

# Effects of Rosin-Type Nucleating Agent on Polypropylene Crystallization

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**ABSTRACT:** In this investigation the effects of a rosin-type nucleating agent, which was prepared from cocrystallizing of dehydroabiatic acid and Na-dehydroabietate, on polypropylene (PP) crystallization were studied. The results of differential scanning calorimetry and X-ray diffraction proved that a cocrystal of dehydroabiatic acid and Na-dehydroabietate was formed. The lower melting point of the cocrystal caused it to be uniformly dispersed in PP. When cocrystals were added as nucleating agent, the mechanical properties, heat distortion temperature, and crystallization temperatures of PP were obviously improved, and the size of spherulites was also decreased. This proved that the cocrystals of dehydroabiatic acid and Na-dehydroabietate could act as an effective nucleating agent for PP. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1069–1073, 2002

**Key words:** polypropylene; rosin-type nucleating agent; cocrystal; crystallization

## INTRODUCTION

In the last few years, a new kind of rosin-type nucleating agent for PP, which can greatly improve the transparency of PP, was reported in several patents.<sup>1–3</sup> 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,<sup>4</sup> the effects of alkali dehydroabietate on polypropylene crystallization were investigated. Our further studies found that the nucleating agent prepared from cocrystallizing of dehydroabiatic acid and Na-dehydroabietate was easier to uniformly disperse in PP and significantly improved the properties of PP. Undoubtedly, the studies of effects of

a cocrystal nucleating agent on PP crystallization is meaningful to apply the rosin-type nucleating agent to PP.

## EXPERIMENTAL

### Materials

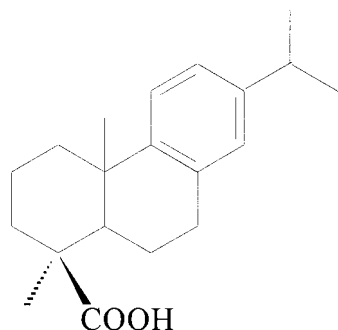
Isotactic polypropylene (injection-molding grade, melting index 7.0 g/10 min) was obtained from Beijing Yansan Petroleum and Chemical Corp. Dehydroabiatic acid (MW 300, m.p. 173°C, UV 268 nm, 276 nm) was separated from disproportionated rosin (Wuzhou Rosin Plant, Guangxi, China) according to the usual procedure.<sup>5</sup>

### Preparation of Nucleating Agents

Sodium dehydroabietate was prepared by reacting dehydroabiatic acid with NaOH in ethanol. Na-dehydroabietate and dehydroabiatic acid were dissolved in a water–ethanol mixture at 70°C,

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**Figure 1** Structure of dehydroabietic acid.

then cocrystallized at 40°C; the cocrystal of Na-dehydroabietate and dehydroabietic acid was separated and dried in vacuum to obtain the nucleating agent. Dehydroabietic acid, Na-dehydroabietate, blends of dehydroabietic acid and Na-dehydroabietate, and cocrystal of dehydroabietic acid and Na-dehydroabietate were ground into powder with a nominal particle size of 65  $\mu\text{m}$ , and marked as Nu1, Nu2, Nu3, and Nu4, respectively.

#### Preparation of PP Samples

PP powder was mixed with Nu1–Nu4 in a  $\Phi 30$  twin-screw extruder (SHJ-30, China), respectively. The nucleated PP samples, which were marked as PP–Nu1, PP–Nu2, PP–Nu3, and PP–Nu4, respectively, were dried and injection-molded into standard specimens in an injection-molding machine (SZ-160/68 NB).

#### Measurements

##### Differential Scanning Calorimetry (DSC)

A Perkin–Elmer differential scanning calorimeter (DSC-7; Perkin Elmer Cetus Instruments, Norwalk, CT) interfaced with a BBC-Master computer via analog-to-digital converter, was used to detect the thermal transition and to monitor the rate of heat flow from samples during crystallization. A  $5 \pm 2$  mg quantity of each PP sample was placed in a DSC pan and heated at a rate of 20°C/min under an atmosphere of circulating dry nitrogen. To detect the crystallization temperatures of PP samples, this treatment was followed by cooling at a rate of 10°C/min, from 230°C to room temperature to complete crystallization.

##### X-ray Diffraction (XRD)

X-ray diffraction data between 3.0 and 20° were recorded at 2°/min on a Japan D/max-RB 12-kW diffractometer using  $\text{CuK}\alpha$  radiation at a genera-

tor voltage of 40 kV and a generator current of 100 mA. Samples were powder.

##### Scanning Electron Microscopy

A 1-g sample of each PP was placed in a nitrogen-atmosphere thermal oven and melted at 230°C. Samples were kept for 10 min to remove all memory of previous thermal and mechanical history, and then quickly transferred to another thermal oven kept at a constant temperature of 131°C for 2 h. After that, they were quenched in liquid nitrogen, and  $\text{H}_2\text{SO}_4\text{--H}_2\text{O--CrO}_3$  was used to etch the samples. The surface morphology of spherulites was observed by a Hitachi scanning electron microscope (SEM S-530; Hitachi, Tokyo, Japan).

##### Mechanical Testing

Both tensile testing and flexural testing were carried out on a universal tester (Instron 1122) based on National Standard Testing Methods GB 1040-79 and GB 1042-79, 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 were reported.

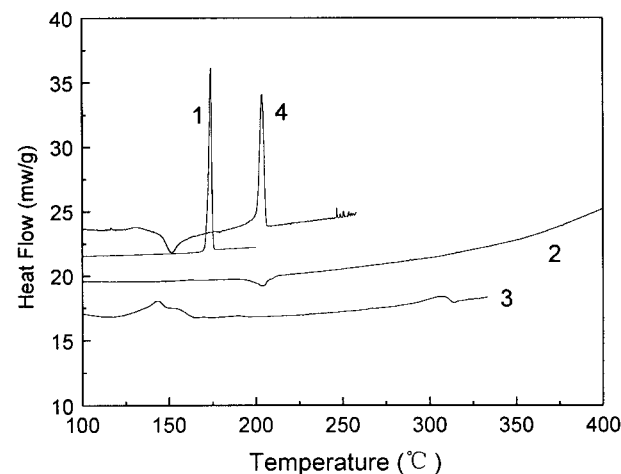
##### Heat Distortion Temperature (HDT)

HDT was measured with a heat distortion testing machine (RW-3, China) according to GB1634-79.

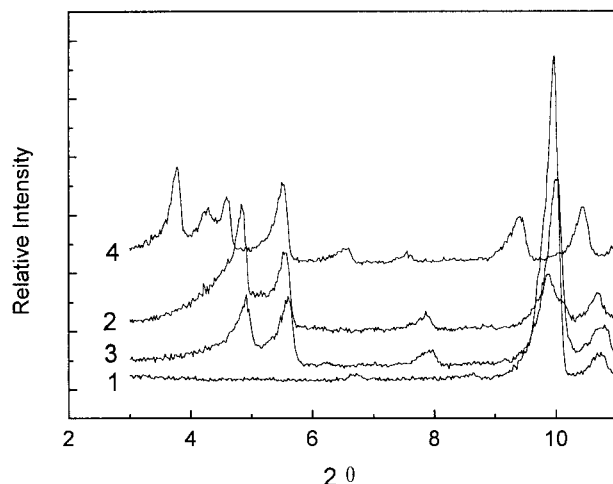
## RESULTS AND DISCUSSION

#### Melting Points of Nucleating Agents

Figure 2 shows DSC curves of Nu1, Nu2, Nu3, and Nu4 at a heating rate of 20°C/min.



**Figure 2** DSC curves of (1) Nu1, (2) Nu2, (3) Nu3, and (4) Nu4.



**Figure 3** XRD patterns of (1) Nu1, (2) Nu2, (3) Nu3, and (4) Nu4.

The melting point of Nu1 was 174.3°C; Nu2 did not melt below 300°C and began to decompose at 300°C; Nu3 had two melting points, 143.6 and 304.9°C, respectively; Nu4 had only one melting point at 203.7°C, which was different from that of Nu3. Thus, it can be concluded that the cocrystal of dehydroabietic acid and Na-dehydroabietate was formed.

#### XRD of Nucleating Agents

The X-ray diffraction patterns of Nu1, Nu2, Nu3, and Nu4 are shown in Figure 3.

The XRD pattern of Nu1 contained a peak at  $2\theta = 9.98^\circ$ ; Nu2 and Nu3 contained three peaks at  $2\theta = 4.86, 5.64,$  and  $10.02^\circ$ . The preceding results showed that the crystals of dehydroabietate acid and Na-dehydroabietate in Nu3 did not affect each other; the XRD pattern of Nu3 was only a simple overlap of that of Nu1 and Nu2. The XRD pattern of Nu4 contained four new peaks at  $2\theta = 3.80, 4.34, 4.62,$  and  $9.48^\circ$  compared to that of

Nu3; meanwhile the peaks at  $2\theta = 4.86$  and  $10.02^\circ$  disappeared. These results meant that the crystal structure of Nu4 was completely different from that of Nu1, Nu2, and Nu3; therefore, it can also be concluded that a cocrystal of dehydroabietic acid and Na-dehydroabietate was formed.

#### Mechanical Properties and HDT of Nucleated PP

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

The results show that PP–Nu1, PP–Nu2, and PP–Nu3 underwent only limited improvements in mechanical properties and HDT compared to that of pure PP, whereas the mechanical properties and HDT of PP–Nu4 were substantially improved. Generally, the skin layer of PP was enhanced through nucleation; the highly oriented skin layer resulted in the higher mechanical properties and HDT of PP.<sup>6,7</sup> Nu1 could be uniformly dispersed in PP, but it had poorer nucleating effect. Nu2 and Nu3 both had a higher melting point, although they were difficult to uniformly disperse in PP, which also affected the nucleating effects. Thus the mechanical properties and HDT of PP–Nu1, PP–Nu2, and PP–Nu3 experienced only slight improvements compared to that of pure PP. The preceding results showed that, among the four nucleating agents, Nu4 had the best nucleating effect on PP.

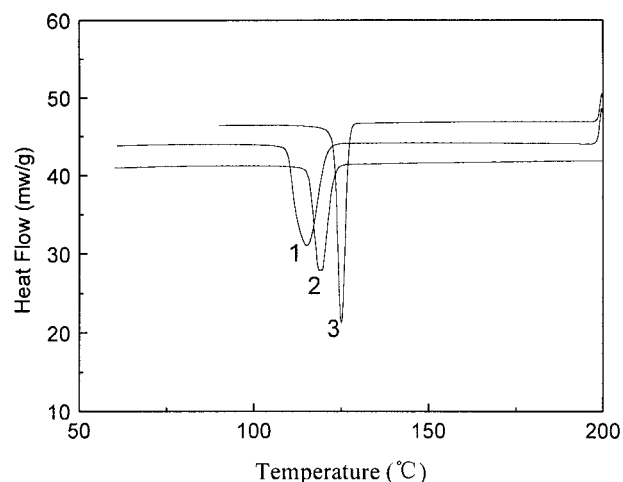
#### Crystallization Temperatures of PP Samples

Figure 4 shows DSC cooling curves of pure PP, PP–Nu3, and PP–Nu4 at a rate of 10°C/min.

An exothermic peak occurred at  $T_c = 115.1, 118.5,$  and  $125.1^\circ\text{C}$ , for pure PP, PP–Nu3, and PP–Nu4, respectively. Compared with pure PP, the increase in  $T_c$  was 3.4°C for PP–Nu3 and 10.0°C for PP–Nu4. The larger  $T_c$  values of PP–Nu4 indicate that the rate of crystallization increased with the addition of Nu4. The in-

**Table I** Mechanical Properties of Nucleated PP Samples

PP Samples	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	HDT (°C)
PP	39.4	44.1	1460	121
PP–Nu1	40.7	45.3	1470	124
PP–Nu2	41.6	46.5	1580	127
PP–Nu3	41.3	46.7	1560	128
PP–Nu4	44.1	54.2	1990	139



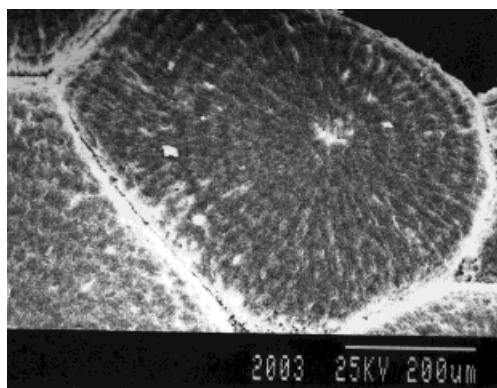
**Figure 4** DSC cooling curves of (1) pure PP, (2) PP-Nu3, and (3) PP-Nu4.

crease in  $T_c$  can be considered to be attributable to the lower melting point of Nu4, which could be uniformly dispersed in PP. At the same time, the peaks of PP-Nu4 became much sharper than that of pure PP. Thus, it can be concluded that Nu4 can act as an effective nucleating agent for PP.

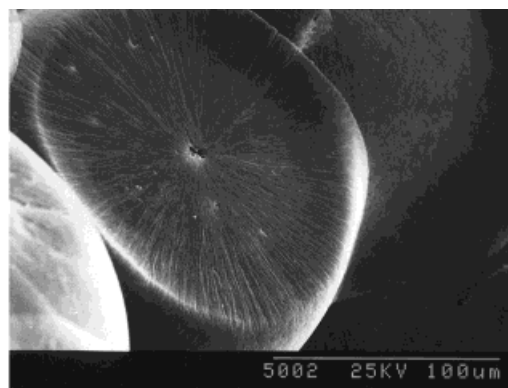
#### SEM Micrographs of PP-Nucleated Samples

Figure 5 shows SEM micrographs of PP samples.

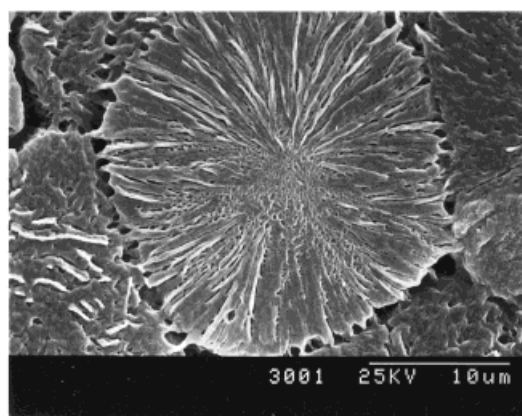
The average diameter of spherulites of pure PP, PP-Nu3, and PP-Nu4 are 200, 150, and 15  $\mu\text{m}$ , respectively. The size of spherulites is the smallest when the nucleating agent Nu4 was added. The reason might be that Nu4 substantially enhanced the numbers of heterogeneous nuclei of crystallization because of its good disper-



(a) Pure PP



(b) PP-Nu3



(c) PP-Nu4

**Figure 5** SEM micrographs of (a) Pure PP, (b) PP-Nu3, and (c) PP-Nu4.

sion. The greater the number of nuclei, the smaller the diameter of the spherulites.

## CONCLUSIONS

When a cocrystal of dehydroabiatic acid and Na-dehydroabietate was formed, the melting point of the nucleating agent was lowered, which caused Nu4 to be uniformly dispersed in PP. The rosin-type nucleating agent Nu4 substantially improved the mechanical properties, HDT, and crystallization temperatures of PP, and also decreased the size of spherulites. Therefore, Nu4 could act as an effective nucleating agent for PP.

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