4.10 Effect of Isotacticity on Radiation Stability of Polypropylene

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Abstract: The relationship between radiation stability and isotacticity of polypropylene(PP), such as isotactic pentad ratio, was studied in this paper. It was found that the higher the isotacticity, the better the radiation stability. Compared with normal PP powder which has normal isotacticity, the special PP powder with higher isotacticity, such as, isotactic pentad ratio > 98%, can keep the Melting Index change less than normal PP after UV-light-oxygen aging or γ-irradiation in air. Furthermore, the special PP powder with higher isotacticity has lower intention of crosslinking or branching after 1KGy γ-irradiation in vacuum and has lower intention of degradation after 5KGy γ-irradiation in vacuum. The special PP powder with higher isotacticity also has lower content of carbonyl after 25 KGy γ-irradiation in air. These demonstrated that the special PP with higher isotacticity made from "special catalyst" is more suitable as the material for radiation sterilization than normal PP, because there are less "week points" in PP with higher isotacticity than that in PP with lower isotacticity. The random copolymer with 2.7% ethylene units made from the "special catalyst" mentioned above is even more stable in irradiation sterilization than homopolypropylene with higher isotacticity; therefore, it is reasonable that a random copolypropylene with about 4%wt ethylene made from the "special catalyst" should be the much more suitable PP material than normal PP for irradiation sterilization.

Introduction: Radiation sterilization of medical supplies made of polypropylene(PP) has been carried out widespreadly. Compared with ethylene oxide-sterilization method, radiation sterilization is a very safe method, but people still want better products, such as, the medical supplies made of PP with less additives. For this purpose, the PP resin(without additives) which has better radiation stability has to be used; therefore, it is important to know what kind of PP has better radiation stability.

The effect of PP microstructure on its radiation stability has been studied widely[1-9]. For example, it was said that the copolypropylene with 6% ethylene units has better radiation stability[8][9], the PP with lower crystallinity[5][8] or with larger spherulite size[9] has better radiation stability, adding nucleate agent can make PP's radiation stability become worse. Besides, the effect of quenching[8], molecular weight[7] ect. on radiation stability of PP has also been studied However, the study of effect of isotacticity of PP, such as, isotactic pentad ratio, relative length of helix structure, ect., on radiation stability has not been found up to now; therefore, this paper will discuss the effect of isotactic pentad ratio of PP on its radiation stability.

Experiment: 1. Material: HPP-1 is a homopolypropylene with higher isotacticity and MI=1.0 g/10min.; HPP-2 is also a homopolypropylene with general isotacticity and MI=2.0 g/10min.; HPP-3 is also a homopolypropylene with lower isotacticity and MI=2.0 g/10min.; And RPP is a random copolypropylene with about 2.7% ethylene units made from N-catalyst from which HPP-1 was made.

2. Experiment: The samples were irradiated with ^{60}Co γ-ray in air or in vacuum; Melting Index(MI) was measured at 230°C and antioxidant with ethanol was added into PP powder before measurement. The measurement was carried out after the sample was completely dried; The content of

carbonyl and relative length of helix structure were measured by FT-IR; The isotactic pentad ratio was measured by 100 MHz ^{13}C-NMR at 135°C; Rheograph was obtained by Rheometer at 230°C.

Result and Discussion: 1. Expression of isotacticity of PP: Isotacticity of PP is usually expressed by Isotactic Index which is measured by extraction with boiling n-heptane and this method is not precise enough; therefore, the isotacticity of PP will be expressed by isotactic pentad ratio and relative length of helix structure(10 or more isotactic units' relative contents) in this paper. Table 1 shows the isotacticity result of different commercial PP powder made from different commercial catalysts. In Table 1, HPP-1 with higher isotacticity was made by using N-catalyst and HPP-2 with general isotacticity was made by using GF-2A catalyst. It is obvious that isotacticity of HPP-1 made from N-catalyst is higher than that of HPP-2 made from general high efficiency catalyst.

Table 1. Isotacticity of Different PP

	HPP-1	HPP-2
Isotactic Pentad Ratio %	>98	95.2
Relative Length of Helix	95.7	92.3

2. Effect of isotacticity on ultraviolet ray stability of PP powder: HPP-1, HPP-2 and HPP-3 powder with different isotaticity were irradiated by outdoor sunlight and MI of these PP was measured every other day. It is found that PP with different isotacticity has different ultraviolet ray stability (See Fig.1).

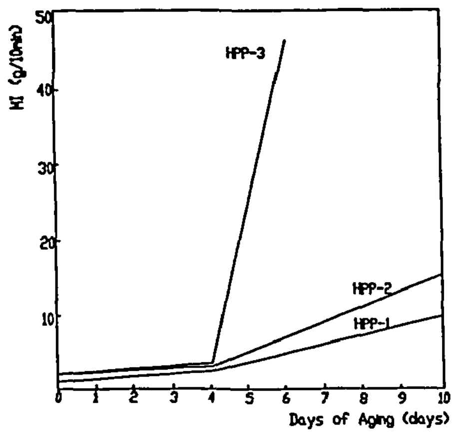

Figure1. MI Change of PP Powder During Ultraviolet Ray Ageing

It can be seen from Fig.1 that all 3 PP powders did not degrade obviously in 4 days' ageing; therefore, these 4 days could be called induction time of ultraviolet ray ageing. After 4 day-ageing, the speed of degradation is increased obviously and the speed of 3 different PP powders is much different: the slope(tgθ) of HPP-1 with higher isotacticity is only 1.2, and the slopes of HPP-2 and HPP-3 are 2.0 and 21.3 respectively; therefore, it is obvious that PP with higher isotacticity has better UV-stability.

3. Effect of isotacticity on γ-radiation stability of PP powder: PP powders were irradiated by γ-ray in air and in vacuum. The result is shown in Table 2. Normally the higher the crystallinity of PP is, the worse its radiation stability is. The abnormal phenomenon occurs here: the crystallinity of HPP-1 powder is 60.2%, and that of HPP-2 powder is only 54.3%, however the radiation stability of HPP-1 is better than that of HPP-2. This phenomenon suggests that isotacticity plays a very important role in radiation stability of PP and the higher the isotacticity of PP, the better the radiation stability of PP.

Table 2. Relationship Between Isotacticity and γ-radiation Stability ($\dot{D}$=1.0 Gy · s^{-1})

MI g/10min.	Before Irradiation	1KGy in Air	1KGy in Vacuum	5KGy in Vacuum
HPP-1	1.0	6.5	0.9	3.2
HPP-2	2.0	13	1.4	4.4

The result of radiation in vacuum is little bit different from that in air. Although PP belongs to crosslinking type polymer[8], it is easy to degrade during and after irradiation. It is largely dependent on the radiation condition of PP whether crosslink or degradation occurs predominantly. From the data in Table 2, it could be found that crosslinking or branching is predominant as the absorbed dose is less than 1KGy in vacuum, while the degradation becomes important as the absorbed dose increases. Rheology measurement conforms that PP powder has indeed been crosslinked or branched after 1 KGy irradiation in vacuum and the crosslinking or branching is more obvious in HPP-2 which has general isotacticity, than that in HPP-1 which has higher isotacticity (see Fig.2). For linear polymer molecule,

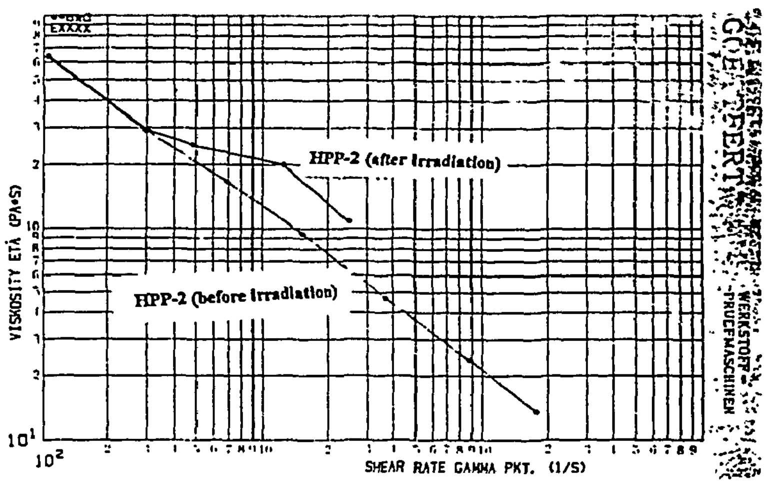

Figure 2. Rheograph of HPP-2 before and after irradiation at 230°C
(D=1.0KGy, $\dot{D}$=1Gy · s^{-1}, in vacuum)

such as, polypropylene, its molecule can be oriented gradually when shear rate of rheometer is increased; therefore, the apparent viscosity of linear polymer can be found to decrease gradually. For the polymer with crosslinking or branching structure, the molecule is difficult to be oriented when shear rate of rheometer is increased; therefore, its apparent viscosity can be found to decrease less than that of linear polymer. Accordingly, Figure 2 indicates that HPP-2 has indeed been crosslinked or branched after 1 KGy irradiation in vacuum. Compared with HPP-2, only a little crosslinking or branching occurs in HPP-1 after 1 KGy irradiation in vacuum(see Fig.3). Apparent viscosity of it appears little increased

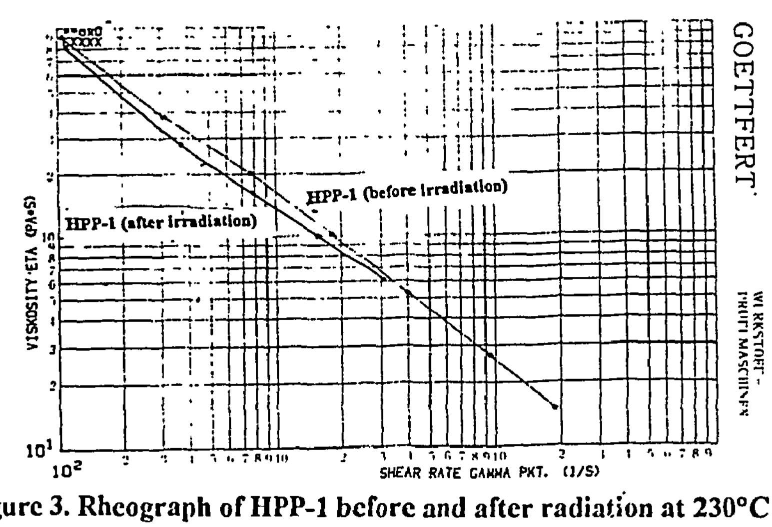

Figure 3. Rheograph of HPP-1 before and after radiation at 230°C
(D=1.0 KGy, $\dot{D}$=1Gys^{-1}, in vacuum)

only when the shear rate of rheometer is very high. According to above information, it is not difficult to find that radiation stability of HPP-1 with higher isotacticity is better than that of HPP-2 with general isotacticity. For instance, molecular weight of HPP-1 is reduced less than that of HPP-2 after 1 KGy irradiation in air; Crosslinking or branching of HPP-1 is less than that of HPP-2 after 1 KGy irradiation in vacuum, and the degradation of HPP-1 is also less than that of HPP-2 after 5 KGy irradiation in vacuum.

4. Effect of isotacticity on the content of carbonyl of PP after irradiation: HPP-1 and HPP-2 with same kinds of additives were extruded at same condition, and then were compressed into film samples under same condition. These samples were measured by FT-IR immediately after 25 KGy irradiation in air The relative content of carbonyl S was obtained

$$S = \frac{\text{Peak area of } 1700\ cm^{-1}}{\text{Peak area of } 1460\ cm^{-1}}$$

S was measured every month and the results are shown in Table 3 and Fig..4. The result further confirms that the PP with higher isotacticity made from N-catalyst has better radiation stability than the PP with general isotacticity.

Table 3 Effect of Isotacticity on Content of Carbonyl of PP after 25 KGy Irradiation

S	Immediately	1 Month	2 Month	3 Month	4 Month
HPP-1	0.082	0.088	0.109	0.113	0.135
HPP-2	0.067	0.101	0.133	0.135	0.147

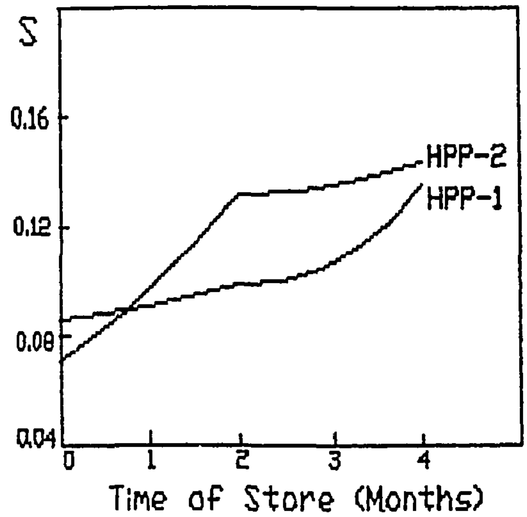

Figure 4. Effect of isotacticity on content of carbonyl after 25 KGy irradiation

5. Mechanical properties of PP with higher isotacticity after irradiation: In order to compare with commercial product Himont PD 626 which is a random copolypropylene and a special type for radiation sterilization, a special homopolypropylene was made from N-catalyst which has higher isotacticity (Isotactic pentad ratio is over 98%) and similar MI to that of PD 626. A certain type of additives were added to this homopolymer and test pieces were made by injection moulding. The measurement result is shown in Table 4. It can be seen that retaining rate of mechanical properties of the special

Table 4. Comparison of Mechanical properties between special homopolypropylene and commercial PP for irradiation sterilization

	PD 626, MI=12.7			Homopolypropylene, MI=13.2		
25KGy irradiatio	before	after 5 days	after 3 months	before	after 5 days	after 3 months
Flexural Modules10^3 MPa	1.1	1.1	1.2	1.6	1.7	1.8
Flexural Strength MPa	28.6	29.3	30.6	42.8	43.6	45.7
Izod Impact Notched, J/M	31.7	29.8	24.5	26.2	25.5	19.2
Tension Strength MPa	30.7	30.0	30.2	38.0	39.1	38.6

homopolypropylene listed in Table 4 are similar to that of PD 626, such as, the retaining rate of impact strength with notch which is considered to have closest relationship with practical use (see Table 5).

Table 5. Retaining rate of impact strength with notch after irradiation

	PD 626	Homopolymer
5 days after irradiation	94%	97%
3 months after irradiation	77%	73%

Why does the PP with higher isotacticity have so excellent radiation stability? It is proposed by the authors that there are less weak points(stress concerning points) in the PP molecule with higher isotacticity than that in normal PP molecule with general isotacticity and amount of weak points is the key factor which can make PP stable or not(see Fig. 5). It can be seen from Fig.5 that there are more weak points in the PP with general isotacticity because there are more trans-form units in this kind of PP.

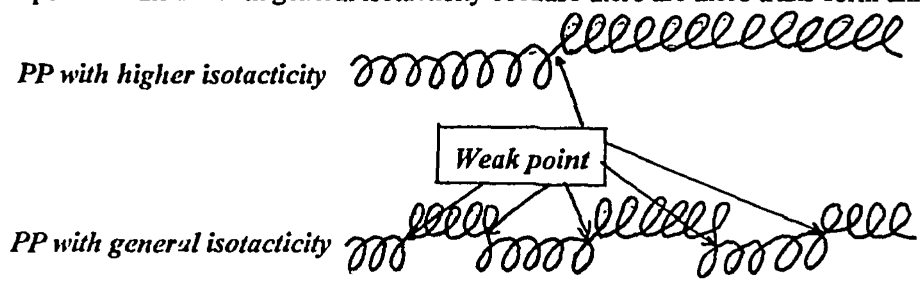

Figure 5. Sketch of PP molecular helix with different isotacticity

The weak points are easy to be broken when PP molecule is exposed to γ-ray; therefore, chemical reaction, such as, crosslinking or degradation, is easy to occur in the PP with general isotacticity when this kind of PP is irradiated. On the other hand, the PP with higher isotacticity is different from general PP. It has better radiation stability since there are less weak points in its molecule.

6. The radiation stability of random copolypropylene made from N-catalyst: It is known that the retaining rate of elongation of homopolypropylene is not as high as that of copolypropylene; therefore, a polypropylene with 2.7% ethylene units(RPP) made from N-catalyst was used. Although there is only 2.7% ethylene units in RPP, its radiation stability becomes much better than that of HPP-1 (see Table 6). The retaining rate of elongation of RPP is much higher than that of HPP-1. The result after

Table 6. Radiation stability of homo-PP and Co-PP

MI g/10min.	before irradiation	1 KGy in air	1 KGy in vacuum	5 KGy in vacuum
HPP-1	1.0	6.5	0.9	3.2
RPP	1.2	2.5	1.4	1.8

25KGy irradiation is shown in Table 7. It is proved that the random copolypropylene made from N-catalyst has good radiation stability. The reasons are that (1) the crystallinity of RPP is only 44.2%, much lower than that of HPP-1(60.2%); (2) there are less weak points in crystalline area because the N-catalyst was used. It can be expected that a random copolypropylene with excellent radiation stability can be obtained if the copolypropylene contains about 6% ethylene units as suggested by references <8> and <9>.

Table 7. Retaining rate of elongation of HPP-1 and RPP

elongation %	before irradiation	after irradiation	retaining rate
HPP-1	587	298	51%
RPP	554	480	87%

Conclusion: 1. The PP with higher isotacticity made from N-catalyst has better radiation stability than the PP with general isotacticity. The homopolypropylene with higher isotacticity has already had higher retaining rate of mechanical properties after γ-ray irradiation.

2.. The radiation stability of the PP with higher isotacticity can be improved if a certain amount of ethylene units is randomly copolymerized into its molecule.

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