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THERMAL ANALYSIS OF A POLYETHYLENE GLYCOL (PEG 4000): T-CR-T DIAGRAM CONSTRUCTION

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Abstract

A modified isoconversional method is applied to perform the kinetic analysis of non-isothermal processes. The solidification process of a polyethylene glycol with a mean molecular of 4000 (PEG 4000) was here analyzed. It was stated that the Avrami model provides a good description of the solidification process.

Temperature-cooling rate-transformation diagrams were constructed and there was a good agreement between experimental data and the calculated T-CR-T curves. Moreover, morphological qualitative analysis has been performed by means of scanning electron microscopy.

Keywords: DSC, PEG, T-CR-T

Introduction

Polyethylene glycols (PEG) are polymers from oxyethylene polymerization. These polymers are widely used for pharmaceutical purposes as excipients since they improve dissolution degree and/or time of certain active principles in the gastric medium. Phase diagram knowledge is very important [1, 5]. These materials were also used in the conservation of archaeological waterlogged wood to substitute water by some consolidating material [6, 7]. Thus, knowing both thermodynamic and kinetic aspects of their solidification is fundamental. Solidification process depends on the thermal history of the polymer [8, 9]. In this work, the solidification process of a polyethylene glycol with a mean molecular of 4000 (PEG 4000) was analyzed.

Several models [10–13] have been developed to reproduce experimental data under isothermal or continuous heating/cooling rate conditions. Once a reliable model has been determined, one can construct the transformation diagrams: Time – temperature (T-T-T) and temperature – heating/cooling rate (T-HR/CR-T) transformation diagrams [14–16].

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In our study, a modified method is applied to perform kinetic analysis of non-isothermal processes. As expected, it was stated that the Avrami model provides a good description of the solidification process. Moreover, temperature-cooling rate-transformation diagrams were constructed and there was a good agreement between experimental data and the calculated T-CR-T curves.

Experimental

The solidification process was here analyzed by means of differential scanning calorimetry (DSC). Experiments were carried out in a Mettler DSC30 equipment. Two types of experiments were performed: constant heating rate up to the liquid state, isothermal regime and, constant cooling rate measurements at rates ranging from 10 to 65 K min^{-1}. As an example, Fig. 1 shows several DSC scans of two polyethylene glycols with different average molecular mass (4000 and 6000). These and previous results lead us to state that solidification process depends on the molecular mass as well as on the thermal treatment of the polymer [7, 9].

Thanks to the differential scanning calorimetry technique applied to the study, the whole process, we have obtained data on its temperatures and enthalpies. Similar melting and cooling enthalpy was measured, and samples were crystalline at all cooling rates. Moreover, similar mass (10 mg) was used in all DSC (PEG 4000) experiments. From these data and with an adequate theoretical model, understanding the behaviour of PEG when treated thermally is possible [17].

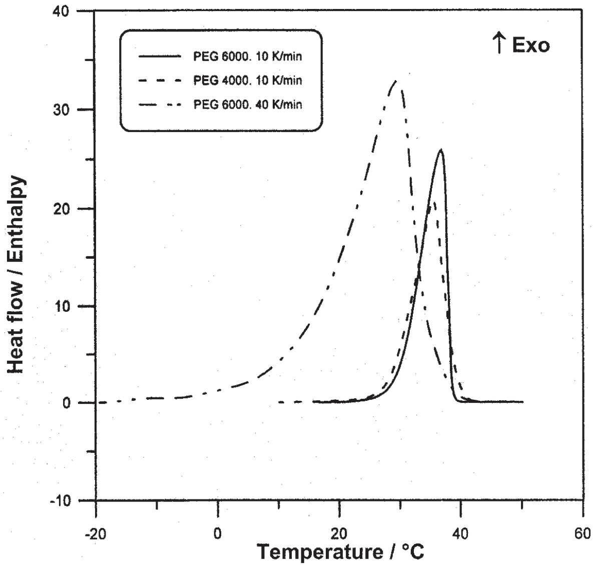

Fig. 1 Several DSC scans for PEG 4000 and PEG 6000

The study is complemented with the scanning electronic microscopy (SEM) technique that produces micrographies allowing morphological qualitative analysis of the substance. A DSM 960A Zeiss microscopy of the *Servei de Microscopia* of the Girona University was utilized.

Kinetic analysis and discussion

The Johnson-Mehl-Avrami (JMA) equation is frequently used for experimental data analysis of isothermal crystallization kinetics.

$$\alpha=1-\exp(-kt)_{\mathrm{n}}$$

where α is the crystalline fraction, k the crystallization rate constant, t the time elapsed from the beginning of the process and n a kinetic exponent depending on the morphology of crystallization growth. k and n are considered as constant with respect to time. Hence, the isothermal crystallization rate equation can be obtained by differentiation with respect to time: $\mathrm{d}\alpha/\mathrm{d}t='kf(\alpha)$ with $f(\alpha)=n(1-\alpha)[-\ln(1-\alpha)]^{1-1/\mathrm{n}}$.

The crystallization rate equation can be extended to the continuous cooling/heating treatment at a constant rate β: $\mathrm{d}\alpha/\mathrm{d}t=\beta'kf(\alpha)$, where T is temperature. Such equation was first introduced by Doyle [18] to derive kinetic data from a thermogravimetric curve. It is usually assumed that the rate constant k has an Arrhenius behavior with respect to the temperature during the crystallization process: $k = A\exp(-E/RT)$, where A is the pre-exponential term, E the apparent activation energy and R is the gas constant. There are various differential and integral methods to calculate these terms from continuous heating data as i.e. Kissinger's [19]. Once E is known, it is possible to construct low temperature parts of the T-T-T and T-HR-T transformation diagrams [13, 20].

Nevertheless, in this work a similar procedure has been applied to analyze solidification data – procedure described in reference [21]. The reason is that in this case the process is not driven by nucleus growth but by nucleation. In the solidification process, a certain amount of undercooling, ($\Delta T=T_{\mathrm{m}}-T$), where T_{m} is the melting temperature is necessary to induce solidification [22]. The driving force for nucleation is Gibbs energy difference between the liquid and the crystal.

The so-called isoconversional method [23] was applied to find the activation energy for a given value of the degree of conversion, $E(\alpha)$. Here, it is adapted to evaluate the constant B, of the constant rate equation, in the case of solidification from an isotropic melt [21].

$$k(T)=A\exp(-B/T\Delta T^2)$$

where A has a smooth dependence on temperature with respect to the exponential factor and B is a constant proportional to $\sigma^3/\Delta S_{\mathrm{m}}^2$, where σ is interface energy between the liquid and the nucleus and ΔS_{m} the melting entropy.

Kinetic model determination has been performed from the knowledge of function $z(\alpha)$,

$$z(\alpha)=\Delta Hf(\alpha)g(\alpha)$$

where α value of the maximum of the function allows us determine the kinetic model. In this expression ΔH is the enthalpy value and $g(\alpha)$ is defined by,

$$g(\alpha)=\int_0^{\alpha}\frac{1}{f(\alpha')}\mathrm{d}\alpha'$$

Figure 2 shows experimental evaluated $z(\alpha)$ functions for PEG 4000, and Johnson-Mehl-Avrami (JMA) model (full line). It can be stated from Fig. 2 that JMA model gives us a good description for PEG 4000. Average kinetic parameter is n=1.35.

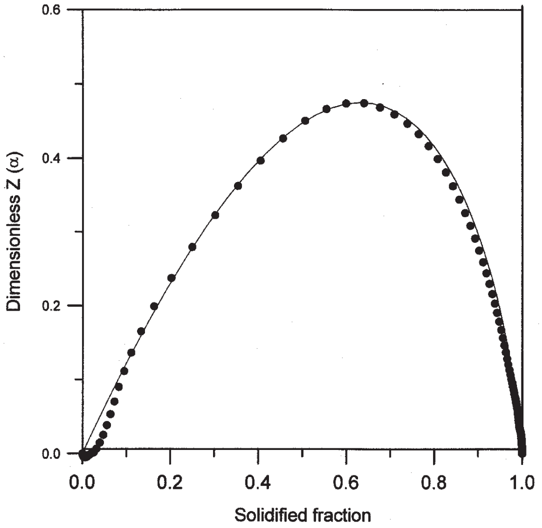

Fig. 2 Dimensionless $z(\alpha)$ function *vs.* α for PEG 4000. Points represent experimental DSC data and solid lines are calculated from JMA model

The experimental DSC (points) and calculated (full lines) heat flow divided by enthalpy and solidified fraction are shown in Figs 3 and 4 for PEG 4000. We can state that the models give a good description of the solidification process.

Once B and T_m are known, temperature-cooling rate-transformation diagrams can be obtained from the kinetic model [21]. Figure 5 shows calculated (T-CR-T) curves (full lines) and several experimental DSC data for α=0.1, 0.3, 0.5, 0.7, 0.9. As expected in any solidification process, the solidification onset shifts to higher temperatures when the cooling rates decreases.

Morphological analysis has been performed by means of SEM. Figure 6 shows PEG 4000 untreated. Figures 7 and 8 show PEG 4000 thermally treated at different cooling rates: 40 and 2.5 K min^{-1}, respectively. Several crystalline zones, with different morphology, are observed. Nevertheless, no significant changes were detected in the crystallization behavior, as DSC results confirm.

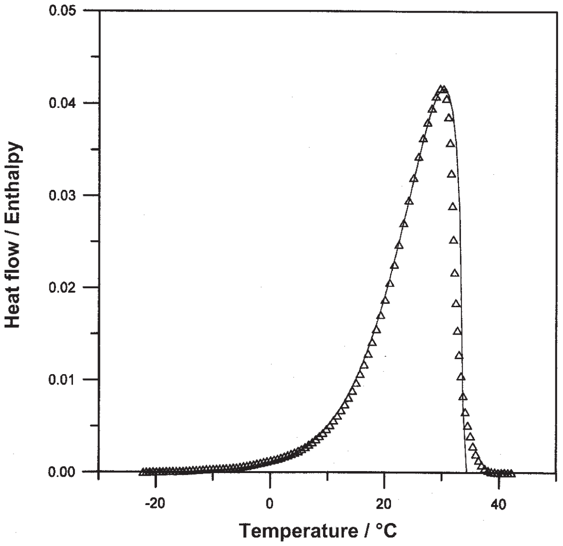

Fig. 3 Heat-flow divided by enthalpy *vs.* temperature. Triangles represent experimental DSC data and solid lines are calculated from the JMA model

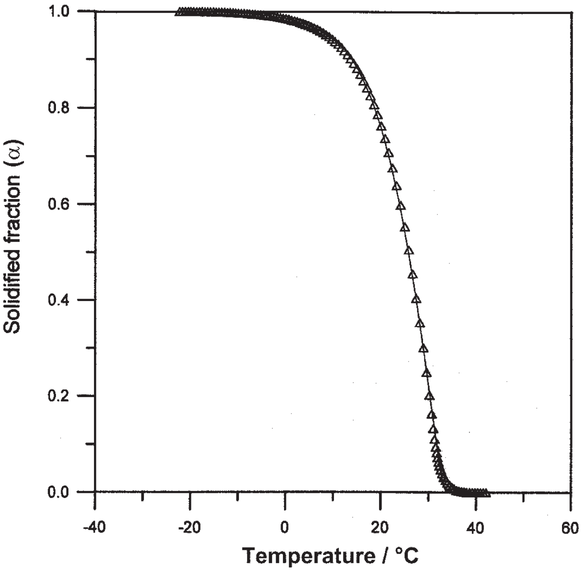

Fig. 4 Solidified fraction *vs.* temperature. Triangles represent experimental DSC data and solid lines are calculated from the JMA model

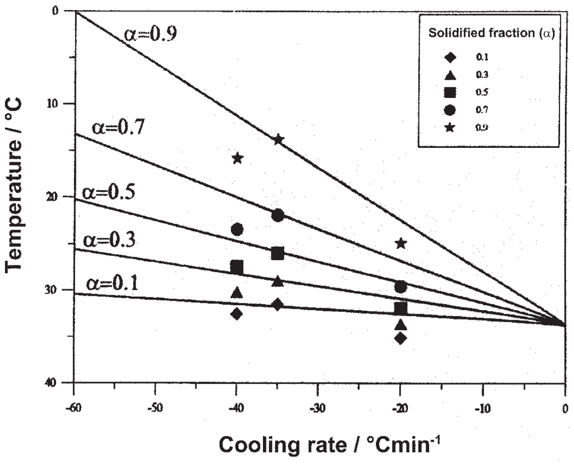

Fig. 5 Calculated T-CR-T curves (solid lines) for the JMA model and experimental DSC data (points)

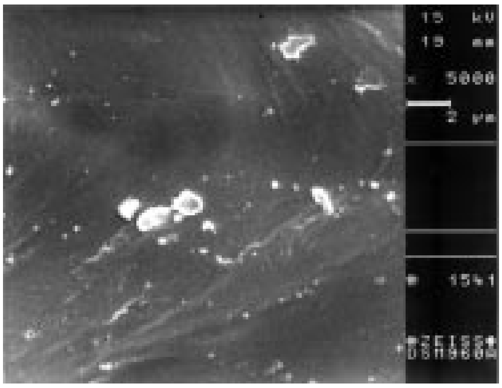

Fig. 6 PEG 4000 micrography. Not thermally treated

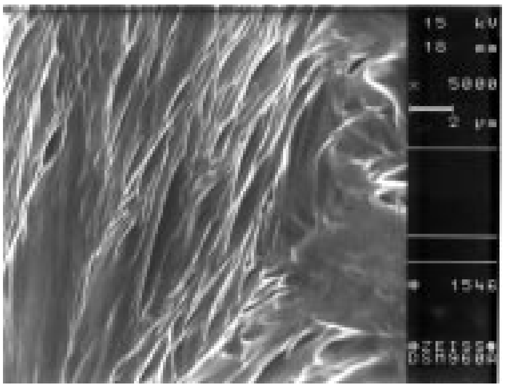

Fig. 7 PEG 4000 micrography. Constant cooling rate: 40 K min^{-1}

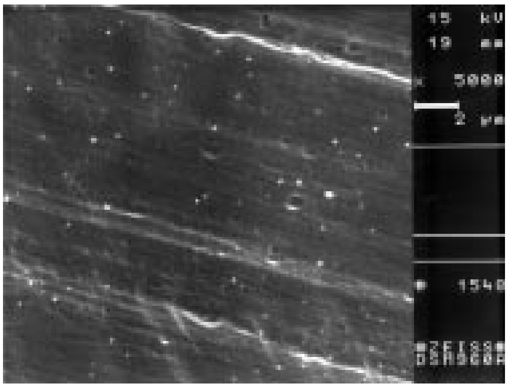

Fig. 8 PEG 4000 micrography. Constant cooling rate: 2.5 K min^{-1}

Conclusions

The thermodynamics and kinetics of the solidification process of a polyethylene glycol (PEG 4000) was here analyzed by calorimetric experiments. The kinetic analysis was performed with a modified isoconversional method. It has been stated that the JMA model gives a good description of the solidification process for PEG 4000. Average kinetic parameter is n=1.35.

Temperature-cooling rate-transformation diagram was constructed for a wide range of conditions and they showed a good agreement between experimental data and T-CR-T curves obtained by calculation. This verifies the reliability of the method utilized and the validity of the constant rate model description.

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