

Influence of Titanium Dioxide on Crystallization Behavior of an Ethylene–Propylene Copolymer

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ABSTRACT: Crystallization of an ethylene–propylene copolymer (E/P) filled with diverse weight percentages of titanium dioxide (TiO₂) was performed under isothermal and nonisothermal conditions to investigate the influence of the inorganic substance on the nucleation and growth mechanisms of the matrix. The overall and radial crystallization rates of the composite materials were measured using, respectively, differential scanning calorimetry (DSC) and optical microscopy. The nucleation density of E/P spherulites as a function of composition was investigated by scanning electron microscopy (SEM), revealing a nucleating effect of TiO₂. A comparison between the spherulitic texture of spec-

imens showed a higher fineness of the composites relative to the neat matrix, whereas no changes of surface nucleation density were appreciable among composites within the explored compositional range. The thermal behavior is discussed in the light of the enhanced thermal conductivity of polymer composites, which conciliates the crystallization kinetics of the matrix, analyzed using the Avrami equation, to optical and SEM observations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3409–3416, 2003

Key words: crystallization; thermal properties; differential scanning calorimetry; kinetics

INTRODUCTION

Titanium dioxide (TiO₂) is an inorganic substance required as an additive from widespread industrial sectors, including food and cosmetic fields, because it combines a set of useful properties, such as opacity, water adsorption, high availability, and low toxicity level. The plastics industry also largely exploits TiO₂ as a whitening pigment, although the effect of TiO₂ upon the structure and physical properties of polymers has not been exhaustively investigated.

An earlier study presented morphological, thermal, and mechanical investigations on a particulate composite made of a propylene copolymer with a low amount of ethylenic units [ethylene–propylene copolymer (E/P)] and titanium dioxide, suggesting usefulness of this material in packaging of agricultural food.¹ The goal of the previous work was the preparation of E/P–TiO₂ composite materials that can be successfully processed and manufactured, as they show a uniform dispersion of the TiO₂ particles within the matrix and a good adhesion between the components. Otherwise, clusters of TiO₂ particles would act as failure regions, worsening thermomechanical resistance of manufactured goods.

The crystallization rate of polymer composites is a very important parameter from an industrial point of

view, as it affects not only the production rate but also the mechanical properties of materials. The overall rate of crystallization depends on two processes: nucleation and subsequent growth of crystals. The rate of nucleation is especially related to the mechanical properties as it determines the number of crystalline nuclei which arise per unit mass and unit time, thus accounting for the final average dimension of spherulites. According to the crystallization theory, the rate of nucleation is proportional to the quantity: $\exp(-\Delta\phi^*/kT)$, where k is the Boltzmann constant; T , the absolute temperature; and $\Delta\phi^*$, the work necessary to form a nucleus of critical dimension. A critical nucleus is large enough to prevent its disruption in the melt and therefore possesses a high probability of growing.² In the presence of foreign particles acting as nucleating centers, a low interfacial energy between the surface particles and the polymer crystal causes a reduction of the work needed to form a critical nucleus so that a higher nucleation density is achieved.

Relative to time dependence, nucleation is generally classified as “instantaneous” if all nuclei form simultaneously in the whole polymer volume and their number does not increase with time or as “sporadic” if nuclei continue to increase. As solidification of materials may take place shell by shell from external surfaces to the interior,^{3,4} to avoid any ambiguity, the above terms must be associated to the thickness of the observed samples. Indeed, instantaneous nucleation may only be observed in thin polymer films a few tens of micrometers thick, whereas in thicker specimens nucleation is necessarily time-dependent.

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The present work investigated the effect of TiO₂ on the crystallization and morphology of E/P. In particular, crystallization of E/P–TiO₂ specimens under isothermal and nonisothermal conditions was carried out as function of the composition and both the overall and radial growth rates of spherulites were measured to draw information on nucleation and growth mechanisms of the E/P copolymer in the presence of TiO₂ particles. A correlation between the thermal behavior and the microstructure was made by applying Avrami analysis and also by taking into account the different values of thermal conductivity of composite specimens.

EXPERIMENTAL

Materials and samples preparation

An isotactic polypropylene copolymer containing 2.4 wt % of ethylene units randomly distributed along the chain, with a weight-average molecular weight $M_w = 216,000$, melt flow index of 9.5 dg/min, and melting point of 154°C, was provided by the Montell Polyolefins Co. (Milan, Italy). Rutile crystalline modification of TiO₂, as granules, with an average diameter of 0.3 μm and a polysiloxanic surface coating, was supplied by Urai S.p.A. (Milan, Italy).

The appropriate weighed amounts of E/P and TiO₂, to make composites containing 1, 5, 10, and 20 wt % of TiO₂, were mixed in a Brabender apparatus for 10 min at 210°C, gradually increasing the mechanical moment of the rotating screw to 32 rotations per minute. Materials were compression-molded at 200°C (ref. 1) in the form of 1.5-mm-thick sheets, from which specimens for differential scanning calorimetry (DSC) measurements were obtained. The designation of specimens indicates the two components and their weight/weight ratio, whereas for the unfilled matrix the wording "neat E/P" is used.

Techniques and procedures

DSC was carried out using a Mettler TA-3000 endowed with a TC 10A temperature control and programming unit and a liquid nitrogen cooling system. The instrument was calibrated, at various scanning rates, with pure indium, lead, and zinc standards. Sample amounts of about 10–15 mg were isothermally crystallized under nitrogen as the purge gas with the following program: heating from 30 to 200°C with a scan rate of 10°C/min and holding at 200°C for 10 min, then cooling with a nominal scan rate of –50°C/min to the prefixed crystallization temperature, in the range 112–122°C. Crystallization temperatures lower than 112°C were not exploited because E/P started to crystallize before the achievement of the set temperature. At temperatures higher than 122°C, crystalliza-

tion is too slow to permit a quantitative determination of crystallization rates.

Samples for nonisothermal crystallization were melted as before, then dynamically cooled from the melt to 30°C with a scan rate of –10°C/min. The surface of DSC crystallized samples was observed using a Philips 501 scanning electron microscope after surface metallization of specimens with an Au–Pd alloy using a Polaron sputtering apparatus.

For optical observations, a small amount of material was squashed between two glass slides to make a few tens of micrometers-thick film and then inserted in a Linkam THMS 600 hot stage programmed by a TMS 91 unit. A Zeiss polarizing microscope equipped with a JVS TK-1085E video camera was used. Samples were heated to 200°C, kept at this temperature for 10 min to destroy any crystalline trace, and then rapidly cooled to the crystallization temperature ranging between 118 and 138°C. The hot stage device was maintained at constant temperature until primary crystallization was completed. Photos at appropriate time intervals were taken and measurements of spherulites diameters were performed with Image Pro-Plus software. The radial growth rate G of spherulites at each temperature was obtained as the slope of radius versus time plot.

RESULTS AND DISCUSSION

Isothermal crystallization

Radial growth rate

Optical observations of spherulites isothermally developed in the range 118–138°C from neat E/P and E/P–TiO₂ 99/1 films showed that nucleation is instantaneous in both samples as all spherulites appear contemporaneously after an induction period. At each temperature, the induction time required by nucleation is not affected by the presence of TiO₂ and no difference of radial growth rates, as shown in Figure 1, was found. Measurements of growth rates were not possible in the presence of a TiO₂ content higher than 1%, because the high refractive index of TiO₂ hinders the observation under light-transmission microscopes.

Young et al.⁵ measured the radial growth rate of isotactic polypropylene in the presence of 2.5 wt % of TiO₂ particles without observing any variation in the growth rate of spherulites relative to neat polypropylene. The authors therefore assumed that even a TiO₂ percentage as high as 40% would not change the spherulite growth rate. The conclusion that the growth rate of E/P spherulites at a certain temperature is independent of the TiO₂ amount was also drawn by the present authors, extending the finding obtained for E/P–TiO₂ 99/1 to composites with a higher TiO₂ percentage.

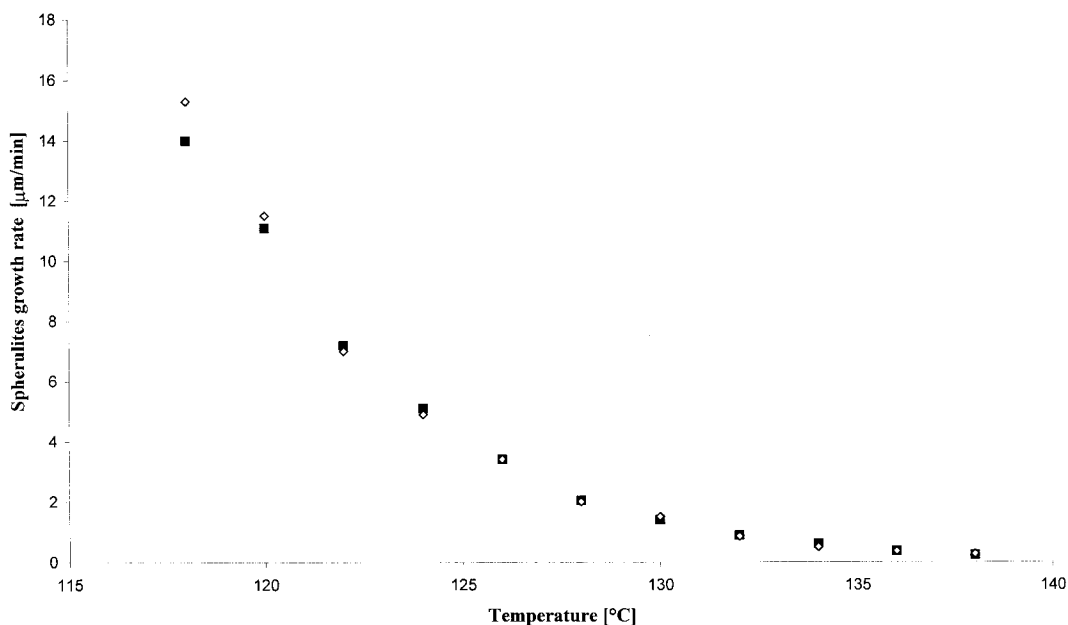


Figure 1 Spherulites growth rate versus temperature (■) for neat E/P and (◇) in the presence of 1% of TiO₂.

Scanning electron microscopy (SEM) investigations on surface morphology

The influence of foreign TiO₂ particles on the mechanism of nucleation of E/P was investigated by SEM analysis of the upper surface of isothermally crystallized specimens. The surface of specimens consists of flat circular spherulites, in conformity with a time-dependent nucleation mechanism. A bidimensional growth of spherulites indicates that spherulites simultaneously nucleated in the bulk lay in a plane and, therefore, successive nucleating events take place in different planes, according to a layer-by-layer crystallization. This kind of crystallization has also been visually observed in E/P films hundreds of micrometers thick using an optical microscope.

SEM examination showed a fine spherulitic texture of the E/P matrix in the presence of TiO₂, even at a percentage as low as 1%, demonstrating a nucleating effect of TiO₂. In Figure 2, the surfaces of E/P-TiO₂ 80/20 and neat E/P crystallized at 116°C in a DSC cell are shown for the comparison. Figure 2 also shows that the nucleation capability of TiO₂ is effective even in E/P-TiO₂ 99/1, in conformity with the usual behavior of nucleating agents.²

Moreover, from SEM analysis, it appears that the enhancement of the nucleation density of E/P spherulites in the presence of TiO₂ is not related to the TiO₂ content, that is, the nucleating effect remains quantitatively the same with an increasing TiO₂ %. Indeed, the level of the fineness of spherulitic textures of E/P-TiO₂ 99/1 and 80/20 crystallized at the same temperature appears to be equal.

Calorimetric behavior

Notwithstanding the similarity of the texture fineness of the surface of E/P-TiO₂ 99/1 and E/P-TiO₂ 80/20 crystallized at the same temperature, these specimens show very different DSC curves. On the contrary, composites containing up to 10% of TiO₂ at $T_c \leq 118^\circ\text{C}$ show crystallization peaks almost overlapping that of neat E/P despite the higher superficial nucleation density of the composites. Apparently, the enhancement of nucleation density in composites evidenced by SEM does not appreciably modify the overall crystallization rate of the polymer matrix in the temperature range 112–118°C and in the presence of a low percentage of TiO₂. Indeed, the heat evolution during crystallization of E/P follows almost identical patterns independently of the TiO₂ content to 10%, while an increase of the heat-evolution rate is evident only for E/P-TiO₂ 80/20, as shown in Figure 3 for the isothermal crystallization at 116°C. The latent heat of E/P crystallization in the presence of 20% of TiO₂ is released in a time shorter than that required from neat E/P and, as expected, the shifting of the crystallization peak to earlier time is accompanied by the enhancement of the height of the crystallization peak.

In Table I, the semitransformation time $t_{0.5}$ of E/P-TiO₂ composites (i.e., the time needed to crystallize 50% of the polymer, whose inverse value gives an estimate of the overall crystallization rate²) is reported as function of the crystallization temperature and composition. From the data, it emerges that E/P-TiO₂ 80/20 shows the shortest semitransformation time at each temperature, whereas no substantial difference

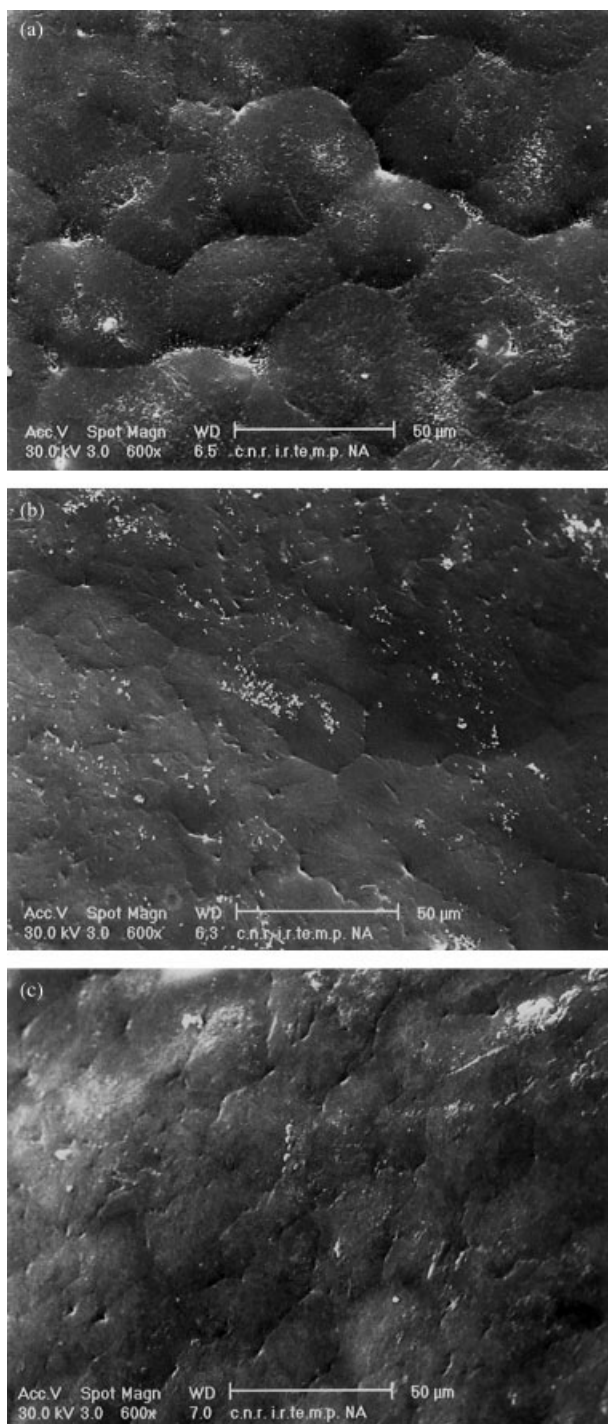


Figure 2 SEM micrographs of the surface of (a) neat E/P, (b) E/P-TiO₂ 80/20, and (c) E/P-TiO₂ 99/1 isothermally crystallized in a DSC pan at 116°C. Magnification 600×.

among the semitransformation times of specimens exists in the temperature range 112–118°C to a content of 10% of TiO₂. At $T_c \geq 120^\circ\text{C}$, differences among semitransformation times of composites with different TiO₂ content become evident. Furthermore, the reduction of $t_{0.5}$ observed for E/P-TiO₂ 80/20 with respect to neat E/P increases with an increasing temperature

and, therefore, the increase in the overall crystallization rate should be more evident with an increasing temperature. This apparent temperature influence can be easily understood by noting that the difference between $t_{0.5}$ observed for E/P-TiO₂ 80/20 and neat E/P is fairly constant with the temperature when expressed as percentage reductions (reductions of $t_{0.5}$ for E/P-TiO₂ 80/20 relatively to neat E/P of about 30% at each temperature can be derived from data in Table I).

When nucleation may be assumed as instantaneous in the whole mass of a polymer, the enhancement of the overall crystallization rate is generally interpreted following two hypotheses: an increase of either the nucleation density or the growth rate of spherulites.² However, the above assumption does not conform to the present case. For instance, by only comparing crystallization peaks of the composites at 116°C, it could be thought that a nucleating effect only exists when the TiO₂ percentage is equal to 20%, in contrast to SEM observations which reveal a higher surface density of E/P spherulites even for the composite with 1% of TiO₂. Alternatively, one could explain the high overall growth rate of E/P-TiO₂ 80/20 by admitting an acceleration of spherulite growth in the presence of TiO₂ if optical evidence for this acceleration would were achieved. Analogously, by comparing the crystallization peaks at temperatures $T_c \geq 120^\circ\text{C}$, it should be inferred that the increase in nucleation density of composite specimens depends on the TiO₂ content. Since none of the quoted possibilities matches microscopic observations, thermal data must be processed in such a way to account for the time dependence of the nucleation by considering the apparent movement of the solidification front along the thickness of the specimens.

From a theoretical point of view, the essential feature of the change of state is the existence of a moving surface of separation, on which heat is liberated or absorbed, between the two phases with different thermal properties and different temperature distributions $T_1(x,t)$ and $T_2(x,t)$.⁶ Assuming that the surface of separation between the solid and the liquid phases is at $X(t)$, a boundary condition to be satisfied at this surface is

$$T_1(X,t) = T_2(X,t) = T_f$$

where T_f is the fusion temperature of the substance. When the surface of separation moves a distance dX , a quantity of heat $L\rho dX$ (where L is the latent heat of fusion per unit mass, and ρ , the density of the substance) is liberated per unit area and must be removed by conduction.⁶

As the way in which this surface moves is complicated and leads to no linear differential equations, special solutions for such problems are generally determined.⁶ For instance, O'Neill⁷ analyzed the fusion

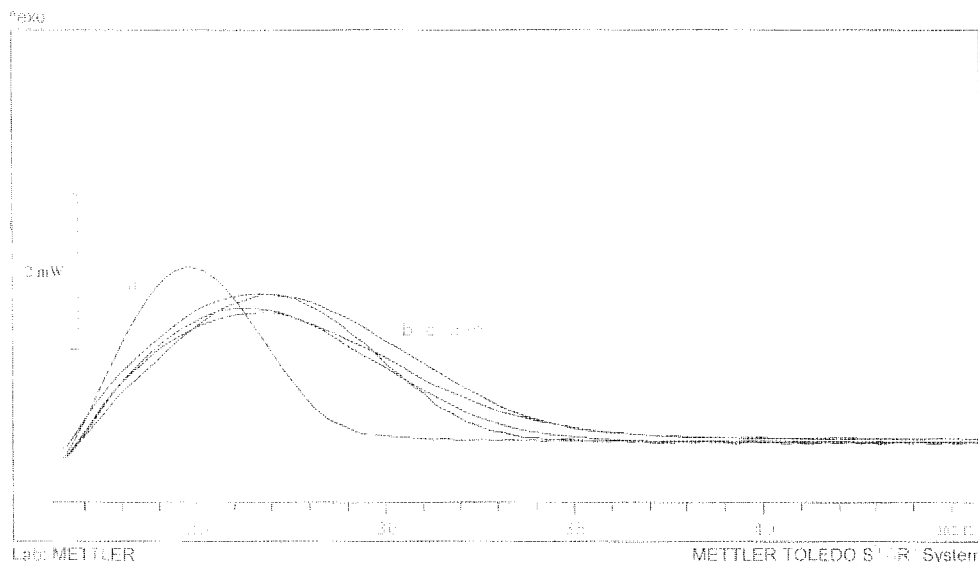


Figure 3 DSC crystallization curves of E/P-TiO₂ composites obtained at 116°C: (a) E/P-TiO₂ 80/20; (b-e) E/P-TiO₂ 90/10, E/P-TiO₂ 95/5, E/P-TiO₂ 99/1, and neat E/P.

process of a small specimen in a DSC pan by assuming that the rate at which the sample melts is proportional to the interface velocity. For polymers, searching for an exact solution for crystallization is even more complicated, as they require supercooling at a temperature far below the fusion temperature to crystallize. Nevertheless, the impossibility to achieve an exact expression for the time dependence of the heat-flow rate, a relative comparison between rates of the heat dissipation may be qualitatively obtained for neat E/P and E/P-TiO₂ composites as follows.

In agreement with the conclusions drawn by several authors on the importance of thermal conductivity in the DSC of polymers⁸⁻¹³ and in determining the heat-transport properties of composites,^{14,15} the present thermal behavior could be related to the higher thermal conductivity and the lower specific heat of E/P-TiO₂ 80/20 relative to compositions with smaller TiO₂ contents. Assuming a value of 6.5 W m⁻¹ K⁻¹ at 373 K (ref. 16) for the thermal conductivity of TiO₂, an average value of 0.12 W m⁻¹ K⁻¹ reported for polypropylene¹⁷ as a reliable value for the present E/P, the thermal conductivity of E/P-TiO₂ 80/20 calculated

according to the mixture rule¹⁴ results: 1.4 W m⁻¹ K⁻¹, that is, an order of magnitude higher than the value of neat E/P. Furthermore, the specific heats of solid TiO₂ and polypropylene are, respectively, 0.703 J g⁻¹ K⁻¹ (ref. 18) and 1.92 J g⁻¹ K⁻¹ (ref. 16), so that in the composites the specific heat is reduced in respect to the neat matrix. For instance, for E/P-TiO₂ 80/20, the value of the specific heat calculated with the mixture rule results: 1.68 J g⁻¹ K⁻¹. Thermal parameters of E/P-TiO₂ specimens are reported in Table II.

Considering the formed solid phase of the specimen as a cylinder, heat developed from the solid is removed with a rate proportional to both the temperature difference ΔT between the sample and the furnace and the thermal conductivity K of the solid and inversely related to the thickness d of the cylinder⁶:

$$Q = K\Delta T/d \quad (1)$$

where Q is the heat flow for time unit and area unit. Therefore, differences in the bulk nucleation rate of the composites may be associated to differences in the rate of heat removal caused by thermal property

TABLE I
Semitransformation Time $t_{0.5}$ of E/P-TiO₂ Composites as Function of Temperature

T_c (°C)	$t_{0.5}$ (neat E/P) (min)	$t_{0.5}$ (E/P-TiO ₂ 99/1) (min)	$t_{0.5}$ (E/P-TiO ₂ 95/5) (min)	$t_{0.5}$ (E/P-TiO ₂ 90/10) (min)	$t_{0.5}$ (E/P-TiO ₂ 80/20) (min)
122	29.5	28.0	28.0	25.5	21.5
120	20.0	17.0	18.0	16.2	12.5
118	9.3	9.9	10.2	9.6	7.2
116	6.0	6.7	6.0	6.3	4.3
114	3.6	3.6	3.4	3.8	2.5
112	2.2	2.3	2.3	2.1	1.5

TABLE II
Thermal Parameters of E/P-TiO₂ Specimens Derived from the Mixture Rule

Parameter	Neat E/P	E/P-TiO ₂ 99/1	E/P-TiO ₂ 95/5	E/P-TiO ₂ 90/10	E/P-TiO ₂ 80/20	TiO ₂
Conductivity (W K ⁻¹ m ⁻¹) × 10	1.20	1.84	4.39	7.58	14.0	65.0
Specific heat (J g ⁻¹ K ⁻¹)	1.92	1.91	1.86	1.80	1.68	0.703
Conductivity/specific heat (g m ⁻¹ s ⁻¹) × 10	0.625	0.963	2.36	4.22	8.33	92.5

changes. Differences in the bulk nucleation rate between an E/P-TiO₂ composite and neat E/P may be ascribed to both differences in the nucleation density and in the rate of heat removal.

Under the same temperature difference ΔT , the respective heat-flow rates for neat E/P and E/P-TiO₂ 80/20 differ by an order of magnitude as a consequence of the different thermal conductivity. The differences between the heat-flow rates of neat E/P and E/P-TiO₂ composites with the TiO₂ content $\leq 10\%$ are less pronounced than is the difference between the heat-flow rate of E/P-TiO₂ 80/20 and neat E/P. Equation (1) only accounts for the difference in thermal conductivity, which regulates heat propagation only under steady-state conditions. Under transitory conditions, the quantity diffusivity: $k = K/\rho c$ (where ρ is the density; c , the specific heat; and K , the thermal conductivity), must be involved in the mathematical treatment of heat propagation. Notwithstanding that the thermal conductivity differences between sample couples [(E/P-TiO₂ 80/20, E/P-TiO₂ 90/10) and (E/P-TiO₂ 90/10, neat E/P)] are the same, different values come out by subtracting the corresponding thermal conductivity/specific heat ratios for the two couples. From data reported in Table II, it can be derived that the difference between the K/c ratios for E/P-TiO₂ 80/20 and E/P-TiO₂ 90/10 is higher than is the difference between E/P-TiO₂ 90/10 and neat E/P. Therefore, at a low crystallization temperature, E/P-TiO₂ 90/10 and neat E/P may show similar crystallization rates despite their different conductivity.

This analysis leads one to conclude that there is excellent agreement between the experimental crystallization rates of the composites and the theoretical expectations derivable from the data in Table II. Indeed, the longer time needed to crystallize neat E/P and composites with a low TiO₂ percentage, relative to a highly filled matrix, can be related to the slow propagation of heat through specimens with a low thermal diffusivity. The diverse ability of polymer composites to dissipate heat according to their thermal conductivity or diffusivity justifies not only the remarkable difference between the semitransformation time of neat E/P and E/P-TiO₂ 80/20, but also the slight difference between the semitransformation time of neat E/P and the other E/P-TiO₂ compositions. In conclusion,

E/P-TiO₂ specimens are thought to crystallize in a shorter time than does neat E/P because of the fast heat delivery during crystallization, accordingly to their high thermal conductivity. The time differences found in the present work among samples with different thermal conductivities are in good agreement with the values predicted by the simulation method developed by Schenker and Stager⁹ and the mathematical model proposed by Seferis et al.^{11,12}

Avrami analysis

The fractions $Y(t)$ of E/P crystallized at time t at constant temperature T_c , obtained as function of the TiO₂ concentration from the DSC measurements, using the formula

$$Y(t) = \frac{\int_0^t (dH/dt)dt}{\int_0^\infty (dH/dt)dt} \quad (2)$$

(where the numerator is the enthalpy developed during crystallization up to time t , whereas the denominator is the heat generated on complete crystallization), were interpreted by using the Avrami equation:

$$1 - Y(t) = \exp(-ht^n) \quad (3)$$

where n gives indications of the type of nucleation and the geometry of the growing crystals, whereas the constant h is related to the global crystallization rate and depends on both the nucleation density and growth rate.

TABLE III
Avrami Exponent of E/P-TiO₂ Composites
as Function of Temperature

Composite	T_c (°C)					
	112	114	116	118	120	122
n (neat E/P)	1.9	1.9	1.8	2.0	2.1	2.0
n (E/P-TiO ₂ 91/1)	2.0	2.0	2.2	1.9	2.2	2.3
n (E/P-TiO ₂ 95/5)	2.1	2.2	2.2	2.2	2.1	2.4
n (E/P-TiO ₂ 90/10)	2.3	2.2	2.2	2.2	2.3	2.3
n (E/P-TiO ₂ 80/20)	2.5	2.4	2.4	2.4	2.6	2.4

TABLE IV
Temperature and Time Values Relative to Crystallization
Peaks of Specimens Cooled at $-10^{\circ}\text{C}/\text{min}$ After Being
Kept at 180°C for 10 min

Composition (wt/wt)	T_{max} ($^{\circ}\text{C}$)	T_i ($^{\circ}\text{C}$)	t_{max}^* (min)	t_i^* (min)
Neat E/P	97.5	103.7	8.3	7.6
E/P-TiO ₂ 99/1	97.6	104.4	8.3	7.6
E/P-TiO ₂ 95/5	98.3	104.8	8.2	7.5
E/P-TiO ₂ 90/10	99.8	104.7	8.0	7.5
E/P-TiO ₂ 80/20	102.9	106.8	7.7	7.3

T_{max} and t_{max} are associated to the maximum of the crystallization peak, whereas T_i and t_i are the onset temperature and time, respectively.

* $t = 0$ corresponds to the beginning of the cooling.

Defining the global crystallization rate as the inverse of the semitransformation time $t_{0.5}$, h is given by

$$h = \ln 2 / t_{0.5}^n \quad (4)$$

The Avrami exponent n derived from the slope of the straight lines, $\ln[-\ln(1 - Y(t))]$ versus $\ln t$, is reported in Table III as function of composition and temperature. For neat E/P and E/P-TiO₂ composites with a TiO₂ concentration $\leq 10\%$, the values of n are nearly 2, compatible with a nucleation depending almost linearly on time and a monodimensional growth of the solid phase, as discussed in the above analysis. The higher fractional values of n obtained for E/P-TiO₂ 90/10 and E/P-TiO₂ 80/20 are compatible with a monodimensional growth and a nucleation dependence on $t^{1.3}$ and $t^{1.5}$, respectively. Avrami analysis suggests a higher nucleation rate of E/P-TiO₂ composites, which explains the higher overall crystallization rate observed for composites and allows one to consolidate all data collected with different techniques. It is worth underlining that the present analysis does not consider crystallization to start at once in the whole volume, but assumes instantaneous nucleation occurring gradually in thin sections of the specimens.

Nonisothermal crystallization

The relationship between the crystallization peaks of dynamically crystallized specimens reflects the pattern found under isothermal crystallization, when, instead of time, the temperature differences between the maxima of dynamic peaks of E/P-TiO₂ composites, relative to neat E/P, are considered. In Table IV, the temperature values associated to the maximum and to the onset of the crystallization peaks (calculated as the intersection between the tangent in the inflection point of the crystallization peak and the horizontal baseline¹⁹), obtained by cooling specimens dynamically at

$-10^{\circ}\text{C}/\text{min}$, are reported as a function of the composition, demonstrating that progressive shifts of T_{max} and of the onset temperature at higher temperature are found in the presence of TiO₂.

The analysis of the nonisothermal crystallization peaks conforms to the previous observation that DSC analysis of polymeric samples is limited by thermal resistance of the specimens^{8,12} and as well agree with the above analysis of isothermal crystallization. Indeed, heat flow from the sample to the furnace is revealed to be faster, that is, at a higher temperature, if the conductivity of specimens increases due to the presence of a more conductive filler. In dynamic cooling, the time of crystallization of each specimen is remarkably reduced relative to isothermal crystallizations because the DSC platform is continuously cooled and thereby the rate of heat removal from crystallizing specimens progressively increases according to eq. (1). This also accounts for the minor difference in crystallization time between E/P-TiO₂ 80/20 and neat E/P in dynamic conditions relative to isothermal conditions.

CONCLUSIONS

Analysis of specimens by SEM revealed a higher nucleation density of the polymer matrix in the presence of TiO₂ at any composition, demonstrating that TiO₂ acts as a nucleating agent toward E/P. Optical observations showed that the radial growth rate of E/P spherulites is not altered by the addition of a low percentage of foreign TiO₂ particles, whereas measurements of the overall crystallization rate using DSC showed a significant increase of the bulk crystallization rate in the presence of a TiO₂ percentage $\geq 10\%$, especially at higher crystallization temperatures. Notwithstanding that TiO₂ was found to act as a nucleating agent at a very low percentage, such as 1%, the overall growth rate of composite specimens appears to not substantially differ from the overall growth rate of neat E/P when the TiO₂ percentage is less than 10%. As the composition dependence of the overall crystallization rate of the polymer does not account for the increased number of spherulites nucleated in the composite material, the thermal behavior was discussed in light of the higher thermal conductivity of polymer composites, considering that processes such as phase transitions involve the releasing or absorption of heat. Avrami analysis demonstrated the predominant role of the nucleation on the increase of the overall crystallization rate of E/P-TiO₂ 80/20. The values of the Avrami exponent have led to the conclusion that nucleation occurs instantaneously in thin sections of the specimens, both in neat E/P and in E/P-TiO₂ composites. However, bulk nucleation increases with time as crystallization proceeds layer by layer along the thickness of the specimen. This leads to a time depen-

dence of nucleation relative to the whole polymer mass although nucleation on individual planes is instantaneous. The final reason of the higher crystallization rate of E/P-TiO₂ 80/20 can be ascribed to the higher bulk nucleation rate, demonstrated by the increase of the Avrami exponent.

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