Effect of Nucleating Agents on the Temperature-Dependent Melt Crystallization Kinetics of Poly(1-Butene)*

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Synopsis

The effect of additives (mostly nucleating agents) on the crystallization rate of isotactic poly(1-butene) has been investigated by differential scanning calorimetry. Isothermal crystallization half-times and crystallization temperatures have been measured for polymer-additive blends. The crystallization temperature and the cooling rate at which the ultimate fraction transformed becomes less than 1 is calculated as a function of nucleation density, and this is used to characterize the effect of the additives on crystallization rate. The relationship between the isothermal crystallization half-time and the crystallization temperature is also calculated theoretically and is compared with experimental results.

INTRODUCTION

The effect of additives on the crystallization rate of isotactic poly(1-butene) homopolymer has been investigated. Most of the additives studied increase the rate of crystallization primarily by increasing the density of heterogeneous nuclei.[1] Some of the additives decrease the rate of crystallization, probably by acting as a diluent.[2]

The crystallization process examined here is from an unstressed, unpressurized melt to the form II crystal.[1] The crystallization of the polymer was followed using differential scanning calorimetry.[3] The change in crystallization rate has been determined by measuring both the isothermal crystallization half-time $t_{1/2}$ and the crystallization temperature T_c for both the neat polymer and the polymer blended with the additives. The isothermal crystallization half-time is the time taken by the polymer to complete half of its transformation from the melt to a semicrystalline solid; the crystallization temperature is the temperature at which the heat evolution and, thus, the rate of crystallization reaches a maximum when the material is cooled at a constant rate of cooling.[4] An additive that acts as a nucleating agent will generally decrease the crystallization half-time and increase the crystallization temperature.

The poly(1-butene) homopolymer is the same as that studied in Ref.[4] In that work, it was suggested that the experimental measurements necessary to characterize the crystallization kinetics of a semicrystalline polymer are established by adopting a model for the crystallization of the polymer and

specifying the range in which thermodynamic variables and other field interactions with the polymer will be varied during the processes of interest. Then, by adopting a crystallization model of instantaneous heterogeneous nucleation followed by spherulitic growth, it was shown that, to the extent to which that model accurately describes the crystallization, the determination of the spherulitic growth rate and nucleation density as a function of temperature characterizes the temperature-dependent crystallization kinetics of the polymer. These were measured for poly(1-butene). Given these measurements, the crystallinity as a function of time for any process in which the temperature is varied can in principle be calculated. This was done specifically for a process in which the polymer is cooled at a constant rate from an initial temperature above its thermodynamic melting temperature to a temperature low enough that the material ceases any further crystallization. From this model the crystallization temperature can be calculated. Furthermore, the ultimate fraction transformed X_∞, defined as the fraction of polymer that has transformed by the time the polymer is cooled to the temperature T_∞ at which any further growth of the spherulites ceases, can also be calculated. Both T_c and X_∞ are functions of the cooling rates. This functional dependence was calculated for poly(1-butene).

In this work, this analysis is further developed to analyze the effect of various additives on the crystallization rate of poly(1-butene). The cooling rate at which X_∞ is equal to some value X^* that is close to but less than 1, $s_{X_\infty = X^*}$, gives a measure of the cooling rate at which crystallization becomes rate limiting; this cooling rate is thus a measure of the effect of the crystallization rate on the processing rate of the material.[4] further, it is shown that $s_{X_\infty = X^*}$, T_c, and $t_{1/2}$ can all be calculated as a function of the nucleation density M_0, and thus they can all be calculated as functions of one another. The calculated functional relationship between T_c and $t_{1/2}$ is then compared with experimental results.

EXPERIMENTAL

Materials

The isotactic poly(1-butene) used in this study was an additive-free homopolymer manufactured by Shell Chemical Company. It had a melt flow rate of 0.42 dg/min (ASTM D 1238, Condition E), and its number-average and weight-average molecular weights were 73,000 and 750,000, respectively, as measured by gel permeation chromatography. Based on its carbon-13 nuclear magnetic resonance spectrum, the polymer contained 94% isotactic linkages with an average isotactic (*meso*) sequence length of 32, and 6% syndiotactic linkages with an average syndiotactic (*racemic*) sequence length of 2.0.[5] The ether-soluble fraction of the material was 0.6% by weight. This is the same polymer studied in Ref. 4.

The sources of the some of the additives are given in Refs. 6–8. The source of the other additives studied, which are listed in Table II, are as follows: Polywax 2000 is polyethylene of molecular weight 2000, Polywax 850 is polyethylene of molecular weight 850, both from Petrolite Corporation; HDPE is Union Carbide grade 7006 high-density polyethylene; polypropyl-

ene is Shell Chemical Polypropylene DN 5033, a nonnucleated homopolymer with a melt flow rate of 3.0 dg/min (ASTM D 1238, Condition L); talc-A is Mistron Vapor from Cyprus Industrial Minerals Company, median particle size 1.5 μm; talc-B is Mistron ZSC from Cyprus Industrial Minerals Company, a zinc stearate-coated ultrafine platy talc of median particle size 1.5 μm; TiO_2 is Dupont R-900; Epon 1002 is an epoxy resin from Shell Chemical Company; polycaprolactone is PCL-300 from Union Carbide, weight-average molecular weight 18,000. Other compounds were reagent-grade chemicals. Of these, stearamide, phthalimide, quinizarin, 1,5-dihydroxy-9,10-anthraquinone, 9,10-anthraquinone, sodium 2-anthraquinone sulfonate, 2-methyl-9,10-anthraquinone, 9-methyl anthracene, and anthracene were obtained from Eastmen Organic Chemicals; alizarin was obtained from Mallinckrodt, Inc.; lauroylamide was obtained from Pfaltz and Bauer; 1,8-naphthalimide, quinalizarin, and 9,10-dihydroanthracene were obtained from Aldrich Chemical; anthrone was obtained from Fisher Scientific; and 1,4-naphthoquinone was obtained from McAlister/Bicknell.

Procedure

Blends of the poly(1-butene) and additives were mixed in a Brabender mixing head at 175°C and 60 rpm for 5 min under nitrogen atmosphere to minimize oxidative degradation. Isothermal crystallization half-times and crystallization temperatures were measured by a Perkin-Elmer DSC-2 differential scanning calorimeter using the procedure outlined in Ref. 4.

Each $t_{1/2}$ and T_c value reported here and in Refs. 6–8 is the average of at least two measurements. The precision of the $t_{1/2}$ measurements is 10%; the precision of the T_c measurements is 1°C.

RESULTS AND DISCUSSION

Measurements of spherulitic growth rates and nucleation densities for the base polymer are given in Ref. 4. The model developed in that work requires use of the glass transition temperature T_g and the equilibrium melting temperature T_m; determination of the parameters G_0, C_1, C_2, and C_3 obtained from the measurement of the spherulitic growth rate as a function of temperature,

$$G(T) = G_0 \exp\left(\frac{-C_1 C_2}{(C_2 + T - T_g)}\right) \exp\left[\frac{-C_3}{T(T_m - T)}\right]$$

where G_0, C_1, C_2, and C_3 are defined[4] in terms of the parameters of the model of crystal growth by Hoffmann et al.,[9,10] which describes the spherulitic growth rate as a function of temperature; and the parameters M_0, T, and γ obtained from the measurement of the nucleation density as a function of temperature

$$M(T) = \gamma M_0 \int_\tau^\infty dx \, \exp[-\pi\gamma^2 (x - \mathbf{T})^2]$$

were M_0 is the density of nucleating sites that are active at any temperature, T is the mean tempeature at which sites nucleate, and is a measure of the breadth of nucleating temperatures over which there is an increase in nucleating sites with a decrease in temperature.[4] These parameters for the neat poly(1-butene) are given in Table I. The measured isothermal crystallization half-times and crystallization temperatures for the polymer-additive blends are given in Refs. 6–8 and Table II.

In analyzing the effect of nucleating agents on the crystallization kinetics, it will be assumed that the model of instantaneous heterogeneous nucleation followed by spherulitic growth that was developed in Ref. 4 is an adequate description of the crystallization process. It will be assumed that the additive has no effect on the growth rate of the spherulites; that is, the parameters G_0, C_1, C_2, and C_3 are unaffected by the additive. It will be further assumed that the effect of the additive is to change the density of potential nucleating sites M_0 but that the parameters T and γ characterizing the functional dependence of the nucleation density M on temperature will be unchanged. These are reasonable assumptions when the additive increases the crystallization rate, as a nucleating agent would do. For the case when the additive decreases the crystallization rate it is doubtful that it is doing so by reducing the nucleation density, so in this case the assumptions are doubtful.

Using the parameters tabulated in Table I, we have calculated numerically the dependence of the crystallization temperature (at a cooling rate $s = 10°C/min$) as a function of the nucleation density M_0. This is shown in Fig. 1. We have further calculated the dependence of the cooling rate at which $X_\infty = 0.95$ on M_0, which is shown in Fig. 2. The cooling rate at which $X_\infty = 0.95$ is a measure of the cooling rate at which crystallization becomes rate-limiting. In other words, if the polymer is cooled at about this rate or any faster, then it will not be able to crystallize completely. The effect of adding a nucleating agent on this practical measure of crystallization rate is then given by the relationship shown in Fig. 2.

These two calculations can be combined by eliminating the common variable M_0, which gives us the dependence of $s_{X_\infty=0.95}$ on T_c. This is shown in Fig. 3. Thus, the practical measure of the rate at which crystallization becomes rate limiting, which is difficult to measure directly, can be related to a measurement that can easily be obtained experimentally. This can give

TABLE I
Crystallization Kinetics Parameters for Neat Poly (1-Butene)[a]

T_g	249 K
T'_m	403 K
G_0	6.90×10^2 cm/min
C_1	25
C_2	30
C_3	1.136×10^5 K^2
M_0	6.36×10^5 cm^{-3}
T	357 K
α	0.0586 K^{-1}

[a] Parameters are defined in the text and are from the measurements given in Ref. 4 and literature sources cited there.

TABLE II
Effect of Additives on the Crystallization Rate of Poly(1-Butene)[a]

Additive	T_c (°C)	$t_{1/2}$ (90°C) (min)	$t_{1/2}$ (95°C) (min)
None[b]	65.2	7.6	26.2
None[c]	68.7	8.7	23.7
0.2% Polywax 2000	87.5		1.04
0.5% Polywax 2000	88.0		0.75
1.0% Polywax 2000	88.5		0.83
0.2% Polywax 850	82.0	1.85	9.59
0.5% Polywax 850	84.8	0.31	2.75
1.0% Polywax 850	85.0	0.54	1.58
0.5% HDPE	87.2		1.23
0.5% 1,8-Naphthalimide	82.5	0.60	1.84
0.5% Phthalimide	78.5	1.42	
0.5% Nylon 11	69.0	5.19	
0.5% Alizarin	87.0	0.35	1.43
1.0% Alizarin	88.0	0.11	1.13
2.0% Alizarin	84.3	0.69	2.17
0.5% Quinizarin	72.8	7.46	
0.1% 1,5-Dihydroxy-9,10-anthraquinone	77.5	2.46	
0.3% 1,5-Dihydroxy-9,10-anthraquinone	79.0	1.88	
0.5% 1,5-Dihydroxy-9,10-anthraquinone	89.0		0.77
0.5% Quinalizarin	79.0	1.53	
0.5% 2-Anthraquinone sodium sulfonate	81.2	1.10	
0.5% 2-Methyl-9,10-anthraquinone	66.3	8.66	
0.5% Anthrone	71.0	13.0	
0.5% 9-Methyl anthracene	70.5	17.7	
0.5% Anthracene	70.5	13.5	
0.% 9,10-Dihydro-anthracene	68.8	11.2	
0.5% 1,4-Naphthoquinone	66.0	8.21	
0.5% 1,1-Dinapthyl	69.5	6.48	
0.5% Calcium stearate	70.3	4.83	
0.5% Hydroquinone	75.5	1.84	
0.1% Talc-A	67.2	7.00	
0.5% Talc-A	71.2	3.45	
1.0% Talc-A	74.3	3.15	
1.2% Talc-B	73.3	5.1	
1.7% TiO	77.5	2.3	
0.1% Epo$_n^2$ 1002	74.2	5.8	
0.5% Anthranilic acid	74.5	3.69	
0.5% Polycaprolactone	72.2	7.56	

[a] Crystallization temperature (at a cooling rate of 10°C/min) and isothermal crystallization half-time (at 90 and 95°C) for neat poly(1-butene) homopolymer and poly(1-butene) blended with various additives.
[b] From Ref. 4
[c] Average of four measurements.

an indication of the level of nucleating agent necessary to achieve a desired degree of crystallization rate enhancement.

Similarly, we can calculate $t_{1/2}$ as a function of M_0 and, combining this with the dependence of T_c on M_0, obtain a plot of T_c as a function of $t_{1/2}$. This is shown in Figs. 4 and 5 for the two temperatures at which $t_{1/2}$ measurements were made. The experimental measurements reported in Refs. 6–8 and Table II are plotted in these figures. The agreement between
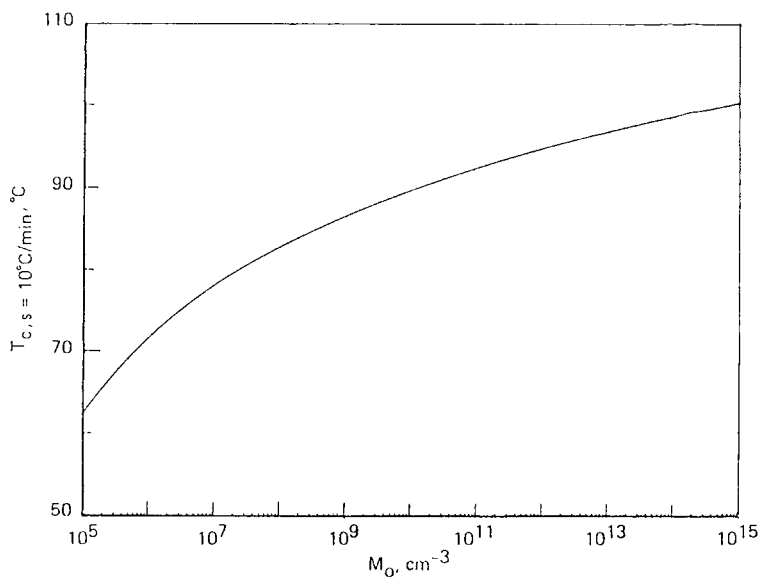
Fig. 1. Crystallization temperature as a function of the density of potential nuclei for poly-(1-butene) cooled at a rate of 10°C/min. The curve was calculated numerically using the expressions given in Ref. 4 and the parameters tabulated in Table I but by varying the density of potential nuclei M_0.
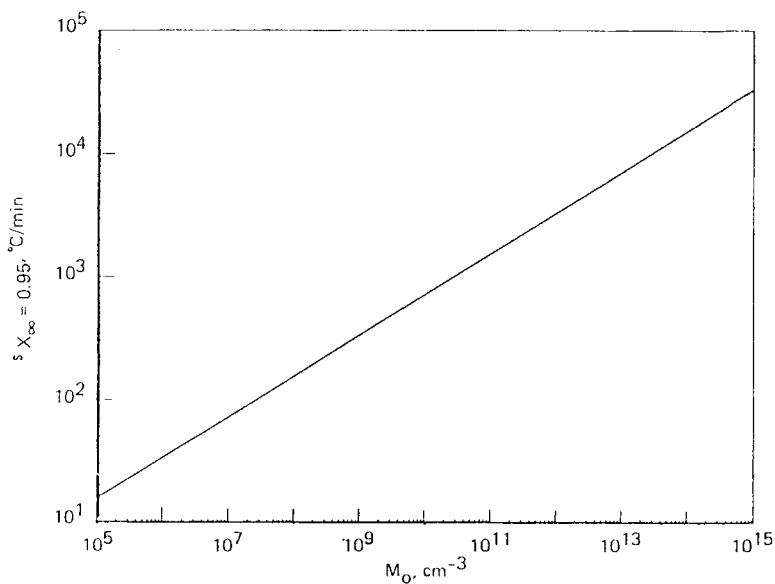

Fig. 2. Cooling rate at which the ultimate fraction transformed equals 0.95 as a function of the density of potential nuclei in cooling at a constant rate for poly(1-butene). The curve was calculated numerically using the expressions given in Ref. 4 and the parameters tabulated in Table I but by varying the density of potential nuclei M_0.
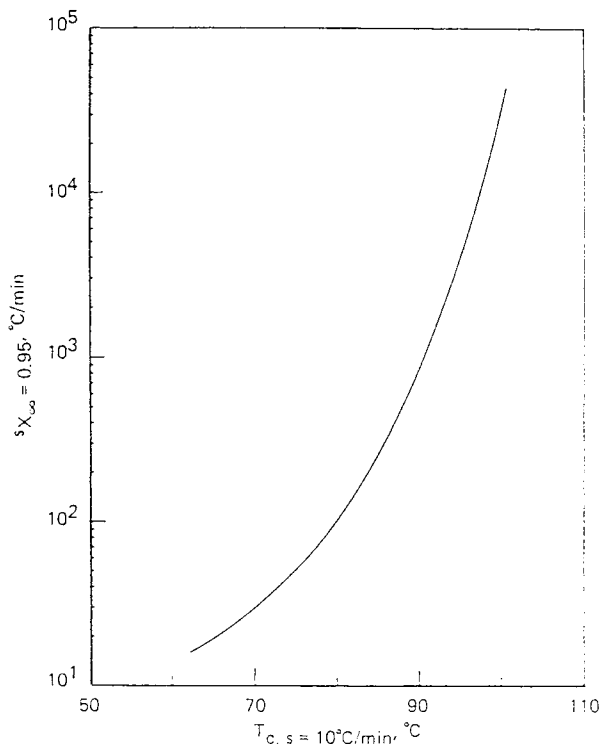
Fig. 3. Cooling rate at which the ultimate fraction transformed equals 0.95 as a function of the crystallization temperature at a cooling rate of $s = 10°C/min$ for a cooling at a constant rate for poly(1-butene). The curve was calculated from the curves shown in Figs. 1 and 2 by elimination of the common variable m_0.

the experimental data and the theoretical prediction depends on the validity of the assumptions underlying the analysis. The agreement between experiment and theory shown in Figs. 4 and 5 is reasonably good, with the theory slightly overestimating the crystallization temperature at a given $t_{1/2}$. The degree to which the crystallization temperature is overestimated is comparable to that found previously.[4] The functional relationship between T_c and $t_{1/2}$ seems to be best for blends with low $t_{1/2}$ and high T_c. This is reasonable, since in this case the additive is probably acting primarily as a nucleating agent. If there is a great deviation between theory and experiment, then the interaction between additive and polymer is probably more complex than just a change in the nucleation density. This obviously must be the case when the $t_{1/2}$ is increased or the t_c decreased from that of the neat polymer, since this indicates that the crystallization rate is reduced. For anthrone, 9-methyl-anthracene, anthracene, and 9,10-dihydroanthracene there is a small effect on T_c but a pronounced retarding of $t_{1/2}$, which indicates that these additives have a complex interaction with the polymer.

In practical applications of making poly(1-butene) pipe, we find that we are unable to cool poly(1-butene) that does not contain good nucleating additives much faster than about 25°C/min without the material remaining
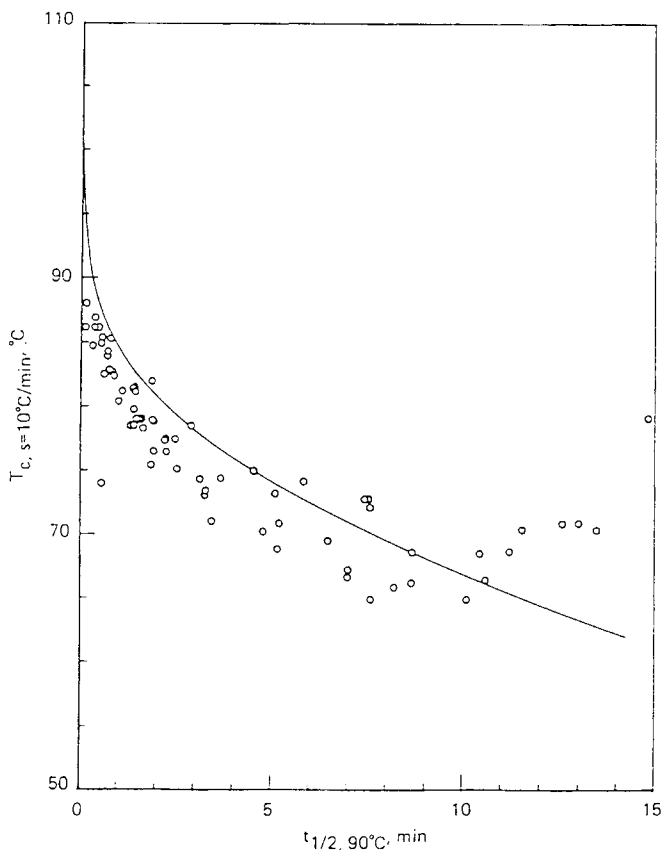
Fig. 4. Crystallization temperature at a cooling rate of $s = 10°C/min$ as a function of the isothermal crystallization temperature at 90°C for poly(1-butene). The curve was calculated numerically using the expressions given in Ref. 4 and the parameters tabulated in Table I by first calculating $t_{1/2}$ and T_c as a function of M_0 and then eliminating the common variable M_0. Experimental points are for blends of poly(1-butene) with various additives, as given in Refs. 6–8 and Table II.

tacky, indicating lack of complete crystallization. Since the neat polymer has a crystallization temperature of about 65°C, from Fig. 3 we see that the rate at which crystallization becomes rate limiting is about 25°C/min. This suggests that the reason for the tacky material is that the polymer cannot crystallize at such a fast rate. By adding nucleating agents, we can enhance the crystallization temperature to almost 90°C. From Fig. 3, such a nucleated polymer should have a crystallization rate-limiting cooling rate of about 800°C/min. However, in practical applications even this highly nucleated blend cannot be cooled much faster than about 60°C/min without evidence of tackiness and, thus, lack of crystallization. Since the material can clearly crystallize at this rate of cooling, it is evident that the source of the problem is other than a slow inherent rate of crystallization. In this case, it has been determined that the problem is the slow rate of heat transfer, which limits the ability of the nucleated blend to cool faster than this rate.
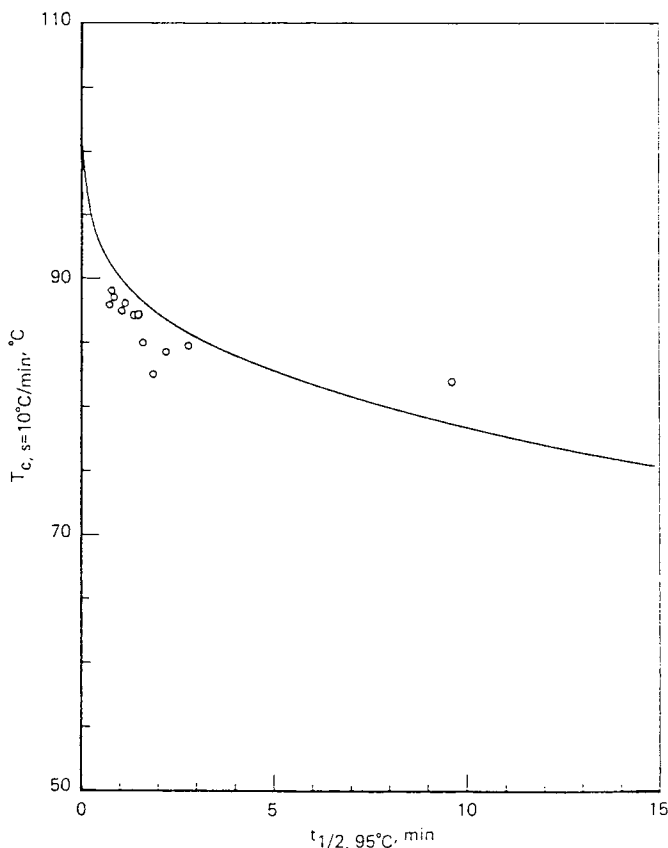
Fig. 5.   Crystallization temperature at a cooling rate of $s = 10°C/min$ as a function of the isothermal crystallization temperature at 95°C for poly(1-butene). The curve was calculated numerically using the expressions given in Ref. 4 and the parameters tabulated in Table I by first calculating $t_{1/2}$ and T_c as a function of M_0 and then eliminating the common variable M_0. Experimental points are for blends of poly(1-butene) with various additives as given in Refs. 6–8 and Table II.

SUMMARY AND CONCLUSION

A theoretical analysis has been made of the crystallization kinetics of neat poly(1-butene) and blends of poly(1-butene) with additives that is most cases act as nucleating agents. This analysis yields a practical measure of the effect of these additives on the processability of the polymer and also a relationship between the isothermal crystallization half-time and crystallization temperature. Experimental measurements are in reasonable agreement with this theory. This analysis is useful in analyzing the effect of additives on the crystallization of a polymer and optimizing the concentration of nucleating agent needed for a polymer.

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