

Influence of Solvent Precipitation on the Isothermal and Non-isothermal Crystallization Behavior of Nylon 6,6

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Abstract

A semi-crystalline Nylon 6, 6 was widely used in many engineering applications due to its excellent mechanical strength, dimensional stability at elevated temperature, chemical resistance and other advantages. In practical processing such as extrusion, molding and film forming, crystallization usually proceeds under isothermal and non-isothermal conditions. In this study, the effect of solvent precipitation on the crystallization behavior and morphology of nylon 6, 6 was studied. Analysis of isothermal and non-isothermal crystallization kinetics of nylon 66 was carried out by using DSC. Isothermal crystallization of nylon 6, 6 by the solvent precipitation process fit the Avrami equation, and non-isothermal crystallization of nylon 6, 6 fit Mo method. These results suggest that polymer entanglements in solution also affect the crystallization behavior and morphology of the solvent-precipitated nylon 6,6.

Theory

$X(t) = 1 - \exp(-Kt^n) \rightarrow \lg\{-\ln[1 - X(t)]\} = n \lg t + \lg K$ $X(t)$ is relative crystallization, t is crystallization time

Avrami equation

Avrami equation can be used to analyze the isothermal crystallization process, the slope n is Avrami exponent and the intercept K is the crystallization parameter.

The crystallization half-time $t_{1/2}$ is defined as the time at which the extent of crystallization is completed 50% and determined from the measured kinetics parameter. $\rightarrow t_{1/2} = (\frac{\ln 2}{K})^{1/n}$
 $t_{Max} = (\frac{n-1}{nK})^{1/n}$, $t_{1/2}$ is the crystallization half-time, t_{Max} is the necessary time for maximum crystallization, $G = \tau_{1/2}^{-1} = (t_{1/2})^{-1}$ is the rate of crystallization.

Ozawa equation

$1 - C(t) = \exp[-K(T)/\Phi^m]$ $\lg\{-\ln[1 - C(T)]\} = -m \lg \Phi + \lg K(T)$, Φ is cooling rate

MO method

Combined Avrami equation and Ozawa equation, $\lg Z_t + n \lg t = \lg K(T) - m \lg \Phi$ Let $F(T) = \{K(T)/Z_t\}^{1/m}$, $a = n/m$ $\rightarrow \lg \Phi = \lg F(T) - a \lg t$

Experimental

Neat Nylon-6,6 was dissolved in concentrated formic acid solution at room temperature.

The formic acid solution-Nylon-6,6 was dried in a oven at 80°C.

The sample was swollen in distilled deionized water some hours or some days.

The sample was dried by vacuum oven at 80°C 24 h before DSC test.

The sample was heated quickly to 300°C, stayed 10mins, then cooled (-80 °C/min to 6 different temperature for isothermal in the range of 229-239°C, and 6 different cooling rate (2.5 · 5 · 10 · 20 · 30 · 40 °C/min) test non-isothermal crystallization process.

Results And Discussion

Isothermal Crystallization Kinetic Analysis

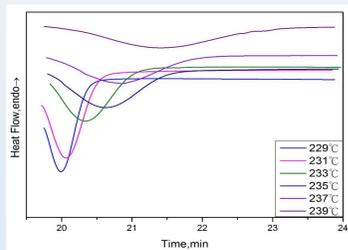


Figure 1 Heat flow versus time during isothermal crystallization of solvent-precipitated Nylon-6,6 at the different crystallization temperatures by DSC. The crystallization exothermic of solvent-precipitated Nylon-6,6 shifted to higher temperature and became smooth when the crystallization temperature was increased.

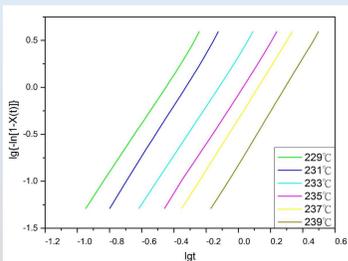


Figure 2 Plots of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ for isothermal crystallization at the indicated temperature of solvent-precipitated solvent-precipitated Nylon-6,6. was described by Avrami equation $n = 2.4 \sim 2.7$ and $K = 37 \sim 0.1835$, $t_{Max} = 0.19 \sim 1.58$ min, $t_{1/2} = 0.2 \sim 1.65$ min from 229°C to 239°C.

Nonisothermal Crystallization Kinetic Analysis

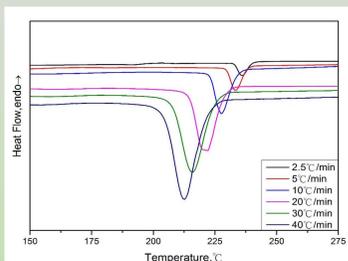


Figure 3 Heat flow versus temperature during non-isothermal crystallization of solvent-precipitated Nylon-6,6 at different cooling rates by DSC; The peak temperatures were shifted to low temperatures when the cooling rate increased.

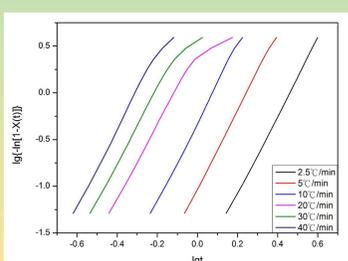


Figure 4 Plot of $\lg\{-\ln[1 - X(t)]\}$ versus $\lg t$ for the non-isothermal crystallization process of solvent-precipitated Nylon-6,6; was described by Avrami equation The values of primary stage n_1 are $3.5 \sim 4.3$, and the values of second stage n_2 are $1.06 \sim 2.45$.

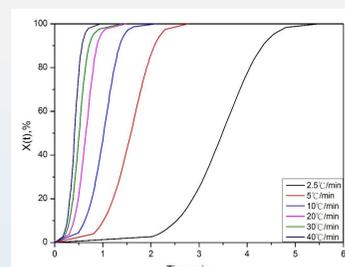


Figure 5 Relative crystallinity $X(t)$ at different crystallization times t in the process of non-isothermal crystallization for solvent-precipitated Nylon-6,6. The non-isothermal crystallization process of the time was short when the cooling rate was fast.

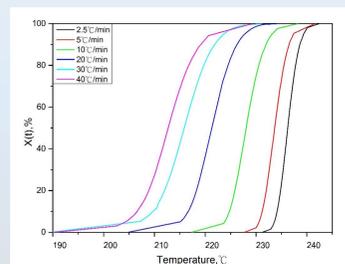


Figure 6 Relative crystallinity $X(t)$ at different crystallization temperature T in the process of non-isothermal crystallization for solvent-precipitated Nylon-6,6.

- The spherulites are impinged in the later stage, so the curves trended smooth and became S-shaped (or reversed S-shaped) in Fig. 5 and Fig. 6.

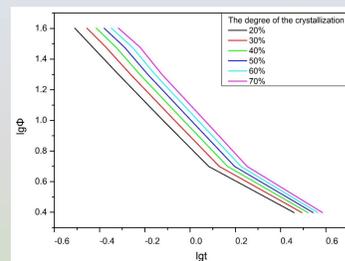


Figure 7 Plot $\lg \Phi$ versus $\lg t$ from the combined Avrami and Ozawa equation for solvent-precipitated Nylon-6,6, was described by Mo method, and the values of $F(T)$ and a were $7.9 \sim 13.96$ and $1.2 \sim 1.37$, the values of $F(T)$ increased, the cooling rate increased.

Conclusion

- The Avrami exponent $n=2.4 \sim 2.7$ in the isothermal crystallization process for solvent-precipitated Nylon-6,6, and the process of crystal nucleation and growth was two-dimensional, circular, diffusion-controlled process.
- In the non-isothermal crystallization process for solvent-precipitated Nylon-6,6, the primary stage was spherulites nucleation and growth, and the spherulites were impinged and crowded at the second stage, so the crystallization rate decreased; and the Avrami exponent of primary stage n_1 is $3.5 \sim 4.3$ and second stage n_2 is $1.06 \sim 2.45$.
- Fig. 7 showed that a high cooling rate should be obtained a higher degree of crystallinity at same crystallization time.