

# Effects of an Organic Phosphorus Nucleating Agent on Crystallization Behaviors and Mechanical Properties of Poly(propylene)

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Received 5 December 2001; revised 11 April 2002; accepted 11 April 2002

**ABSTRACT:** The effects of an organic phosphorus nucleating agent on the crystallization behavior and mechanical properties of poly(propylene) were investigated. As the concentration of nucleating agent increased from 0 to 0.8%, the tensile and flexural strengths of the nucleated poly(propylene) resin increased by 15%, the flexural modulus increased by 35%, the crystallization peak temperature increased by 10°C, and the nucleation density (calculated with

the nonlinear Volterra integral equation) increased by 10<sup>6</sup> times. Mechanical properties increased with nucleation density. Linear equations between the mechanical properties and the logarithmic nucleation density were revealed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 297–301, 2003

**Key words:** poly(propylene); crystallization; nucleation; mechanical properties

## INTRODUCTION

Recently, more and more attention has been focused on the study of crystallization of nucleated poly(propylene) for its excellent mechanical, optical, and processing properties. A great amount of research<sup>1, 2</sup> has been conducted on isothermal crystallization kinetics in search of the nucleation theory. However, there are two deficits in this past research: (1) most of research was focused on sorbitol derivatives, with little research on organic phosphorus nucleating agents, for its complex crystal structure; and (2) there has been little systemic research on the relation between mechanical properties and crystallization behaviors of nucleated poly(propylene), which is necessary for the improvement of mechanical properties and is the major aim of researching nucleated poly(propylene).

In this paper we investigated the effect of concentration of nucleating agent (NA-40) on the crystallization behavior and mechanicals properties of poly(propylene). Compared with virgin poly(propylene), the crystallization temperature of nucleated poly(propylene) can be improved by 10–20°C, the crystallization process cycle can be shorten by two times, the tensile and flexural strengths of poly(propylene) can be increased by 10–40%, and the transparency is increased. By simulating the crystallization differential scanning calorimetry (DSC) curve of poly(propylene)

with a nonlinear Volterra integral equation, nucleation density was calculated, and the correlation between mechanical properties and nucleation density was studied. Some new information on the process of crystallization of poly(propylene) has been obtained.

## EXPERIMENTAL

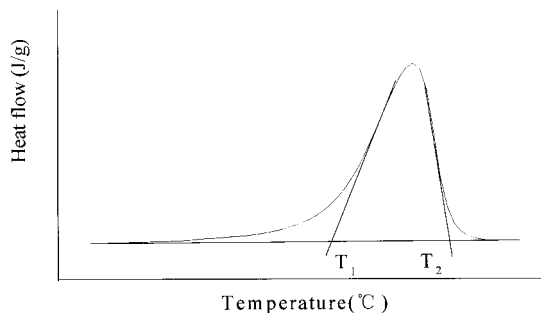
### Materials

A commercial grade homo-isotactic poly(propylene) PP-401 powder, without additives and with a melt index of 2.5 g/min, was supplied by Yangzi Petrochemical Company, Ltd. (China). A commercial grade homo-isotactic poly(propylene) PP-140 powder, without additives with a melt index of 13–15 g/min, was supplied by Jinlin Petrochemical Company, Ltd. (China). Nucleating agent NA-40 (12*H*-dibenzo [*d*,*g*][1,3,2] dioxaphosphocin,2,4,8,10-tetrakis (1,1-dimethylethy)-6-hydroxy-6-oxide, sodium salt) was prepared by reacting sodium hydroxide with the condensation of 2,2'-methylene-bis(4,6-di-butyl phenol) with phosphorus oxychloride, sodium salt. NA-40 has a melting point of >400°. Elemental analysis showed that NA-40 is composed of C68.37, H8.26, P6.2 in comparison with the calculated values from the chemical formula C<sub>29</sub>H<sub>41</sub>O<sub>4</sub>Pn<sub>a</sub>, which are C68.53, H8.26, P6.09, Na 4.52. The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra, measured in DMSO-d<sub>6</sub> at a frequency of 500 MHz, show chemical shifts at 1.32 (s,18H), 1.43 (s,18H), 3.42 (s,2H), 7.12 (d,2H), and 7.31 (d,2H) ppm.

### Preparation of nucleated poly(propylene)

Different amounts of NA-40 powder were dispersed in 1 kg of PP-140 powder in a high-speed mixer at a

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**Figure 1** Calculation of width of crystallization temperature area (WCTA).

rotating speed of 160 revolutions (rev)/min for 15 min. Next, the dispersion was allowed to dry in air for 48 h. The dry mixture was kneaded and extruded with a twin-screw extruder (Nanjing Rubber and Plastic Machinery Plant, China) with a vent at a kneader temperature of 190°C and an extruder temperature of 220°C. The strands produced by this procedure and water-cooling were cut into pellets of ~3 mm size with an automatic cutter.

#### Preparation of specimens and test of standard mechanical properties

Standard specimens were injection-molded in an injection molding machine at a cylinder temperature of 215° and an injection pressure of 55 MPa. Tensile strength was measured according to the ASTM D638-84, flexural modulus and strength were determined according to the ASTM D790-84a, and Charpy impact strength was assessed according to the ASTM D256-64.

#### Differential scanning calorimeter (DSC)

Isothermal crystallization behaviors were measured with a Perkin-Elmer DSC-4 calorimeter (Norwalk, CT) using a specimen (~7 mg) that was cut from a compression-molded film of 0.2–0.3-mm thickness. After melting the specimen at 200°C for 10 min, it was cooling at rates of 2, 4, 8, and 16°C/min until the end of crystallization. The kinetic parameters for eq. 6 were determined by Marquardt's nonlinear regression of the dynamic DSC data obtained from the crystallization conditions, without superposition of two competing processes.

The width of crystallization temperature area (WCTA) is the difference between the temperatures of the points where the tangent of the base and the curve intersect (WCTA =  $T_2 - T_1$ , as shown in Figure 1).

#### Calculation of crystallization kinetics

Avrami analysis is a useful and convenient tool to study the crystallization kinetics of a polymer. How-

ever, a fit between experiment and equation can be obtained only at a conversion of <30% because the equation does not compensate for the hindered crystal growth caused by the growth site impingement.<sup>3</sup>

For the purpose of resolving this problem, the theory of phase transition kinetics with growth site impingement was reported by Tobin.<sup>4</sup> The theory leads to nonlinear Volterra integral equations, which may be solved by iteration or by transformation to differential equations. For the cases of heterogeneous and homogeneous nucleation, the equation is expressed as follows:

$$\alpha'(t) = kNA \quad (1)$$

where  $\alpha'(t)$  is the relative crystallization rate,  $k$  is a constant that is determined by temperature,  $N$  is the initial number of nuclei, and  $A$  is the tangency area between spherulites and isotactic poly(propylene) (iPP) melt.<sup>5</sup>

$$k = k_0 \exp\left(-\frac{E_d}{RT}\right) \exp\left(-\frac{\Phi}{T(T_m^0 - T)}\right) \quad (2)$$

where  $k_0$  is a constant independent of temperature,  $E_d$  is the activation energy of diffusion of crystallizing segments across the phase boundary, and  $\Phi$  is a constant related to the free energy of formation of critical nucleus.

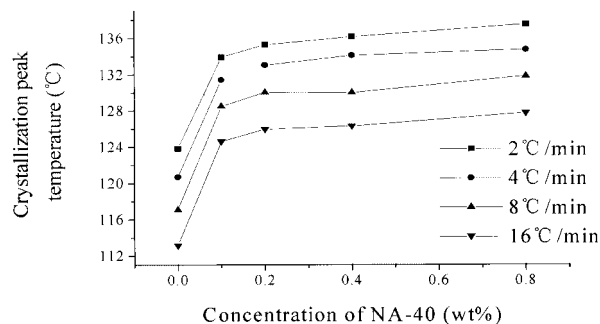
When the relative crystallization degree is small at a low cooling rate, and the impingement can be ignored,<sup>1, 6</sup> then eqs. 3–5 apply:

$$A = 4\pi r^2(1 - \alpha(t))^{3/2} \quad (3)$$

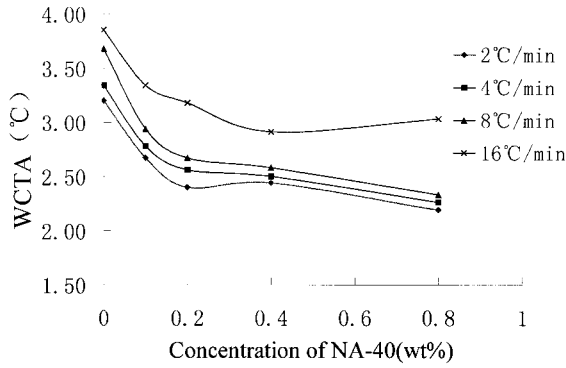
where  $r$  is the radius of spherulite, and  $\alpha(t)$  is relative crystallization degree;

$$r = r_0 vt \quad (4)$$

where  $r_0$  is the critical radius,  $v$  is radial growth rate, and  $t$  is crystallization time; and



**Figure 2** The effect of nucleating agent concentration on the crystallization peak temperature of PP-401.



**Figure 3** The effect of nucleating agent concentration on the WCTA of PP-401.

$$\nu = \nu_0 \exp\left(-\frac{E_d}{RT}\right) \exp\left(-\frac{\phi_l T_m^0}{T(T_m^0 - T)}\right) \quad (5)$$

where  $\nu_0$  is a universal constant of a semicrystalline polymer ( $\nu_0 \approx 7.5 \times 10^8 \mu\text{m/s}$ ).

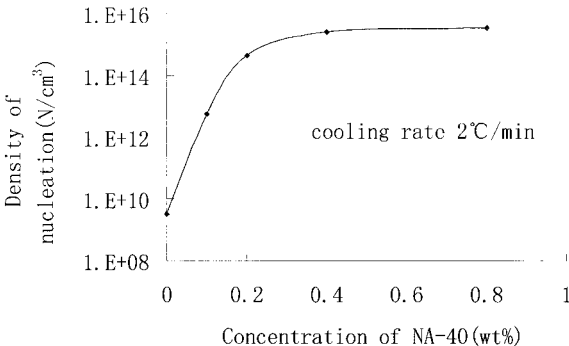
Substituting eqs. 2–5 into eq. 1, we find

$$\alpha'(t) = 4\pi N k_0 r_0^2 \nu_0 \exp\left(-\frac{3E_d}{RT}\right) \times \exp\left(-\frac{3\phi}{T(T_m^0 - T)}\right) t^2 (1 - \alpha(t))^{3/2} \quad (6)$$

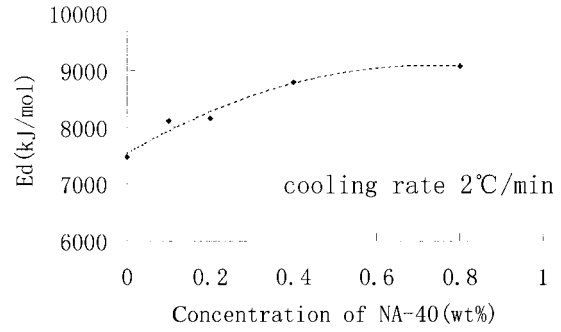
Equation 6 is similar to eq. 12 in the literature (shown here as eq. 7,<sup>7</sup>

$$\alpha'(t) = 4\pi N \nu_0^3 \exp\left(-\frac{3E_d}{RT}\right) \times \exp\left(-\frac{3\phi}{T(T_m^0 - T)}\right) t^2 (1 - \alpha(t))^2 \quad (7)$$

We can assume that  $k_0 r_0^2 = \nu_0^2$ , and therefore,



**Figure 4** The effect of nucleating agent concentration on the nucleation density of PP-401.



**Figure 5** The effect of nucleating agent concentration on the  $E_d$  of PP-401.

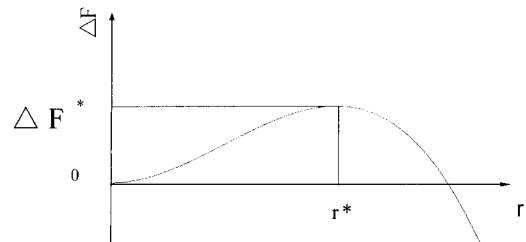
$$\alpha'(t) = 4\pi N \nu_0^3 \exp\left(-\frac{3E_d}{RT}\right) \times \exp\left(-\frac{3\phi}{T(T_m^0 - T)}\right) t^2 (1 - \alpha(t))^{3/2} \quad (8)$$

So, the value of  $N$  can be calculated from eq. 8.

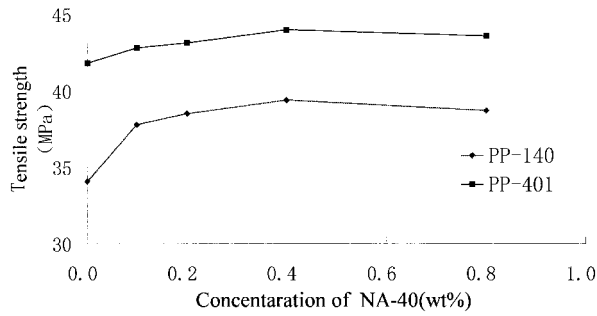
## RESULTS AND DISCUSSION

### Effect of NA-40 concentration on crystallization behavior

The crystallization peak temperature decreases with an increase of cooling rate and increases with rising the nucleating agent concentration, as shown in Figure 2. When the concentration of nucleating agent increases from 0 to 0.2%, the crystallization peak temperature rises  $\sim 10^\circ\text{C}$ . However, when the concentration is  $>0.2\%$ , the rising trend of the crystallization peak temperature is unremarkable, which suggests that 0.2% is probably a “saturated concentration”.<sup>1</sup> It is assumed that at concentrations greater than this saturated concentration, the nucleating agent agglomerates itself because the chance of impinging on a nucleating agent particle is too large. Too rapid cooling rate will increase the ratio of homogeneous crystallization to the overall crystallization, which will decrease the crystallization temperature and also broaden the range of crystallization temperature. As shown in Figure 3, the range of crystallization temperature widens with an increase of cooling rate and



**Figure 6** Graph of  $\Delta$  versus  $r$ .



**Figure 7** The effect of concentration of NA-40 on the tensile strength.

narrows with increase of concentration of NA-40. Accordingly, the addition of NA-40 can accelerate crystallization, as already discussed.

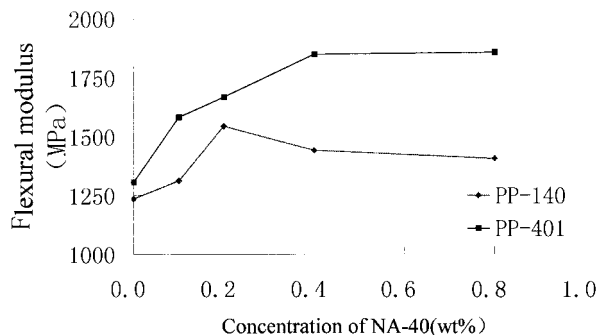
#### Effect of NA-40 concentration on crystallization kinetics

The results calculated with eq. 8 by simulating the Marquart's nonlinear multivariable regression method,<sup>8</sup> are shown in Figures 4 and 5. The nucleation density increases from  $10^9$  to  $10^{16}$  when the NA-40 concentration is increased from 0 to 0.8%, indicating that the addition of NA-40 increases the number of seeds (Figure 4). However, when the concentration is greater than the "saturated concentration", the nucleation density levels off because of the agglomeration of nucleating agent.

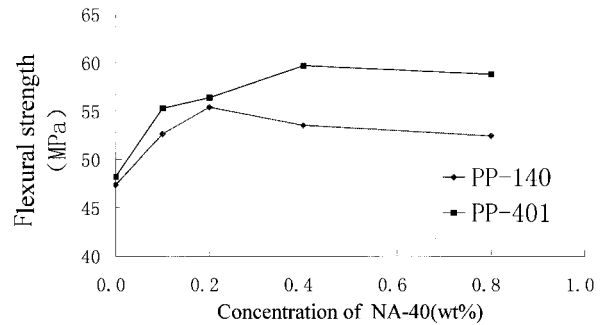
The free energy of forming a spherulite whose radius is  $r$  can be expressed as follows:

$$\Delta F = -\frac{4}{3}\pi r^3 \Delta f_v + 4\pi r^2 \gamma \quad (9)$$

where  $\Delta f_v$  is the free energy of the crystallization per unit volume and  $\gamma$  is the surface active energy per unit area. The function is graphed in Figure 6, where  $\Delta F^*$  is the critical free energy of nucleus, and  $r^*$  is the critical radius. When  $r > r^*$ , a smaller average radius will result in a larger free energy. This relationship ex-



**Figure 8** The effect of concentration of NA-40 on the flexural modulus.



**Figure 9** The effect of concentration of NA-40 on the flexural strength.

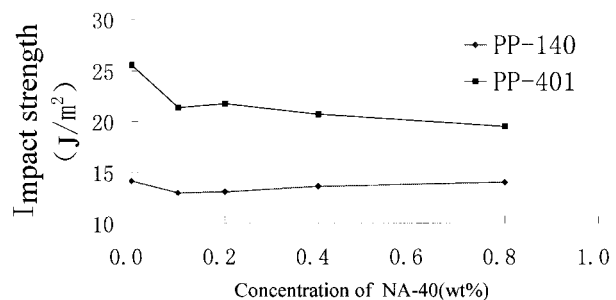
plains the fact that free energy ( $E_d$ ) rises with an increase of NA-40 concentration at a  $2^\circ/\text{min}$  cooling rate, as shown in Figure 5, because the increased concentration of NA-40 produces more nuclei, resulting in smaller spherulites.

#### Effect of NA-40 on mechanical properties of poly(propylene)

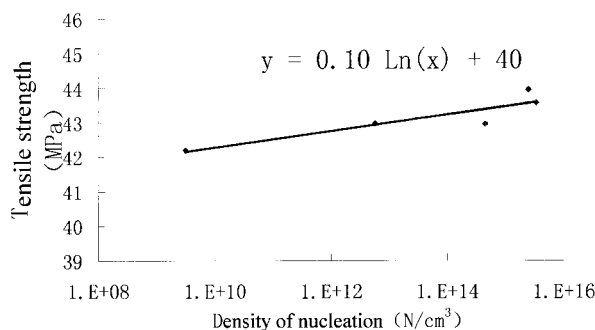
The results in Figures 7–10 show that addition of NA-40 at  $<0.2\text{--}0.4\%$  (by weight) improves the tensile and flexural properties of poly(propylene). Above this range of concentrations, there is little further increase in the mechanical properties, which may be because of the "saturated concentration". We can assume that spherulites would impinge on each other when the concentration of NA-40 is  $>0.4\%$ , so further addition of nucleating agent neither increases the number of nuclei or the degree of crystallization. Also, the addition of nucleating agent can improve impact strength by minimizing the size of the spherulites. However, the impact strength of the specimens in this study decreases with the addition of NA-40 because the size of NA-40 is too big.

#### Correlation between crystallization behavior and mechanical properties

Linear correlations exist between the nucleation density and mechanical properties, as shown in Figures 11–13. The common correlations are as follows:



**Figure 10** The effect of concentration of NA-40 on the impact strength.



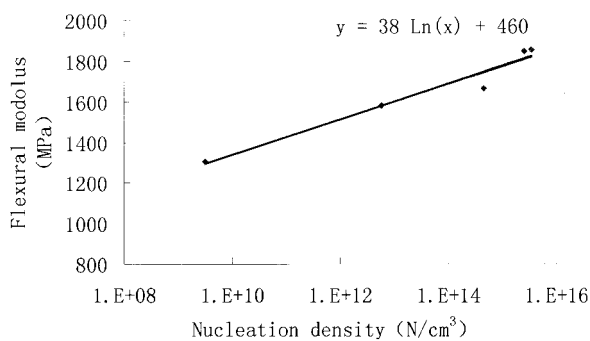
**Figure 11** The effect of nucleation density on the tensile strength of PP-401.

$$\sigma = k \ln(N) + b \quad (10)$$

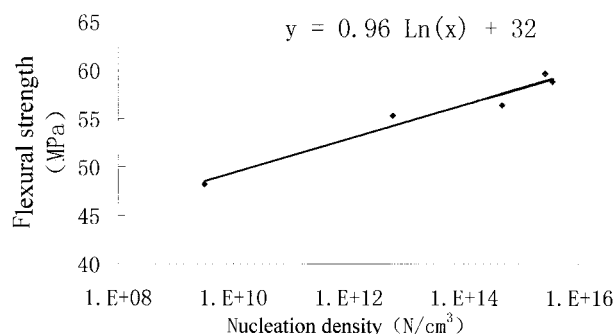
where  $\sigma$  represents the mechanical properties and  $N$  is the nucleation density. Equation 10 implies that spherulites may act as crossed networks, and  $k$  is a constant that reflects the cohesion between spherulites and amorphous compound. When  $N = 1$ , then  $\sigma = b$ , which implies that  $b$  is a theoretical value of  $\sigma$  of amorphous isotactic poly(propylene).

## CONCLUSIONS

With an increase in the concentration of NA-40 from 0 to 0.8%, the crystallization peak temperature of the resin rises from 125 to 137°C, and the range of crystallization temperature decreases from 4 to 3°C. Furthermore, nucleation density increases from  $10^9$  to  $10^{15}$  unit/cm<sup>3</sup> as NA-40 concentration is increased. The improvement in crystallization properties is unre-



**Figure 12** The effect of nucleation density on the flexural modulus of PP-401.



**Figure 13** The effect of nucleation density on the flexural strength of PP-401.

markable when the concentration of NA-40 is  $>0.2\%$ . Mechanical properties also increase with increasing NA-40 concentration: tensile and flexural properties increase by 20–40%.

Linear equations between the nucleation density and the mechanical properties exist. The mechanical properties increase with the increase of nucleation density. The correction can be expressed as follows:

$$\sigma_t = 0.10 \ln(N) + 40 \quad (11)$$

$$E = 38 \ln(N) + 460 \quad (12)$$

$$\sigma_f = 0.96 \ln(N) + 32 \quad (13)$$

where  $\sigma_t$ ,  $E$ ,  $\sigma_f$  are tensile intention, flexural modulus, and flexural strength, respectively, and  $N$  is the number of nuclei per unit volume.

The financial support for this work by the State Education Commission of China and China Petroleum and Chemical Corporation is gratefully acknowledged.

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