

Nonisothermal Crystallization of Reprocessed Poly(ethylene Terephthalate)

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ABSTRACT: Poly(ethylene terephthalate) was submitted to five reprocessing cycles by extrusion. The materials were analyzed with oligomer and after oligomer extraction. The nonisothermal crystallization of the five samples was investigated by differential scanning calorimetry. Samples with oligomer content and carboxylic end group concentrations between 44 and 98 eqw $\times 10^6$ g presented a nonlinear correlation with the crystallization temperature. After the oligomer extraction of the polymer, this correlation is linear. The nonisothermal crystallization results were analyzed using the Ozawa model. The polymers containing oligomers obey the Ozawa model for the first reprocessing cycle. After

oligomer extraction, the polymers obey the Ozawa model from the first to the third reprocessing cycle. In both cases, the exponential n values are close to 2.0. For the other cycles, deviations from this model occur. The activation energy was calculated using the Kissinger and Varma models. The values obtained for the five reprocessed samples were inversely proportional to the molar mass when analyzed by both models. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 525–531, 2004

Key words: crystallization; polyesters; recycling

INTRODUCTION

The end properties of consumer goods produced with semicrystalline polymers are strongly influenced by the degree of crystallinity. The study of the crystallization kinetics thus has a considerable practical importance. Polymer crystallinity has a significant effect on properties such as toughness, elasticity, transparency, and permeability. Poly(ethylene terephthalate) (PET) shows a low crystallization rate and low crystallinity degree compared to other polymeric materials such as polypropylene (PP) and polyethylene (PE). The maximum radial growth of PET crystals is 10 $\mu\text{m min}^{-1}$, which is very low when compared with the rate of PE, 5000 $\mu\text{m min}^{-1}$.^{1,2} This low crystallization and nucleation rate is advantageous for the manufacture of transparent materials.³ The crystallization kinetics of PET depend on many factors, such as temperature, molar mass, amount and type of catalyst residue, terminal groups, and additives.⁴

Inorganic salts or organic substances that act as nucleating agents are added in small concentrations (<1% in mass) to produce polymers with a high crystallinity degree and excellent spherulitic morphology. This improves the mechanical properties and in-

creases the crystallization rate, consequently resulting in an increase of the density of nuclei and a decrease of the injection cycle time, with evident economical advantages.¹

Crystallization in a polymer processing operation occurs under nonisothermal conditions and, frequently, in the presence of molecular orientation. A study of the crystallization kinetics can be used to elucidate the nucleation mechanism and the growth of the polymeric crystals.⁵ Several models are used to explain the crystallization kinetics of polymers. One of these used for nonisothermal crystallization was proposed by Ozawa,⁶ who considers that the Avrami^{3,7,8} and Evans⁹ models have the same mechanism for isothermal processes, described by the Avrami equation, eq. (1).

$$1 - \alpha_{\text{rel}} = \exp[-K(T)^n] \quad (1)$$

In isothermal crystallization kinetic analysis, there is a dependence between crystallization time and the fraction in volume of the crystallized material. In this equation, α_{rel} is the relative crystallinity degree, n is the Avrami exponent related to the mechanism of nucleation and crystal dimension, and K is related to the crystallization rate constant as a function of the isothermal crystallization $k(T)$ where $K = k(T)^{1/n}$.

The crystalline fraction is defined as a function of the crystallization time, as shown in eq. (2), where dH_c/dt is the rate of heat evolution and t_0 and t_∞ represent the initial and final time of crystallization. Isothermal measurement is possible only when the

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thermal response time of the measured system is small compared to the rate of the process.¹⁰

$$\alpha(T) = \frac{\int_{t_0}^t (dH_c/dt) dt}{\int_{t_0}^{t_\infty} (dH_c/dt) dt} \quad (2)$$

Ozawa modified the Avrami model for nonisothermal crystallization, and a method for the kinetic analysis of the thermoanalytical data of the process is derived from this theory.¹⁰ This model supposes a constant cooling rate and extended the mathematical derivation proposed by Evans.⁹ Eq. (2) is rewritten as eq. (3), where T is the crystallization temperature and T_0 and T_∞ represent the initial and final crystallization temperatures.

$$\alpha(T) = \frac{\int_{T_0}^T (dH_c/dT) dT}{\int_{T_0}^{T_\infty} (dH_c/dT) dT} \quad (3)$$

During the nonisothermal crystallization process, a temperature change with time occurs, leading to the dependence of the crystallization rate on time. The Ozawa model, considering a constant rate of temperature change, is given by eq. (4), where $C = dT/dt$.

$$t = \frac{|T_0 - T|}{C} \quad (4)$$

Thus eq. (1) is rewritten as eq. (5),

$$1 - \alpha_{\text{rel}}(T) = \exp\left(-\frac{\kappa(T)}{C^n}\right) \quad (5)$$

where $\kappa(T)$ is the so-called cooling function of nonisothermal crystallization at temperature T , and the Avrami exponent, n , can be calculated from the plot of $\ln[-\ln(1 - \alpha_{\text{rel}}(T))]$ as a function of $\ln C^{-1}$, eq. (6). A straight line is obtained, and n and $\kappa(T)$ are determined from the slope and intercept, respectively. κ is related to the overall crystallization rate and indicates how fast the crystallization process is.¹¹ The exponent n is usually found between 1 and 4, depending on the type of nucleation and the growth dimension.¹²

$$\ln[-\ln(1 - \alpha_{\text{rel}}(T))] = \ln \kappa(T) - n \ln C \quad (6)$$

Polymer crystallization is composed of two phenomena. The first is related to the nucleation of the crystalline phase, called the primary crystallization re-

gime, followed by growth of semicrystalline entities originating from the nuclei, called the secondary regime. The secondary crystallization is caused by the collision of the spherulites at the end of the crystallization and is usually related to the perfection of the crystal. In deriving eq. (5), Ozawa ignored secondary crystallization and the dependence of the fold length on the temperature. In nonisothermal crystallization, the crystallization rate depends on the cooling rate. Consequently, the crystallization rate constant, K , can be appropriately correlated.¹³

As a generalization of the Avrami equation (eq. (1)) for nonisothermal situations, the equation of Nakamura et al.^{14,15} is given by the following:

$$1 - \alpha_{\text{rel}} = \exp\left\{-\left[\int_0^t K(T) dt\right]^n\right\} \quad (7)$$

In nonisothermal conditions, eq. (7) can be reformulated as a function of T and reduces to the Ozawa equation, eq. (5), with integration between temperatures T_0 and T_t .

$$\left[\int_{T_0}^{T_t} K(T) dT\right]^n = \kappa(T) \quad (8)$$

Using the equation from Nakamura et al., it is possible to find the relation between the Avrami and Ozawa parameters; thus eq. (8) can be rewritten as eq. (9).

$$\int_{T_0}^{T_t} K(T) dT = \kappa(T)^{1/n} \quad (9)$$

Integration of eq. (9) with respect to the temperature allows the determination of the crystallization rate K . From the known value of the Ozawa cooling function, κ is found for nonisothermal crystallization.

$$K = -d[(\kappa(T)^{1/n})/dT] \quad (10)$$

The Ozawa model has some limitations; for example, the secondary crystallization process is not taken into account, the exponent n is considered constant, and, finally, effects such as transcrystallization, in which crystals grow preferentially normal to the surface, are not considered.^{16,17}

Activation energy

The activation energy can be calculated using the methods of Kissinger¹⁸ and Varma.¹⁹ In the Kissinger method, the activation energy for the transport of the macromolecular segments to the growing surface (ΔE) was graphically calculated through eq. (11) where T_c is

the crystallization temperature, C is the cooling rate, and R is the gas constant. ΔE can then be obtained from the slope of the plot of $\ln(C/T_c^2)$ versus $(1/T_c)$.

$$\frac{d(\ln C/T_c^2)}{d(1/T_c)} = \frac{\Delta E}{R} \quad (11)$$

Varma et al.¹⁹ use eq. (12), relating the rate of conversion to the crystalline structure, where K is the rate constant, α is the degree of conversion, t is time, and n is the crystallization order.

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n \quad (12)$$

The crystallization rate is represented by eq. (13), where K_0 is a pre-exponential constant, ΔE is the activation energy of crystallization, T is temperature, and R is the universal gas constant.

$$K = K_0 e^{(-\Delta E/RT)} \quad (13)$$

Eq. (14) is obtained by substituting eq. (13) into eq. (12).

$$\frac{d\alpha}{dt} = K_0 e^{(-\Delta E/RT)} (1 - \alpha)^n \quad (14)$$

Under nonisothermal conditions, eq. (14) can be rearranged and, in this analysis, the authors¹⁹ have assumed Arrhenius behavior and first-order reaction kinetics; thus, n is 1. Assuming that the time change is proportional to the temperature change in differential scanning calorimetric DSC, $\beta = dT/dt$, giving eq. (15).

$$\frac{d\alpha}{dt} = \frac{K_0}{\beta} e^{(-\Delta E/RT)} (1 - \alpha) \quad (15)$$

Linearizing eq. (15) we have

$$\ln \left[\frac{d\alpha/dt}{1 - \alpha} \right] = \ln \left(\frac{K_0}{\beta} \right) - \left(\frac{\Delta E}{R} \right) \frac{1}{T} \quad (16)$$

The ΔE for the initial step of the crystallization can be obtained from the plot of $\ln[(d\alpha/dt)/(1-\alpha)]$ versus $1/T$, which yields a straight line with slope $(-\Delta E/R)$ and an intercept equal to $\ln(K_0/\beta)$.

In this work, we have analyzed the effects of carboxylic end group concentrations and molar masses of reprocessed PET on the crystallization temperature. Ozawa's model was used to observe the changes in the values of exponent n as a function of the degradation degree of the material reprocessed by extrusion. The activation energy related to the crystallization process for each reprocessing cycle was calculated using the Kissinger and Varma models. These results are used for evaluation of the reprocessing of PET.

EXPERIMENTAL

Materials

Pellets of virgin PET (RHOPET® S80, $[\nu] = 0.80 \text{ dL/g}^{-1}$) were supplied by Rhodia-Ster S.A. (Poços de Caldas, Brazil). All samples were dried at 160 °C for 6 h prior to processing. PET pellets were processed by extrusion for five cycles using a Wortex single-screw laboratory extruder (screw diameter 32 mm, screw length/diameter ratio (L/D) = 30) with double fillet Davis Standard Barrier type screw.²⁰ The thermal profile used was 220, 260, 275, 280, and 280 °C from feeding to the die, and the screw rotational speed was 102 rpm. The reprocessed PET samples were finely ground (1 mm). The oligomers were extracted from the samples of the first, third, and fifth processing cycles using chloroform (p.a., Merck) in a Soxhlet apparatus for 24 h. After that, all samples, with and without oligomers, were dried in a vacuum oven at 160 °C and $1.0 \times 10^4 \text{ Pa}$ for 4 h (Tecnal model EDG-CON 5P) prior to measurements of $[\nu]$, carboxylic end group (CEG) concentrations, and DSC.

Methods

The intrinsic viscosities $[\nu]$ were measured in a Ubbelohde viscometer at 30 °C using a 60/40 (m/m) phenol / 1,1,2,2-tetrachloroethane solvent mixture, according to American Society for Testing and Materials (ASTM) standard D 4603. The molar mass was calculated from $[\nu]$ data according to the Berkowitz relation,²¹ eq. (17).

$$M_w = 6.58 \times 10^{-4} [\eta]^{1.54} \quad (17)$$

The CEG concentrations were determined by titration in alcoholic solution at 109 °C according to the optimized Pohl method.^{22,23}

The DSC measurements (TA Instruments 2910; Texas Instruments, Dallas, TX) were carried out under an argon flow (50 mL/min^{-1}). The instrument was calibrated with indium during heating at the rate of 10 °C min^{-1} . PET samples (about 10 mg) were quickly heated up to 300 °C, kept at this temperature for 5 min, and cooled with constant cooling rates of 6, 8, 10, 12, 14, or $16 \text{ °C}^{-1} \text{ min}$ to 30 °C. The temperatures were corrected for thermal lag between the samples and the calorimeter furnace according to the relation used by Mubarak et al.²⁴

RESULTS AND DISCUSSION

The values of intrinsic viscosity, molar mass, and CEG concentrations for samples with oligomers as a function of processing cycle are shown in Table I.²² The molar mass values decrease 19, 27, 33, 44, and 53 %, and CEG values increase 20, 70, 105, 125, and 168 % with each processing cycle, respectively (Table I). The

TABLE I
Values of Intrinsic Viscosity $[\eta]$, Molar Mass (M_w) and CEG for Reprocessed PET Samples

Processing cycle	$[\eta]/\text{dL g}^{-1}$	$M_w/\text{g mol}^{-1} \times 10^3$	CEG/eqw $\times 10^6$ g	Oligomer (% m/m)
0	0.7800 (± 0.0021)	45	36.5 (± 2.4)	0.07
1	0.6910 (± 0.0019)	37	44.0 (± 4.1)	0.20
2	0.6443 (± 0.0044)	33	62.0 (± 7.8)	0.38
3	0.6051 (± 0.0011)	30	75.0 (± 1.4)	0.45
4	0.5289 (± 0.0047)	25	82.0 (± 0.7)	0.47
5	0.4780 (± 0.0006)	21	98.0 (± 0.5)	0.61

oligomer content also increases approximately 10 times from the first to the fifth cycle.²² This behavior is probably caused by thermomechanical chain scission leading to hydrolysis of the ester bonds that occurred during the extrusion, drying, and milling of the material.²⁵

The variation of crystallization temperature (T_c) with the molar mass and CEG are shown in Figure 1 for cooling rates from 6 to 16 °C min⁻¹. The increase of the molar mass [Figure 1(a)] causes a significant decrease in the crystallization temperature for molar masses larger than 32×10^3 g/mol⁻¹. Similar behavior was observed by other authors using different techniques and with isothermal or nonisothermal experiments.¹⁶ The opposite tendency was found for the T_c variations as a function of CEG, although there is a decrease of T_c at increasing heating rates. This drastic increase of the CEG indicates an increase of the polydispersity; consequently, an increase of the oligomer content occurs as a function of the degradation degree.

The increase of the CEG as a function of the number of reprocessing cycles from 44 to 98 eqw $\times 10^6$ g [Figure 1(b)] causes a sharp increase of T_c , indicating a molar mass reduction and, consequently, an increase

in the mobility of the chains. T_c is apparently constant above a limiting CEG value. Pilati et al.¹⁶ synthesized PET with a larger range of molar mass ($[\nu]$ from 0.252 to 0.962 dL/g⁻¹) and a narrower CEG range (from 12 to 40 eqw $\times 10^6$ g) and studied the effects of $[\nu]$ and CEG on T_c by a multiple linear regression. The observed effects were interpreted assuming that the interaction of the CEG on PET chains (mutual or with residual catalyst) led to an apparent increase of molar mass in the molten state, which produced a decrease in chain mobility and was responsible for the decrease in the rate of crystallization. Our material was processed five times at high temperature and, consequently, had a greater CEG range (44 to 98 eqw $\times 10^6$ g) and oligomer content. The oligomer content was determined and separated from the molar mass and CEG effects by using the multiple linear regression method, resulting in eq. (18), which describes the dependence of T_c with $[\nu]$ and CEG.

$$T_c = 186.7 + 0.074(\text{CEG}) - 0.02[\eta] \quad (18)$$

According to eq. (18), the effect of CEG and $[\nu]$ on T_c is low in comparison to the values proposed by Pilati

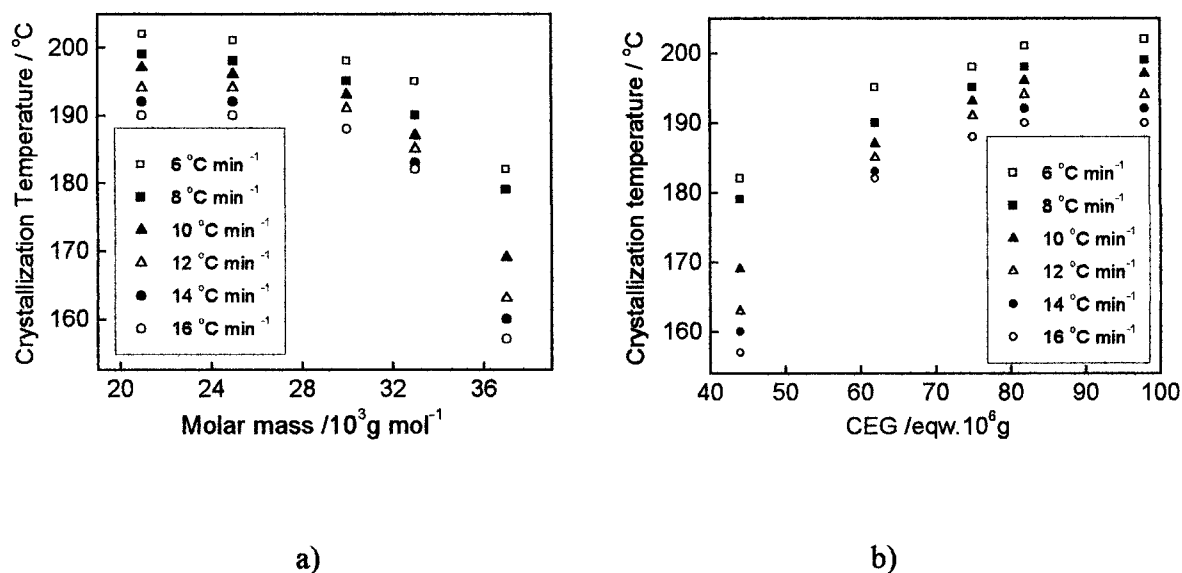


Figure 1 Crystallization temperature (T_c) as a function of (a) molar mass, and (b) CEG for the five processing cycles.

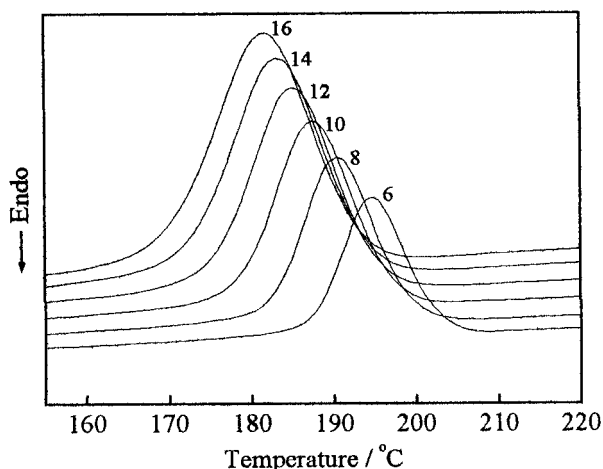


Figure 2 DSC crystallization exotherms for PET reprocessed five times (cooling rates from 6 to 16 °C min⁻¹).

et al.,¹⁶ who observed a higher influence of CEG and $[\nu]$ for values of CEG below $40 \text{ eqw} \times 10^6 \text{ g}$ and $[\nu]$ between 0.25 and 0.962 dL/g. However, our samples were obtained by reprocessing in order to estimate the life cycle of the plastic goods. These results are very important for the recycling industry, which works with reprocessed material containing oligomers, whose concentration increases as a function of degradation degree (i.e., reprocessing cycles).

Nonisothermal crystallization

The crystallization exotherms of processed PET at various cooling rates are presented in Figure 2. The baseline is the continuation of the straight lines observed on the DSC thermograms before and after completion of crystallization heat evolution. The increase of cooling rate causes a shift of the crystallization exothermic peak to lower temperatures. The crystallization is controlled by nucleation and growth; consequently, at low cooling rates there is enough time for the nuclei to be activated.

Values of relative crystallinity calculated from the cooling exotherms as a function of temperature are shown in Figure 3. The curves have practically the same sigmoid dependence, which would indicate that only the retardation effect of the cooling rate on crystallization is observed for these curves.²⁷

For the polymer containing oligomers, in the first reprocessing cycle the crystallization rate is slower, because the crystallization occurs at a lower temperature compared with other cycles, indicating more difficulty for chain crystallization with greater molar mass. The values of the exponential n values for all cycles are shown in Figure 4.

For the range of temperature between 150 and 178 °C, the material of the first processing cycle presented practically constant exponential n values close to 2.0,

indicating disklike morphology formed by heterogeneous nucleation. Similar values were obtained by other authors.^{23–27} The materials from other cycles presented deviation from the model, because the exponential n values change from 2.0 to 3.5 and occur in a narrow range of temperature. Fractional n values are generally attributed to the simplification assumptions made in the model, such as constant radial growth rate, constant density and shape of the growing nuclei, uniqueness of the nucleation, no secondary crystallization process, and no volume change during phase transformation/crystallization. Consequently fractional n values cannot be explained on any physical basis.²⁸

The Ozawa model considers only primary crystallization, that is, the main part of the whole process. Secondary crystallization becomes dominant in the final stage of crystallization where a crystal interference in interspherulitic regions occurs and the crystallization is more difficult. In our material, secondary crystallization has not been detected, probably because it would be associated with a very small heat effect. Secondary crystallization affects principally the more degraded material. The temperature where the maximum crystallization rate occurs was determined for each processing cycle using eq. (10). For the first cycle, this temperature is 165 °C and this value increases to 185, 189, 190, and 193 °C, respectively, from the second to the fifth reprocessing cycle.

After oligomer extraction, the polymer showed crystallization behavior according to the Ozawa model until the third processing cycle, and the exponential n values were close to 2.0. For the other cycles, a deviation from this model occurs and the n values change from 2.0 to 3.5. These results indicate that the nucleation and growth mechanisms of PET spherulites are very dependent on the processing cycle or, more specifically, on the oligomer content.

The degree of crystallinity was determined considering a baseline for crystallization on heating in the second heating rate to eliminate the thermal history.²⁹ The degree of crystallinity (α_c^∞) for PET samples was calculated using eq. (19), where ΔH_m^0 is the melting heat of a pure crystal (100 J/g)³⁰ and Δh is the difference between melting and crystallization enthalpies.

$$\alpha_c^\infty(\%) = 100(\Delta h / \Delta H_m^0) \quad (19)$$

The values of $\alpha_c^\infty(\%)$ obtained for processed PET were 27, 35, 38, 38, and 38 % from the first to fifth processing cycles.

Activation energy (ΔE) of the crystallization process

Using the Kissinger model, we observed that, for the five processing cycles, the curves of $\ln(C/T_c^2)$ as a function of $10^3 T_c^{-1}/K^{-1}$ present good linearity (R^2

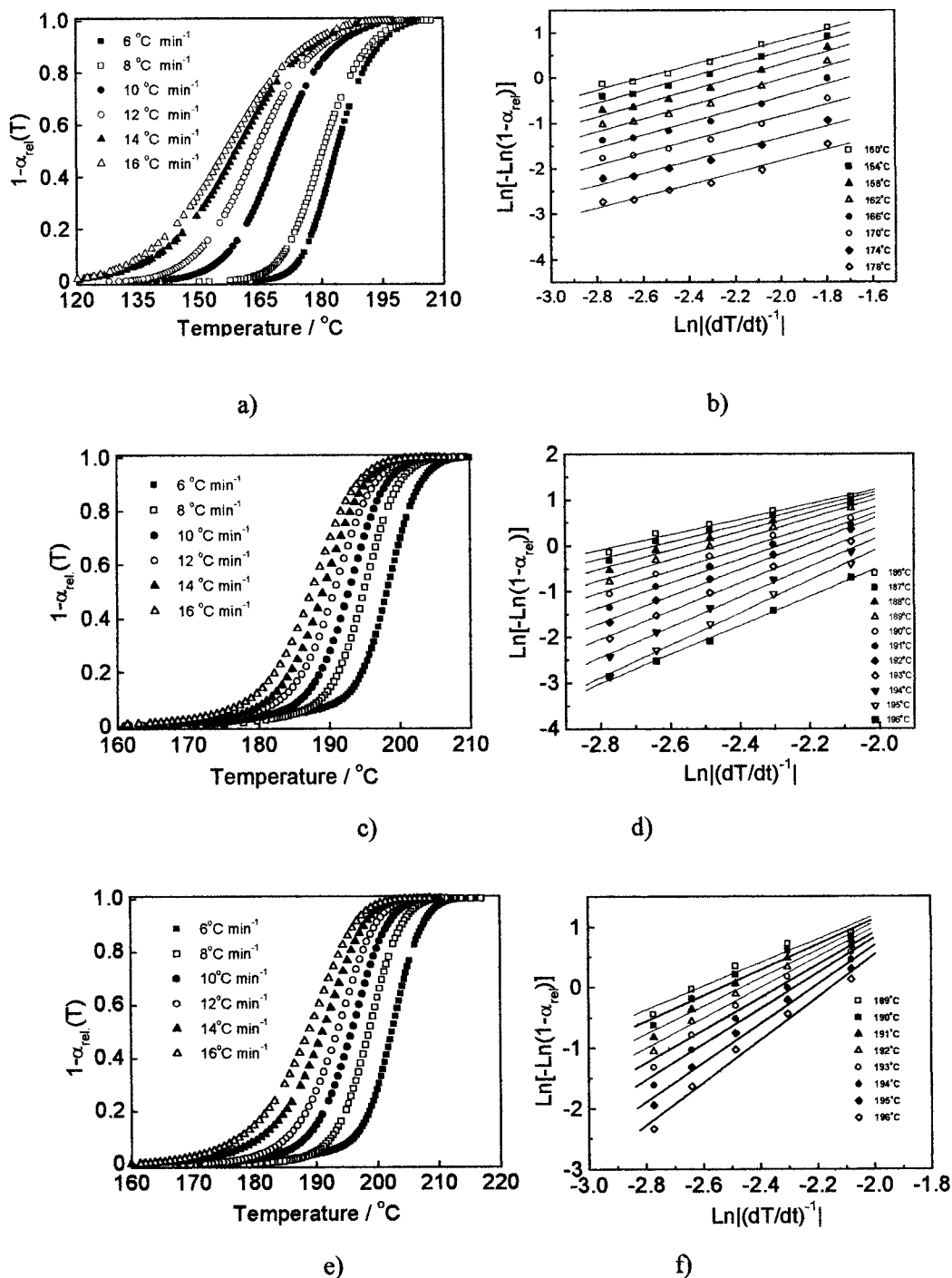


Figure 3 Ozawa plots: (a) and (b) first, (c) and (d) third, (e) and (f) fifth reprocessing cycle for the material with oligomers.

> 0.99) (Figure 5). The ΔE values obtained were -230 , -391 , -483 , -459 , and -436 kJ/mol^{-1} for the first to the fifth cycle, respectively. The value obtained for the first cycle is close to the one for virgin PET.²⁷ For the other cycles, the activation energy values are smaller, favoring the global crystallization process, which is related to self-diffusion of the molecules in the growing crystal. Thus, ΔE is dependent on the molar mass, chain rigidity, and entanglements of the polymer

chains. The mobility of the polymer chains increases for polymers with lower molar mass; consequently, self-diffusion of the molecules is favored and the energy necessary for the crystallization is smaller.

Using the Varma model, the ΔE values obtained were -171 (± 21), -181 (± 35), -275 (± 50), -285 (± 55), and -285 (± 54) kJ/mol^{-1} from the first to the fifth cycle, respectively. These values are within the range of values (155 – 268 kJ/mol^{-1}) reported in the

literature for similar materials.¹⁹ The Kissinger and Varma models showed different activation energy values. This difference is probably related to the considerations made in the Varma model to calculate the activation energies. This model uses data from the initial step of the crystallization process. On the other hand, the Kissinger model uses only the crystallization temperature peak data, and, at this temperature, secondary crystallization processes may also occur.

CONCLUSIONS

Reprocessed PET with high values of CEG, from 44 to $98 \text{ eqw} \times 10^6 \text{ g}$, presented a nonlinear correlation with the crystallization temperature, probably because of the effect of oligomer content. When the oligomer content was reduced, it was possible to observe that the effect of CEG and molar mass is very small. This result is very important for the recycling industry, which works with reprocessed materials with higher CEG values and oligomer contents.

The polymer containing oligomers obeys the Ozawa model for the first cycle. After oligomer extraction, the polymer obeys the Ozawa model from first to third cycle. In both cases the exponential n value near 2.0 indicates disklike morphology, formed by heterogeneous nucleation. For the other processing cycles, the exponential n values changed from 2.0 to 3.5, indicating deviation from the Ozawa model. This indicates that the crystal dimensions change as a function of these molar mass ranges (from 21 to $45 \times 10^3 \text{ g/mol}^{-1}$) and of the higher oligomer content.

The values of activation energy obtained for the five reprocessed PET samples were inversely proportional to the molar mass, confirming that crystallization is more difficult for the polymer processed for one cycle than for the polymer processed for five cycles. The calculated values of activation energy are influenced by the models, which use different temperature data.

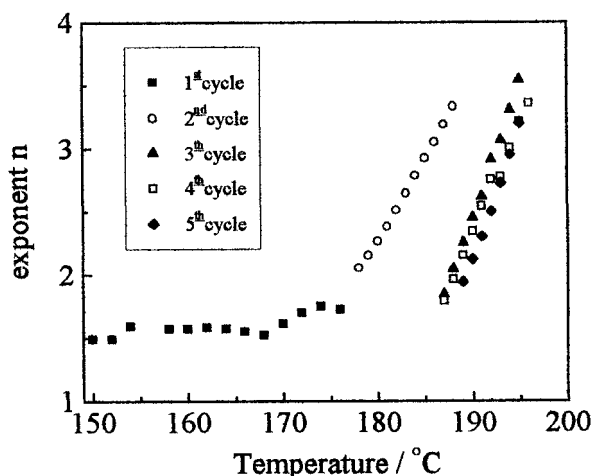


Figure 4 Exponent n for reprocessed PET with oligomers.

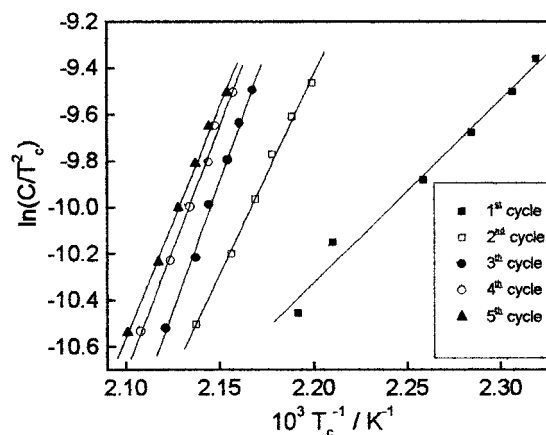


Figure 5 Kissinger plot for reprocessed PET samples.

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