Controlling of Degradation Effects in Radiation Processing of Polymers

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ELECTRON BEAM RADIATION EFFECTS ON POLYAMIDE-6

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Abstract

The polyamide-6 is a semicrystalline material with a high degree of crystallinity, and it is among the top of three engineering plastics due to its use in high performance machine parts. The recycling process needs special attention, because successive recycling cycles promote changes in several properties of the material, as structures break down, decrease of molecular weight, increase of melting index and decrease of mechanical resistance. This polymer was irradiated with a 1.5 MeV electron beam at different doses. The glass transition of the samples was determined by dynamic mechanical analyses (DMA) measurements. The crystallinity was observed through the X ray diffraction method. It was observed that cross-linking may have occurred in the irradiated samples of virgin and recycled polyamide-6 and the crystallinity has not changed. The density of cross-linking was calculated through the equilibrium swelling experiments, using the Flory-Rehner theory. The objective of this work was to investigate the cross-linking and degradation in the virgin and recycled polyamide-6 induced by ionizing radiation

1. INTRODUCTION

Polyamide-6 is a semicrystalline polymer with a long-chain synthetic polymeric amide that has recurring amide groups as an integral part of the main polymer chain. The polyamide-6 is among the top three engineering thermoplastics due to its use in high performance machine parts [1]. It has a wide range of applications in its many forms and replaces metals in components and assemblies, which need excellent mechanical, chemical and physical properties [2]. Its limitations are high moisture absorption resulting in dimensional and mechanical property changes, high mold shrinkage, and notch sensitivity unless suitably blended for toughness [3].

Successive recycling cycles promote changes in polymer properties, such as structure breaking, molecular weight reduction, melt index increase and mechanical resistance reduction. Wiebeck and co-workers [4] found that the melt index was increased after three times recycling process and the stress-strain properties decreased at the first recycling process. Machado and co-workers [6] studied the crystallinity of polyamide-6 without additives in nineteen successive recycling cycles and concluded that the level of crystallinity of the samples did not change significantly.

Applications of electron beam processing in the treatment of polymers are commonly used. The interaction of high energy radiation with polymers may cause permanent modifications in the polymer's physicochemical structure. The induced modifications may result in degradation of the polymer or in improvement of its properties (cross-linking), which are simultaneous and competing processes, depending on the radiation dose utilized. Cross-linking occurs more readily in the polymer's amorphous phase and this process makes the glass transition temperature (Tg) increase [6, 7]. In these regions, the molecular chains are mobile, and after a short time period they move to meet new partners. Within the crystalline regions, molecular rearrangements are necessary to permit a cross-linking and these are more difficult for geometrical regions. The glass transition temperature (Tg) is not dependent upon chain scission at a very high molecular weight of a linear chain polymer but is affected by cross-linking [8].

The polymeric materials exhibit an enhancement in their resistances to heat, oil, water, shock, abrasion and fatigue as an increase in their crosslinkages occur. In addition, since they are resistant to chemicals and solvents, the crosslinked polymeric materials are not only used for common articles but have a wide use as industrial materials as well.

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This work presents results of dynamic mechanical analyses (DMA) and X-ray diffraction analyses of the virgin and recycled irradiated polyamide-6. The polymer with high degree of crystallinity has a reduced amorphous phase, nevertheless a weak physical transition. DMA is more sensitive to it than other thermal analyses [9].

The X-ray diffraction method is a powerful tool for investigating orderly arrangements of atoms or molecules through the interaction of electromagnetic radiation with structures comparable in size to the wavelength of the radiation resulting in interference. Extensive cross-linking in a crystalline polymer may cause loss of crystallinity [10]. X-ray diffraction diagrams of partially crystalline polymers such as polyamides show peaks of high intensity corresponding to the crystalline regions [2].

This work also presents the results of effective chains concentration (v_e) and number-average molecular weight between cross-linking ($\overline{M_c}$) of irradiated virgin and recycled polyamide-6. These results were calculated through the equilibrium swelling experiments, using the Flory-Rehner theory.

2. MATERIALS AND METHODS

The polyamide-6 resin (Tg=50°C, T_m=220°C e ρ= 1,13 g/cm^3) without additives has been dried for 4 hours at a temperature of 100°C. This dried resin was submitted to three successive recycling cycles in a 90/110 mm multiple-screw extruder. The work temperature varied from 250 to 260°C. The virgin and recycled polyamide-6 were molded by the process of injection molding.

This polyamide were irradiated at the Nuclear and Energy Research Institute (IPEN) radiation facility, on a JOB 188 model accelerator, with a 1.5 MeV electron beam, at doses of 200, 300, 500 and 600 kGy, and dose rate of 22.61 kGy/s.

The DMA tests were performed using DMA-983 equipment from TA Instruments. The specimens were held in the equipment by vertical clamps under a 6 in/ lb torque separated 15mm from each other. A procedure was adopted in order to eliminate the moisture absorption effect on the DMA data. The polyamide specimens were cooled to -70°C using liquid nitrogen (LNCA), kept in isotherm for 3 minutes and heated to 130°C at 3°C/min. Then, they were cooled to -70°C, kept in isotherm for 3 minutes and heated to 200°C at 3°C/min. A 1Hz frequency was utilized along with a 0.3 mm oscillation amplitude, length correction of 0.5 and Poisson's constant of 0.5.

For X-ray diffraction experiments a diffractometer URD 63 (Seifert-fpm) in Bragg-Brentano geometry in combination with an IRIS generator (40 kV, 30 mA) was used. The wavelength of irradiation was 1.5418 A (CuKα, Ni- filtered) and X-rays were detected by a position sensitive detector (STOE). The detector (at the fixed position) facilitates the simultaneous measurement of 7 deg 2 θ angular range with a resolution of 0.02 deg Δ2θ (the diameter of the diffractometer circle was 360 mm). Typical counting times were between 15 and 60 s per diagram. The experiments were done in Philips X- Ray Diffraction equipment, model PW 1830 at 40 KV/ 20 mA. The scanning range was between 10° and 80° with exposure time of 1°/sec.

According to the ASTM D3616-88, the dry samples were allowed to stand in the formic acid for 72 hours in the dark [11]. The solvent was removed and the swollen samples were weighted.

The cross-linking density in a polymer network is inversely proportional to the number average molecular weight between cross-linking ($\overline{M_c}$) [12, 13]:

$$\overline{M_c} = \frac{M_n}{(v_e M_n + 2)}$$

According to the Flory-Rehner model, $\overline{M_c}$ can be estimated from the equation; where W_2, V_1 and ρ are the polymer volume fractions in the swollen gels at equilibrium, the molar volume of solvent and the polymer density, respectively. According to the regular solution theory by Hildebrand and colleagues and the Bristow and Watson semiempirical equation, the equation for the interaction parameter becomes:

$$v_e = -\left[\frac{\ln(1-W_2)+W_2+\chi W_2^{\,2}}{\overline{V}_1\rho\left(W_2^{\frac{1}{3}}-\dfrac{W_2}{2}\right)}\right]$$

$$\chi = \frac{\overline{V}_1}{RT}(\delta_S-\delta_P)^2+0.34$$

where δ_s and δ_p are solubility parameter of solvent and polymer, respectively. The calculated interaction parameter χ for the system polyamide-6 -formic acid is 0.485.

3. RESULTS AND DISCUSSION

TABLE I.   THE GLASS TRANSITION TEMPERATURE TG AT DIFFERENT DOSES FOR THE VIRGIN AND RECYCLED POLYAMIDE-6 SAMPLES OBTAINED THROUGH THE DMA.

Dose (kGy)	Tg virgin (º C) first heating	Tg virgin (º C) second heating	Tg recycled (º C) first heating	Tg recycled (º C) second heating
0	70.8	70.0	72.7	72.6
200	71.3	69.9	74.9	74.2
300	72.7	67.6	76.4	74.0
500	74.2	69.4	78.9	77.7
600	76.0	71.4	76.4	74.9

It is well known from the literature that moisture strongly affects the polyamide-6 T_g leading to plasticity, which leads to a higher chain mobility, reducing T_g. It may be observed in Table 1 that after the second heating, Tg decreased, specially in the virgin polyamide-6. The cooling process was very slow (~40 min), so that modifications should have been introduced into the polymer's molecular structure and this affects the glass transition temperature. For this reason, only the first heating DMA data was considered. The recycled and virgin samples present an increase in Tg as a function of the radiation dose. With the results obtained by DMA one can conclude that there was a change in the molecule structure of poliamide-6. The molecular mobility is hindered by cross-linking, shifting the glass transition temperature to higher values. Cross-linking can be formed by macronetwork or micronetwork. The micronetwork can be several nanometers to several micrometers small and the functional micronetwork can serve as a precursor for macronetworks [11]. The glass transition temperature of the recycled samples increases as the dose is brought up to 500 kGy. It suggests that the cross-linking process is occurring.

$$\overline{M}_c = \frac{M_n}{(v_e M_n+2)}$$

Figures 1 and 2 present the X-ray diffraction diagrams of polyamide-6, virgin and recycled, irradiated at different doses. It was observed that the radiation process at doses up to 600 kGy did not affect the crystallinity of the irradiated specimens.
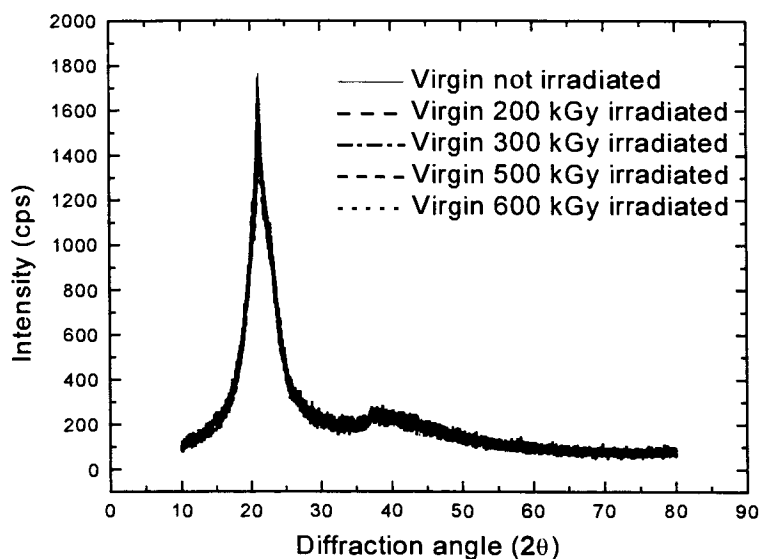

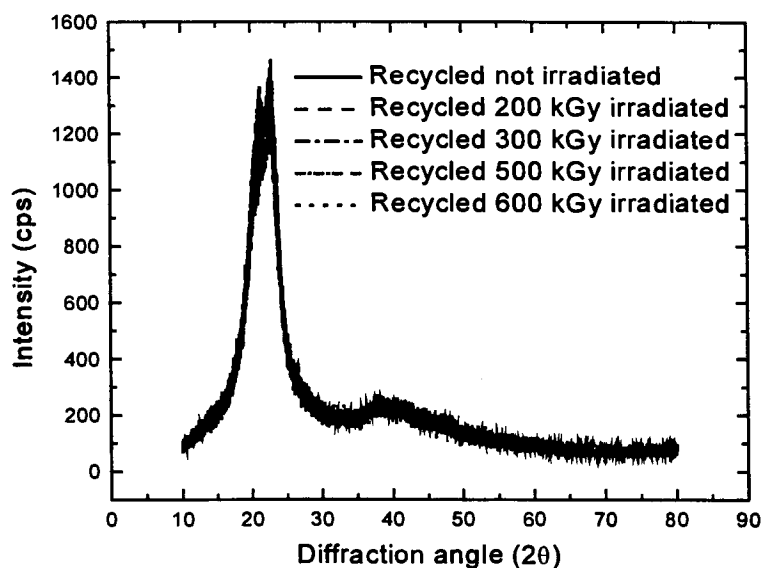FIG. 1.   X-ray diffraction diagrams of virgin polyamide-6 irradiated at different doses.

FIG. 2.   X-ray diffraction diagrams of recycled polyamide-6 irradiated at different doses.

The Figures 3, 4 and 5 present the results of the concentration of effective chains, number average molecular weight between cross-linking and swelling percentage in function of the dose, respectively.
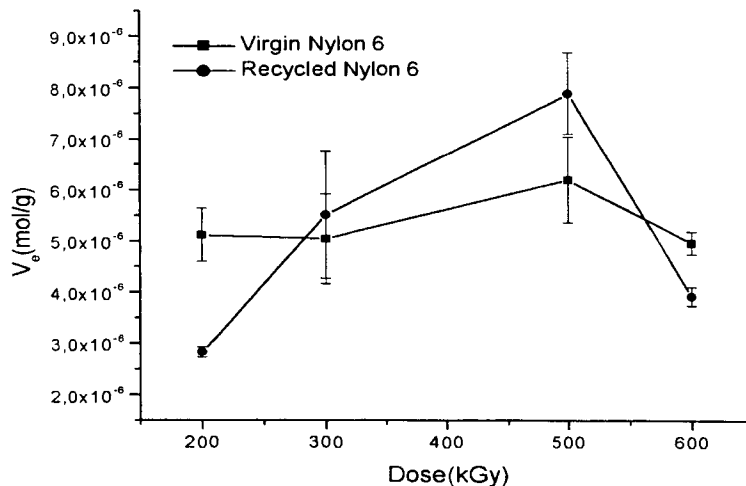

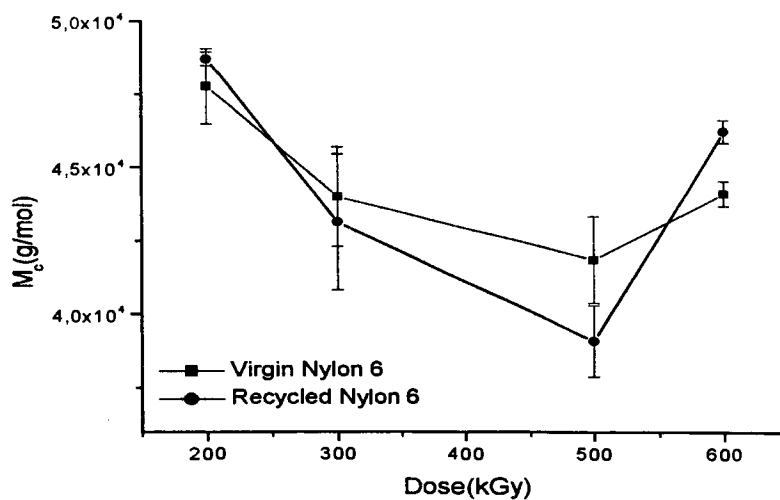*FIG. 3.   Concentration of effective chains versus dose.*

FIG. 4.   Number average molecular weight between cross-linking versus dose.

In Figure 3, the results showed that for doses up to 500 kGy, the concentration of effective chains increased while for higher doses this value decreased. This variation is more pronounced for the recycled samples.

In Figure 4 the results showed that for doses up to 500 kGy the number average molecular weight between cross-linking decreased while for higher doses this value increased. This variation is more pronounced for the recycled samples.
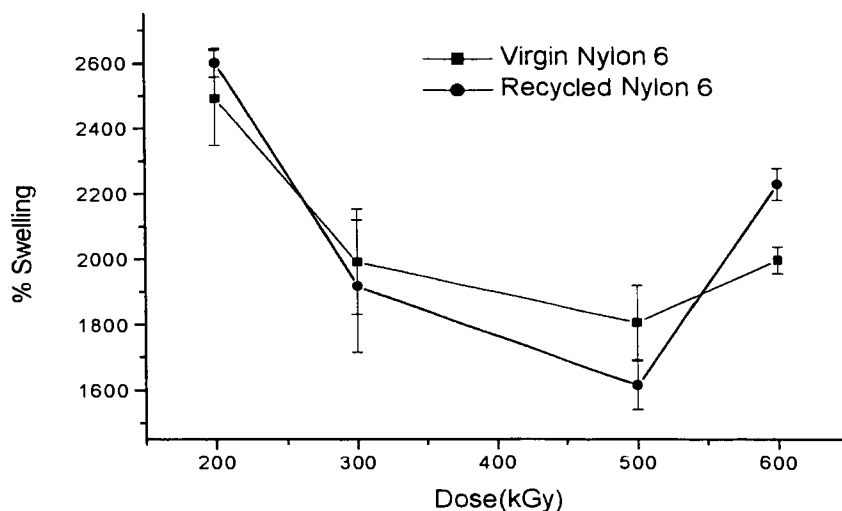
FIG. 5. Swelling percentage versus dose.

In the Figure 5, the results confirmed the behaviour of the curves presented in Figures 3 and 4. When the swelling percentage decreases it means that the chains are more interlaced. All these results suggest that the recycled polyamide-6 can be cross-linked up to 500 kGy. The predominance of the degradation process was also observed in the swelling percentage curves at doses over 500 kGy.

These are partial results from a set of experiments to confirm the recycled polyamide-6 cross-linking.

4. CONCLUSIONS

The T_g values obtained by DMA increased with the increasing of radiation dose for the virgin and recycled polyamide-6, it may confirm the occurrence of network in the samples.

By the X-ray diffraction, it was observed that the radiation process did not affect the crystallinity of these irradiated polyamide-6.

For doses up to 500 kGy it was observed that the number average molecular weight between cross-linking (M_c) decreased in both virgin and recycled polyamide-6 samples indicating the cross-linking of polyamide-6. For higher doses the (M_c) increased indicating the degradation of polyamide-6.

The predominance of the degradation process was also observed in the swelling percentage curves at doses over 500 kGy.

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