

Nonisothermal Crystallization of Highly-Filled Polyolefin/Calcium Carbonate Composites

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ABSTRACT: Nonisothermal crystallization kinetics of highly-filled polyolefin composites was studied by means of differential scanning calorimetry (DSC). Two types of commercial calcium carbonate based fillers (modified with stearic acid and nonmodified one) were used for our investigations. In order to evaluate the crystallization kinetics changes of composites, the Avrami theory modified by Jeziorny was used. Validity of mineral fillers modification with stearic acid has been proved by thermal analysis. Because of the suppression of the heterogeneous nucleation effect resulting from calcium carbonate with stearic acid modification, an increase in the processability of highly-filled polyolefin cast films might occur. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41201.

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INTRODUCTION

The main reason for polymer composite development is a need to improve mechanical, thermal, electrical, and processing properties.^{1,2} Composites preparation, including physical modification of polymers, is designed to develop materials that have predefined properties. Composite properties are a combination of polymeric matrix and filler properties, as well as a result of interfacial polymer–filler interactions. The addition of fillers into the polymeric matrix may also generate different transformations of the polymer supermolecular structure, such as: an increase in a crystallinity degree or changes in melting (T_m) and crystallization temperatures (T_c).^{3–5} Nowadays, highly-filled polyolefin composites with organic fillers (e.g., wood-polymer composites) or inorganic ones (e.g., talc, calcium carbonate), excluding nanocomposites, are the fastest developing group of polymeric materials.^{6–12} Mechanical properties of polyolefin and calcium carbonate composites have been a topic of numerous scientific papers.^{13–19} Moreover, polyethylene and polypropylene composites that contain modified and nonmodified CaCO₃, where calcium carbonate is limited to 50 wt %, have been widely studied. Thus, significant changes in composite properties have been noted.

On the contrary, only few papers deal with the effect of CaCO₃ addition on the thermal properties and the crystallinity degree of polyethylene and polypropylene.^{5,20–24} Tiemprateeb et al.²⁰ compared the properties of polyethylene composites filled with calcium carbonate with a pure one. The authors claimed that the addition of

CaCO₃ filler does not influence the melting point or the crystallinity degree of polyethylene composites. According to Refs. 21 and 22, calcium carbonate used as a filler has only a slight influence on the polyethylene crystallinity. Thus, bearing in mind the crystallization of polymeric matrix it can be considered as an inactive filler. However, it was also noted²² that the presence of small CaCO₃ particles might have led to an increase of calcium carbonate activity as nucleation centers. The authors²³ proved that the addition of 10 vol % calcium carbonate to high-density polyethylene caused a slight increase in the composite melting temperature. An opposite effect, that is, a decrease in the melting point, was observed for the polypropylene and calcium carbonate composites.²⁴ Moreover, a slight increase in the crystallization temperature, in comparison to the pure polymer, was also noted.

In other papers,^{23,25,26} a reduction in nucleation efficiency was noted for calcium carbonate whose surface was modified with stearic acid. However, this surface modification is usually applied in order to increase a filler's dispersion degree in polymeric matrix. The WAXD analysis carried out by the authors²⁵ showed an increase in the crystallinity degree of polypropylene that was modified with pure CaCO₃ and a certain decrease in case of the modified filler. In the study published by Zuiderdiun et al.,²⁶ it was found that calcium carbonate modified with stearic acid did not affect the melting temperature of polypropylene composite. The authors also stated that the calcium carbonate surface modification led to an increase in the melting enthalpy of the

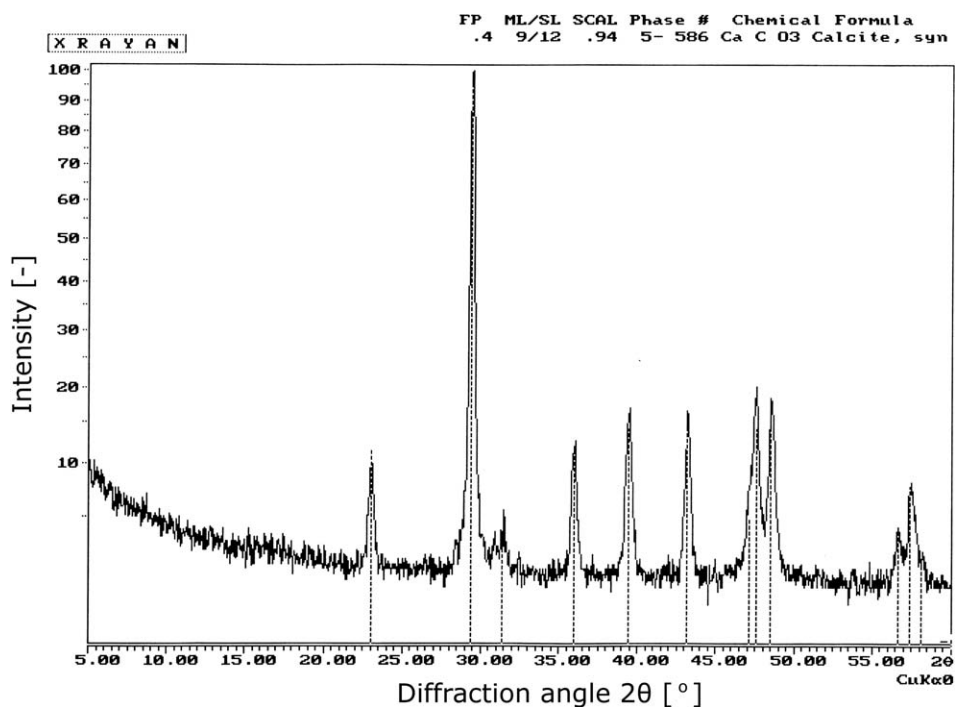


Figure 1. WAXS pattern of CaCO_3 -XRAYAN software analysis showing calcite type.

composite, in comparison to the nonmodified filler. However, a negligible effect of calcium carbonate content and its particle size on the melting enthalpy was also proved.

Owing to different statements regarding the influence of calcium carbonate on thermal properties and crystallinity degree of polyethylene and polypropylene, the main task of our studies was to determine the influence of CaCO_3 and its surface modification on nonisothermal crystallization of highly-filled polyolefin composites (HFPCs). The HFPCs are ternary composites (PE-MD/iPP/CaCO_3) that may be used in the production of paper-like films.^{27,28}

One of the most significant difficulties occurring in the production of oriented materials, like films and fibers, is early viscosity increase caused by additives acting as nucleating agents on the semicrystalline polymeric matrix. In case of highly-filled composites (that contain between 30 and 50 wt % of the filler) designated for cast film production, the evaluation of crystallization kinetics, especially during primary crystallization, is necessary. Various papers present the application of the modified Avrami theory with regards to nonisothermal crystallization of several polymers.^{29–38} It should be mentioned that only few papers focused on crystallization kinetics behavior of highly-filled composites.^{31,32} The main issue was the nonlinearity of Avrami crystallization curves that led to some problems with function fitting and interpretation of crystallization parameters. In our studies, observations of the nonlinear shape of Avrami curves allowed to examine the modification effectiveness.

The main aim of our studies was to evaluate the structure, thermal properties, and crystallization kinetics of polyolefin composites highly-filled with calcium carbonate modified with stearic acid. The modified Avrami theory was applied to evaluate the effectiveness of stearic acid compatibilization on polyolefin-

calcium carbonate composites. The investigations were conducted to determine the potential application of HFPCs as highly oriented composites in polymer film processing.

EXPERIMENTAL

Materials

The following polymeric materials were used as the matrix:

- polyethylene (MDPE) HF 513 (manufactured by the Total Petrochemicals, Feluy, Belgium) with a low density of 0.934 g/cm^3 (23°C) and a melt flow rate ($\text{MFR}_{2;16; 190}$) of 0.15 g/10 min ;
- isotactic polypropylene (iPP) MOPLEN HP 456J (manufactured by the Basell Orlen Polyolefines, Plock, Poland) with a density of 0.915 g/cm^3 (23°C) and a melt flow rate ($\text{MFR}_{2;16; 230}$) of 3.4 g/10 min .

Physicochemical Analysis of CaCO_3

Two calcium carbonates Calplex Extra and Calplex Extra T modified with stearic acid (produced by Calcit D.o.o. Slovenia) were used as inorganic fillers. Calcium carbonate occurs in nature in three crystalline forms: orthorhombic aragonite, hexagonal vaterite, and rhombohedral calcite, which is the most durable one.^{39,40} The crystallographic form of CaCO_3 utilized in our experiments was determined by means of wide angle X-ray scattering (WAXS) where $\text{CuK}\alpha$ radiation monochromatized with Ni filter was used. The measurements were performed within a diffraction angle 2θ between 5 and 60° and the results were analyzed employing XRAYAN software. It was found that both calcium carbonates were of calcite type. An example of the WAXS pattern of calcium carbonate (Calplex Extra) was shown in Figure 1.

The aim of calcium carbonate surface modification was to increase the interface adhesion between filler and polymeric

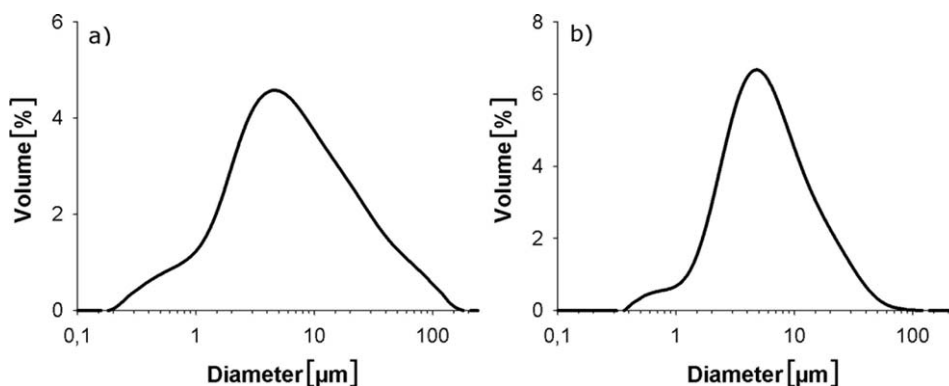


Figure 2. Volume contribution of CaCO_3 versus the particle size distribution: (a) nonmodified (the Calplex Extra); (b) modified (the Calplex Extra T).

matrix.^{14,15} It should be noticed that stearic acid is the most frequently used CaCO_3 modifier. According to Rothon,⁴¹ carboxyl ion (a derivative of stearic acid) may react with calcium carbonate surface as well. The ion is in contact with the filler surface and the rest of the chain juts out forming a monolayer and has a significant influence on the chemical affinity between the filler and the polymer. Because of the modification of calcium carbonate with stearic acid, a reduction of CaCO_3 particles agglomeration effect has been observed.

The impact on the calcium carbonate grain size characteristics was clearly presented in the investigations. The particle size distribution of CaCO_3 was measured by Mastersizer 2000 (manufactured by Malvern Instrument Ltd., UK) employing laser diffraction technique, which allowed to capture figures ranging from 0.02 to 2000 μm . As presented in Figure 2(a), the size distribution of the nonmodified CaCO_3 was in the range of 0.2–158.5 μm . Smaller particle dimensions that varied between 0.4 and 104.7 μm and narrower distribution were observed for CaCO_3 modified with stearic acid [Fig. 2(b)].

The modification with stearic acid also had a significant influence on the surface properties of calcium carbonate. On the basis of the adsorption isotherm of the stearic acid organic solution combined with calcium carbonate in the form of calcite (as elaborated by Suess⁴²), it was shown that one acid molecule covers about 0.21 nm^2 of calcium carbonate. It was also noted that the high degree of monolayer coverage was a result of numerous calcium atoms on the surface of the filler. The possibility of several filler layers creation⁴³ was confirmed by the results of specific surface area investigations conducted with the multipoint BET measurement technique that used adsorption under relative pressure (p/p_0). On the basis of nitrogen adsorption/desorption curves, it was possible to determine the BET specific surface area for nonmodified CaCO_3 equal to 9.2 m^2/g and at the same time equal to 7.8 m^2/g for modified fillers. Therefore, the modification of calcium carbonate surface with stearic acid caused a specific reduction of CaCO_3 surface by 1.4 m^2/g , that is, by 15%.

Samples Preparation

The structural investigations were carried out for medium density polyethylene, polypropylene, and ternary polyolefin

composites (MDPE/iPP/ CaCO_3) with the components weight ratio of 40/12/48. The polymer blend MDPE/iPP (77/23 wt %) was used as a reference material. The composites compositions were summarized in Table I.

The MDPE/iPP polymer blend (R1) and MDPE/iPP/ CaCO_3 composites (C1 and D1) were processed by means of a corotating twin-screw extruder, model PRISM EUROLAB DIGITAL 16 XL (L/D = 40), manufactured by Thermo Electron Corporation (Germany), with temperature profile set between 210 and 230°C and screw speed of 150 rpm. The polymers and fillers (in case of composites) were dosed to the first zone of the barrel (there were 10 zones in total). The extruded material was solidified by quenching in a 10–12°C water bath and chopped up into pellets by a granulator, followed by drying at 80°C for 5 hours. Polymeric materials that were tested using DSC were in a form of granules.

Scanning Electron Microscopy

Surface fracture observations were performed by means of scanning electron microscopy to evaluate the homogeneity of the CaCO_3 distribution in the polymeric matrix and to estimate the role of calcium carbonate surface modification with stearic acid. The apparatus applied to observe the powder filler dispersion level at cryogenic fractured surfaces was SEM Zeiss EVO40 (Germany), with a secondary electrons (SE) contrast and acceleration voltage of 17 kV. SEM micrographs were presented in

Table I. Compositions of the Investigated Materials

Sample	Materials (wt %)			
	MDPE HF 513	iPP HP456J	Calplex Extra (nonmodified CaCO_3)	Calplex Extra T (modified CaCO_3)
MDPE	100	–	–	–
iPP	–	100	–	–
R1	77	23	–	–
C1	40	12	48	–
D1	40	12	–	48

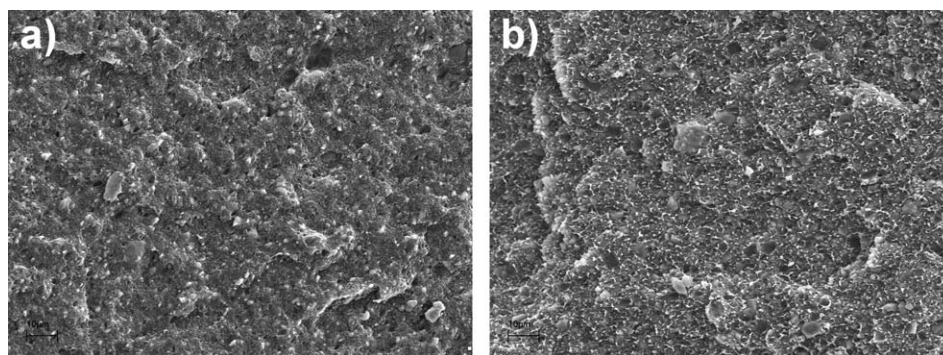


Figure 3. SEM micrographs of MDPE/iPP/CaCO₃: (a) C1; (b) D1.

Figure 3. As shown in Figure 3(b), a more homogenous distribution of modified CaCO₃ filler was achieved.

The applied instrumental investigation methods demonstrated direct influence of calcium carbonate (calcite) modification with stearic acid upon physical properties and structure of composites (C1, D1). In the next part of this article, a modification of the filler as well as its influence on the crystallization process of composites shall be analyzed.

Differential Scanning Calorimetry

Differential scanning calorimetry measurements were carried out using a NETZSCH DSC204 F1 Phoenix apparatus with aluminum crucibles and 5 ± 0.1 mg samples under nitrogen flow. Nonisothermal crystallization processes were performed at certain programmed temperatures. All samples were heated up to 220°C and held in a molten state for 5 minutes. Then the samples were cooled to 60°C with constant cooling rates $\Phi = 5, 10, 20,$ and $30^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

DSC investigations were used to determine stearic acid influence on the polyolefin-calcium carbonate composites crystallization behavior. After converting DSC crystallization curves at different cooling rates ($\Phi = 5, 10, 20, 30^\circ\text{C}/\text{min}$), relative crystallinity as a function of time and temperature was determined.^{29–38} Calculations were based on the following equations:

$$X(t) = \frac{X_i(t)}{X_i(\infty)} = \frac{\int_0^t (dH(t)/dt) dt}{\int_0^\infty (dH(t)/dt) dt} \quad (1)$$

$$X(T) = \frac{X_T(T)}{X_T(\infty)} = \frac{\int_0^T (dH(T)/dT) dT}{\int_0^\infty (dH(T)/dT) dT} \quad (2)$$

where $X_i(t)$, $X_T(T)$, and $X_i(\infty)$, $X_T(\infty)$ indicated relative crystallinity at time t and temperature T and at the end of the crystallization process, whereas $dH(t)/dt$ and $dH(T)/dT$ were the heat flow rates. The relationship between relative crystallinity of pure polyolefins, polymer blends and highly-filled modified and

nonmodified polymer-calcium carbonate composites in a function of temperature was presented in Figure 4.

Various crystallization behaviors of investigated samples could be observed. In case of polyethylene–polypropylene immiscible blend, the effect of separate polypropylene crystallization could be noted in Figure 4(c). Calcium carbonate introduced into polymer melt acted as a nucleating agent and caused a significant increase of the crystallization onset to higher temperature values (Fig. 4d). The addition of stearic acid could prevent the effect of crystallization temperature increase that was caused by a high amount of inorganic filler [Fig. 4(e)]. The course of relative crystallization curves for composites, where stearic acid was present, was similar to those obtained for pure polyolefin blends (Fig. 4c). However, the effect of earlier polypropylene crystallization was not observed. The appearance of additional crystallization peaks (early the crystallization onset) observed for polypropylene based composites filled with calcium carbonate was ascribed to self-nucleation effect by Supaphol et al.⁴⁴ Presented by the authors' hypothesis explained that residual polypropylene crystallites become entrapped along the rough surface of nonmodified CaCO₃ particles and became active nucleation centers during subsequent crystallization. This phenomenon can be clearly observed for composites containing more than 20 wt % of calcium carbonate.⁴⁴ Therefore, the effect described in presented studies was reasonable higher because composites contain high amount of inorganic filler (48 wt %). In our study the 15% reduction of CaCO₃ specific surface area caused by stearic acid addition leads to decrease the possibility of crystallites entrapment on the rough surface of unmodified inorganic filler. It is important to mention the fact that the effect of modification was almost time-independent; and only in case of curve obtained at the lowest cooling rate $\Phi = 5^\circ\text{C}/\text{min}$, the inflexion of the relative crystallization curve could be observed.

To analyze the mechanism of crystallization at its early stage, crystallization kinetics analysis was undertaken by applying Avrami theory⁴⁵ modified by Jeziorny.^{29–38} The model of crystallization that was used allowed to determine crystallization kinetics parameters during nonisothermal crystallization after an adequate correction of the crystallization rate:

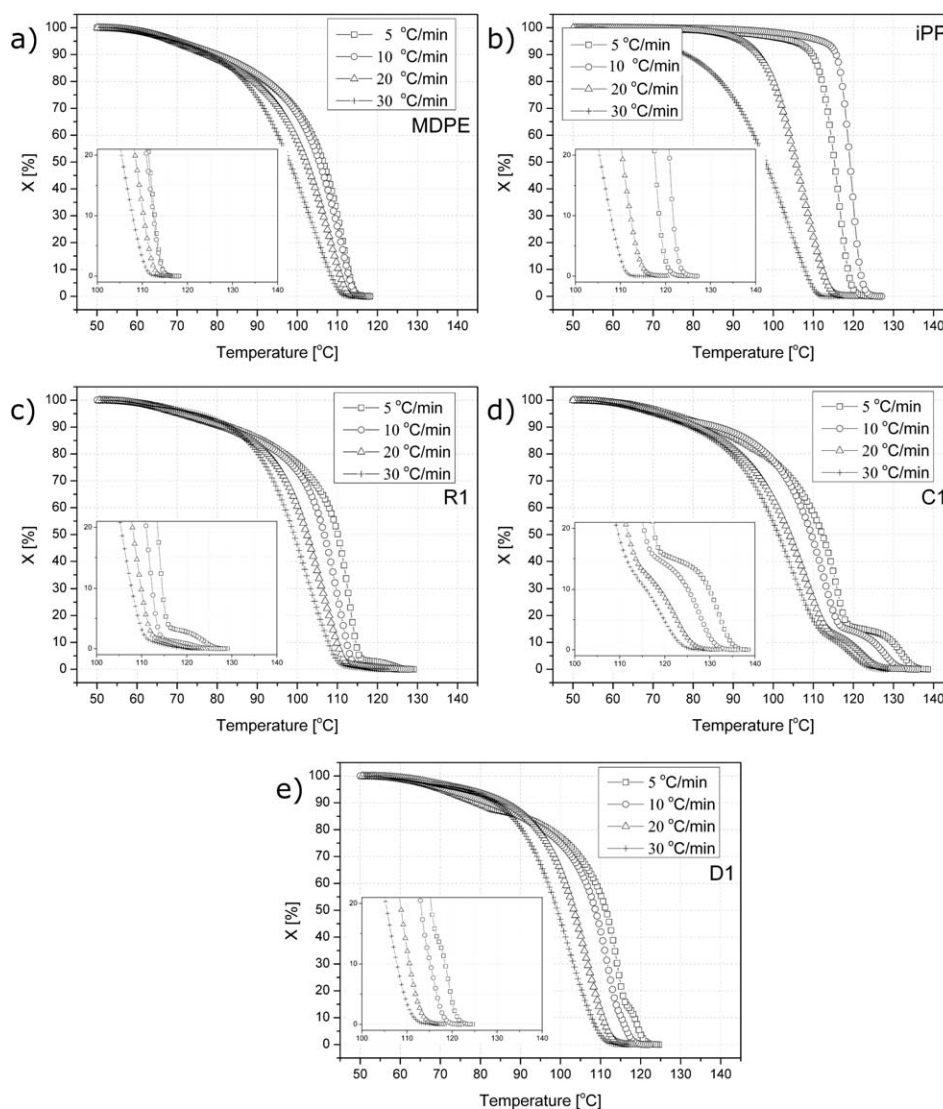


Figure 4. Relative crystallinity as a function of temperature of pure MDPE and iPP, MDPE/iPP blends, polyolefin blends filled with calcium carbonate, and calcium carbonate modified with stearic acid.

$$1 - X(t) = \exp[-Z_t t^n] \quad (3)$$

By rearranging the eq. (2), the following can be presented:

$$\ln[-\ln(1 - X(t))] = \ln Z_t + n \ln t \quad (4)$$

where Z_t is the Avrami constant rate, n is the Avrami exponent, and $X(t)$ is the relative crystallinity at time t evaluated from temperature T , which can be defined in the following way:

$$t = \frac{(T_0 - T)}{\Phi} \quad (5)$$

where T is the temperature at time t , T_0 is the initial temperature (shown at the start of the crystallization process) and ϕ is the true cooling rate calculated as a derivative of DSC temperature signal.

In order to correct the Avrami constant Z_t that was affected by non-isothermal crystallization process, Jeziorny proposed to take into account the cooling rate as a factor that could lead to significant changes.

$$Z_c = \frac{\ln Z_t}{\Phi} \quad (6)$$

The analysis of nonisothermal crystallization kinetics, based on Avrami theory modified by Jeziorny, did not describe crystallization in a quantitative way. However, it was possible to obtain information about some changes in crystallization kinetics, even that crystallization parameters did not have a clear meaning as in case of isothermal crystallization. The Avrami curve nonlinearity caused by the complicated crystallization behavior of highly-filled polymeric composites was analyzed, which allowed to evaluate the effectiveness of stearic acid as a compatibilizer. Therefore, the modified Avrami theory analysis was applied as a sensitive tool that allowed to observe changes in crystallization behavior, as well as interactions between composite elements. The $\ln[-\ln(1-X(t))]$ versus $\ln t$ Avrami plots of polymer blend [R1-Fig. 5(a)], nonmodified [C1-Fig. 5(b)] and modified [D1-Fig. 5(c)] MDPE/iPP/ CaCO_3 composite were presented in Figure 5.

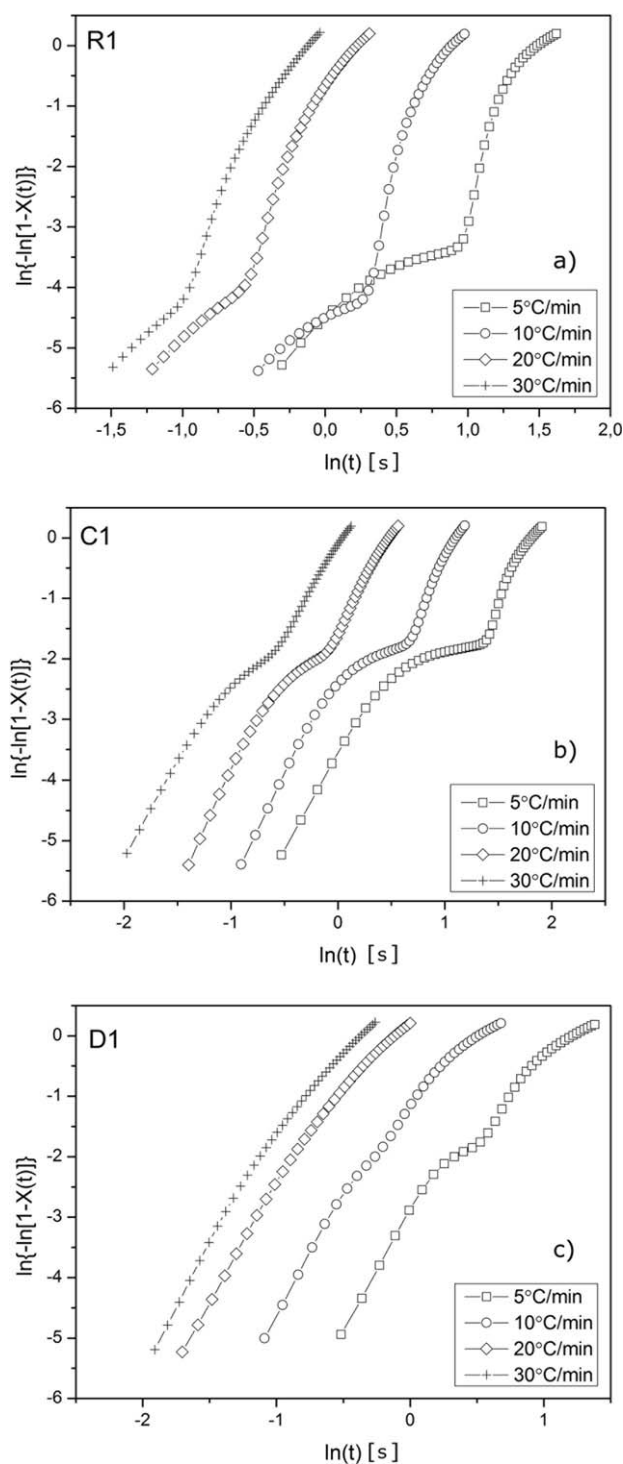


Figure 5. Plots of $\ln[-\ln(1-X(t))]$ versus $\ln t$ for (a) R1-MDPE-iPP; (b) C1-MDPE-iPP-nonmodified CaCO_3 ; (c) D1-MDPE-iPP-modified CaCO_3 .

For samples marked as R1, that is, nonfilled MDPE-PP blends, the inflexion of $\ln[-\ln(1-X(t))]$ versus $\ln t$ curve was observed [Fig. 5(a)]. It was caused by the earlier crystallization of isotactic polypropylene [up to the relative crystallinity level of 2%, Fig. 5(c)]. For C1 samples, at all applied cooling rates, the first inflexion of the $\ln[-\ln(1-X(t))]$ versus $\ln t$ curves that was a

result of the crystallization changes caused by a presence of calcium carbonate was observed. In case of D1 samples, changes in crystallization were obtained only for one sample cooled with $5^\circ\text{C}/\text{min}$ rate. The crystallization behavior of the remaining D1 samples that were cooled with higher cooling rates were similar to nonfilled materials (pure PP or MDPE) — the earlier crystallization of composites was entirely suppressed. It is important to mention that in case of modified samples filled with calcium carbonate (marked as D1) early crystallization was not observed neither for the relative crystallinity curves nor in a form of inflexion of the $\ln[-\ln(1-X(t))]$ versus $\ln t$ curves. The nonisothermal crystallization parameters for the R1, C1, and D1 samples were presented in Table II.

The Avrami exponent n and the parameters Z_t and Z_c can be evaluated by analyzing approximated functions obtained from the eq. (4). The mean values of the Avrami exponents obtained for polyolefin blends were much higher than for filled samples ($n_{R1} = 3.78$). However, it should be noticed that in case of samples filled with modified calcium carbonate the n value is higher than for the nonmodified ones ($n_{D1} = 3.13$, $n_{C1} = 2.57$). For C1 samples, the n value was close to $n = 2$, therefore, it could be emphasized that the addition of the nonmodified inorganic filler led to fibrillar or lamellar crystal growth. A higher n value, observed for polyolefin blend R1, that was almost equal to 4, indicated that the crystallization changed its character to a thermal one. In case of the samples filled with modified calcium carbonate the n value was close to 3. This value was mostly observed during a thermal heterogeneous nucleation. Considering the Z_c parameter, it should be underlined that the nonmodified filled samples (C1) were almost insensitive to thermal conditions. This could be assigned to a strong heterogeneous influence of the mineral filler. The Z_c values for modified and nonfilled polyolefin blends showed a similar increasing tendency that matched an increasing cooling rate. However, for D1 samples the Z_c values were slightly higher and the value of 1 was achieved at a cooling rate of $20^\circ\text{C}/\text{min}$. The values of crystallization half-time indicated that the fastest crystallization was observed for D1 samples. Owing to the complex polymeric system and its nonlinear crystallization character, it was difficult to compare these crystallization parameters in a quantitative way. The onset of the crystallization in other cases (R1, C1) occurred much earlier. The modification of calcium carbonate resulted in less complex crystallization behavior of polymeric composite.

It is important to outline that in case of highly-filled polymer composites that consisted of two immiscible semicrystalline polymers and an inorganic filler, a description of crystallization kinetics using standard crystallization parameters n , Z_t , and Z_c was performed in the following way: a visual analysis of $\ln[-\ln(1-X(t))]$ versus $\ln t$ plots was done, in comparison to relative crystallization versus time curves. The inflexion of $[-\ln(1-X(t))]$ versus $\ln t$ curves caused by the earlier crystallization of isotactic polypropylene [Fig. 5(a)] or the addition of calcium carbonate [Fig. 5(b)] and its suppression in the presence of stearic acid [Fig. 5(c)] were difficult to describe in a quantitative way by using standard crystallization kinetics parameters. Therefore, the analysis of regression coefficient could be proposed as a tool to determine the inflexion presence

Table II. Non-Isothermal Crystallization Parameters of Investigated Composites

Sample	Φ (°C/min)	n	\bar{n}	Z_t	Z_c	$t_{1/2}$	R^2
R1	5	3.18	3.78	0.025	0.477	2.854	0.89
	10	4.649		0.014	0.653	2.313	0.92
	20	4.23		0.411	0.957	1.131	0.97
	30	4.339		1.923	1.022	0.790	0.98
C1	5	1.901	2.57	0.025	1.13	5.781	0.93
	10	2.333		0.062	0.758	2.809	0.95
	20	2.601		0.265	0.936	1.448	0.98
	30	2.409		0.817	0.993	0.934	0.98
D1	5	2.663	3.13	0.044	0.536	2.807	0.97
	10	2.852		0.26	0.874	1.410	0.98
	20	3.118		1.692	1.027	0.751	0.98
	30	3.14		3.732	1.045	0.585	0.98

of $[-\ln(1-X(t))]$ versus $\ln t$ curves in case of blends and filled composites. The high regression coefficient of D1 curves meant that Avrami nonlinearities, caused by immiscible composite ingredients, were suppressed. This might lead to a statement that the effectiveness of stearic acid as a compatibilizer was sufficient.

A comparison of relative crystallinity versus temperature curves up to 20% of crystallinity [Fig. 4(c-e)], with regression coefficient values evaluated for approximate functions obtained from the modified Avrami theory analysis (Fig. 5), indicated that the suppression of early crystallization effects was successful.

CONCLUSIONS

The nonisothermal crystallization behavior of polyolefin–calcium carbonate composites was investigated. In this article the application of crystallization kinetics analysis based on Avrami equation modified by Jeziorny enabled a description of relationship between the modification of calcium carbonate with stearic acid and the crystallization of entire composites. Two methods of interpretation of the signals obtained from differential scanning calorimetry during cooling were used to prove the effectiveness of stearic acid modification on the nucleating effect suppression. The effect of modified and nonmodified fillers addition upon polyolefin composites crystallization behavior could be observed not only as a shift of $\ln[-\ln(1-X(t))]$ versus $\ln t$ curves but also as inflections of the Avrami plots. The evaluation of regression coefficient of linear approximated functions that was conducted for $\ln[-\ln(1-X(t))]$ versus $\ln t$ curves in the primary crystallization part curve have supplied additional information about crystallization of immiscible polymer blends and highly filled polymeric composites. The new way of interpretation of the Avrami plots presented in this study allowed to achieve the modification assessment both in a quantitative and qualitative way.

Moreover, the effect of suppressed crystallization behavior of composites filled with physically modified calcium carbonate calcite led to their processability increase. It is also important to

notice that when crystallization of processed materials was delayed, the viscosity increase was also delayed and reached lower temperatures. Therefore, products in a form of films or blow molded films could obtain significantly higher draw ratios. Conscious limitations that occurred during the primary crystallization were in line with the expectations that materials appropriated for orientation technologies should fulfill.

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