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γ-Radiation-Induced Crystallinity Changes and Thermal Behavior of Low-Crystalline Polypropylene Films

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Abstract
Low-crystalline polypropylene films (PP) were irradiated with different doses of γ-radiation (0, 1, 2.5, 5, 7.5 and 10 Mrad). Differential scanning calorimetry, (DSC), wide-angle X-ray diffraction (WAXD) and FT-IR measurements were used to study the effects of γ-radiation on crystallinity, crystalline structure and thermal changes. It was found that crystalline structure, thermal behavior and crystallinity significantly changed with γ-irradiation. The crystallinity changes mainly depend on γ-irradiation dose, chain scission and crosslinking. The rise in crystallinity was found to be limited and related to chain scission. However, the reduction was accompanied by formation of crosslinking.

1. Introduction

The effects of gamma radiation on the morphology and thermal behavior of polypropylene have been subjected to study over many years [1-3]. The influence of γ-radiation on crystallinity changes and the mechanism that takes place in polypropylene is still quite unclear. Some studies, estimated a decrease in crystallinity [1, 4, 5], while others were found an increase in crystallinity [2, 6]. Many studies have shown that the change in crystallinity can affect the resistance of polypropylene to radiation-induced degradation. The smectic mesomorphic phase of PP, obtained by fast quenching from high-melts has been shown to withstand much higher doses than the monoclinic form [7, 8]. Nishimoto and Kagiya [3] have established that the critical dose, (*DC)* of irradiation, decreases with an increase in the monoclinic crystalline content. Consequently, it is important to investigate the effects of γ-radiation on the morphology, mechanism and the crystallinity changes in the low-crystalline polypropylene. Most of previous studies did not concern on the irradiation with low γ-dose rate. Irradiation with low-dose rate consumed long time which allowed good monitoring for the morphological changes occurred during γ-irradiation. Thus, the purpose of the present work is to investigate the effect of irradiation with low γ-dose rate on the crystallinity, crystalline structure and thermal behavior of low-crystalline polypropylene using Differential Scanning Calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and FT-IR.

2. Experiments

2.1. Material

The polymer used in this study was commercial sample of polypropylene (PP). These

polymer pellets were purified by dissolving in refluxing xylene under nitrogen atmosphere. The solution was precipitated with cold methanol, filtered and dried at 50 °C in vacuum oven. The sample was assumed to be "additive-free" and designated as purified sample.

2.2. Films Preparation

The purified sample was molded into 100 ±10 mm thickness films in aluminum foil between two plates by first heating at 210 °C and holding for 7 min and then increasing the molding pressure to 15,000 pounds. The temperature was maintained for further 5 min to erase the thermal history. The pressure was allowed to fall, the mold was then immediately quenched into a large bath filled with water at 15 °C. Quenching was used to produce a lower order crystalline structure, thereby increasing the amorphous region and the number of tie-molecule chains. These film specimens were used for further γ-radiation and other characterizations.

2.3. Gamma Irradiation

The films were kept in the γ-radiation chamber in the position which allows a uniform irradiation for all films. The source of radiation was Cobalt-60. The samples were irradiated at different doses; 0, 1, 2.5, 5, 7.5 and 10 Mrad with dose rate 0.10 Mrad / hr at room temperature in an air environment.

2.4. Characterization

2.4.1. Differential Scanning Calorimetry (DSC)

Thermal characterization studies were determined on a Perkin-Elmer Model DSC-7 differential scanning calorimeter equipment. The melting point (T_m), the heat of fusion (ΔH_f), the peak crystallization temperature (T_c), the heat of crystallization (ΔH_c), and the onset temperature (T_{on}) were computed from the melting endotherms and cooling exotherms. A rate of 10 ºC/min was used for heating and cooling cycles. Samples were analyzed by heating from 50 ºC to 250 ºC and kept at for 5 min and cooled to 50 ºC. The degree of crystallinity was calculated:

$$Crystallinity (\%) = H_f / H_{f0}$$

Where H_f is the heat of fusion of a perfectly crystalline polypropylene (assumed to be 209 Jg^{-1}) [9].

2.4.2. Wide-Angle X-Ray Diffractometer (WAXD)

The WAXD experiments were performed using Rigaku Dmax 2500 diffractometer from 2θ 10º to 35º at an interval of 0.05º at 40 kV and 100 mA, using Cu K-Alpha 1 radiation at a scan rate of 5º /min. Four major characteristic peaks for polypropylene at 2θ values of 14º, 17º, 18.5º and 21º for (110), (040), (130) and (041) reflections, respectively, were identified. The half-width for (110) and (040) reflections were measured to obtain an estimate of average-crystallites sizes.

2.4.3. FT-IR Spectroscopy

IR spectra were recorded with Fourier transform infrared 16 PC spectrometer. The crystallinity content of the samples was calculated from IR data as an average of the values provided by using equations (1) [10] and (2) [11].

$$C (\%) = 1.2 + 15.2 \times D_{1894} \tag{1}$$

Where D_{1894} is the absorbance per unit sample thickness (cm) of the crystalline band at 1894 cm^{-1}.

$$C(\%) = \frac{D_{1894}}{D_{1894} + k/A} \cdot 100 \tag{2}$$

Where $D_{1894} = E_{1894}/E_{1306}$.

K and A *are* the extinction coefficients corresponding to a totally crystalline one (6.2 cm^{-1}) and a totally amorphous one (17 cm^{-1}), respectively.

3. Results and Discussion

3.1. Thermal Analysis (DSC)

Thermal characterization gives good information on the morphological changes taking place after irradiation. Fig. 1. Shows the melting endotherms of the PP specimens before and after irradiation. It is seen that melting temperature (T_m), were reduced from 160.8 ºC to 154.8 ºC with increasing the time of irradiation. The melting peak significantly reduced at low doses, while an increase was observed at 2.5 and 10 Mrad. The reduction at low doses is attributed to chain scission. This is evidence that the process of γ-degradation starts with scission of the strained tie-molecules. It was reported [1, 12] that the effect of crosslinking on the ability of the samples to crystallize is indicated by the decrease in the crystallization temperature (T_c). On other hand, crosslinking will hinder crystallization. Since there is an increase in (T_m), a corresponding decrease in (T_c) and (ΔH_c) at 2.5 and 10 Mrad, that means crosslinking is dominant at those doses. DSC heating thermograms of PP show that a gradual broadening and appearance of shoulders towards the left of the peaks for the irradiated films is also observed at 2.5, 5, 7.5 and 10 Mrad. This indicates that the reduction in the crystallites average-size take place (or broadening of crystallites size distribution). This confirms that the crystalline region is effected with irradiation which is the confirmation of Kushal's observation [13]. The changes in the heat fusion (ΔH_f), were listed in Table.1. It is clearly seen that (ΔH_f) initially increases to 68.75 J/g and 67.63 J/g, at 1 and 7.5 Mrad against 63.20 J/g for the unirradiated sample. However, it is reduced to 62.30 and 63.05 at 2.5 and 10 Mrad. The reduction of (ΔH_f) indicates the breaking of crystallites, while an increase indicates a build up. The crystallization thermograms (Fig. 2.) were sharp single peaks and no significant changes observed after irradiation. The crystallization temperature (T_c), and crystallization enthalpies (ΔH_c), obtained by cooling from 250 ºC to 50 ºC

were increased at 1, 5 and 7.5 Mrad, while a decrease was found at 2.5 and 10 Mrad. The broadening of crystallization peaks steadily increased with the irradiation from 5 to 10 Mrad. This indicates a decrease in the average-size of crystallites. The data obtained from DSC explain that an increase in crystallinity was found, which is accompanied by chain scission. However, a decrease in crystallinity at 2.5 and 10

Mrad was accompanied by crosslinking, where a breakdown of crystallites occurred. The changes in the onset temperature (T_{on}), which is the temperature at which the sample starts to exhibit structural changes, decrease with irradiation except at 2.5 and 10 Mrad. This is conforming that structural changes occurred at 2.5 and 10 Mrad.

Table 1. *The effect of γ-irradiation on the thermal behavior of polypropylene during heating and cooling cycles (In Air).*

Dose (Mrad)	T_m (ºC)	T_{on} (ºC)	ΔH_f (Jg^{-1})	T_c (ºC)	T_{on} (ºC)	ΔH_c (Jg^{-1})
0	160.86	147.56	63.20	111.28	116.72	64.35
1	157.83	145.84	68.75	112.44	115.88	75.48
2.5	158.75	148.47	62.30	110.74	117.11	63.05
5	156.36	146.98	66.79	110.80	115.33	73.42
7.5	154.86	143.03	67.64	109.13	113.85	75.34
10	154.98	148.35	63.05	109.80	116.40	64.14

Table 2. *The effect of γ-irradiation on d-spacing and peak position for the reflections (110) and (040).*

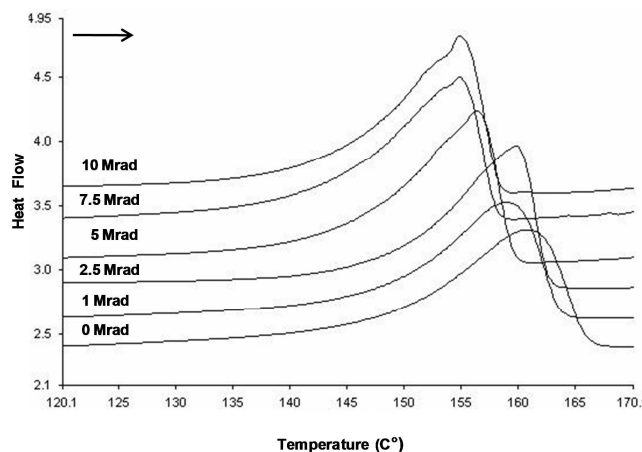| Irradiation Dose (Mrad)	d-spacing		2θ	
	(110)	(040)	(110)	(040)
0	6.121	5.1961	14.1	17.05
1	6.187	5.2419	14.02	16.98
2.5	6.077	5.1811	14.3	17.10
5	6.143	5.2113	14.84	17.00
7.5	6.187	5.2574	14.02	16.85
10	6.077	5.1811	14.3	17.10

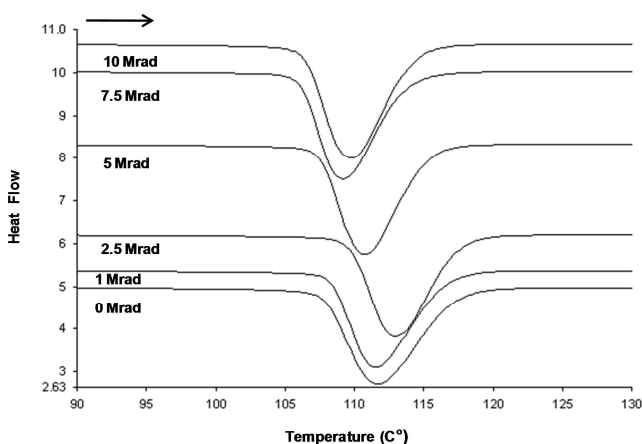**Fig. 1.** *Melting endotherms of γ-irradiated polypropylene films.*

Fig. 2. *Crystallization Exotherms of γ-irradiated polypropylene films.*
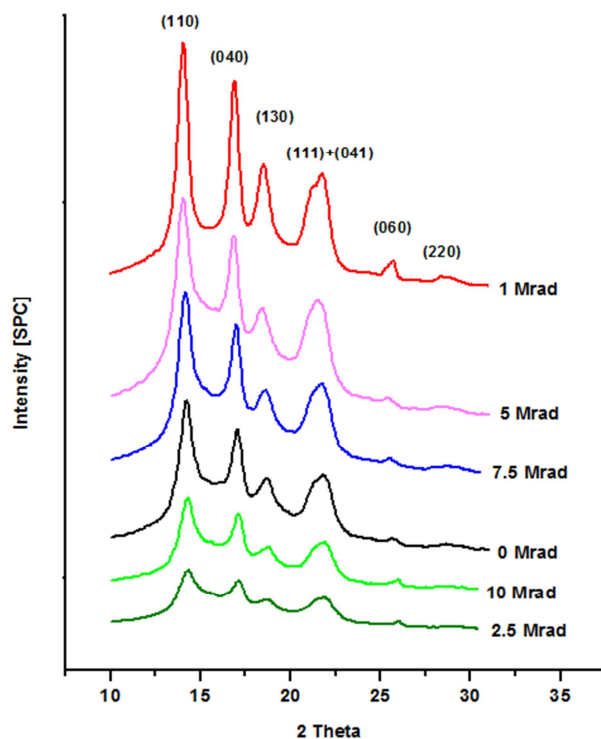
3.2. Wide-Angle X-Ray Diffraction (WAXD)

Fig. 3. *X-ray diffractograms of γ-irradiated polypropylene films.*

Fig. 3. Illustrates the diffractograms of neat and irradiated polypropylene films. Four sharp peaks can be identified, corresponding to the reflections of (110), (040), (130) and (041) at 2θ values of 14º, 17º, 18.5º, and 21.5º, respectively. The other peaks of small intensity correspond to the reflections of (150), and (220). Fig. 3. Shows the influence of the absorbed dose on the shape of peaks. It is well known that an increase in width and decrease in number of reflections of X-ray pattern are due to smaller crystallite sizes and disturbance of the three-dimensional arrangement of their atoms and molecules [14]. The broadening of the major peaks was observed at 2.5 and 10 Mrad. The half-width of the (110) and (040) peaks which are related to the average size of crystallites were higher at 2.5 and 10 Mrad. It means

that crystallites break down at those doses. Oppositely, the half-width were smaller at 1, 5 and 7.5 Mrad, which indicates a maximum increase at those doses. These observations agree with experimental results of d_{hkl} spacing (d is the distance between two successive planes), which shows the similarly increased to 6.187 at 1 and 7.5 Mrad, while it decreased to 6.077 at 2.5 and 10 Mrad against to 6.121 of unirradiated sample. This is confirming the results of DSC that the crystalline region is definitely effected. However, shift occurring in the peaks position were minimum (14.02º) at 1 and 7.5 Mrad and maximum (14.3º) at 2.5 and 10 Mrad. The intensities of (110) and (040) were maximum at 1 Mrad and minimum at 2.5 Mrad. These changes are attributed to an increase in the crystallinity at 1 and 7.5 Mrad and diminish the crystallites at 2.5 and 10 Mrad. The parameters of the X-ray diffraction pattern such as number of diffraction patterns, peak position (2θ) and width of the diffraction pattern support the results of DSC measurements. The changes in crystallinity with absorbed dose were calculated from WAXD, DSC and FT-IR data (Table 3). The crystallinity changes which obtained by three different methods was identical to the variation of 2θ and d-values. Crystallinity rises to a maximum value 43.49 at 1 Mrad followed by diminish to 26.52, approaching the crystallinity of the unirradiated film. This variation in crystallinity seems to be similarly repeated with irradiation from 5 to 10 Mrad. It was reported [15, 16] that, small molecules formed by chain scission have a freedom to move and to order themselves in the solid phase resulting perfect crystallites increasing the crystallinity. Consequently the shorter chains that are produced from chain scission associated with the original crystalline region, forming larger crystallites with irradiation up to 1 Mrad. The rise occurred seems to be limited where a breakdown of the associated crystallites (new crystal lamellae) was found with irradiation up to 2.5 and led to return the crystallinity to slightly less to the original value. The previous process repeatedly occurred with irradiation from 5 to 10 Mrad. This is confirming the DSC results that a defect was occurred in the original crystalline region at 2.5 and 10 Mrad. The above analysis of X-ray diffraction patterns and DSC versus irradiation does show two kinds of processes: built up and breakdown of crystalline region. This reflects that the structural changes occurring due to γ-irradiation differ depending on the absorbed dose. Chain scission (degradation) is most probable at a low dose and leads to the growth of the crystalline region, while crosslinking is accompanied with a decrease in crystalline region. The small molecules that produced by scission get associated with the original crystalline region forming lager crystallites. This growth continues till certain size and then broken to approaching the original crystalline content. These results make us more confident to say that the rise in the crystallinity is temporary. The results of this work supported to that propose of Horracks et al. [15] that the rise in crystallinity occurring due to the association of small molecules to the original crystalline region but our study proved that this rise is temporary and limited. Thus, one can say that radiation-induced degradation of polypropylene occurs exclusively in the amorphous phase. The presence of the defects or the action of the radiation led to an increase in the parameters of the unit cell, 2θ and to decrease in the crystallites packing d.

Table 3. *Effect of γ-radiation dose on the degree of crystallinity (%) using WAXD, FT-IR and DSC techniques.*

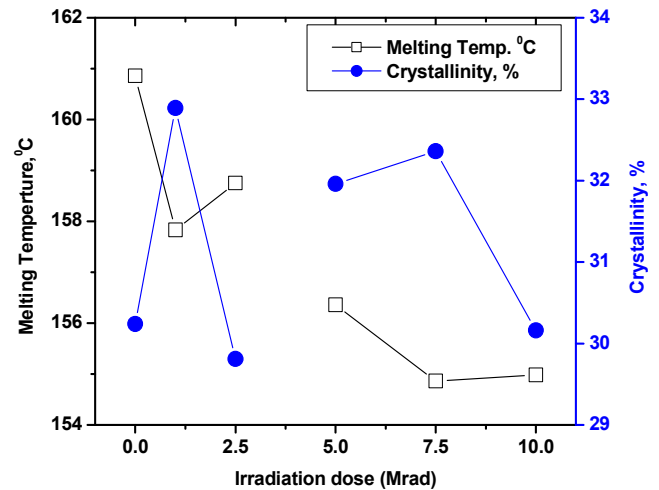| Method	Crystallinity (%) at different irradiation Doses (Mrad)					
	0	**1**	**2.5**	**5**	**7.5**	**10**
FT-IR	34.33	43.49	26.52	31.28	37.10	28.10
WAXD	33.01	41.81	29.11	32.81	34.21	30.29
DSC	30.24	32.89	29.81	31.96	32.36	30.16

Fig. 4. *The relationship between the changes in crystallinity (●) and melting temperature (□) during γ-irradiation.*

Fig. 4. depicts the T_m and the crystallinity variation along the γ-oxidation process. A relationship between T_m and crystallinity is found. It is worth remarking that, crystallinity and T_m vary in opposite directions. The temporary crystallinity increase, and the T_m decrease detected together at the beginning of induction period can only be accounted for by the shortening of the polymer chains, which promotes a closer intermolecular arrangement. These indicate that the increase in crystallinity is attributed to the scission of tie-molecules which located in amorphous phase followed by crystalline reorganization forming new perfect lamella in the form of α-crystal chains, while the reduction in crystallinity is due to crosslinking which can cause a defect in the crystalline lamellae.

4. Conclusions

The effect of γ-radiation on the crystallinity, structure, and thermal behavior of low-crystalline polypropylene were studied. γ-radiation causes significant changes in crystallinity, crystalline structure, and thermal behavior. The changes in crystalline structure were found to include two processes; build up of the crystalline region, and occurrence of a defect within the original crystalline region. The change in crystallinity does not show absolute increase or decrease. Two possible explanations can be given in this study: the first chain scission mechanism leading to increase in the

crystallinity and the second implies the occurrence of a defect in the original crystalline region due to the formation of crosslinking, leading to the decrease of crystallinity. The crystallinity changes depend on irradiation dose, chain scission and crosslinking.

Acknowledgement

References

[1] Zhang X.C., R.E. Cameron. J Appl Polym Sci., 74 (9) (1999) 2234–42.

[2] Kostoski D., Stojanovic Z., *Polym. Degrad. Stab.* 47 (1995) 353.

[3] Kagiya T., Nishimoto S., Watanabe Y., Kato M., *Polym. Degrad. Stab.*, 14 (1986) 199.

[4] Rolando, R. J., *Tappi J.* 74 (1991) 213.

[5] Kostoski D., Stojanovic Z., Gal O., Stannett V.T., *Radiat. Phys. Chem.* 32 (1988) 667.

[6] Mateev M., Karageorgiev S., *Radiat. Eff. Defects Solids.* 152(2) (2000) 109–38.

[7] Nishimoto, S., Kitamura K., Watanabe Y., Kagiya T. *Radiat. Phys. Chem.* 37 (1991) 71.

[8] Rolando, R. J. J Plastic Film Sheeting, 9 (1993) 326.

[9] Kostoski D., Stojanovic Z., *Polym. Degrad. Stab.*, 47 (1995) 353-356.

[10] Cernia, E., Mancini C., Montaduo G., *Polymer Letters.* 1 (1963) 371.

[11] Hendus, H., Schell G., *Kunststoffe*, 51 (1961) 6397.

[12] Chappell S. E., Sauer J. A., Woodward A. E., *J. Polymer Sci.* 13 (1969) 505.

[13] Sen K., Kumar P., *J. Appl. Polym. Sci.* 55 (1995) 857-863.

[14] Badr Ali, Zahran, Khafagy RM., *Polym. Int.* 49 (2000) 1555-1560.

[15] Horrocks A. R., D'Souza J. A., *J. Appl. Polym. Sci.* 52 (1991) 243

[16] Alariqi S.A.S., Rao B.S.M., Pratheep Kumar A., Singh R. P., *Polym. Degrad. Stab.* 94 (2009) 272–277.