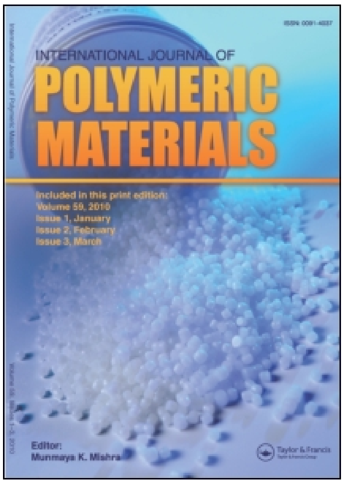

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Structural Analysis of Crystalline Nylon 6,12 Exposed to Gamma Radiation

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Characterisation of crystalline poly(amide 6, 12)fibers subjected to various γ-irradiation doses is presented. The specimens were analysed through their thermal, vibrational and morphological properties. All the experimental evidence points to the conclusion that chain scission may have occurred, forming low molecular weight species (oligomers) due to the degradation of the neat polymer chain. The thermal behaviour (fusion point and crystallinity) provides evidence that the oligomers formed act as plasticifing agents. The observed melting point depression of the irradiated poly(amide 6, 12) samples is explained by Flory's theory [1]. The vibrational properties studied by Infrared spectroscopy (FT-IR) show the increase in crystallinity; the images obtained by atomic force microscopy (AFM) are also an evidence of the surface pattern modification by γ-irradiation.

Keywords: Gamma irradiation; Nylon (6-12); Surface pattern; Crystallinity

1. INTRODUCTION

The interaction of matter with electromagnetic radiation is of both scientific and practical interest because of its broad range of applications, among which one can mention spectroscopic characterization techniques, such as, IR [2], microwaves [3], *etc.*, which are waves

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[*] Corresponding author.

of relatively low-energy. On the other hand, the uses of high-energy electromagnetic waves include many industrial processes such as curing of polymers by UV [4], inspection of baggage in airports by X-rays, *etc.* One kind of radiation with the highest energy range that has recently found useful applications is the γ-radiation, since it has been employed to increase the conductivity of polymer films [4], as an antiseptic method [5, 6], as well as a characterization technique [8, 9]. Also, the elimination of dangerous organic contaminants has been reported [10], along with many other applications related to various synthesis routes [7, 8, 11 – 14].

On the other hand, there is a fundamental interest in the structural changes in polymeric materials [15 – 19], aiming to develop novel ways to produce materials with improved properties.

Accordingly, the present work is aimed to study the structural changes in crystalline Nylon 6, 12 fibers as induce by γ-irradiation, and to attempt to explain them based on available fundamental theories.

2. EXPERIMENTAL

2.1. Materials

Crystalline 0.2 mm diameter Nylon 6 – 12 fibers were obtained from Dupont (Zytel). Various types of samples were studied, one of which was chosen as reference (that is, without applying radiation), and the others were exposed to 15, 50, 100, 200 and 300 kGy doses of γ-irradiation from a ^{60}Co source. The samples were identified as follows, based on the final dose: NY stands for Nylon 6, 12 fiber followed by VIR (reference) or 15, 50, 100, 200 or 300 which indicates the irradiation dose; for example, NY50 indicates a Nylon 6, 12 fiber, 50 kGy γ-irradiated.

2.2. Sample Irradiation Procedure

Polyamide fibers were submitted to γ-irradiation doses of 15 – 300 kGy under room conditions. The dose rate was 3.64 kGy/h (*i.e.*, 0.364 Mrad/h) in a 55 – 6500 Atomic Energy of Canada Limited (AECL) γ-irradiator using a ^{60}Co source. The dosimetry of irradiation process was verified through a red acrylic dosimeter L9-C1 (Nordion, 1994).

2.3. Characterization Techniques

2.3.1. *Calorimetric Behaviour*

The melting temperatures and crystallinity degree of the irradiated fibers and neat fibers were obtained from a DuPont differential scanning calorimeter (DSC), 2100 model, under the following conditions: N_2 atmosphere, a heating rate of 20°C/min from room temperature up to 170°C, then 5°C/min up to 230°C.

2.3.2. *Infrared Spectroscopy*

A Nicolet Fourier Transform Infrared Spectrophotometer (FT-IR) equipment was used for this analysis. Scrapes of the Nylon 6, 12 surface were mixed with KBr powder to produce a tablet in the standard way.

2.3.3. *Surface Pattern*

The morphological changes in Nylon 6, 12 gamma irradiated fibers were observed with an Autoprobe C.P. Force Atomic Microscopy (AFM) from Park Scientific Instruments, in the Contact mode, using gold-coated contact ultralevers. The preferential magnification was 10 μm, scanning along the *Y*-axis.

3. RESULTS AND DISCUSSION

In order to quantitatively determine the induced structural changes in the fiber as a consequence of the γ-radiation dose, differential scanning calorimeter and infrared spectroscopy measurements were done, as mentioned. Figure 1 shows the evolution of crystallinity of the sample upon irradiation, as obtained from the corresponding DSC thermograms. The degree crystallinity of the irradiated samples tends to be

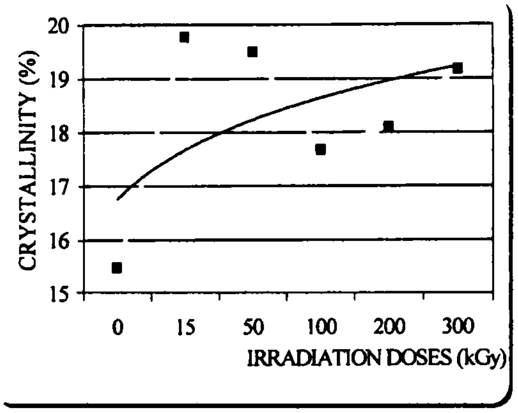


FIGURE 1 Degree of crystallinity of the irradiated specimens as function of irradiation dose.

higher than that of the neat fibers, indicating that indeed, structural changes are occurring in the fibers as a consequence of the γ-irradiation. This is probably due to the effect of low molecular weight species (oligomers) which are formed by chain scission processes within the polymer. Therefore, a completely miscible blend is formed of the new oligomeric Nylon 6, 12 (ON6, 12) and the remaining Nylon 6, 12 (N6, 12) polymer. The net result of the oligomer is the increase in the entropy of the blend with the Nylon 6, 12 polymer. As a consequence of this, the crystallinity of the sample has to increase, as DSC crystallinity reveals. The effect of incorporating oligomeric additives in polymers has been well-studied [1, 19–21] and it is not surprising to find such an increase in the crystallinity. This finding can be explained by the following scheme: at the range studied, very low molecular weight species are formed. These species can be easily packed within the Flory's Lattice [1], thus, a crystallinity increase is expected. That is, there exist an increase in the entropy. This phenomenon is supported by the FT-IR (Fig. 2) measurements, where a sharper peak around 3300 cm^{-1}, is observed as the gamma radiation dose increases.

Figure 3 shows the corresponding melting points of the Nylon 6, 12 fibers as a function of radiation dose. A melting point depression is observed when the dose increases. This melting point depression has been extensively studied in various polymers [1, 19–21] and is due to

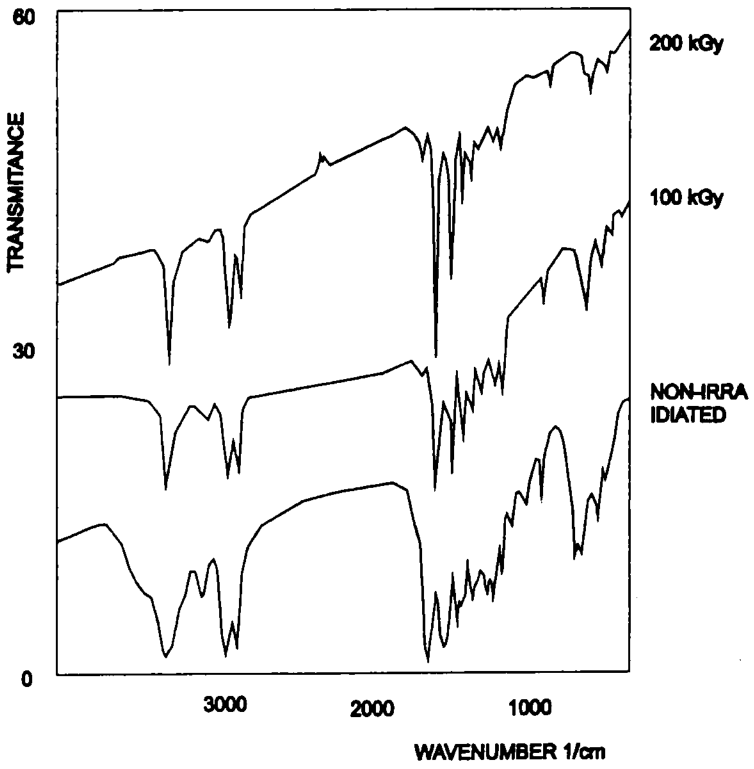


FIGURE 2 Infrared spectres of samples with different levels of irradiation.

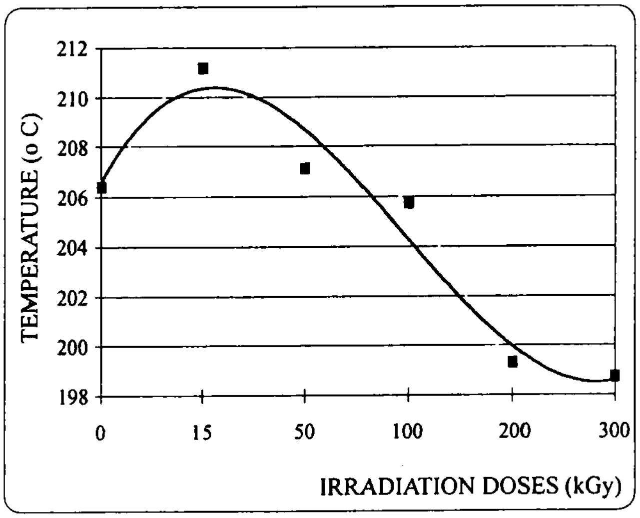


FIGURE 3 Melting temperatures as a function of irradiation dose.

the addition of low molecular weight compounds. In this case, the low molecular weight compounds are the oligomeric nylon 6, 12 formed through the irradiation, providing additional evidence of chain scission.

It must be emphasized that the melting point of the NY15 sample is higher than that of the neat fiber. This phenomenon may be explained by repolymerization theory. It can be said that 15 kGy is the threshold energy to break the C—N bond, and to form free radicals which react immediately. However, that energy is not enough to break bonds repeatedly until small species are formed, as it happens with greater doses.

The change of the crystallinity in the irradiated samples must cause a change in the density of the samples, which in turn must be reflected in the corresponding morphologies. Figures 4(a) through 4(d) show AFM micrographs from the samples irradiated at 0, 25, 200 and 300 kGy. As observed there, the higher the radiation dose, the bigger the damage to the fiber surface, as revealed by the diagonal strips, caused by the degradation process. These damages are likely related to the changes in crystallinity since the oligomer formation during the

NYLON 6,12 NON-IRRADIATED

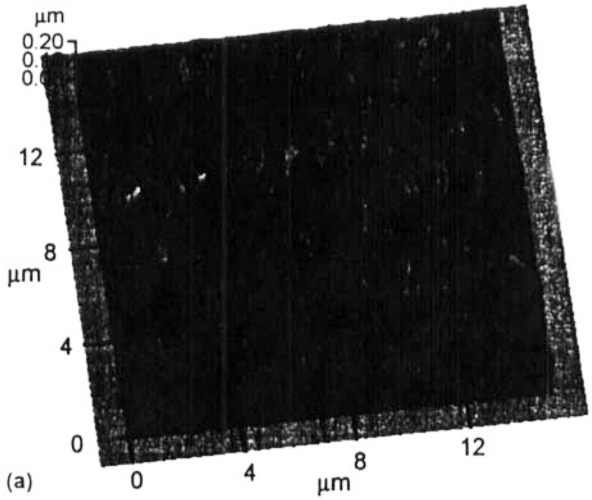
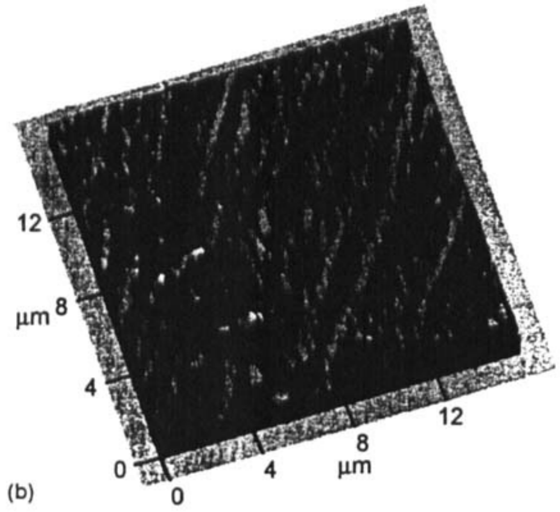


FIGURE 4 (a) through (d) Atomic force microscopy images of samples with various levels of irradiation.

NYLON 6,12 25 kGy



NYLON 6,12 200 kGy

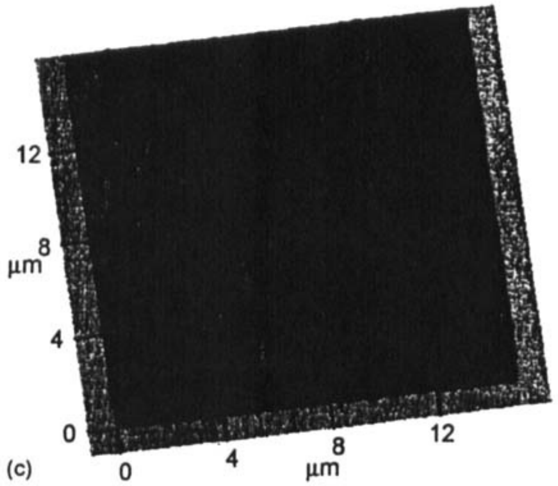


FIGURE 4 (Continued).

NYLON 6,12 300 kGy

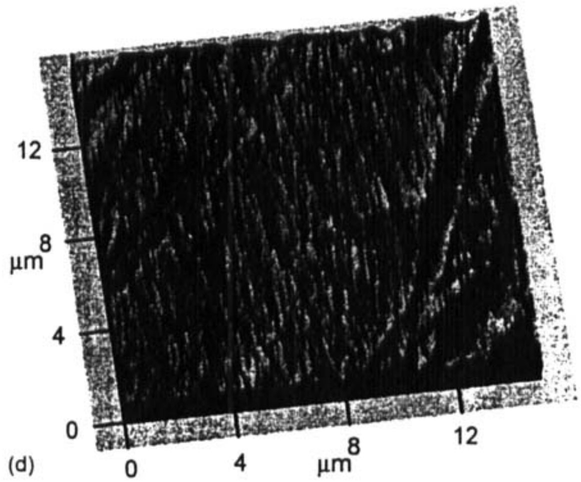


FIGURE 4 (Continued).

exposure to γ-irradiation induces changes also in the corresponding viscoelastic, rheological and mechanical properties of these materials. When the polymer suffers the aforementioned change in crystallinity, changes in density are observed. Therefore a swelling or shrinkage due to these changes can be expected. This swelling or shrinkage is responsible for the strip formation along the sample.

4. CONCLUSIONS

All the experimental evidence gathered, including thermal behaviour and morphological characteristics leads to the conclusion that, first, chain scission has occurred, forming low molecular weight species (oligomers), due to the γ-degradation of the neat polymer chain. Second, the thermal behaviour (melting point and heat of crystallisation) provides evidence that the oligomers formed are acting indeed as plasticiting agents. These structural changes are observed also by FT-IR and AFM measurements. Mechanical characterisation and positron annihilation lifetime measurements are currently under way, aiming to provide a deeper insight into the molecular details of these phenomena, and shall be reported separately.

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