

Morphological, Structural, and Interfacial Changes Produced in Composites on the Basis of Polypropylene and Surface-Treated Sepiolite with Organic Acids. III. Isothermal and Nonisothermal Crystallization

J. L. ACOSTA, M. C. OJEDA, E. MORALES and A. LINARES, *Instituto de Plásticos y Caucho, Juan de la Cierva 3, 28006 Madrid, Spain*

Synopsis

Two kinetics studies with regard to isothermal and nonisothermal crystallization were conducted on composites samples containing polypropylene and sepiolite surface-treated with isobutyric acid. Comparison of both studies allows us to demonstrate that isobutyric acid-treated sepiolite incorporated to the polypropylene at different ratios acts as an effective nucleating agent and, due to its surface activity, generates two different crystalline structures, one of which is attributable to the formation of a mesophase on the periphery of the sepiolite particle.

INTRODUCTION

In many studies dealing with crystalline polymers it has been shown that the size of both spherulites and crystallites was affected by the presence of a filler.¹ Furthermore, it has been demonstrated² that the energy surface of the filler may completely suppress or accelerate the formation of crystalline structures, or influence the type and dimensional distribution of spherulites. Consequently, and as a result of the effect of the interface with the solid, the conditions of supermolecular structure formation in the boundary layer are altered, and this change can be evidenced when studying the crystallization kinetics of the composites.

In the crystallization of composites on the basis of polypropylene and different sepiolites surface-treated with organic acids it is possible to differentiate between two behavioral patterns vis à vis the crystallization process: in the first, no splitting-up into the corresponding crystallization isotherms can be appreciated,³ whereas in the second pattern, referring to a composite consisting of polypropylene and a sepiolite surface-treated with isobutyric acid, a bimodal composition in isothermal crystallization is noticeable at all crystallization temperatures tested. Apart from this behavioral pattern, the process undergoes a change in the crystallization kinetics in the composites on the basis of polypropylene and sepiolite treated with isobutyric acid compared to the composites that contain sepiolites surface-treated with the remaining organic acids, as well as to filler-free polypropylene, all of which translates into an alteration of the crystalline structure of the composite.

In this paper isothermal and nonisothermal crystallization kinetics are studied for polypropylene composites containing sepiolite surface-treated with isobutyric acid. In the light of the data obtained, it is possible to demonstrate the existence of a complex interface (mesophase) in the terms established by several authors.^{4,5}

EXPERIMENTAL

Raw Materials

The raw materials in this study were polypropylene ISPLEN (Spain) and sepiolite (delivered by TOLSA, Spain) surface treated with isobutyric acid according to a procedure described elsewhere.⁶ The composites containing different filler portions were obtained on a Brabender Plasticorder rheometer following the method specified in a previous publication.⁷

MEASUREMENTS OF CRYSTALLIZATION CHARACTERISTICS

The course of isothermal crystallization was followed through differential scanning calorimetry (DSC) measurements, on a Perkin Elmer DSC-2. Prior to isothermal crystallization at the chosen temperature, the samples were heated to 473°K in the apparatus and held there for about 5 minutes to minimize the effect of any previous history on the crystallization. The crystallinity of the samples was determined taking the enthalpy value 33 cal/g⁸ as fully crystalline.

Likewise the course of nonisothermal crystallization was followed on a Perkin Elmer DSC-4. All the samples were first heated to 473°K in the apparatus, held there for about 5 minutes and then cooled at a rate of 10, 5, and 2.5°K/min. During the cooling cycle the crystallization exotherms were recorded.

RESULTS AND DISCUSSION

Isothermal crystallization of all polypropylene composites containing different amounts of sepiolite surface-treated with isobutyric acid yields thermograms analogous to the one shown in Figure 1, where the bimodal composition can be observed in the graphs registered at three different crystallization temperatures. The thermograms corresponding to polypropylene composites containing sepiolite treated with the remaining organic acids under study and recorded in the same conditions, however, show one single peak only.

On the basis of the thermograms recorded at the four selected crystallization temperatures it is possible to calculate for the three filler ratios used the maximum degree of crystallinity reached by the different samples in the thermic conditions imposed by the test. Likewise the kinetic crystallization parameter can be inferred from the graphic representation of Avrami's equation.⁹ Figure 2 shows the respective curves from Avrami's equation for the polypropylene composites containing sepiolite surface-treated with isobutyric acid in comparison with the graph corresponding to filler-free

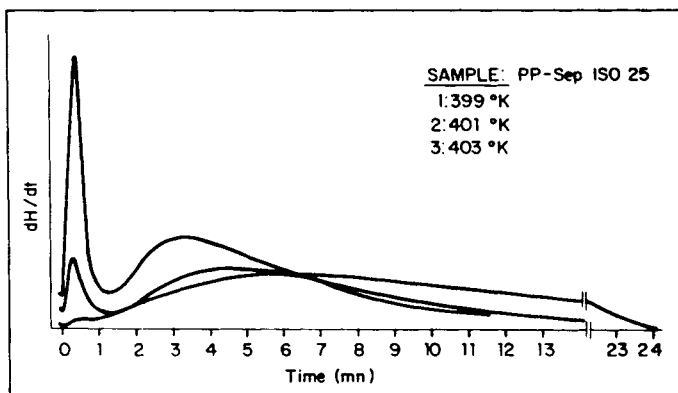


Fig. 1. DSC thermograms recorded by isothermal analysis at three different crystallization temperatures for PP-Sep ISO 25 composites.

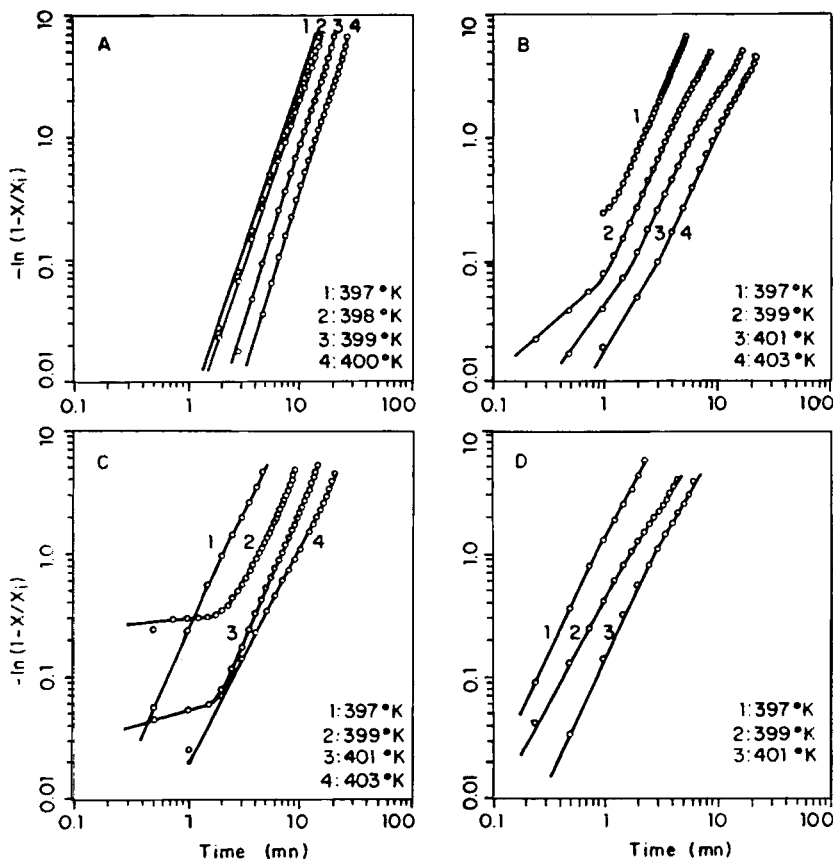


Fig. 2. Representation of Avrami's equation at the tested temperatures for: (a) filler-free polypropylene; (b) PP-Sep ISO 10 composites; (c) PP-Sep ISO 25 composites; and (d) PP-Sep ISO 40 composites.

polypropylene in the same conditions. Table I furnishes an overview with regard to the crystallinity levels reached, as well as to the kinetic parameters derived from the graphic representation, all values being interpreted as a function of the sections they generate in the graphs.

The comparative survey of Figure 2 and the data contained in Table I highlight several facts regarding crystallinity and kinetic parameters. Our attention was especially drawn to the findings of the kinetics crystallization study. On the one hand, a standard behavioral pattern in the crystallization process of filler-free polypropylene can be observed in Figure 2, Avrami's equation yielding a straight graph with a slope of ~ 2.5 over the whole crystallization temperature range tested, values which are similar to other described in the literature.¹⁰ This confirms the fact that isothermal crystallization of polypropylene responds to an athermal nucleation with a growth morphology determined by $n(\sim 2.5)$, i.e., it is bidimensional or tridimensional.

On the other hand, and in contrast to the former, the composite samples tested (Figs. 2a–c) show a remarkable change in the slope, more pronounced in most of the samples with lower filler contents (10 and 25%) and at conversion rates below 20%. The slope in the first section of the straight line in all cases shows values between 0.5 and 1, and in the second section it reaches approximately 1.5. As can be observed, in neither section do the n values coincide with those found for filler-free polypropylene crystallized in the same conditions. This may be taken as conclusive evidence of the fact that during the isothermal crystallization process of the composites under study takes place the growth of two or more ordered structures within the polypropylene matrix, one of which derives from the formation of the mes-

TABLE I
Crystallinity and Kinetic Parameters for All the Samples at the Four Tested Crystallization Temperature

Samples	Filler wt %	Crystallization temp. (°K)	Crystallinity (%)	Avrami			
				1st step		2nd step	
				n	log K	n	log K
PP	—	397	35.39	2.58	-2.33	—	—
PP	—	398	37.08	2.61	-2.41	—	—
PP	—	399	35.11	2.78	-2.97	—	—
PP	—	400	33.59	2.59	-2.99	—	—
PP-Sep ISO	10	397	37.44	1.36	-0.65	2.16	-0.78
PP-Sep ISO	10	399	51.26	0.86	-1.16	2.17	-1.24
PP-Sep ISO	10	401	72.98	1.29	-1.40	1.96	-1.55
PP-Sep ISO	10	403	74.18	1.35	-1.74	2.05	-2.02
PP-Sep ISO	25	397	16.36	2.10	-0.62	1.88	-0.59
PP-Sep ISO	25	399	31.36	0.49	-0.55	1.58	-0.98
PP-Sep ISO	25	401	31.22	0.26	-1.27	2.10	-1.75
PP-Sep ISO	25	403	59.06	1.73	-1.68	—	—
PP-Sep ISO	40	397	7.54	1.98	0.16	1.70	0.12
PP-Sep ISO	40	399	10.04	1.65	-0.37	1.41	-0.32
PP-Sep ISO	40	401	8.42	1.98	-0.85	1.66	-0.74
PP-Sep ISO	40	403	—	—	—	—	—

ophase on the particle periphery, as has been suggested by recent interface theories.⁴

With regard to the crystallinity percentages reached by the isothermally crystallized samples in the test conditions defined, Table I shows that the crystallinity values of the composites with the lowest sepiolite content at all crystallization temperatures tested are significantly higher than those reached by unfilled polypropylene crystallized in the same conditions. In addition, crystallization times are shorter for composites as compared to those required by polypropylene proper, facts that can be predicted by means of the kinetic constant K obtained from Avrami's equation (Table I). This may give us some idea of the strong nucleating influence exerted by the sepiolite surface-treated with isobutyric acid on isothermal polypropylene crystallization. Crystallinity decreases markedly with increasing filler ratio (Table I) reaching very low values for composites containing 40% surface-treated sepiolite over the whole crystallization temperature range tested. The only reason that might explain these facts, in our opinion, is kinetic and instrumental. If supposedly the treated sepiolite, once it is incorporated to the polypropylene and subjected to isothermal crystallization, induces the building-up of different ordered structures in the matrix and in the mesophase, each one with proper growth capacity as a function of the nature of the micelles, the surface activity of the filler and the thermal conditions imposed, when the respective samples are heated to the melting point and subsequently the temperature is lowered to the crystallization temperature by means of sudden cooling in the same DSC oven, a point has been reached where growth and build-up structures sets in or finalizes. As a consequence, a residual crystallization curve is recorded (which fact explains the extremely low values obtained). This graph does not represent the actual crystallinity of the sample. Proof confirming this assumption was obtained when determining crystallinity again for all samples, this time by means of their melting enthalpy, which gave values in the order of those obtained for the low filler content samples.

The study of nonisothermal crystallization kinetics conducted on the same samples supplied data in support of the theory that two or more structures are being formed in the polypropylene matrix. For this purpose we used the method developed by Harnisch and Muschik,¹¹ which allows the determination of Avrami's exponent during nonisothermal crystallization of the polymers using the equation:

$$n = 1 + \left(\ln \frac{\dot{x}_1}{1 - x_1} - \ln \frac{\dot{x}_2}{1 - x_2} \right) / \ln(\beta_2/\beta_1); \quad T = T_c \quad (1)$$

where $\dot{x} = \dot{x}(t, T) = dx/dT$ and β is a constant cooling rate. All quantities on the right-hand side are known or can be determined from the \dot{H} -graph of DSC analysis for the chosen T_c . In order to determine the value of the exponent n by means of this method it is necessary to record the nonisothermal crystallization thermograms of each sample for at least two different cooling rates. We have, however, used three cooling rates: $\beta_1 = 10^\circ\text{K}/\text{min}$, $\beta_2 = 5^\circ\text{K}/\text{min}$, and $\beta_3 = 2.5^\circ\text{K}/\text{min}$.

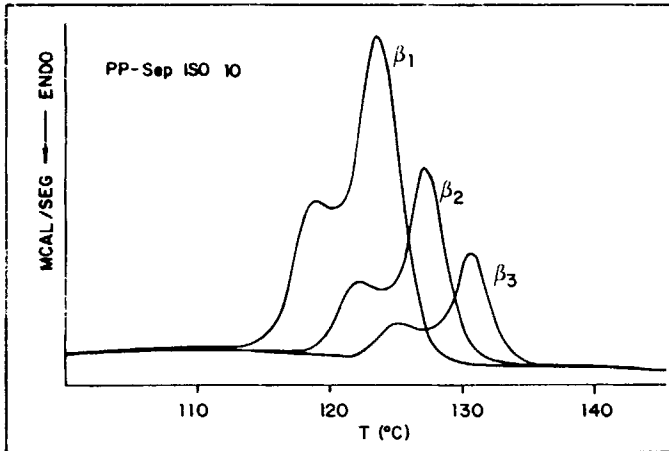


Fig. 3. DSC-thermograms recorded by nonisothermal analysis at the three different cooling rates used for PP-Sep ISO 10 composites.

Figure 3 shows a representative sample of the cooling rates we used. As can be observed, a similar phenomenon occurs as had been noted for isothermal crystallization (i.e., two peaks appear in the graph), which is unequivocal evidence of the formation of two structures during the nonisothermal crystallization process. On the basis of the respective thermograms, the magnitudes compiled in Table II are determined. The graphs deriving from these values are shown in Figure 4, where filler-free polypropylene is compared to the composite at the three filler ratios employed.

Again the graphs show two differentiated sections for the composite samples, while polypropylene has but one. The value of n as determined for polypropylene was 4.3–5.2 while for the composite samples the first slope showed values between 4 and 5.4 and the second section moved between 2 and 2.7. According to these magnitudes, filler-free polypropylene crystallization would be of the thermal type, in contrast with the respective findings by Harnisch and Muschik. These authors determined the nature of polypropylene crystallization to be athermal.

TABLE II

Values Corresponding to the Temperature Where Crystallization Velocity Has Its Maximum (T_{max}) and Values of the Avrami Exponent (n) Determined by Nonisothermal Analysis at Different Cooling Rates β , ($i = 1, 2$, and 3)

Samples	Filler wt %	T_{max} (°C)			Avrami			
		β_1	β_2	β_3	1st step		2nd step	
					n_{1-2}	n_{2-3}	n_{1-2}	n_{2-3}
PP	—	112.2	115.8	119.0	5.2	4.3	—	—
PP-Sep ISO	10	123.5	127.2	130.3	4.9	4.4	2.4	2.0
PP-Sep ISO	25	127.0	130.8	133.9	5.2	5.4	2.6	2.1
PP-Sep ISO	40	125.8	129.2	132.0	5.4	4.0	2.7	2.7

Note: n_{i-j} is the Avrami exponent obtained by application of Equ. (1) between the different cooling rates β_1 – β_2 and β_2 – β_3 .

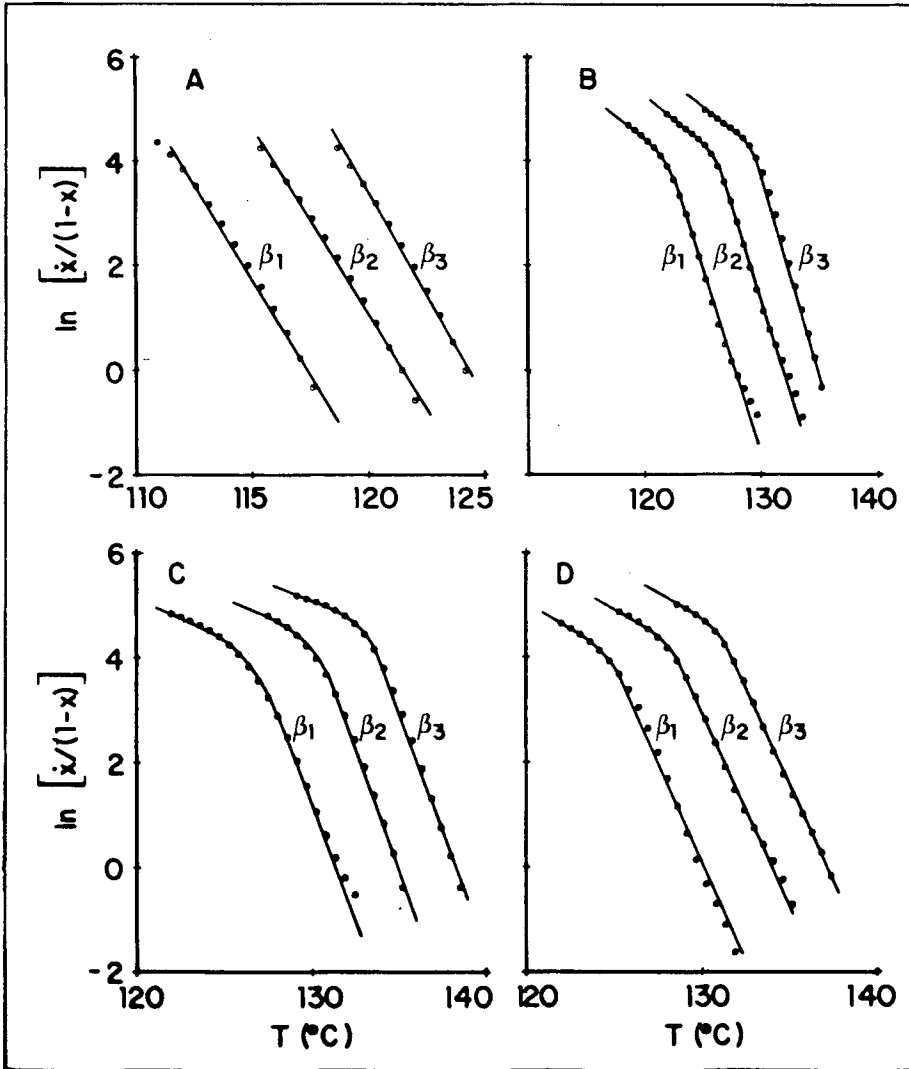


Fig. 4. Representation of $\ln(\bar{x}/1-x)$ values versus temperature at the three cooling rates for: (a) filler-free polypropylene; (b) PP-Sep ISO 10 composites; (c) PP-Sep ISO 25 composites; and (d) PP-Sep ISO 40 composites.

In any case, the data obtained in the nonisothermal crystallization study clearly demonstrate that the same type of behavior as was described for isothermal crystallization is reproduced at a different scale. In other words, two structures are formed which become manifest through the different nucleation and growth mechanisms in the crystallization process of the composites studied, as well as through the separation into two phases at the melting peak. Obviously two different values of Avrami's exponent are indicated here for each individual sample.

In light of the above, the following conclusions may be arrived at:

1. The sepiolite treated with isobutyric acid acts as a nucleating agent

increasing both, crystallinity ratio and rate (K values), with regard to the unfilled polypropylene.

2. The sepiolite treated with isobutyric acid induces the formation of two ordered structures in the polypropylene composites containing them: one that corresponds to spherulite development of the micelles which build up spontaneously in the matrix, and another ordered structure pertaining to the mesophase formulated according to the theoretical criteria established elsewhere.⁴ Such ordering is satisfactorily demonstrated by means of the graphic representation of Avrami's equation, which shows two well-differentiated slopes defining a particular growth rate and geometry.

References

1. V. I. Grigoriev, V. P. Gordienko, and A. N. Tynnyi, *Sov. Mater. Sci.*, **9**, 672 (1973).
2. Yu. M. Malin Skii and I. V. Epel'Baun, *Vysokomol. Soyed.*, **314**, 911 (1972).
3. A. Linares, M. C. Ojeda, and J. L. Acosta, Spanish Pat., 504509 (1981).
4. Yu. S. Lipatov and E. V. Lebedev, *Makromol. Chem. Suppl.*, **2**, 53 (1979).
5. G. C. Papanicolau, S. A. Paipetis, and P. S. Theocaris, *Coll. Polym. Sci.*, **256**, 625 (1978).
6. J. L. Acosta, M. C. Ojeda, E. Morales and A. Linares, *J. Appl. Polym. Sci.*, submitted for publication.
7. J. L. Acosta, M. C. Ojeda, E. Morales and A. Linares, *J. Appl. Polym. Sci.*, submitted for publication.
8. J. G. Fatou, *Eur. Polym. J.*, **7**, 1057 (1971).
9. M. Avrami, *J. Chem. Phys.*, **9**, 177 (1941).
10. B. Wunderlich, *Macromolecular Physics*, Academic Press, New York, 1976.
11. K. Harnisch and H. Muschik, *Coll. Polym. Sci.*, **261**, 908 (1983).
12. J. M. Majer, *Kunststoff*, **50**, 565 (1960).
13. XX Biennial Symposia R.S.E.Q., Morphological and structural changes in isotactic polypropylene observed by adding surface-treated and untreated sepiolite, Castellón 1984, Spain.

Received July 2, 1985

Accepted October 16, 1985