PP/L Blends

PP/L	100/0					95/5					85/15					
	T_c °C	n	$t_{0.5}$ (min)	$k_n \cdot 10^5$ (min ⁻ⁿ)	$\Gamma \cdot 10^4$ (cm/min)	$N \cdot 10^{-3}$ (cm ⁻³)	n	$t_{0.5}$ (min)	$k_n \cdot 10^5$ (min ⁻ⁿ)	$\Gamma \cdot 10^4$ (cm/min)	$N \cdot 10^{-3}$ (cm ⁻³)	n	$t_{0.5}$ (min)	$k_n \cdot 10^5$ (min ⁻ⁿ)	$\Gamma \cdot 10^4$ (cm/min)	$N \cdot 10^3$ (cm ⁻³)
123	2.9	8.0		135.6												
124	2.7	9.7		74.9												
125	2.8	11.4		46.9	21.1											
126	2.5	13.7		27.1	16.6	3.6										
127	3.0	17.2		13.6	14.4	3.8										
128	2.9	21.0		7.4	11.4	3.2										
129	2.8	27.1		3.5	9.5	3.0	2.6	5.8	706.4	12.1	505	3.1	3.4	1708	8.1	4185
130	3.0	32.1		2.1	7.3	3.0	3.1	6.1	303.1	8.5	631	3.0	4.6	729	7.6	2143
131					6.0		3.1	9.2	87.0	7.4	272	3.0	5.6	386	5.8	2519
132							3.0	13.2	29.7	6.1	169	2.5	7.6	156	4.6	2068
133							3.0	15.5	18.4	4.6	237	2.9	9.1	92	3.7	2235
134							3.2	24.9	4.5	3.7	114	3.0	11.1	50	3.1	2244
135							3.0	26.4	3.8	3.2	146	3.0				
136										2.0						

crystals. Values of n and K_n , reported in Table II, were determined for each T_c from the slope and the intercept, respectively, of the straight lines obtained by plotting $\log[-\ln(1 - X_t)]$ versus $\log t$. In Figure 5, the straight lines obtained for pure PP and PP/L blends, at a T_c of 130°C, are reported. A strong increasing effect on K_n following the blending of L with PP can be observed. The value of the Avrami exponent, n , about 3 for pure PP and PP/L blends, indicates the three-dimensional growth of crystalline units, developed by heterogeneous nucleation.

Assuming spherulitic spherical growth with instantaneous nucleation, the number of primary nuclei per unit volume N can be calculated by the relation:¹⁷

$$N = (K_n/\Gamma^3)[3\rho_a(1 - \lambda_\infty)/4\pi\rho_c] \quad (4)$$

where ρ_c and ρ_a are the density of the crystalline and the amorphous phases respectively, and $(1 - \lambda_\infty)$ is the crystalline weight fraction at time $t = \infty$. Γ and K_n were measured at the same T_c . The N values calculated for the PP/L 95/5 and 85/15 blends were higher by two and three orders of magnitude than the ones calculated for plain PP, respectively (Table II). For a given T_c , the enhancement of the overall crystallization rate of PP is strictly related to the nucleating action of L particles.

Non-Isothermal Crystallization Kinetics

The development of relative crystallization with temperature for the non-isothermal melt crystallization of PP/L blends at different cooling rates was determined by DSC and is presented in Figure 6. The temperature of crystallization of PP/L blends cooled at the same rate, $T_{c(1)}$, were influenced by composition, according to the heterogeneous nucleating action of L particles (Table III).

The kinetics of non-isothermal crystallization can be characterized by the application of the approximate theory formulated by Ziabicki, in which the crystallization can be presented by means of the equation for first order kinetics:¹⁸⁻²⁰

$$dX_r/dt = [1 - X_r]K(T) \quad (5)$$

where the rate constant, $K(T)$, is dependent only on temperature and X_r is the relative crystallinity calculated from DSC thermograms by the relation:

$$X_r = \int_{T(0)}^{T(t)} [(dQ/dt)/(dT/dt)]dt$$

$$\div \int_{T(0)}^{T_\infty} [(dQ/dt)/(dT/dt)]dt \quad (6)$$

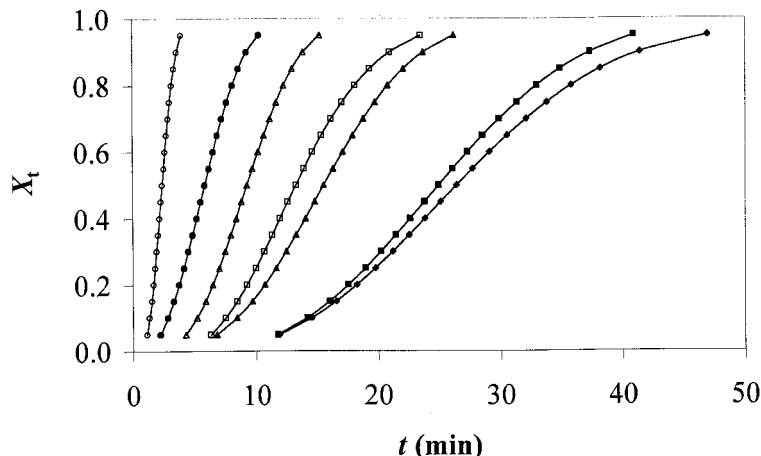


Figure 3 Relative crystallinity (X_t) versus time (t) during isothermal melt crystallization process of PP/L 95/5 blend at different T_c values: (○) 126°C, (●) 130°C, (△) 131°C, (□) 132°C, (▲) 133°C, (■) 134°C and (◆) 135°C.

where (dQ/dt) is the rate of evolution of crystallization heat, which, after being divided by the cooling rate, (dT/dt) , is integrated over the range from the temperature $T(0)$, at which crystallization starts, to the actual temperature $T(t)$ and to the end temperature of crystallization, T_∞ .

A $K(T)$ value can be determined at a temperature T in the range of temperatures between glass transition and melting temperatures.

According to Ziabicki's theory, Jeziorny derived an equation to calculate the quantity G , defined as the kinetic crystallizability, by means of non-isothermal crystallization:²¹

$$G = \int_{T_g}^{T_m} K(T)dT = (\pi/\ln 2)^{1/2}K_{max}D/2 \quad (7)$$

where K_{max} is the value of $K(T)$ at the maximum crystallization rate, and D is the half-width of the crystallization peak. The parameter G must be cor-

rected considering the effect of cooling rate (dT/dt) , and its final form is as follows:

$$G_c = G/(dT/dt) \quad (8)$$

where G_c is the kinetic crystallizability at unit cooling rate.

Calculation of the G_c parameter was made possible by knowing the D and K_{max} values appearing in eq. (4). The half-width, D , can be directly determined from the thermogram, while the K_{max} value can be calculated as follows:

$$K_{max} = C_k/t_{max} \quad (9)$$

where

$$C_k = \int_0^{t_{max}} (dH/dt)dt / \int_{t_{max}}^{\infty} (dH/dt)dt \quad (10)$$

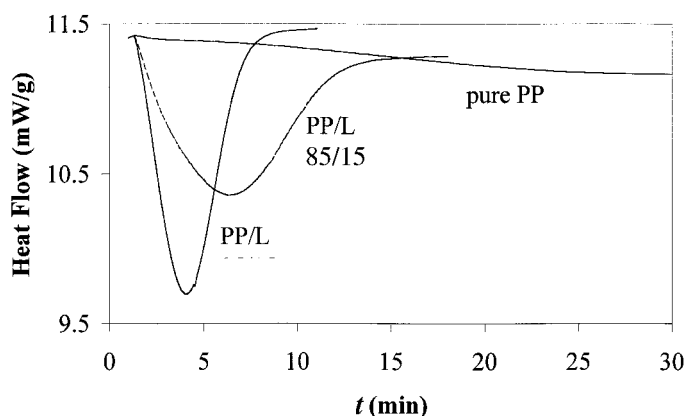


Figure 4 DSC. crystallization curves of PP/L blends at a T_c of 130°C.

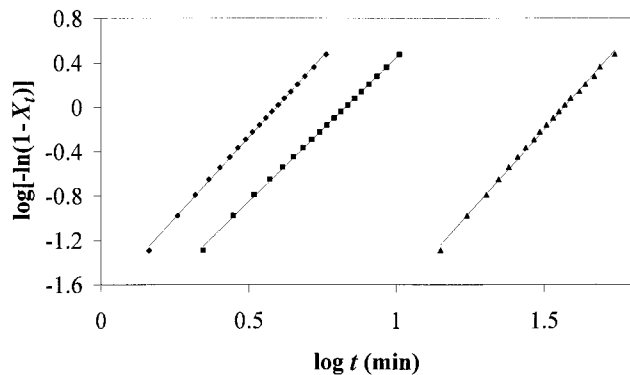


Figure 5 Avrami plots for PP/L blends at a T_c of 130°C: (▲) pure PP, (■) PP/L 95/5 and (◆) PP/L 85/15.

where t_{\max} is the time from the start of crystallization to the maximum rate of crystallization.

The G_c values reported in Table III show a constant value for all investigated PP/L compositions. The kinetic crystallizability, which is related only to the intrinsic structure of the polypropylene, is not influenced by the presence of L.

Glass Transition Temperatures and Melting Behavior

The T_g values determined by means of DSC for both PP/L blends were very close to the value of -13°C recorded for plain PP, as was expected considering the two separated phases, PP and L, in the blends.

For all DSC isothermal crystallization temperatures investigated, the pure PP showed a single peak of melting, while two overlapping melting peaks were observed for PP of both PP/L blends. This result could be ascribed to two different PP crystalline forms, as

TABLE III
Parameters Characterizing Kinetics of Non-Isothermal Crystallization of Pure PP and PP/L Blends

PP/L	Cooling Rate (°C/min)	$T_{c(0)}$ (°C)	G (°C/min)	G_c
100/0	5	113.0	7.05	1.41
	10	109.7	13.61	1.36
	20	106.2	25.74	1.29
95/5	5	119.4	7.00	1.40
	10	116.5	13.28	1.33
	20	112.5	27.49	1.37
85/15	5	122.3	7.00	1.40
	10	118.6	12.63	1.26
	20	114.5	26.81	1.34

has been confirmed by WAXD analysis. In fact, pure PP crystallizes from the melt in the α -form, while when the PP crystallizes in the presence of L, it simultaneously crystallizes in both the α and the β form.

The observed melting temperature of the alpha phase, $T_{m,\alpha}$ linearly increases with the crystallization temperature for pure PP. The experimental data can be fitted to the equation of Hoffmann-Weeks:²²

$$T_m = 1/\gamma T_c + (1 - 1/\gamma)T_m^0 \quad (11)$$

where γ is the morphological factor and T_m^0 is the equilibrium melting temperature.

In Figure 7, the melting temperatures registered at the maximum of the peak relative to the melting of the α -form for the isothermally crystallized pure PP and PP/L blends, are reported. A straight line was extrapolated from the experimental $T_{m,\alpha}$ values of the pure PP, and the calculated T_m^0 was equal to 193°C . This value is well within the equilibrium melting temperatures calculated for α -modification of different iso-

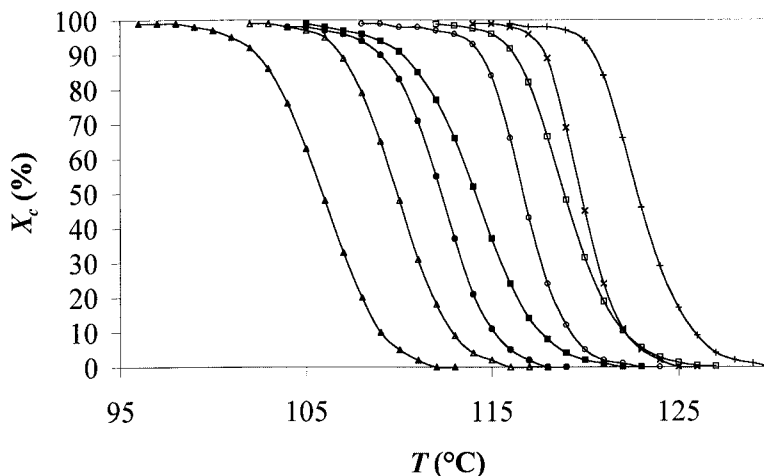


Figure 6 Relative crystallinity (X_c) versus temperature (T) during non-isothermal melt crystallization process at different cooling rates (CR) for pure PP: (▲) 20°C/min, (△) 10°C/min, PP/L 95/5 blends: (●) 20°C/min, (○) 10°C/min, (×) 5°C/min and PP/L 85/15 blends: (■) 20°C/min, (□) 10°C/min, (+) 5°C/min.

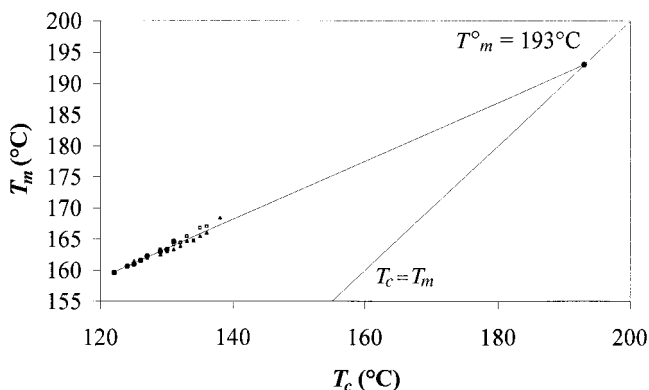


Figure 7 Apparent melting temperature (T_m) versus crystallization temperature (T_c) for pure PP and PP/L blends: (●) pure PP, (▲) PP/L 95/5 and (□) PP/L 85/15.

tactic PPs, as reported by Varga.⁶ In the picture, the $T_{m,\alpha}$ values relative to the melting peaks obtained for the PP/L blends, are also reported. These values are well distributed around the straight line extrapolated for pure PP.

The $T_{m,\beta}$ values relative to the melting of the β -form of PP/L blends increased with crystallization temperature, as shown in Figure 8. The observed $T_{m,\beta}$ values are in good agreement with the ones reported in the literature, even if the presence of the $\beta\alpha$ -recrystallization phenomenon prevents the extrapolation of an equilibrium melting temperature.²³

X-ray Diffraction Analysis

The samples submitted to X-ray diffraction analysis were prepared by cooling pure PP and PP/L blends from 200 to 50°C, at cooling rates of 5, 10 and 20°C/min. In the presence of L, PP can crystallize in both α and β crystalline forms. The ratio between the α and β forms is influenced by the amount of lignin in the PP/L blend and by the crystallization conditions. The

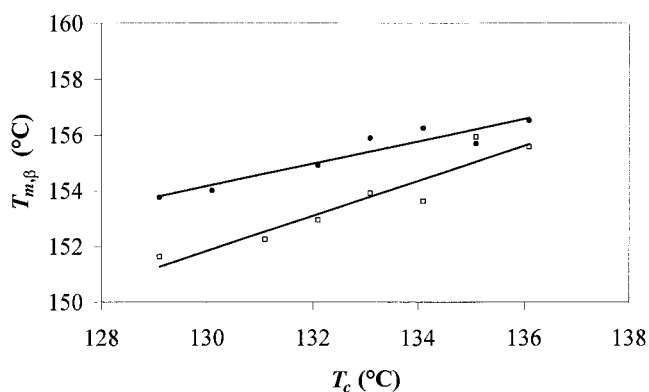


Figure 8 Apparent melting temperature of β -form ($T_{m,\beta}$) for (◆) PP/L 95/5 and (□) PP/L 85/15 blends.

TABLE IV
Crystallinity (X_c) and β -Form Crystalline Fraction (β_{index}) for Pure PP and PP/L Blends

PP/L	Cooling Rate (°C/min)	β_{index}	$X_c^{(a)}$ (%)	$X_{c,PP}$ (%)
100/0	5	0.00	60	60
	10	0.00	60	60
	20	0.00	57	57
95/5	5	0.00	56	59
	10	0.00	54	56
	20	0.04	52	55
85/15	5	0.09	56	66
	10	0.29	57	67
	20	0.39	51	60

(^a) $\pm 2\%$

β index was calculated according to the empirical relation proposed by Turner, Jones, et al.:⁴

$$\beta_{\text{index}} = H\beta_1/H\beta_1 + (H\alpha_1 + H\alpha_2 + H\alpha_3) \quad (12)$$

where $H\alpha_1$, $H\alpha_2$ and $H\alpha_3$ are the intensities of the three α -form peaks (110), (040) and (130), and $H\beta_1$ is the intensity of the single (hk0) peak at $d = 5.495 \text{ \AA}$. The intensity values were measured after amorphous contribution subtraction. An increase of β_{index} was observed with the increase of cooling speed for the PP/L 85/15 blend, while the β crystalline form is present in the PP/L 95/5 blend crystallized at the higher adopted cooling speed (Table IV).

As reported in the literature,¹³ the amount of β -form produced during PP crystallization in the presence of a nucleating agent can be strongly influenced by thermal conditions. In Figure 9, the diffractograms of pure PP and PP/L 85/15 crystallized from melt under isothermal conditions at 125°C are reported. Pure PP reached complete crystallization in about 34 min, while the PP/L 85/15 sample reached complete crystallization in less than 2 min. A β_{index} of 0.58 was calculated for the PP/L 85/15 sample, while pure PP crystallized in the pure α -form.

The degree of crystallinity was calculated from diffracted intensity data over the range from 7 to 36° of 2θ , by using the area integration method.²⁴ The percent crystallinity calculated for pure PP and its blends (X_c) and the percent crystallinity for PP ($X_{c,PP}$) are reported in Table IV. An increase of PP crystallinity was observed for the PP/L 85/15 samples.

CONCLUSIONS

L has been shown to increase the degradation temperature of PP in air. The temperature at which 50% of the initial mass of the material has been lost increased with respect to the amount of PP, with values of 32 and of 72°C for PP/L 95/5 and for PP/L 85/15, re-

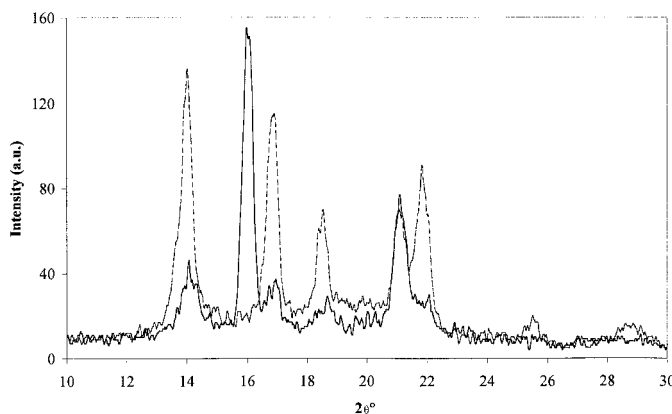


Figure 9 X-ray diffractograms of (---) pure PP and (—) PP/L 85/15, crystallized from melt under isothermal conditions at 125°C.

spectively. During the isothermal crystallization process, the L acts as a nucleant and does not interfere with the spherulitic growth rate and the three-dimensional growth of crystalline units of PP, as indicated by the values of the Avrami exponent. The rate of crystallization of PP is strongly enhanced by the nucleation action of L particles. The number of nuclei per unit volume calculated for PP/L blends were higher by some order of magnitude than the ones calculated for plain PP.

The heterogeneous nucleation action of L particles was confirmed by the process of non-isothermal melt crystallization, giving values of PP crystallization temperatures related to blend composition.

In the presence of L, PP simultaneously crystallizes into two crystalline forms, α and β , for all isothermal crystallization temperatures investigated. The observed melting temperatures relative to both crystalline forms linearly increased with the crystallization temperature for the PP/L blends. The melting temperatures relative to the α -form are in good agreement with the ones observed for the pure isotactic PP.

An increase of β -form fraction was observed with an increase in cooling speed and L content of the PP/L blends when crystallized from melt under non-isothermal conditions.

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