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Development of an Advanced Engineering Polymer from the Modification of Nylon 66 by e-Beam Irradiation

N.K. Pramanik, R.S. Haldar*, U.K. Niyogi, and M.S. Alam #

Shriram Institute for Industrial Research, Delhi- 110 007, India
#Jamia Hamdard, Delhi-110 062, India
**E-mail : rshaldar@shriraminstitute.org*

ABSTRACT

When Nylon 66 was irradiated by an optimum dose of e-beam in presence of polyurethane as impact modifier in combination with triallyl isocyanurate as cross-linker, a superior performance was observed for the irradiated nylon 66. Significant improvement of properties, such as hardness, tensile strength, flexural modulus and impact strength was obtained on radiation processing of nylon 66 by e-beam. More interestingly, percent water absorption of such irradiated nylon 66 was reduced substantially. Improvement of mechanical properties and reduction of water absorption of irradiated nylon 66 were due to the cross-linking of the polymer system. Increase of cross-linking with dose of e-beam was verified by the increased gel content at higher doses. Irradiated nylon 66 showed better dimensional stability than those achieved with pristine nylon 66. The increase in dimensional stability may be attributed to reduction in crystallinity with increasing dose of e-beam as revealed by DSC studies.

Keywords: Nylon 66, e-beam irradiation, radiation cross-linking, polyurethane, crosslink network

1. INTRODUCTION

Nylon 66 being a versatile engineering polymer is widely used in various engineering applications. But due to its hygroscopic nature nylon 66 is not very successful in outdoor uses, especially in the environment where humidity, high temperature and repeated impact are encountered[1]. It absorbs moisture from atmosphere, which affects badly on a range of its important properties resulting in poor processibility, dimensional instability, weak mechanical and chemical properties and finally on the performance of products made out of it[2]. Despite a few drawbacks, nylon 66 possesses superior physico-mechanical properties and could be a potential material of choice in many critical applications, if the above shortcomings are suitably overcome. Some emerging modern techniques for material modification are achieved through electron beam irradiation and ion beam sputtering[3,4] technique. Several efforts have been put forth to minimize the limitations of nylon 66; and one of the most convenient ways to overcome the limitations is crosslinking among the polyamide chains brought out by using high energy ionizing radiation like gamma rays or electron beam[5,6]. The feasibility of crosslinking on nylon 66 have been studied by number of researchers starting with Charles by, who for the first time successfully crosslinked nylon 66 with high energy radiation coming from an atomic piles[7]. Later Lawton, *et al.* and Valentine and coworkers on irradiation of nylon 66 using high-energy pile radiation showed that the primary effect was cross-linking accompanied by considerable degradation and loss of crystallinity[8-10]. Radiation cross-linking of nylons reported recently by several other researchers[11-13], but in most of the cases they used either extruded films or yarns or fibers. Only a few works reported the effect of e-beam irradiation on injection molded specimens[14-15]. In this study we report quite extensively the investigation of the effect of e-beam irradiation on nylon 66 blended with triallyl isocyanurate (TAIC) as crosslinker and polyurethane (PU) as impact modifier towards the improvement of its physico-mechanical properties and modification of morphological parameters.

2. EXPERIMENTAL

2.1 Materials

Injection molding grade Nylon 66, Zytel 101L from DuPont, USA was used as base polymer in this study. Molding grade Polyurethane, Estane GP 92 AE procured from Lubrizol Advanced Materials Inc, USA was used as impact modifier. LR grade Triallyl isocyanurate from Acros Organics, Belgium was used as crosslinker. Formic acid (85 per cent), LR grade from SD Fine- Chem limited, India was used as solvent in this study.

2.2 Specimen Preparation

Nylon 66 granules were dried in an air circulated oven at 80 °C for 4 h before the start of actual operation of injection molding. The dried granules were mixed with 2 phr of Triallyl-isocyanurate (TAIC) and 3 phr of polyurethane (PU) in a rotating tumbler at room temperature. The proportions of the additives mixed with the base polymer were optimized at the beginning in a separate study, which is not included in this paper. As TAIC was liquid at room temperature uniform physical blends were prepared by tumbler mixing. The mixed materials were injection molded at 270 °C on a microprocessor-

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based reciprocating screw-type horizontal injection molding machine of clamping force 40 MT and shot capacity 25 g of Joy D'zine, India, into various test specimens. The pristine nylon 66, and its modified form such as nylon 66/TAIC and nylon 66/PU/TAIC were molded using the same processing conditions to make the test specimens. A circular band with OD 120 mm x ID 110 mm x width 15 mm (CB1) was molded from the above three materials for the study of dimensional stability. The molded specimens were packed in polyethylene pouch and sealed immediately after molding in order to prevent moisture absorption.

2.3 E-beam Irradiation of the Molded Specimens

Nylon 66 specimens of different compositions were irradiated by e-beam at BRIT, Vashi, Mumbai using 2 MeV e-beam accelerator in air at ambient temperature. The specimens were arranged in arrays inside stainless steel trays attached to the conveyor system running at a speed of 3 cm/s and received 10 kGy dose of e-beam per pass. The penetrability of electrons in nylon 66 molded specimens was insured by optimizing the beam energy. For the test specimens, single-side radiation was enough for complete penetration. The values of radiation doses were 50 kGy, 100 kGy, 150 kGy, 200 kGy, 250 kGy and 300 kGy. As soon as the irradiation was over, the specimens were repacked in polyethylene (PE) zipper bags to minimize the moisture absorption.

2.4 Mechanical properties

Tensile strength, percent elongation and tensile modulus were determined following ASTM D 638-94 using type IV specimens on a Universal Testing Machine, Model 4302, Make Instron, UK. Flexural strength and flexural modulus were determined on the same Universal Testing Machine as per ASTM D 790-92. Rockwell Hardness was determined as per ASTM D785-93 following procedure 'B' using 'R' scale with a 12.7 mm diameter Indenter and 60 kg major load on a Rockwell hardness tester, Model RAB 250, Make Saroj Engg. Udyog, India. Impact strength was measured at room temperature on notched specimens according to ASTM D256-93 on the Ceast Universal Pendulum, Model 6545 in the Izod mode.

Ten specimens were tested for each mechanical property and the average of all values was reported. Standard deviation was calculated over the entire range of data against each of the above properties at every dose of radiation and in every case the error was found to be less than 1 per cent of the value reported.

2.5 Water Absorption

Water absorption was determined following ASTM D570-98 on molded sample pieces using a Mettler balance, Model AG 204, where the conditioned specimens were dipped in a container of distilled water maintained at a temperature of 23 ± 2°C for 24 h. The percent water absorption was calculated using the following equation

$$\%\ \text{water absorption} = \frac{\text{final weight - Initial weight}}{\text{Initial weight}} \times 100$$

The values obtained are the average of three readings.

2.6 Gel Content

Percent gel content was determined by using about 0.5 g sample pieces collected from the molded specimens and dipped in 85 per cent formic acid[16]. After extraction at room temperature for three days the insoluble gels were collected by filtering through a fritted glass crucible and weighed followed by determining their percentages in the respective samples. Three samples were extracted to determine gel/sol fraction and the average was reported.

$$\%\ \text{Gel content} = \frac{\text{weight of the unextractable fraction}}{\text{Initial weight of sample}} \times 100$$

2.7 G(S)/G(X) Ratio

Radiation chemical yield of crosslinking and chain scission were calculated by using Charlesby-Pinner equation[17]

$$S + S^{1/2} = (p_0 / q_0) + 1 / (q_0 UD)$$

where S is the sol fraction, p_0 and q_0 are the chain scission density and crosslink density per unit dose (kGy^{-1}) respectively, U is the number-average degree of polymerization of the polymer before irradiation, and D is the dose (kGy) of radiation. The values of p_0/q_0 were obtained graphically from the intercept of the experimental curve of ($S + S^{1/2}$) versus 1/D. G(S), the number of polymer chain scission per 100 ev energy absorbed and G(X), the number of polymer crosslink site per 100 ev energy absorbed are related to p_0 and q_0 by the relation[11,15]

$$G(S) / G(X) = 2\,(p_0/q_0)$$

2.8 Dimensional Stability

Dimensional stability was studied on circular band CB1 at two different temperatures, 0 °C and 50 °C. Two sets of sample for each composition were taken and their initial inner diameter (ID) and outer diameter (OD) were recorded. One set of samples were then placed in a digitally controlled low temperature cabinet at 0 °C for low temperature dimensional stability study and the other set kept in a programmable oven at 50 °C for high temperature dimensional stability study. After a fixed period of time (24 h) the samples were taken out and immediately their final ID and OD were measured by a calibrated inspection gauge to determine the dimensional change. The changes between final and initial dimensions were reported. The less the change in dimension, the more is the dimensional stability of the sample.

2.9 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) study was carried out with the samples under nitrogen atmosphere on a Differential Scanning Calorimeter, Model Q200 of TA instruments, USA. About 8 mg of samples were taken in an aluminum DSC pan for these experiments. The samples were heated from room temperature to 300 °C at a heating rate of 10 °C/min, kept at 300 °C for five minutes and finally cooled down to room temperature at a cooling rate of 10 °C/min. Percent crystallinity was calculated using the following equation

$$\text{Crystallinity}\,(\%) = \frac{\Delta H\,\text{exp}}{\Delta H} \times 100$$

where ΔH exp is heat of fusion of the sample under study, and ΔH is heat of fusion of the 100 per cent crystalline nylon 66.

Heat of fusion of the 100 per cent crystalline nylon 66 was taken as 196 J/g in the calculation of percent crystallinity[18].

3. RESULTS AND DISCUSSION

3.1 Tensile Properties

Different sets of dumbbell specimens were prepared by injection molding of three different nylon 66 compositions followed by irradiating them under electron beam at various doses. The first set was of virgin nylon 66, while the second set was made from the combination of nylon 66 and 2 per cent TAIC. On the other hand the 3rd set comprises a blend of nylon 66, 3 per cent PU and 2 per cent TAIC respectively. The results obtained for tensile strength (TS), tensile modulus (TM), and percent elongation for different compositions are shown in Figs. 1, 2, and 3, respectively.

Figure 1. shows that the tensile strength of TAIC mixed nylon 66 increases steadily with increasing radiation dose and 21 per cent improvement is observed at 300 kGy. On the other hand, for nylon 66 blended with PU and mixed with TAIC tensile strength improves up to 100 kGy followed by a gradual fall thereafter. However, for virgin nylon 66, tensile strength remains almost unchanged up to 150 kGy and thereafter starts decreasing gradually. The increase of tensile strength on irradiation is due to the inter-chain cross-linking of poly(hexamethylene adipamide) molecules, while the chain scission plays important role in the fall of tensile strength during irradiation. Interestingly, at 0 kGy, tensile strength of nylon 66/TAIC composition is 6.6 per cent higher than that of virgin nylon 66, which may be due to the thermal crosslinking of the polyamide molecules by isocyanutate crosslinker during molding. But, Nylon 66/ PU /TAIC blend composition before irradiation shows tensile strength 9 per cent lower than that of the virgin and this may be due to the presence of the low tensile polyurethane as impact modifier.

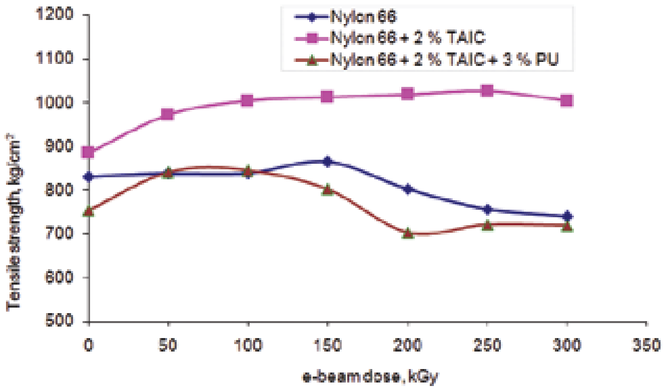

Figure 1. Tensile strength of different nylon 66 compositions *vs* dose of e-beam.

The variation of tensile modulus with dose of e-beam is shown in Fig. 2, where in all the three cases tensile modulus was found to increase with increasing radiation up to 300 kGy. Maximum 28 per cent improvement was observed for nylon 66/TAIC composition, whereas 13 per cent and 12 per cent improvement were observed for virgin nylon 66 and nylon 66/ PU/ TAIC composition respectively at 300 kGy e-beam. Fig. 3 shows the fall of percent elongation with increasing dose of e-beam for the three nylon 66 compositions. Here in all the cases as expected, modulus was increased, while elongation decreased with increasing dose of radiation as the material transformed into a more rigid state due to inter-chain cross-linking after absorbing radiation energy.

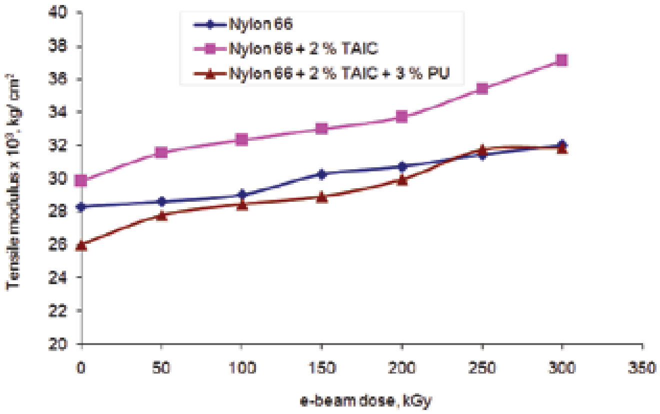

Figure 2. Tensile modulus of various nylon 66 compositions *vs* dose of e-beam.

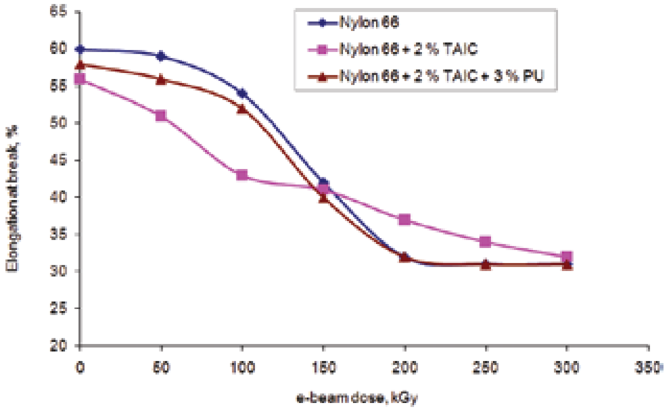

Figure 3. Percent elongation of different compositions *vs* dose of e-beam.

Table 1 presents a summary of the results obtained after the tensile experiment of various nylon 66 compositions. It reveals that the composition where 2 per cent TAIC was added to nylon 66 generates important results only. This composition leads to an improvement of 21 per cent in tensile strength and 28 per cent in modulus and a decrease of percent elongation by 28 per cent at 300 kGy of e-beam when compared with the corresponding values of pristine nylon 66. Such a significant increase in tensile strength and modulus of nylon 66 when irradiated by e-beam at 300 kGy in presence of TAIC as cross-linker as compared to un-irradiated virgin nylon 66 is really remarkable. It is evident from these results that the irradiation by e-beam can be used for modifications of the tensile properties of nylon 66. The incorporation of cross-linker leading to further improvement of the tensile properties of nylon 66 is indeed an achievement. Necking was observed in all the specimens before the rupture. This implies the mode of deformations was of yielding type, thus undergone ductile failure; and interesting the extent of yielding decreased with the increasing dose of

Table 1. Summary of tensile properties for various nylon 66 compositions

Nylon 66 compositions	Change in tensile strength wrt unirradiated virgin nylon 66, %		Change in tensile modulus wrt unirradiated virgin nylon 66, %		Change in percent elongation wrt unirradiated virgin nylon 66, %	
	300 kGy	0 kGy	300 kGy	0 kGy	300 kGy	0 kGy
Nylon 66	(-) 11	0	13	0	(-) 29	0
Nylon 66/TAIC	21	6.6	28	5	(-) 28	(-) 4
Nylon 66/PU/TAIC	(-) 13	(-) 9	12	(-) 11	(-) 29	(-) 2

e-beam. The drop in percent elongation and the rise in tensile strength and modulus certainly signify that nylon 66 became stronger and more rigid on irradiation by e-beam in presence of cross-linker. However, blending of PU did not show any improvement of tensile properties of nylon 66, irrespective of whether it was irradiated in presence of cross-linker by e-beam or not.

3.2 Flexural Properties

Figure 4 shows the increase of flexural modulus of various nylon 66 compositions with increasing dose of e-beam**.** Table 2 gives a summary of the flexural properties of all the compositions. TAIC mixed nylon 66 showed the maximum improvement compared to the other two compositions; 21 per cent improvement in flexural modulus with respect to pristine nylon 66 was observed as compared to 4.4 per cent increase for virgin nylon 66 and 16 per cent increase for nylon 66/ PU/ TAIC at 300 kGy dose of e-beam. Apart from flexural modulus, the flexural strength of TAIC mixed nylon 66 was also superior to other compositions. This composition undergoes an improvement of flexural strength of 3 per cent even at 0 kGy and 35 per cent at 300 kGy of e-beam when compared with the value of pristine nylon 66. The observations of flexural strength and modulus of nylon 66/TAIC are in line with the results of its tensile strength and modulus and are due to the thermal crosslinking of polyamide chains before irradiation, while e-beam induced inter-chain crosslinking after irradiation. Mode of deformation in the flexure of all the compositions was yielding-type, indicating ductile failure and the trend was like that of tensile properties.

3.3 Rigidity

The results obtained from Rockwell hardness indicate that surface hardness increases in every composition as the dose of e-beam increases. As shown in Fig. 5, maximum improvement in Rockwell hardness is observed for TAIC mixed nylon 66 composition and it is 9 per cent at 300 kGy e-beam irradiation. On the other hand, 6 per cent improvement of hardness for nylon 66/ PU/ TAIC composition and 4 per cent increase for nylon 66 are observed at 300 kGy e-beam compared to the pristine nylon 66. The rise in hardness being in line with the rise in tensile and flexural modulus and drop in percent elongation as mentioned earlier clearly indicates that the polymer has become more rigid on irradiation. Increased

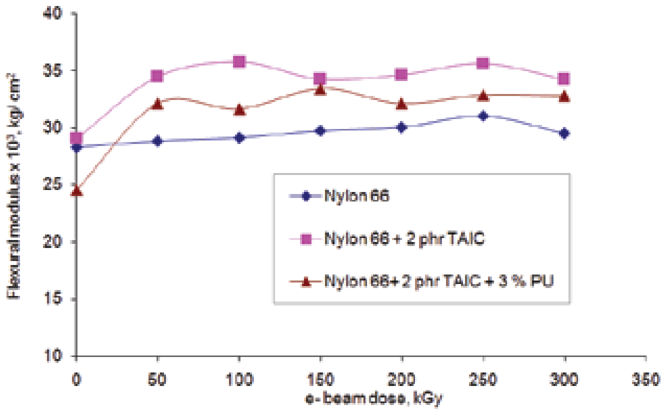

Figure 4. Flexural modulus of various nylon 66 compositions *vs* dose of e-beam.

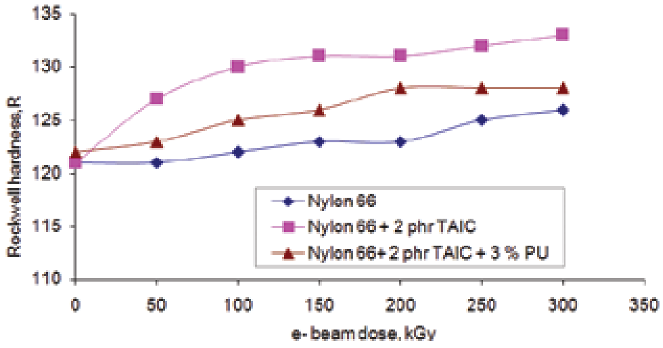

Figure 5. Rockwell hardness of various compositions *vs* dose of e-beam.

Table 2 . Summary of flexural properties for various nylon 66 compositions

Nylon 66 compositions	Increase in flexural strength wrt unirradiated virgin nylon 66, %		Increase in flexural modulus wrt unirradiated virgin nylon 66, %	
	300 kGy	0 kGy	300 kGy	0 kGy
Nylon 66	12	0	4.4	0
Nylon 66/TAIC	35	3	21	3
Nylon 66/PU/TAIC	17	(-) 24	16	(-) 13

rigidity improves the machinability of nylon 66, which is one of the most desirable characteristics for a plastic material for engineering applications.

3.4 Izod Impact Strength

The results of Izod impact strength for various nylon 66 compositions are shown in Fig. 6. For all the compositions, Izod impact strength was decreased with increasing dose of e-beam. However the impact strengths of TAIC mixed nylon 66 and TAIC mixed nylon 66/PU blend remained much higher compared to virgin nylon 66 in the entire range of e-beam irradiation. At lower doses (less than 100 kGy), the PU blended composition showed maximum improvement in impact strength compared to the other two compositions. The remarkable increase of impact strength of nylon 66 in the PU-modified composition at lower doses may be due the presence of rubbery PU phase, which remains immiscible to nylon 66 and absorbs the impact energy. The increase of impact strength of nylon 66 in presence of TAIC may be attributed to the absorption of impact energy by the three dimensional network structure of polyamide chains developed by isocyanurate crosslinker. On the other hand, at higher doses of e-beam may cause polyamide chain scission adversely to effect deterioration of impact strength.

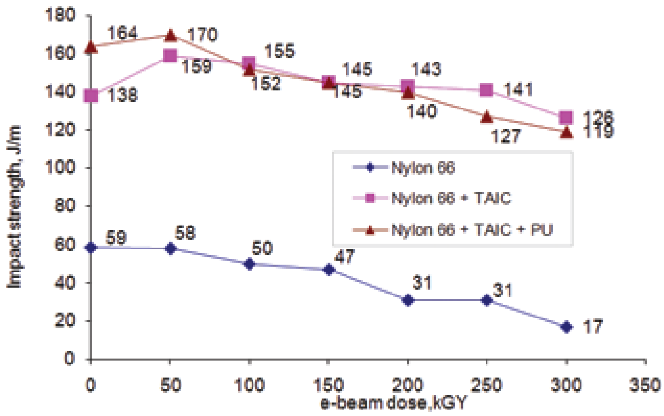

Figure 6. **Izod impact strength of various compositions *vs* dose of e-beam.**

Fracture surfaces of impact specimens for all compositions of nylon 66 were observed smooth over the entire doses of irradiation till 300 kGy, which indicates ductile failure of the samples. There were no cavities observed at the broken surfaces indicating that the specimens were free of porosity. It is worthy to note that the impact strength of both nylon 66/TAIC and nylon 66/PU/TAIC at 300 kGy are 126 J/m and 119 J/m respectively, which are even much higher than the impact strength value of 59 J/m of pristine nylon 66. Hence nylon 66/TAIC irradiated by 300 kGy e-beam or nylon 66/PU/TAIC by 100 kGy e-beam may be chosen as a suitablel material for many important industrial applications where rigidity, tensile and flexural strength and impact resistance are the critical requirements.

3.5 Water Absorption

The most significant observation in this study is the decrease of water absorption of nylon 66 with increasing dose of e-beam for all the compositions as can be seen in Fig. 7, which is very much desired as far as the performance of the product of these materials is concerned. Percent water absorption was decreased by 30 per cent at 300 kGy for nylon 66 /TAIC and 29 per cent for nylon 66/ PU/TAIC as compared to 14 per cent decrease for virgin nylon 66. Even at 0 kGy irradiation (i.e., before irradiation) the percent water absorption value of TAIC mixed nylon 66 was 6 per cent less and TAIC mixed nylon 66/ PU blend was 10 per cent less than that of the pristine nylon 66.

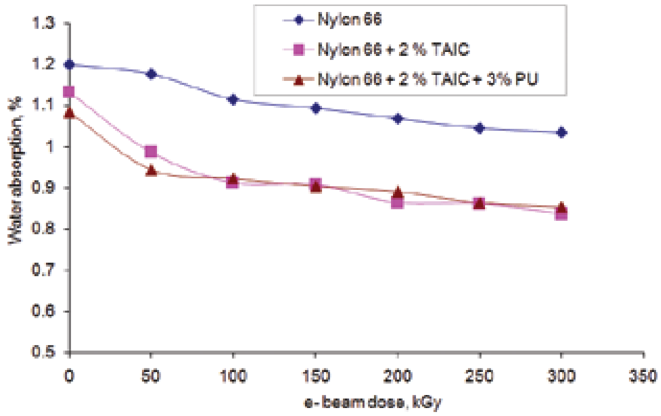

Figure 7. **Percent water absorption of various compositions *vs* dose of e-beam.**

Sengupta and coworkers[18] also found that water uptake was less for the films that received a radiation dose of 200 and 500 kGy than the un-irradiated nylon 66 film. Reduction of water absorption may be attributed to the crosslinking of polyamide chains. This is further evident from the fact that melt mixing of TAIC with nylon 66 leads to thermal crosslinking to effect a 6 per cent reduction of water absorption, even when it was not irradiated by e-beam.

3.6 Dimensional Stability

Figure 8 represents the dimensional stability at 0 °C of circular band, CB1 made out of all three compositions of nylon

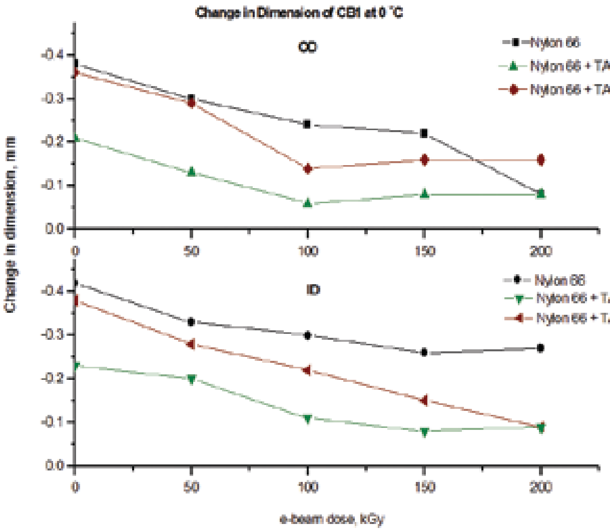

Figure 8. **Change in dimension of circular band CB1 at 0 °C with e-beam dose.**

66. The changes in ID and OD, before and after the experiment, decreased with increasing dose of e-beam and this is indicative of improved dimensional stability of the bands when irradiated by e-beam. Out of the three materials, namely virgin nylon 66, nylon 66/TAIC and nylon 66/PU/TAIC, the dimensional changes are minimum for CB1 made up of nylon 66 mixed with TAIC followed by e-beam irradiation. The maximum dimensional stability was achieved at 100 kGy e-beam, beyond which no significant dimensional change observed. Dimensional stability of CB1 made from virgin nylon 66 is poorer than the blend of nylon 66 with PU mixed with TAIC after irradiation at all doses of e-beam. Fig. 9 shows the dimensional change at 50 ^{0}C of circular band, CB1 made out of different nylon 66 compositions. Similar to the low temperature results, when the experiment was done at 50 °C the maximum dimensional stability for CB1 made from nylon 66/TAIC composition was observed at 100 kGy dose of e-beam. Dimensional stability of CB1 made from the blend of nylon 66/ PU mixed with TAIC after irradiation at all doses of e-beam was poorer compared to nylon 66 mixed with TAIC. CB1 made from virgin nylon 66 showed minimum high temperature dimensional stability at all doses of e-beam irradiation. The increased dimensional stability with the nylon 66/TAIC composition may be attributed to the three dimensional cross-link network due to irradiation, which in turn reduced the crystallinity of nylon 66. The more amorphous the material, the better is its dimensional stability. However, in the nylon 66/PU/TAIC composition, the immiscible component, PU restricts the development of crosslink structure in the blend, thereby reducing its dimensional stability compared to that observed in nylon 66/TAIC.

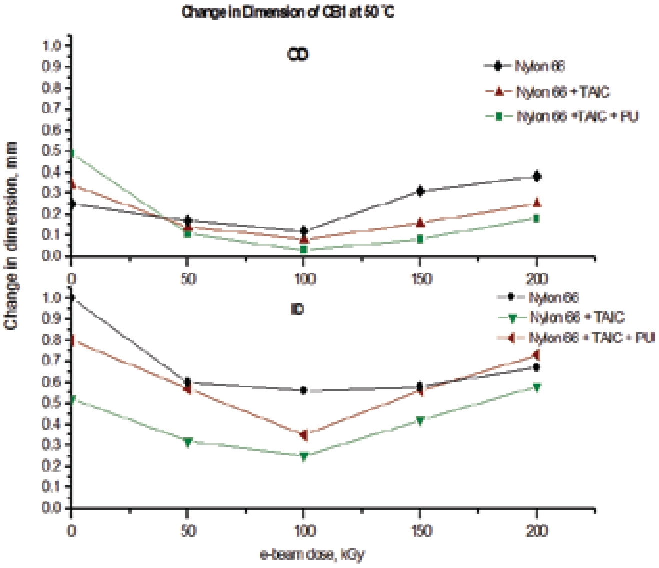

Figure 9. Change in dimension of circular band CB1 at 50 ^{O}C with e-beam dose.

3.7 Gel Content

Figure 10 shows the extent of gel formation in virgin nylon 66 /TAIC sample irradiated with varying doses of e-beam. In case of virgin nylon 66, there was no gel formation till 50 kGy, followed by 48 per cent gel at 100 kGy and thereafter gradual increase to 70 per cent gel at 300 kGy. TAIC mixed nylon 66, on the other hand, underwent gel formation from the beginning of irradiation and showed 76 per cent gel at 50 kGy followed by gradual increase of gel content to 80 per cent at 300 kGy e-beam.

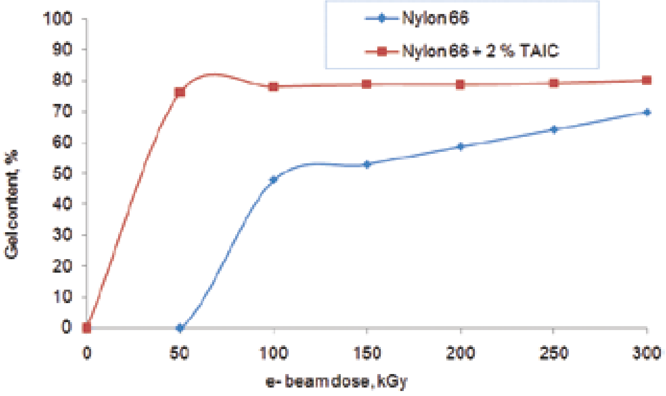

Figure 10. Percent gel content as a result of different doses of e-beam.

Gels are insoluble and infusible fractions constituting three dimensional crosslink network structures which are generated by crosslinking of linear polymer chains. Post polymerization crosslinking in nylon 66 is possible by high energy irradiation when crosslinking of polyamide molecules may proceed through free radical reactions in the solid phase resulting in the formation of gels. Increase of crosslinking of nylon 66 with increasing dose of e-beam has been verified by the increase of gel content in nylon 66 as the dose of e-beam increases. Formation of gel on irradiation has been enhanced further in presence of TAIC as crosslinker as was seen in case of TAIC mixed nylon 66 composition where all the mechanical properties were improved more than the improvement observed in virgin nylon 66.

As is shown in Fig. 11(a) and (b), the G(s)/G(x) value of virgin nylon 66 as determined from Charlesby-Pinner plot was 1.40, whereas it was decreased to 1.32 for nylon 66/ TAIC. This decrease in G(s)/G(x) value is due to more cross-linking in nylon 66 when TAIC was added as cross-linker which played very important role in accelerating the process of cross-linking because of generation of more free radicals during irradiation. The more the decrease of G(s)/G(x) value, the better is the efficiency of the cross linker to enhance the properties of nylon 66 through more cross-linking.

Table 3. Change in properties of different nylon 66 compositions before irradiation as compared to the respective values of virgin nylon 66

Properties	Nylon 66/TAIC % change	Nylon 66/PU/TAIC % change
Hardness	2.0	4.0
Tensile strength	6.6	-9.0
Tensile modulus	5.0	-11.0
Percent elongation	-4.0	-2.0
Flexural strength	3.0	-24.0
Flexural modulus	3.0	-13.0
Impact strength	133.0	178.0
Water absorption	-6.0	-10.0

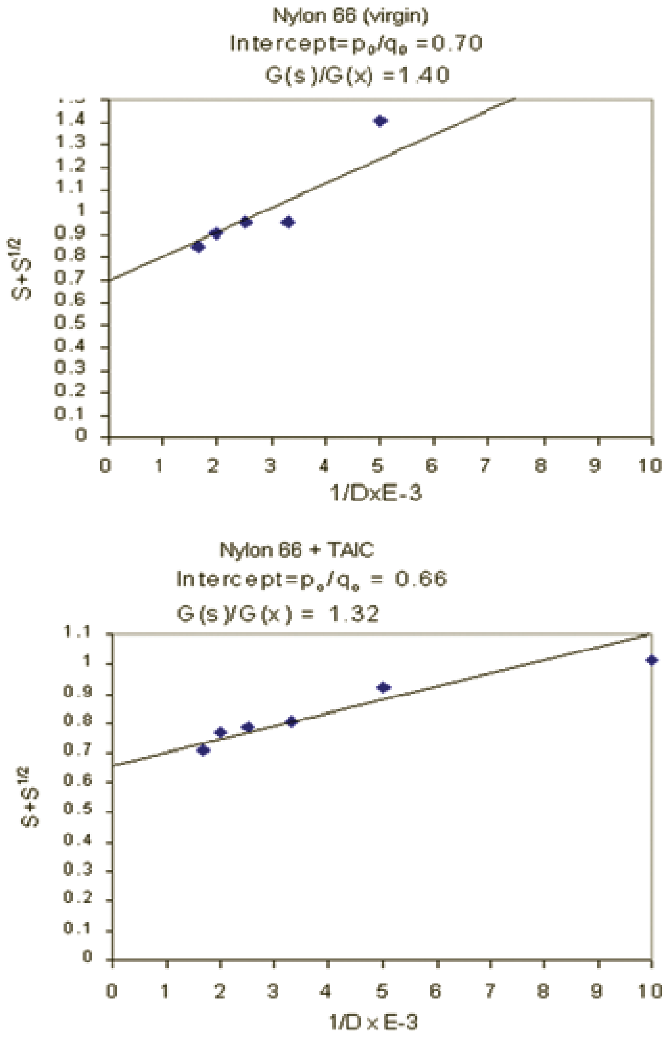

Figure 11. (a) Charlesby-Pinner plot of virgin nylon 66 to determine G(s)/G(x) and (b) Charlesby-Pinner plot of nylon 66/TAIC to determine G(s)/G(x).

It is interesting to note that when TAIC was blended with nylon 66 by melt mixing, the mechanical properties of nylon 66 were much affected, even though it was not irradiated by e-beam. As shown in Table 3, before the irradiation by e-beam there were significant changes in various properties of different nylon 66 compositions compared to the corresponding values of virgin nylon 66. The improvement in mechanical properties as well as decrease of water absorption at zero irradiation when cross-linker was incorporated into nylon 66 by melt mixing might be attributed to the thermal cross-linking of polyamide molecules. However, the extent of thermal cross-linking of polyamide molecules during melt mixing is not enough to form insoluble and infusible nylon 66 gel. This may be advantageous as far as the processibility of nylon 66/TAIC is concerned since thermal cross-linking will not affect the melt processing of this material for making products.

3.8 Crystallinity

DSC thermograms of TAIC mixed nylon 66 as presented in Fig. 12 reveal that crystalline melting temperature (T_m) and crystallization temperature (T_c) of nylon 66 in presence of TAIC have decreased considerably with the increase of dose of e-beam irradiation. T_m of nylon 66 was reduced from 263 °C to 250 °C while its T_c was decreased from 234 °C to 219 °C, when irradiated by 0 to 300 kGy e-beam in presence of TAIC. The decrease of T_m and T_c of nylon 66 with increasing dose of e-beam may be due to the chain scission effect of e-beam at higher doses causing reduction in size of molecular chains of nylon 66, which melt faster and crystallize slowly at comparatively lower temperature.

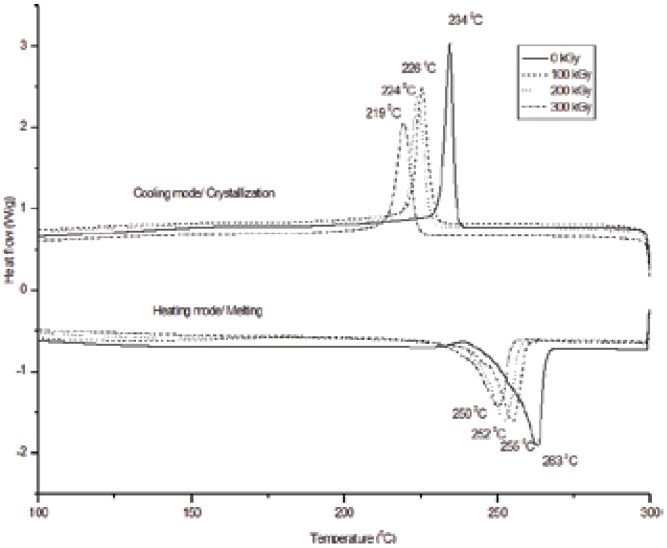

Figure 12. DSC Thermograms for TAIC mixed Nylon 66 at 0, 100, 200 and 300 kGy.

The reduction of crystallinity of nylon 66 is evident from the plot of percent crystallinity versus dose of e-beam as shown in Fig. 13. Virgin nylon 66 undergoes a reduction of 14.2 per cent crystallinity at 300 kGy irradiation. On the other hand, the crystallinity of nylon 66/TAIC has decreased by 26.4 per cent at 300 kGy e-beam and by 7.6 per cent at zero irradiation when compared with the values of un-irradiated virgin nylon 66. The decrease of percent crystallinity of nylon 66 with increasing dose of e-beam may be due to the fact that the growth of crystalline structure in the crosslinked mass of nylon 66 due to e–beam irradiation is not favorable.

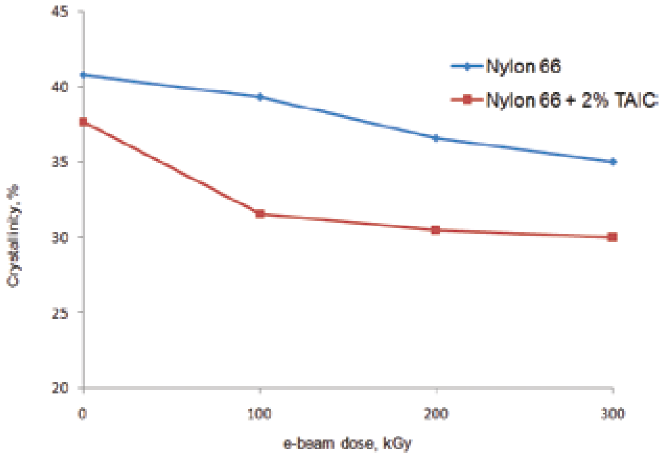

Figure 13. Percent crystallinity of samples as a result of application of different doses of e-beam.

Sengupta[12], *et al.* studied on injection molded nylon 66, where specimens were dipped in triallyl cyanutate solution before irradiation by e-beam at ambient temperature and found that crystallinity decreased with increasing radiation. The decrease of percent crystallinity is indicative of the development of more amorphous nature in nylon 66. The improvement of dimensional stability in irradiated nylon 66 as seen earlier may be due to the increase of its amorphous nature. In previous sections we have already discussed that water absorption of nylon 66 decreases with the increasing dose of irradiation. Reduction of percent crystallinity of nylon 66 with increasing dose of e-beam can thus be correlated with the decrease of water absorption. Similarly, the reduction of percent crystallinity of nylon 66 may be correlated with the increase of its gel content. This indicates that as the dose of e-beam increases, there occur more crosslinking resulting in increased gel formation, which is responsible for increase in amorphous nature and decrease in hygroscopicity of irradiated nylon 66.

4. CONCLUSIONS

Electron beam radiation is proved to be a powerful means to improve the mechanical properties of nylon 66, thus can overcome the inherent limitations of such polymer. This radiation processing technique is highly beneficial since all the changes are brought about in solid-state, as opposed to inconvenient alternative chemical and thermal reactions processes.

Physical and mechanical properties improved significantly when nylon 66 irradiated by electron beam in presence of TAIC as crosslinker. Such crosslinked Nylon 66 may be useful for preparing rigid and dimensionally stable articles with superior mechanical properties and improved serviceability.

Blending of PU with nylon 66 in presence of TAIC at lower doses of e-beam improved the impact resistance of pristine nylon 66 manifold. PU modified e-beam crosslinked nylon 66 may find applications in high impact industrial products

Decrease of water absorption of e-beam irradiated of nylon 66 in presence of crosslinker is another important achievement as it helps reduce the inherent hygroscopic nature of nylon 66 to effect improved dimensional stability and enhanced shelf life of the product.

Development of cross-linked structure in irradiated nylon 66 is evident from the formation of infusible and insoluble gel where gel content increased with increasing dose of e-beam irradiation. Presence of crosslinker has decreased G(s)/G(x) value in irradiated nylon 66 indicating occurrence of more cross-linking than chain scission in irradiated sample than that occurred in virgin nylon 66.

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CONTRIBUTORS

Mr Nilay Kanti Pramanik completed Master of Science in Polymer Science from Tezpur University, Assam. He is pursuing Ph.D from Jamia Hamdard on radiation processing of polyamides using gamma rays and e-beam. He has more than six years research experience in polymer processing and fabrication. Polymer characterization using state of the art instrumentation facility is also a subject of his interest. He was the Young Scientist Award Winner in Engineering Sciences, 2010 organized by Indian Science Congress Association. He has six publications in international journal to his credit.

Dr R.S. Haldar received his MTech (Polymer Science & Technology) and PhD from IIT Delhi. He is presently working as Senior Assistant Director at Shriram Institute for Industrial Research, Delhi. He has an experience of twenty eight years in the field of polymer processing technology. His areas of interest include: New product development in polymers, engineering polymers, polymer blends and alloys, radiation processing of polymers, shape memory polymers, shear thickening polymers, biocompatible polymers, bioresorbable polymers and morphology of polymers. He has published 30 research papers, filed two patents, edited two books.

Dr U.K. Niyogi obtained MSc (Tech) (Technology of Plastics) from U.D.C.T, Mumbai and was awarded PhD (Tech.) from University of Calcutta. He is presently working as Joint Director and Head, Material Science Division of Shriram Institute for Industrial Research, Delhi and engaged in various R&D projects on polymeric materials, specialty chemicals and waste utilization. He has more than thirty years of experience in the field of R&D, synthesis and processing of polymers and resins. He is life member of various professional institutes such as Institution of Materials, Minerals and Mining, U.K., Indian Plastics Institute, Indian Institute of Chemical Engineers, Institution of Engineers, India, etc. He has 47 research papers to his credit.