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## Effects of electron beam irradiation on thermal and mechanical properties of nylon 6, nylon 66 and nylon 1212

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### ABSTRACT

Effects of electron beam (EB)-irradiation at different doses up to 600kGy on nylon 6 (PA6), nylon 66 (PA66) and nylon 1212 (PA1212) films have been investigated by FTIR, TGA, DSC and UTM. From FTIR spectra analysis, it was found that crystallinity of PA6, PA66 and PA1212 was considerably affected upon EB irradiation. As expected both DSC melting and crystallization temperature along with percent crystallinity of PA6, PA66 and PA1212 were decreased with the EB-irradiation dose. Tensile strength of all nylon samples was significantly increased at low EB irradiation dose whereas elongation at break of sample films was decrease continuously with increasing irradiation dose. However, EB-irradiated PA6, PA66 and PA1212 exhibited somewhat improved thermal stability compared with their parent nylons. © 2016 Trade Science Inc. - INDIA

#### INTRODUCTION

Polyamides are one of the most commonly used polymers. They were the first engineering thermoplastics produced specifically by design as a plastic and are the largest family in both production volume and number of applications. Due to their very high strength and durability polyamides are commonly used in textiles, carpets and floor coverings or automotive<sup>[1, 2]</sup>.

Nylon is a generic name referring to a series of aliphatic polyamides. These polymers contain the recurring amide group, -CONH-. The usual method for describing a particular type of nylon is by at-

#### taching a number designation to the word nylon that represents the number of carbons in the repeating units of the raw stock. For example, nylon 6 (PA6) made of [-caprolactam that contains six carbon atoms. PA6 is the most common polyamide and offers a balanced combination of all typical characteristics of this group of materials. PA6 are characterized by their possessing of high tensile strength, elasticity, tenacity and resistance to abrasion. These mechanical properties are maintained even under high temperatures and therefore, the polyamides can be used in temperatures up to 200°C in applications of short-term<sup>[3]</sup>. Nylon 66 (PA66) is synthesized by condensation polymerization of

KEYWORDS

Nylon, Irradiation; Crystallization; Melting; Electron beam; Mechanical property; Cross-link.

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hexamethylenediamine and adipic acid. It is crystalline, and the crystals melt at a high temperature. This makes it a good candidate for applications where properties such as high strength, excellent chemical and abrasion resistance, and toughness are sought<sup>[2]</sup>. In spite of its superior properties, they are very sensitive to moisture absorption<sup>[1]</sup>. Indeed, moisture content must be controlled during melt processing of them. Nylon 1212 (PA1212) is a semicrystalline thermoplastic material which is polymerized from 1,12-dodecanedioic acid and dodecamethylenediamine with excellent dimensional stability, good chemical stability and low temperature stability<sup>[4]</sup>. PA1212 is also a good electrical insulator and as other polyamide insulating properties will not be affected due to moisture. In comparison with PA6 and PA66, PA1212 has lower melting point and density, with very high moisture regain.

The effects of high-energy irradiation on polymers can lead to changes in their properties, and their interaction with high-energy electrons is a complex and random process<sup>[5]</sup>. The changes resulting from irradiation are mainly a consequence of electron absorption followed by bond cleavage to give radicals, radical recombination leading to the formation of crosslinks and end-links or disproportionation to give chain scission and gas evolution, mainly by radical recombination<sup>[6, 7]</sup>. The final result depends on the nature of the material, on the dosage, dosage rate and the energy of the radiation. Thus, there are many ways to exploit these processes technologically, such as crosslinking<sup>[8-11]</sup> and surface modification<sup>[12-14]</sup>.

Through radiation crosslinking, thermoplastic polyamides are turned into plastics which behave like elastomers over a wide temperature range. Crosslinking makes the originally thermoplastic product able to withstand considerably higher temperatures of up to 350°C. The dimensional stability under thermal stress is also improved<sup>[15]</sup>. The aim of this paper is to study the effect of electron beam (EB) radiation with different doses, on microstructures, thermal and mechanical properties of PA6, PA66 and PA1212 and compare these results with those of un-irradiated samples.

#### EXPERIMENTAL

#### Materials

PA6 (1022-HSM, Solvay Chemicals Korea Co., Ltd., Korea) and PA1212 (PA1212BR-3, Shandong Dongchen Engineering Plastic Co., Ltd., China) were used as received. PA66 granules (Zytel 103HSL, DuPont, USA) were used as received. This is a lubricated and heat stabilized PA66 resin for extrusion. The nylon resins were pre-dried in a convection oven for at least 12h at 100°C to remove any moisture from the pellets before processing.

#### **EB-irradiation of hot-pressed film**

EB-irradiation of hot-pressed films was carried out using an EB accelerator (ELV 4, EB tech Co., Ltd., Daejeon, Korea). The samples were placed on a tray on a conveyer and irradiated in air at room temperature. The conveyer speed was kept constant at 1 m/min. The applied irradiation dose was varied from 100 to 600 kGy by increasing the number of passes. The doses were verified using Cellulose Triacetate (CTA) dosimeter film based on ISO/ ASTM51650<sup>[16]</sup>.

#### Characterization

The Fourier transform infrared (FTIR) spectra of the EB-irradiated samples were measured with a Thermo Scientific Nicolet 6700 FTIR spectrometer (Waltham, MA, USA) in attenuated total reflection (ATR) mode. The spectra were measured in the wavenumber range from 4000 to 400 cm<sup>-1</sup> and analyzed using commercial software.

Thermal properties of the specimen were determined by differential scanning calorimetry (DSC) (Perkin Elmer DSC 7, Norwalk, CT, USA). Thermal history of the samples was removed by scanning from 30°C to 300°C (PA6: 275°C, PA66: 300°C and PA1212: 250°C) with the heating rate of 20°C/ min. After cooling down the specimen at the rate of -10°C/min to 30°C, it was reheated at 30°C to 300°C (PA6: 275°C, PA66: 300°C and PA1212: 250°C) with the heating rate of 20°C/min and the DSC curves were obtained. The heat of melting and the heat of crystallization were calculated from the areas under the melting and cooling peaks, respectively. The per-

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cent crystallinity ( $\chi_c$ ) was calculated by integrating the second-scan DSC melting curves for obtaining the sample heat of melting ( $\Delta H_m$ ) and dividing by the heat of melting of 100% crystalline ( $\Delta H_{m100}$ ) PA6, PA66 and PA1212, taken as 241 J/g<sup>[17]</sup>, 197J/g<sup>[18]</sup> and 279.2J/g<sup>[19]</sup>, respectively.

Thermal stability of samples was determined by on a thermogravimetric analyser TGA7 (Perkin Elmer, Norwalk, CT, USA). The thermogravimetric analysis (TGA) curves were obtained under a nitrogen ( $N_2$ ) atmosphere at a flow rate of 4 ml/min and a scanning from 20°C to 800°C with the heating rate of 20°C/min.

The tensile properties of samples were determined with a universal test machine (DEC-A500TC, Dawha Test Machine, Buchun, Korea) at a cross head speed of 500 mm/min. Dumbbell specimens for tensile tests were prepared in accordance with the IEC 60811-1-1 specification. The mean value of at least five specimens of each sample was taken, although specimens that broke in an unusual manner were disregarded.

#### **RESULTS AND DISCUSSION**

#### FTIR study of nylon samples after EB-irradiation

Figure 1 shows FTIR spectra of pristine and EBirradiated nylon film samples. The infrared spectra of EB-irradiated samples were identical with the pristine samples, no new bands were observed. Comparison of the major frequency bands of sample films with the reference PA66<sup>[20]</sup> confirm that the unirradiated films are those for PA6, PA66 and PA1212 with band shifts not exceeding  $\pm$  5cm<sup>-1</sup>. This is characterized by the major band: the amide bands at 1640 and 1540 cm<sup>-1</sup> and N-H, CH<sub>2</sub> (asymmetric stretching) and CH<sub>2</sub> (symmetric stretching) at 3300, 2930 and 2860cm<sup>-1</sup> respectively. The CH<sub>2</sub> asymmetric and symmetric stretching appear as strong broad bands in the 2800–3000 cm<sup>-1</sup> region. The bands at ~1540cm<sup>-1</sup>, ~1640cm<sup>-1</sup> and ~3300cm<sup>-1</sup> are of special interest because they are related to hydrogen bonding<sup>[21]</sup>. The relative changes in absorbance intensity taking place in some characteristic band during irradiation, are summarized in TABLE 1.

In case of PA66, when the irradiation dose increased from 0 to 600kGy, there was a sharp decrease in peak intensity at ~ 3300cm<sup>-1</sup> from 0.287 to 0.143. This is due to loss of N-H stretching absorbance which arises due to loss of hydrogen bonding after EB-irradiation. But at higher EB-irradiation dose, the decrease in intensity at ~3300cm<sup>-1</sup> is less which is due to the decrease in number of N-H bonds. The intensity of peak at ~934cm<sup>-1</sup> and ~1200cm<sup>-1</sup> which are assigned for the crystalline phase of PA66 was also found to decrease with increasing irradiation dose. EB dosage increase from 0 to 600 kGy, the peak intensity at ~934cm<sup>-1</sup> was decreased from 0.128 to 0.073 and at ~ 1200 cm<sup>-1</sup> the peak intensity value decreases from 0.257 to 0.137. This indicates that the crystalline phase of PA66 has been changed significantly by EB-irradiation. In sharp contrast, the decrease in peak intensity at ~3300, ~1200 and ~934cm<sup>-1</sup> of PA6 and PA1212 is less than those of PA66. The intensity difference near ~930cm<sup>-1</sup> of the un-irradiated and 600kGy-irradiated sample was 0.004 for PA6, 0.055 for PA66 and 0.01 for PA1212. Similarly, the intensity difference at ~1200cm<sup>-1</sup> (1240cm<sup>-1</sup> for PA1212) of the un-irradiated and

 TABLE 1 : Change in relative FTIR absorbance of nylon samples at different band position before and after EB-irradiation

	Relative intensity (cm <sup>-1</sup> )								
Radiation dose (kGy)	PA6			PA66			PA1212		
	3300	1200	930	3300	1200	934	3304	1240	940
0	0.124	0.159	0.050	0.287	0.257	0.128	0.123	0.104	0.046
100	0.121	0.158	0.048	0.216	0.203	0.103	0.112	0.102	0.046
200	0.118	0.147	0.047	0.149	0.142	0.086	0.111	0.097	0.042
400	0.115	0.137	0.046	0.144	0.138	0.074	0.093	0.094	0.037
600	0.114	0.136	0.046	0.143	0.137	0.073	0.092	0.093	0.036
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Figure 1 : FTIR spectra of pristine and EB-irradiated nylon film samples

Research & Reviews On Polymer 600kGy-irradiated sample was 0.023 for PA6, 0.120 for PA66 and 0.011 for PA1212. These results indicated that the crystal structure of PA6 and PA1212 does not significantly affect the up to 600kGy irradiation dose comparing with PA66. The chain scission phenomenon which predominantly occurred in crystalline phase produced crystal defect and reduced the crystallite size upon EB-irradiation<sup>[22]</sup>. Decrease in crystallinity of PA66 upon EB-irradiation has been reported by several workers<sup>[23]</sup>. Pramanik et al. reported that PA66 when irradiated by EB radiation at 600kGy shows a decrease in  $\chi_c$  from 40.8 to 20.4%<sup>[20]</sup>.

# Thermal properties of EB irradiated nylon samples

To evaluate how the thermal properties of the PA6, PA66 and PA1212 are affected by high-energy EB-irradiation, DSC was used to determine the  $T_m$ ,  $T_c$  and the  $\chi_c$  of both pristine and EB-irradiated ny-lon film samples. Figure 2 illustrates the first-scan and second-scan DSC thermograms of PA6, PA66 and PA1212 as a function of the EB-irradiation dose and the results of DSC thermal properties of samples are summarized in TABLE 2. The abbreviation of the sample code in TABLE 2, PA66-100kGy, for example, means that the PA66 film was EB-irradiated at 100kGy.

DSC heating curves on the EB-irradiated PA6 with different doses are shown in Figure 2a, together with that for the un-irradiated PA6 film. The firstscan DSC thermogram of un-irradiated PA6 film shows a single melting peak at 220.3°C. In contrast the second-scan DSC thermogram of un-irradiated PA6 exhibits multiple endotherms with a small shoulder at 192.5°C, and double peaks at 215.1 and 218.9°C in which the low-temperature peak corresponds to the y-form and high-temperature peak corresponds to the  $\alpha$ -form. The presence of broad melting endotherms, endotherms with shoulders, and double peak structures are usually interpreted as indicating different populations of lamellae thicknesses. Thus, the unusual small shoulder is observed at 192.5°C which is attributed to the thin lamellae formed during cooling. According to the literature<sup>[24]</sup>, the T<sub>m</sub> for the  $\gamma$  and  $\alpha$  form crystal of PA6 are ~215

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	DSC thermal properties								
Sampla anda	First-scan	Crystall	lization	Se	Second-scan				
Sample Code	T <sub>m1</sub>	Tc	-AHc	$T_{m2}$	$\Delta H_{m}$	Xc			
	(°C)	(°C)	( <b>J</b> /g)	(°C)	( <b>J</b> / <b>g</b> )	(%)			
PA6	220.1	187.1	57.6	218.1	60.0	24.9			
PA6-100KGy	218.5	186.0	56.0	217.2	57.8	24.0			
PA6-200KGy	217.6	183.9	55.8	216.6	56.6	23.5			
PA6-400KGy	215.2	181.7	52.8	213.7	53.3	22.1			
PA6-600KGy	213.8	178.2	51.2	211.5	53.3	22.1			
PA66	262.2	233.9	44.8	262.0	61.0	31.0			
PA 66-100KG y	261.1	232.2	43.9	260.8	55.8	28.3			
PA 66-200KG y	259.3	231.5	43.0	258.7	55.2	28.0			
PA 66-400KG y	257.2	229.0	42.6	255.9	50.3	25.5			
PA 66-600KG y	255.5	226.7	40.3	253.4	50.0	25.4			
PA1212	190.1	161.8	42.7	190.3	44.3	15.9			
PA1212-100KGy	188.8	159.6	42.5	188.4	44.2	15.8			
PA1212-200KGy	187.6	157.4	41.8	187.1	44.0	15.8			
PA1212-400KGy	184.8	153.8	41.0	183.9	43.9	15.7			
PA1212-600KGy	182.3	150.0	40.5	180.8	40.6	14.5			

TABLE 2 : DSC thermal properties of pristine and EB-irradiated nylon samples

and ~220 °C, respectively. The  $\alpha$  crystalline form is most commonly observed at room temperature and can be obtained slowly cooling from the melt state<sup>[25, <sup>26]</sup>. The crystal structure of  $\alpha$  crystalline phase is monoclinic, and consists of anti-parallel extended zigzag chains. While the  $\gamma$  crystalline form is less stable with the hydrogen-bonding forming between parallel chains and almost perpendicular to the carbon plane. The  $\gamma$ -crystals of PA6 can be obtained by fiber spinning at high speed or through fast quenching from the melts. The  $\gamma$  crystalline phase can be converted to the  $\alpha$ -phase by phenol treatment<sup>[27]</sup> or by stretching<sup>[28]</sup>.</sup>

As the EB-irradiation dose is increased, the  $\alpha$ form melting peak is gradually diminished but the  $\gamma$ form melting shoulder almost remains. Finally the two melting peaks merge into one peak. Moreover, the melting peak shifts to lower temperatures and becomes broader. The decrease of  $\alpha$ -form melting peak with increasing dose of EB may be due to the growth of crystalline structure in the cross-linked mass of samples through EB-irradiation is not favorable. When the polymer chains are cross-linked the mobility is compromised, and the rate of lamellar thickening is reduced due to significantly inhibit the ability of the polymer molecules to crystallize from the melt. In addition, either EB or gamma rays, on the crystalline region of polymer is to cause some imperfection. It is noted that the first-scan DSC thermogram of PA6-400kGy and PA6-600kGy, a melting shoulder near 199°C is seen in addition to the main melting peak of the  $\alpha$ -form at 215.2 and 213.8°C respectively. The appearance of the shoulder peak in the first-scan DSC thermogram of PA6-400kGy and PA6-600kGy could be attributed to an unstable crystallized region. At the higher EB-irradiation dose, chain scission phenomenon which occurred in crystalline phase produced crystal defect and reduced the crystallite size upon EB-irradiation<sup>[22]</sup>.

DSC results of PA1212 are almost similar to those of PA6. With first-scan DSC heating curve of un-irradiated PA1212, only one endothermic peak was observed at 190.1°C (Figure 2c). The secondscan DSC thermogram of PA1212 exhibits with a small shoulder at 168.2°C, and double peaks at 182.1 and 190.3°C in which the lower-temperature peak assigned to  $\beta$ -phase crystals, and another peak reflecting the melting of  $\alpha$ -phase crystals. According to Jones et al.<sup>[29]</sup>, PA1212 exhibits both the  $\alpha_n$  and

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Figure 2 : First- and second-scan DSC thermo gram of pristine and EB-irradiated nylon film samples

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 $\beta_p$  structures in room temperature. Unit cell dimensions are as follows:  $\alpha_p$  structures: a=0.49 nm, b= 0.52 mm, c=3.23 nm,  $\alpha$ =50°,  $\beta$ =77°,  $\gamma$ =64°, and  $\beta_p$  structures: a=0.49 nm, b=0.802 nm, c=3.23 nm,  $\alpha$ =90°,  $\beta$ =77°,  $\gamma$ =67°. The Brill transition temperature of PA1212 is about 130°C when heated from room temperature to  $T_m^{[29]}$ . EB-irradiation results in an increase of the intensity of the low-temperature peak while that of the high-temperature peak decreases. With the increasing dose of EB-irradiation the peak intensity of high-temperature peak is significantly reduced and the peak position of high-temperature peak value of un-irradiated PA1212.

Further the small shoulder peak of second-scan DSC thermogram for PA6 and PA1212 almost did not change in the peak position or size with increasing EB-irradiation dose. This indicated that the shoulder peak does not relate to the chain scission reaction caused by EB-irradiation.

Figure 2b shows two melting peaks with different intensity for un-irradiated PA66 at 247.1 and 262.2°C when the sample is first-scanned at a heating rate of 20°C/min. Because no cold crystallization was observed during the heating run, it was assumed that melting of the PA66  $\alpha$ -phase gave rise to these two endotherms. The low-temperature peak



Scheme 1 : Schematic representation of mechanism of EB-irradiation induced reactions in nylon

was attributed to the melting of imperfect  $\alpha$ -crystals, which re-crystallized into more perfect  $\alpha$ -crystals; these last ones, by its turn, melted absorbing the high-temperature peak. As the EB-irradiation dose increases, the relative intensity of low-temperature peak increases, reflecting decrease in perfect  $\alpha$ -crystals, as expected, since EB-irradiation should facilitate development of crystal imperfections and reduction of the lamellar thickening rate.

In the most stable PA66 crystalline structure, the triclinic a-phase, crystallites are comprised of stacks of crystalline sheets<sup>[30, 31]</sup>. The sheets are formed by individual PA66 molecules hydrogen-bonded in alltrans conformations. Adjacent sheets are also regularly and cumulatively offset, tilting 42° relative the lamellar plane, resulting in a pleated crystallite. The second crystalline phase found in PA66, the  $\beta$ -phase, is also triclinic and characterized by sheets that shear alternately in the c-direction, resulting in a 13° offset from the lamellar normal. A third, non-equilibrium crystal phase is observed in PA66 at temperatures near the melting point. The  $\gamma$ -phase, or pseudohexagonal phase, begins to form when PA66 is heated through the Brill transition. For PA66, the Brill transition temperature occurs between 170°C and 220°C, well below the T<sub>m</sub>, which is in the range of 250°C to 272°C<sup>[31, 32]</sup>.

Regarding the melting of the samples, it was observed that the second-scan DSC thermogram of unirradiated PA66 also had two melting endotherms: one between 210 and 256°C and the other one between 256 and 268°C. The low-temperature peak was attributed to the melting of  $\beta$ -crystals and hightemperature peak was attributed to the melting of  $\alpha$ crystals. With the increasing dose of EB-irradiation the peak intensity of high-temperature peak is significantly reduced and the peak position of high-temperature peak indeed shifts to low-temperature peak value of un-irradiated PA66. That is, EB-irradiation of PA66 gave rise to the formation of imperfect  $\alpha$ -crystals which melted between 210 and 256°C.

Figure 3 shows the relationship between the EBirradiation dose and crystallization temperature ( $T_c$ ) of PA6, PA66 and PA1212. It can be seen that the un-irradiated PA6, PA66 and PA1212 had only a crystallization peak temperature at 187.1, 233.9 and



Figure 3 : Crystallization behaviors of the pristine and EB-irradiated nylon film samples



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161.8°C, respectively. With the EB-irradiation does, the  $T_c$  of all nylon samples shifted to a lower temperature, and the  $T_c$  range became broader.

The reduction of  $\chi_c$  of PA6, PA66 and PA1212 is evident from the plot of  $\chi_c$  versus dose of EB as shown in Figure 4. The  $\chi_c$  of un-irradiated PA66 was 31.0%, while the  $\chi_c$  of PA66-600kGy decreased to 25.4%. Un-irradiated PA66 undergoes a reduction of 18%  $\chi_c$  at 600kGy irradiation. On the other hand, the  $\chi_c$  of PA6-600kGy and PA1212-600kGy has decreased by 11.2% and 9.9% when compared with the values of un-irradiated PA6 and PA1212 respectively. These findings are in good agreement with the result of the FTIR peak reduction listed in



Figure 4 :  $\chi_c$  of the pristine and EB-irradiated nylon film samples





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TABLE 1.

The decrease in  $\chi_{\rm c}$  as a function of irradiation dose can be explained by chain cross-linking and scission mechanism. As shown in Scheme 1, in the process of EB-irradiating, two main reactions may occur in the nylons, especially in the polymer phase, that is, cross-linking and chain scission reactions, both of which take place at the same time<sup>[33-35]</sup>. When the samples were irradiated by intermediate doses in air, the EB-irradiation enhances the crosslinking degree of the polymer chains, which results in the decrease in the crystallinity. The crystallization is affected by the presence of cross-links which reduce chain mobility and reputation needed for lamellae to form. Consequently, crystallization of a crosslinked polymers results in a lower crystallinity in comparison of to the un-irradiated polymer. At the high irradiation dose, for example, 600 kGy. the oxidative degradation may occur, which may produce more shortened chains, enhance the crystal imperfections, and consequently lower the  $\chi_c^{[36]}$ . The increased irradiation dose causes the large raccumulation of reactive intermediates such like peroxyl radicals and hydroperoxides, which promote the chain process of degradation<sup>[37]</sup>.

The TGA is a useful technique to determine the quantitative degradation based on the weight loss of a polymer material as a function of temperature. Figure 5 shows the TGA thermogram resulting from the analysis of the PA6, PA66 and PA1212. The PA6 and PA66 show a small and very gradual weight loss between ambient and 300°C. This weight change is most likely due to the evolution of traces of moisture, volatiles or unreacted monomer. Above 300°C the PA6 and PA66 decompose in a single smooth step as shown by the symmetrical derivative profile with peak temperature of ~410 °C. This weight change corresponds to the decomposition of the base polymer to leave residual carbon char from the polymer back bone. This carbon char is quantified as 0.51% for PA6 and 1.79% for PA66 at 590°C where the weight profile is at a plateau under the N<sub>2</sub> atmosphere. Weight loss of nylons is associated with evolution of small molecules initially beginning with water and then low molecular weight oligomers and finally HCN. The thermal decomposition of nylons





has been shown to begin with a primary scission reaction of an -NHCO- bond followed by a complex series of secondary reactions<sup>[38]</sup>. Subsequent intermediate mechanisms of decomposition depend upon the specific structure of the nylon, but decomposition products do not differ greatly among the nylons studied. Vacuum decomposition of nylons, at 300~400°C, produced large quantities of CO<sub>2</sub> and  $H_2O$ . In some cases,  $NH_3$  was detected in significant amounts. At higher temperature several researchers have shown that HCN, NH<sub>3</sub> and NO<sub>2</sub> were produced during thermal degradation in both inert and air atmospheres<sup>[39]</sup>. The TGA curve of PA1212 also exhibit single-stage degradation with well defined initial and final degradation temperatures without gradual weight between ambient and 300°C. Because of the PA1212 has lower water absorption than PA6 and PA66. The decomposition of PA1212 occurs in the range of 400 - 511 °C and the char residue at 590°C was 0.3%.

TGA data relating to the temperatures corresponding to initial weight loss, such as  $T_0$  (temperature of onset decomposition),  $T_{10}$  (temperature for 10% weight loss),  $T_{20}$  (temperature for 20% weight loss),  $T_{50}$  (temperature for 50% weight loss) and  $T_{max}$  (temperature for maximum weight loss) are the main criteria to indicate the thermal stability of the poly-

mers. The relative thermal stability of PA6, PA66 and PA1212 has been evaluated by comparing the decomposition temperatures at different percentage weight loss (TABLE 3). The higher the values of  $T_{10}$ ,  $T_{20}$ ,  $T_{50}$  and  $T_{max}$  were the higher the thermal stability of the polymer material.

TGA measurements are also conducted on the EB-irradiated samples to elucidate their thermal degradation behaviors. Some typical weight-loss curves as a function of temperature are shown in Figure 6. The thermal stability of the PA66 is improved with the increase in irradiation doses from 0 to 400kGy, whereas an irradiation dose of 600kGy leads to an obvious decrease in thermal stability as evidenced by a completely reverse trend of the rage of degradation temperature (Figure 6b). For PA66-400kGy, the TGA traces show a maximum shift of the weight loss towards higher temperature with stabilization 20°C higher than un-irradiated PA66. At the irradiation dose of 600kGy, the weight loss shifted towards lower temperatures with 10°C than PA66-400kGy. The thermal stability decreased after 600kGy irradiation whereas the amount of nonvolatile residue at 590°C significantly increased. Similarly, it is also found from Figure 6c and TABLE 3 that the irradiation dose has almost similar effect on PA1212. The thermal stability increased slightly

Comunito ao dia	Temper	rature at differ	Char radiduo at 500°C (%)		
Sample code –	T <sub>10</sub>	T <sub>20</sub>	T <sub>50</sub>	T <sub>max</sub>	- Char residue at 590°C (%)
PA6	428	447	470	504	0.51
PA6-100kGy	435	453	476	506	0.67
PA6-200kGy	436	455	478	507	0.84
PA6-400kGy	435	455	477	505	1.18
PA6-600kGy	435	455	476	504	7.25
PA66	425	437	451	493	1.79
PA66-100kGy	429	440	457	494	1.90
PA66-200kGy	430	443	462	501	1.95
PA66-400kGy	431	449	470	514	3.32
PA66-600kGy	433	445	461	503	2.62
PA1212	449	462	478	506	0.30
PA1212-100kGy	449	462	482	510	0.30
PA1212-200kGy	455	468	484	512	0.28
PA1212-400kGy	449	465	483	509	0.41
PA1212-600kGy	449	463	480	508	0.25

TABLE 3 : Thermal data obtained from TGA thermograms of PA6, PA66 and PA1212



Figure 6 : TGA thermograms of EB-irradiated PA6, PA66 and PA1212

Research & Reviews On Polymer with increasing EB-irradiation dose up to 200kGy, thereafter decreased with further increase in dose (Figure 6c). In sharp contrast, PA6 shows quite different behavior as shown in Figure 6a. When irradiated at 100kGy, the weight loss is shifted toward about 5°C higher temperatures in comparison with that of pristine PA6 and thereafter almost maintained regardless of irradiation doses. These results are explained by the higher radiation stability of PA6 in comparison with PA66 and PA1212.

## Mechanical and thermal properties change after EB-irradiation

TABLE 4 summarized the effect of EB-irradiation on the tensile properties of three nylon samples. The tensile properties of samples were determined with a UTM at a cross head speed of 500mm/min. It is noteworthy that tensile strength of PA6 and PA66 improves up to 200kGy followed by a gradual fall thereafter (Figure 7a). The irradiation with a higher dose of 600kGy decreases the tensile strength of PA6 and PA66 by 28.6% and 22.9%, respectively than those with dose of 200kGy. For PA1212, tensile strength increased by 19% at 100kGy and slightly decrease by 17.0% when the EB-irradiation dose is increased from 100 to 600kGy for PA1212.

In sharp contrast, the elongation at break of EBirradiated three nylon samples was decreased gradually with irradiation does (Figure 7b). It is noted that the reduction of elongation at break for PA66 and PA1212 is more conspicuous than that of PA6. In case of PA6-600kGy, an approximately 41% decrease in the elongation at break of 198% was observed relative to that of pristine PA66. In sharp contrast after irradiation at 600kGy, the elongation at break of PA66 film was decreased by 87.4% to 42%, whereas PA1212 film decreased the elongation at break by 88.5% to 42% compared to the un-irradiated one.

The enhanced tensile strength of nylon samples at lower EB-irradiation can be explained by the inter-chain cross-linking of polymer molecules. Higher cross-link density of polymer leads to improved mechanical properties, which explains the increase in mechanical stiffness and strength of material. Here



Dadiation	Tensile properties									
dose – (kGy)		PA6	]	PA 66	PA1212					
	Tensile strength	Elongation at break	Tensile strength	Elongation at break	Tensile strength	Elongation at break				
0	41.6±1.8	336±45	46.9±2.5	334±50	24.2±1.8	364±40				
100	43.6±3.2	327±89	51.7±3.2	279±93	$28.8 \pm 1.8$	321±64				
200	48.3±6.0	321±50	52.8±5.3	$171 \pm 48$	24.5±1.4	220±29				
400	37.4±3.2	258±41	48.7±1.3	75±10	24.1±1.6	163±42				
600	34.5±2.3	198±65	40.7±7.6	42±5	23.9±1.8	42±30				

TABLE 4 : Change in tensile properties of nylon samples before and after EB-irradiation



Figure 7 : Variation of the tensile properties of three nylon samples before and after EB-irradiation

in all the cases as expected, elongation at break decreased with increasing dose of EB-irradiation as the material transformed into a more rigid state due to inter-chain cross-linking after absorbing radiation energy. While the chain scission plays important role in the fall of tensile properties during irradiation. Irradiating nylon smaples with high irradiation dose, for example, 600 kGy, lead to significant decrease in tensile strength and elongation at break may be caused by oxidative degradation which usually coexists with chain scission in the presence of oxygen resulting in the decrease in the crystallinity<sup>[40]</sup>.

Further it reveals that the PA6 generates important results. The tensile strength and elongation at break of PA6 was 41.6MPa and 336%, respectively but it decreased little even after irradiated at 200kGy. It leads to an improvement of 16% in tensile strength and a decrease of elongation at break by 4.5% at 200kGy when compared with the corresponding values of un-irradiated PA6. In sharp contrast the tensile strength improved 12.6% for the PA66-200kGy and 1.2% for the PA1212-200kGy. But, the decrease in elongation at break of the PA66-200kGy and PA1212-200kGy is 47.4% and 39.6%, respectively.

#### CONCLUSIONS

In this study investigated the influence of EBirradiation on microstructure, mechanical and thermal properties of PA6, PA66 and PA1212. FTIR, TG, DSC, and mechanical testing were employed to assess the influence. FTIR study reveals that after EB-irradiation the morphological structure of PA6, PA66 and PA1212 was changed. The decrease of crystalline absorption band intensity after irradiation indicates crystallinity of PA66 significantly decreases than that of PA6 and PA1212. The decrease of N-H stretch absorbance value of irradiated nylon

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samples indicates the loss of hydrogen bonding due to irradiation which resulted in decrease in crystallinity. Both the DSC  $T_m$  and  $T_c$  along with  $\chi_c$  of all nylon samples were decreased with the increasing dose of EB-irradiation leading to the development of more amorphous character in these semi-crystalline polymers. TGA traces showed that EB-irradiated PA6, PA66 and PA1212 exhibited the improved thermal stability compared with their parent nylons. The thermal stability of PA66 and PA1212 increased up to 400 and 200kGy irradiation dose, respectively and thereafter decreased whereas PA6 exhibited same thermal stability regardless of irradiation doses. The mechanical testing results show that an intermediate dose of EB-irradiation could enhance the mechanical strength of PA6, PA66 and PA1212, while a high dose leads to a decrease in tensile properties of the three nylon samples. It was found that the drop in elongation at break of PA66 and PA1212 undergoing higher EB-irradiation dose was much more conspicuous than those of PA6. These results can be explained by the higher radiation stability of PA6 in comparison with PA66 and PA1212.

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