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STUDY OF THE CRYSTALLIZATION KINETICS
Poly(ethylene oxide) and a blend of poly(ethylene oxide) and poly(bisphenol A-co-epichlorohydrin)

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Abstract

A kinetic study of the crystallization of poly(ethylene oxide) (PEO) and of a blend of PEO+poly-(bisphenol A-co-epichlorohydrin) (PBE) was performed by using DSC in a non-isothermal program at constant cooling rates. The curves obtained were analyzed by the Kissinger, Ozawa and Friedman methods, with determination of the kinetic parameters in each case. As a consequence of the presence of PBE, the kinetic parameters were altered, leading to the conclusion that PBE has some influence on the crystallization of PEO, modifying its mechanism.

Keywords: crystallization, non-isothermal kinetics, poly(ethylene oxide)

Introduction

The crystallization of low molecular mass poly(ethylene oxide) (PEO) has previously been studied by means of optical microscopy [1], isothermal methods in DSC [2–4], DSC with tri-block copolymers [5] and temperature-modulated calorimetry [6]. Studies on the crystallization of high molecular mass PEO have also been performed by using atomic force microscopy [7].

In the present work, the crystallization of high molecular mass PEO is studied by using non-isothermal DSC measurements at constant cooling rates, and the effect of blending with poly(bisphenol A-co-epichlorohydrin) (PBE) is investigated. Among various methods suggested in the literature [8], we chose to apply the one peak maximum evolution method (Kissinger method) and two isoconversional methods (Ozawa and Friedman methods).

Kissinger method

Kissinger [9] derives an expression (1) which makes it possible to calculate the activation energy of a process by analyzing DSC or DTA curves obtained at a number of heating or cooling rates, regardless of the reaction order:

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$$\frac{\mathrm{d}\left[\ln\left(\frac{\beta}{T_\mathrm{p}^2}\right)\right]}{\mathrm{d}\left(\frac{1}{T_\mathrm{p}}\right)}=-\frac{E}{R} \tag{1}$$

where β is the heating rate, T_p is the absolute temperature of the peak, E is the activation energy, and R is the gas constant. In this work, as the temperature was decreased, the limits of integration had to be changed and, instead of using $1/T_\mathrm{p}$ in Eq. (1), $-1/T_\mathrm{p}$ was used.

Some assumptions were made to derive Eq. (1): the reaction rate at the peak is maximum; the order of the reaction remains constant during the process; and the integral of the expression that describes the reaction rate was approximated, dropping the terms after the second in a converging series.

Ozawa method

Ozawa proposes an extension of the Avrami equation (2) to non-isothermal conditions [10, 11]:

$$-\ln(1-\alpha)=Zt^{\mathrm{n}} \tag{2}$$

where α is the crystallized fraction, t is time, Z is a constant, and n is the Avrami exponent, related to nucleation and growth dimension.

From Eq. (2), the non-isothermal Eq. (3) is derived, and Avrami's exponent can be determined:

$$\ln(-\ln(1-\alpha))=\ln\chi(T)-n\ln\beta \tag{3}$$

where T is the absolute temperature, $\chi(T)$ is the cooling crystallization function, and β is the cooling rate.

Friedman method

Adopting the suppositions that crystallization is a single-step reaction and that the rate constant obeys the Arrhenius law, Friedman [8] proposed an isoconversional method for kinetic studies involving the use of DSC measurements, which is described by Eq. (4).

$$\ln\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)_\alpha=\ln(QA_\alpha f(\alpha))-\frac{E_\alpha}{RT_\alpha} \tag{4}$$

where R is the gas constant, A_α is the pre-exponential factor at a given conversion, E_α is the activation energy at a given conversion, $(\mathrm{d}H/\mathrm{d}t)_\alpha$ is the heat flux at a given conversion, T_α is the absolute temperature at a given conversion and Q is the total heat of reaction.

Equation (4) allows determination of the different activation energies for each degree of conversion directly from the DSC data, without a knowledge of the conversion function and is not restricted to use of the linear cooling rate.

Materials and methods

Films of high molecular mass PEO (Fig. 1a) with MW=4·10^6 g mol^{-1} and d=1.19 g ml^{-1}, provided by Aldrich, were cast from methyl ethyl ketone (MEK) on glass plates. Blends of PEO with 20% PBE (Fig. 1b), EPON® 1004, with d=1.19 g ml^{-1}, epoxy-equivalent 800–950 g equiv^{-1}, donated by Shell Chemical, were prepared by co-dissolution of the polymers in MEK and casting on glass plates.

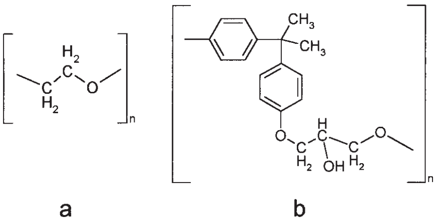

Fig. 1 Chemical structures of (a) PEO and (b) PBE

Optical micrographs of the samples were taken in an Olympus BX-50 microscope, using polarized light.

Preliminary DSC scans were performed with a DuPont 2000 DSC. The temperature program for these scans contains an isotherm at 100°C during 5 min, followed by quenching to –100°C with liquid nitrogen, and a ramp of 20°C min^{-1} to 100°C. T_g, T_m and ΔH_m were determined by using a second heating scan.

A Perkin Elmer DSC7 instrument was used for the kinetic study. The samples were maintained at 100°C during 5 min and then cooled at constant rates to 0°C. Multiple scans were made with cooling rates of 15, 10, 7.5, 5, 2.5 and 1°C min^{-1}.

Preliminary results

The optical micrographs (Fig. 2) reveal PEO spherulites occupying all of the observed field of the microscope in both samples. A slight modification in the morphology of the crystals is observed, with the presence of bigger crystals in the blend as a consequence of the presence of the amorphous polymer (PBE). The surface seems to be cracked in both cases, which may be due to a volumetric shrinkage during crystallization, as described by Phillips and Manson [12].

The preliminary DSC analysis (Table 1) demonstrates the presence of a single glass transition and a lower temperature of melting for the blend, which indicates its miscibility. The enthalpy of melting (ΔH_m) of the blend is smaller than that of pure PEO. This occurs partly because of the lower crystallizable material content in the blend, and partly because of the effect of PBE, preventing the crystallization of PEO.

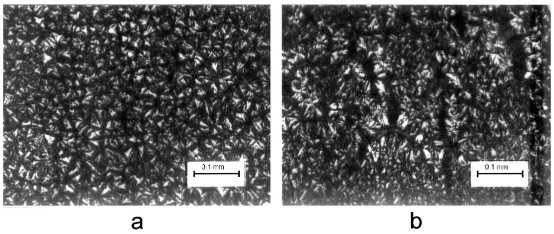

Fig. 2 Optical micrograps of (a) pure PEO and (b) 20 wt% PBE blend

Table 1 Preliminary DSC results for the samples under study

Sample	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	Crystallinity/%	
				total	corrected
PEO	–59	69	132	70	70
Blend	–50	66	94	50	63

Results and discussion

Figures 3 and 4 show DSC plots for the process of crystallization of PEO (Fig. 3) and of the blend (Fig. 4), at different cooling rates. There is a shift in the temperature of the peak to higher values when the cooling rate is decreased. This behaviour occurs because the samples are closer to thermal equilibrium at lower cooling rates.

The shapes of the peaks in Figs 3 and 4, especially at higher cooling rates, indicate that there may be a superposition of crystallization peaks due to the occurrence of more than one mechanism for the process; however, this feature was neglected in this study.

From the DSC curves at the same cooling rate for the two samples, it can be observed that the peak temperature is shifted to lower values as the amount of PEO is decreased. This shift can be interpreted in terms of slower crystallization in the blend, indicating that it is more difficult for its crystals to nucleate and grow.

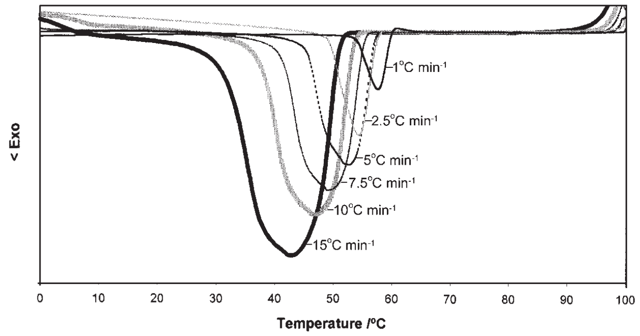

Fig. 3 DSC plots for the process of crystallization of pure PEO at cooling rates of 15, 10, 7.5, 5, 2.5 and 1°C min^{-1}

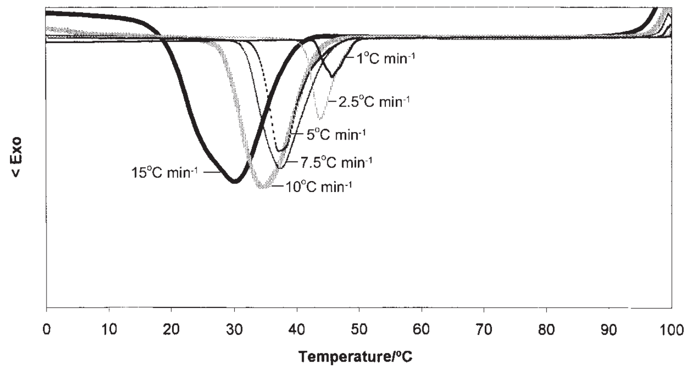

Fig. 4 DSC plots for the process of crystallization of 20 wt% PBE blend at cooling rates of 15, 10, 7.5, 5, 2.5 and 1°C min^{-1}

Integration of the DSC curves leads to plots of the degree of conversion *vs.* temperature for each cooling rate (Fig. 5) showing their typical S shape.

Kissinger plots of $\ln(\beta/T_p^2)$ *vs.* $-1/T_p$ are shown in Fig. 6a and 6b. Ozawa plots were made for temperatures varying from 330 to 315 K (pure PEO) and from 322 to 308 K (blend) (Fig. 7). The results do not converge to parallel straight lines. Thus, the Avrami exponents were calculated as the average of the slopes for each set of curves. In this way, the physical meaning was lost, and this procedure is useful only as a tool for comparison between the two samples.

Friedman analysis was conducted, considering $\alpha=0.5$ and plotting $\ln(dH/dt)$ *vs.* $1/T$, as shown in Fig. 8.

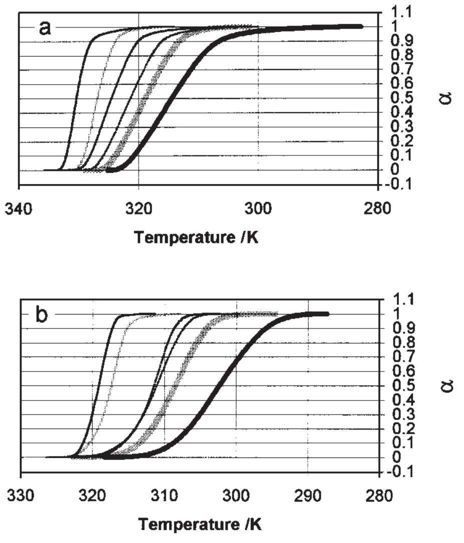

Fig. 5 Plots of the degree of conversion (α) as a function of cooling rate for (a) pure PEO and (b) 20 wt% PBE blend

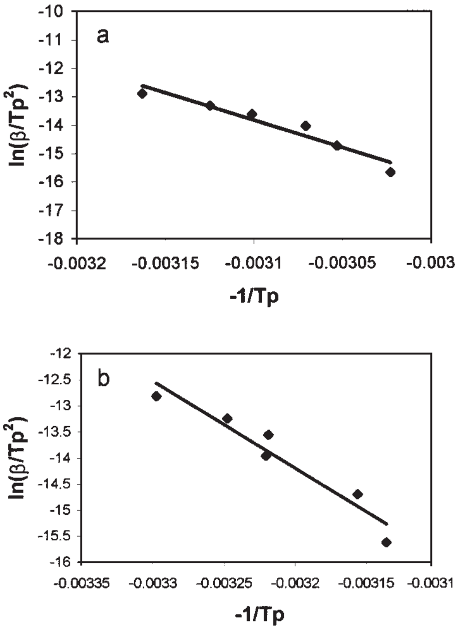

Fig. 6 Kissinger plots of ln(β)/T_p^2 as a function of (–1/T_p) for (a) pure PEO and (b) 20 wt% PBE blend

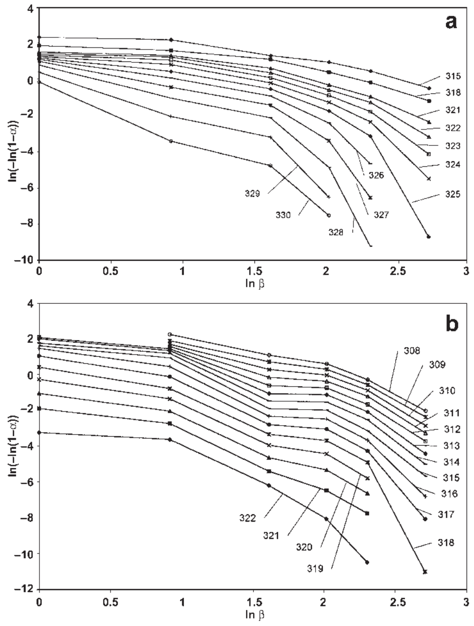

Fig. 7 Plots of ln(–ln(1–α)) as a function of lnβ for (a) pure PEO at different temperatures and (b) 20wt% PBE blend at different temperatures. Used in the Ozawa analysis

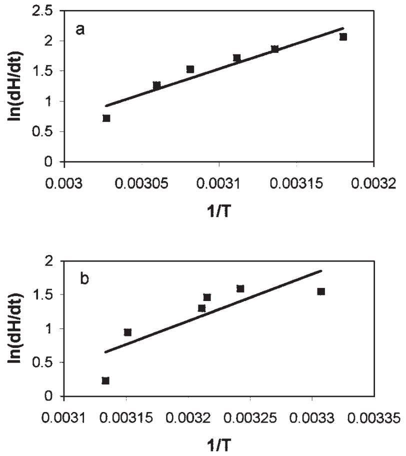

Fig. 8 Plots of ln(d*H*/d*t*) as a function of 1/*T* for (a) pure PEO and (b) 20 wt% PBE blend. α=0.5. Used in the Friedman analysis

Table 2 Kinetic parameters of crystallization calculated using the three methods proposed

Sample	Method		
	Kissinger	Ozawa	Friedman (α=0.5)
PEO	E_a=161 kJ mol^{-1}	n_{av}=1.5	E_a=69.5 kJ mol^{-1}
Blend	E_a=138 kJ mol^{-1}	n_{av}=2.6	E_a=57.4 kJ mol^{-1}

The results of the three methods of analysis are presented in Table 2. These results show that the kinetic parameters of crystallization vary with the composition of the sample. The different values obtained for n_{av} with the method of Ozawa indicate a change in the mechanism of the process of crystallization.

It is important to note that the activation energy values obtained from the Kissinger and Friedman methods, using the same raw data, are very different. This difference is attributed to the initial assumptions for each method and the choice of the kinetic model applied to perform the calculations in each case. Ortega [13] describes the same behaviour in kinetic calculations when TG curves are used. Although different for the two methods, the activation energies indicate a constant ratio between PEO and the blend for the two methods, indicating that they converge to similar results, differing only by a constant factor.

Conclusions

There are differences in the crystallization of PEO as a pure polymer and as a blend containing 20% of PBE, indicating that the amorphous polymer alters the rate and mechanism of the process. In the system under study, this is a complex process, dependent on the temperature and degree of conversion. It is also important to define the kinetic model to be used, as different assumptions lead to different results.

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