



Journal Homepage: - www.journalijar.com
**INTERNATIONAL JOURNAL OF
 ADVANCED RESEARCH (IJAR)**

Article DOI: 10.21474/IJAR01/3821
 DOI URL: <http://dx.doi.org/10.21474/IJAR01/3821>



RESEARCH ARTICLE

AVRAMI MODEL DEVIATIONS IN POLYOLEFINS AS FUNCTION OF THE COMPLEXITY OF THE MOLECULAR STRUCTURES.

Hector Yznaga Blanco¹, Jose Carlos Ortiz Cisneros¹, Felipe Avalos Belmonte¹ and Roberto Zitzumbo Guzman².

1. Chemical sciences faculty, Autonomous University of Coahuila, UAC, Blvd. V. Carranza, sn, Saltillo, Coahuila, Mexico.
2. Center for Applied Innovation in Competitive Technologies, CIATEC, omega no. 201, industrial delta, León, Guanajuato, Mexico.

Manuscript Info

Manuscript History

Received: 08 February 2017
 Final Accepted: 06 March 2017
 Published: April 2017

Key words:-

Avrami analysis, crystallization, polypropylene, polyethylene

Abstract

The influence of the complexity of the molecular structure and the cooling rate in the Avrami model fitting has been studied. Kinetics of non-isothermal crystallization of polypropylenes (with different molecular weights), polyethylenes (High Density Polyethylene, HDPE and Low Density Polyethylene, LDPE) and polyethylene wax from molten state were performed under non-isothermal conditions at cooling rates of 3, 10, and 50 °C min⁻¹. Differential scanning calorimetry (DSC) was used to monitor the crystallization. The results showed that the predicted evolution of relative crystallinity using the Avrami model was a better fit for the polypropylenes and polyethylene wax than for the polyethylenes due to their molecular structure much more simple and regular. The fitting for higher cooling rates was better than for lower cooling rates for all the materials analyzed and this could be attributable to a predominant homogeneous nucleation at higher cooling rates and predominant heterogeneous nucleation at lower cooling rates. The fitting for HDPE was better than for LDPE at the final stage of crystallization for various cooling rates due to the phenomenon of a slower secondary crystallization. The results showed a better fitting of the Avrami equation for the polypropylenes and polyethylene wax than for the polyethylenes due to the influence of the branching degree in lamellar thickness and amorphous-layer thickness as the main contributor to secondary process.

Copy Right, IJAR, 2017,. All rights reserved.

Introduction:-

Conducting research on the phenomenon of crystallization in crystalline polymers is of great importance because of the physical and mechanical properties in the processes of transformation of plastics, since it depends on the crystal structures formed which are dictated by the kinetics of the crystallization, depending on aspects such as molecular symmetry (tacticity) and the molecular weight of the material^{1,2}.

Corresponding Author:- Hector Yznaga Blanco.

Address:- Chemical sciences faculty, Autonomous University of Coahuila, UAC, Blvd. V. Carranza, sn, Saltillo, Coahuila, Mexico.

Among the crystalline polymers, the polyolefins, like polypropylenes (PP) and polyethylenes (PE) are some of the most widely used commercial polymers because of their high-performance for engineering thermoplastics and the crystallization is ideal for the final properties of the parts being processed with it ³.

The effects of molecular weight ^{4,5}, molecular weight distribution ⁶ and tacticity ^{7,8} on the crystallization have been investigated by several authors for the polypropylenes. The results indicate that the growth rate of crystals markedly decreases when the molecular weight increases and the degree of crystallinity is usually in the range 40-70% depending on the level of tacticity of the polymer.

For the polyethylenes the first detailed study of the non-isothermal crystallization was conducted in the 70s by Nakamura et al. ^{9,10}. In the 80's the nonisothermal crystallization of PE as a function of molecular mass was also investigated by Minkova and Mihailov ¹¹, who studied the kinetics of crystallization of ultra-high molecular mass polyethylene (UHMWPE), high density polyethylene with usual mass (HDPE), and their blends. In the same decade, Eder and Wlochowicz ¹² crystallized HDPE at constant cooling rates ranging from 0.5 to 10 °C min⁻¹. However their experimental data did not conform to the theoretical treatment developed by Ozawa ¹³ due to factors as secondary crystallization. The modeling of the PE crystallization is however still a challenge as most of the existing models are not adapted, as shown by Shan et al ¹⁴.

Polyethylene waxes are highly crystalline materials with a large melting enthalpy ¹⁵. Wax encompasses a wide range of substances that may be of organic, natural (animal, vegetable or mineral) or synthetic origin including paraffin and polyethylene waxes that has a molecular mass between 200 and 1000 g mol⁻¹, whereas the molecular mass of the polymer is between 10,000 and 6000,000 g mol⁻¹. The difference between the polymer and the waxes is in the number of repeating units in the ethylene monomer, which directly affects the molecular mass.

Many of the papers concerning the problem of correcting of the known theoretical approaches to the overall crystallization rate were published more than 2–3 decades ago. However, growing interest in modeling of semicrystalline polymer solidification during complex processing conditions again drew attention to the subject ¹⁶.

The majority of methods for describing the crystallization kinetics are based on the Avrami equation ^{17,18} or its modified forms ^{9,10,13,19,20}. Ozawa ¹³ accounted for the effect of cooling rate on dynamic crystallization by properly modifying the Avrami equation to include the constant cooling rate. Nakamura et al. ^{9,10} proposed an isokinetic approach derived from Avrami's works in which additional assumptions about the relation between the nucleation and the growth rate are introduced. Liu et al. ¹⁹ proposed a different kinetic equation by combining Ozawa and Avrami equations. Phillips and Manson²⁰ described isothermal crystallization as a linear combination of homogeneous and heterogeneous nucleation, including the growth process, by using two modified Avrami equations.

Other models, derived from Avrami equation, have been proposed^{12,13,21-23} applying this equation to the data obtained from the non-isothermal crystallization thermograms. However, none of these models consider the effects of secondary crystallization.

It is often erroneously considered that the Avrami equation is valid only for the isothermal conditions, although such an assumption was never made by Avrami. It is equally applicable to isothermal as well as to non-isothermal crystallization. Avrami model is based on the iso-volume assumption and its limits are set after considering the domains having equal rates of growth and not considering the invasion of the spherulites ^{16,21}. A good prediction with Avrami can be obtained only for up to 30% of relative crystallinity, since it does not consider the impingement of spherulites.

The crystallization process proceeds in two steps: nucleation and crystal growth ²⁴. Nucleation is either homogeneous or heterogeneous; during homogeneous nucleation, nuclei are formed randomly throughout the molten material, whereas during heterogeneous nucleation the crystals grow from inclusions such as impurities, fillers and fibers ^{20,25}. The Avrami expression takes different forms for homogeneous and heterogeneous nucleation.

In this study, the influence of the complexity of the molecular structure and the cooling rate in the Avrami model fitting for the prediction of the crystallization kinetics of polypropylenes with different molecular weights, polyethylenes (HDPE, LDPE) and polyethylene waxes were studied and compared under non-isothermal conditions

at different cooling rates. The comparison of the Avrami model predictions, taking into account the molecular weight as well as the complexity of the molecular structure, can contribute to explaining the influence of these factors in the fitting of the Avrami model applied to the non-isothermal crystallization of the most commonly used polyolefins.

Materials and Methods:-

The materials used in this research were: polypropylenes, PP250, isotactic, weight average molecular mass $M_w \approx 250000$, number average molecular mass $M_n \approx 67000$ and PP190, weight average molecular mass $M_w \approx 10000$, number average molecular mass $M_n \approx 50000$ (Sigma Aldrich) and polyethylenes, HDPE (PEMEX) under the commercial denomination PADMEX65050, density of 0.965 g cm^{-3} , melt flow index of 2 g (10min)^{-1} ; LDPE, (PEMEX) under the commercial denomination PX20020, density of 0.920 g cm^{-3} , melt flow index of 5 g (10min)^{-1} and polyethylene waxen powder (Multiceras SA de CV), under the commercial denomination 9090. All of this materials were used as received. Two types of polypropylenes with different molecular weights were used considering that the ends of the molecular chains do not fall within the crystalline entities. Two types of polyethylenes, a high density (HDPE) and low density (LDPE) and a Polyethylene Waxen, were used as a second type of material. Both molecules have branching unlike polypropylenes. The branches in HDPE are controlled in length and LDPE has longer branches and a more disordered molecular structure.

For this study the following work plan was proposed. A Perkin Elmer DSC7 thermal analyzer was used to measure the thermal behavior of the samples during crystallization in the cooling mode from the molten state (melt-crystallization). Melt crystallization: non-isothermal crystallization was carried out first by maintaining the sample at $200 \text{ }^\circ\text{C}$ for 10 min, in order to eliminate the thermal history of the material and then cooling the DSC cell to ambient temperature at controlled cooling rates of 3, 10, and $50 \text{ }^\circ\text{C min}^{-1}$. The samples were maintained in a pure nitrogen atmosphere. The exothermal trend lines of heat flow as a function of temperature were recorded and the enthalpy of crystallization on each run was measured as a function of temperature and time. Sample size was between 7 - 8 mg.

The relative degree of crystallinity, X_t , (Eq. 1) and absolute degree of crystallinity, X_c , (Eq. 2) as a function of crystallization temperature T are defined as:

$$X_t = \int_{T_0}^T (dH_c/dT) dT / \int_{T_0}^{T_\infty} (dH_c/dT) dT \quad (\text{Eq. 1})$$

$$X_c = \int_{T_0}^T (dH_c/dT) dT / \Delta H_m^0 \quad (\text{Eq. 2})$$

where T_0 and T_∞ represent the onset and the end of crystallization temperatures, respectively. ΔH_m^0 is the heat of fusion of a perfect crystal. Most studies on the polymer crystallization rely on the Avrami equation (Eq. 3) to analyse the data, which provides the information of nucleation and the crystallization rate.

The basic isothermal expression is:

$$X_t = \frac{X_c}{X_{c\infty}} = 1 - \exp(-kt^m) \quad (\text{Eq. 3})$$

where $X_{c\infty}$ is the equilibrium crystallinity; the exponent m is a mechanism constant, the value of which depends on the type of nucleation and growth-process parameters; parameter k is a composite rate constant involving both nucleation and growth rate parameters. The half- time of crystallization, $t_{1/2}$ (Eq. 4), is calculated from:

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{\frac{1}{m}} \quad (\text{Eq. 4})$$

Using Eq. (3) in double-logarithmic form, and plotting $\log(-\ln(1-X_t))$ against $\log(t)$ for each cooling rate, a straight line is obtained, from which values of the two adjustable parameters, k and m , can be obtained. It must be taken into account that in nonisothermal crystallization, the values of k and m do not have the same physical significance as in the isothermal crystallization, due to the fact that under nonisothermal conditions the temperature changes constantly. So, m and k , are two adjustable parameters to be fit to the data [17, 27].

The data predicted by the Avrami equation with the parameters k and m , previously obtained, was placed with the experimental data on the same graph to visualize the differences in fitting between them.

Results and Discussion:-

Integration of the exothermic peaks during the non-isothermal scan gives the relative degree of crystallinity as a function of temperature. The peak temperature for maximum crystallization to occur, T_p , shifted to a low temperature region as the cooling rate increased. The values of T_p , the corresponding peak times, t_{max} , the crystallization enthalpies, ΔH_c , and relative crystallinity, X_t , of non-isothermal melt crystallization under different cooling rates are listed in Table 1.

Table 1:- Peak Temperature (T_p), Time (t), Crystallization Enthalpy (ΔH_c), Relative Crystallinity (X_t) at Maximum Rate of Heat Flow during Nonisothermal Crystallization.

| Cooling rate/ $^{\circ}\text{C min}^{-1}$ | $T_p / ^{\circ}\text{C}$ | t / min | $\Delta H_c / \text{J g}^{-1}$ | $X_t / \%$ |
|---|--------------------------|------------------|--------------------------------|------------|
| -3 | 125.8 | 1.43 | 79.95 | 56.86 |
| -10 | 119.7 | 0.68 | 80.53 | 47.95 |
| -50 | 105.4 | 0.20 | 84.28 | 54.24 |

In Figure 1 it can be observed that all the trend lines have the same sigmoidal shape on the whole implying that only the lag effects of the cooling rates during crystallization were observed for these trend lines. As was previously explained by Hoffman and Miller²⁶ this retardation effect is the result of rate-dependent induction time preceding the initiation of the crystallization stage.

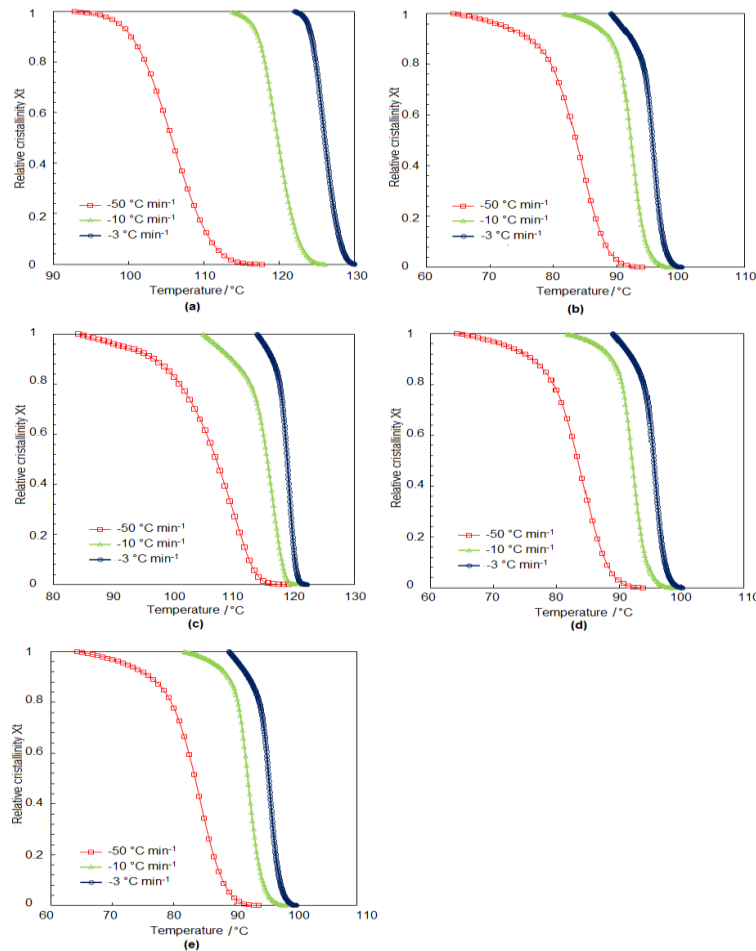


Figure 1: Relative degree of crystallinity vs. temperature during nonisothermal crystallization at 3 °C min⁻¹, 10 °C min⁻¹, 50 °C min⁻¹. Samples cooled from the melt. (a) Polypropylene PP250, (b) Polypropylene PP190, (c) Polyethylene HDPE, (d) Polyethylene LDPE, (e) Polyethylene Waxen.

The sigmoidal shape of the trend lines suggests that an analysis for non-isothermal data based on the Avrami analysis (Eq. 3) might be applicable. The Avrami exponent *m* and the rate parameter *k* could be estimated from the slope and intercept respectively, of the plot for $\log [-\ln (1-X_t)]$ vs. $\log (t)$ in the crystallization process from Figure 2. It can be observed in the plots that the linear portions of each region are parallel to each other, shifting to shorter times by increasing the cooling rates and it suggests that the nucleation mechanism and crystal growth geometries were similar at all cooling rates consistent with conclusions reported in the literature¹⁹.

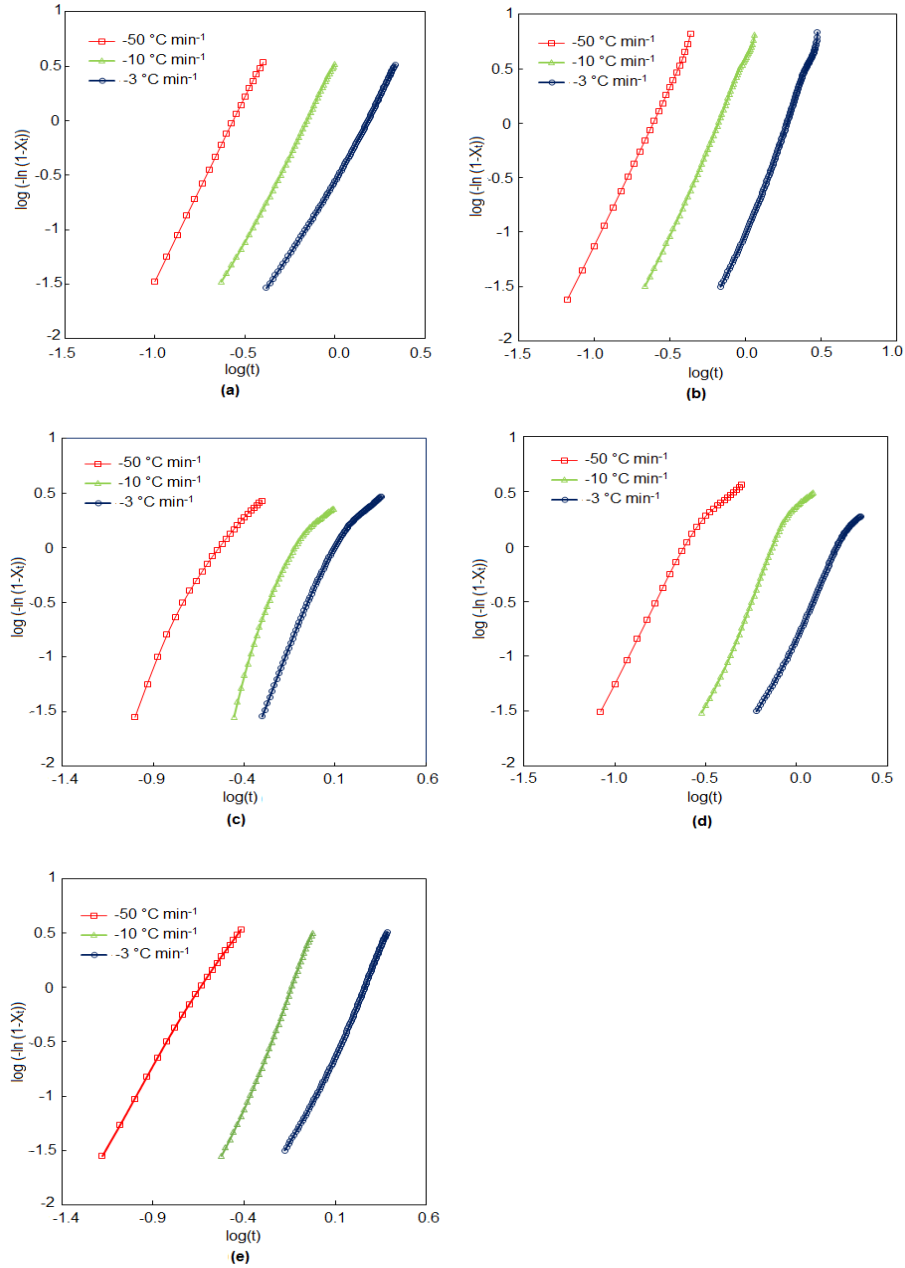


Figure 2:- Plots of $\log [-\ln (1-X_t)]$ vs. $\log (t)$ for nonisothermal melt crystallization. (a) Polypropylene PP250, (b) Polypropylene PP190, (c) Polyethylene HDPE, (d) Polyethylene LDPE, (e) Polyethylene Waxen.

Figure 3 also shows that for the polypropylenes and the polyethylene waxen, no deviation was observed in the trend lines implying that for these materials the secondary crystallization process was not evidenced. The trend line for the polyethylenes shows two regions: an initial linear portion (primary stage), followed by a levelling off (secondary stage). This roll-off occurred at 65% of relative crystallinity for both polyethylenes. The linear portions of each region in the plots were parallel to each other, shifting to shorter times by increasing the cooling rates. From each region different values for m (m_1 and m_2) and k (k_1 and k_2) were obtained. The exponent m_2 might correspond to the formation of new and a more stable lamellae as a result of the lamella-thickening effect²⁷, i.e., the possibility of lamella thickening was the main contributor to the secondary process²⁸, however the plots for polypropylene and polyethylene waxen didn't show this phenomenon. The values of the rate constants k and Avrami exponent m as a function of the cooling rate for the materials used by Equation (3) are listed in Table 2.

Table 2:- Values of the Avrami exponent m and Rate Constant k used by Eq. (3) as a function of the cooling rate, the half-time of crystallization $t_{1/2}$ and the Root Mean of the Squared Error, $RMSE$.

| Cooling rate/ °C min ⁻¹ | Primary stage | | | Secondary stage | | RMSE |
|------------------------------------|---------------|-------|-----------------|-----------------|-------|-------|
| | m_1 | k_1 | $t_{1/2}$ / min | m_2 | k_2 | |
| PP250 | | | | | | |
| -3 | 3.14 | 0.27 | 0.81 | - | - | 0.008 |
| -10 | 3.48 | 3.23 | 0.73 | - | - | 0.005 |
| -50 | 3.35 | 78.7 | 0.01 | - | - | 0.002 |
| PP190 | | | | | | |
| -3 | 4.01 | 0.08 | 2.16 | - | - | 0.008 |
| -10 | 3.42 | 4.18 | 0.05 | - | - | 0.006 |
| -50 | 2.95 | 63.0 | 0.004 | - | - | 0.002 |
| HDPE | | | | | | |
| -3 | 2.84 | 0.48 | 0.51 | 1.68 | 0.11 | 0.03 |
| -10 | 2.74 | 1.83 | 0.14 | 1.55 | 0.23 | 0.04 |
| -50 | 2.32 | 16.4 | 0.02 | 1.79 | 0.98 | 0.02 |
| LDPE | | | | | | |
| -3 | 2.89 | 0.20 | 1.20 | 2.02 | 0.41 | 0.03 |
| -10 | 3.75 | 2.88 | 0.06 | 1.97 | 0.34 | 0.02 |
| -50 | 2.72 | 47.2 | 0.005 | 1.63 | 1.06 | 0.02 |
| PE Waxen | | | | | | |
| -3 | 4.02 | 0.09 | 1.91 | 2.58 | 0.48 | 0.008 |
| -10 | 4.54 | 4.32 | 0.03 | 2.63 | 0.55 | 0.007 |
| -50 | 2.62 | 46.8 | 0.005 | 2.98 | 1.76 | 0.008 |

The values of the Avrami exponent m expressing crystallization through tridimensional spherulitic growth with a predominantly heterogeneous nucleation at low cooling rates (3°C min⁻¹) and a predominantly homogeneous nucleation at high cooling rates (50°C min⁻¹) for the four polymers and the polyethylene waxen.

The average values of the Avrami exponent for each material were $m_1 = 2.63$ and $m_2 = 1.67$ for HDPE, $m_1 = 3.12$ and $m_2 = 1.87$ for LDPE and $m_1 = 3.72$ and $m_2 = 2.73$ for polyethylene waxen. These values have different implications for the growth mechanisms; $m_1 \approx 4$ corresponds to the three dimensional spherical growth and thermal nucleation in the primary crystallization stage, it also indicates the dominant super-structural morphology is spherulitic and that nucleation is near instantaneous^{15, 27}; $m_2 \approx 2$ correspond to the one-dimensional linear growth and thermal nucleation during the secondary stage and the changing values of k indicate the variation of dominance of two competing nucleating and growth processes as have been reported in literature on this subject^{1, 19, 20, 29}.

According to Equation (3), the horizontal axis of Figure 1 was substituted by a time scale of Figure 3, so that the experimental and the predicted kinetics are reported in it. This graph shows that the higher the cooling rate, the shorter the completion of the crystallization.

The plots in Figure 3 show that the prediction based on the Avrami model stands out from the experimental data all along the time scale; the crystallinity is underestimated for the short times and overestimated for the longer times.

The variations of the experimental data can be compared to the theoretical data obtained with the use of Equation (3). The values of the *RMSE* are reported in Table 2 and it shows that there is concordance exists between the experimental and the predicted data for the polypropylenes and polyethylene waxen but not for polyethylenes. The *RMSE* values for the polyethylenes are of one order higher than those for the polypropylenes and the polyethylene waxen, reflecting greater deviation of the model prediction for the polyethylenes.

The results confirm that the Avrami equation does not predict correctly the final stage of the crystallization. The deviation of the Avrami plots are attributable to spherulite impingement, which indicates that the form of crystal growth transformed from the primary crystallization into the secondary one. The secondary stage was generally considered the result of the slower crystallization or crystal perfection, which were caused by the spherulite impingement in the later stage of crystallization process or by the further reorganization of an initially poorly crystallized macromolecules or small and metastable crystals according with previous works^{19, 23, 24}.

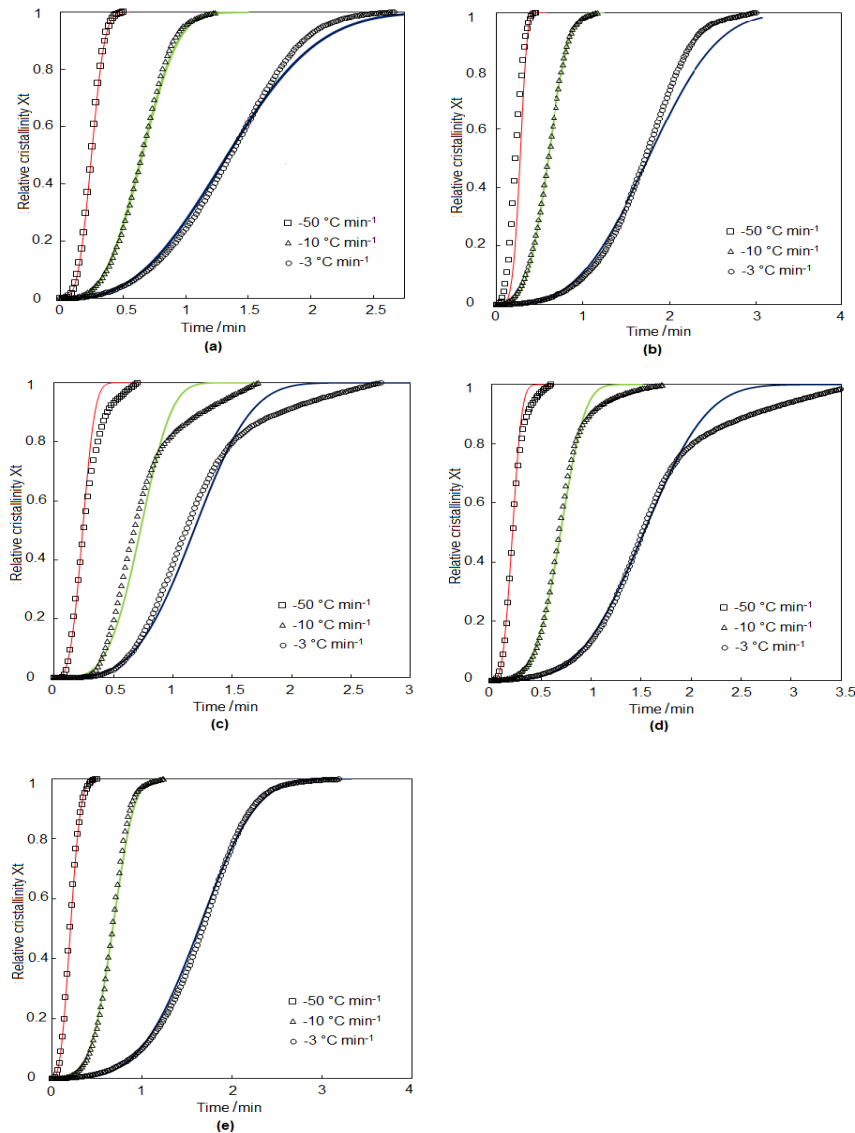


Figure 3: Relative crystallinity vs. time for nonisothermal crystallization at $3\text{ }^{\circ}\text{C min}^{-1}$, $10\text{ }^{\circ}\text{C min}^{-1}$, $50\text{ }^{\circ}\text{C min}^{-1}$. Samples cooled from the melt. (a) Polypropylene PP250, (b) Polypropylene PP190, (c) Polyethylene HDPE, (d) Polyethylene LDPE, (e) Polyethylene waxen. The symbols and the lines represent experimental data and predicted data using Eq. (3), respectively.

The results in Figure 3 also shows that the prediction for low cooling rates is less accurate than for high cooling rates at the final stage of crystallization for the four polymers and the polyethylene waxen which is consistent with the type of nucleation phenomena prevailing in each case. The homogeneous nucleation dominates at higher cooling rates and it is the speed of heat transfer which equalizes any differences in spherulite growth domains, decreasing the average spherulite size and the anisotropy and this characteristics makes the Avrami model a better fit. The heterogeneous nucleation predominates at lower cooling rates and the nucleation of the spherulites no longer occurs simultaneously at the start of crystallization so the prediction of the Avrami model fails in the final stage of crystallization.

The Avrami model fitting for polypropylenes, PP250 and PP190, was very good as it is shown in Figure 3a and Figure 3b and there weren't significant differences between them despite their different molecular weights. Similar results were obtained by Wunderlich³⁰ who states that, Avrami plots obtained by DSC data were the only convenient means to represent the empirical data of crystallization for polypropylenes. Regarding the influence of molecular weight for polypropylenes, other authors obtained contradictory results. Hoffman and Miller²⁶, using the reptation concept, predicted that the growth rate, G , would be inversely proportional to molecular weight, M_w . The results obtained in this work were consistent with the work of Pospisil and Rybnikar³¹ which concluded that there was no dependence of G on M_w and did not show any difference between the two polypropylenes (the difference in the $RMSE$ was only 0.0001 in the Avrami fitting for them). In this case the crystallization behaviour and the crystal form of the polymer are strongly affected by the configuration or tacticity and the conformational structure of the polypropylene chain and not by the molecular weights³².

Also it can be observed in Figure 3 that the Avrami model fits better for the case of polypropylenes (Figure 3a and Figure 3b) than for polyethylenes (Figure 3c and Figure 3d). This could be explained by the differences in the shape of the molecules and the chains of monomers in both cases. The isotactic polypropylenes have chains of monomers with a greater regularity, so their linear growth rate and the overall crystallization rate are higher due to an increasing number of intramolecular folded-chain nuclei that could result in a higher nucleation density.

The molecules in the polyethylenes samples used have different branching degree (DB). Recently, Luo et al.³³ explained that the crystallization and the glass transition processes of branched polyethylenes are correlated with each other and because of that the crystallization ability of PE chains can be reduced by increasing the content of branched structure, accordingly the content of amorphous domains in all PE samples increased. For branched PE's, the α -transition became weak or disappeared, while the β -transition resulted gradually stronger with an increasing DB. So the β -transition of branched PEs was greatly dependent on the DB, as the content of amorphous structure proves. The results of this work agree with Tardiff et al.²⁷ which showed that the DB has influence in lamellar thickness and amorphous-layer thickness and is the main contributor to secondary process resulting in a higher deviation of the Avrami equation.

The results for polyethylenes were similar to Eder and Wlochowicz¹²; they obtained that for a fast crystallizing polymers, like HDPE, great discrepancies remained between the experimental and predicted data and the deviation from the model is related to factors such as secondary crystallization, which in some cases, like with polyethylenes, it can be greater than 40% of the total, dependence of the lamellar thickness on crystallization temperature and the occurrence of different mechanisms of nucleation.

The crystallization trend lines for HDPE had a configuration with a lower slope than that of LDPE in the latter stage, so the fitting of the Avrami equation for HDPE is slightly worse than for LDPE. This can be explained by the fact that in the secondary crystallization the macromolecular chains have more time to perfect the crystals structure at lower cooling rates, forming thicker lamellae and the crystallinity rise is only driven by this mechanism for HDPE as was considered by Marand et al.³⁴. As was calculated above, the average Avrami exponent m_2 for HDPE was lower than for LDPE implying a slower crystallization or crystal perfection caused by the spherulite impingement in the later stage of crystallization process. This is consistent with observations reported in previous research³⁵.

The results for the polyethylene waxen (Figure 3e) were similar to those of LDPE in terms of degree of crystallinity but the Avrami model fitting was better in comparison with the two polyethylenes (HDPE and LDPE) due to its low molecular weight, and long molecular chains with short branches which has influence on the low crystallinity and viscosity. The value of the $RMSE$ of the fitting was similar to the polypropylenes. Its low molecular weight and regularity of the molecular chains allows greater mobility through the melting process, with nucleation mechanism

and crystal growth geometries for the primary crystallization process similar to the polypropylenes. In this study, the secondary crystallization does not manifest itself for the polyethylene waxes, which is in contradiction with what has been reported by Gumede³⁶.

Conclusions:-

The differences in the fitting of the Avrami equation between polymers with simpler molecular structure like polypropylenes (PP250, PP190) and polymers with more complex structure like polyethylenes (HDPE, LDPE) and polyethylene waxes have been investigated by cooling the melt at various scanning rates by DSC technique. The homogeneous nucleation dominates at higher cooling rates and heterogeneous nucleation dominates at lower cooling rates. The results showed a better fitting of the Avrami equation for higher cooling rates than for lower cooling rates for all materials. A higher heat transfer intensity had influence in the spherulite growing, diminishing the impingement effect, which is not considered by Avrami equation. The difference in molecular weight for polypropylenes had no influence in the fitting of the Avrami equation. A crystallization process with primary and secondary stages have been observed in the polyethylenes. The results showed a better fitting of the Avrami equation for the polypropylenes and polyethylene waxes than for the polyethylenes due to the influence of the branching degree in lamellar thickness and amorphous-layer thickness as the main contributor to secondary process. A better fitting was obtained for LDPE than for HDPE caused by a slower secondary crystallization process.

References:-

1. Avalos, F., Lopez-Manchado, M., and Arroyo, M. (1996): Crystallization kinetics of polypropylene: I. Effect of small additions of low-density polyethylene. *Polymer*. 37(25): p. 5681-5688.
2. Liang, G.-D., Qin, W.-P., Liu, T.-T., Zhu, F.-M., and Wu, Q. (2011): Nonisothermal Crystallization Kinetics of Low-Density Polyethylene Inside Percolating Network of ZnO Nanoparticles. *J Appl Polym. Sci.* 125: p. E113-E121.
3. Lamberti, G. (2011): Isotactic polypropylene crystallization: Analysis and modeling. *Eur Polym J.* 47: p. 1097-1112.
4. Carvalho, B.D. and Bretas, R.E.S. (1998): Quiescent crystallization kinetics and morphology of isotactic polypropylene resins for injection molding. I. Isothermal crystallization. *Journal of Applied Polymer Science.* 68(7): p. 1159-1176.
5. Hoffman, J.D. and Miller, C. (1988): Test of the reptation concept: crystal growth rate as a function of molecular weight in polyethylene crystallized from the melt. *Macromolecules.* 21(10): p. 3038-3051.
6. Phillips, P.J. and Vatansever, N. (1987): Regime transitions in fractions of cis-polyisoprene. *Macromolecules.* 20(9): p. 2138-2146.
7. Janimak, J., Cheng, S., and Giusti, P. (1991): Isotacticity Effect on Crystallization and Melting in Poly(propylene) Fractions. 2. Linear Crystal Growth Rate and Morphology Study. *Macromolecules.* 24: p. 2253-2260.
8. Janimak, J., Cheng, S., and Zhang, A. (1992): Isotacticity effect on crystallization and melting in polypropylene fractions: 3. Overall crystallization and melting behaviour. *Polymer.* 33(4): p. 728-735.
9. Nakamura, K., Katayama, K., and Amano, T. (1973): Some aspects of nonisothermal crystallization of polymers. II. Consideration of the isokinetic condition. *Journal of Applied Polymer Science.* 17(4): p. 1031-1041.
10. Nakamura, K., Watanabe, T., Katayama, K., and Amano, T. (1972): Some aspects of nonisothermal crystallization of polymers. I. Relationship between crystallization temperature, crystallinity, and cooling conditions. *Journal of Applied Polymer Science.* 16(5): p. 1077-1091.
11. Minkova, L. and Mihailov, M. (1989): Kinetics of nonisothermal crystallization and melting of normal high density and ultra-high molecular weight polyethylene blends. *Polymer Science.* 267(7): p. 577-582.
12. Eder, M. and Wlochowicz, A. (1983): Kinetics of non-isothermal crystallization of polyethylene and polypropylene. *Polymer.* 24(12): p. 1593-1595.
13. Ozawa, T. (1971): Kinetics of non-isothermal crystallization. *Polymer.* 12: p. 150.
14. Shan, H. and Lickfiel, G. (2007): Crystallization Kinetics Study of Polyethylene. *International Journal of Polymer Analysis and Characterization* 12(4).
15. Gumede, T.P., Luyt, A., Perez-Camargo, R., and Muller, A. (2017): The influence of paraffin wax addition on the isothermal crystallization of LLDPE. *Journal of Applied Polymer Science.* 134.
16. Piorkowska, E., Galeski, A., and Galeski, J. (2006): Critical assessment of overall crystallization kinetics theories and predictions. *Progress in Polymer Science.* 31: p. 549-575.

17. Avrami, M. (1939): Kinetics of phase change. I General theory. Chem Phys. 7: p. 1103.
18. Avrami, M. (1940): Kinetics of phase change. II transformation time relations for random distribution of nuclei. Chem Phys. 8: p. 212.
19. Liu, T., Mo, S., Wang, S., and Zhang, H. (1997): Nonisothermal Melt and Cold Crystallization Kinetics of Poly(Aryl Ether Ether Ketone). Polym Eng Sci. 37(3): p. 568-575.
20. Phillips, R. and Manson, J.A. (1997): Prediction and Analysis of Nonisothermal Crystallization of Polymers. Journal of Polymers Sciences B: Polymers Physics. 35: p. 847-888.
21. Choe, C.R. and Lee, K.H. (1989): Nonisothermal crystallization kinetics of poly(etheretherketone)(PEEK). Polym Eng Sci. 29(12): p. 801.
22. Patel, R.M. and Spruiell, J.E. (1991): Crystallization kinetics during polymer processing-analysis of available approaches for process modeling. Polym Eng Sci. 31(10).
23. Young, R.J. and Lovell, P.A. (2011): Introduction to polymers. Third ed: Taylor and Francis Group.
24. Wang, W., Dang, G., Jia, H., Li, Q., Zhou, H., et al. (2011): Non-isothermal crystallization kinetics of a typical semicrystalline polyimide. Acta Polimérica Sinica. 11(11): p. 1273-1277.
25. Strobl, G. (2006): Crystallization and melting of bulk polymers: New observations, conclusions and a thermodynamic scheme. Prog Polym Sci. 31: p. 398-442.
26. Hoffman, J.D. and Miller, R.L. (1997): Kinetics of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment Polymer. 38(13): p. 3151-3212.
27. Tardif, X., Pignon, B., Boyard, N., Schemelzer, J., Sobotka, V., et al. (2014): Experimental study of crystallization of PolyEtherEtherKetone (PEEK) over a large temperature range using a nano-calorimeter. Polymer Testing. 36: p. 10-19.
28. Kolb, R., Wutz, C., Stribeck, N., Krosigk, G., and Riekkel, C. (2001): Investigation of secondary crystallization of polymers by means of microbeam X-ray scattering. Polymer. 42(12): p. 5257-5266.
29. Avalos, F., Lopez-Manchado, M., and Arroyo, M. (1998): Crystallization kinetics of polypropylene III. Ternary composites based on polypropylene/low density polyethylene blend matrices and short glass fibres. Polymer. 39(24): p. 6173-6178.
30. Wunderlich, B. (1976): Macromolecular Physics: Crystal nucleation, growth, annealing New York: Academic, Press.
31. Pospíšil, L. and Rybníkař, F. (1990): Crystallization of controlled rheology type polypropylene. Polymer. 31(3): p. 476-480.
32. Amer, I. (2011): Molecular weight effects on crystallization of polypropylene, in *Chemistry and Polymer Science* University of Stellenbosch.
33. X., L., Xie, S., Hu, H., Jiang, J., Huang, W., et al. (2013): The relationship between the degree of branching and glass transition temperature of branched polyethylene: experiment and simulation. Polymer Chemistry.
34. Marand, H. and Huang, Z. (2004): Isothermal Lamellar Thickening in Linear Polyethylene: Correlation between the Evolution of the Degree of Crystallinity and the Melting Temperature. Macromolecules. 37: p. 6492-6497.
35. Giboz, J., Copponnex, T., and Mele, P. (2017): Analysis of the influence of the injection molding process on the crystallization kinetics of a HDPE. Journal of Applied Polymer Science. 134.
36. Gumede, T.P. (2014): Kinetic study of the crystallization of LLDPE and wax in LLDPE/Wax phase change blends used for thermal energy storage University of the free state (Qwaqwa campus).