

The Effects of Alkaline Earth Dehydroabietate on the Crystallization Process of Polypropylene

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Received 12 June 2001; accepted 28 August 2001

ABSTRACT: In this article, the influence of alkaline earth dehydroabietates, which were prepared from Na-dehydroabietate, on crystallization of polypropylene (PP) from the melt state was studied by differential scanning calorimetry and polarization microscopy. It was found that magnesium dehydroabietate could improve mechanical properties and crystallization temperatures of PP and also decrease the size of spherulites. Kinetic analysis of PP isothermal crystallization showed that magnesium dehydroabietate decreased the fold surface energy of the developing crystals of PP and promoted the nucleation and crystallization of PP. However, calcium dehydroabietate increased the fold surface energy of the developing crystals of PP, but had no nucleation effect on PP. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2644–2651, 2002

Key words: polypropylene; nucleation; crystallization

INTRODUCTION

In the last few years, a new kind of rosin-type nucleating agent for polypropylene (PP), which can greatly improve the transparency of PP, was reported in several patents.^{1–3} Other than the conventional nucleating agents widely used before, this compound has a framework of phenanthrene, as shown in Figure 1. In our earlier works,⁴ the effects of alkali dehydroabietate on PP crystallization was studied and it was found that alkaline dehydroabietate increased the fold surface energy of the developing crystals of PP, but accelerated the overall crystallization rate of PP. In this article, the effects of alkaline earth dehydroabietate on the crystallization process of polypropylene were also studied, and the results were found that magnesium dehydroabietate de-

creases the fold surface energy and accelerates the overall crystallization rate of PP, meaning that magnesium dehydroabietate has a nucleating mechanism different from that of alkaline dehydroabietate.

Therefore, the study of effects of alkaline earth dehydroabietate on PP crystallization is meaningful to evaluate the effectiveness of rosin-type nucleating agent for application.

EXPERIMENTAL

Materials

Isotactic polypropylene (injection-molding grade, melting index 7.0 g/10 min) was obtained from Beijing Yansan Petroleum and Chemical Corp. Dehydroabietic acid (M_w 300, m.p. 173°C, UV 268 nm, 276 nm) was separated from disproportionated rosin (Wuzhou Rosin Plant, Guangxi, China) according to the usual procedure.⁵ Sodium dehydroabietate was prepared by reacting dehydroabietic acid with NaOH in ethanol according to our earlier works.⁴

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50043017.

Journal of Applied Polymer Science, Vol. 85, 2644–2651 (2002)
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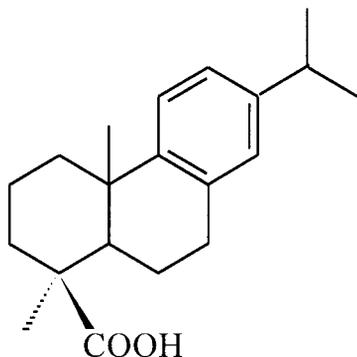


Figure 1 Structure of dehydroabietic acid.

Preparation

Preparation of Nucleating Agents

Magnesium dehydroabietate was prepared by reacting sodium dehydroabietate with MgSO_4 in H_2O ; the precipitation of magnesium dehydroabietate was separated and dried in vacuum. By the same method, calcium dehydroabietate was prepared by reacting sodium dehydroabietate with CaCl_2 in H_2O . For magnesium dehydroabietate and calcium dehydroabietate, they were ground into powder with a nominal particle size of $65 \mu\text{m}$ and marked as Nu-Mg and Nu-Na, respectively.

Preparation of PP Samples

PP powder was mixed with Nu-Mg and Nu-Ca in a $\Phi 30$ twin-screw extruder. The nucleated PP samples, marked as PP-Nu-Mg and PP-Nu-Ca, respectively, were dried and then injection molded into standard specimens in an injection-molding machine (SZ-160/68 NB) at 230°C .

Measurements

Differential Scanning Calorimeter (DSC)

A Perkin-Elmer differential scanning calorimeter, DSC-7, interfaced with a BBC-Master computer via analogue-to-digital converter, was used to detect the thermal transition and to monitor the rate of heat flow from samples during crystallization. A sample of $5 \pm 2 \text{ mg}$ was placed in a DSC pan and quickly heated at a rate of $80^\circ\text{C}/\text{min}$ to 230°C for 10 min to remove all memory of previous thermal and mechanical history.

To detect the crystallization temperatures of PP samples, this treatment was followed by cooling at a rate of $10^\circ\text{C}/\text{min}$ to room temperature to complete the crystallization.

In the experiments performed to study kinetics of isothermal crystallization, the samples were submitted to the same thermal treatment in melt state and then cooled at a rate of $200^\circ\text{C}/\text{min}$ to the appropriate crystallizing temperature, T_C . The rate of heat flow during the development of crystalline phase against time was recorded up to a vanishing thermal effect and analyzed according to the usual procedure to give the relative degree of crystallinity as a function of time.

Polarization Microscope (PLM)

Each PP sample, measuring 0.1 g, was placed in a nitrogen-atmosphere oven and melted at 230°C . Each PP sample was pressed between glass slides and coverslips and kept there for 10 min to remove all memory of previous thermal and mechanical history, and then quickly transferred to another thermal oven and kept at a constant temperature of 130°C for 0.5 h. After that, they were quenched in liquid nitrogen. The thickness of the PP samples was about $20 \mu\text{m}$. The morphology of spherulites was observed by a polarization microscope, Leica MPS30.

Mechanical Testing

The tensile and flexural testing was carried out on an universal tester (Instron 1122) on the basis of National Standard Testing Methods GB 1040-79 and GB 1042-79, respectively. The tensile strength was measured at a crosshead speed of $50 \text{ mm}/\text{min}$; the flexural strength and modulus were measured at a crosshead speed of $2 \text{ mm}/\text{min}$. The average values of at least five tests were reported. The notched impact strength was measured with an impact testing machine (CSI-137C) according to National Standard Testing Methods GB 1843-80.

RESULTS AND DISCUSSION

Mechanical Properties of Nucleated PP

The effects of nucleating agents on the mechanical properties of PP are shown in Table I.

The results showed PP-Nu-Ca had little improvement in mechanical properties compared to the pure PP; however, the mechanical properties of PP-Nu-Mg were improved substantially. Generally, the skin layer of PP was enhanced and size of spherulites was reduced through nucleation; the highly oriented skin layer and smaller spherulites resulted in the higher mechanical

Table I Mechanical Properties of Nucleated PP Samples

PP Samples	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Izod Impact Strength (J/m)
PP	39.4	44.1	1460	25.3
PP-Nu-Mg	44.7	58.9	2069	24.5
PP-Nu-Ca	40.1	45.5	1545	26.0

properties of PP.⁶⁻⁷ The results above indicated that Nu-Mg had a better nucleating effect on PP than Nu-Ca.

Crystallization Temperatures of PP Samples

Figure 2 shows DSC cooling curves of pure PP, PP-Nu-Mg, and PP-Nu-Ca at a rate of 10 °C/min.

An exothermic peak occurs at T_{CP} (crystallizing peak temperature) = 115.4, 127.8, and 113.9°C, for pure PP, PP-Nu-Mg, and PP-Nu-Ca, respectively. Compared with pure PP, the crystallization temperature of PP-Nu-Mg was increased 12.4°C. The larger T_{CP} values of PP-Nu-Mg indicate that the rate of crystallization increased with the addition of Nu-Mg. At the same time, the peak of PP-Nu-Mg became much sharper than that of pure PP. Thus, it can be concluded that magnesium dehydroabietate can act as an effective nucleating agent for PP. Oppositely, the T_{CP} of PP-Nu-Ca was decreased 1.5°C compared with pure PP. The decrease in T_{CP} indicates that calcium dehydroabietate has no nucleating effect on PP.

Kinetic Analysis of PP Crystallization

Isothermal crystallization of polymers can be described by the Avrami equation. The relative degree of crystallinity θ at time t is given by⁸:

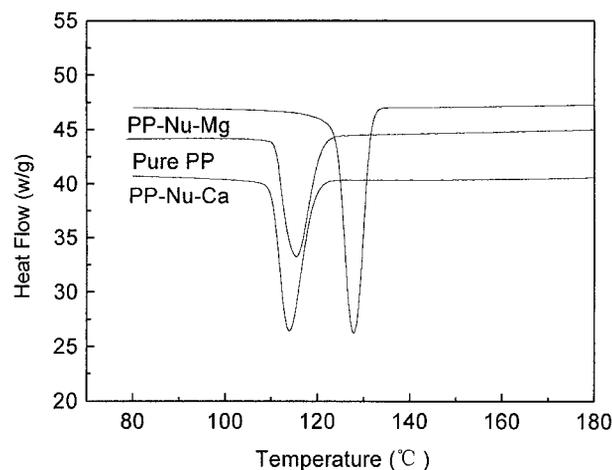


Figure 2 DSC cooling curves of pure PP, PP-Nu-Mg, and PP-Nu-Ca.

$$\theta = \frac{X_C(t)}{X_C(\infty)} = \int_0^t \frac{dH(t)}{dt} dt / \int_0^\infty \frac{dH(t)}{dt} dt \quad (1)$$

where $X_C(t)$ and $X_C(\infty)$ are the absolute degrees of crystallinity at time t and the completing crystallization time, respectively, and $dH(t)/dt$ is the rate of heat flow in the process of isothermal crystallization at time t . Time t was measured from the moment when the sample was cooled to the appropriate crystallization temperature. θ can also be obtained from the expression⁸⁻⁹

$$1 - \theta = \exp(-Kt^n) \quad (2)$$

$$\ln[-\ln(1 - \theta)] = n \ln t + \ln K \quad (3)$$

where n is the Avrami exponent, which is determined by the mode of crystal nucleation and the crystal growth geometry in actual circumstance, and K is the rate constant, which is also a function of nucleation and growth of crystals. The plot of $\ln[-\ln(1 - \theta)]$ against $\ln t$ is a straight line whose slope is n and its intercept on ordinate is $\ln K$.

Figure 3 shows curves of the relative degree of crystallization θ against time t for three PP samples. Figure 4 shows lines of $\ln[-\ln(1 - \theta)]$ versus $\ln t$.

When $\theta = 0.5$ in eq.(3), it gives out the data of crystallization half-time $t_{1/2}$, which is the time taken for 50% of the total crystallization to occur:

$$t_{1/2} = \left(\frac{\ln 2}{K} \right)^{1/n} \quad (4)$$

Results of $t_{1/2}$, n , and K are listed in Table II.

In the ideal state of heterogeneous nucleation of PP crystallization,⁸ n should be exactly 3. In the actual process of crystal growth, the real circumstance cannot satisfy the ideal state that the Avrami equation supposes it to have. In addition, the practical measurement is determined by both

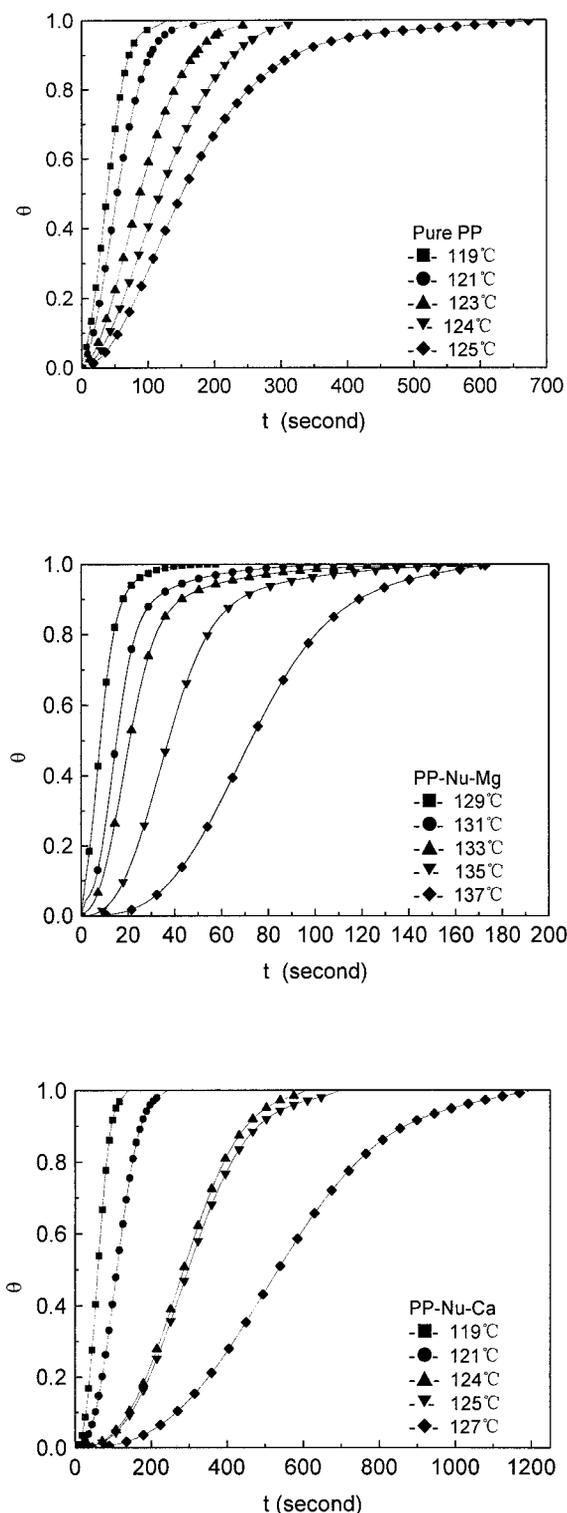


Figure 3 Curves of relative degree of crystallization θ versus time t .

the temperature and the thermal history of crystal growth.⁹

In Table I, the rate constant K decreases as temperature increases. Temperatures at which

isothermal crystallization was conducted are higher than that of the maximum rate of crystallization. Consequently, the higher the temperature of isothermal crystallization, the larger the distance from the temperature of the maximum

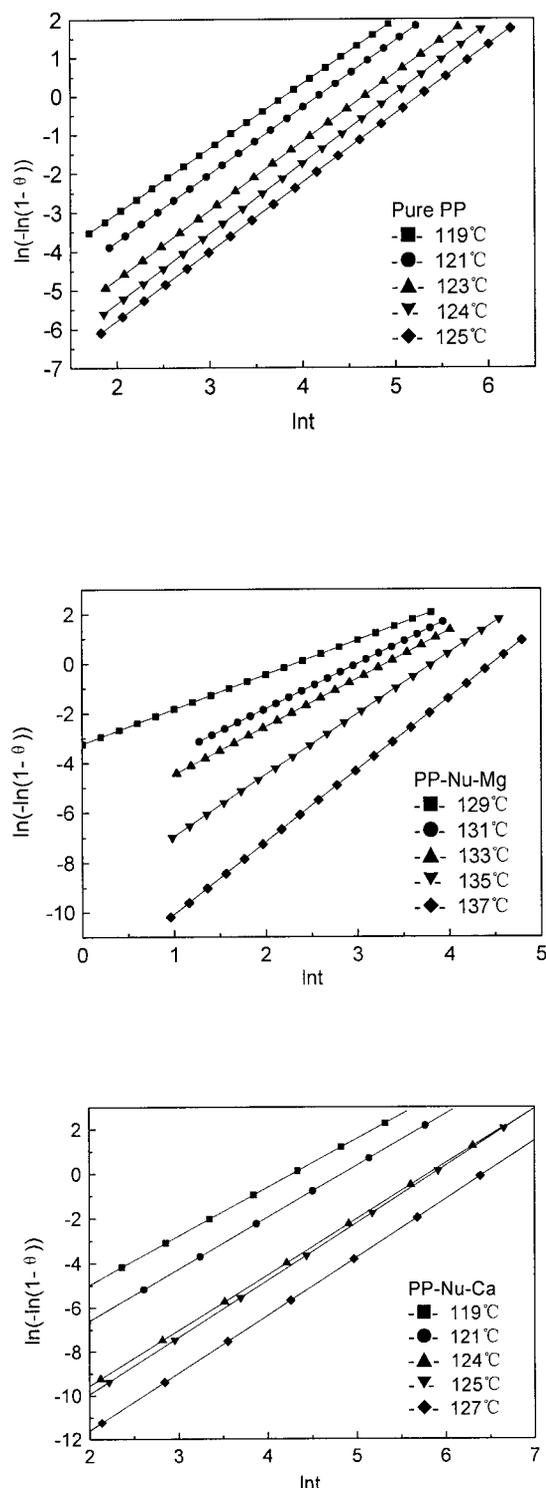


Figure 4 Curves of $\ln[-\ln(1-\theta)]$ versus $\ln t$.

Table II Avrami Values of n and K , $t_{1/2}$

Sample	T_C (°C)	n	K (second $^{-n}$)	$t_{1/2}^*$ (s)
Pure PP	119	1.7	1.71×10^{-3}	37
	121	1.7	0.73×10^{-3}	53
	123	1.8	0.26×10^{-3}	87
	124	1.8	0.13×10^{-3}	118
	125	1.8	0.09×10^{-3}	157
PP-Nu-Mg	129	1.4	3.86×10^{-2}	8
	131	1.8	0.42×10^{-2}	17
	133	1.9	0.16×10^{-2}	23
	135	2.5	0.81×10^{-4}	39
	137	2.9	0.23×10^{-5}	78
PP-Nu-Ca	119	2.4	3.07×10^{-5}	60
	121	2.5	5.46×10^{-6}	111
	124	2.6	2.81×10^{-7}	287
	125	2.6	1.89×10^{-7}	300
	127	2.7	3.78×10^{-8}	540

rate of crystallization and the lower the rate of crystallization.

Figure 5 shows the crystallization half-time $t_{1/2}$ versus temperature. The rate of crystallization of polymers can be estimated by the crystallization half-time, when the crystallization temperature is the same, or by the excessive cooling degree (ΔT) that the crystallization needs, when the rate of crystallization is the same (same crystallization half-time). The excessive cooling degree is defined as the difference between the equilibrium melting temperature (T_m^0) and crystallization temperature (T_C):

$$\Delta T = T_m^0 - T_C, \quad (5)$$

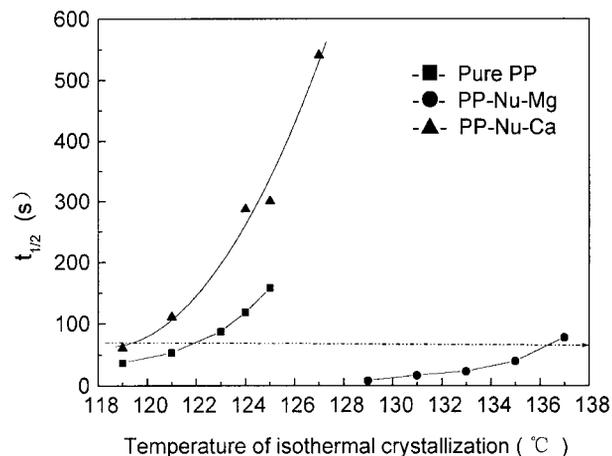


Figure 5 Curves of half-time of isothermal crystallization versus temperature.

The excessive cooling degree that the different samples need at the same rate of crystallization is different. The sample that needs smaller excessive cooling degree has a faster rate of crystallization if they crystallize at the same crystallization temperature. When $t_{1/2}$ of PP samples is 70 s, for pure PP, PP-Nu-Mg, and PP-Nu-Ca, T_C is 121.5, 136.4, and 119.0°C, respectively. Obviously, PP-Nu-Mg has the smallest excessive cooling degree; this indicates that Nu-Mg can accelerate the rate of crystallization for PP and acts as an effective nucleating agent of PP. Oppositely, Nu-Ca has a poorer nucleation effect on PP.

The Fold Surface Energy of the Developing Crystals

According to the Hoffman nucleation theory of isothermal crystallization, the dependence of growth rate G on crystallization temperature T_C and on excessive cooling degree ΔT is described by the following equation^{10–13}:

$$G = G_0 \exp\left[-\frac{U^*}{R(T_C - T_\infty)}\right] \exp\left(-\frac{K_g}{fT_C\Delta T}\right) \quad (6)$$

where G_0 is a preexponential factor containing quantities not strongly dependent on temperature, U^* is the activation energy of polymer segments transporting to the crystal front through the subcooled melt, R is the gas constant, T_∞ is a theoretical temperature at which all motion associated with viscous flow ceases, f is the correction factor for temperature dependence of heat of fu-

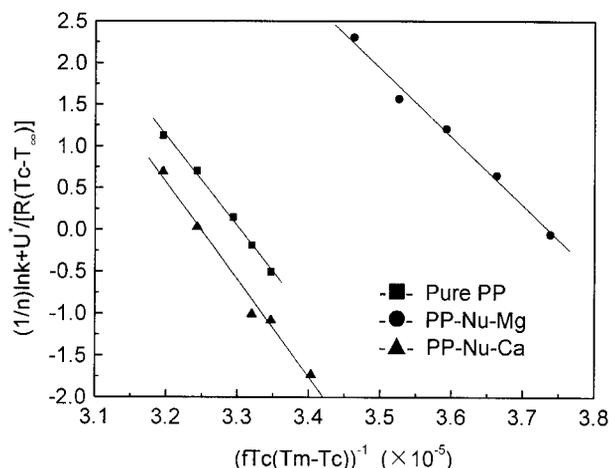


Figure 6 Curves of $1/n \ln K + U^*/[R(T_C - T_\infty)]$ versus $(fT_C \Delta T)^{-1}$.

sion, and K_g is a constant for a given growth regime.

According to the Avrami equation, it can be shown that¹⁴:

$$G \propto K^{1/n} \quad (7)$$

By combining eqs. (6) and (7) and after some rearrangements, it gives:

$$\frac{U^*}{R(T_C - T_\infty)} + \frac{1}{n} \ln K \propto - \frac{K_g}{fT_C \Delta T} \quad (8)$$

So, for a given growth regime, the plot of $1/n \ln K + U^*/[R(T_C - T_\infty)]$ against $(fT_C \Delta T)^{-1}$ is a straight line the slope of which gives the value of K_g . To analyze experimental results by using eq. (8), the following standard values were employed¹⁵: $U^* = 6270$ J/mol, $T_\infty = T_g - 30$ K = 239.6 K, $T_m^0 = 481$ K, and $f = 2T_C/(T_m^0 + T_C)$.

Figure 6 shows the curves of $1/n \ln K + U^*/[R(T_C - T_\infty)]$ versus $(fT_C \Delta T)^{-1}$ for the three PP samples.

K_g is the associated thermal dependence of growth rate upon $1/T_C \Delta T$:

$$K_g = \frac{C \sigma \sigma_e b_0 T_m^0}{K_b \Delta H_m^0} \quad (9)$$

where K_b is the Boltzmann's constant, b_0 is the thickness of surface monolayer, ΔH_m^0 is the theoretical heat of fusion per unit mass, σ and σ_e are

the lateral and fold surface energies of the developing crystals in PP bulk, respectively, C is a coefficient which is determined by the growth regime: $C = 4$ in Regimes I and III, and $C = 2$ in Regime II.¹⁶

Knowing the values of K_g from the slopes in Figure 6, the values of σ_e can be derived from eq. (9) with $T_m^0 = 481$ K, $b_0 = 6.56 \times 10^{-10}$ m, $\sigma = 8.79 \times 10^{-3}$ J/m², $\Delta H_m^0 = 134.0$ J/cm³, $C = 4$, and $U^* = 6270$ J/mol.¹⁵ The values of K_g and σ_e are listed in Table II.

For pure PP, PP-Nu-Mg, and PP-Nu-Ca, the fold surface energy is 0.180, 0.137, and 0.193 J/m², respectively. Obviously, Nu-Mg decreases the fold surface energy of the developing crystals in PP bulk.

Usually, an effective nucleating agent should decrease the interfacial surface energy. Nu-Mg decreases the fold surface energy, so it promotes the nucleation of PP and accelerates the overall crystallization rate of PP. At the same time, Nu-Ca increases the interfacial surface energy of PP somewhat, so it reduces the overall crystallization rate of PP.

Compared with our previous works, it can be found that magnesium dehydroabietate and alkaline dehydroabietate all accelerate the overall crystallization rate of PP, but the latter increases the fold surface energy of PP. This means magnesium dehydroabietate has a nucleating mechanism different from that of alkaline dehydroabietate. Magnesium dehydroabietate accelerates the overall crystallization rate of PP from promoting the nucleation; however, alkaline dehydroabietate does it largely from increasing number of nuclei. It could be proven by that the size of spherulites in PP-Nu-Na (15 μm)⁴ was far smaller than those in PP-Nu-Mg (150 μm).

PLM Photographs of PP Nucleated Samples

Figure 7 shows PLM photographs of PP samples. The average diameter of spherulites of pure PP, PP-Nu-Mg, and PP-Nu-Ca are 300, 150, and 300 μm , respectively. The size of spherulites is smallest when the nucleating agent Nu-Mg was added. It is well known that the spherulite will continue growing until it impinges on another spherulite and then stops augmentation, so the more the nuclei, the smaller the spherulite. The results above prove that Nu-Mg promoted the nucleation of PP.

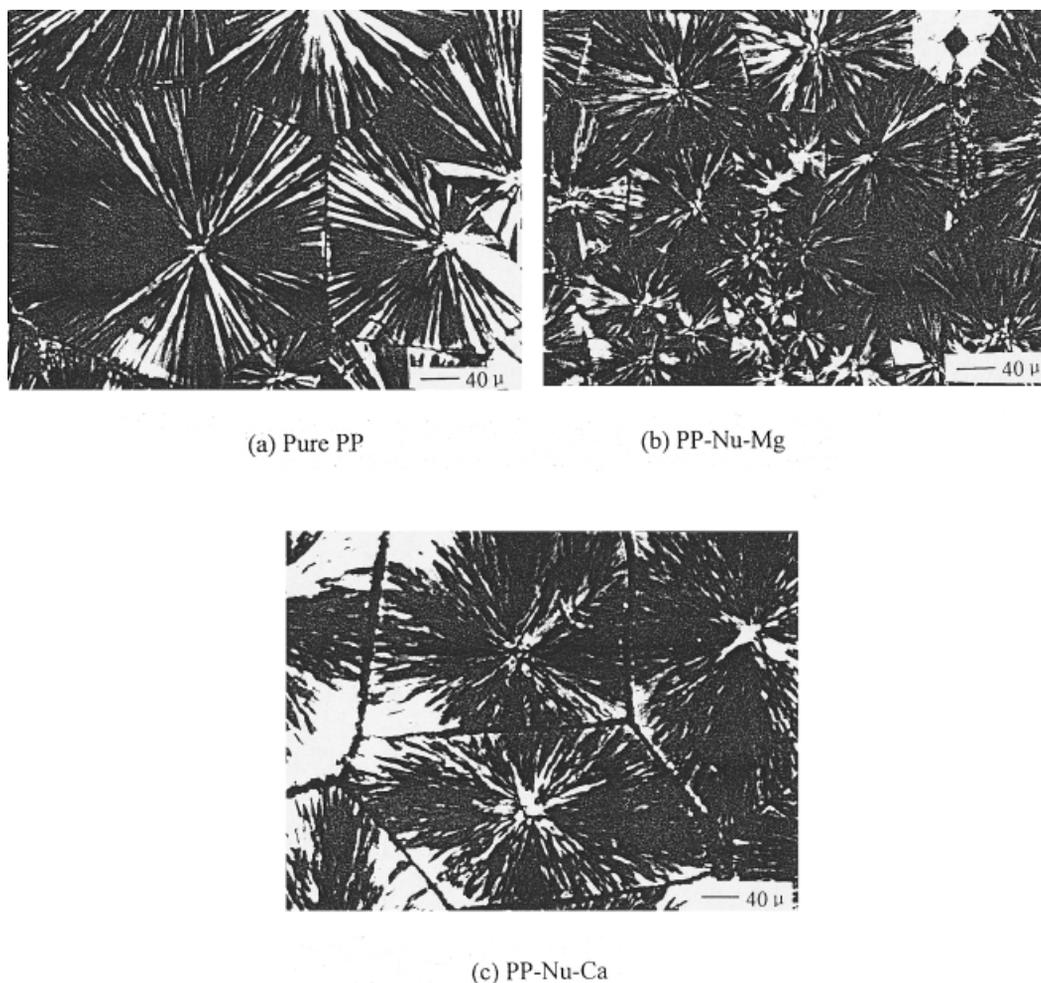


Figure 7 PLM micrographs of (a) pure PP, (b) PP-Nu-Mg, and (c) PP-Nu-Ca.

CONCLUSION

The rosin-type nucleating agent Nu-Mg substantially improves the mechanical properties and crystallization temperatures of PP and decreases the size of spherulites also. Kinetics analysis of PP isothermal crystallization proves that Nu-Mg decreases the fold surface energy and accelerates

the overall crystallization rate of PP. Therefore, Nu-Mg could act as an effective nucleating agent for PP. Oppositely, Nu-Ca increases the fold surface energy of PP and has no nucleation effect on PP.

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Table III Values of K_g and σ_e

Sample	K_g ($\times 10^6$ K ²)	σ_e (J/m ²)
Pure PP	1.08	0.180
PP-Nu-Mg	0.82	0.137
PP-Nu-Ca	1.16	0.193

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