

Application of the NPK Method in the Crystallization Kinetics of High-Density Polyethylene.

Frida Monzón^{a*}, María Dolores Rovira^a, Julià Sempere^b, Rosa Nomen^b

^a Universidad Centroamericana José Simeón Cañas. Bulevar Los Próceres, Antiguo Cuscatlán, La Libertad, El Salvador.

^b IQS School of Engineering. Universitat Ramon Llull. Via Augusta, 390, 08017 Barcelona

Aplicación del Método NPK en la Cinética de Cristalización de Polietileno de Alta Densidad.

Aplicació del mètode NPK a la cinètica de crist·lització de polietilè d'alta densitat.

RECEIVED: 6 OCTOBER 2023; ACCEPTED: 21 DECEMBER 2023; [HTTPS://DOI.ORG/10.55815/424211](https://doi.org/10.55815/424211)

ABSTRACT

The Non-Parametric Kinetics (NPK) method, developed in 1998, by Serra, R., Sempere, J. and Nomen, R. has been used by them and other research groups to analyze the thermal behavior of a physical or chemical transformation and thermal stability. However, it was until 2021 that the method was applied for the first time in a cooling process for the determination of the crystallization kinetics of polypropylene, obtaining satisfactory results.

The advantage of the NPK method is that it does not assume any model for the temperature function, nor for the conversion function to describe the crystallization kinetics. Through a mathematical process, the method provides two vectors: the vector \mathbf{u} , which contains the information about the kinetic model, and the vector \mathbf{v} , which contains the information about the temperature function.

The aim of this work is to verify that the NPK method is applicable to the crystallization of high-density polyethylene by comparing the results with the most commonly used models to describe the crystallization kinetics of polymers. The fits obtained were very good and the vector \mathbf{u} and \mathbf{v} allow us to reproduce the original curves from DSC.

Keywords: High-Density Polyethylene, NPK Method, Polymer Crystallization, Thermal Analysis.

RESUMEN

El método de Cinética No Paramétrica (NPK), desarrollado en 1998 por Serra, R., Sempere, J. y Nomen, R., ha sido utilizado por ellos y otros grupos de investigación para analizar el comportamiento térmico de una transformación física o química y estabilidad térmica. Sin embargo, fue hasta el año 2021 que se aplicó por primera vez el método en un proceso de enfriamiento para la determinación de la cinética de cristalización del polipropileno, obteniendo resultados satisfactorios.

La ventaja del método NPK es que no asume ningún modelo para la función de temperatura ni para la función de conversión para describir la cinética de cristalización. Mediante un proceso matemático, el método proporciona dos vectores: el vector \mathbf{u} , que contiene la información sobre el modelo cinético, y el vector \mathbf{v} , que contiene la información sobre la función de temperatura.

El objetivo de este trabajo es verificar que el método NPK es aplicable a la cristalización de polietileno de alta densidad comparando los resultados con los modelos más utilizados para describir la cinética de cristalización de polímeros. Los ajustes obtenidos fueron muy buenos y los vectores \mathbf{u} y \mathbf{v} nos permiten reproducir las curvas originales de DSC.

Paraules clau: Polietileno de Alta Densidad, Método NPK, Cristalización de Polímeros, Análisis Térmico.



*Corresponding author: fmonzon@uca.edu.sv

RESUM

El mètode de Cinètica No Paramètrica (NPK), desenvolupat l'any 1998 per Serra, R., Sempere, J. i Nomen, R. ha estat utilitzat per ells i altres grups de recerca per analitzar el comportament tèrmic d'una transformació física o química i estabilitat tèrmica. No obstant això, va ser fins al 2021 que el mètode es va aplicar per primera vegada en un procés de refrigeració per a la determinació de la cinètica de cristallització del polipropilè, obtenint resultats satisfactoris.

L'avantatge del mètode NPK és que no assumeix cap model per a la funció de temperatura, ni per a la funció de conversió per descriure la cinètica de cristallització. Mitjançant un procés matemàtic, el mètode proporciona dos vectors: el vector **u**, que conté la informació sobre el model cinètic, i el vector **v**, que conté la informació sobre la funció de temperatura.

L'objectiu d'aquest treball és comprovar que el mètode NPK és aplicable a la cristallització de polietilè d'alta densitat comparant els resultats amb els models més utilitzats per descriure la cinètica de cristallització dels polímers. Els ajustos obtinguts van ser molt bons i el vector **u** i **v** ens permeten reproduir les corbes originals a partir de DSC.

Paraules clau: Polietilè d'alta densitat, mètode NPK, cristallització de polímers, anàlisi tèrmica.

INTRODUCTION

Within olefins, polyethylene (PE) is the most produced and used polymer worldwide. PE is a thermoplastic polymer with unique properties, such as fast crystallization rate and a low glass transition temperature, which can be used in multiple applications [1].

The different types of PE are classified based on their density, which varies according to the different amounts of molecular branches. These include high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). HDPE is a copolymer of ethylene with short-chain branches, with an amount of up to 3% molar of an α -olefin comonomer. This material is semi-crystalline, with an average density of 0.935-0.975 g·cm⁻³ [2].

Understanding the kinetic parameters that influence the crystallization process is crucial, as they play a significant role in determining the conditions necessary for product preparation. The final characteristics of the product, including its degree of crystallinity and crystalline structure, are significantly impacted by these parameters [3]. By gaining insights into these factors, adjustments can be made to the production conditions, allowing for the attainment of the desired properties in the finished product.

The crystallization process involves three steps: The first two refer to primary crystallization, in which the formation of active nuclei and growth of crystals from the nuclei occurs; and the third, named secondary crystallization, occurs in the amorphous phase trapped in the crystals, producing an increase in crystallinity [4].

In polyethylene, spherulites are the structures formed in crystallization [5].

As crystallization is a kinetic phenomenon, it can be examined by considering three key parameters: temperature (T), degree of conversion (α) and pressure (P), as shown in Eq. 1 [6]:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \cdot h(P) \quad (\text{Eq. 1})$$

Since the pressure dependence is usually neglected in the condensed phase, this expression is only a function of two variables (Eq. 2):

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (\text{Eq. 2})$$

To describe the conversion function $f(\alpha)$ for the crystallization of the polymers several models are used [6]. Among these options, the Avrami equation, Eq. 3, is the most widely used to describe the crystallization kinetics [7]:

$$\alpha = 1 - \exp(-k^m t^m) \quad (\text{Eq. 3})$$

Where α is the degree of conversion from the amorphous to the crystalline phase, m is the Avrami exponent associated with the crystallization mechanism, and k is the general rate constant.

This equation is applicable to data obtained by differential scanning calorimetry (DSC), since the heat released in the crystallization process is directly proportional to the volume of the crystalline phase formed [8].

A modification of the previous equation is the Avrami-Erofeev model (Eq. 4)

$$f(\alpha) = cn(1 - \alpha)[- \ln(1 - \alpha)]^{(1-\frac{1}{n})} \quad (\text{Eq. 4})$$

Where $f(\alpha)$ is the conversion function, n is the Avrami kinetic parameter, α is the degree of conversion, and c is the empirical factor parameter recommended by Vyazovkin et al. [6] to adjust the other parameters of the equation.

Since it involves both the nucleation and growth of crystals, the Šesták-Berggren model is also used to quantitatively describe the crystallization phenomenon as a function of conversion. The representation of this model is shown in Eq. 5:

$$f(\alpha) = c\alpha^m(1 - \alpha)^n[- \ln(1 - \alpha)]^p \quad (\text{Eq. 5})$$

Where m , n , and p are the kinetic parameters. Šesták and Berggren [9] assign m values between 0 and 1, and n values greater than 1.

Normally, equation 5 tends to be used in its truncated form ($p=0$) [6], known as two-parameter Šesták-Berggren, as shown in Eq. 6:

$$f(\alpha) = c\alpha^m(1 - \alpha)^n \quad (\text{Eq. 6})$$

This equation is used for both isothermal and non-isothermal mode studies.

The temperature dependence in crystallization kinetics is commonly explained by the Hoffman-Lauritzen (HL)

theory [10], also referred to as the Lauritzen-Hoffman (LH) theory. This theory provides an analytical vision by connecting microscopic parameters with macroscopic quantities [11], where the growth rate of the spherulites depends on the temperature [8], as shown in Eq. 7:

$$G = G_0 \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \exp\left(\frac{-K_g}{T\Delta T f}\right) \quad (\text{Eq. 7})$$

Where G_0 is the preexponential factor, U^* is the activation energy of the elementary jump, $\Delta T = T_m^0 - T$ is the subcooling, T_m^0 is the equilibrium melting temperature, $f = 2T/(T_m^0 + T)$ is the correction factor, T_∞ is a hypothetical temperature usually 30 K below the T_g , and K_g the kinetic parameter.

This theory yields to 3 crystallization regimes that depend on the nucleation rate and the lateral propagation of the crystal [11]. Regime I, where the nucleation rate is less than the lateral growth rate; regime II, in which the nucleation rate occurs by a lateral propagation; and regime III, where nucleation is faster. These regimes depend on temperature, so regime III transitions to regime II and then to regime I as the crystallization temperature increases [5].

In the traditional kinetic analysis, a fundamental requirement is the prior knowledge of the model governing the conversion function $f(\alpha)$ and the temperature function $f(T)$. However, in 1998, Serra, R., Sempere, J., and Nomen, R. introduced the NPK method [12], [13], [14], which stands out for its distinctive feature, it doesn't assume any predefined model to describe the behavior of the kinetic model or the kinetic constant [15].

Using a set of experimental measurements, and applying the mathematical approach of Singular Value Decomposition (SVD), the model can decompose any matrix whose rows correspond to different degrees of conversion, from 0 to 1, and whose columns correspond at different temperatures, to a matrix product of three matrices (Eq. 8) [13]:

$$\mathbf{A} = \mathbf{U} \cdot \mathbf{W} \cdot \mathbf{V}^T \quad (\text{Eq. 8})$$

Where \mathbf{U} and \mathbf{V} are orthonormal matrices and \mathbf{W} is a diagonal matrix, whose elements are the singular values of matrix \mathbf{A} . If only the first singular value, w_1 , is significant, matrix \mathbf{A} can be expressed as the product of the first column of the matrix \mathbf{U} , now called vector \mathbf{u} , the first singular value, now called W , and the first column of the matrix \mathbf{V} , now vector \mathbf{v} , as shown in Eq. 9:

$$\mathbf{A} \cong \mathbf{u} \cdot W \cdot \mathbf{v}^T \quad (\text{Eq. 9})$$

Therefore, by applying the SVD to the matrix, two matrices \mathbf{U} and \mathbf{V} are obtained, whose first columns are the vectors \mathbf{u} and \mathbf{v} . The first vector contains the numerical information about the kinetic model and the second the temperature dependence, W is a scalar. Once the vector \mathbf{u} and \mathbf{v} containing discrete points of $f(\alpha)$ and $f(T)$ are known, the simulation is immediate [15].

Since no assumption is made about temperature dependence, the method avoids the problem of calculating

the kinetic constant and can be applied to any reaction or kinetic process, even if its mechanism is unknown.

Another feature of the NPK method is that based on the data of each of the vectors \mathbf{u} and \mathbf{v} , the experimental data of the original DSC curves can be reproduced [16].

In the years leading up to 2021, the NPK method primarily found application in assessing the kinetics of chemical reactions. However, in a crucial development in 2022, Monzon et al. [17] expanded the utility of the NPK method by successfully applying it to the crystallization process of polypropylene, showcasing its versatility.

This study aims to further extend the scope of the NPK method by investigating its suitability for analyzing the crystallization of high-density polyethylene. The primary objective is to evaluate the method's efficacy in this specific context by comparing the obtained results with those derived from widely accepted models commonly employed to describe the crystallization kinetics of polymers.

MATERIALS AND METHODS

High-density polyethylene from Dow was used in pellets, with a melting point of $T_m = 132.5^\circ\text{C}$. The analysis was performed on a Mettler-Toledo DSC 3+ using a nitrogen atmosphere. The equipment was calibrated by Mettler Toledo personnel with zinc and indium references. A short check-in with indium is carried out prior to each new register.

A ~10 mg sample of HDPE was rapidly heated to 150°C in a 40 μL aluminum crucible at $10 \text{ K}\cdot\text{min}^{-1}$ and held for 5 minutes to eliminate thermal history. Then the sample was cooled to 10°C at speeds of -2.5, -5, -10, -15 y -20 $\text{K}\cdot\text{min}^{-1}$.

The DSC recordings were processed with the NPK method to obtain the vectors \mathbf{u} and \mathbf{v} . Then the vector \mathbf{u} was fitted to the Avrami and Šestak-Berggren models and the vector \mathbf{v} was fitted to the Lauritzen-Hoffman model. Both adjustments were made in order to verify that data obtained through the NPK method fits well with the models most accepted by the literature. Finally, the original calorimetric curves were reconstructed using only the information in vectors \mathbf{u} and \mathbf{v} .

Results and Discussion

Thermal analysis of the HDPE sample was performed in the DSC and the calorimetric curves are shown in Figure 1.

As recommended by ICTAC [6], at least three temperature programs must be carried out, but in the case of NPK a minimum of five temperature programs are required at different cooling rates [18], since it is necessary to calculate parameters that are valid and reliable, in addition to being statistically correct.

According with He et al. [19], Figure 1 shows that the temperature of the crystallization peak decreases with increasing cooling rate, while the crystallization temperature range widens with increasing cooling rate.

The enthalpies of crystallization (Q_c) for each of the velocities, obtained from the integrals of the peaks of each DSC record, are shown in Table 1.

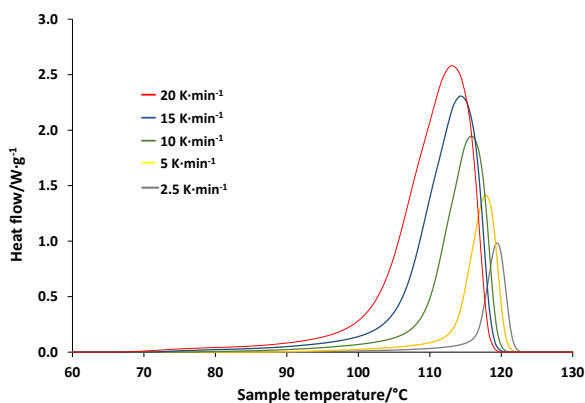


Figure 1. Calorimetric curves of HDPE at cooling rates of -2.5, -5, -10, -15 y -20 K·min⁻¹

Table 1. Enthalpies of crystallization for HDPE at the cooling rates used

| Cooling speed (K·min ⁻¹) | Q _c (J·g ⁻¹) |
|--------------------------------------|-------------------------------------|
| -2.5 | 88.12 |
| -5 | 86.51 |
| -10 | 86.30 |
| -15 | 86.52 |
| -20 | 86.33 |

The average Q_c is 86.8 ± 0.8 J·g⁻¹. Taking the value of ΔH₁₀₀ = 293 J·g⁻¹ reported by Li et al. [20] for polyethylene, a crystallinity percentage of 31% is obtained.

Then the data from the curves obtained in DSC were processed in the NPK program, obtaining vectors **u** and **v**.

First, the fitting of the vector **u** with respect to the conversion functions was performed using the equations of the 2 and 3 parameter Šesták-Berggren kinetic model (Eq. 5 and Eq. 6) and the Avrami equation (Eq. 4). The analysis was performed between conversions of 0.02 and 0.98. By using the Solver tool of Excel and error minimization, the kinetic parameters of the model equations are obtained. These parameters are shown in Table 2.

Table 2. Parameters of in the equation of the 2 and 3 parameter Šesták-Berggren and Avrami model

| Parameter | Šesták-Berggren 2 parameters | Šesták-Berggren 3 parameters | Avrami |
|-----------|------------------------------|------------------------------|--------|
| c | 0.96 | 0.94 | 0.42 |
| m | 0.43 | 0.00 | |
| n | 1.53 | 1.70 | 1.20 |
| p | | 0.42 | |

Figure 2 shows the vector **u** and its fit obtained with the equations of the 2 and 3 parameter Šesták-Berggren and Avrami models.

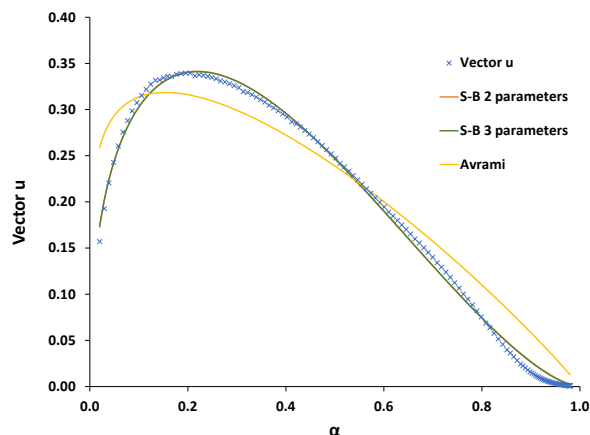


Figure 2. Fit vector **u** with equation of the 2 and 3 parameters Šesták-Berggren and Avrami model

Figure 2 shows that the best fit is given by the Šesták-Berggren equations for 2 and 3 parameters, with absolute average errors of ±5.3·10⁻³ and ±5.1·10⁻³, respectively. These values fulfill with the intervals proposed by Šesták-Berggren [9], for parameters *n* and *m*.

For the Avrami equation, the fit is not good. As reported by Feng [4], this deviation may be taken place because the Avrami model generally fits in the initial stage of crystallization only, as it does not consider some factors, such as the effect of secondary crystallization and the decrease in growth rate. This deviation is reflected with the obtained value of *n* = 1.20 with an absolute average error of ±2.3·10⁻². This value differs from the values reported by other authors such as Huang et al. [21] which reports a value of *n* = 2.04 for cooling rates -5, -10, -15, -20 and -25 K·min⁻¹ and, in the case of Yanjun et al. [22], *n* = 2.87 for cooling rates -2.5, -5, -10, -20 and -35 K·min⁻¹.

The adjustment of the temperature function was also performed. The NPK data for the vector **v** and the corresponding temperature values were taken and the adjustment was made with the Hoffman-Lauritzen equation (Eq. 7) and the parameters corresponding to the pre-exponential factor (*G*₀) and the kinetic factor (*K*_g) were found.

The constants used are those shown in Table 3.

Table 3. Constants used to determine the parameters of the Lauritzen and Hoffman equation.

| Constant | Value |
|------------------------------------|---|
| <i>U</i> [*] | 6280 J mol ⁻¹ |
| <i>R</i> | 8.314 J mol ⁻¹ K ⁻¹ |
| <i>T</i> _α | 203.15 K |
| <i>T</i> _m ⁰ | 417.65 K |

In the case of the value of *U*^{*}, the value of 6280 J·mol⁻¹ is used as reported by several researchers [23], [24] y [25]. The value of *T*_m⁰ used is the one reported by Patel [24].

The parameters obtained from the fit of the vector \mathbf{v} with the equation of the Lauritzen-Hoffman model are shown in Table 4.

Table 4. Parameters obtained from the fit of the vector \mathbf{v} with the equation for of Lauritzen and Hoffman

| Parameter | Value |
|-----------|----------------------------------|
| G_0 | $9.35 \cdot 10^5 \text{ s}^{-1}$ |
| K_g | $9.24 \cdot 10^4 \text{ K}^2$ |

Values reported by Patel [24] for the pre-exponential factor (G_0) is $1.70 \cdot 10^5 \text{ s}^{-1}$ and for the kinetic factor (K_g) is $1.30 \cdot 10^4 \text{ K}^2$, for a sample of HDPE of $M_w=65,000$ at cooling rates of -2, -5, -10, -20 and -40 $\text{K} \cdot \text{min}^{-1}$, and although they are of the same order, they differ significantly.

The representation of the fit to the vector \mathbf{v} with the Lauritzen-Hoffman equation is shown in Figure 3.

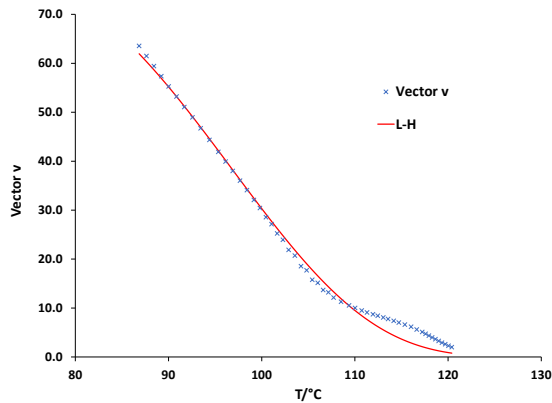


Figure 3. Fit vector \mathbf{v} with the equation of the Lauritzen and Hoffman model

Figure 3 illustrates that the fit is not good in the initial phase of crystallization. In this case, an absolute average error of ± 1.4 is obtained.

To better visualize this trend, the equation of the Lauritzen and Hoffman model is linearized, obtaining the graph shown in Figure 4.

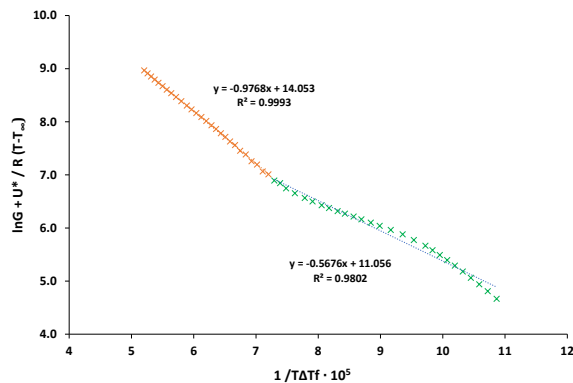


Figure 4. Linearization of the Lauritzen and Hoffman model equation

In Figure 4, two slopes are observed around 106.6°C . This transition temperature may vary. As demonstrated

by Fatou and Mandelkern [26], this value depends on the molecular weight of the polymer.

With these results, the vector \mathbf{v} is analyzed into two segments. The first one from 86.85°C to 106.6°C , and the second from the latter temperature up to 120.40°C . As demonstrated by Supaphol and Spruiell [23], this trend shows regime II (segment a) and regime III (segment b) of the secondary nucleation theory of Lauritzen and Hoffman.

Vyazovkin et al. [7] recommended to parameterize the segments separately. Doing that, the new parameters obtained are shown in the Table 5.

Table 5. Parameters obtained with the Lauritzen and Hoffman equation for segment a (regime II) y segment b (regimen III)

| Parameter | Segment (a) | Segment (b) |
|-----------|----------------------------------|----------------------------------|
| G_0 | $4.48 \cdot 10^4 \text{ s}^{-1}$ | $1.18 \cdot 10^6 \text{ s}^{-1}$ |
| K_g | $5.27 \cdot 10^4 \text{ K}^2$ | $9.65 \cdot 10^4 \text{ K}^2$ |

Supaphol and Spruiell [23] report values of the K_g parameter for regimes II of $1.01 \cdot 10^5 \text{ K}^2$ and for regime III de $2.42 \cdot 10^5 \text{ K}^2$, for HDPE sample of T_m^0 of 142.7°C and 141.3°C .

Figure 5 shows the graphic representation of each of the two segments obtained against the vector \mathbf{v} .

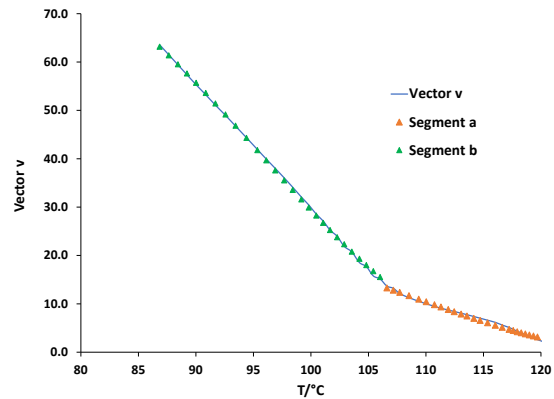


Figure 5. Fit of vector \mathbf{v} with two regimes of the Lauritzen and Hoffman equation

The ratio of the K_g parameter obtained in the two segments gives a value of 1.83. According to Vyazovkin et al. [7] this value obtained has to be approximately 2, to establish that there is a change in different crystallization regimes, but it allows values of up to 1.5.

To reproduce the experimental data of the DSC curves with the values obtained from the vectors and for each calorimetric curve at the different cooling rates, the vector \mathbf{u} corresponding to each conversion and the vector \mathbf{v} corresponding to each temperature are found.

Since w in equation 9 is a constant and not a vector, its value, 0.013 is the average of all its values. Once the value of w is calculated, the values of da/dt are found and the resulting curves at the different cooling rates for the HDPE are shown in Figure 6.

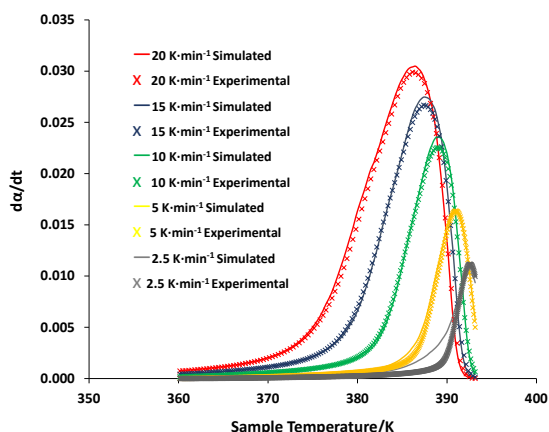


Figure 6. Comparison of the experimental curves with the simulated using the NPK method.

CONCLUSIONS

The NPK method has once again proven its efficacy in determining the crystallization kinetics of polymers. This is evident from the vector \mathbf{u} 's strong alignment with the Šestak-Berggren model of 2 and 3 parameters. Despite a minor deviation with the Avrami method, this anomaly appears to be exclusive to high density polyethylene. In addition, the vector \mathbf{v} aligns well with the Lauritzen-Hoffman model, clearly exhibiting the two characteristic regimes II and III in HDPE.

The vectors \mathbf{u} and \mathbf{v} carry ample information to reproduce the original curves. This eliminates the necessity of fitting the data to a specific model for both temperature dependence and conversion dependence.

ACKNOWLEDGMENT

To the Universidad Centroamericana José Simeón Cañas and IQS, Universidad Ramón Llull with the funds that allowed FM to participate in the 15th Mediterranean Congress of Chemical Engineering, May 30th to June 2nd, 2023, Barcelona, Spain.

REFERENCES

- Depan D, Khattab A, Simoneaux A, Chirdon W. Crystallization kinetics of high-density and low-density polyethylene on carbon nanotubes. 2019; 2:e10062
- McDaniel MP, DesLauriers PJ. Ethylene polymers, HDPE. 2000:1-40
- Wang S, Zhang J. Non-isothermal crystallization kinetics of high density polyethylene/titanium dioxide composites via melt blending. 2014; 115:63-71
- Feng L. Melting and crystallization behavior of linear low-density polyethylene. 2004
- Feng L, Kamal MR. Spherulitic crystallization behavior of linear low-density polyethylene. Polym Eng Sci. 2005; 45:74-83;
- Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. 2011; 520:1-19
- Vyazovkin S, Stone J, Sbirrazzuoli N. Hoffman-Lauritzen parameters for non-isothermal crystallization of poly (ethylene terephthalate) and poly (ethylene oxide) melts. 2005; 80:177-80
- Vyazovkin S. Nonisothermal crystallization of polymers: Getting more out of kinetic analysis of differential scanning calorimetry data. Polymer Crystallization. 2018; 1:e10003; doi: 10.1002/pcr2.10003.
- Šesták J, Berggren G. Study of the kinetics of the mechanism of solid-state reactions at increasing temperatures. 1971; 3:1-12
- Lauritzen, J., Hoffman, J. Theory of Formation of Polymer Crystals with Folded Chains in Dilute Solution. 1960;64: 73-102
- Zhang MC, Bao-Hua Guo, Xu J. A Review on Polymer Crystallization Theories. 2016:4; doi: 10.3390/cryst7010004.
- Serra R, Sempere J, Nomen R. A new method for the kinetic study of thermoanalytical data: The non-parametric kinetics method. 1998; 316:37-45; doi: [https://doi.org/10.1016/S0040-6031\(98\)00295-0](https://doi.org/10.1016/S0040-6031(98)00295-0).
- Sempere J, Nomen R, Serra E, Sempere B. Nonparametric Kinetic Methods. In: Anonymous Thermal analysis of Micro, Nano-and Non-Crystalline Materials. Springer; 2012. pp. 351-369.
- Ferrer N, Serra E, Sempere J, Nomen R. Non-parametric kinetic analysis of autocatalytic reactions. J Loss Prev Process Ind. 2017; 49:357-66
- De Armas D (2016) Síntesis de macrolactonas cíclicas. Dissertation, Universidad Ramón Llull.
- Sempere J, Nomen R, Serra R, Soravilla J. The NPK method: An innovative approach for kinetic analysis of data from thermal analysis and calorimetry. 2002; 388:407-14; doi: [https://doi.org/10.1016/S0040-6031\(02\)00037-0](https://doi.org/10.1016/S0040-6031(02)00037-0).
- Monzón F, Rovira MD, Sempere J, Nomen R. Determination of polymer crystallization kinetics with the NPK method. 2022:1-5
- Sempere J, Nomen R, Serra E, Sempere B. Non-parametric kinetic analysis of the oxidation of TiN and TiC nanoparticles. Int J Chem Kinet. 2012; 44:147-54; doi: 10.1002/kin.20606.
- He C, Cao X, Huo G, Luo S, He X. Non-isothermal crystallization behaviour and kinetics of LLDPE/REDMUD blends. 2015; 23:483+
- Li D, Zhou L, Wang X, He L, Yang X. Effect of crystallinity of polyethylene with different densities on breakdown strength and conductance property. 2019; 12:1746
- Huang J, Wen Y, Kang C, Tseng W, Yeh M. Nonisothermal crystallization of high density polyethylene and nanoscale calcium carbonate composites. 2008; 48:1268-78
- Li Y, Du L, Zhang Z, Wu Q. High-density polyethylene and heat-treated bamboo fiber com-

- posites: nonisothermal crystallization properties. 2015;2015
23. Supaphol P, Spruiell JE. Nonisothermal bulk crystallization studies of high density polyethylene using light depolarizing microscopy. 1998; 36:681-92
 24. Patel RM. Crystallization kinetics modeling of high density and linear low density polyethylene resins. *J Appl Polym Sci.* 2012;124: 1542-52; doi: <https://doi.org/10.1002/app.35177>.
 25. Treviño-Quintanilla CD, Krishnamoorti R, Bonilla-Ríos J. Flash DSC crystallization study for blown film grade bimodal HDPE resins. I. Isothermal kinetics and its application of the blown film modeling. 2016; 54:2425-31
 26. Fatou JG, Marco C, Mandelkern L. The influence of molecular weight on the regime crystallization of linear polyethylene. 1990; 31:1685-93