

Influence of Gamma-Irradiation on Structural and Mechanical Properties of Polypropylene Yarn

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SYNOPSIS

Polypropylene multifilament yarn samples were irradiated by gamma rays in air. The effect of radiation dose on thermal, structural, and mechanical properties was studied. Melting endotherms and crystallization exotherms gave useful information regarding the structural changes. X-ray diffraction, infrared spectroscopy, density, and viscosity data of the irradiated samples were analyzed. Although viscosity and mechanical properties decreased with irradiation, the density marginally increased. Breaking elongation has been found to be a sensitive parameter for assessing deterioration. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Although polypropylene fibers have not yet established themselves in the apparel sector, they have steadily and surely gained acceptance in the industrial and geotextile arena, due mainly to their superior mechanical properties, chemical and biological inertness, and relatively low cost compared to other textile fibers.¹ Applications such as tentage, wind sails, twines, cords, and geotextiles demand long-term stability and serviceability. All polymeric materials degrade and polypropylene is no exception, even if heavily loaded with stabilizers.² This has initiated many studies on the durability and aging behavior of polypropylene.³⁻⁸ Of particular interest are studies involving high-energy gamma-irradiation of plastics, which leads to chain scission, cross-linking, or both, depending on the environment.⁹⁻¹² Gee and Melia¹³ in their work on polyethylene showed that irradiation leads to intermolecular cross-linking and ordering in the solid phase. Spadaro et al.¹⁴ showed that a cross-linking reaction predominates when polyethylene is irradiated under vacuum, while oxidative degradation prevails in air, and its kinetics depends on the diffusion of atmospheric oxygen in the bulk of the material. The extent to which the polymer is affected depends upon the type of poly-

mer, general morphology, type, and dose of irradiation.^{3,15} Black and Lyons¹⁶ showed that the chain scission is disproportionately higher at low doses of high-energy radiation on polypropylene. This is associated with changes in mechanical properties as well.^{12,16,17} It may here be mentioned that fibers are highly anisotropic and, being fine, have enormously large surface areas. This is likely to affect the degree of damage due to irradiation. Although some studies have been conducted on fibers,^{9,18} the effect of irradiation on structural features has not been dealt with in depth. The present work has evolved around the effect of the dosage of gamma-irradiation on thermal, structural, and mechanical properties.

EXPERIMENTAL

Material

Throughout this study, commercial polypropylene multifilament yarn (328 denier and 80 filaments) obtained from Rajasthan Petrosynthetics Ltd., India, was used. The diameter of a single filament was 25 μm .

Gamma-Irradiation

The samples were taken in hank form in a glass container that was kept in the gamma chamber. The source of radiation was Cobalt-60, radiating at a dose rate of 0.12 Mrad/h. The samples were irradiated

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for periods ranging from 5 to 200 h at room temperature in an air environment.

Physicomechanical Characterization

The samples thus irradiated were characterized and evaluated as follows:

Thermal Characterization

Differential scanning calorimetric studies were conducted on a Perkin-Elmer DSC-7 series equipment. A rate of 10°C/min was used for both the heating and cooling cycles. The melting peak temperature (T_m), the heat of fusion (ΔH_f), the temperature for onset of crystallization (T_{on}), the peak crystallization temperature (T_c), the heat of crystallization (ΔH_c), and half-width were computed from melting endotherms and cooling exotherms. An estimate of the rate of crystallization (R_c) was computed from the slope of the crystallization curve.¹⁹

X-ray Diffractometric Studies

The X-ray diffractograms of the powdered samples were recorded on Philips Norelco equipment. Radial scans with a diffraction angle (2θ) ranging from 10° to 35° using CuK α radiation were recorded at a scan rate of 2°/min. Four major characteristic peaks for polypropylene at 2θ values of 14°, 17°, 18.5°, and 21° for (110), (040), (130), and (041) reflections, respectively, were identified. The half-widths for (110) and (040) reflections were measured to obtain an estimate of average crystallite size.

Density

The density of the samples was determined by a density gradient column prepared with an isopropanol (0.785 g/cc) and diethylene glycol (1.116 g/cc) mixture. An average of four samples is reported.

Infrared Spectroscopy

The IR spectra of the samples were recorded on an FTIR (Nicolet Instruments Ltd.) in the wavenumber range from 400 to 4800 cm⁻¹ at a rate of 200 cm⁻¹ per second. Relevant portions of the spectra depicting the changes in the carbonyl content and hydroxyl content have been compared.

Viscosity

Four percent (w/w) solutions of samples were prepared in boiling decalin or xylene and the viscosities of these solutions were measured by a Brookfield viscometer at 125°C, keeping a constant rpm of 20.

Tensile Behavior

The tenacity and breaking elongation (%) were computed from the tensile results obtained on an Instron 4201 Model at a gauge length of 10 cm and a rate of extension of 20 cm/min.

RESULTS AND DISCUSSION

Thermal Characterization

Thermal characterization gives a fairly good idea of the changes taking place in irradiated polypropylene yarn. Figure 1 compares the melting endotherms of the exposed samples. It is clearly evident from these that the melting peak temperature (T_m) steadily reduces as the dose or exposure time is increased. In fact, after 200 h, the T_m reduces by about 20°C, i.e., from 169.2 to 149.7°C. The high-energy gamma-radiation seems to have inflicted heavy damage, which is to be expected. This large reduction can be attributed to severe chain scission, cross-linking, or branching. An interesting aspect of the endotherms is the gradual broadening and appearance of a shoulder toward the left of the peak. This indicates that the average size of the crystallites is changing. Normally, one believes that molecular degradation, as a result of exposure, is restricted to amorphous regions of the polymer, being less ordered and more accessible. The present study indicates that the crystalline regions are definitely affected. It is possible that larger crystallites break at or around the defects, resulting not only in the reduction of average size but also in the broadening of the crystallite-size distribution.

Another interesting observation during the heating cycles related to changes in heat of fusion values (ΔH_f). These results are presented in Table I. It was expected that, as a result of the breaking up of the crystallites, ΔH_f will either reduce or remain the same. However, after showing a small decrease, the heat of fusion values increased to 125.4 J/g as against 96.2 J/g for the control sample. The above scans were run in air. To ascertain the reason for the above observations, the scans were rerun in a nitrogen atmosphere. In this case, too, the ΔH_f values showed an increase after an initial dip (Table I). As the amount of the dose of gamma-radiation increases, it is expected that the chain scission would result in smaller molecules with higher freedom of movement, which may allow them to rearrange and order themselves in the solid phase, leading to perfect crystallite formation. This has also been reported

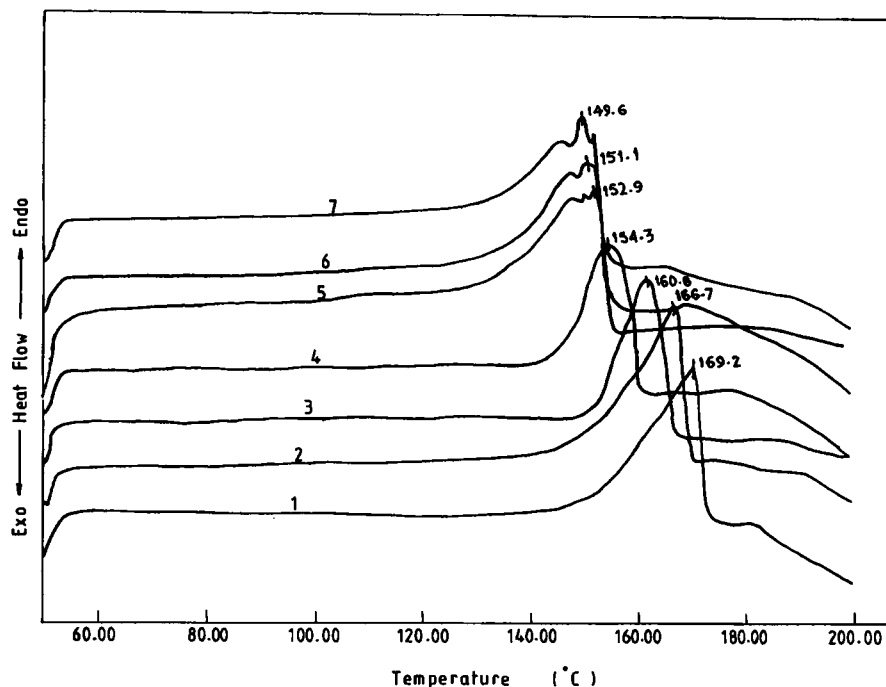


Figure 1 Melting endotherms of irradiated polypropylene multifilament yarn samples exposed for (1) 0 h, (2) 5 h, (3) 25 h, (4) 50 h, (5) 100 h, (6) 150 h, and (7) 200 h.

by Gee and Malia in the case of polyethylene¹³ as well as Horrocks and D'Souza⁴ in their studies on the aging of polypropylene.

DSC crystallization exotherms were obtained by cooling the samples from 200 to 50°C. (Fig. 2). These exotherms also provide interesting information. As the time of exposure is increased, the temperature of peak crystallization steadily decreases from 117.6 to 107.6°C. This clearly speaks of molecular cleavage. Here, too, one may observe broadening of the crystallization peak as the radiation dose or time of exposure is increased. The half-width of the peak,

which is indicative of the average size of crystallites, steadily increases with the dosage (Table II). Interestingly, not only the heat of crystallization, (ΔH_c) but also R_c , an estimate of the rate of crystallization, fall appreciably. The molecular restructuring as a result of cleavage, cross-linking, or even some recombination may be responsible for these changes. Although irradiation in air predominantly leads to oxidative degradation,^{16,17} some cross-linking is not ruled out. Such a cross-linked molecular structure would definitely hinder crystallization as well as the rate of crystallization.

Table I The Effect of Irradiation on Heat of Fusion, Melting Temperature (in Air and Nitrogen), and Density of Polypropylene Yarn

Irradiation Time (h)	Radiation Dose (Mrad)	T_m	ΔH_f	T_m	ΔH_f	Density (kg/m ³)
		(°C)	(J/gm)	(°C)	(J/gm)	
		(In Air)		(In Nitrogen)		
0	0.0	169.2	96.2	168.8	96.9	904
5	0.6	166.7	91.6	165.3	86.3	902
25	3.0	160.8	97.8	161.6	90.5	905
50	6.0	154.3	99.8	—	—	908
100	12.0	152.9	108.8	155.3	111.9	911
150	18.0	151.1	119.7	153.3	121.4	915
200	24.0	149.6	125.4	152.5	126.8	916

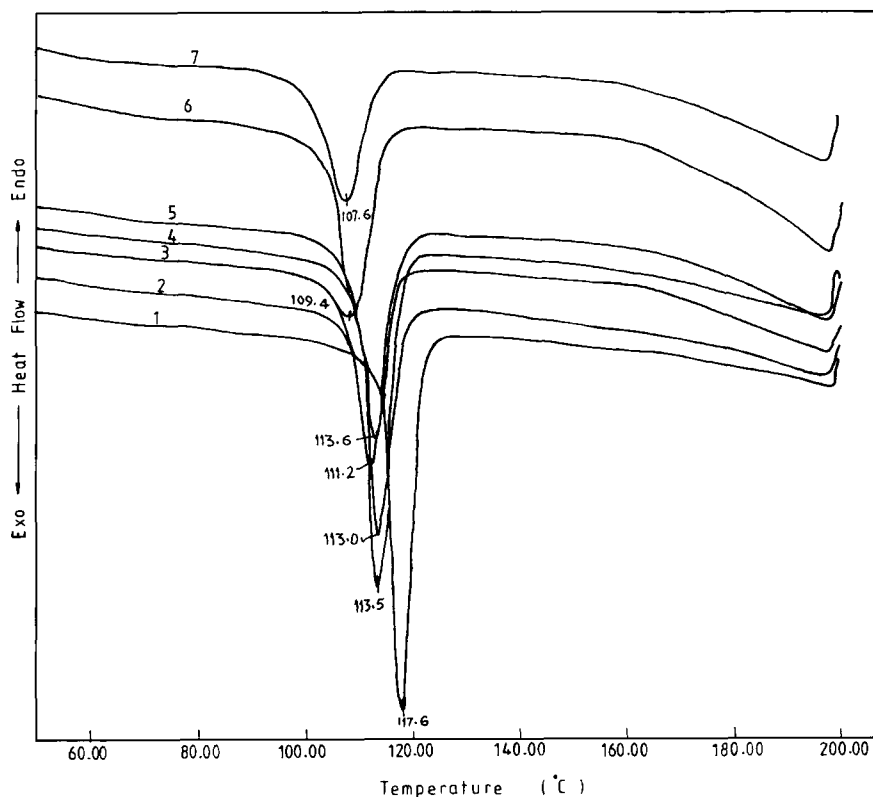


Figure 2 Crystallization exotherms of irradiated polypropylene multifilament yarn samples exposed for (1) 0 h, (2) 5 h, (3) 25 h, (4) 50 h, (5) 100 h, (6) 150 h, and (7) 200 h.

Density

Density of the irradiated samples also showed a marginal increase (Table I) with increasing dosage. This may also be a result of a possible densification due to rearrangement of smaller molecular chains. However, some contribution of oxygen uptake during irradiation as a result of oxidation cannot be discounted.

Table II Effect of Irradiation on the Thermal Behavior of Polypropylene Multifilament Yarn During Cooling Cycle (In Air)

Irradiation Time (h)	T_c (°C)	T_{on} (°C)	R_c (J/°C)	Half-width (°C)	ΔH_c (J/g)
0	117.8	121.8	0.87	3.9	92.2
5	113.5	118.5	0.51	4.4	81.0
25	113.0	118.1	0.47	5.0	73.9
50	113.6	118.0	0.34	5.3	67.0
100	111.2	116.2	0.29	5.8	65.8
150	109.4	114.5	0.26	6.3	64.8
200	107.6	113.4	0.18	7.7	53.3

X-ray Diffraction Studies

X-ray diffractograms (Fig. 3) show typical polypropylene reflections at 2θ values of 14° , 17° , 18.5° , and 21° representing (110), (040), (130), and (041) reflections, respectively. Irradiation does not seem to bring about any identifiable crystallographic transitions. However, one notices a little broadening of major peaks. The half-widths of (110) and (040) peaks, which can be related to the average size of crystallites, seem to be higher for irradiated samples (Table III). This means crystallites do break down upon irradiation. One may point out here that smaller structural entities, which result in increased ΔH_f values, are not perfect enough to be picked up in X-ray diffraction. For this case, therefore, one may say that the differential scanning calorimetric technique is more sensitive than is x-ray analysis.

Infrared Spectroscopy

Infrared spectra match that of a typical isotactic polypropylene. Figure 4(a) and (b) compare typical portions of IR spectra related to carbonyl and hy-

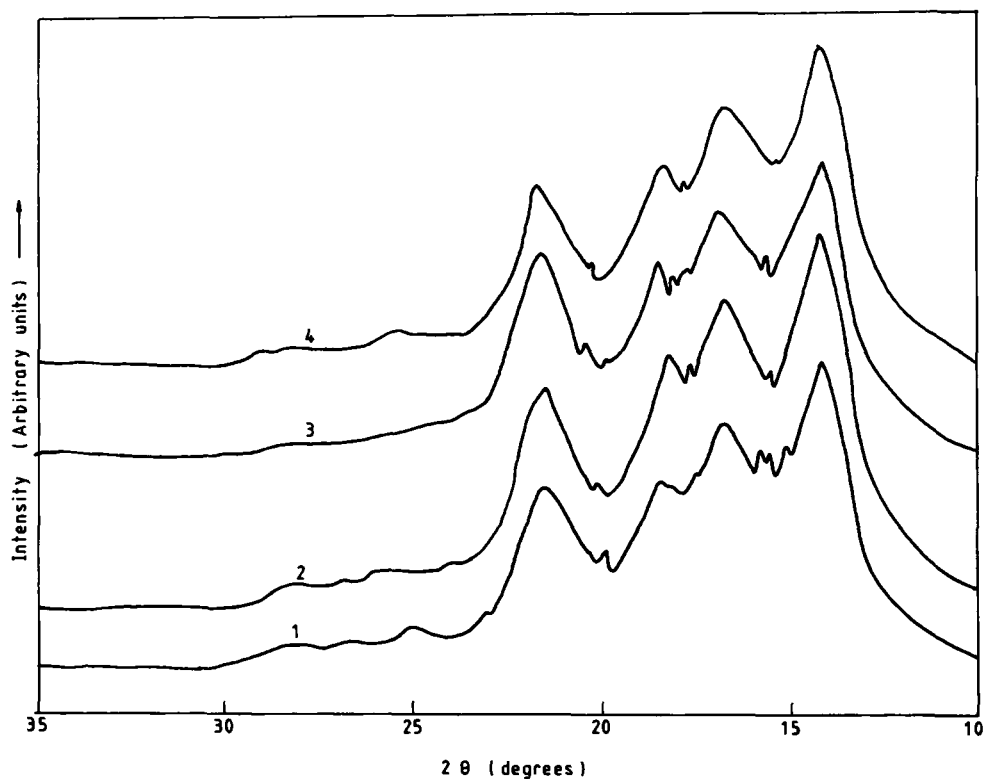


Figure 3 X-ray diffractograms of irradiated polypropylene multifilament yarn samples exposed for (1) 0 h, (2) 5 h, (3) 100 h, and (4) 150 h.

droxyl absorption. Both the carbonyl (around $1650\text{--}1800\text{ cm}^{-1}$) and the hydroxyl (3400 cm^{-1}) content show a steady increase with the irradiation time. This reflects oxidative degradation, which was expected.

Viscosity

The viscosity was measured by dissolving the polypropylene samples in two solvents, viz., decalin and xylene. All the samples dissolved completely at the boil in the solvents and there was no gelation or

undissolved mass. The viscosity of the clear solutions (4% w/w) was measured at 125°C in a Brookfield viscometer at a fixed rpm. It is evident from the data (Table IV) that the viscosity of the solutions decreased upon irradiation, clearly depicting a decrease in the molecular weight. The radiation dose

Table III Effect of Irradiation Dose on the Half-Width of Reflections in the X-ray Diffraction Patterns

Irradiation Time (h)	Half-width (Rad)	
	(110)	(040)
0	0.023	0.017
5	0.022	0.021
100	0.025	0.029
150	0.027	0.030

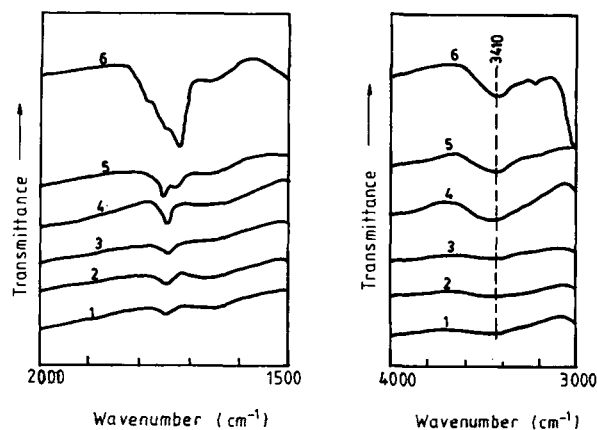


Figure 4 Infrared spectra of irradiated polypropylene multifilament yarn samples exposed for (1) 0 h, (2) 5 h, (3) 25 h, (4) 50 h, (5) 100 h, and (6) 200 h. (a) Effect on carbonyl content; (b) Effect on hydroxyl content.

Table IV Effect of Irradiation on Viscosity and Mechanical Properties of Polypropylene Yarn^a

Irradiation Time (h)	Radiation Dose (Mrad)	Viscosity ^b (CP)		Tenacity (gpd)	Breaking Elongation (%)
		In Decalin	In Xylene		
0	0.0	1574.0 (1.24)	1482.0 (1.0)	4.34 (2.5)	32.6 (2.6)
5	0.6	1548.0 (1.2)	1422.7 (1.3)	4.17 (1.8)	31.0 (2.2)
25	3.0	1363.0 (2.2)	1185.6 (1.1)	4.14 (2.8)	28.0 (2.9)
50	6.0	1211.9 (1.5)	1067.7 (1.3)	3.01 (2.9)	16.4 (3.1)
100	12.0	1018.3 (2.5)	928.8 (2.4)	2.10 (3.3)	12.8 (4.2)
150	18.0	640.6 (3.4)	712.6 (3.9)	1.25 (6.7)	6.5 (4.6)
200	24.0	546.9 (4.1)	385.3 (3.9)	0.81 (7.0)	3.3 (5.1)

^a Coefficient of variation (%) is shown in parentheses.

^b Viscosity of 4% (w/w) solution of polymer in decalin or xylene was measured at 125°C.

vs. viscosity as percentage of control has also been plotted in Figure 5. It may be noted that both solvents are equally effective for measurement of viscosity. It is expected that the major chemical reaction during irradiation in air is oxidative cleavage. However, the absence of gel formation does not indicate absence of cross-linking. As the degradation is severe, minor cross-linked networks formed during

exposure may not stand out and are likely to remain in the dissolved phase.

Mechanical Properties

The effect of irradiation on mechanical properties was as expected (Table IV). Both the tenacity and the breaking elongation decrease drastically, which has also been reported by many workers.^{9,10,20-22} These changes in tensile properties are attributed to a decrease in the average molecular length by the cleavage of macromolecular chains. It may be noticed from Figure 5 that after 50 h exposure, while the tenacity and viscosity (in decalin) retained are 68 and 77%, respectively, the elongation drops to about 51% of the unirradiated sample. It may, therefore, be inferred that elongation at break is a more sensitive indicator of degradation. This fact has also been reported by Wilski¹² and recommended by IEC.²³

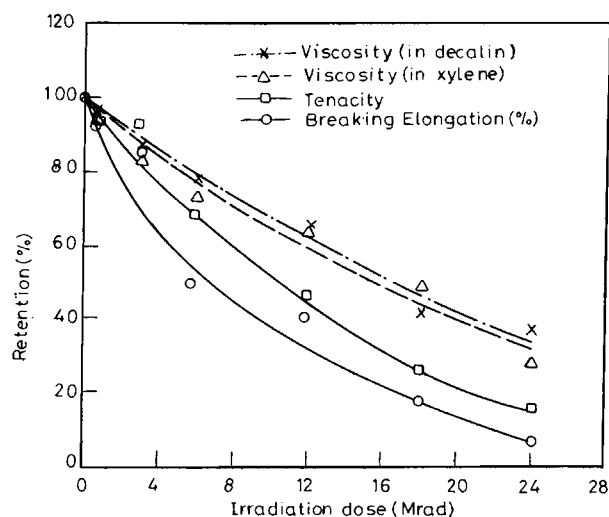


Figure 5 Effect of irradiation on polypropylene multifilament yarn: (—·×—) viscosity (in decalin) retention (%); (---Δ---) viscosity (in xylene) retention (%); (—□—) tenacity retention (%); (—○—) breaking elongation retention (%).

CONCLUSIONS

Upon irradiation, although the mechanical properties of polypropylene yarn deteriorate, the density does not decrease; in fact, it shows a marginal increase. Heat of fusion increases with irradiation dose, although peak melting temperature falls steadily. This may be related to the breakdown of crystallites with a concomitant formation of smaller

crystalline entities. Crystallization exotherms hint at molecular cleavage and possible cross-linking or branching. X-ray diffraction analysis also shows broadening of the peaks. The carbonyl and hydroxyl content increase with an associated fall in the molecular weight as evidenced from the viscosity data. Breaking elongation is a more sensitive parameter than is tenacity for assessing degradation.

Thanks are due to Rajasthan Petrosynthetics Ltd. India for supplying the required PP multifilament yarn. The authors would like to thank Prof. P. Bajaj from IIT Delhi for the helpful discussion during the work.

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Received November 11, 1993

Accepted August 3, 1994