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Electron beam induced crosslinking of nylon 6 with and without the presence of TAC

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Abstract

The influence of electron beam irradiation on neat nylon 6 was manifested by formation of molecular branches deduced from increase in melt flow index and intrinsic viscosity. Crosslinking of nylon 6 was carried out using electron beam irradiation in presence of triallyl cyanurate (TAC). The crosslinked samples showed a high level of gel content. At a given dose, increasing the TAC level from 1% to 3% increased the gel content of the samples slightly and correspondingly decreased the percent of water absorption. The melting temperature decreased with increasing the dose and the TAC level. All samples containing TAC showed some decrease in crystallinity under exposure to electron beam. The crosslinked nylon 6 samples showed higher thermal stability as it was verified by its heat deflection temperature. Elongation at break decreased while the tensile strength and yield stress increased as a function of TAC level and absorbed dose.

Keywords: Nylon 6; Triallyl cyanurate; Electron beam; Crosslinking; Heat deflection temperature

1. Introduction

Nylons are the most widely used engineering thermoplastic. They are tough, strong and abrasion resistant. Nylons as aliphatic polyamides have the highest softening points amongst aliphatic polymers owing to their high melting points, which are generally above 200 °C. These high values arise from the complete hydrogen bonding of the amide groups in the crystalline regions. However, even the highest melting polymer, nylon 6.6 ($T_m = 264$ °C) has a maximum continuous-use temperature of only about 120 °C even when filled with glass-fibers [1]. This shortcoming may be overcome by crosslinking nylon under high-energy electrons. The overall effect of crosslinking is that the molecular weight of the polymer steadily increases with dose, leading to branched chains, until ultimately a tridimensional network is formed when on the average each polymer chain is linked to another chain. The resulting structure corresponds to that of a polymer, which no longer melts above its normal melting temperature and does not dissolve in its usual solvents completely [2].

Aspects of polyamide radiolysis have been studied by a number of researchers since Charlesby who first reported crosslinking of nylon 6.6 [3]. In an investigation carried out by Valentine in order to determine the solvent–polymer interaction parameter, he used irradiated nylon 6.6 and found that it had been crosslinked under reactor radiation [4]. Deeley et al. [5], from a study of irradiated nylon 6.6 concluded that the degree of crosslinking is not proportional with radiation dose, suggesting main-chain scission also plays an important role in the reaction. Majury and Pinner [6] investigated the irradiation of polycaprolactam with both gamma

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rays and 2 MeV electrons. The gel fraction of polymer was measured as a function of radiation dose. The critical gel dose was found to be 350 kGy. These investigators also reported that the radiation behavior of polycaprolactam was similar at different temperatures whether the irradiation was carried out at −80 °C, at room temperature, or at 100 °C [6]. Pinner has studied the effect of ionizing radiation on gel formation in nylon and derived a value of 0.35 for $G(x)$ (number of polymer crosslink sites per 100 eV absorbed dose) at irradiation doses above 300 kGy [6]. Lyons and Glover studied the dependence of radiation crosslinking and chain scissioning on the molecular structure of the repeat unit in certain polyamides [7,8]. Also the radiation effects on nylon 10.10 have been investigated in recent years [9–12]. To our best knowledge no investigation has been reported so far regarding the effects of high-energy electron beam (5 MeV) on nylon 6 compounded with TAC.

In the present work, the effect of 5 MeV electrons on the crosslinking of pure polyamide 6 and compounded with triallyl cyanurate (TAC) has been investigated. The effects of absorbed dose and the level of TAC weight percent on mechanical properties, density, crystallinity and thermal stability of the irradiated nylon samples have been also examined.

2. Experimental

2.1. Materials

The material used in this project was nylon 6 of density 1.1262 g/cm^3, melt flow index 13.87 g/10 min and melting point 221.85 °C produced by Parsylon Company, Khoramabad, Iran. Merck triallyle cyanurate (TAC) was used as a crosslinking agent.

2.2. Sample preparation

Nylon 6 granules were dried in an oven for 24 h at 80 °C and then blended with a mixture of nylon 6 powder and TAC. The compound then was injection molded into the dumbbell shape samples.

2.3. Irradiation

Irradiation of the nylon samples was carried out in the Yazd Radiation Processing Center using Rhodotron TT200 electron accelerator with energy of 5 MeV under various irradiation doses ranging from 40 kGy to 150 kGy.

2.4. Melt flow index

Melt flow index (MFI) of the samples was determined according to ASTM D1238 using a Zwick 4100 made of Germany. The MFI of nylon 6 samples were measured in gram per 10 min when the tests run at the temperature of 235 °C under the load of 1 kg.

2.5. Gel content

The gel content of the electron beam treated samples was determined using solvent extraction method according to ASTM D2765 method. The samples were refluxed with *m*-cresol at 70 °C for 20 h.

2.6. Viscosity measurement

Viscosity of the dilute solutions of nylon 6 in formic acid was measured using Ubbelohde viscometer. Intrinsic viscosity was determined using dual Huggins–Kraemer plot.

2.7. Differential scanning calorimetry

Thermal analysis was carried out on a Shimadzu DSC-50 differential scanning calorimeter. The test was performed under nitrogen environment and the heating rate of 20 °C/min between 20 °C and 400 °C. The melting temperature and heat of fusion of the samples were determined from the DSC thermograms. The degree of crystallinity, X_c, was calculated as:

$$X_c = \Delta H / \Delta H_m^\circ$$

where ΔH is the heat of fusion and ΔH_m° is the heat of fusion of 100% crystalline nylon 6 equal to 188.1 J/g [13].

2.8. Thermal gravimetric analysis

Thermal Gravimetric Analysis was performed on a Shimadzu DTG 50/50H thermal analysis system between room temperature and 630 °C under air and heating rate of 10 °C/min.

2.9. Heat deflection temperature (HDT)

Heat deflection temperature of nylon 6 samples was determined according to ASTM D648-95 on a Ceast model 6505 HDT/VCAT instrument under a load of 66 psi (0.489 MPa) and heating rate of 50 °C/h. This test method determines the temperature at which a test bar, loaded to the specified bending stress, deflects by 0.25 mm.

2.10. Mechanical properties

The stress–strain properties were determined according to ASTM D638 on an Instron model 4411 testing machine. The test procedure was carried out at a