EFFECT OF ELECTRON-BEAM IRRADIATION ON NYLON-6/DIAMOND COATED CNTS COMPOSITE FIBER

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ABSTRACT

Polyamides (Nylon-6) are engineering plastic with excellent properties which are useful in several industrial applications and are valued for their high strength and processability. The addition of filler such as diamond coated Carbon Nano Tubes (CNTs) to form molded composites has increased the range of polyamide applications due to the resulting increase in strength. The effects of electron-beam irradiation on these thermoplastic nanocomposites are either increases the cross-linking or causes chain scission. In this study, DN-coated CNTs were synthesized using sonochemical technique in the presence of cationic surfactant CTAB. These hybrid nanoparticles were characterized using TEM analysis. The nanoparticles were then introduced into Nylon-6 polymer through a melt extrusion process to form nanocomposite fibers that were tested for their mechanical & thermal properties (e.g. tensile and Differential Scanning Calorimetry). These composites were further exposed to the electron-beam (160 KGy, 132 KGy and 99 KGy) using a 1.5 MeV electron beam accelerator, at room temperature, in presence of air and tested for their thermal and mechanical properties. The ultimate tensile strength were found to be 521 MPa, 690 MPa and 425 MPa for radiated (99 KGy,132 KGy and 160 KGy) DN/CNTs/Nylon-6 single fibers as compared to 346 MPa for DN/CNTs/Nylon-6 single fibers without irradiation and 240 MPa for neat Nylon-6 single fibers respectively. Differential Scanning Calorimetry (DSC) analysis results were showed that degree of cure was increased because of cross-linking which was expected at high electron-beam radiation dose.

1. INTRODUCTION

Different types of fillers are used in polymeric materials to widen its application for various engineering purposes. Nylon-6 is one of the most important crystalline engineering thermoplastics. The amide groups in its chain structure are separated by alkane sequences in regular arrangements[1]. Carbon based filler materials such as CNTs, Diamond nanoparticles or diamond coated CNT are added to the Nylon-6 to produce the more rigid structure to increase its tensile strength and modulus[2]. These increased mechanical properties are assigned to the exceptional hardness of diamond and the superior tensile strength of CNTs [3]. To increase the mechanical properties further we study the effect of electron beam irradiation on these polymer nanocomposites fibers.

Nylon-6 is a wide used polymer in the field of engineering application. The presence of nanomaterials as fillers in highly cross-linked polymers can increase its scope of applications such as wear-resistant coatings, integrated circuits (ICs), multifunctional polymer fabrics, and

composites, where it requires a combination of good mechanical, thermal and electrical properties.

It is well known that the liner polyethylene properties could be improved by structural modification such as radiation-induced cross-linking; chemical-induced cross-linking and silane compound induced cross-linking [4]. Nylons are slightly different from linear polyethylene because of –CONH-groups in its chain. Apart from this amide group in nylons have similar structure like linear polyethylene. Using high-energy radiation to increase the cross-linking is innovative process and short time consuming technique than the chemical induced and silane compound induced crosslinking process. Using high-energy radiation from an atomic pile Nylon 6, 6 was cross-linked [5].For cross-linking of nylon 6, 6 Lawton et. al. irradiated it by high-energy electrons [6]. Subsequent studies on irradiation of Nylon 6, 6 showed that the primary effect was cross-linking accompanied by considerable degradation and loss of crystallinity [7-9]. Bernstein et. al., shown that efficient cross-linking of Nylon 6,6 could be attained upon straight radiation [10].

Ionizing radiation treatment of nano-filled polymer based nano-composites [11-14] are limited in the literature. Dintcheva et al. reported a study on molecular modification and mechanical properties of polyethylene (LDPE) and polyethylene/commercial organo-modified montmorillonite (LDPE/OMMT) nanocomposite upon electron-beam radiation[11]. Lu et al. studied the mechanical and morphological variations of the HDPE/EVA blend with and without nano-clays upon γ-irradiation[12]. Gad also studied the thermal and mechanical properties of electron-beam irradiated poly(ethylene-co-vinyl acetate) (EVA)/clay composites[13]. Jiau et. al. also studied the thermal and fire retardant properties of γ-irradiated ethylene vinyl acetate copolymer (EVA) composites using Mg-Al-CO_3 hydrotalcite (MALDH) and microcapsulated red phosphorus (MRP)[14]. However, there are some studies on cross-linking behavior of Nylon-6 and Polyethylene but the effect of γ-irradiation on DN-coated CNTs/Nylon-6 nanocomposites are not found in literature.

In this study, DN-coated CNTs were synthesized using the sonochemical technique in the presence of cationic surfactant CTAB. These DN-coated CNTs were then infused into Nylon-6 polymer fiber [2]. These DN-coated CNTs/Nylon-6 and diamond/Nylon-6 nanocomposites fibers were exposed to electron beam radiation using 1.5 Mev electron beam. Differential Scanning Calorimetry studies were carried out to understand the cross-linking of DN-coated CNTs/Nylon-6 nanocomposites after radiation and compare it with the without radiation sample. These fibers were also tested for their tensile response.

2. EXPERIMENTATION

2.1 Materials

In this study, multiwalled carbon nanotube (CNTs) was used with a density 0.04-0.05 g/cm3, 10-20 nm in diameter and ~15 μm in length (purchased from Nanostructured & Amorphous Materials). Diamond (DN) coated CNTs, diamond was used with a size of 2-20 nm (provided by the Lavrentiev Institute of Hydrodynamics). Nylon 6, commercial grade UBE Nylon P1011F, (Procured from UBE America, Inc), a density of 1.09-1.19 g/cm^3, and melting point is around 115-250 °C was used.

2.2 Synthesis of DN Coated CNTs

Diamond nanoparticles were cleaned in a solution of $HClO_4$ and H_2SO_4 acids and washed with HCl acid and distilled water [15]. The DN coated CNTs were synthesized as described below and schematically represented in Figure 1.

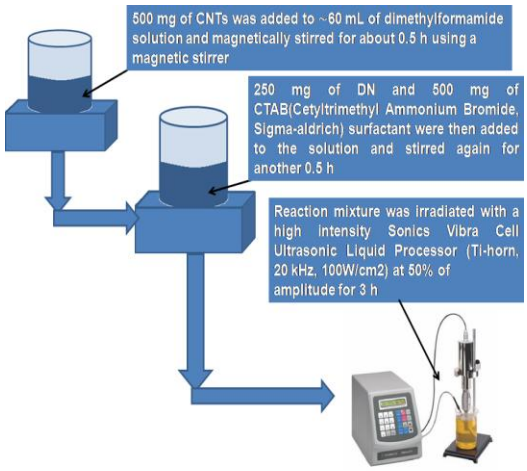

Figure 1. Schematic view of synthesizing process of Diamond coated with the CNTs

A 500 mg of CNTs were dispersed in 60 mL of dimethyl formamide using a magnetic stirrer for 0.5h to form a uniform CNTs deagglomerated solution. 250 milligrams of DN and 500 mg of CTAB (Cetyltrimethyl AmmoniumBromide, Sigma-aldrich) surfactant were then added to the solution and stirred for another 0.5h to obtain a uniform dispersed solution. This reaction mixture was then sonicated with a high intensity Sonics Vibra Cell Ultrasonic Liquid Processor (Ti-horn, 20 kHz, 100W/cm^2) at 50% of amplitude for 3 h. To avoid a temperature increase during the sonication process, external cooling was employed by circulating cooled liquid (kept at 10 °C by a thermostat control) through a jacketed reaction vessel for the entire period of reaction time. The reaction product was later washed with ethanol and centrifuged at 12000 rpm at 12 °C for about 10 min to separate the nanoparticles from the solution. The procedure was repeated 4-5 times to remove the excess surfactant. The precipitate was then dried under a vacuum at room temperature for overnight.

2.3 Fabrication Process

1wt% of DN-CNTs nanoparticles were measured carefully and then mixed with Nylon-6 powder using the dual centrifugal Thinkymachine at 2000 rpm for about 10min. This procedure was repeated for 5-6 times to achieve a uniform mixture. The dry powder mixture of nanoparticles and Nylon-6 polymer were dry mixed using a hot air dryer for another 24 h, and extruded directly without exposing to the air using a Wayne yellow label table top extuder. The extruder has a 19 mm diameter screw, which is driven by a 2HP motor. This fabrication process is schematically shown in the Figure 2.

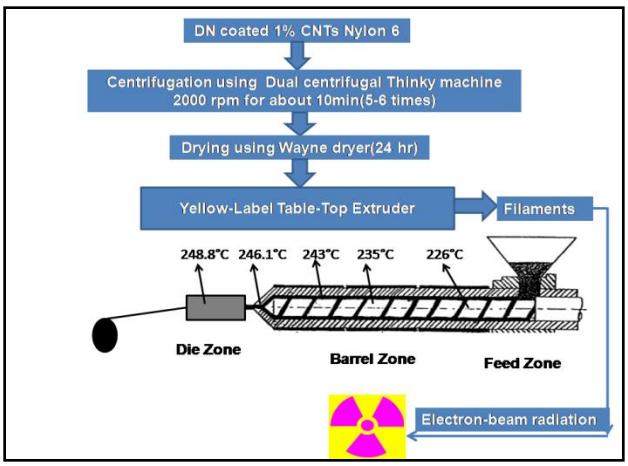

Figure 2. Schematic view of fabrication process using Wayne yellow label table top extruder

In this extruder five heating zones were used to melt the mixture before extrusion of single fiber, three inside the barrel and two in the die zone at set temperatures of 226, 235, 243, 246, and 248 °C, respectively. After extruding DN-Coated CNTs/Nylon-6 nanocomposite filament was exposed to the various dosages of electron-beam radiation.

2.4 Electron-Beam Irradiation

The DN-Coated CNTs/Nylon-6 nanocomposite filament and neat Nylon-6 were irradiated with electron beam radiation at Instituto de Pesquisas Energeticas e Nucleares-IPEN, São Paulo, Brazil, using a 1.5 MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.499 MeV energy, 5.62 mA current and 37.5 kW power), at room temperature, in the air, dose rate 22.42 kGy/s and radiation dose of 99 kGy, 132 kGy and 160 kGy. Irradiation doses were measured using cellulose triacetate film dosimeters ‘‘CTA-FTR-125’’ from Fuji Photo Film Co. Ltd. Mechanical and thermal properties of all irradiated DN coated CNTs/Nylon 6 nanocomposites were evaluated and compared with un-irradiated material.

2.5 Characterization

X-ray Diffraction analysis was used to confirm the presence of DN in the DN-coated CNTs and these results were presented in our previous studies [2]. In this study, thermal analysis (Differential Scanning Calorimetry, DSC) and tensile response was carried out to confirm the effect of radiation on the cross-linking and the mechanical properties.

2.5.1 Differential Scanning Calorimetry Analysis

DSC analysis was carried out for neat and DN coated CNTs/ Nylon6 fiber with irradiation and and without irradiation. In a typical experiment ~10-15 mg sample was placed in a small aluminium pan, which was subsequently covered with a lid and tightly crimped around the edge. It was then transferred into the METTLER Toledo DSC cell and heated from 25°C to 300°C at 10°C per min and also collected the cooling data from 300° C to 25° C at 10°C per min.

2.5.2 Tensile Analysis

Tensile tests of single-fiber specimens of the Nylon-6 composites infused with 1 wt % DN-coated CNTs were carried out before and after irradiation to estimate the increase in mechanical properties, such as tensile strength and modulus, due to cross-linking. The tests were performed using a Zwick/Roell single filament testing equipment according to the ASTM standard D 3379 75 **[16]**.

3.RESULTS

3.1 Differential Scanning Calorimetry Analysis

Differential Scanning Calorimetry was carried out to study the cross-linking behavior of 1% DN coated CNTs/Nylon-6 nanocomposites before and after different doses of electron-beam irradiation *i.e.* 99KGy, 132KGy and 160 KGy. Neat Nylon-6 also exposed to the same radiation doses to understand the cross-linking without filler content. In figure 3., DSC analysis for 1% DN coated CNTs/Nylon-6 is shown with different radiation doses. These results are also summarized in table 1.

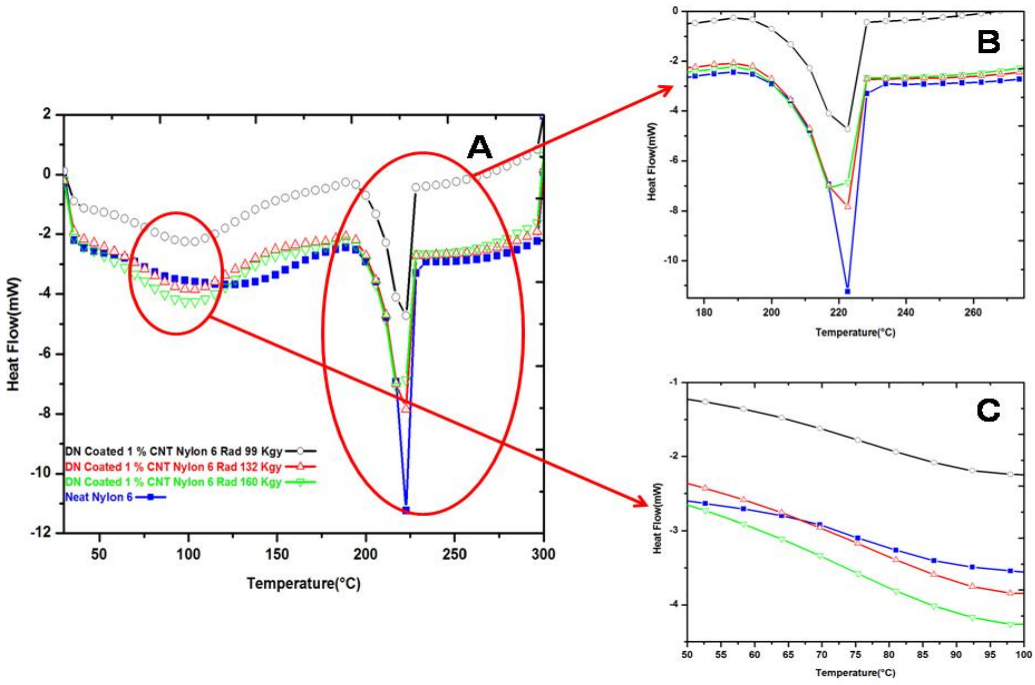

Figure 3. DSC analysis of DN-coated CNTs/Nylon-6 composite A) Heating curve for different radiation , B) Magnifying view of melting point zone and C) Magnifying view of Tg zone

From figure 3, it is clear that the endothermic melting enthalpy decreased for DN-coated CNTs/Nylon-6 composite compared with neat Nylon-6 at 99KGy. This indicates the increase in

cross-linking of the polymer. **The T_g also increase in case of 99 KGy and 132 KGy doses. Whereas the160 KGy dose the melting enthalpy also decreased, this may be due to the start of chain scission because at that stage Tg was decreased at high doses of radiation and further studies in this direction are under progress.**

Table 1. DSC analysis of DN Coated 1 % CNTs/Nylon 6

Filaments	Melting point (ºC)	Glass Transition Temperature (ºC)
Neat Nylon 6	222	78
DN Coated 1 % CNTs Nylon 6 (99 KGy)	222	81
DN Coated 1 % CNTs Nylon 6 (132KGy)	222	82
DN Coated 1 % CNTs Nylon 6 (160KGy)	219	74

A summary of DSC analysis of neat Nylon-6 with and without radiation is shown in figure 4. In

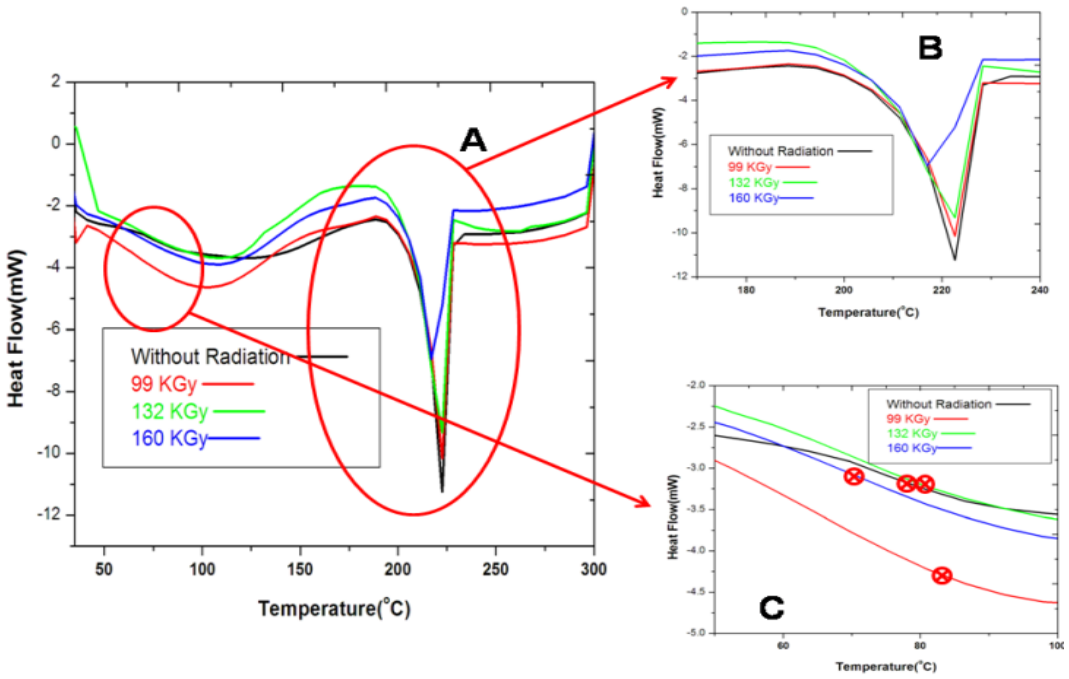

Figure 4. DSC analysis of neat Nylon-6 with and without irradiation A) Heating curve for different radiation dose ,B) Magnifying Melting zone and C) Magnifying Tg zone

this case the melting enthalpy also decreases with the radiation which indicates the cross-linking of the neat Nylon-6 while exposed to electron beam radiation. Table 2 represents the thermal

behavior results obtained for different radiation doses of neat nylon-6. At very high doses of electron beam radiation *i.e.* 160KGy the melting and glass transition temperature decreased.

Table 2. DSC analysis of neat Nylon 6

Filaments	Melting point (°C)	Glass Transition Temperature (°C)
Without Radiation	222	78
99 KGy	222	80
132KGy	222	81
160KGy	217	70

3.2 Tensile Response

The tensile response of both DN coated 1% CNTs/Nylon-6 nanocomposite and neat Nylon-6 with different dosage of radiation is shown in figure 5. From figure 5 it can be inferred that tensile strength and modulus increase significantly after irradiation with respect to un-irradiated sample. Table 3 presents the tensile response obtained for with and without radiation. For 132 KGy irradiation dose, it shows highest improvement in mechanical properties (*i.e.* tensile strength 253 MPa and 690 MPa and tensile modulus 3.47 GPa and 26.54 GPa) both neat and DN coated 1% CNTs/Nylon-6 nanocomposite sample. This improvement indicates the increased cross-linking of the Nylon-6 composite after irradiation.

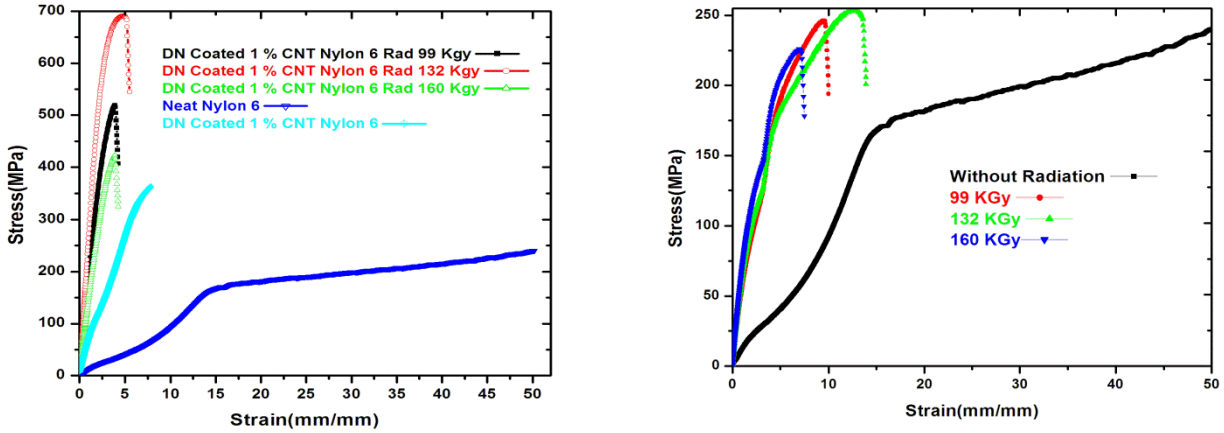

Figure 5. Tensile Response of A) DN-Coated 1% CNTs/Nylon-6 composite with and without irradiation B) Neat Nylon-6 with and without irradiation

But after a certain level of irradiation the chain scission occurs at 160KGy dose and the properties decreased. The further studies are under progress to understand the irradiation dose and time of exposure.

Table 3. Tensile response of neat and DN coated 1% CNTs/Nylon-6 nanocomposite

Filaments		Ultimate Tensile Strength (MPa)	Modulus (GPa)
Neat Nylon 6	Without irradiation	240	0.84
	99KGy	246	3.52
	132 KGy	253	3.47
	160 KGy	225	3.13
DN Coated 1 % CNTs Nylon 6	Without irradiation	346	6.7
	99 KGy	521	19.75
	132KGy	690	26.54
	160KGy	425	14.68

4. CONCLUSIONS

The DSC results suggest that the 132KGy electron beam dose is required to increase the glass transition temperature (T_g) of Nylon 6 polymer and higher than 132KGy dose decreases the T_g and starts scission of polymer chains. The melting enthalpy of irradiated DN coated 1% CNTs /nylon 6 and irradiated neat nylon-6 decreased compared to neat nylon 6. The highest ultimate tensile strength was found 690 MPa and 253 MPa respectively both for DN coated 1% CNTs/Nylon-6 nanocomposite and neat nylon-6 for radiated dose of 132 KGy which was higher than the radiated dose 99 KGy (*i.e.* 521 MPa, 246 MPa) & 160 KGy (*i.e.* 425 MPa, 225 MPa), whereas at higher doses of electron-beam radiation (*i.e.*160 KGy), the ultimate tensile strength decreased due to chain scission. Tensile modulus also increased with irradiation doses at a certain level. In both the cases 132 KGy showed higher tensile modulus which is consistent with the other results. **Though irradiated DN coated 1% CNTs/Nylon-6 nanocomposite filaments are expensive compare with the neat Nylon-6 filament but it had increased its mechanical properties significantly for advanced engineering applications which were mentioned earlier**.

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