

# Effects of Rosin-Type Cocrystal Nucleating Agents on the Crystallization Process and the Properties of Polypropylene

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**ABSTRACT:** A new kind of rosin-type nucleating agent for polypropylene (PP), the cocrystal of dehydroabietic acid, potassium dehydroabietate, and sodium dehydroabietate, was prepared, and the effects of the nucleating agents on the mechanical and crystallization properties of PP were also studied. The results of differential scanning calorimetry and X-ray diffraction proved that the cocrystal of dehydroabietic acid and compound alkali dehydroabietate was formed rather than a simple blend of dehydroabietic acid and single

alkali dehydroabietate. When it was added to PP, the size of the PP spherulite decreased; the mechanical properties, crystallization temperature, and transparency of PP were substantially improved. Thus, the cocrystal of dehydroabietic acid, potassium dehydroabietate, and sodium dehydroabietate acted as a more effective nucleating agent for PP. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2137–2141, 2003

**Key words:** poly(propylene) (PP); nucleation; crystallization

## INTRODUCTION

The crystallization and mechanical properties of polypropylene (PP) are related to its crystal structure. When PP is crystallized from a melt, it easily forms large spherulites, which leads to some negative effects on the crystallization process of PP.<sup>1</sup>

Nucleating agents are routinely used to accelerate the rate of crystallization and improve the mechanical and optical properties, by the reduction of spherulite size, in the crystallization process of PP. In the recent years, some new kinds of rosin-type nucleating agents for PP have been reported in several patents. In contrast to conventional nucleating agents used widely before, these nucleating agents have some advantages, such as low production cost, high nucleating efficiency, and no irritating odor.<sup>2–4</sup> In our earlier studies, we prepared some good nucleating agents from the cocrystal of dehydroabietic acid and single alkali dehydroabietate, which were easier to uniformly disperse in PP and which improved the properties of PP.<sup>5,6</sup> In further studies, we found that the cocrystal nucleating agent comprising dehydroabietic acid and compound alkali dehydroabietate was more easily dispersed in PP, so the crystallization and mechanical properties of PP were significantly improved.

## EXPERIMENTAL

### Materials

Isotactic PP (grade F401, melt index = 2.5 g/10 min, and density = 0.91 g cm<sup>-3</sup>) was supplied by Beijing Yansan Petroleum and Chemical Corp. (Beijing, China) Dehydroabietic acid (molecular weight = 300, melting temperature = 173°C, and ultraviolet wavelength = 268 and 276 nm) was separated from disproportionated rosin (Wuzhou Rosin Plant, Guangxi, China) according to the usual procedure;<sup>7</sup> the structure of dehydroabietic acid is shown in Figure 1.

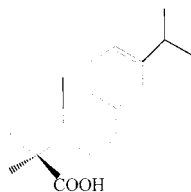
### Preparation

Preparation of the nucleating agents

A rosin-type nucleating agent was prepared by the reaction of 1 mol of dehydroabietic acid with 0.25 mol of potassium hydroxide and 0.15 mol of sodium dehydroabietate in ethanol to neutralize the acid to 40%; the mixture was then cocrystallized at 40°C. The cocrystal of dehydroabietic acid, potassium dehydroabietate, and sodium dehydroabietate was separated, dried in vacuum and was then ground into powder with a nominal particle size of 65 μm; it was marked as Nu-(K + Na). With the same method, 1 mol of dehydroabietic acid was reacted with 0.4 mol of potassium hydroxide or sodium dehydroabietate. The cocrystal of dehydroabietic acid and potassium dehydroabietate or sodium dehydroabietate was produced; these were marked as Nu-K and Nu-Na, respectively.

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**Figure 1** Structure of dehydroabietic acid.

### Preparation of the PP samples

PP powder was mixed with 0.6 wt % Nu-Na, Nu-K, and Nu-(K + Na) in a SHJ-30  $\Phi$ 30 twin-screw extruder (Light Industry Machinery Mould Factory, Shanghai, China), respectively. The PP samples, which were marked as PP/Nu-Na, PP/Nu-K, and PP/Nu-(K + Na), were dried and injection-molded into standard specimens in an SZ-160/68NB injection-molding machine (Rubber Plastics Machinery Plant, Linzhou, China) at 230°C.

### Measurements

#### Differential scanning calorimetry (DSC)

A PerkinElmer differential scanning calorimeter (DSC-7, USA) interfaced with a BBC-Master computer via an analog-to-digital converter was used to detect the thermal transition and to monitor the rate of heat flow from the samples during crystallization. The more detailed test method was described in previous articles.<sup>6</sup>

#### X-ray diffraction (XRD)

A Rigaku (Japan) D/max-RB X-ray diffractometer was used to characterize the patterns of the nucleating agents from 3 to 35°. The operation parameters were Cu K $\alpha$  radiation, a generator voltage of 40 kV, and a current of 100 mA. The scanning rate was 2°/min, and the diffraction intensity was automatically recorded.

#### Mechanical testing

Both tensile testing and flexural testing were carried out on a universal tester (Instron 1122, UK) on the basis of National Standard Testing Methods GB1040-79 and GB1042-79, respectively. The tensile strength was measured at a crosshead speed of 50 mm/min; the flexural strength and modulus were measured at a crosshead speed of 2 mm/min. The average values of at least five tests and the standard deviations are reported. The notched impact strength was measured with an impact testing machine (CBI-137C, USA) according to National Standard Testing Method GB1843-80.

### Haze measurement

The nucleated PP samples were injection-molded into a 1 mm thick sheet in an SZ-160/68 NB injection-molding machine (Rubber Plastics Machinery Plant, Liuzhou, China) at 230°C. The haze was measured by a WGT-S hazemeter (Precision & Scientific Instrument Co. Ltd., Shanghai, China) according to National Standard Testing Methods GB 2410-80, and the average values of at least five tests and the standard deviations are reported.

### Polarizing light microscopy (PLM)

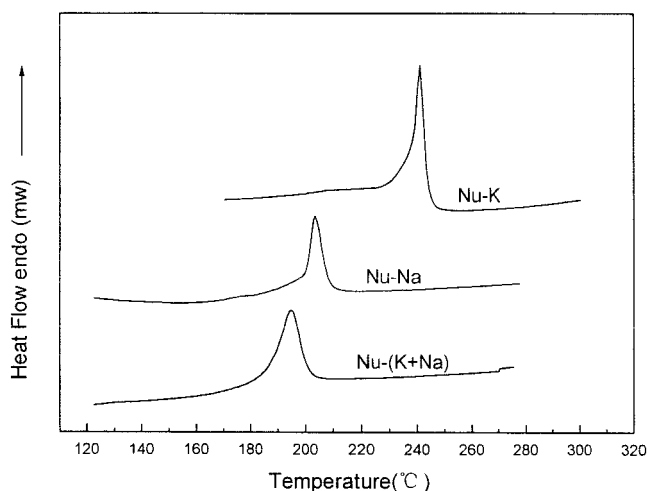
Each PP sample (0.1 g) was placed on a hot stage and melted at 230°C. Each PP sample was pressed between glass slides and cover slips and kept there for 10 min to remove all the memory of its previous thermal and mechanical history and was then quickly transferred to another hot stage and kept at a constant temperature of 130°C for 1 h. After that, the sample was quenched in liquid nitrogen. The thickness of the PP samples was about 20  $\mu$ m. The morphology of the spherulites was observed with a polarizing microscope (Leica MPS30, Germany).

## RESULTS AND DISCUSSION

### Melting points of the nucleating agents

Figure 2 shows the curves of Nu-Na, Nu-K, and Nu-(K + Na) at a heating rate of 10°C/min.

The melting points of Nu-Na and Nu-K were 203.6 and 241.2°C, respectively; the single melting points meant that the cocrystal of dehydroabietic acid and alkali dehydroabietate was formed.<sup>6</sup> Nu-(K + Na) had only one melting point at 194.9°C, which meant that Nu-(K + Na) was a unique phase and not a physical mixture of the two cocrystals, Nu-K and



**Figure 2** DSC curves of the nucleating agents.

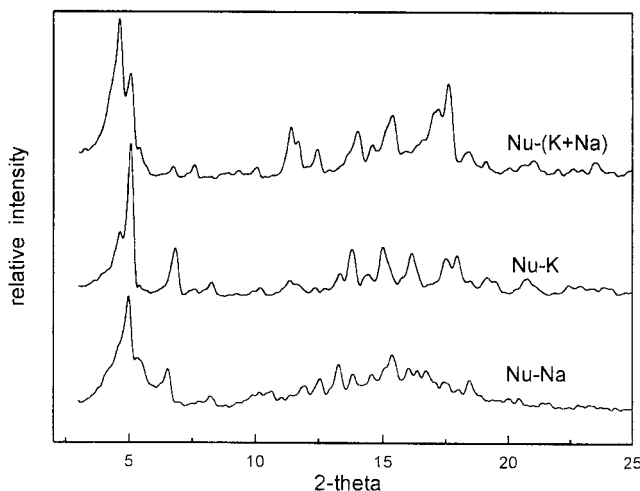


Figure 3 XRD patterns of the nucleating agents.

Nu-Na. Thus, we concluded that a new cocrystal of dehydroabiatic acid, potassium dehydroabietate, and sodium dehydroabietate was formed.

**XRD of nucleating agents**

The XRD patterns of the nucleating agents are shown in Figure 3.

As shown in Figure 3, the XRD pattern of Nu-Na contained two peaks at  $2\theta = 5.00$  and  $6.54^\circ$ ; Nu-K had three peaks at  $2\theta = 4.64$ ,  $5.08$ , and  $6.81^\circ$ , but the intensity of the diffraction peaks that appeared at  $2\theta = 4.64^\circ$  was very weak, which was only a shoulder peak near the main peak at  $2\theta = 5.08^\circ$ . The pattern of Nu-(K + Na) was not a simple overlap of that of Nu-K and Nu-Na; two new, sharp diffraction peaks appeared at  $2\theta = 4.66$  and  $5.11^\circ$ . This result also meant that a new cocrystal of dehydroabiatic acid, potassium dehydroabietate, and sodium dehydroabietate had formed.

**Mechanical properties of the PP samples**

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

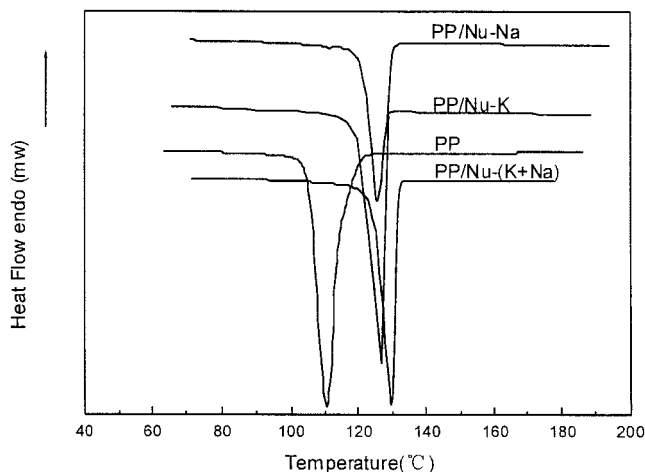


Figure 4 DSC curves of the PP samples.

The results showed that the addition of each nucleating agent to PP gave rise to an increase in its mechanical properties, especially the flexural modulus. Generally, the better the effect of a nucleating agent is, the thicker the high-oriented skin layer of PP will be, and the better the mechanical properties of the PP samples will be. When Nu-Na, Nu-K, and Nu-(K + Na) were added to PP, the flexural modulus of PP improved from 1457 to 1649, 1750, and 2020 MPa, respectively. It is obvious that the effect of Nu-(K + Na) was more noticeable than that of the others. Furthermore, the addition of Nu-(K + Na) increased the notched impact strength of PP from 20.8 to 23.9 J/m. This was because Nu-(K + Na) had a better distribution in PP, it decreased the size of spherulites greatly, and the interaction between the PP matrix and Nu-(K + Na) was enhanced; thus, the notched impact strength increased.

**Crystallization temperatures ( $T_c$ 's) of the PP samples**

Figure 4 shows the DSC cooling curves of the PP samples at a cooling rate of  $10^\circ\text{C}/\text{min}$ .

TABLE I  
Mechanical Properties of The Nucleated PP Samples

	PP sample			
	PP	PP/Nu-Na	PP/Nu-K	PP/Nu-(K + Na)
Tensile strength (MPa)	35.9	40.2	40.7	41.3
Standard deviation	0.780	0.731	0.970	0.707
Flexural strength (MPa)	36.6	38.1	40.8	45.3
Standard deviation	0.781	1.09	0.772	0.361
Flexural modulus (MPa)	1457	1659	1750	2020
Standard deviation	25.8	25.7	22.5	27.5
Notched impact strength (J/m)	20.9	21.0	22.6	23.9
Standard deviation	1.54	1.44	0.525	0.862

**TABLE II**  
Haze Values of the PP Samples

Sample	Haze (%)	Standard deviation
PP	70	0.049
PP/Nu-Na	40	0.065
PP/Nu-K	31	0.045
PP/Nu-(K + Na)	24	0.066

Exothermic peaks occurred at  $T_c = 111, 125, 126,$  and  $129^\circ\text{C}$  for PP, PP/Nu-Na, PP/Nu-K, and PP/Nu-(K + Na), respectively. The crystallization process of pure PP was homogeneous nucleation. The intense thermal motion of the molecular chain segment made it difficult to form stable crystal nuclei at high temperatures, so its  $T_c$  was very low. When the cocrystal nucleating agents were added to PP, the crystallization of PP turned into heterogeneous nucleation. Because the melting points of the nucleating agents were higher than that of PP, stable crystal nuclei of PP could be formed on the nucleating agent surfaces at high temperatures; this led to an increase in the  $T_c$  of PP. In general, the higher the  $T_c$  is, the faster the crystallization rate will be. Compared with pure PP, the increase in  $T_c$  was  $18^\circ\text{C}$  for PP/Nu-(K + Na), which demonstrated that this nucleating agent improved the crystallization rate of PP remarkably. In addition, the exothermic peak of PP/Nu-(K + Na) became much sharper than that of the others; this also showed that the nucleating ability of Nu-(K + Na) was more notable.

### Transparency of the PP samples

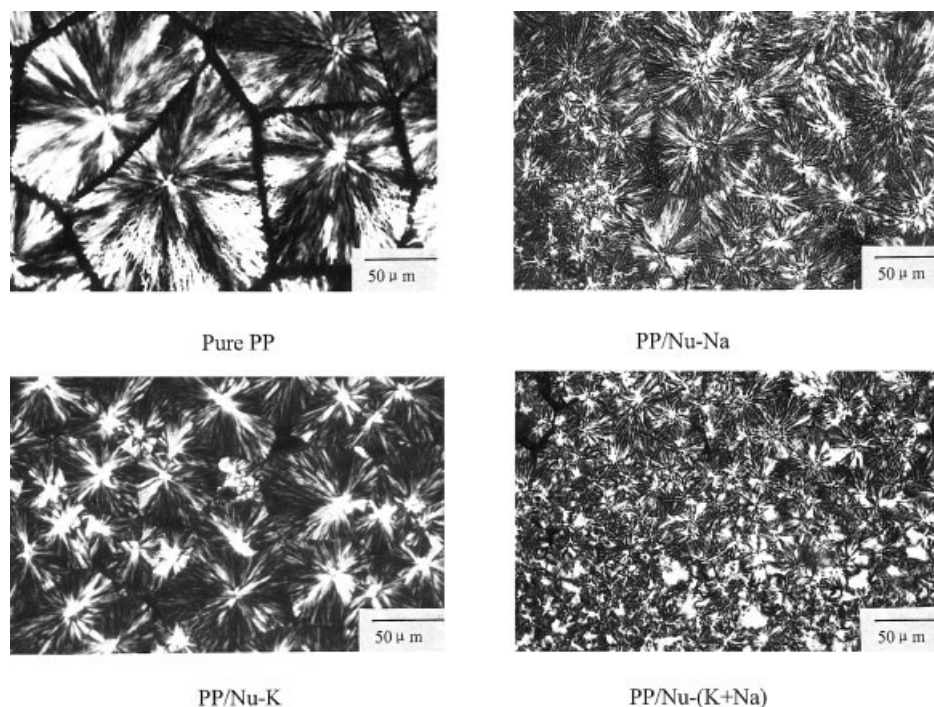
Table II lists haze values of PP, PP/Nu-Na, PP/Nu-K, and PP/Nu-(K + Na).

The haze value of pure PP was 70%; its transparency was worst among the four PP samples. When Nu-Na or Nu-K was added to PP, the transparency of PP was improved to some extent; with the addition of Nu-(K + Na), the haze value of PP decreased to 24%, and the PP specimens looked quite glossy. This result showed that the nucleating ability of Nu-(K + Na) was superior to those of Nu-Na and Nu-K. Because Nu-(K + Na) could disperse well in PP, it provided a larger number of heterogeneous nuclei; the size of the spherulites were much smaller than those in pure PP, PP/Nu-Na, and PP/Nu-K. When the light passed through the PP samples, the light scattering from the spherulitic interfaces decreased, so the transparency of PP increased. This was proven by PLM photographs.

### Morphological study of the PP samples

Figure 5 shows the PLM photographs of the PP samples.

For PP, the average diameter of the spherulites was  $200\ \mu\text{m}$ , and the spherulitic interface was very clear. The addition of Nu-Na or Nu-K reduced the average diameter of the spherulites to  $50\text{--}70\ \mu\text{m}$ , but the interface was still distinct; when Nu-(K + Na) was added to PP, the spherulites were as small as  $5\text{--}10\ \mu\text{m}$ , and the boundaries became blurry. This indicated that



**Figure 5** PLM photographs of the PP samples.

Nu-(K + Na) provided more heterogeneous nuclei; it had a better nucleating effect on PP than Nu-Na or Nu-K. These results agreed with the aforementioned results.

### CONCLUSIONS

Nu-(K + Na) was not a simple blend of Nu-Na and Nu-K because its melting point, crystal pattern, and  $T_c$  were different from those of the others. Meanwhile, the nucleating ability of Nu-(K + Na) was more notable because of its good dispersion. The addition of Nu-(K + Na) improved the flexural modulus, notched impact strength,  $T_c$ , and transparency of PP remark-

ably. Therefore, Nu-(K + Na) should be a promising nucleating agent for PP.

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