Study on Radiation Crosslinking of a Bio-based Polyamide—I: Characterization by X-ray Diffraction

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Abstract. Biomass is a feasible substitute for petrochemicals, providing many of the same chemical building blocks that are required to fabricate durable and high-performance materials. In this paper, the radiation crosslinking of a bio-based polyamide has been investigated over a range of irradiation dose (50–250 kGy) with limited air. The crystallinity variations were studied using infrared (IR) spectroscopy and X-ray diffraction (XRD). The presence of both α and γ phase was seen in all the polyamide fibers at room temperature. Generally, the irradiated BDIS fibers had lower crystallinity levels than that in the unirradiated one (F0) except for the fibers irradiated at the dose of 200kGy (F200). F200 possessed the maximum crystallinity. In addition, gel content of the irradiated fibers was measured. It was concluded that the relation between sol fraction and radiation dose followed the Charlesby–Pinner equation, the ratio of degradation to crosslinking (p_0/q_0) decreased with the increase of molecular weight.

Introduction

Semicrystalline polyamides are typical gamma-radiation crosslinkable polymer, including PA11, PA12, PA6, PA610，PA6,6 and PA10,10.[1] Extensive work has been carried out so far in the field of gamma-radiation of polyamide materials and their properties.[2] The crystallinity and structural changes resulting from gamma-irradiation were explored by Lihua Zhang et al. using wide angle X-ray diffraction (WAXD), electron spin resonance (ESR) and DSC. It was concluded that free radicals produced were trapped mainly in the interface between crystalline and amorphous regions wherein free radicals were mainly in the form of $-CH_2-CO-NH-CH\bullet-CH_2-$, which showed a quartet in the ESR spectrum.[3] In our lab, a bio-based polyamide (BDIS) based on renewable monomers has been synthesized and characterized.[4] In this study, the crystallinity variations of BDIS were studied using infrared (IR) spectroscopy and X-ray diffraction (XRD).

Materials

The biobased BDIS polyamides were synthesized through a two-step process: the formation of ammonium salts and subsequent melting-polycondensation at high temperature. Equimolar amounts of diacids (sebacic acid-SA and itaconic acid-IA) and diamines (1, 10 diaminodecane-DD and 1, 4 diaminobutane-BD) were dissolved in absolute ethanol to form ammonium salts, with which polymer were synthesized at 180~210 °C using hydroquinone as inhibitors. [4]

In this experiment, the BDIS polyamide was prepared with a mole ratio of BD to DD of 1:1 and a mole ratio of IA to SA of 1:1. The viscosity-average molecular weight of the obtained polyamide were 50000(M1), 64000(M2), 70000(M3) and 75000(M4) Da.

Preparation of sample

BDIS polyamides with different molecular weight were extruded through a double screw extruder (Haake Mini Lab II) to form fibers. The drawing of fibers was carried out by a two-stage draw process. In the first-stage drawing, the fibers were stretched to certain times of their original length at ambient

temperature. In the next step, the second-stage drawing was carried out at 115°C to their optimum draw ratios. Then the finished fibers were formed after 1-2min heat-setting at 125°C.

The samples, enclosed in a PE bag with limited air, were irradiated with a cobalt-60 plate source which was supplied by National Institute of Metrology, at a dose rate of 3.2×10^{3}Gy/h. The irradiation doses used were 50, 100, 150, 200 and 250 kGy. The sample designations are given in Table 1.

Table 1 Designation and irradiation dose of bio-based BDIS samples

Sample Code	Radiation Dose/ kGy
F0	0
F50	50
F100	100
F150	150
F200	200
F250	250

Characterizations

Measurement of the gel content (Gel/%) was determined by Soxhlet extractor with dimethylformamide (DMF) (refluxing 30–40 h). The ratio of the remaining mass of insoluble material (dried to constant weight in a vacuum oven) to original mass was defined as Gel% by the Eq. 1. The sol content (sol%) was then calculated via Eq. 2.

$$Gel(\%) = \frac{mass\ residue(g)}{originalmass(g)} \times 100. \tag{1}$$

$$100 - Gel(\%) = sol(\%). \tag{2}$$

Measurement of X-ray diffraction (XRD) was carried out using a Rigaku X-ray diffractometer (Japan) with curved crystal monochromatized Cu Kα radiation (1.54Å) generated at 40 kV and 50mA. Equatorial scans were obtained in the 2θ range of 6-36° with intensity data collected. The crystallinity (Xc), crystal forms and crystal size of the sample were calculated with XRD processing software of device.

Fourier transform infrared (FTIR) spectra were obtained from attenuated total reflectance (ATR) on a Nicolet nexus 670 spectrometer (Thermo Co., USA). At least 64 scans were obtained at ATR to achieve an adequate signal to noise ratio. Absorption spectra were acquired in the wavenumber range of 600-4000 cm^{-1}.

Results and discussion

Gel Content

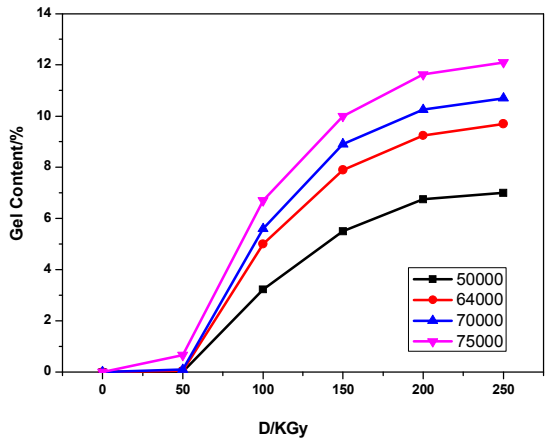


Fig. 1 Gel content of the BDIS fibers with different molecular weight at varying radiated doses

As shown in Figure 1, the gel content is strongly dependent on the radiation dose. In general, the gel content corresponds with the network structure in the amorphous region of BDIS fibers, which is insoluble in solvents. The higher the gel content is, the higher the degree of crosslink density in amorphous regions is.

It can be seen that below 50 kGy, there is no gel detected for BDIS with molecular weight from 50,000 to 70,000. In the case of BDIS with high molecular weight, such as 75000, the gel content is detected after radiation of 50kGy but it is less than 1%. Above 50kGy, when the radiation doses increase, the gel content of BDIS fibers show a rapid increase. The highest gel content obtained in this experiment is 13% in the BDIS with the largest molecular weight after radiation of 250kGy, as displayed in Figure 1.

However, for all 4 samples, there is only slight increase of gel content when the radiation increased from 200kGy to 250kGy, which suggested that chain scission reactions were getting predominant over crosslinking reactions.

It may be stated that the influence of radiation doses on crosslinking or chain scission is more likely attributed to the consumption of dissolved oxygen in the polymer by reaction with free radicals to form peroxides. At high doses (200 kGy and above), all the dissolved oxygen gets consumed and fresh oxygen cannot diffuse in from the outside of PE bag fast enough to replace it so that further peroxidation ceases.[5]

Thus, the increase of gel content slows down with the increasing of radiation dose when it reached above 200kGy, because the crosslinking reaction and the decomposition reaction coexist, and at high doses the decomposition reaction became substantial. In addition, it can be found at the same dose, the greater the BDIS molecular weight is, the more the gel content is, and the better the radiation crosslinking is. According to the theory of random crosslinking, this is because polymer with higher molecular weight possesses long molecular chain, wherein the number of monomeric unit is greater, so the probability of its molecular chain in connection with the crosslinked network is higher.

According to the classical Charlesby–Pinner equation (Charlesby, 1960)

$$S+S^{1/2}=p_0/q_0+1/(q_0\ \mu_1\ D), \quad (3)$$

where S is the sol fraction (S = 1–gel fraction), p_0 and q_0 are constants which indicate sensitivity of chain scission and crosslinking to radiation, respectively. In this study, the relationships between $S+S^{1/2}$ and 1/D are shown in Figure 2.

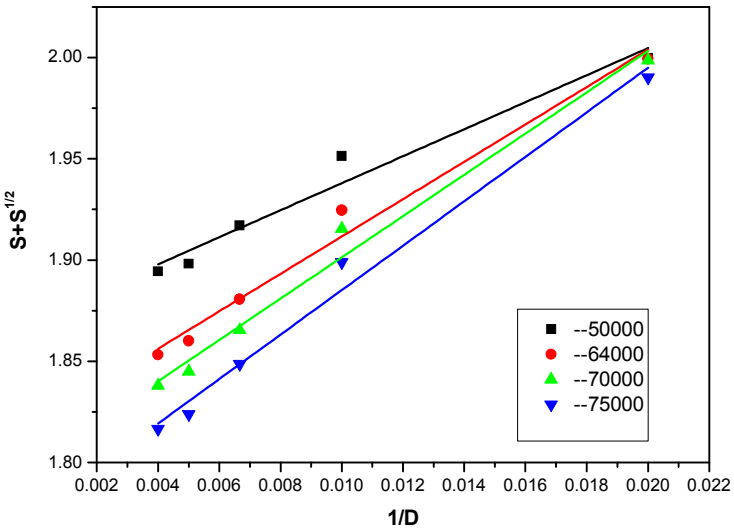
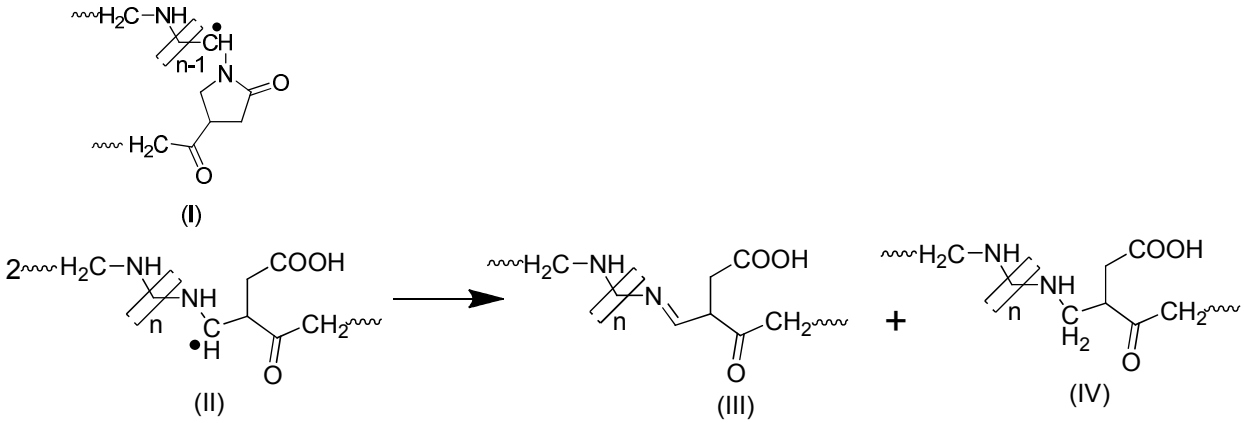


Fig. 2 The relationships between $S+S^{1/2}$ and 1/D

According to the classical Charlesby–Pinner equation, when the relationships between $S+S^{1/2}$ and 1/D are linear, it shows that radiation crosslinking follows a random crosslinking law. However, in the present system, the data points depart partly from straight lines, and this might be because the C=N double bonds of BDIS as shown in Scheme 1(III) are known to enhance the radical formation and react rapidly at the initial irradiation stage.

An extrapolation of these lines to 1/D=0 gives p_0/q_0. It can be concluded that the value of p_0/q_0 for the BDIS with lower molecular weight is larger compared with the one with higher molecular weight, showing that the BDIS with higher molecular weight is easier to crosslink.

In this system, the predominant free radical produced is one with the unpaired electron on the carbon adjacent to the amide nitrogen as shown in Scheme 1(I).[6] Scheme 1(II) may be produced from the combination of bio-based polyamide and water in air.[7] And then, disproportionation reaction occurs leading to the possible formation of Scheme 1(III) and Scheme 1(V).



Scheme 1. Radiation mechanism of BDIS polyamides

FTIR

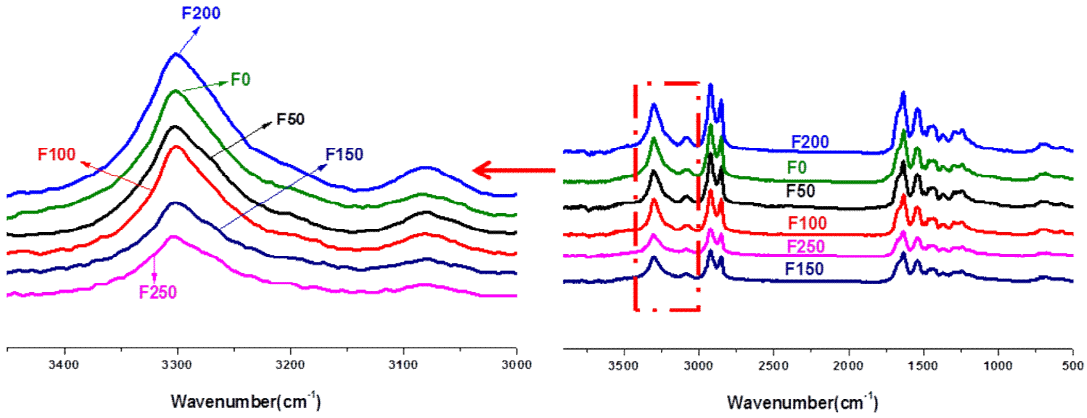


Fig. 3 FTIR spectra of the BDIS polyamides and hydrogen-bonded N-H stretching absorption region of FTIR spectra

The spectra of F0, F50, F100, F150, F200 and F250 are shown in Figure 3. The absorption bands that represent the hydrogen-bonded N-H stretch, overtone of N-H in plane bending, C=O stretching (amide I), C-N stretching and in-plain N-H deforming associated with the amide groups (amide II) are located at around 3300 cm^{-1}, 3090 cm^{-1}, 1635 cm^{-1} and 1540 cm^{-1}, respectively. In addition, the absorption bands in the wave number ranging from 2852 to 2854 cm^{-1} and from 2923 to 2926 cm^{-1} represent the symmetric and the asymmetric stretching of methylene, respectively.

The spectrum of F0 does not show any absorption bands above 3400 cm^{-1} indicating the absence of free N–H. This aspect remains the same in the other spectrum also. From Figure 3, it can be found that for F50, F100 and F150 there is a drop in absorbance values compared with F0 in the 2850–3350cm^{-1} region. So N–H stretch absorbance values are severely diminished. This means that the amount of hydrogen bonding is reduced which suggests a loss of crystallinity in F50, F100 and F150. Again from Figure 3, we see that the N–H stretch absorbance values in F200 and F250 increase and the N–H stretch value in F200 is nearly equal to that in F0. For comparison of the absorbance values we have chosen the Amide I band at 1640 cm^{-1} as an internal reference band as it is stated to be independent of crosslinking to account for variations in the amount of polymer analyzed.

XRD

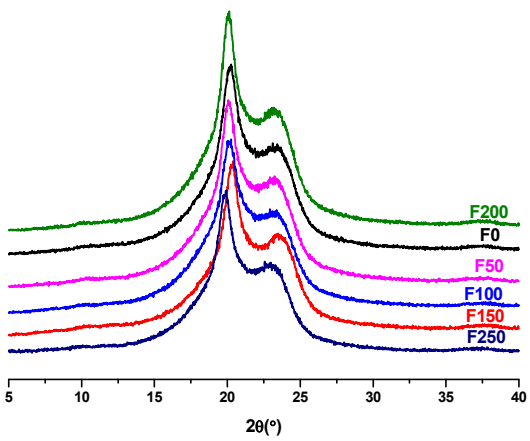


Fig. 4 XRD patterns of bio-based BDIS polyamide samples at different irradiated doses

Figure 4 shows the XRD patterns of bio-based BDIS polyamide samples prepared from the BDIS with molecular weight of 75000 and with different irradiated doses. In each XRD pattern, two diffraction peaks located at 19° and 23°, which are designated as α_1 and α_2 respectively, can be easily distinguished, confirming the significant presence of α crystallites for polyamides.

The area under the crystalline and amorphous proportions is determined in arbitrary units and the crystallinity was calculated using the following equation:

$$\text{Crystallinity} = Ic \times 100/(I_C + I_A), \quad (4)$$

Where I_A and I_C are the integrated intensity corresponding to the amorphous and crystalline phases, respectively.

Table 2 Percent crystallinity of the bio-based BDIS polyamide as obtained from WAXS

Sample Code	Crystallinity (%)
F0	37
F50	36
F100	35
F150	30
F200	40
F250	24

In this experiment, it was found that the variation in molecular weight had no significant effect on the crystallinity of the fibers, so the irradiated study of BDIS with molecular weight of 75000 was just carried out. It is obvious from Table 2 that generally the irradiated BDIS fibers have lower crystallinity levels than that in the unirradiated one (F0) except for F200. F200 shows the maximum crystallinity, which coincides with the result of FTIR. And the reason is that at some irradiated dose radiation may lead to the decomposition of entangled molecular chain in amorphous region; the molecular chains with shorter length after decomposition are easier to move, correspondingly, folding and orientation are easier, so that the degree of crystallinity will increase.

Moreover, any shifting of the α_2 peak towards the α_1 peak is not seen at low irradiated dose (<200 kGy), thereby indicating that the degree of perfection of the formation of hydrogen-bonded sheets is more or less same at lower radiation doses.

Conclusions

In summary, it can be concluded that: (i) For BDIS with higher molecular weight of 75000, the minimum dose for the gel to appear is 50 kGy and the gel content at this dose is ~1%, and at a radiation dose of 250 kGy a gel content of 13% is observed. While in the case of BDIS with lower molecular weight of 50000, 64000, 70000, there is absence of any gel for below 50 kGy. In addition, it can be found at the same dose, the greater the BDIS molecular weight is, the more the gel content is. (ii) Generally, the irradiated BDIS fibers have lower crystallinity levels than that in the unirradiated one (F0) except for F200. F200 shows the maximum crystallinity.

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