

Crystallization Kinetics of Poly(ethylene Terephthalate). III. Effect of Moisture on the Crystallization Behavior of PET from the Glassy State

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INTRODUCTION

The crystallization kinetics of poly(ethylene terephthalate) (PET) has been studied as a function of various parameters affecting the molecular structure of the polymer.¹⁻⁷ The effects of physical factors such as the previous melt history,² additives and nucleating agents,⁶ the extrusion conditions,⁸ and orientation⁹ on the crystallization behavior of PET have been documented.

PET is known to be a hygroscopic thermoplastic. The water absorption characteristics of PET and their effects on orientation and physical properties were previously studied.¹⁰ Very little has been documented concerning the effects of moisture on the crystallization kinetics of PET. The present investigation was undertaken in order to establish the effects of moisture content on the crystallization behavior of PET from the glassy state.

EXPERIMENTAL

Poly(ethylene terephthalate) material used for this study was supplied by Eastman in the form of an amorphous sheet of 10 mils thickness and 0.68 IV. The IV (inherent viscosity) was measured in 60/40 phenol/tetrachloroethane at 25°C using a Cannon-Ubbelohde dilution viscometer. Samples were stored at room temperature in chambers having different relative humidity in order to achieve different moisture levels as was described previously.¹⁰ Percent moisture absorbed was measured by weighing.

Isothermal crystallization from the glassy state was followed using the depolarized light intensity (DLI) technique. In this technique, the intensity of transmitted light from samples placed between crossed polaroids was measured by using an instrument similar to that described in the literature.^{11, 12}

The light scattering data were obtained by using a laser, small-angle, photographic, light scattering apparatus which has been described earlier.^{12, 13}

RESULTS AND DISCUSSION

The variation of the half-time, $t_{1/2}$, and the induction time t_0 of crystallization with percent moisture at various crystallization temperatures are given in Figures 1 and 2. It is seen that the moisture content affects both of these parameters very strongly. The effects are larger at the higher crystallization temperatures. For example, the half-time at 120°C for the dry sample is 170 s,

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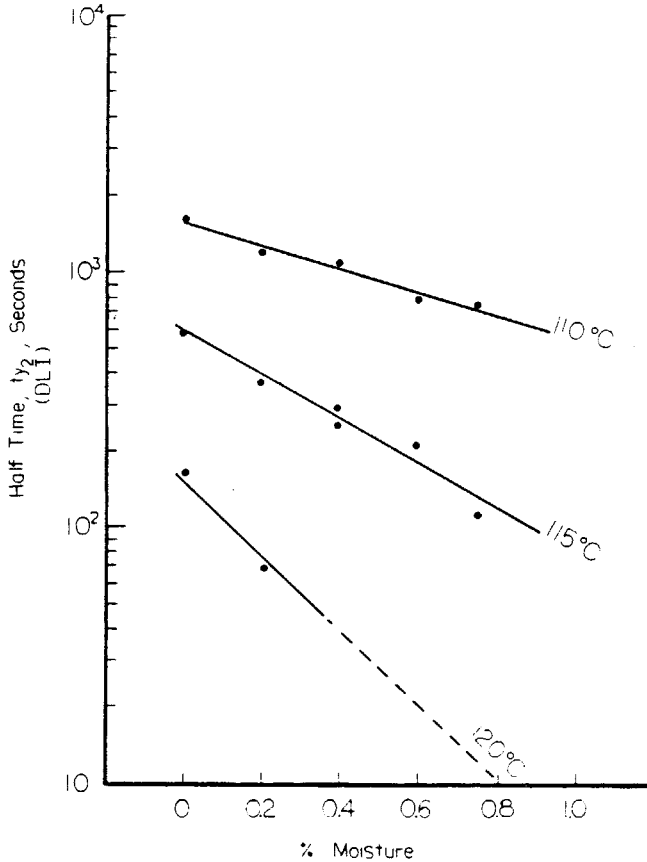


Fig. 1. Half-time of crystallization of PET ($IV = 0.68$) vs. percent moisture at various temperatures.

and it reduces to 70 s when the sample contains 0.2% moisture. Higher moisture content reduces the half-time to the order of a few seconds. Similar decrease in induction time with moisture has been observed for nylon 6.¹⁴

The crystallization isotherms at crystallization temperatures of 110 and 115°C are given in Figure 3 as a function of moisture content. In this figure, Θ_a is the fraction of uncrystallized material. The isotherms are sigmoidal in shape, typical of polymer crystallization behavior. It should be noted that these isotherms, for samples containing different amounts of moisture, can be superposed by shifting horizontally along the axis of $\ln(t)$, indicating similar crystallization mechanisms.

The crystallization kinetics of polymers are generally analyzed in terms of the Avrami expression:⁶

$$\Theta_a = e^{-kt} \quad (1)$$

where Θ_a is the fraction of untransformed material, k is the crystallization rate constant, t is the time, and n is the Avrami exponent describing the mechanism of crystallization.

Figure 4 shows a plot of the crystallization isotherms according to eq. (1). All lines exhibit the same slope, which indicates similar crystallization mecha-

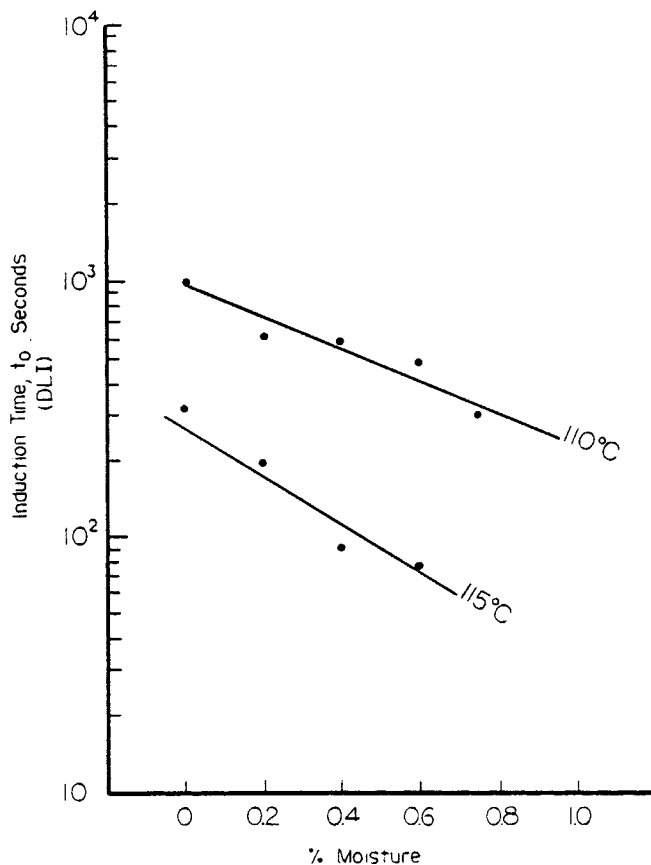


Fig. 2. Induction time of crystallization of PET ($IV = 0.68$) vs. percent moisture at various temperatures.

nism. In other words, the moisture does not change the nature of crystallization, only the rate.

Since all of the crystallization isotherms give the same Avrami exponent, $n = 2$, the half-time can be used directly⁷ to compare the rates of crystallization. From eq. (1), at half-time, the equation for the rate can be written as

$$k = 0.69 / (t_{1/2})^n \quad (2)$$

At 115°C, the half-time for dry samples is 600 s and that for 0.6% moisture is 200 s. Therefore,

$$R = k_{0.6} / k_0 = 9 \quad (3)$$

In other words, the rate for the wet samples is nine times greater than the dry sample when crystallizing at 115°C.

The overall rate of crystallization k is composed of two quantities: the spherulite growth rate G and the nucleation rate \bar{N} . In order to determine the relative contribution of the growth rate and nucleation rate to the overall rate of crystallization, another independent method is needed. For this purpose,

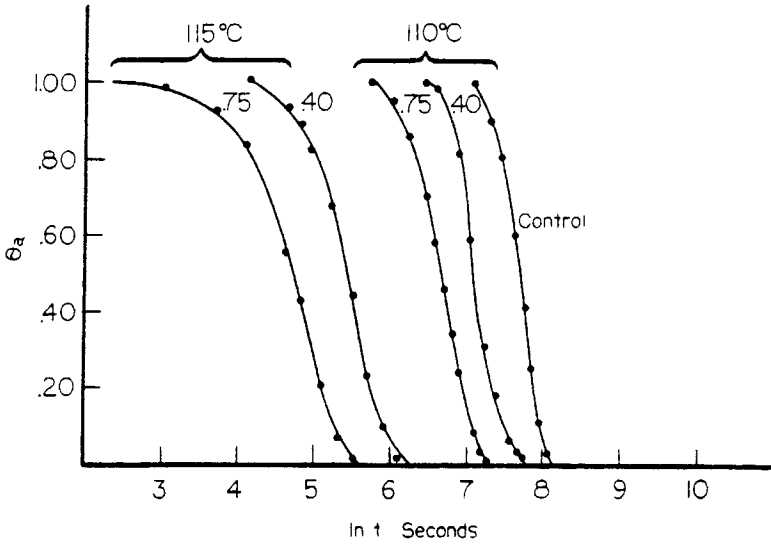


Fig. 3. Crystallization of PET (IV = 0.68) as a function of moisture content and various crystallization temperatures.

the spherulite radius was determined by light scattering as a function of crystallization time. Figure 5 gives the spherulite radius in microns as a function of time (s) at 110 °C for wet and dry samples. The spherulite growth rate is the slope of the line. It is seen that the growth rate is the same for dry and wet samples. Therefore, the increase in the overall rate of crystallization of wet samples results from an increase in the rate of nucleation.

In the process of polymer crystallization, two steps are usually required: formation of nuclei which are thermodynamically stable after they reach a

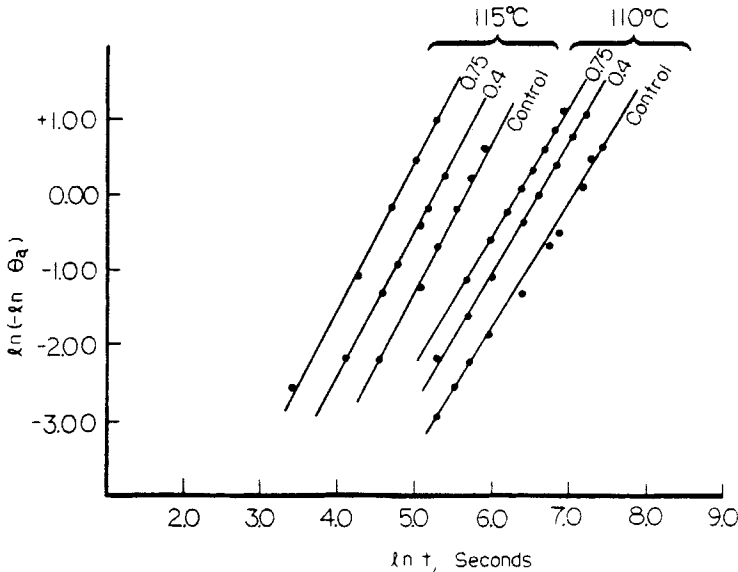


Fig. 4. Avrami plot of PET (IV = 0.68) as a function of moisture contents and crystallization temperatures.

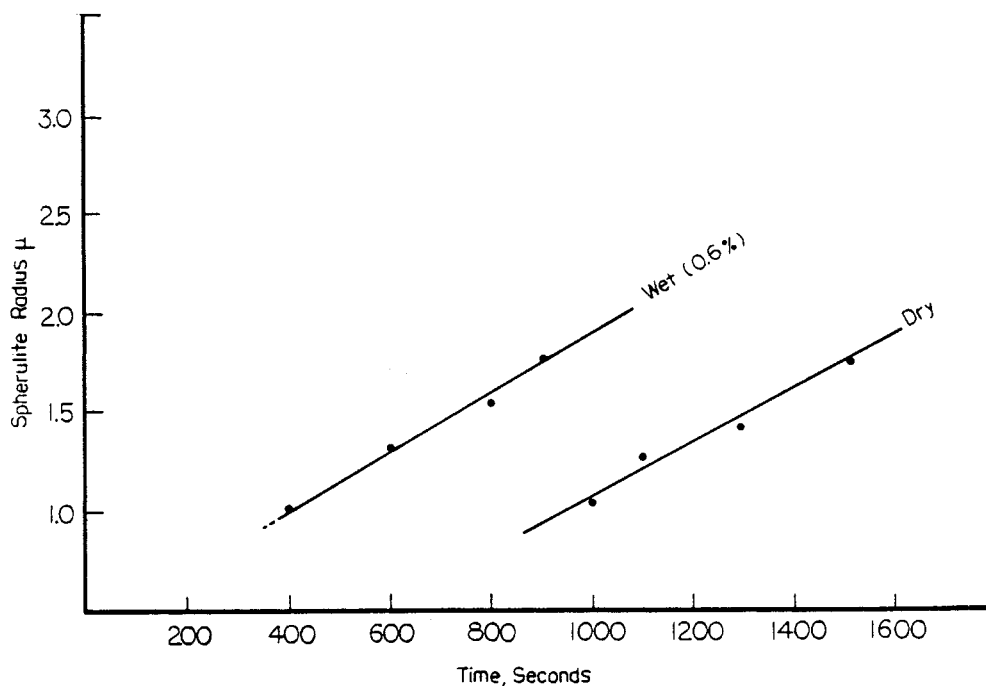


Fig. 5. Radial growth rate of PET ($IV = 0.68$) at 110°C for dry and wet samples.

critical size and the growth of these nuclei to form spherulites. The effect of moisture on the crystallization appears to have the following effect. Absorbed water causes a plasticizing effect, as seen by the decrease in the glass transition temperature T_g ,¹⁰ thus causing an increase in the frequency of formation of more stable nuclei which grow into spherulites. Once the nuclei are formed they grow at the same rate.

CONCLUSIONS

1. The half-time and the induction time of crystallization decrease significantly with increasing moisture content.
2. At crystallization temperatures of about 120°C , small amounts of moisture exhibit a very significant effect on the rate of crystallization.
3. Spherulite growth rate appears to be independent of moisture. However, the nucleation rate increases significantly with moisture.
4. The increase in the overall rate of crystallization of wet samples is primarily due to an increase in the nucleation rate.

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