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Structural Changes of PP with Different Isotacticity Induced by γ-Irradiation

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Abstract

The morphology of i-PP with different isotacticity under high absorbed dose were studied with the measurements of cystallinity, crystallite size, melting heat and melting point by x-ray diffraction and DSC methods respectively. The results indicate that the changes are not only related to the heat history but also related to the isotacticity of i-PP. In generally, the higher the isotacticity of i-PP, the less morphology changes, and the morphology of annealing samples change less than the virgin powder samples. It means that the annealed i-PP with higher isotacticity is more stable to radiation both in air and vacuum conditions.

Keywords

Polypropylene, isotacticity, crystallinity, crystallite size, radiation stability.

Introduction

Research on radiation effects on morphological structure of iso-polypropylene (i-PP) has been widely carried out. It has been demonstrated that some microscopic changes occur in the solid state structure, as a result of the radiation induce crosslinking and degradation (Nishimoto, 1991; Chappell et al, 1963; Busfield et al, 1979; Gee et al,1970; Babic et al, 1983). Such microstructure changes may give rise to various macroscopic physical property changes. Recently, relationship between radiation stability and isotacticity of i-PP was reported (Qiao et al, 1996; Wei et al, 1998). Since the degree of crystallinity of i-PP and the perfectness of crystalline of it are closely related to its isotacticity, and generally, an increase in crystallinity corresponds to an increase in isotacticity(Quynn et al, 1959). The higher isotacticity of i-PP is, the more perfect crystalline content and the less morphous content tend to be formed. In another word, isotacticity of i-PP may potentially affects its morphology. As well known that the stability of i-PP toward ionizing radiation shows a significant relationship with the primary morphology (Nishimoto, et al, 1991,1992). So a compare study of morphological structure changes of polypropylene with different isotacticity induced by γ-irradiation should be meaning.

Experimental

(1) Materials: PB-281, PB-278, PB-280, PB-289 and HB-289 are all homopolyproylene with isotacticity of 86.3%, 90.2%, 93.9%, 96.9% and 99.0% respectively. Both powder samples and sheet samples were used here. Sheet samples were prepared by compression molding at 220°C under 50kgf/cm^2 and then cooling to room temperature under 150 kgf/cm^2 at ambient rate. A small amount of antioxidant was added.

(2) X-ray diffraction: X-ray diffractogram were recorded before and after γ-irradiation on a Rigaku D/max-RB diffractometer (Ni-filtered, Cu Kα radiation, 12kV, 80mA) at a scanning rate of $2\theta=2^{\circ}$ per minute. Determination of percent crystallinity was carried out by peak-separation method from X-ray diffraction measuring. And that of crystal size was calculated according to the half-peak-width in the spectra diffracted by the (110) plane which situates at about $2\theta\approx15^{\circ}$.

(3) Differential scanning calorimetry: Differential scanning calorimetry measurements were made with a Dupint-1090 DSC under purging into nitrogen stream: about 3-5mg of samples were heated at a rate of 10°C/min up to 200°C. In order to ensure a relative constant post-irradiation thermal history for each sample, a standard scanning procedure was used.

(4) Irradiation: Samples were irradiated with ^{60}Co γ-ray in air or in vacuum. Irradiation in vacuum was carried out as followed: glass tubes containing PP powders or sheets were evacuated at ambient temperature for no less than 20 minutes at 10^{-2} Pa before sealing, and after irradiation at dose rate of 501Gy/min for 16 hours and 40 minutes, the tubes were stored for more than a week before further experiments.

Result and Discussion

Crystallinity: The crystallnities of PP with different isotacticity before and after γ-irradiation in air or vacuum are shown in Fig.1. It can be seen that the crystallinity of virgin powder PP is linearly increased from 31% to 44% with the increasing of isotacticity from 86.3% to 99.0%, which is expectant that the higher isotacticity of PP, the easier is can crystallize under the polymerization conditions. The crystallinities of annealing samples of PP with different isotacticity are nearly the same and expectantly higher than powder samples, and do not change after γ-irradiation no matter what they are irradiated in air or vacuum. However, the crystallinities of powder PP are increased to a different degree after irradiation in air, and in fact, the crystallinity increase more for powder sample with higher and lower isotacticity than that with middle one. The increase of crystallinity of powder PP may be ascribed to the transition from amorphous phase because there are more amorphous phase and low crystallinity in virgin powder PP. This result indicates that the crystalline structure in annealing PP is more perfect and stable to radiation than that in powder sample.

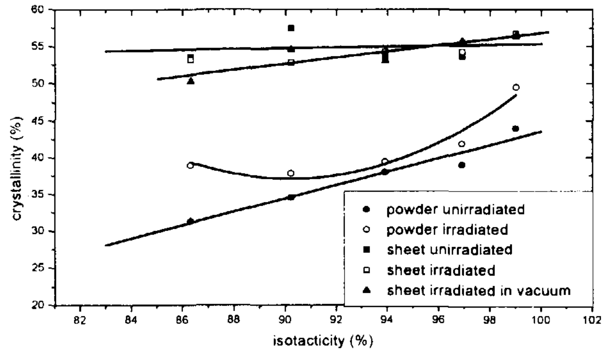
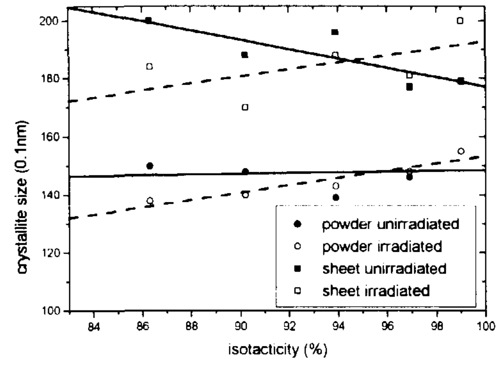


Fig.1. The crystallinity of PP before and after γ-irradiation in air or vacuum

Crystallite size: The crystallite sizes of PP with different isotacticity before and after irradiation are shown in Fig.2 and Fig.3. The results indicate that the crystallite size for both



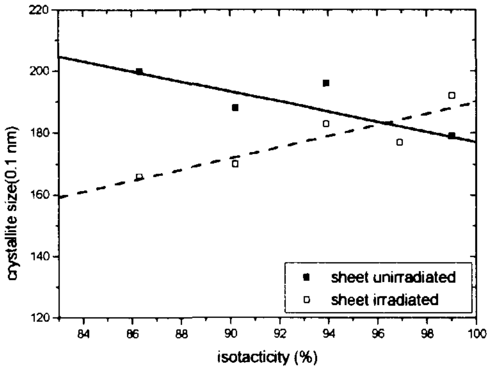


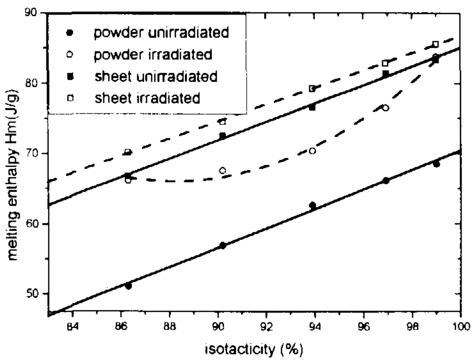
Fig.2. The crystallite size of PP before and after irradiation in air

Fig.3. The crystallite size of PP before and after irradiation in vacuum

powder PP and annealing PP changes seemingly with the same tendency after irradiation in air or in vacuum. The crystallite size of samples with lower isotacticity decreases, those with higher isotacticity increases, and that with middle almost does not change. This result indicates that there are two competition process simultaneously, one is damage of crystalline, the other is the transition process from amorphous phase to crystal phase. When the crystallinity is higher, and the crystallite size is larger, the damage process of crystalline should be dominant and as the crystalline is smaller and perfect, the transition from amorphous to crystalline should be dominant, which may explain for the effect of nucleating agent and the isotacticity of PP on the radiation resistance (Qiao et al, 1996).

From all these above, it should be concluded that the PP, either powder or annealing sample, with higher isotacticity, has better radiation resistance, since it is apt to crystallize in small crystallite size and perfectness, which may compensate the morphological structure damages (Nishimoto et al, 1992), while the PP with lower isotacticity has relatively more amorphous content which is more sensitive to radiation (Chappell et al, 1963).

Melting Characteristic: The study of melting characteristic differs from the x-ray diffraction in one important respect in which the sample has to be heated to the initial melting point before the information is obtained, and significant changes in structure can occur in the heating process and the observations may not be directly comparable with the results obtained by the other methods. A lot of previous investigations of the effect of γ-irradiation on the



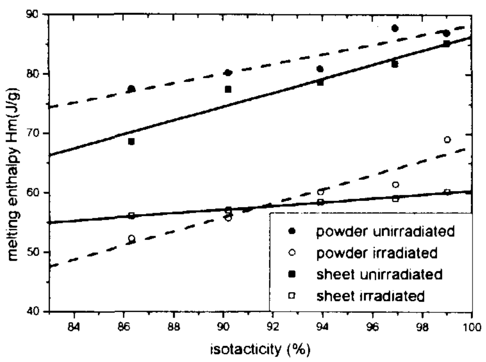


Fig.4. The dependence of the melting heat on isotacticity (first scanning, irradiated in vacuum).

Fig.5. The dependence of the melting heat on isotacticity (second scanning, irridiated in vacuum).

melting characteristics of isotactic PP has been reported (Gee et al, 1970; Busfield et al, 1979: Tommlinson et al, 1967). Decrease of melting point and broadening of fusion curves were observed everywhere. In present work, double melting thermogram in accord with double DSC scanning were obtained for each samples and shown in Fig.4 and Fig.5. According to Fig.4 and Fig.5, the melting heat of both powder and sheet samples are increased after irradiation during first and second scanning. The increments of ΔH of powder PP are more than sheet's; which suggests that the phase transition from smectic to crystal occurs (Nishimoto, 1995) and which is consistent with the result obtained by x-ray diffraction method. The melting points, shown in Fig.6 and Fig.7 are significantly decreased and expectantly increased with the isotacticity of i-PP for both powder and sheet samples, but the decrement of sheet sample is less than the powder samples. This result also indicates that the perfectness of crystalline of PP significantly effects the radiation resistance of PP.

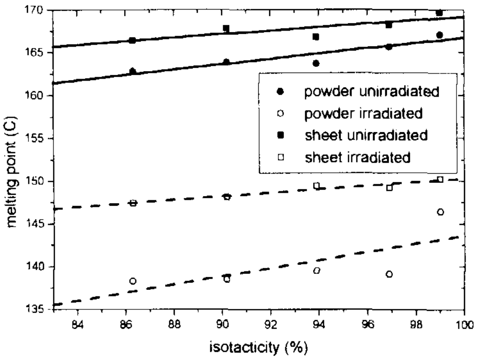


Fig.6.The dependence of melting point on the isotacticity(first scanning, in vacuum).

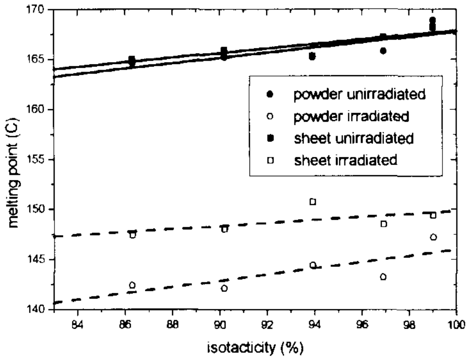


Fig.7.The dependence of melting point on the isotacticity(second scanning, in vacuum)

Conclusion

From the results above mentioned, it should be concluded that, (1) γ-radiation can induce the morphology changes of i-PP. (2) the radiation resistance of i-PP is significantly related to its isotacticity and the conditions of preparing the samples.

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