

Study on Transparent Poly(propylene) Nucleated by the "in Situ" Reaction Products of Dehydroabietic Acid and Sodium Stearate

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ABSTRACT: Dehydroabietic acid (DHA), sodium stearate (NaSt), DHA/NaSt (1/1 wt/wt) mixture, the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min and sodium dehydroabietate (DHAA-Na) were qualitatively analyzed by Fourier transform infrared spectrometry (FTIR) and wide angle X-ray diffractometry (WAXD). The crystallization behavior, spherulitic morphology, optical and mechanical properties of iPP samples nucleated by DHA, NaSt, DHA/NaSt (1/1 wt/wt) mixture, and DHAA-Na under the same concentration (0.3 wt %) were investigated by differential scanning calorimetry (DSC), polarized light microscope (PLM), optical and mechanical measurements. The results showed that an "in situ" reaction occurred between DHA and NaSt, and an effective transparent nucleating agent (DHAA-Na) was

produced during the melting blending of iPP and DHA/NaSt (1/1 wt/wt) mixture in the twin screw extruder. The crystallization onset and peak temperatures, the gloss and the mechanical properties were improved markedly; the crystallization half-time, the spherulitic size, and the haze were reduced substantially when iPP samples are nucleated by DHA/NaSt (1/1 wt/wt) mixture. The optimum composition ratio of DHA/NaSt should be kept at \approx 1/1 wt/wt and above 0.4 wt %/0.4 wt %. The DHA/NaSt bi-component nucleator was effective for iPP with different MFR values. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2436–2444, 2009

Key words: poly(propylene); nucleating agent; dehydroabietic acid; sodium stearate; transparency

INTRODUCTION

As a new kind of transparent material, clarified polypropylene has many outstanding properties such as excellent transparency and gloss, enhanced mechanical properties, and nontoxicity, and has been developed fast in recent years.^{1,2} Nucleating agents such as sorbitol acetals,^{3–5} organic phosphate salts,⁶ salts of rosin acid,^{7–15} trisamides¹⁶ were usually used to improve the transparency of polypropylene. Among them, rosin-based nucleating agents reported by Arakawa Chemical firstly are nontoxic natural products and were approved by the U.S. Food and Drug Administration (FDA) for manufacture of food containers.¹⁷ As a new type of transparent nucleating agents for PP, they attracted several researchers' interests. Li and coworkers^{7–12} prepared a series of rosin type nucleating agents (potassium, sodium, magnesium, and calcium salts of dehydroabietic acid; the cocrystal of dehydroabietic acid and Na-dehydroabietate; the cocrystal of dehydroabietic acid, potassium dehydroabietate, and

sodium dehydroabietate), and studied the effects of these nucleating agents and the cocrystals/LDPE blends on the crystallization and properties of PP. They found the mechanical properties, heat distortion temperature (HDT), crystallization temperatures, and transparency of PP were improved obviously, and the size of spherulites was decreased with the addition of these nucleating agents. LDPE and the cocrystals had the cooperative effects on the crystallization and transparency. Liang and Zhang¹³ studied the effect of two kinds of modified abietates, cocrystals of dehydroabietic acid with sodium dehydroabietate and tetrahydroabietic acid with sodium tetrahydroabietate on the properties of PP. The results showed that HDT, transmittance, crystallizing point, the degree of crystallinity, and mechanical properties were enhanced obviously, the size of spherulites decreased by addition of the modified abietate cocrystals. Wang et al.^{14,15} studied the nonisothermal crystallization, morphology, and properties of iPP containing different concentrations of nucleating agent potassium dehydroabietate (DHAA-K) or sodium dehydroabietate (DHAA-Na). It was found that the peak temperature of crystallization shifted to a higher region by about 13.7–16.9°C, and the rate of crystallization became faster for iPP doped with DHAA-K or DHAA-Na. The size

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of spherulites marginally decreased, and the transparency, gloss, and flexural modulus increased with increasing nucleating agent concentration before its optimal concentration. From the researches mentioned above, the rosin-type nucleating agents used in the literatures were alkali or alkaline earth dehydroabietate and cocrystals of dehydroabietic acid or tetrahydroabietic acid with alkali dehydroabietate or tetrahydroabietate.

The “*in situ*” nucleating agent cited in the literatures was rare. The sole one was the bicomponent β -nucleator (consisting of equal amount of pimelic acid and calcium stearate) firstly reported by Shi and coworkers.^{18–22} The effective component of pimelic acid/calcium stearate mixture was calcium pimelate produced “*in situ*” during the melt mixing of iPP and the bicomponent nucleator.²³ Compared with the nucleating agents traditionally synthesized in the reactor, the merits of the “*in situ*” nucleating agent produced in the melting blending were high efficiency, low cost, and no pollutant. Recently, another new bicomponent nucleating agent composed of dehydroabietic acid and sodium stearate was found in our laboratory.²⁴ The effective component of it was qualitatively analyzed by Fourier transform infrared spectrometry (FTIR) and wide angle X-ray diffractometry (WAXD). The effect of the “*in situ*” nucleating agent on the crystallization behavior, spherulitic morphology, optical and mechanical properties of iPP was studied in this article.

EXPERIMENTAL

Materials

iPP-1 powder (MFR = 11.4 g/10 min at 230°C and 21.2N load, according to ISO 1133-1997), iPP-2 powder (MFR = 1.9 g/10 min), iPP-3 powder (MFR = 6.8 g/10 min), and iPP-4 powder (MFR = 19.2 g/10 min) were obtained from Jinling Plastics and Rubber Chemical Co, China. Dehydroabietic acid (DHA, m.p. 170–172°C, MW 300.45) and sodium dehydroabietate (DHAA-Na, MW 322.45) were prepared according to the methods described in the literature.¹⁴ Antioxidant B215 {tetrakis [methylene (3, 5-di-*tert*-butyl-4-hydroxyhydrocinnamate)] methane/tris(2, 4-di-*tert*-butylphenyl) phosphate (1/2 wt/wt) mixture, industrial product} and sodium stearate (NaSt, chemical pure reagent, m.p. 205–210°C, MW 306.46) were commercially available.

Characterization of the “*in situ*” reaction product of DHA and NaSt (1/1 wt/wt)

Five grams of DHA and 5 g of NaSt were intensely mixed in a mini-mixer at the speed of $\sim 25,000$ rpm for 1 min. The mixture was poured into a test tube

purged with N₂ atmosphere, and the tube is immersed in a silicone oil bath kept at 220°C for 10 min. The tube was taken out and cooled to room temperature. The DHA, NaSt, and the DHA/NaSt (1/1 wt/wt) mixture before and after heating were analyzed by FTIR (Nexus670, Nicolet Corporation) and WAXD (ARL X'TRA, Thermo Electron Corporation), respectively. FTIR spectrometer was operated in transmission mode using KBr pellets with the measuring range of 400–4000 cm⁻¹. The X-ray diffractometer using a Cu K α source was operated in reflective mode at 45 kV and 35 mA under ambient temperature, the scanning range (2θ) was 2–50°, and the scanning rate was 2°/min.

Preparation and characterization of nucleated iPP samples

Five hundred grams of iPP powder was intensely mixed with 0.5 g B215, variable amount of the nucleator in a mixer at the speed of $\sim 25,000$ rpm for 1 min. The mixture was compounded in a corotating twin screw extruder [TE-20, $D = 20$ mm, $L/D = 32/1$, Coperion Keya (Nanjing) Machinery Co, China]. The rate of the feeder screw and the main screw was set at 20 and 200 rpm, and the temperature from the hopper to the die was set at 210, 220, 220, and 210°C, respectively. The melt was cooled and pelletized. iPP without nucleating agent was also prepared in a similar way to produce the blank control sample.

Crystallization behaviors of the blank and the nucleated iPP-1 samples were performed in a differential scanning calorimetry (DSC) instrument (Perkin-Elmer Pyris 1) under a dry nitrogen atmosphere. The instrument was calibrated with pure indium for temperature and heat flow. About 5–10 mg of each sample was sealed into an aluminum pan, heated from 50 to 220°C at the rate of 60°C/min, and held at 220°C for 5 min to erase the thermal memory, then cooled to 50°C at the rate of 10°C/min. The crystallization onset and peak temperatures of the samples were recorded. The crystallization half-time ($t_{1/2}$), which is defined as the time interval from the onset of crystallization to the time at which the crystallization process is half completed, was calculated from the crystallization curve.

A granule of the blank or the nucleated iPP-1 sample was placed between two glass slides on a hot stage kept at $220 \pm 2^\circ\text{C}$ for 10 min to allow the sample to melt completely and remove thermal memory, squeezed on the top slide to form a film, then cooled in air to room temperature. The thickness of samples was between 20 and 40 μm . Spherulitic morphology of the blank or the nucleated iPP-1 sample was observed on a polarized light microscope (PLM, LW-200-4JS, Shanghai LW Scientific Co, China)

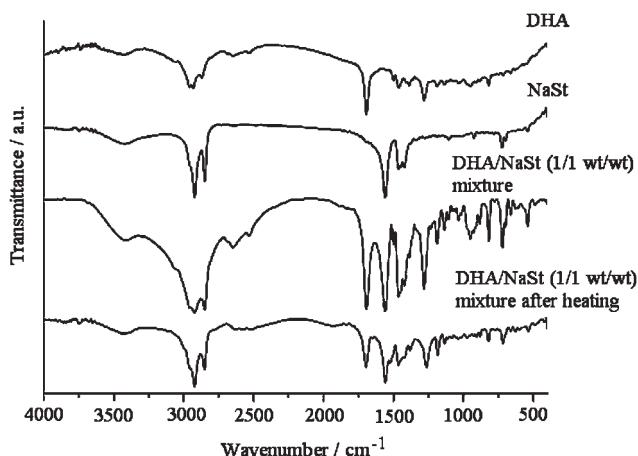


Figure 1 FTIR spectra of DHA, NaSt, DHA/NaSt (1/1 wt/wt) mixture, and the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min.

equipped with cross polars and a CCD camera. Pictures were captured and stored in a computer.

Optical and mechanical measurements

Standard test specimens for optical and mechanical characterization were injection-molded with a reciprocating-screw injection molding machine (CJ80M3V, Chen De Plastics Machinery Co., China) at the temperature range of 190–210°C and the injection pressure of 70 MPa. The hazes of the samples were measured by a photoelectrical hazemeter (WGW, Shanghai Precision and Scientific Instrument Co., China) according to ISO 14782 : 1999. The thickness of the test pieces was 1 mm. The glosses were tested using a glossmeter (WGG60-Y4, Keshijia Institute of Photoelectrical Instrument, Quanzhou, China) according to ISO 2813 : 1994. Tensile strength, tensile strain at break, and flexural modulus were measured on a electromechanical universal testing machine (CMT5254, Shenzhen SANS Testing Machine Co., China) according to ISO527-2/1BA/50: 1996 and ISO178: 2003, respectively. The testing speed of tensile and flexural test was 50 mm/min and 2 mm/min, respectively. The specimens for Izod notched impact test were notched on a plastic specimen notcher (MZ2061, Jiangdu Mingzhu Testing Machine Factory, China) and were measured on a pendulum impact testing machine (MZ2056, Jiangdu Mingzhu Testing Machine Factory, China) according to ISO180/A: 2000.

RESULTS AND DISCUSSION

Qualitative analysis of the “*in situ*” reaction products of DHA and NaSt (1/1 wt/wt) mixture after heating

The FTIR spectra of DHA, NaSt, DHA/NaSt (1/1 wt/wt) mixture, the reaction products of DHA/NaSt

(1/1 wt/wt) mixture after heating at 220°C for 10 min were shown in Figure 1. The characteristic absorption bands related to carboxyl of DHA and NaSt were listed as follows: DHA: ν (dimeric COOH) at 2532 and 2648 cm^{-1} , ν (C=O) at 1693 cm^{-1} , δ (OH) and ν (C–O) at 1281 cm^{-1} ; NaSt: ν_{as} (COO⁻) at 1558 cm^{-1} , ν_{s} (COO⁻) at 1463 and 1423 cm^{-1} . The FTIR spectrum of DHA/NaSt (1/1 wt/wt) mixture included the characteristic absorption bands of DHA and NaSt. The absorption bands of ν (dimeric COOH) at 2532 and 2648 cm^{-1} , and δ (OH) and ν (C–O) at 1281 cm^{-1} disappeared and three new weak absorption bands at 2628, 2578, and 2518 cm^{-1} appeared, the absorption bands of ν (C=O) at 1693 cm^{-1} and ν_{as} (COO⁻) at 1558 cm^{-1} became small in the spectrum of the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating. Moreover, the wide absorption band of ν_{s} (COO⁻) at 1463 and 1423 cm^{-1} of DHA/NaSt (1/1 wt/wt) mixture weakened after heating. It was shown that some new substances were produced in the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating. The operation of subtraction DHA and NaSt from DHA/NaSt (1/1 wt/wt) mixture after heating was done on the FTIR spectrometer by means of OMNIC 6.0 software. The FTIR spectra of the subtraction result and DHAA-Na were shown in Figure 2. The FTIR spectrum of the new substance was similar to that of DHAA-Na. The characteristic absorption bands related to carboxyl of DHAA-Na were: ν_{as} (COO⁻) at 1552 cm^{-1} , ν_{s} (COO⁻) at 1470 and 1442 cm^{-1} . They also could be found on the subtraction curve. The WAXD spectra of DHA, NaSt, DHA/NaSt (1/1 wt/wt) mixture, the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min and DHAA-Na were

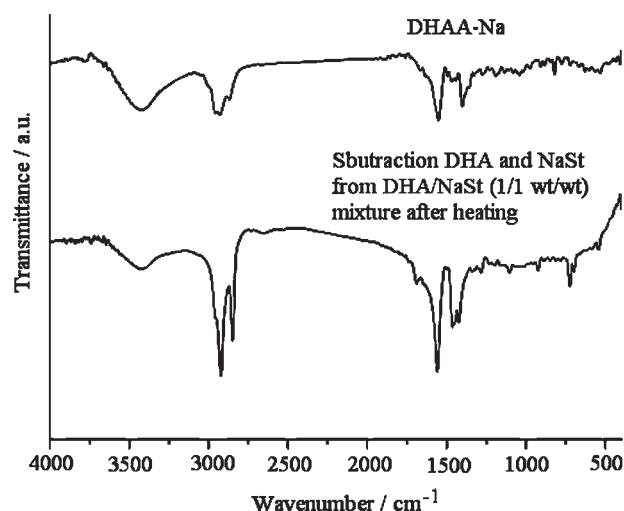


Figure 2 FTIR spectra of the result of subtraction of DHA and NaSt from DHA/NaSt (1/1 wt/wt) mixture after heating, and DHAA-Na.

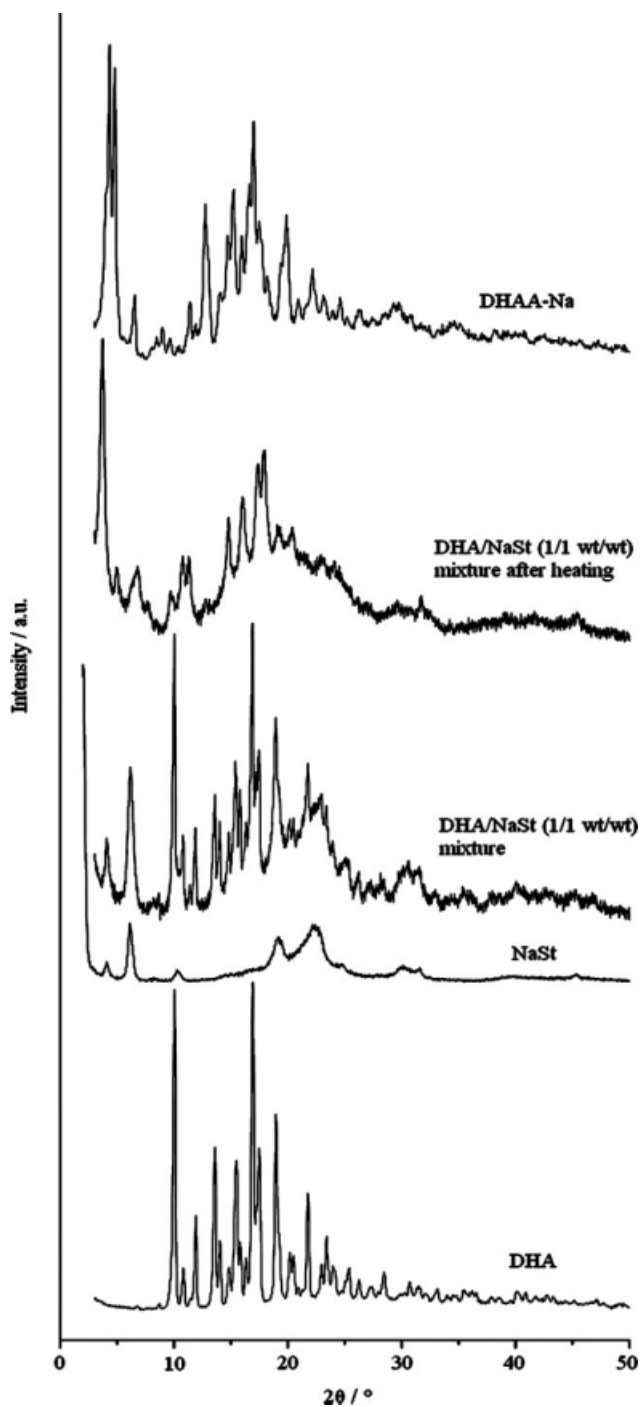


Figure 3 WAXD diffraction patterns of DHA, NaSt, DHAA-Na, DHA/NaSt (1/1 wt/wt) mixture, and the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min.

shown in Figure 3. The obvious diffraction peaks of DHA, NaSt, and DHAA-Na were listed as follows: DHA: 10.1°, 11.9°, 13.6°, 15.5°, 16.9°, 17.5°, 19.0°, and 21.8°; NaSt: 4.1°, 6.1°, 10.2°, 19.1°, 22.2°, 30.0°, and 31.6°; DHAA-Na: 4.4°, 4.8°, 6.6°, 12.8°, 14.7°, 15.3°, 17.0°, 19.9°, and 22.2°. The WAXD pattern of DHA/NaSt (1/1 wt/wt) mixture included the diffraction

peaks of DHA and NaSt. The diffraction peaks at 4.1°, 6.1°, 10.1°, 13.6°, 16.9°, 19.0°, and 22.0° of DHA/NaSt (1/1 wt/wt) mixture weakened after heating at 220°C for 10 min. It was also indicated that some new substances were produced in the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating. The WAXD pattern of the reaction product of DHA/NaSt (1/1 wt/wt) mixture after heating had some similarity to that of DHAA-Na. The diffraction peaks at 4.8°, 6.6°, 14.7°, and 17.0° of DHAA-Na also could be found on the curve of the reaction product of DHA/NaSt (1/1 wt/wt) mixture after heating.

Characterization of the nucleated IPP-1 samples

It was found that sodium dehydroabietate was an efficient nucleator for polypropylene; it increased the rate of crystallization, decreased the size of spherulite, and improved the transparency, gloss, and flexural modulus.^{7,14,15} Therefore, the crystallization behavior, spherulitic structure, mechanical and optical properties of iPP-1 samples nucleated by 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture, and 0.3 wt % DHAA-Na were compared. If there was a complete reaction between 0.3 wt % DHA and 0.3 wt % NaSt during extrusion, the calculated stoichiometric amount of "in situ" DHAA-Na that would be produced was 0.32 wt %. The actual amount of the "in situ" DHAA-Na should be lower than 0.32 wt % because it was difficult to regulate the "in situ" reaction in the extruder completely.

The DSC cooling curves of the blank iPP-1 and the iPP-1 samples doped with 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture, and 0.3 wt % DHAA-Na were shown in Figure 4. The relevant crystallization parameters were listed in Table I. The crystallization peak temperatures (T_{cp}) and enthalpies (ΔH) of iPP-1 nucleated with 0.3 wt % DHA and 0.3 wt % NaSt were lower than those of the blank iPP-1. The crystallization half times ($t_{1/2}$) of iPP-1 nucleated with 0.3 wt % DHA and 0.3 wt % NaSt were greater than that of the blank iPP-1. It was shown that DHA and NaSt had no nucleating ability for iPP-1. Compared with the T_{cp} , $t_{1/2}$, and ΔH of the blank iPP-1, the T_{cp} , $t_{1/2}$, and ΔH of iPP-1 nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na increased by 15.7°C and 16.5°C, decreased by 19.8 s and 33.6 s, and increased by 1.4 J/g and 5.6 J/g, respectively. It was indicated that DHA/NaSt (1/1 wt/wt) mixture and DHAA-Na were good nucleating agents for iPP-1, the nucleating ability of the latter was superior to that of the former. The crystal structure of the reaction products of DHA/NaSt was different from that of DHAA-Na (as Fig. 3 shown); the crystal lattice

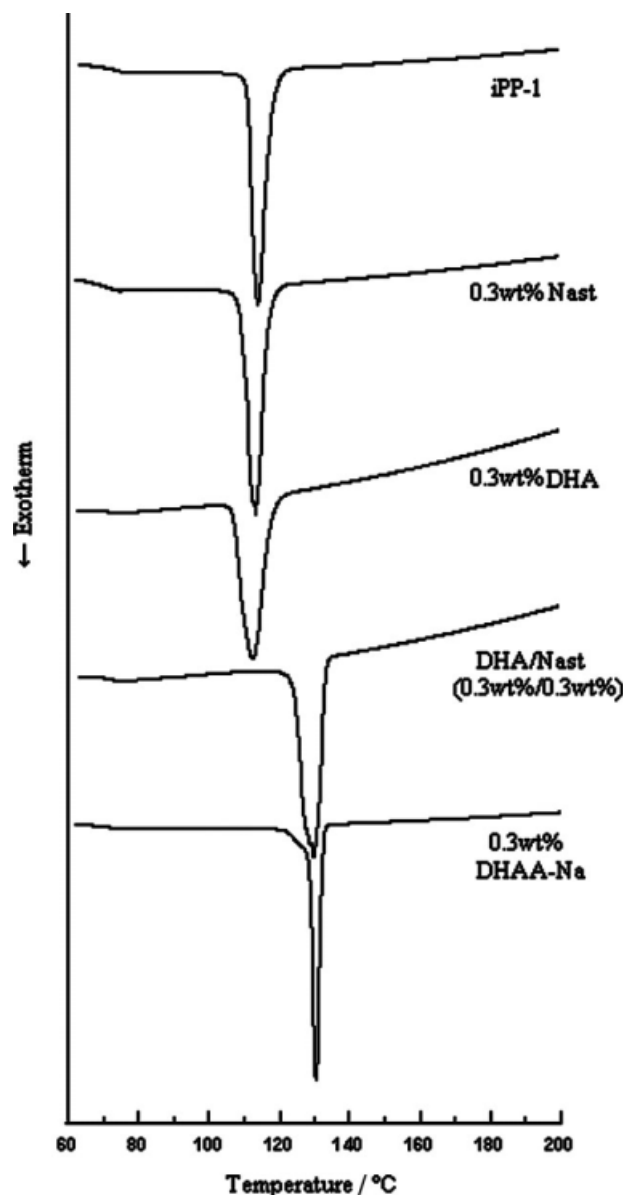


Figure 4 DSC cooling curves of iPP-1 samples doped with 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture, and 0.3 wt % DHAA-Na.

matching between the reaction products of DHA/NaSt (1/1 wt/wt) mixture and iPP (i.e., epitaxy) is different from that of DHAA-Na and iPP. Therefore, the nucleating ability of DHAA-Na was different from that of DHA/NaSt (1/1 wt/wt) mixture.

The PLM photographs of the blank iPP-1 and the iPP-1 samples doped with 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were shown in Figure 5. The radial spherulites with the diameter of about 10 μm were easily discerned in the photographs of the blank iPP-1 and iPP-1 doped with 0.3 wt % NaSt. The intact spherulites were rare, only the irregular crystals existed in the photograph of iPP-1 doped with 0.3 wt % DHA. The spherulitic sizes of iPP-1 nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were reduced obviously; especially, the spherulites in the former were undiscernible.

The mechanical and optical properties of the blank iPP-1 and the iPP-1 samples doped with 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture, and 0.3 wt % DHAA-Na were listed in Table I. The tensile strength, flexural modulus, and gloss of iPP-1 doped with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were greater than those of the blank iPP-1 and iPP-1 doped with 0.3 wt % DHA and 0.3 wt % NaSt. The hazes of iPP-1 doped with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were lower than those of the blank iPP-1 and iPP-1 doped with 0.3 wt % DHA and 0.3 wt % NaSt.

From the results mentioned above, it was shown that an "*in situ*" reaction occurred between DHA and NaSt, and DHAA-Na was produced during the melting blending in the twin screw extruder. Hence, the FTIR and WAXD spectra of the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min were similar to those of DHAA-Na. The "*in situ*" reaction formula was shown in Figure 6. The T_{cp} and ΔH of iPP-1

TABLE I
Crystallization Parameters, Mechanical and Optical Properties of iPP-1 Nucleated with Different Nucleators

Properties	Blank	0.3 wt % DHA	0.3 wt % NaSt	DHA/NaSt (0.3 wt %/0.3 wt %)	0.3 wt % DHAA-Na
Crystallization onset temperature (T_{co} , °C)	118.0	117.7	116.9	133.1	132.2
Crystallization peak temperature (T_{cp} , °C)	114.0	112.6	113.3	129.7	130.5
Crystallization half time ($t_{1/2}$, s)	58.2	62.1	59.4	38.4	24.6
Crystallization enthalpy (ΔH , J/g)	94.9	93.8	93.0	96.3	100.5
Tensile strength (MPa)	36.7 \pm 1.6	38.3 \pm 1.8	36.2 \pm 1.0	40.9 \pm 1.1	40.4 \pm 1.7
Tensile strain at break (%)	307 \pm 10	305 \pm 19	302 \pm 16	295 \pm 18	305 \pm 12
Flexural modulus (MPa)	1092 \pm 28	1269 \pm 29	1218 \pm 32	1410 \pm 42	1480 \pm 39
Izod notched impact strength (kJ.m ⁻²)	1.75 \pm 0.05	2.72 \pm 0.11	2.41 \pm 0.09	2.41 \pm 0.12	1.87 \pm 0.06
Haze (%)	37.0 \pm 1.3	42.5 \pm 1.1	49.6 \pm 1.2	10.5 \pm 0.5	11.2 \pm 0.3
Gloss (%)	104.7 \pm 2.3	105.9 \pm 2.4	103.3 \pm 3.2	133.2 \pm 2.8	131.2 \pm 1.7

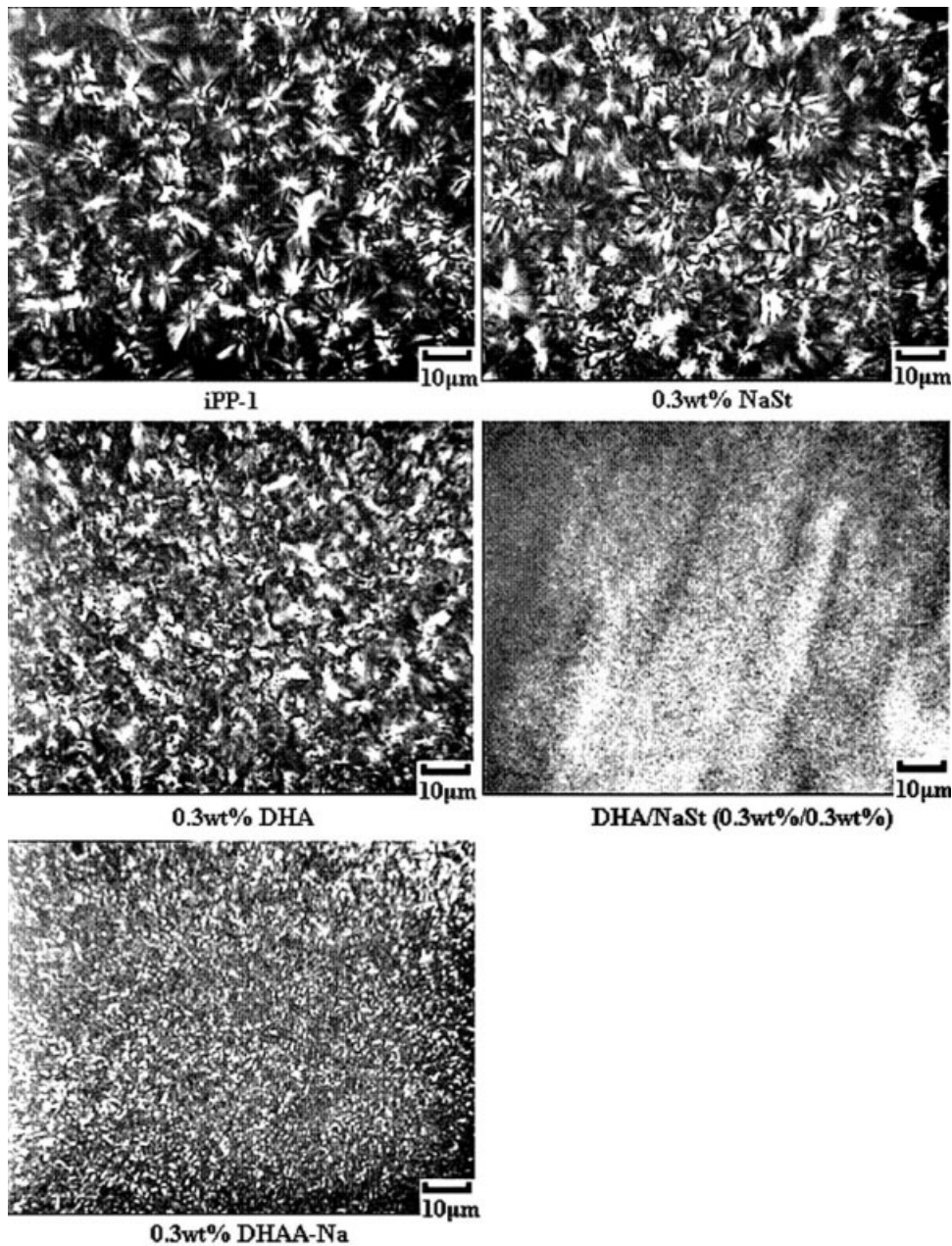


Figure 5 PLM photographs of iPP-1 samples doped with 0.3 wt % DHA, 0.3 wt % NaSt, DHA/NaSt (0.3 wt %/0.3 wt %) mixture, and 0.3 wt % DHAA-Na.

nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture was lower than that of iPP-1 nucleated with 0.3 wt % DHAA-Na, the $t_{1/2}$ of the former was greater

than that of the latter. It was ascribed to the “*in situ*” reaction product was a mixture (DHAA-Na, stearic acid, DHA and NaSt), and its nucleating ability was

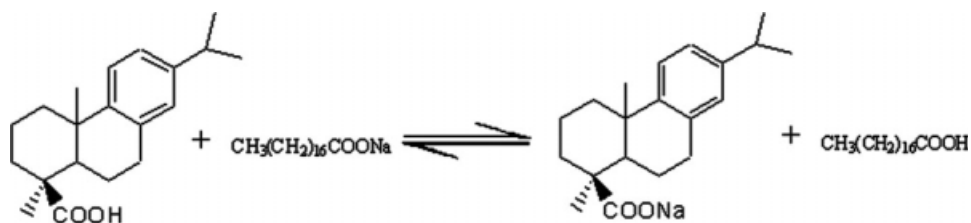


Figure 6 The “*in situ*” reaction formula.

TABLE II
L₉ (3⁴) Orthogonal Experiment Results

DHA (wt%)	NaSt (wt%)	C	D	Tensile strength (MPa)	Tensile strain at break (%)	Flexural modulus (MPa)	Izod notched impact strength (kJ m ⁻²)	Haze (%)	Gloss (%)
1 (0.2)	1 (0.2)	1	1	40.7 ± 1.8	226 ± 10	1491 ± 43	2.12 ± 0.10	12.3 ± 0.8	134.6 ± 1.6
1 (0.2)	2 (0.4)	2	2	40.1 ± 1.2	262 ± 12	1439 ± 28	2.50 ± 0.09	18.1 ± 1.1	128.2 ± 1.9
1 (0.2)	3 (0.6)	3	3	40.5 ± 1.4	247 ± 12	1424 ± 37	2.72 ± 0.11	23.3 ± 1.0	122.7 ± 3.0
2 (0.4)	1 (0.2)	2	3	38.9 ± 1.4	271 ± 16	1451 ± 42	2.37 ± 0.07	10.3 ± 0.3	138.6 ± 2.6
2 (0.4)	2 (0.4)	3	1	39.1 ± 1.7	293 ± 20	1464 ± 36	2.19 ± 0.11	9.9 ± 0.4	138.9 ± 3.2
2 (0.4)	3 (0.6)	1	2	39.7 ± 2.0	170 ± 16	1480 ± 22	2.41 ± 0.12	10.7 ± 0.2	136.7 ± 1.5
3 (0.6)	1 (0.2)	3	2	39.4 ± 1.9	283 ± 18	1421 ± 59	2.38 ± 0.09	9.4 ± 0.3	139.8 ± 1.8
3 (0.6)	2 (0.4)	1	3	39.3 ± 1.1	199 ± 21	1455 ± 46	2.28 ± 0.08	7.5 ± 0.2	143.7 ± 2.2
3 (0.6)	3 (0.6)	2	1	39.7 ± 1.4	295 ± 14	1459 ± 38	2.31 ± 0.09	7.6 ± 0.3	141.7 ± 2.4

inferior to that of DHAA-Na. It was known that an efficient nucleating agent could produce heterogeneous nuclei and increased the amount of nuclei in the system substantially; thus, it accelerated the crystallization rate of iPP, resulting in smaller spherulites and highly oriented skin layer. Hence, the optical and mechanical properties of iPP were improved.⁸⁻¹⁰ The crystal size of iPP-1 nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture was smaller than that of iPP-1 nucleated with 0.3 wt % DHAA-Na; so, the haze of the former was lower than that of the latter, and the gloss and Izod notched impact strength of the former was superior to that of the latter. Perhaps, the mixture of the "in situ" reaction products improved the dispersion of "in situ" DHAA-Na in iPP. The mechanical properties, especially the tensile strength and flexural modulus of iPP-1 nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture were also improved, compared with those of the blank iPP-1, DHA and NaSt nucleated iPP-1.

Effect of the composition ratios of DHA and NaSt on the properties of IPP-1 samples

Tensile strength, tensile strain at break, flexural modulus, Izod notched impact strength, haze and gloss were chosen as six main indicators to evaluate the properties of the nucleated iPP-1 samples. DHA and NaSt were chosen as two factors, each factor containing three levels (as shown in Table II). Therefore, L₉ (3⁴) orthogonal table was selected for the experiment. The arrangements and results of each experiment were displayed in Table II. The range analysis results were shown in Table III. DHA was the main factor affecting the evaluating indicators (tensile strength, haze, and gloss) because the R value of DHA was the biggest one among the R values of DHA, NaSt, columns C and D, while NaSt was the minor factor. The interaction columns of DHA and NaSt were columns C and D. The interac-

tion of DHA and NaSt was important for all evaluating indicators and it was the main factor affecting the evaluating indicators (tensile strain at break and flexural modulus). The R difference of Izod notched impact strength among DHA, NaSt, columns C and D was small; indicating that the effect of the influencing factors was almost same. To obtain nucleated iPP-1 samples with low haze and

TABLE III
Range Analysis of the Orthogonal Experiment Results

Evaluating indicators		DHA	NaSt	C	D
Tensile strength (MPa)	K ₁	121.3	119.0	119.7	119.5
	K ₂	117.7	118.5	118.7	119.2
	K ₃	118.4	119.9	119.0	118.7
	R	3.6	1.4	1.0	0.8
Tensile strain at break (%)	K ₁	735	780	595	814
	K ₂	734	754	828	715
	K ₃	777	712	823	717
	R	43	68	228	99
Flexural modulus (MPa)	K ₁	4354	4363	4426	4414
	K ₂	4395	4358	4349	4340
	K ₃	4335	4363	4309	4330
	R	60	5	117	84
Izod notched impact strength (kJ m ⁻²)	K ₁	7.34	6.87	6.81	6.62
	K ₂	6.97	6.97	7.18	7.29
	K ₃	6.97	7.44	7.29	7.37
	R	0.37	0.57	0.48	0.75
Haze (%)	K ₁	53.7	32.0	30.5	29.8
	K ₂	30.9	35.5	36.0	38.2
	K ₃	24.5	41.6	42.6	41.1
	R	29.2	9.6	12.1	11.3
Gloss (%)	K ₁	385.5	413.0	415.0	415.2
	K ₂	414.2	410.8	408.5	404.7
	K ₃	425.2	401.1	401.4	405.0
	R	39.7	11.9	13.6	10.5

K₁, K₂, and K₃ represent the sum of tensile strength, tensile strain at break, flexural modulus, Izod notched impact strength, haze and gloss at level 1, 2, and 3, respectively. R represents the maximum difference among K₁, K₂, and K₃.

TABLE IV
Effect of DHA/NaSt (0.5 wt %/0.5 wt %) Mixture on the Properties of iPP with Different MFR Values

MFR (g/10 min)		Tensile strength (MPa)	Tensile strain at break (%)	Flexural modulus (MPa)	Izod notched impact strength (kJ m ⁻²)	Haze (%)	Gloss (%)
1.9	Blank	39.9 ± 1.8	190 ± 15	1076 ± 34	2.50 ± 0.12	30.4 ± 0.7	113.3 ± 2.5
	Nucleated	41.3 ± 1.7	191 ± 12	1329 ± 32	2.47 ± 0.11	10.8 ± 0.4	129.2 ± 1.7
6.8	Blank	38.2 ± 1.2	270 ± 20	1000 ± 42	2.03 ± 0.07	34.0 ± 1.1	108.2 ± 3.0
	Nucleated	40.0 ± 1.4	257 ± 18	1359 ± 33	2.01 ± 0.10	6.1 ± 0.2	140.0 ± 2.4
11.4	Blank	36.7 ± 1.6	307 ± 10	1092 ± 28	1.75 ± 0.05	37.0 ± 1.3	104.7 ± 2.3
	Nucleated	39.0 ± 1.6	251 ± 12	1410 ± 43	2.16 ± 0.09	7.3 ± 0.4	137.5 ± 2.8
19.2	Blank	35.8 ± 1.3	295 ± 18	1044 ± 26	1.66 ± 0.10	44.6 ± 1.1	101.6 ± 2.1
	Nucleated	38.3 ± 1.6	293 ± 21	1429 ± 45	1.72 ± 0.08	7.9 ± 0.5	134.0 ± 2.3

high gloss, the DHA content should be kept at 0.6 wt %. But if the NaSt content was chosen as 0.2 wt % as Table III suggested, the haze and gloss of the nucleated iPP-1 samples were not good. Thus, the NaSt content should be kept at ≥ 0.4 wt % as Table II revealed. Because the molecular weights of DHA (300.45) and NaSt (306.46) were approximately equal, their molar quantities were approximately equal too. The “*in situ*” reaction demanded the approximately equal weights of DHA and NaSt. Therefore, transparent iPP with low haze and high gloss was produced when the content of the bi-component nucleator ($\approx 1/1$ wt/wt) was adequate (≥ 0.4 wt %/0.4 wt %).

Effect of DHA/NaSt (0.5 wt %/0.5 wt %) mixture on the properties of iPP samples with different MFR values

The effects of DHA/NaSt (0.5 wt %/0.5 wt %) mixture on the mechanical and optical properties of iPP samples with different MFR values were listed in Table IV. The tensile strength, flexural modulus, and gloss of the nucleated iPP samples were greater than those of the blank ones. The haze of the nucleated iPP samples decreased markedly. Therefore, the bi-component nucleator was effective for iPP with different MFR values.

CONCLUSIONS

The FTIR and WAXD spectra of the reaction products of DHA/NaSt (1/1 wt/wt) mixture after heating at 220°C for 10 min were similar to those of DHAA-Na. DHA/NaSt (1/1 wt/wt) mixture and DHAA-Na were good nucleating agents, whereas DHA and NaSt had no nucleating ability for iPP-1. The spherulitic sizes of iPP-1 samples nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were small, when compared

with the coarse spherulites of the blank iPP-1 and iPP-1 doped with 0.3 wt % NaSt and 0.3 wt % DHA. The tensile strength, flexural modulus, the haze and the gloss of iPP-1 nucleated with DHA/NaSt (0.3 wt %/0.3 wt %) mixture and 0.3 wt % DHAA-Na were improved markedly, when compared with those of the blank iPP-1 and iPP-1 doped with 0.3 wt % DHA and 0.3 wt % NaSt. It was shown that an “*in situ*” reaction occurred and the effective transparent nucleating agent (DHAA-Na) was produced during the melting blending of iPP and DHA/NaSt (1/1 wt/wt) mixture. DHA was the main factor affecting the tensile strength, the haze and gloss. The interaction of DHA and NaSt was important for all evaluating indicators, and it was the main factor affecting the tensile strain at break and flexural modulus. Transparent iPP with low haze and high gloss was produced when the content of the bi-component nucleator ($\approx 1/1$ wt/wt) is above 0.4 wt %/0.4 wt %. The DHA/NaSt (0.5 wt %/0.5 wt %) bi-component nucleator was effective for iPP with different MFR values (1.9–19.2 g/10 min).

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