Full Length Research Paper

Gamma-irradiation induced property modification of polypropylene

A. Adurafimihan Abiona* and A. Gabriel Osinkolu

Materials Science and Electronic Division Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria.

The effects of γ-irradiation on the physico-chemical stability and mechanical properties of commercial polypropylene (PP) have been investigated using X-ray diffraction analysis, Raman spectroscopy, ultraviolent visible spectroscopy and tensile test. The γ-irradiation of polypropylene led to remarkable changes in the physico-chemical properties of the material due to chain scission, oxygen effects and cross-linking activities. These changes result in the production of degraded products such as water vapor, carbon monoxide from hydroxyl and carbonyl groups as confirmed by Raman and Ultraviolent Visible spectroscopic analyses. It was observed that the melting temperature and crystallinity reduce as radiation doses increases. Likewise, there were losses in mechanical properties of the polymer as indicated by reduction in elongation to fracture and reduction in tensile strength of the materials as dose increases.

Key words: γ-Irradiation, Raman spectroscopy, ultraviolent visible spectroscopy tensile test.

INTRODUCTION

Polypropylene (PP) is an attractive thermoplastics with cheap production cost, low density, excellent mechanical properties and wide industrial and commodity applications such as textile fibers, hygiene (diapers, disposals), medical devices (operation gowns and covers and drug packaging), food packaging, absorbents, wipes, filters or battery separators several of which require high energy radiation.

PP are mainly synthesized in three tactic forms namely isotactic, syndiotactic and atactic. But the most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of low density polyethylene and high density polyethylene. Isotactic polypropylene (iPP) is a polymorphic that crystallizes in three crystalline forms namely: α (monoclinic), β (hexagonal) and γ (triclinic) (Lezak and Bartczak, 2005).

The most common crystal modification, formed under normal processing conditions for commercial grades of iPP, is the monoclinic α form with lattice parameter of a =

6.65Å, b = 20.96Å, c = 6.50Å, β = 99.8°(Lezak and Bartczak, 2005).

The use of ionizing radiation on polymeric materials will continue to draw great attentions because it currently represents the only technique, which allows introducing energy into materials to generate favorable changes, provided it is used in the proper doses. Irradiation of polymeric materials with ionizing radiations (e.g. γ-rays) produces ionization and excitation in them. According Kassem et al. (2002), this irradiation leads to the formation of very reactive intermediates, free radicals, ions and excited states.

These intermediates can follow several reaction paths, which result in disproportion, hydrogen abstraction, arrangements and/or the formation of new bonds. The degree of these transformations depends on the structure of the polymer and the conditions of treatment before, during and immediately after or even days, weeks, or months after irradiation. This transformation often lead to resultant physical changes such as embrittlement, strength, discolouration, odour generation, stiffening, softening, increase or decrease in melting point, enhancement or reduction of resistance to chemical attacks and chemical changes such as molecular weight,

*Corresponding author. E-mail: adurafimihan.abiona@gmail.Com, aabioan@cerd.gov.ng. Tel: +2348068565788.

chain length, entanglement, branching, pendant functionality, chain termination (Hemmerich, 2000).

Adequate knowledge of beneficial radiation-induced effects is essential in many applications of plastics radiation technology. For instance, ionizing radiations (such as γ-rays and electron beams) are employed in sterilization of medical devices and their packaging which are mostly plastics against virulent microorganisms. Definitely, right choices of appropriate polymer, total absorbed and irradiation time for specific medical product sterilization is invaluable to ensure that critical elements of materials and product performance are not compromise for their reuse. Also, irradiation is an effective form of food preservation that extends the shelf life of food and therefore reduces its spoilage. This process is of great benefits to the consumer by reducing the risk of illness caused by food-borne diseases. Following the 1997 US Food and Drug Administration approval of irradiation for pathogen control in unprocessed red meat and meat products, there has been a great interest in the use of food irradiation. However, to prevent recontamination, food is usually packaged mostly in plastic materials before irradiation.

Adequate knowledge of ionizing radiation effects on plastics can be explored in the recycling processes of polymeric waste to create new recycled products with enhanced properties from either single or blend of polymers (Jacobo et al., 2001; 2004). Irradiation enhances the compatibility, which depends on the physical and chemical interactions across the phase boundaries of polymer blends by improving the dispersion and the adhesion of the blend phase (Eddy and Marcos, 2007). Irradiation avoids the use of chemical additives forbidden in some areas (pharmaceutical industry and medicine) and the emission of gas pollutants, which are of great concern in global warming and ozone layer depletion, during heat treatment in polymeric waste recycling processes.

The interaction of ionizing radiation on polymer produces ionization and excitation in polymer molecules making the material to be chemically unstable. During the process of regaining chemical stability the polymeric materials undergo chemical reactions such as abstraction, addition reaction, resulting in chain scission or cross-linking. The two mechanisms of chain scission and cross-linking usually occur simultaneously but depending on the radiation dose level one mechanism becomes more prominent than the other. The cross-linking is prevalent in vacuum environment while the presence of oxygen enhances chain scission and gas formation (Popok et al., 2004). The cross-linking leads to better mechanical strength and lower permeability and chain scission vice versa.

The aim of this work is to study the effects of γ-radiation doses on the physico-chemical, thermal and mechanical properties of commercial polypropylene. The Raman and UV-Visible spectroscopic analyses wee used to evaluate the effects of γ-irradiation on the chemical structure of PP. Tensile strength and degrees of crystallinity were also studied.

EXPERIMENTAL

Materials

Pieces of polypropylene product, 0.8 mm in thickness, were cut into 8 x 1 mm from commercially available materials and were individually subjected to gamma irradiation.

Methods

Gamma-irradiation

Pieces of polypropylene product, 0.8 mm in thickness, were cut into 8 x 1 mm from commercially available materials and were individually subjected to gamma irradiation. The samples were irradiated at different doses at room temperature in air using a ^{60}Co gamma cell model 220, with dose rate of 6.05 Gy/s, manufactured by Atomic Energy of Canada Ltd.

Energy dispersive x-ray spectroscopy

The elemental composition of the sample was determined by Energy Dispersive x-ray Spectroscopy (EDS) coupled to Scanning Electron Microscope (SEM) at Physics Department of University of Cape Town. The EDS was run at current of 1000 pA, voltage of 20 kV, working distance of 25 mm, tilt angle of 0°, takeoff angle of 35° and acquisition time of 30 s.

X-ray diffraction

The X-ray diffraction (XRD) analyses of the PP samples were determined by using X-Ray Diffractometer model Bruker AXS D8 Advance at Ithemba LABS, South Africa. It was run with kα-radiation λ = 1.5406 Å and running generating voltage = 45 kV, current = 40 µA. Specimens of dimensions 3 x 1 mm were cut the PP and were scanned in 2θ ranges from 6 – 80° at rate of 1°/min. Measurement were recorded at every 0.03°.

Raman spectroscopy

Raman spectra of the irradiated PP were obtained using Micro-Raman Spectroscopy with laser excitation source of 785 nm from laser diode at the chemistry department of Tshwane University of Technology, Pretoria, South Africa. It is equipped with Confocal Olympus microscope with spatial resolution of 1 µm and micro-motorized XY stage autofocus.

Differential Scanning Calorimetry

The thermal properties of the polypropylene samples were carried out by using Differential Scanning Calorimeter (DSC) of Netzsch Differential Thermal Analyzer (DTA) 404 PC Eos at Centre for Energy research and development (CERD), Obafemi Awolowo University, Ile-Ife. The temperature and the heat flow calibration of the instrument were carried using indium standard. The samples were heated from room temperature to 200°C at a rate of 10°C/min
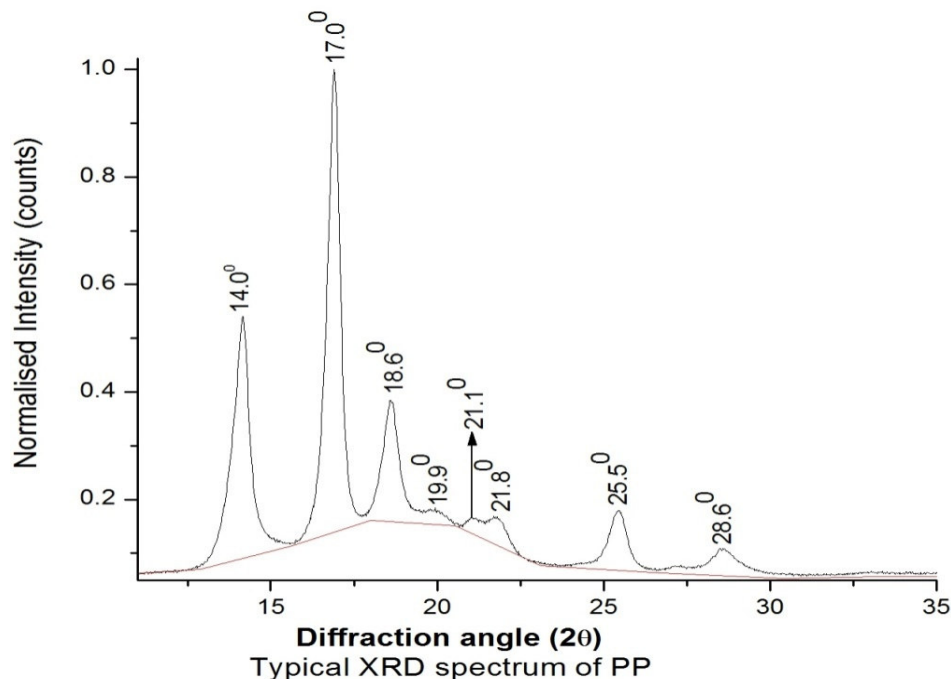
Figure 1. XRD spectrum of γ-irradiated iPP showing 2θ angles and red baseline for crystallinity calculation

under nitrogen atmosphere.

Ultraviolent visible spectroscopy

The absorption spectra of the samples were obtained using CECIL Ultraviolent Visible spectrophotometer (Figure 3.5) at CERD. The samples were scanned from 200 – 800 nm.

Mechanical properties

The mechanical properties of the samples were determined by subjecting them to tensile test using computerized dual column Table-Top 3369 model of Instron's electromechanical testing machine at CERD. The 8 x 1 mm polypropylene pieces were subjected to tension at the rate of 10 mm/min.

RESULTS AND DISCUSSION

Energy dispersive spectroscopic and x-rays diffraction analyses

Polypropylene identification

The commercial PP sample was analyzed for its elemental compositions using EDS in order to assay its elemental contents. The analysis showed that PP contains some elements like zinc, copper, chlorine and silicon apart from the major elements - carbon and hydrogen. Zinc and copper stearates are very common additives use in plastics industries. As such the presence

of these metals in the material under study can be attributed to be from the additives added to the polymer to improve the performance properties of the material. It was identified by X-Rays Diffraction (XRD) analysis that the plastic sample is α (monoclinic) isotactic poly-pro-pylene because there is a good agreement between the peaks of the XRD spectrum and those reported in the literature. The peaks reported by Grady et al. (2002) appeared at 2θ = 14.0°, 17.0°, 18.5°, 21.0°, 22.0° while the sample spectrum peaks are at 2θ = 14.0°, 17.0°, 18.6°, 21.1°, 21.8°, 22.5°, 28.6° as shown in Figure 1.
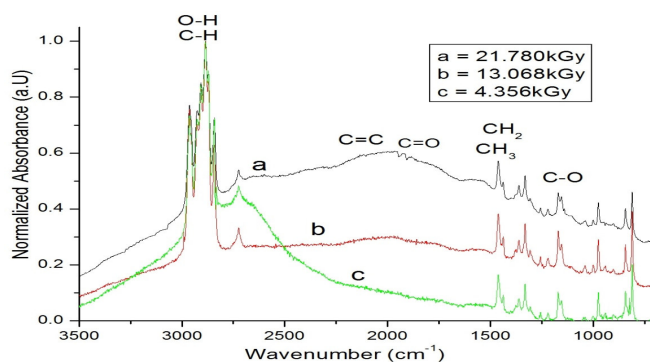
Crystallinity variation in terms of XRD analysis

The X-ray diffraction pattern of typical irradiated sample is shown in Figure 1. The crystallinity of the X-ray diffraction patterns of the samples were calculated from the XRD spectra using Origin 7.0 software to estimate the areas of the crystalline region which is the region above a baseline (a red line in Figure 1) joining the troughs of all the peaks and the total areas of both the crystalline plus amorphous region which is area above the linear baseline (X-axis in Figure 1) according to equation 1. It is observed that the crystallinity decreases with increase in irradiation doses as shown in Table 1. The decrease in crystallinity is a result of degradation activities which reduces the size of crystallites of the materials and eventually enlarges the amorphous region. This is also confirmed by the increase in the broad absorption band of the Raman spectroscopic analysis.

Table 1. Variations of crystallinity with doses from XRD spectra.

Doses (kGy)	Total area (a.u.)	Crystalline area (a.u.)	Crystallinity (%)
0.000	2.30128	1.53181	66.56
4.356	2.26071	1.38815	61.40
13.068	2.67846	1.53901	57.46
21.780	3.36082	1.57241	46.77

Table 2. DSC analysis of Polypropylene.

Doses (kGy)	Melt onset temp.(°C)	Melt peak temp. (°C)	Enthalpy (J/g)	Degree of crystallinity α (%)
0.000	132.5	155.3	91.65	44.23
4.356	150.4	153.8	83.87	40.52
13.068	147.4	152.2	78.37	37.86
21.780	129.1	150.9 (147.4)	108.3	52.32

Figure 2. Raman spectra showing the effects of γ-irradiation on iPP.

$$\alpha = \frac{Ac}{At} \times 100 \qquad (1)$$

Where α = degree of crystallinity, Ac = area of crystalline region, At = total area of amorphous + crystalline regions.

Raman spectroscopic analysis of polypropylene

The effects of γ-irradiation on the chemical structure were studied using Raman spectroscopy. The Raman absorbance spectra of the irradiated PP are shown in Figure 2. The spectra showed an absorption band at 2960 - 2885 cm^{-1}. This band is an overlapped band of C-H and O-H (hydroxyl) stretching vibrations. The symmetric CH$_3$ bending vibration band appearing around 1470 cm^{-1}, is a fingerprint of a helix conformation, which confirmed the presence of a carbon atom with one methyl group which also proves that the sample is most likely a PP (George et al., 2007).

In the presence of atmospheric oxygen, γ-irradiation cause oxidative degradation through simultaneous activities of oxygen effect, scission and cross linking. As

the dose increases there is a gradual appearance of a broad absorption band (between 1700 cm^{-1} and 2270 cm^{-1}) which could be an overlap of C = O (carbonyl group around 1750 cm^{-1}) and C = C (around 1990 cm^{-1}) as shown in Figure 3.

This can be as a result of production of secondary alkyl radicals by γ-irradiation on the surface of polyolefins. These alkyl radicals immediately react with oxygen to form peroxy radicals. Peroxy radicals can react or combine to form carbonyls and hydroxyls (Yeom et al., 1998). Some of these free radicals eventually form water and carbon dioxide. This explained some water vapour that was seen on the sample after irradiation. At higher dose around 21 kGy, the broad absorption band like a halo gets more pronounced and this results in the enlargement of the amorphous region of the spectrum. As the dose increases with time, the size of the crystallites of the sample reduces due to the degradation activities of the γ-irradiation, which results in the increase of the amorphous region and eventual reduction in crystallinity.

Differential scanning calorimetric analysis

The melting profile and the crystallinity in relation to the thermal properties of the irradiated PP were studied using Differential Scanning Calorimetry (DSC). The DSC thermogram of the un-irradiated PP exhibited a melting peak temperature at 155.3°C as shown in Figure 3 and it was found to decrease as irradiation doses increased as shown in Table 2 (Lu et al., 2002). This can be attributed to modification occurring in the crystal structure of iPP which resulted in the mobility of the iPP molecules as doses increases. At higher dose around 21 kGy, there are two melting peaks at 147.4 and 150.9°C in the thermogram (Figure 4) instead of one peak in lower dose thermograms. This additional peak is more enhanced and conspicuous with the first derivative of the thermogram
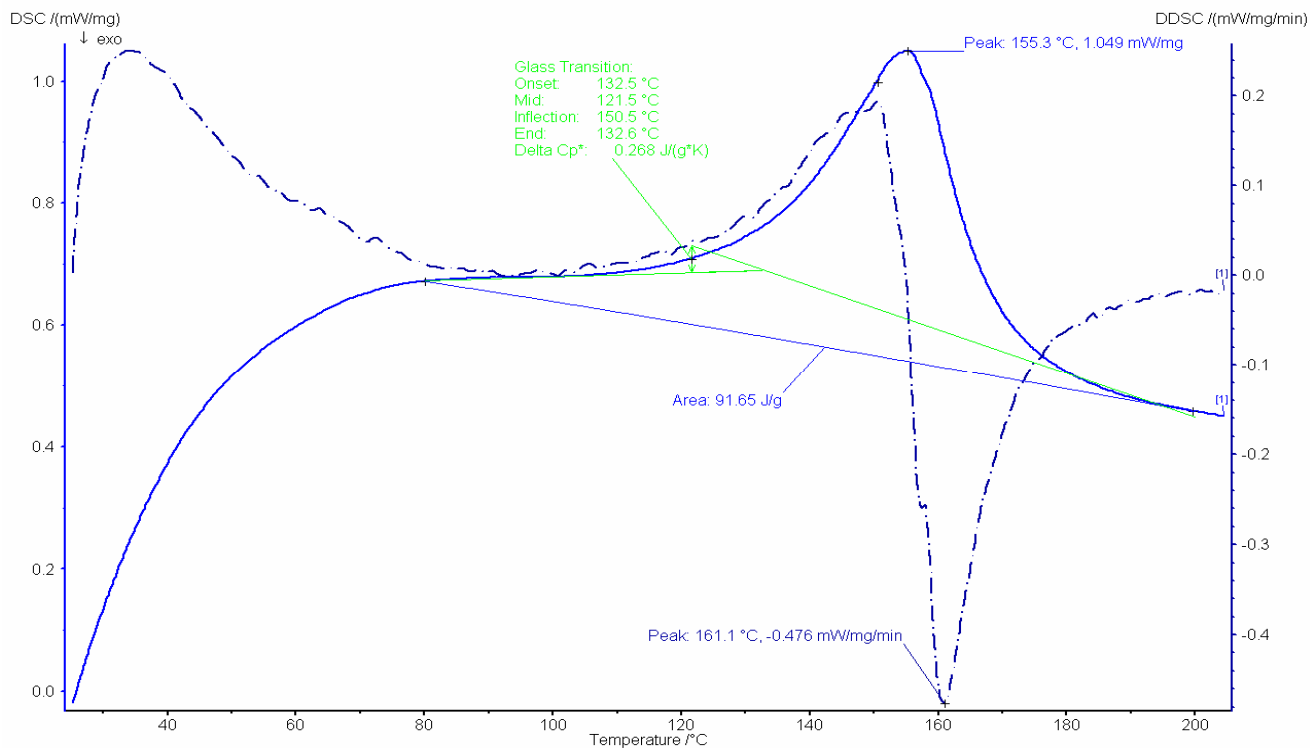
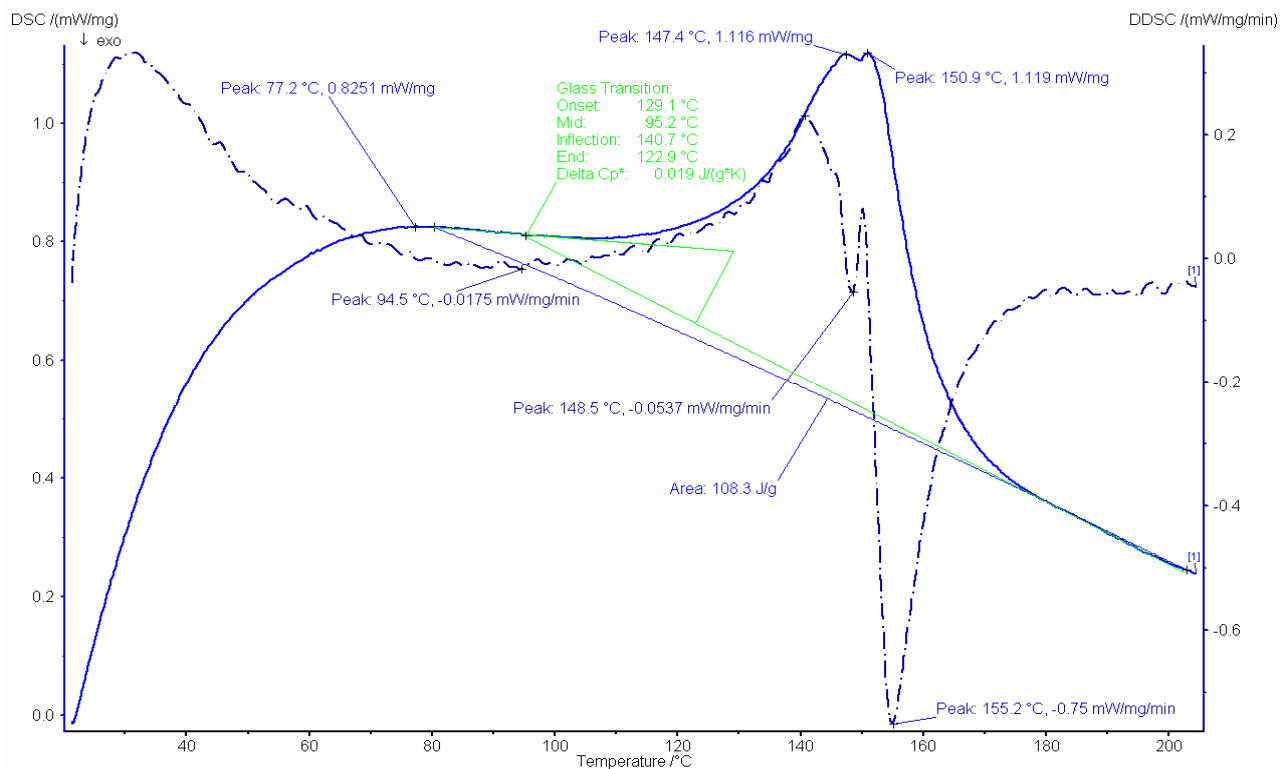**Figure 3.** Typical DSC thermogram of un-irradiated iPP.

Figure 4. DSC thermogram showing the second emerging peak at 21.780 kGy dose.
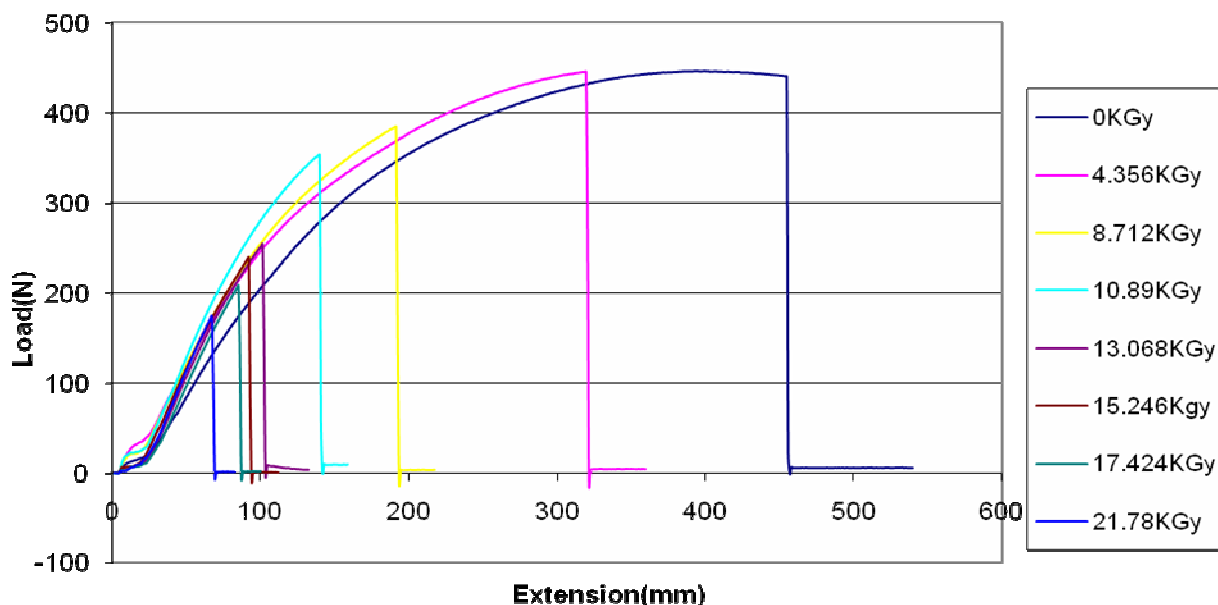
Figure 5. The effect of γ-irradiation on the elongation at fracture of iPP.

(dashed curve in Figure 4). The appearance of the second peak at 147.4°C could be as result of crystalli-zation of another phase of iPP modification from the sample or from the additives added to the sample which could serve as a nucleating agent.

It is well reported that most commercial iPP are usually blends of different crystal species (modifications) of iPP (Lu et al., 2002) and additives which could serve as nucleating agents (Durmus and Yalcinnyuva, 2008). Therefore, combination of higher doses and the presence of additives serving nucleating agents could have favored the crystallization of this another modification. There were broad shoulders between 50 and 110°C in all the thermograms which could be attributed to internal stresses due to a common thermal history in the polymeric samples.

It was also observed that the change in enthalpy (the baselines for the calculation of these enthalpies were straight line taking between 80 and 200°C) and degree of crystallinity (according to equation 2) were decreasing initially as dose increases but at about 21 kGy there is an unusual increase in the change in enthalpy and degree of crystallinity as shown in Table 2. This can be attributed to the appearance of the second peak as doses increases because change in enthalpy is calculated from the area of the melting peak which eventually influenced the calculation of degree of crystallinity.

$$\alpha = \frac{\Delta Hs}{\Delta Hu} X \ 100 \qquad (2)$$

Where α = degree of crystallinity, ΔHs = change in fusion enthalpy of the sample and ΔHu = change in fusion

enthalpy of 100% crystalline sample (usually the literature value of 207J/g is used).

UV-spectroscopic analysis

The optical properties were studied by UV-Vis Spectro-scopy. The absorption spectra of typical spectra are shown in Figure 5. The absorption spectra have essentially two absorption maxima. The first absorption maximum occurs at a wavelength of about 248 nm, the absorbance increases with dose without a shift in the maximum wavelength. The degree of absorption at the wavelength of 248 nm with increase in dose is shown in Figure 6. The absorbance versus dose initially has a linear dependence but subsequently become non-linear as the radiation dose exceeds about 13 kGy (Figure 6). For the initial irradiation doses, the second absorption maximum occurs at wavelength of about 307 nm and the degree of absorption increases with irradiation doses. Another distinctive feature of the second absorption maximum is hypsochromic shift in the second maximum wavelength (λ_{max}) as the radiation dose increases. As shown in Figure 7, the shift in λ_{max} is gradual, changing from 307 nm to 290 nm and at a dose of about 13 kGy the spectrum showed no well defined maximum wavelength λ_{max}. There are essentially two electronic transitions that are feasible, in wavelengths with the UV range examined in this work. The first absorption maximum with λ_{max} = 248 nm corresponds to non-bonding to anti-bonding sigma (n →σ* transition) while the second absorption maximum with varying λ_{max} (307 nm to 290 nm) corresponds to transition of non-bonding
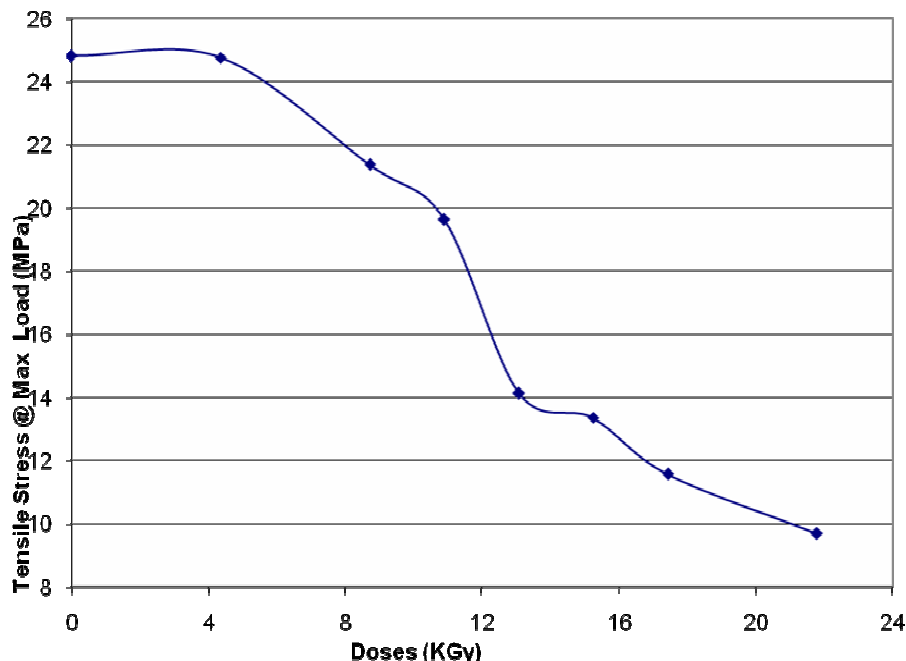
Figure 6. Graph of tensile stress at maximum load.

to anti-bonding pi (that is, $n \rightarrow \pi^*$ transition). The increase in the degree of absorption with dose of the first absorption maximum ($\lambda_{max} = 248$ nm) is due to continuous formation of the hydroxyl group as the dose increases. The hypsochromic shift (towards shorter wavelength) in the second maximum wavelength, λ_{max} is due to the increase in the formation of the carbonyl group (C = O) induced by gamma irradiation of the polymer in the presence of oxygen. This was also confirmed in the Raman spectroscopic analysis earlier. The initial increase in absorption as dose increases is usually associated with chain scission. The sample with the maximum absorption actually presents the most yellowish colour, when physically observed, suggesting severe degradation.

Mechanical properties

The mechanical properties are studied by carrying out tensile test on irradiated samples. It was observed that as the dose increases the iPP becomes more brittle and breaks as indicated by the reduction in elongation to fracture in Figure 8 and 9. The mechanical properties of iPP were also assessed based on its tensile strength as shown in Figure 10. In this case, the tensile strength seems to remain constant at lower doses. However, the elongation to fracture showed a reduction as dose increases. This contradiction in the two parameters that measure mechanical properties that is, elongation at fracture and tensile strength can be resolved as follows: in general both chain scission and cross linking take place simultaneously. It is plausible to say that the chain

scission process is yet to take prominence at these low doses. In general, the process of the degradation of polyolefins which resulted in this tensile behaviour could be as a result of secondary alkyl radicals produced by γ-irradiation on the surface of iPP quickly reacting with oxygen in the atmosphere peroxy radicals. Peroxy radicals can react or combine to form carbonyls and hydroxyls which eventually react to form water vapour (seen on the surface of highly irradiated iPP) and oxides of carbon (Jacobo et al., 2001).

Conclusion

The XRD analysis clearly confirmed that the material under study is an isotactic polypropylene (iPP) with α (monoclinic) crystalline form. Raman spectroscopic analysis also corroborates the confirmation of iPP with the conspicuousness of the methyl group (which is like a fingerprint of PP) peak in its spectra.

The γ-irradiation of polypropylene led to remarkable changes in the physico–chemical properties of the material due to chain scission, oxygen effects and cross-linking activities. These changes result in the production of the degradation products such as water vapour, carbon monoxide from hydroxyl and carbonyl groups as confirmed by Raman and UV-visible spectroscopic analyses. The absorption maximum of the second peaks have hypsochromic shift due to the formation of the carbonyl group. It was also observed that the melting temperature and crystallinity reduces as radiation doses increases. Likewise, there were losses in mechanical

properties of the polymer as indicated by reduction in elongation to fracture and tensile strength of the materials as dose increases.

ACKNOWLEDGEMENTS

REFERENCES

Durmus A, Yalcinnyuva T (2008). Effects of Additives on Non-Isothermal Crystallization kinetics and morphology of Isotactic Polypropylene. In press.

Eddy SP, Marcos AFF (2007). Mechanical Properties of Polyamide 6,6/Low density Polyetheylene Blend by Ionizing Radition, International Nuclear Atlantic conference (INAC).

George J, Kumar R, Sajeevkumar VA, Sabapathy SN, Vaijapurkar SG, Kumar D, Kchawahha A, Bawa AS (2007). Effect of γ-Irradiationon Commercial Polypropylene Based Mono and Multi-Layered Retortable Food Packaging Materials, Radiation Phys. Chem., 76:1205-1212.

Grady BP, Pompeo F, Shambaugh RL, Resasco DE. (2002). Nucleation of polypropylene crystallization by single-walled carbon nanotubes, in press.

Hemmerich KJ (2000). Polymer Materials Selection for Radiation Sterilized Products, Medical Device and diagnostic Industry Magazine.

Jacobo R, Carmen A, Ernesto D, Rebeca P, Jeanette G, Miren I, Magdalena C (2001). Effects of Gamma Irradiation on Polypropylene, Polypropylene + High Density Polyethylene and Polypropylene + High Density Polyethylene + Wood Flour. Mat. Res. Innovat., 4:294-300.

Jacobo R, Carmen A, Delfin M, Ernesto D, Jeanette G, Miren I,Marianella H (2004). ESR Investigatio on Gamma Irradiation on Blends of PP/Virgin HDPE and PP/Recycled HDPE. Revista de la Facultad de Ingenieria de la U.C.V., 19: 115-122.

Kassem ME, Bassiouni ME, El-Muraikhi M (2002).The Effect of γ-Irradiation on the Optical Properties of Polyoxymethylene Compacts, J. Materials Sci.: Materials electronics, 13: 717-719.

Lezak E, Bartczak Z (2005). Experimental Study of the Formation of β- and γ-Phase Isotatic Polypropylene and Estimation of the Phase Composition by Wide-Angle X-Ray Scattering, Fibres and Textiles in Eastern Europe, 13: 51-56.

Lu H, Qiao J, Xu Y, Yang Y (2002). Effects of Isotacticity Distribution on the Crystallization and Melting Behaviour of polypropylene, J. Applied Polymer Sci., 85: 333-341.

Popok VN, Azarko II, Khaibullin RI, Stepanov AL, Hnatowicz V, Mackova A, Prasalovich SV (2004). Radiation-induced change of polyimide properties under high-fluence and high ion current density implantation, Appl. Phys. A: Mat. Sci. Process, 78:1067-1072.

Yeom B, Yu YJ, McKellop HA, Salovey R (1998). Profile of oxidation in irradiated polyethylene, J. Polymer Sci. A: Polymer Chem., 36:329-339.