JOURNAL OF
Applied Polymer
SCIENCE

Characterization of Degradation of Polypropylene Nonwovens Irradiated by γ-Ray

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ABSTRACT: Polypropylene is a leading commercial, fiber-forming polymer due to its low cost and potential for making high strength fibers. As the polymer of choice in the biomedical field, polypropylene contains only two elements, namely carbon and hydrogen. As a result, it is very hydrophobic and bio-inert lacking biodegradability in the landfill. Meltblown and spunbond polypropylene nonwovens were exposed to γ-radiation doses up to 25 kGy. The changes in morphology, chemical, thermal, and tensile properties were characterized by various analytical techniques. Following γ-radiation, the FTIR spectrum illustrated an increase in carbonyl groups suggesting radio-oxidation. Additionally, there was a decrease in thermal and tensile properties indicating deterioration of the polymer. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39917.

KEYWORDS: fibers; degradation; polyolefins; textiles

Received 13 March 2013; accepted 28 August 2013
DOI: 10.1002/app.39917

INTRODUCTION

Since the initial production of nonwovens more than two decades ago, the nonwoven industry remains to be the fastest growing sectors of textile materials in the world. Global consumption of nonwovens will reach 15.6 billion pounds in 2015, an increase from 11.9 billion pounds in 2010. In North America, the demand for nonwoven materials reached 2.2 billion pounds in 2010 and is expected to reach 2.6 billion tons in 2015, a compound annual growth of 3.4%.[1,2] As the nonwovens market continues to expand, the introduction of biodegradable, sustainable raw products to create nonwovens remains unchanged.

Nonwovens exhibit specific features such as strength, elongation, resilience, liquid repellency, softness, washability, filtering capacity, bacteria barrier, and sterility.[3] Among the various applications, many of the products are classified as disposable products which account for nearly two-thirds the demand of nonwovens fabrics.[1] Disposable products such as diapers, feminine pads, medical gowns, drapes, filters etc are often used during a single time and then discarded in the landfill. In 2010, 1.5 billion tons of disposables were produced and disposed in the landfill globally. By 2015, it is projected to increase by 3.2% sending an additional 1.8 billion tons to the garbage.[4] Considering the projected growth in "throw-away" nonwoven sector, it is imperative that issues related to waste disposal be addressed.

Due to its ease of proccessability, polypropylene is the most widely used resin in the nonwoven industry. According to INDA, polypropylene accounts for 70% of the spunlaid resins used to manufacture nonwovens in North America.[5] Employed in nonwoven applications such as medical supplies, filtration, and hygiene products, isotactic polypropylene is a thermoplastic, high molecular weight polymer. Containing namely carbon and hydrogen elements, micro-organisms are unable to digest high molecular weight polymers lacking hydrophilicity. Currently, polypropylene nonwovens are discarded in the landfill where decomposition starts after approximately 100 years. Consequently, a large accumulation of these thermoplastic materials in the environment is an issue of increasing concern. As a result, there is an increasing need to develop polypropylene nonwovens with increased biodegradability, which can be further made into nonwoven products for use in products like face masks, filters, wipes etc.

One approach to enhancing the biodegradability of polypropylene is by application of γ-rays. The most widely used form of ionizing radiation sterilization; γ-rays are an alternative compared to the use of ethylene oxide/CFC mixtures incineration techniques which emit toxic gases leading to carcinogenic and mutagenic effects in humans. In fact, gamma radiation has become the industry standard for high-energy sterilization especially in medical textiles due to the convenience, low cost, and sterilization results. Gamma rays are photons of electromagnetic radiation emitted from the nucleus during radioactive decay and occasionally accompanying the emission of an alpha or beta particle.[6] The rays are identical in nature to other electromagnetic radiations such as light or microwaves. However, they are much higher in energy.

Irradiation has become popular method of altering the molecular structure of polymers particularly polypropylene, to increase the degradability due to recent environmental concern. After exposure to gamma irradiation, polypropylene is subjected to oxidative degradation in the presence of air and during storage after irradiation. Similar to photo-oxidation and thermal oxidative degradation, the mechanism of gamma radiation is fundamentally free radical in nature. The action of ^{60}Co radiation on polypropylene in the presence of air gives rise to a series of processes characterized by a free radical auto-oxidation scheme.[7]

Radiation degradation and stabilization due to gamma rays of polypropylene were extensively investigated because of an application of radiation treatment for the sterilization of disposable biomedical supplies.[5,8–14] It has been reported[15–17] that as an effect of gamma irradiation, polypropylene physical properties deteriorate leading to embrittlement, discoloration, stiffening, softening, odor generation, and loss of molecular weight leading suggesting chain scission and/or cross-linking may have happened. However, sol–gel analysis showed, despite the fact that doses of irradiation are relatively high, no gel was formed and cross-linking was therefore ineffective. The reason is that the cross-linking of polypropylene is complicated by a sizable portion of macro-radicals decaying by beta scission and disproportionate in the absence of an effective cross-linking co-agent.[10] Thus, polypropylene is degraded by chain scission.

Following exposure to gamma rays polypropylene films show a significant reduction in intrinsic viscosity (~90%), elongation at break (~80%), and toughness (~90%).[1] These changes in viscosity and tensile properties are attributed to a decrease in the average molecular length by the cleavage of macromolecular chains. Abiona et al.[18] confirmed auto-oxidation of commercial polypropylene after γ-radiation by production of degraded products such as water vapor, carbon monoxide from hydroxyl and carbonyl groups with Raman and ultraviolet visible light spectroscopic analyses. Alariqi et al.[5] studied the effect of gamma dose on polypropylene films. Surprisingly, surface crack of the samples increased with a decreasing γ-dose rate which indicates that the degradation is more severe at lower dose rates. The cracked (amorphous) surface accelerated the degradation further because the oxidative degradation is initiated at surface. However, a drawback to this study is the lack of surface characterization of polypropylene films before γ-sterilization.

It has been well documented that polypropylene biomedical polymers undergo oxidative degradation.[1,5–7,9–14] Upon exposure to γ-radiation, previous studies have indicated modification in properties such as molecular weight, crystallinity, tensile strength, color, stiffness, and morphology in polypropylene films.[1,5] Sen et al.[8] documented the deterioration of mechanical, structural, and thermal properties in multifilament polypropylene yarns. Recently, Alariqi et al.[1] concluded that the biodegradability of polyolefin particularly polypropylene were accelerated with the pre-treatment of γ-radiation in composting and fungal environments. It was observed that γ-sterilized polypropylene films were colonized by *Aspergillus niger* fungus after 6 weeks of incubation. After 5 months of composting, polypropylene films showed a 75% weight loss, visible surface cracking, and increased carbonyl index indicating susceptibility by microorganisms. Hence, the modification of polypropylene products by γ-radiation appears to be a method to conserve landfill space and encourage biodegradability by micro-organisms.

Though tremendous research has been published examining the effect of γ-radiation on polypropylene, the studies are limited to polypropylene films.[6,7,9–14,18] To date, little literature has been published which evaluates the effect of γ-radiation on textile fabrics. Moreover, to the best of our knowledge, there is no published scientific data on degradation of polypropylene nonwoven materials. Thus, the aim of this study is to investigate the effect of the γ-radiation on the mechanical and thermal properties of polypropylene spunbond and meltblown nonwovens including the effect on the polymer fine structure.

EXPERIMENTAL

Materials

Spunbond polypropylene (PP3155) of melt flow rate 36 (g/10 min) and meltblown polypropylene (6936G1) of melt flow rate 1550 (g/10 min) were supplied by Exxon Mobil for this research. Spunbond and meltblown polypropylene nonwovens were produced in the Nonwoven Cooperative Research Center (NCRC) Pilot facilities located in the College of Textiles at North Carolina State University.[19] The fabric basis weight was 36 and is 25 GSM (g/m^2) respectively for the spunbond and meltblown nonwovens fabrics.

Gamma Irradiation

The spunbond and meltblown nonwovens were secured in jars (constructed of glass) and placed in a ^{60}CO gamma radiation chamber for exposure. The samples were exposed to various doses with largest dose being 25 kGy at a dose rate of 1.36 kGy/day at room temperature.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were collected to study the chemical changes post exposure to γ-radiation. Similar to previous studies, changes in carbonyl (~1760 cm^{-1}) and hydroxyl (~3200 cm^{-1}) groups were evaluated and used to calculate carbonyl and hydroxyl indices to monitor polypropylene γ-induced oxidation. Attenuated total reflectance (ATR) spectra were collected on a Nicolet 560 FTIR spectrometer, with a germanium crystal, equipped with an Advantage microscope, using liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. At least 32 scans were obtained to achieve an adequate signal to noise ratio. The spectral resolution was 8 cm^{-1}. As noted below, the carbonyl index and hydroxyl indices were calculated as a ratio of absorbance at wavenumbers of ~1760 and ~3200 cm^{-1} to the absorbance of the methylene group at absorbance of 2920 cm^{-1} respectively.

$$\text{Carbonyl Index} = A_{1740}/A_{2920}$$

$$\text{Hydroxyl Index} = A_{3200}/A_{2920}$$

Mechanical Properties

Mechanical properties were measured on the Instron MTS Q-Test/5 Universal tensile machine to evaluate the tensile properties and elongation at break as a function of gamma dose. The samples (1 × 6″) were conditioned at 70°F and 65% RH prior to testing. The mechanical properties were evaluated according to the ASTM D5034-09 "Standard Test Method for Breaking Strength and Elongation of Textile Fabrics (Grab Test)." A gauge length of 3 inch, with a break sensitivity of 50% and a cross head speed of 12 inch/min was used for this method. Each sample had ten replicates to obtain a reliable and accurate standard deviation.

Differential Scanning Calorimetry

Thermal properties of γ-irradiated polypropylene were studied by differential scanning calorimetry (DSC). The melting and crystallization temperatures were evaluated as an effect of γ-radiation on a Perkin-Elmer DSC equipped with DSC-7 software. The measurements were carried out under atmospheric nitrogen at a heating rate of 20°C/min. Initially the sample was heated to 180°C and maintained at this temperature for 5 min, then the γ-irradiated sample was cooled to room temperature. The heat of melting and crystallization was calculated from the peak area of the corresponding DSC scans.

Crystallinity Measurements

The degree of crystallinity was determined by differential scanning calorimetry using the following equation:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f \times 100}{\Delta H_f^0}$$

where ΔH_f represents the heat of fusion of PP nonwoven sample and ΔH_f^0 is the heat of fusion of a perfect polypropylene crystal (taken as $\Delta H_f^0 = 209$ J/g[20]).

Wide Angle X-ray Scattering (WAXS)

Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku SmartLab X-ray Diffractometer (XRD) equipped with Cu $K\alpha$ radiation source, $\lambda = 1.542$ Å, generated at 40 kV and 44 mA. The diffracting intensities were recorded every 0.02° from 2θ scans in the range from 5 to 30° with an Omni Instruments Wide Angle XRD device.

Crystallite sizes can be determined from the Scherrer equation:

$$L_{hkl} = \frac{K\lambda}{\beta \cos\Theta}$$

where β is the peak half width, and λ is the radiation wavelength (1.542 Å), and Θ is the Bragg angle of incidence. Half-widths (FWHM) of (110), (040), and (130) reflections for spunbond and meltblown polypropylene nonwovens are reported in Tables IV and V.

The Bragg's law was used to calculate d-spacing for different diffraction patterns:

$$n\lambda = 2d\sin\Theta$$

where n (an integer) is the "order" of reflection.

Scanning Electron Microscopy

The SEM micrographs were taken on a Hitachi S-3200 Scanning Electron Microscope equipped with the "Resolution" software. SEM micrographs were obtained under standard vacuum conditions, with a 5 kV potential difference with magnifications from 50× to 1,000×.

RESULTS AND DISCUSSION

FTIR Studies of γ-Irradiated Polypropylene Nonwovens

In oxidation degradation studies, FTIR monitors structural changes which are usually attributed to carbonyl and hydroxyl functional groups. Similar to studies reported by Alariqi et al.[5] and Meligi et al.,[4] the obtained spectrum in this study for spunbond and meltblown polypropylene nonwovens suggested that absorbance of carbonyl and hydroxyl groups increased after γ-irradiation. The appearance of peaks in the carbonyl region (1500–1800 cm^{-1}), more specifically at 1710 and 1720 cm^{-1} corresponded to the ketone which is attributed to radio-oxidative degradation of spunbond and meltblown polypropylene nonwovens respectively. During the onset of sterilization in spunbond and meltblown polypropylene nonwovens, the concentration of the carbonyl increased significantly as noted by the higher absorbance. Likewise, the hydroxyl (3400–3500 cm^{-1}) concentration also increased tremendously as a result of gamma oxidation. This increase in hydroxyl groups is the outcome of neighboring intermolecular hydrogen bonded hydroperoxides and alcohols. The changes in carbonyl and hydroxyl functional groups collectively in polypropylene nonwovens are represented by the respective hydroxyl and carbonyl indices as shown in Figure 1.

Mechanical Properties of γ-Irradiated Polypropylene Nonwoven

The mechanical properties of polypropylene polymers are profoundly affected by gamma radiation. Similar to other studies on polypropylene films,[1,5,8] the peak load and elongation at break of meltblown and spunbond polypropylene nonwovens decreased tremendously as the gamma dose is increased, as shown in Figures 2 and 3. This dramatic loss of mechanical properties is attributed to the reduction of average molecular length as a result of chain scission after γ-irradiation. Hence, the decrease in elongation at break suggests reduction in molecular weights of both the spunbond and meltblown polypropylene nonwovens. Moreover, the peak load and elongation of the meltblown polypropylene nonwovens show a more dramatic deterioration because the sample had much lower molecular weight. Interestingly, we observed complex mathematical relationships for the peak load and elongation at break as a function of gamma dose for both nonwoven fabrics. The

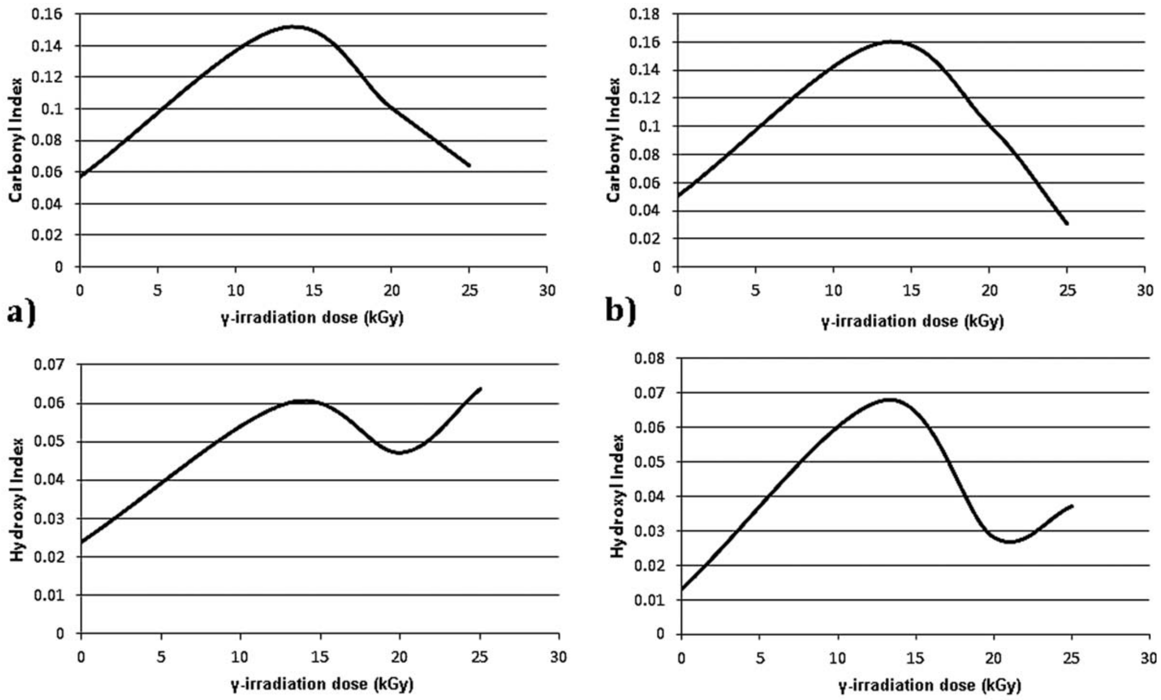

Figure 1. Carbonyl (top) and hydroxyl (bottom) indices of (a) spunbond and (b) meltblown polypropylene nonwovens respectively at multiple γ-irradiation doses.

simplest regression equation was obtained for spunbond nonwovens:

$$y=6.2233e^{-0.043x}$$

where y is the peak load and x is the γ-irradiation dose. The other equations are shown in Figures 2 and 3.

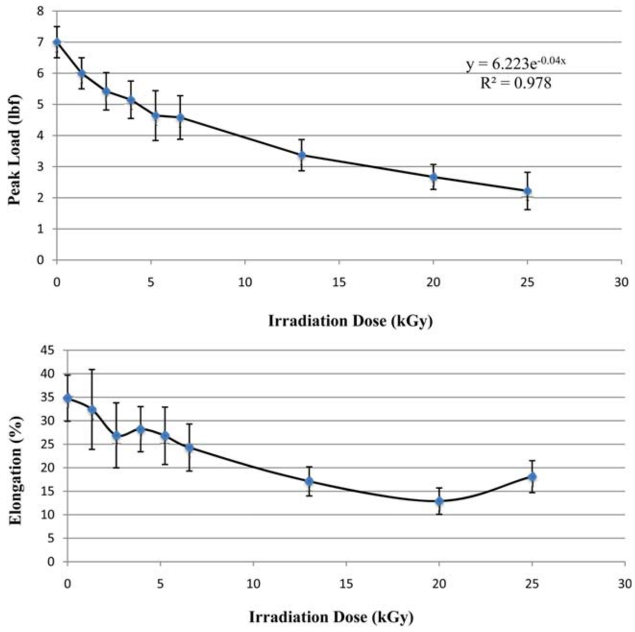

Figure 2. Tensile strength (top) and elongation at break (bottom) of spunbond polypropylene nonwoven at multiple γ-irradiation doses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I lists the elongation at break (%) and peak load (lbf) for spunbond and meltblown polypropylene nonwovens at various γ-irradiation doses. Standard deviations are also reported in this table.

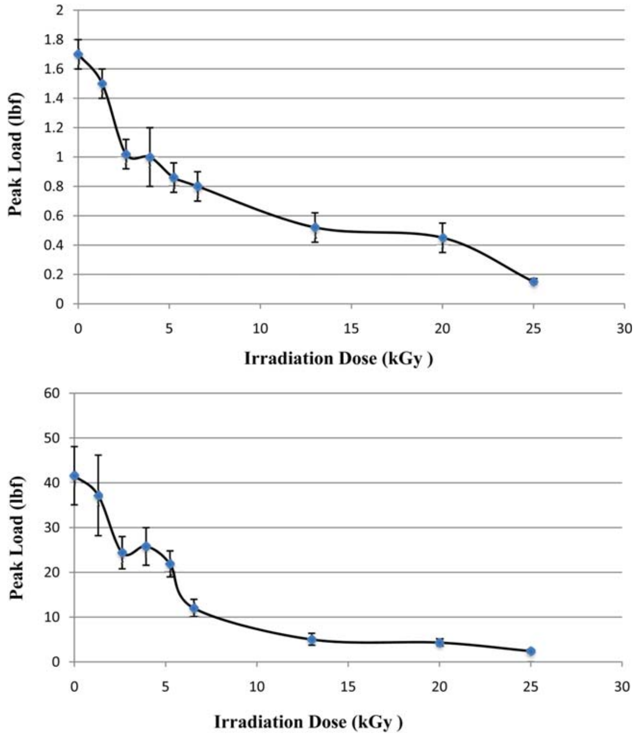

Figure 3. Tensile strength (top) and elongation at break (bottom) of meltblown polypropylene nonwoven at multiple γ-irradiation doses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Effect of Gamma Irradiation on Elongation at Break and Peak Load of Spunbond and Meltblown Polypropylene Nonwovens

	Spunbond		Meltblown	
γ-Irradiation dose (kGy)	Peak load (lbf)	Elongation at break (%)	Peak load (lbf)	Elongation at break (%)
0	7 (0.5)	34.8 (4.9)	1.7 (0.1)	41.6 (6.5)
1.31	6 (0.5)	32.4 (8.5)	1.5 (0.1)	37.2 (9.0)
2.62	5.4 (0.6)	26.9 (6.9)	1.0 (0.1)	24.4 (3.6)
3.93	5.2 (0.6)	28.2 (4.8)	1(0.2)	25.8 (4.2)
5.24	4.6 (0.8)	26.8 (6.1)	0.9 (0.1)	21.9 (2.9)
6.55	4.6 (0.7)	24.3 (5.0)	0.8 (0.1)	12 (2.0)
13	3.4 (0.5)	17.1 (3.1)	0.5 (0.1)	5 (1.4)
20	2.7 (0.4)	12.9 (2.8)	0.5 (0.1)	4.3 (0.9)
25	2.2 (0.6)	18.1 (3.4)	0.2 (0.02)	2.4 (0.4)

Standard deviations are shown in parentheses.

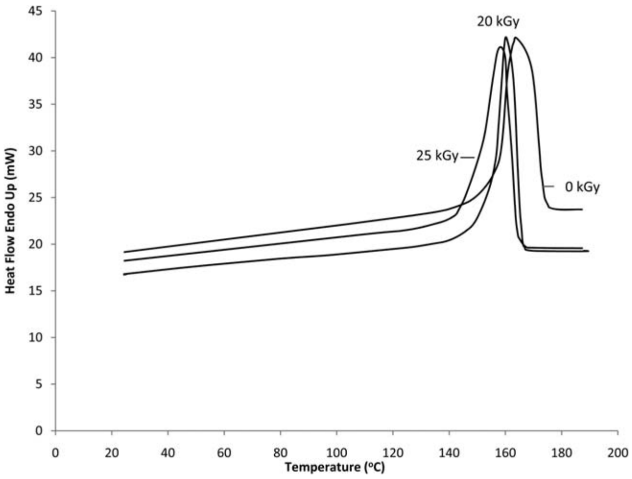

Figure 4. The melting temperature of spunbond polypropylene after γ-irradiation of 0, 20, and 25 kGy.

Differential Scanning Calorimetry

Characterization of changes in thermal properties of spunbond and meltblown polypropylene after γ-irradiation at various doses was studied by differential scanning calorimetry. As illustrated in Figures 4 and 5, the melting temperature (T_m) was steadily reduced in spunbond and meltblown polypropylene nonwovens as the γ-irradiation dose increased. In fact, in the meltblown polypropylene nonwoven (Figure 5), the T_m decreases by nearly 10°C after 25 kGy which suggest that even low doses of γ-irradiation severly deteriorates the polymer. This significant reduction in T_m is a characteristic of cross-linking, chain scission, or branching. The formation of a shoulder at 150°C in spunbond polypropylene (Figure 4) and 165°C in meltblown polypropylene (Figure 5) is observed, which is similar to previous γ-irradiation studies on films.[8] The appearance of the shoulder indicated fluctuations in the size of cystallites.

Similar to the melting temperature, the heat of fusion (Tables II and III) in both spunbond and meltblown polypropylene also rose as the γ-irradiation dose was increased. This observation was interesting because one would expect, the heat of fusion (ΔH_f) to remain unchanged if chain scission is happening, and/or large crystallites are breaking into small crystals.[8] This same phenomenon was observed by Horrocks and D'Souza[2] in their studies on the aging of polypropylene.

In addition to the T_m and ΔH_f, the crystallization temperature (T_c) and heat of crystallization (ΔH_c) were also obtained by cooling the DSC from 180°C to 25°C. Unlike the melting endotherms, the crystallization exotherms (Figures 6 and 7) appeared to remain nearly the same temperature. However, the ΔH_c increased with the γ-irradiation dose for the meltblown polypropylene while the spunbond polypropylene nonwoven increased and then decreased. The results for the crystallization exotherms are interesting compared to previous studies. Alariqi et al.[1,5] and Sen et al.[8] have observed a dramatic decrease in crystallization temperature which attributed to molecular cleavaging. In this study, this phenomenom was not observed. Since the previous studies observed molecular cleavage in polypropylene films after γ-irradiation, it is expected (in this study) that

Table II. Effect of γ-Irradiation Dose on Thermal Properties of Spunbond Polypropylene

	Spunbond polypropylene			
γ-Irradiation dose (kGy)	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)
0	160.8	88.0	107.5	−91.2
13.8	160.1	85.8	108.3	−100
20	157.1	112.7	109.2	−101.5
25	156.0	139.0	109.7	−91.0

Table III. Effect of γ-Irradiation Dose on Thermal Properties of Meltblown Polypropylene

	Meltblown polypropylene			
γ-Irradiation dose (kGy)	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)
0	159.1	90.9	110.0	−101.8
13.8	160.5	87.5	109.0	−99.5
20	154.4	129.2	108.0	−95.3
25	151.7	127.7	107.0	−88.7

Table IV. Peak Position, *d*-Spacing, and Half-Widths of (110), (040), and (130) Reflections of Spunbond Polypropylene Nonwovens

	110			040			130		
Irradiation dose (kGy)	*d*-Spacing (nm)	2θ (°)	FWHM	*d*-Spacing (nm)	2θ (°)	FWHM	*d*-Spacing (nm)	2θ (°)	FWHM
0	6.2	14.4	0.55	5.2	17.2	0.6	4.7	18.8	0.7
13	5.9	15.0	0.7	5.0	17.8	0.7	4.55	19.5	0.9
20	6.1	14.6	0.6	5.1	17.4	0.7	4.7	19.0	0.9
25	6.1	14.5	0.6	5.10	17.3	0.6	4.7	18.9	0.7

FWHM, full width at half maximum.

Table V. Peak Position, *d*-Spacing, and Half-Widths of (110), (040), and (130) Reflections of Meltblown Polypropylene Nonwovens

	110			040			130		
Irradiation dose (kGy)	*d*-Spacing (nm)	2θ (°)	FWHM	*d*-Spacing (nm)	2θ (°)	FWHM	*d*-spacing (nm)	2θ (°)	FWHM
0	5.9	15.0	1.4	5.05	17.6	0.8	4.6	19.4	0.7
13	5.2	14.7	1.6	5.2	17.2	2.0	4.6	19.1	0.2
20	4.6	14.8	1.5	5.1	17.3	1.0	4.05	19.3	0.5
25	6	14.8	1.6	5.2	17.2	2.5	4.6	19.4	0.7

FWHM, full width at half maximum.

cleavage would occur in nonwovens due to the difference of surface area.

The Effect of γ-Irradiation Dose on Crystallinity

The crystallinity of spunbond and meltblown polypropylene nonwovens is greatly affected by γ-irradiation dose. In the spunbond polypropylene nonwoven, as shown in Figure 8, the crystallinity increases tremendously as the increase in the γ-irradiation dose expands. In fact, the crystallinity is increased by 15% with as little as 25 kGy γ-irradiation. The rise in crystallinity is attributed to the reduction in mechanical properties and molecular weight, which confirms the process of chain scission. It can be assumed that the polymer is becoming more brittle.

Compared to the spunbond polypropylene nonwoven (Figure 8), the crystallinity of the meltblown polypropylene nonwoven (Figure 9) also rose with increased γ-irradiation dose. Interestingly, the crystallinity is unchanged at 13 kGy, increases by nearly 20% at 20 kGy, and remains unchanged after the significant increase at 25 kGy. Because the meltblown polypropylene nonwoven is of lower molecular weight then the spunbond polypropylene nonwoven, lower doses can be used to degrade the polymer. Hence, the rise in crystallinity is attributed to chain scission but at a lower irradiation dose and perhaps, the phenomenon of chemi-crystallization as reported by other studies.[1,14] Chemi-crystallization is a form of a secondary crystallization. It is attributed to polypropylene chain scission that releases polymer segments from the non-crystalline phase allowing them to crystallize.[21]

Wide Angle X-ray Scattering

Wide Angle X-ray Scattering (WAXS) was used to study the morphology of the crystalline regions of polypropylene nonwovens. The WAXS diffraction patterns of γ-irradiated and

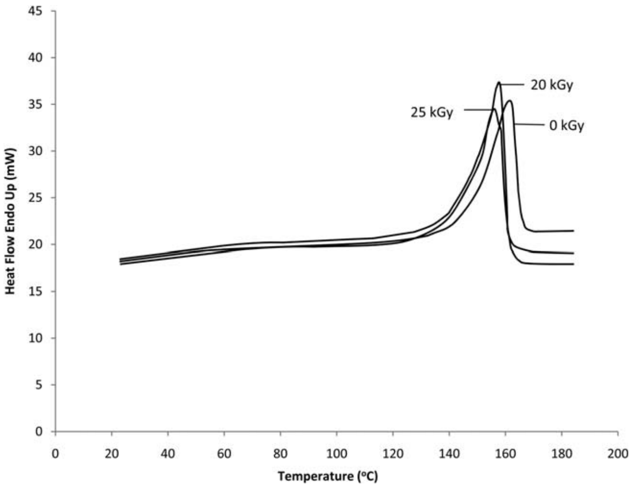

Figure 5. The melting temperature of melt blown polypropylene after γ-irradiation of 0, 20, and 25 kGy.

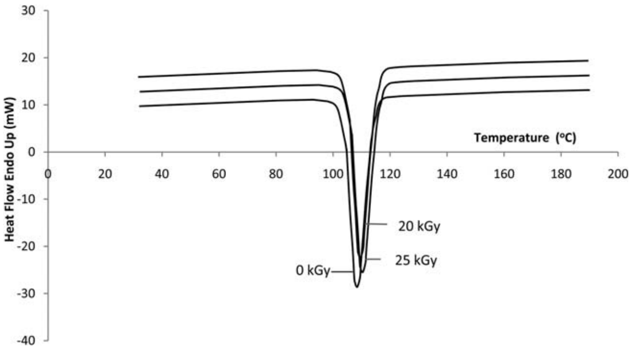

Figure 6. The crystallization temperature of spunbond polypropylene after γ-irradiation of 0, 20, and 25 kGy.

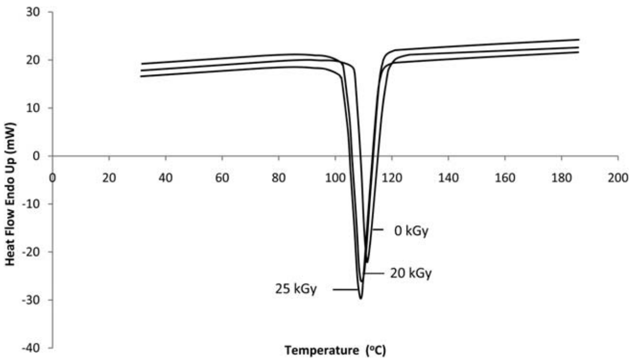

Figure 7. The crystallization temperature of melt blown polypropylene after γ-irradiation of 0, 20, and 25 kGy.

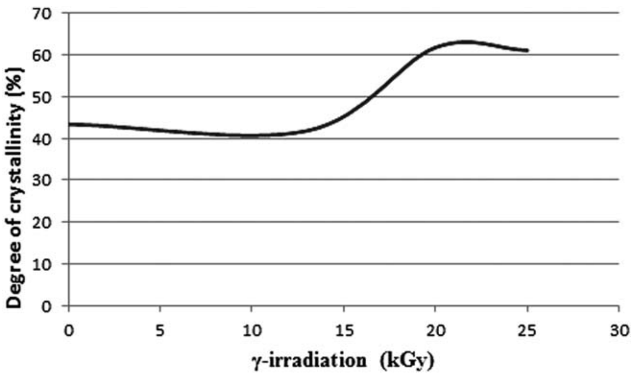

Figure 9. Crystallinity of meltblown polypropylene nonwoven as a function of γ-radiation dose.

unirradiated polypropylene nonwovens show reflections of typical polypropylene monoclinic structure at 2θ values of 14, 17, and 18.5° representing $(110)_\alpha$, $(040)_\alpha$, and $(130)_\alpha$ reflections, respectively. After irradiation by gamma rays, the morphology of spunbond and meltblown polypropylene nonwovens changed significantly.

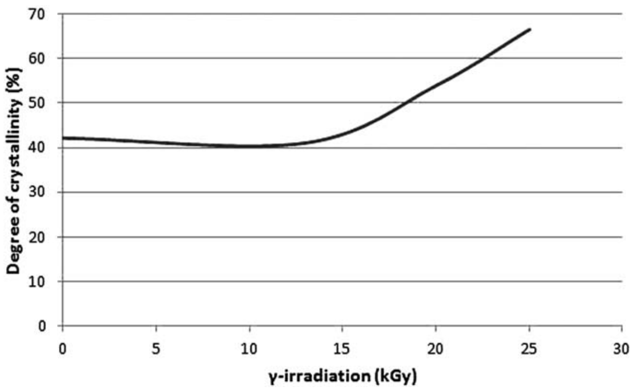

Figure 8. Crystallinity of spunbond polypropylene nonwoven as a function of γ-radiation dose.

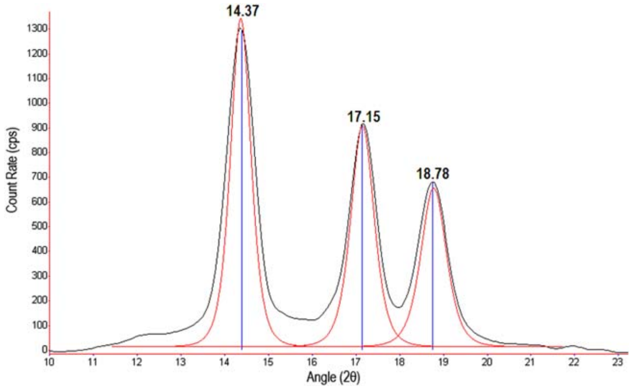

Figure 10. WAXS equatorial scan of spunbond polypropylene nonwoven at 0 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

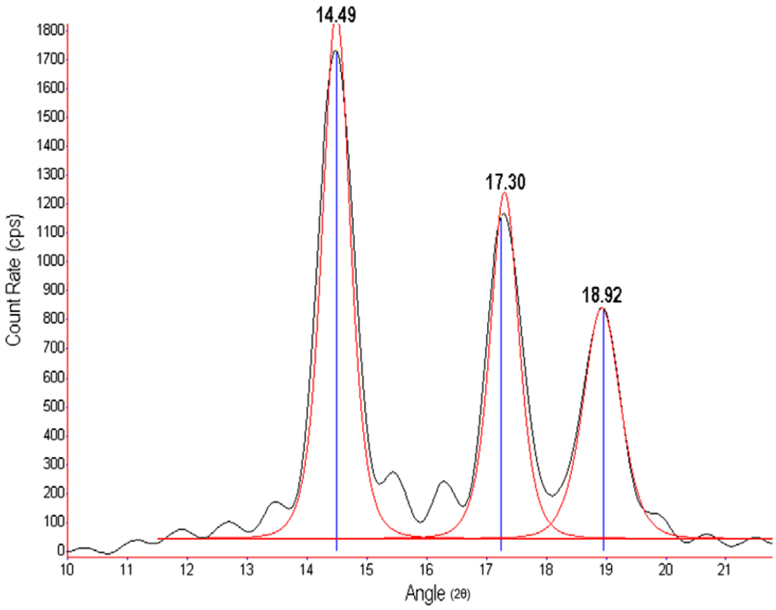

Figure 11. WAXS equatorial scan of spunbond polypropylene nonwoven at 25 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

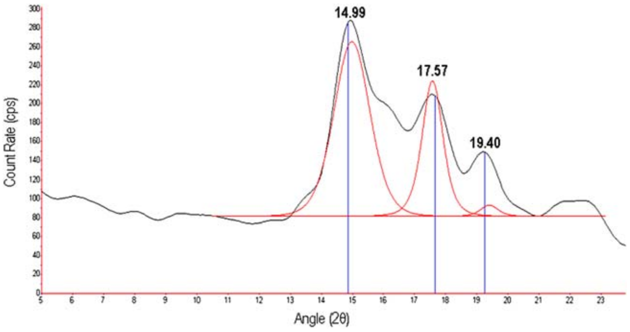

Figure 12. WAXS equatorial scan of meltblown polypropylene nonwoven at 0 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

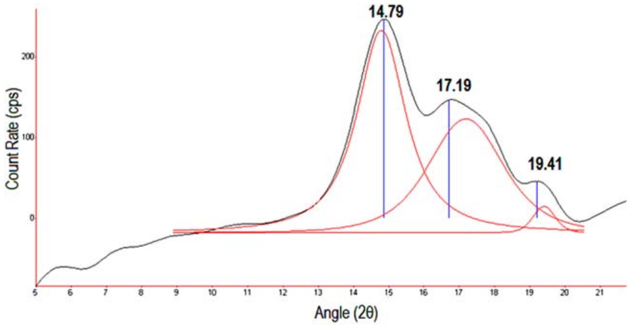

Figure 13. WAXS equatorial scan of meltblown polypropylene nonwoven at 25 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In the spunbond polypropylene nonwoven, the diffraction patterns (Figures 10 and 11) of irradiated and unirradiated samples exhibited similiar 2θ values of 14, 17, and 18.5° while the d-spacing and half-widths are modified with the variation in γ-dose. As indicated in Table IV, the half-widths of (110), (040), and (130) peaks which are used in the determination of crystallites' size appear to be higher for irradiated spunbond polypropylene nonwovens. This is an indication that the crystallites breakdown upon exposure to γ-irradiation. However, there are no hypothesis which suggest morphorlogical transitions as an effect of irradiation dose. These findings are in accordance with earlier studies reported by Sen et al.[8] on polypropylene yarns.

Similar to the spunbond polypropylene nonwoven WAXS pattern, meltblown polypropylene nonwovens (Figures 12 and 13) exhibit 2θ values of 14, 17, and 18.5° simutaneously. The unirradiated meltblown polypropylene contains 2θ values of 14, 17, and 18.5° correlating to the (110), (040), and (130) reflections, respectively. After 13 kGy of γ-irradiation, reflections of the

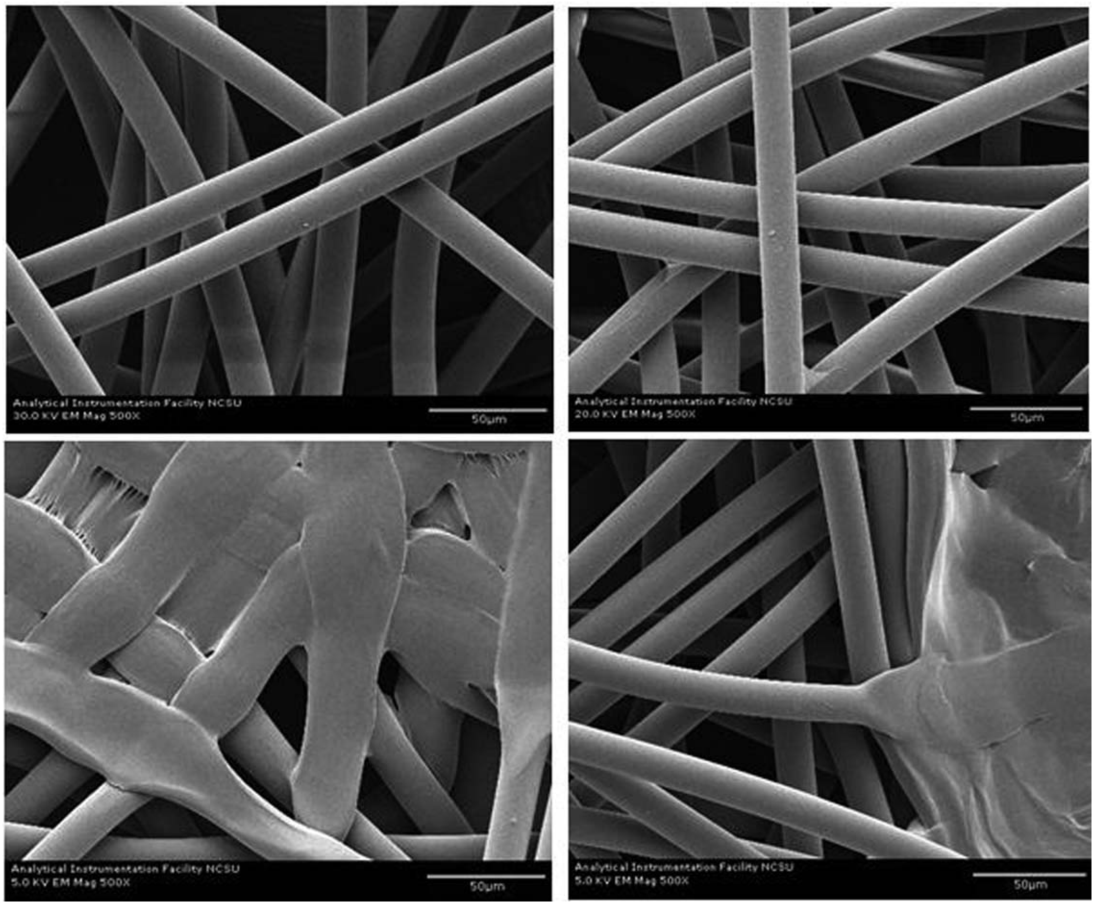

Figure 14. Scanning electron microscopy of spunbond polypropylene nonwoven after (top, left) 0 kGy, (top, right) 13 kGy, (bottom, left) 20 kGy, and (bottom, right) 25 kGy.

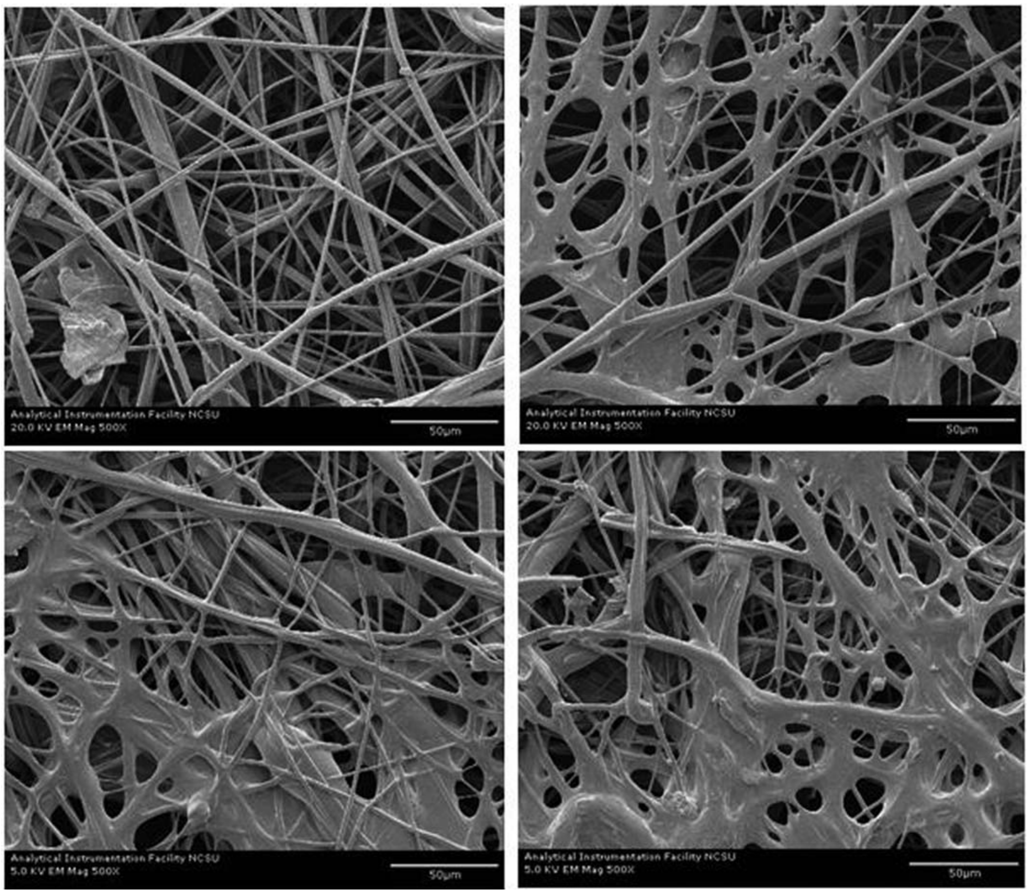

Figure 15. Scanning electron microscopy of meltblown polypropylene nonwoven after (top, left) 0 kGy, (top, right) 13 kGy, (bottom, left) 20 kGy, and (bottom, right) 25 kGy.

α-phase crystal lattice characteristic to α-modification of polypropylene still remain. However, the 2θ angles, *d*-spacing (interplanar distance), and half-widths (Table V) are largely effected after irradiation up the 25 kGy. The 2θangles changed minimally while the *d*-spacing and half-widths are increased. Recall, the half-widths are indicative of crystallite size. The half-width of (110) and (130) peaks up to 20 kGy are smaller than the unirradiated sample. Hence, this is an implication that after 20 kGy irradation, the crystallites of meltblown polypropylene nonwovens increased in size, crystal perfection, and α-phase content. Thus, the irradiation of meltblown polypropylene nonwovens undergo a structural transition from disordered state to the closest packed monoclinic structure at the beginning of irradiation. This finding is confirmed by the increase in crystallinity documented by DSC. Similar results have also been shown by Alariqi et al.[5] and Nishimoto et al.[11] Additionally, small shoulders start to form at 2θ values of 15.2, 16.02, 20.06, and 26.4° suggesting transitioning of α-monoclinic structures to β- and γ-structures as a result of irradiation exposure. It has been reported that the formation of γ-phase was not due to the crystallization of low molecular fraction but also due to the high internal pressure caused by the crosslinking.[22]

Scanning Electron Microscopy of γ-Irradiated Nonwovens

Scanning electron microscopy was used to study the morphology of the surface of spunbond and meltblown polypropylene nonwovens. It is evident, that the surface appears distorted after γ-irradiation to both spunbond and meltblown polypropylene nonwovens, as shown in Figures 14 and 15.

In the spunbond polypropylene nonwoven, the initial observation is that as the irradiation dose increased, the deformity of the surface becomes more apparent. As shown in Figure 14, the control and spunbond polypropylene nonwoven irradiated at 10 kGy appears smooth and free of defects. However, when the spunbond nonwoven is irradiated at 20 kGy, one observes stretching at the bond points which is an indication that the sample is becoming fragile. At 25 kGy, the surface of the spunbond polypropylene nonwoven particularly in the bond point region (bottom, right image in Figure 14) shows deterioration on the surface.

The meltblown polypropylene nonwoven also deteriorated with γ-irradiation, as shown in Figure 15. Prior to irradiation, the control meltblown nonwoven has no defects or cracks. With as little as 10 kGy irradiation, the surface of the meltblown polypropylene nonwoven is transformed into a globular structure. After the highest irradiation exposure (25 kGy), it was noticed that not only is there globular structure but also defects on the surface of the meltblown polypropylene. Other studies[1] have also observed surface deterioration after γ-irradiation.

CONCLUSION

In this study, the effect of γ-irradiation on the degradation of spunbond and meltblown polypropylene nonwovens was studied in great detail. After exposure to γ-irradiation, mechanical properties and molecular weight were greatly reduced suggesting the occurrence of chain scission. Furthermore, the molecular arrangement following γ-irradiation has transition from a more amorphous to crystalline orientation as indicated by the differential scanning and wide angle X-ray scattering. Additionally, γ-irradiation modified the chemical structure of polypropylene by enhancing the content of carbonyl and hydroxyl indices suggesting the occurrence of oxidative degradation.

Nonwoven type and γ-irradiation dose play significant roles in the degradation rate of polypropylene. Repeatedly throughout this study, meltblown polypropylene nonwovens deteriorated faster than spunbond polypropylene because of the lower molecular weight. Also, as the γ-irradiation dose increased the deterioration of the polypropylene polymer increased.

It is planned to study the biodegradation of γ-irradiated spunbond and meltblown polypropylene nonwovens. With the results from this research, we hope to develop an eco-friendly methodology to dispose nonwoven polypropylene waste in a timely manner.

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