The Effects of Ultrasonic Irradiation on the Crystalline Structures of Nucleated Polypropylene

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ABSTRACT: The effects of ultrasonic irradiation on crystallization behavior of polypropylene (PP)-loaded fillers with nucleating activities, such as sodium benzoate, talc (P), talc (A), and mica, are examined. DSC and WAXD analyses demonstrate that the crystalline structure of PP is changed through ultrasonic vibration. Different nucleating systems have their own specific responses to ultrasound. In sodium benzoate-added PP, β-crystal appears when ultrasonic with an appropriate intensity was applied, which alters the growth of PP crystals and favors a special crystal transformation ($\alpha{\rightarrow}\beta$). On the other hand, ultrasonic does not induce β-form in the talc or mica system, but prefers crystal growth of (040) plane. Based on the crystalline structure and structures of nucleating agents, the ultrasonic effects in determination of the crystalline preferential growth are analyzed. © 2002 Wiley Periodicals, Inc. J Appl Polm Sci 84: 1956–1961, 2002; DOI 10.1002/app.10516

Key words: ultrasound; polypropylene; crystalline

INTRODUCTION

High-intensity ultrasonic waves can influence a medium through which the waves propagate by shatter, cavitation, and chemical and mechanical action. The application of ultrasonic in polymer processing is quite attractive because it can accelerate chemical reaction, increase productivity, and soon. Isayev et al.[1,2] introduced ultrasonic vibration to extruder and measured die swell, die pressure drop, mechanical, and rheological properties of polymers with and without ultrasound treatment. When ultrasonic was applied, the polymer exhibited different rheological, physical,

and mechanical properties. In the case of solidifying polymer in a mold, the crystalline structure formed can be well controlled by applying ultrasonic energy.[3] A special ultrasonic process was designed to modify the crystallization of polyolefine-blown films.[4] Khamad et al.[5] investigate an extrusion process of HDPE containing a small amount of butyl rubber under the ultrasonic irradiation; the results of the increase of crystallinity, reduction of structural defects, and enhancement of mechanical properties were observed. However, the information available on crystalline structure of polymers by using ultrasonic is limited, especially for polypropylene (PP). Crystalline isotactic polypropylene (iPP) is of well-known polymorphic structures. There are α, β, γ, δ, and smectic forms involved in the modification of iPP. Of all these crystal structures, the β-form demonstrates the higher performance, such as a higher elongation at break and a higher impact strength.[6]

In addition, the β-form would convert into the α-form, resulting in the formation of pinholes when the β-form iPP experiences an extension or heating treatment, owing to the lower density of the β-form.[7] Because ultrasound can alter the crystal structures of PP, it thus was expected to be an effective method to modified PP.

Our previous work studied PP extrusion with parallel superposition of ultrasonic waves upon the die. Excluding the influence of processing condition, as well as deeply investigating the ultrasonic effects on PP melts, this article focuses on the crystallization behavior of nucleated PP under static ultrasonic irradiation.

EXPERIMENTAL

Materials and Experimental Apparatus

PP, grade F401, with a melt index of 2.0 g/10 min and a density of 0.91 g/cm^3 at 25°C, was commercially available, produced by Lanzhou Chemical Co. (Lanzhou, China). γ-Methacryloxypropyltrimethoxysilane (A174) was the aqueous silane coupling agent, and was acquired from Nanjing Shuguang Chemical Plant (Nanjing, China). Sodium benzoate (NaBz), analytical reagent, was acquired from Chongqing Chemical Agents Plant (Chongqing, China). Mica ($d_{97} < 10 \ \mu$m) from Sichuan Xinju Co. (Sichuan, China) was treated with 1% A174. Talc ($d_{97} < 10 \ \mu$m) was acquired from the Liaoning Haicheng Co. (Haicheng, China). Talc treated with 1% A174 is named talc (A) and without A174 is named talc (P).

The static ultrasound experimental equipment consists of a mold and an ultrasonic generator (Fig. 1). The ultrasonic frequency is 20 kHz and power ranges from 0 to 300 W; the diameter of the horn is 15 mm.

Added to PP were 0.2% nucleating agents, such as NaBz dissolved in water, talc (P), mica, and talc (A) dispersed in alcohol, respectively; after vaporizing dispersion medium, samples were compressed at 180°C into sheets. The sample was cut into small pieces and melted in the static ultrasonic mold at 200°C for 10 min and then irradiated by ultrasonic wave for 5 min. After that, it cooled to room temperature.

Differential Scanning Calorimetry (DSC)

A Perkin–Elmer DSC thermal analyzer was employed to obtain the melting behavior of the samples. The samples were heated under nitrogen atmosphere from 25 to 200°C at a rate of 10°C/min, kept at 200°C for 5 min, and then cooled at the same rate.

X-ray Diffraction

The WAXD patterns of PP were taken on a Philip X'pert prd diffractometer with Ni-filtered CuKα radiation at room temperature. The relative amounts of β-form in PP were determined by using the Turner-Jones equation[8] on the basis of a typical X-ray diffraction diagram:

$$ k = \frac{H_{\beta_1}}{H_{\beta_1} + (H_{\alpha_1} + H_{\alpha_2} + H_{\alpha_3})} $$

where k is the amount of the β-form, H_{β_1} is the height of the strong single β-form peak (300), H_{α} is the heights of the three strong equatorial α-form peaks (110), (040), and (130). The order parameter S of the β-form was calculated by
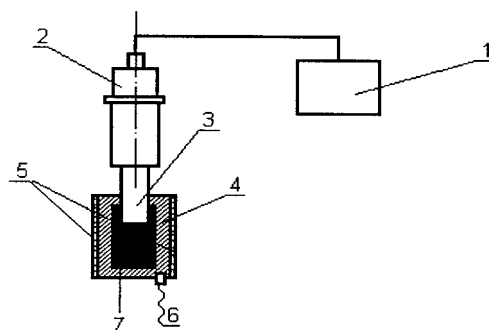
$$ S = H(300)/[H(300) + H(301)] $$

where $H(301)$ is the height of the peak from the (301) crystalline face of the β-form. The higher the S value, the higher the order of the β-form.
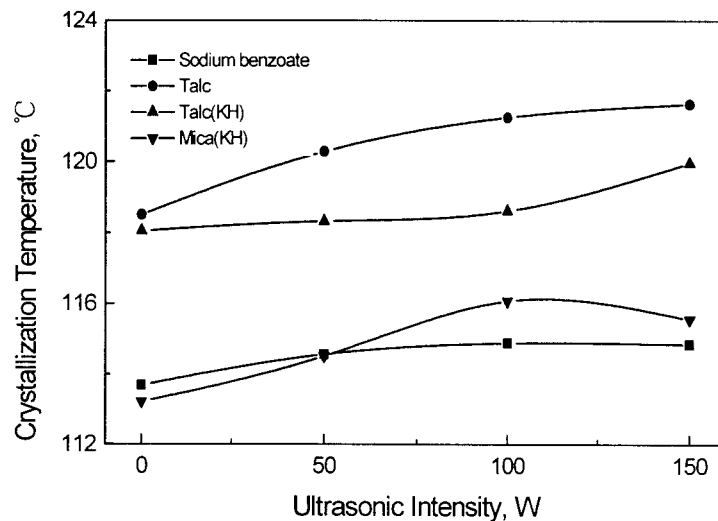
RESULTS AND DISCUSSION

Crystallization Temperature

Figure 2 shows the dependence of crystallization temperature T_c of nucleated PP on the ultrasonic

Figure 1 Scheme of static ultrasonic wave system. 1, Ultrasonic generator; 2, piezoelectric transducer; 3, horn; 4, mold; 5, electric heaters; 6, thermocouple; 7, melt.

Figure 2 Dependence of crystallization temperature on ultrasonic intensity.

intensity. As seen from Figure 2, ultrasonic wave increases T_c by about 1–3°C. Figure 2 shows that ultrasonic wave enhances the crystallization nucleation ability of PP with additives. However, the crystallinity of all the modified PP is decreased with ultrasonic treatment (Table I), which means that the ultrasonic wave influenced the nucleating process of nucleated PP.

Crystalline Form

Figure 3 shows the X-ray diffraction patterns of PP containing NaBz samples with and without ultrasonic treatment, respectively. By introducing appropriate ultrasonic effects, a new peak at θ = 16.5°, which corresponds to the (300) plane, appears. According to Turner-Jones,[8] these undoubtedly indicate the formation of the β-forms of the PP. Table I shows the relative content and order parameter of β-forms. The maximum contribution (K = 12.8%) and maximum order (S = 31.4%) of β phase in the samples are affected by

ultrasonic power of 100 W. All the above imply that ultrasonic vibration can alter the molecular chains' packing geometries from the monoclinic (α) form to the hexagonal (β) form. The enhancement of β-form content combined with the decrease of crystallinity implies that the polymorphic transitions $\alpha \rightarrow \beta$ of PP exist in NaBz-added PP. It may be concluded that by treatment of ultrasonic vibration, the proportion of the monoclinic and hexagonal phases is changed. Generally, the proportion of these two forms depends on the molding conditions and the nucleating process.[9] From our experiments, the molding conditions were the same for all specimens. Therefore, this crystallization behavior can be related to the ultrasonic intensity. Different ultrasonic intensity has a different effect on the formation of α- and β-IPP phase in PP containing NaBz, such as accelerating the growth of only the β-form while repressing the growth of the α-form crystal.
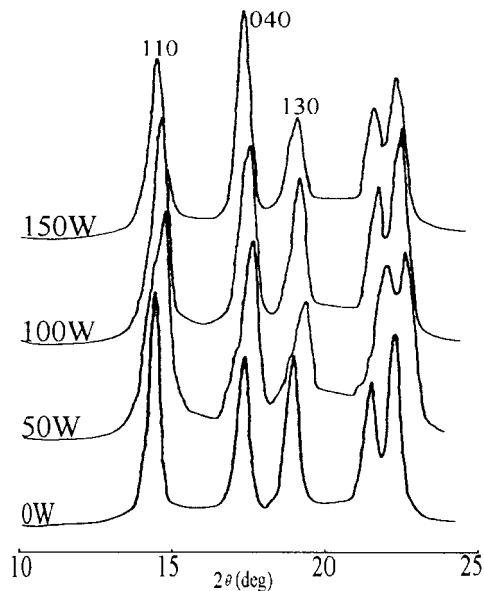
Table I   Crystallinity and Character of β Cryatalline of Filled PP with and without Ultrasonic Wave

UI (W)	PP/Sodium Benzoate			PP/Talc	PP/Talc(KH)	PP/Mica
	K (%)	S (%)	Xc (%)	Xc (%)	Xc (%)	Xc (%)
0	—	—	69.6	69.3	74.4	68.8
50	4.2	16.0	68.3	67.4	66.1	64.4
100	12.8	31.4	59.3	64.7	70.5	70.1
150	7.2	21.2	64.2	65.8	65.9	65.5
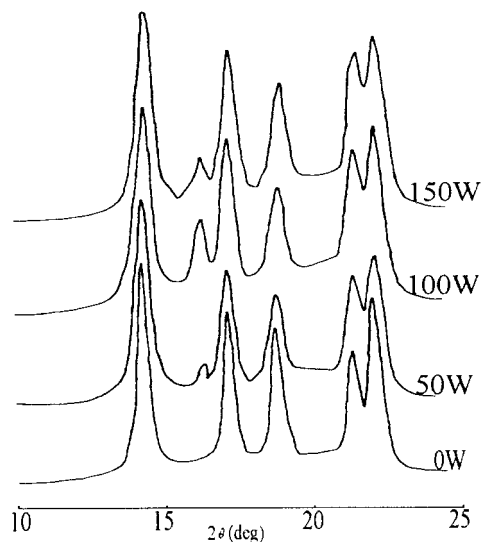
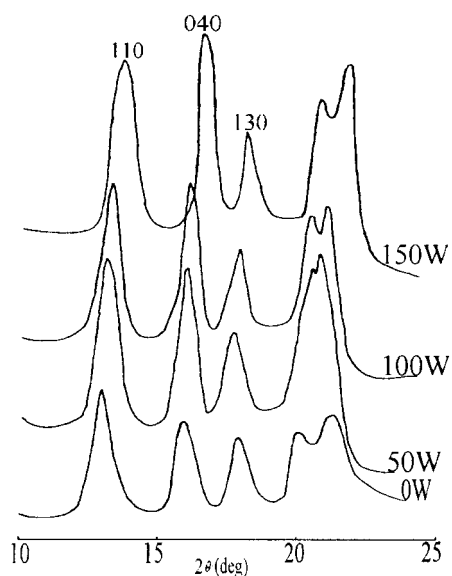**Figure 3** WAXD patterns of PP/sodium benzoate irradiated by ultrasound at different intensity.

Figure 5 WAXD patterns of PP/Talc(A) irradiated by ultrasound at different intensities.

In PP containing talc or mica, ultrasonic vibration does not promote the transition of crystal forms (Figs. 4–6). The reasons are supposed to be that the additives have nonhexagonal crystal form. Talc belongs to the monoclinic crystallographic system and its unit cell has a dimension of a = 0.526 nm, b = 0.910 nm, c = 1.881 nm, β = 100°00′. However, β-form of PP is a hexagonal system and its unit cell has a dimension of a

= 1.908 nm, c = 0.649 nm. From these lattice geometries, it is seen that there is no lattice matching between talc and β-form in PP. Mica also belongs to the monoclinic system, so it behaves similar to talc. According to Mercier,[10] benzoic acid salts allow epitaxial crystallization of polymer. In this manner, the response of NaBz-

Figure 4 WAXD patterns of PP/Talc(P) irradiated by ultrasound at different intensities.
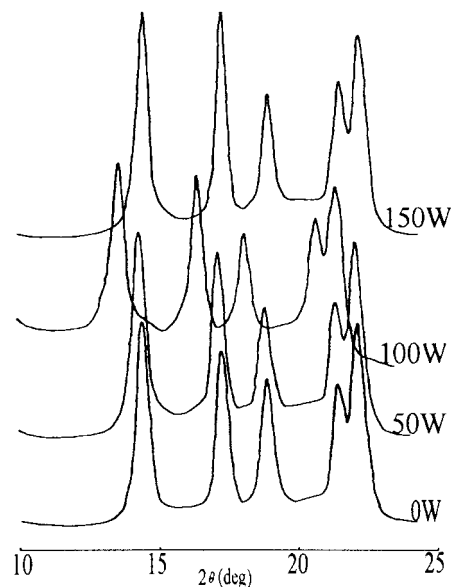
Figure 6 WAXD patterns of PP/Mica irradiated by ultrasound at different intensities.
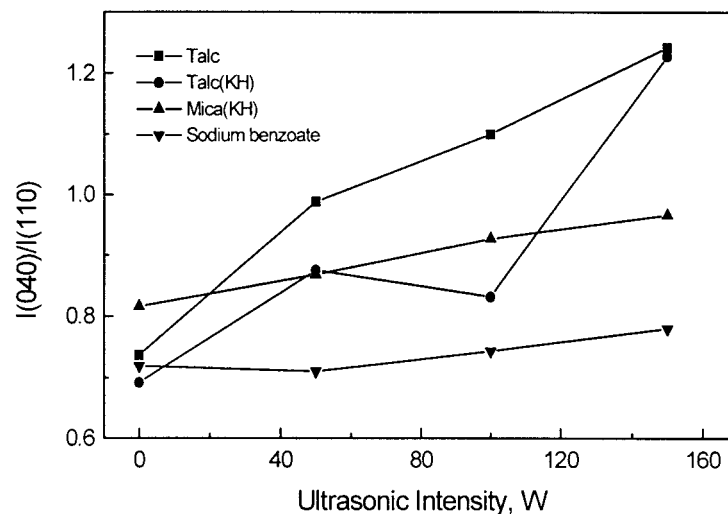
Figure 7 Dependence of reflection intensity ratios $I(040)/I(110)$ on ultrasonic intensity in different nucleating agents filled PP.

added PP to ultrasonic irradiation can be interpreted: PP with helical conformation aligns its —CH_3 groups in rows at the nonpolar benzene rings of NaBz, and ultrasonic vibration and energy may help the chains pack similar to that by changing the structure of the chains. Therefore, it may be concluded that the energy transfer and molecular motion induced by ultrasonic benefit the formation of β-form when nucleated PP crystallize through an epitaxial mechanism.

Crystal Orientation

As mentioned above, talc- or mica-added PP does not change crystal forms after applying ultrasound. However, Figs. 4–6 show that the reflection intensities of the (040) planes become stronger and surpass that of the (110) planes with the increase of ultrasonic intensity, implying that ultrasonic wave results in the orientation of the (040) plane. The ratio of the intensity of the (040) reflection, $I(040)$, to that of the (110) reflection, $I(110)$, can be used to evaluate the orientation degree.

Figure 5 gives the dependence of the ratio $I(040)/I(110)$ on ultrasonic intensity in different nucleating systems. The ratios $I(040)/I(110)$ for talc- and mica-added PP sharply increase with ultrasonic intensity. For example, in talc (P)-added PP, the ratio jumps from 0.69 without ultrasonic wave to 1.23 in the presence of 150-W ultrasonic intensity, but samples containing NaBz show negligible change.

The preferential growth of nucleated PP irradiated by ultrasound may be related to the crystal forms of nucleating agents. Talc and mica have characteristic flaky structures, which are supposed to facilitate the growth of crystals along the (040) plane of PP. The ratio $I(040)/I(110)$ for the mica system is higher than that for NaBz, even with the absence of ultrasound (Fig. 7). Perhaps the free energy required by the piling of (040) crystal is lowered after applying strong ultrasonic vibration. Thus, it is estimated that ultrasonic could promote the (040) plane orientation. Furthermore, talc with or without the coupling-agent system has no difference in crystal orientation caused by ultrasound.

CONCLUSION

The application of ultrasonic to different nucleating agents added to PP has various effects on the crystalline structure of PP.

The results show that ultrasonic vibration can enhance the crystallization nucleation ability while decreasing the crystallinity of nucleated PP. Moreover, influence of ultrasonic wave on crystal form and orientation is related to physical properties of nucleating agents, but has no correction with coupling agent. If there is lattice matching between nucleating agents and PP, just as NaBz, ultrasonic wave is liable to induce the formation of β-form. As

ultrasonic is applied, talc and mica, flaky nucleating agents, become easier to make preferential growth of PP crystals on (040) planes.

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