

Modification of Nylon 66 by Electron Beam Irradiation for Improved Properties and Superior Performances

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ABSTRACT: Nylon 66 has been transformed into a material with significantly improved properties like hardness, tensile strength, and flexural modulus by processing it under the optimized dose rate of electron beam in the presence of suitable crosslinkers. Furthermore, percent water absorption of nylon 66 was reduced substantially on irradiation. Thermogravimetric analysis revealed that thermal stability of nylon 66 improved with increasing dose of radiation. Improvement of mechanical and thermal properties and reduction of water absorption of nylon 66 were due to the crosslinking of polyamide molecules made possible by the high energy radiation. Increase of crosslinking

with increasing radiation dose was verified by the increase of gel content at higher doses. Differential scanning calorimetry showed that both melting and crystallization temperatures along with percent crystallinity of nylon 66 were decreased with the increasing dose of radiation leading to the development of more amorphous character in this semicrystalline polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 193–202, 2011

Key words: e-beam; irradiation; nylon 66; crosslinking; gel content; percent crystallinity; thermal stability

INTRODUCTION

Polyamides (commonly known as nylons) are one of the most exploited plastics due to their structural attributes, which make them suitable for wide range of uses both in domestic as well as engineering applications. The superior physicochemical properties make nylons versatile materials of choice for several applications. Today, in majority of engineering applications, at least one of the nylons is a must in one form or the other. However, there are still certain specific uses, where the nylons cannot meet all the stringent requirements of the application. The major shortcomings that restrict nylons to find uses in several critical areas include:

- After-shrinkage in use
- Poor dimensional stability
- Insufficient rigidity
- Poor machinability
- Higher water absorption
- Porosity in articles
- Poor electrical insulation
- Poor processability

- Poor scratch resistance
- Poor weather resistance
- High-temperature embrittlement
- Color formation at elevated temperature.

Incidentally, all these limitations are also attributed to the unique structural features of nylons. However, in spite of the above, nylons can be the materials of a perfect choice even for the critical applications, provided the already superior bulk properties of nylons are enhanced further substantially and at the same time their inherent drawbacks are overcome to a great extent. There could be many approaches to achieve these, but the most remarkable one pertains to the creation of crosslinked structures in nylons akin to what is being done in the case of several other polymers like polyethylene, which is converted to XLPE on a commercial scale by crosslinking. Presence of the —CONH— groups in nylons make them structurally different from the linear polyethylene. Because the ethylene chains of nylons are similar to those of polyethylene, the assumption that the crosslinking among the ethylene chains of nylons can be achieved would be considered logical. The process of crosslinking of nylons by high energy radiation would be an innovative approach in this context.

Charlesby noted that nylon 66 was crosslinked by high energy radiation from an atomic pile.¹ Lawton and coworkers irradiated nylon 66 by high energy electrons produced by a resonant transformer-type cathode ray equipment to crosslink it.² Subsequent

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TABLE I
Materials Used for the Study

Material used	Grade	Source	Features
Nylon 66	Zytel, 101L	Dupont, USA	Injection molding grade granules
Triallyl cyanurate	Laboratory reagent	Merck, Germany	Boiling point 324°C
Triallyl isocyanurate	Laboratory reagent	Acros Organics, Belgium	Boiling point 315°C
Trimethylolpropane trimethacrylate	Laboratory reagent	Aldrich, USA	Boiling point 310°C
Formic acid	Laboratory reagent	S D Fine Chemical Limited, India	85% (w/v) aqueous solution

studies by Valentine,³ Zimmerman,⁴ and Deely and coworkers⁵ on irradiation of nylon 66 using high-energy pile radiation showed that the primary effect was crosslinking accompanied by considerable degradation and loss of crystallinity. Bernstein and coworkers concluded that efficient crosslinking of nylon 66 where degradation was of little significance was impossible to attain upon straight radiation.⁶ Ferro and Gondim⁷ determined the crosslink density through equilibrium swelling of nylon 66 irradiated by e-beam at different doses. Sengupta and coworkers⁸ studied nylon 66 film irradiated by e-beam at various doses and showed significant improvement of ultimate tensile stress, 10% modulus, elongation at break, and toughness over the unirradiated film. Aytac and coworkers⁹ studied the effects of gamma and e-beam irradiation on nylon 66 and nylon 6 fabrics and found that the deterioration effect of gamma irradiation on mechanical properties of both the polymers was much higher than that of e-beam irradiation. In a recent study, the authors of this work have already demonstrated that nylon 6 can be significantly improved by minimizing most of its deficiencies by the use of radiation processing by e-beam.¹⁰

Because the fact that some of the products (used in railways, automobiles, and defense) based on the crosslinked nylon 6 exhibited unique features, the possibility of exploitation of this polymer for several high-end applications has apparently become feasible. Taking this experience of understanding the process involved in crosslinking of nylon 6, besides the derivable benefits, the present study has been carried out on nylon 66-molded specimens subjecting them to e-beam irradiation to achieve improvements in properties. E-beam-crosslinked structures in nylon 66 are studied to correlate their contribution toward the enhancement of physicomechanical properties.

EXPERIMENTAL

Materials

A commercial grade of nylon 66, Zytel 101L from Dupont, USA, was chosen as the base material for this study. Triallyl cyanurate (TAC) from Merck, Germany, triallyl isocyanurate (TAIC) from Acros

Organics, Belgium, and trimethylol propane trimethacrylate (TMPTMA) from Aldrich, USA, were used as crosslinking aid. The details of all the raw materials used in this study are given in Table I.

Mixing

Nylon 66 granules were dry-blended with 1.0 phr of each of the three crosslinkers separately. The crosslinkers, being liquid at room temperature, formed uniform layers around the surfaces of nylon 66 granules on mixing thoroughly. The blends were prepared at 260°C on a microprocessor-based reciprocating screw-type injection-molding machine of clamping force 40 MT and shot capacity 25 g from M/s Joy d'zine, India, into various test specimens. The specimens were subjected to e-beam irradiation to study the effect of each of the crosslinkers on the properties of nylon 66 at various doses of e-beam.

Irradiation

The specimens of nylon 66 with crosslinkers were irradiated for different radiation doses (100, 200, 300, 400, 500, and 600 kGy) at Bhabha Atomic Research Center, India, using 2 MeV e-beam accelerator in air at ambient temperature. Mechanical properties of all the irradiated specimens were evaluated and compared to the unirradiated virgin material as a reference.

Characterization

The specimens irradiated at various dose levels from 0 to 600 kGy were evaluated for various physicomechanical properties. The tensile properties determined according to ASTM D 638-94b and flexural properties as per ASTM D790-92 were evaluated on a Universal Testing Machine, Model 4302 of Instron, UK. Impact strength was measured at room temperature on notched specimens according to ASTM D256-93a on the Ceast universal pendulum 6545 in the Izod mode. Rockwell "R" hardness was determined as per ASTM D785-93 by Rockwell hardness tester, Model RAB 250 of Saroj Engineering, Udyog, India. Water absorption was determined following ASTM D570-81 using a Mettler balance, Model AG 204 with four decimal accuracies.

All the test specimens before testing were sealed in dry LDPE pouches and stored in a fresh silica gel-filled desiccator as soon as they were released either from the mold after injection molding or from the accelerator after irradiation by e-beam. Ten specimens were tested for tensile properties and impact strength, five specimens for flexural properties and hardness, and three specimens for water absorption, while the average of all the values was reported as the results. We have considered the minimum thickness of a test specimen in the calculation of mechanical strengths, and this is because the weakest point in a specimen lies in its thinnest section. Standard deviation was determined over the entire range of data, and, in every case, the error was calculated to be less than 1% of the value reported. All the properties of nylon 66, filled or unfilled with crosslinker at different doses of e-beam, were evaluated with respect to unirradiated virgin nylon 66 only, unless it was stated otherwise.

Gel Content

Gel content was determined by the method of solvent extraction as followed by Sengupta and co-workers¹¹ where nylon 66 were extracted from a weighed sample by dipping into 85% formic acid at room temperature for 3 days. Gels were collected by filtering through a fritted glass crucible and weighed followed by determining their percentages in the respective samples. Five samples were extracted to determine gel and sol content, and the average was reported. Radiation chemical yields of crosslinking and chain scission were calculated by using Charlesby–Pinner equation¹²:

$$S + S^{1/2} = (p_0/q_0) + 1/(q_0UD)$$

where S is the sol fraction, p_0 and q_0 are the chain scission and crosslinking 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 irradiation. Values of p_0/q_0 were obtained graphically from the experimental curves of $S + S^{1/2}$ versus $1/D$. The number of polymer chain scissions per 100 eV of radiation dose absorbed $G(S)$ and the number of polymer crosslink sites per 100 eV of radiation dose absorbed $G(X)$ are related to p_0 and q_0 as per the equation¹³:

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

Differential scanning calorimetry

DSC studies were carried out with a differential calorimeter, model Q200 of TA Instruments, USA. All

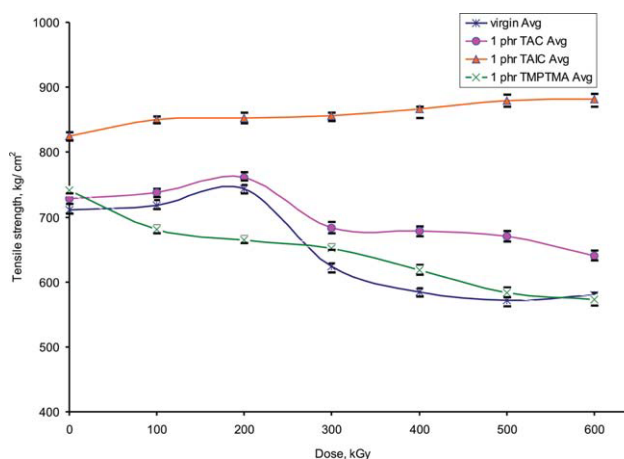


Figure 1 Variation of tensile strength with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the specimens were subjected to the heating and cooling mode under nitrogen purge of 50 mL/min. Rates of heating and cooling in the DSC study were kept at $10^\circ\text{C}/\text{min}$. T_m and ΔH_f were determined from the heating scan, whereas T_c and ΔH_c were determined from the cooling scan. Percent crystallinity was calculated using the following equation:

$$\text{Crystallinity (\%)} = (\Delta H_{\text{Exp}} \times 100) / \Delta H_f$$

where ΔH_{Exp} is the heat of fusion of the sample under study, ΔH_f the heat of fusion of the 100% crystalline nylon 66, and heat of fusion of the 100% crystalline nylon 66 was taken as 196 J/g in the calculation of percent crystallinity.¹⁴

Thermogravimetric analysis

Thermogravimetric analysis was performed on a simultaneous DTA-TGA, Model SDT 2960 of TA Instrument, USA. Heating rate of $10^\circ\text{C}/\text{min}$ was used under nitrogen atmosphere up to 700°C .

RESULTS AND DISCUSSION

Results of tensile strength with varying dose of irradiation for nylon 66 and nylon 66 blended with three different crosslinkers are presented in Figure 1. It may be noted that the tensile strength for the virgin nylon 66 and the nylon 66 with TAC as crosslinker has exhibited a similar pattern of initial rise up to 200 kGy followed by the gradual reduction up to 600 kGy. In the case of nylon 66 with TMPTMA, the tensile strength has undergone a continuous reduction with the increasing dose of irradiation. In the case of TAIC, however, the results have been completely different from the other three cases, exhibiting a continuous rise in tensile strength

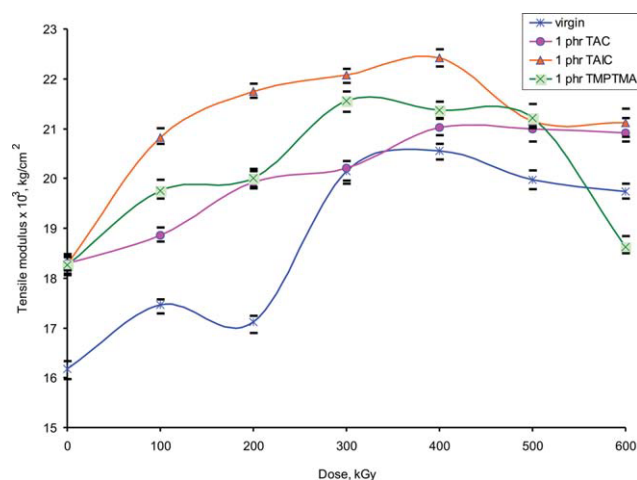


Figure 2 Variation of tensile modulus with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

throughout the whole range of irradiation. An increase in tensile strength of virgin nylon 66 to the extent of 24% from 0 to 600 kGy, when TAIC is used as crosslinker, can be considered as phenomenal. It is evident from the results that the irradiation by e-beam can be used to affect modifications in the tensile strength of nylon 66. The incorporation of crosslinkers leading to further maneuvering of the tensile property of nylon 66 can be described as a break through in this regard. Mode of deformation in tensile testing of virgin nylon 66 was of yielding type indicative of ductile failure at lower doses of e-beam and the extent of yielding decreased with the increasing dose of e-beam showing brittle failure at 400 kGy and more. On the other hand, when crosslinkers were added into the formulation, the deformation of nylon 66 remained ductile throughout the entire range of dose applied. Necking was observed in all the specimens except for virgin nylon 66 at doses of irradiation higher than 400 kGy.

Tensile modulus of virgin as well as crosslinker blended nylon 66 has significantly increased by a maximum of 27% (virgin), 30% (TAC), 32% (TMPTMA), and 38.5% (TAIC) at 400 kGy with respect to unirradiated virgin nylon 66 (Fig. 2). At 500 kGy, the values of virgin and TAIC fall down to 23 and 31%, respectively, while there is no change in value for TAC and TMPTMA. Beyond this, there is no change of tensile modulus till 600 kGy in all the cases except for TMPTMA showing a further drop of 15%. Increase of tensile modulus is indicative of generating harder nylon 66 on irradiation.

In the case of virgin nylon 66, there is a drop of elongation from 31 to 6% up to 300 kGy, beyond which there is almost no change till 600 kGy (Fig. 3). In the case of TAC and TMPTMA, there is a sharp fall in elongation from 31 to 10% when the dose is

increased from 0 to 100 kGy and beyond 100 kGy, the elongation has fallen down gradually to 4% at 600 kGy in both the cases. In the case of TAIC, however, the percent elongation has only gradually dropped from 31 to 17% over the entire range of dosage. The results of the change of percent elongation for TAIC are therefore completely different from the other crosslinkers as has been seen in the case of tensile strength. The drop in percent elongation and the rise in tensile strength and modulus clearly indicate that nylon 66 has become stronger on irradiation by e-beam.

Rigidity of nylon 66 has increased with the dose of e-beam irradiation, and it has been evidenced by an increase of 8% Rockwell R hardness at 600 kGy. TAC, TAIC, and TMPTMA incorporated nylon 66 at 600 kGy have shown a 9, 10, and 11% increase of hardness, respectively, over virgin unirradiated nylon 66. A 2% increase of hardness has also been observed with any of the crosslinkers even when they were not irradiated, that is, at 0 kGy (Fig. 4). The rise in hardness being in line with the rise in tensile modulus and drop in percent elongation as mentioned earlier clearly indicates that the polymer has become more rigid on irradiation. Increased rigidity improves the machinability of nylon 66, which is one of the most desirable characteristics for a plastic material to be used successfully in engineering applications.

Izod impact strength of virgin nylon 66 has fallen down with the dose of e-beam showing a 32% decrease at 100 kGy followed by almost no change till 300 kGy, thereafter a sharp fall of 77% at 400 kGy, beyond which there is no significant change throughout the experiment. In the cases of TAC and TMPTMA-blended systems, Izod impact strength has fallen down by 54% for TAC and 69% for TMPTMA at 400 kGy, and thereafter no major

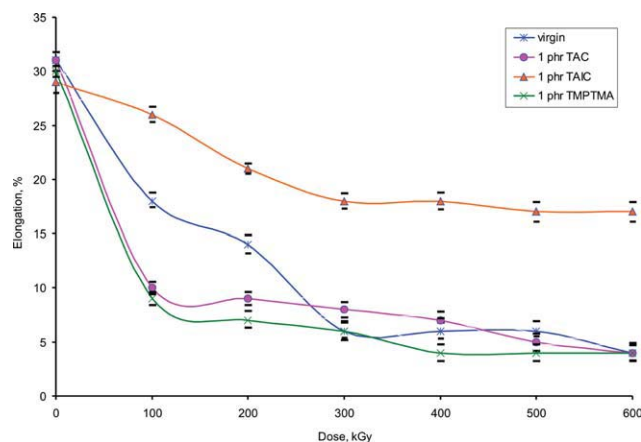


Figure 3 Variation of percent elongation with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

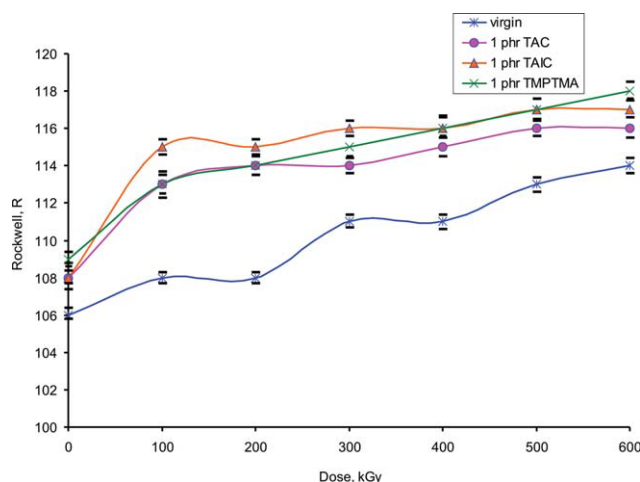


Figure 4 Variation of Rockwell "R" hardness with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change is observed as the dose increases. On the other hand, for TAIC, the behavior is quite different from the other two crosslinkers, showing a 37% reduction of impact strength at 200 kGy, followed by gradual decrease to 57% with the increasing dose through 600 kGy (Fig. 5). Fracture surfaces of all Izod impact specimens, both virgin and crosslinker-filled nylon 66, were observed smooth at lower doses of irradiation till 300 kGy, which is indicative of ductile failure. But at higher doses of e-beam, 400–600 kGy, the broken surfaces were not smooth, rather appeared to be either chipped off or crushed, indicating brittle failure. There were no cavities observed at the broken surfaces, and this proved that the specimens were free of porosity. It may be pointed out in this context that the absolute values of impact strength of all nylon 66 samples even at 300 kGy are quite substantial (80 J/m for virgin while 45–58 J/m for crosslinkers) for selecting them

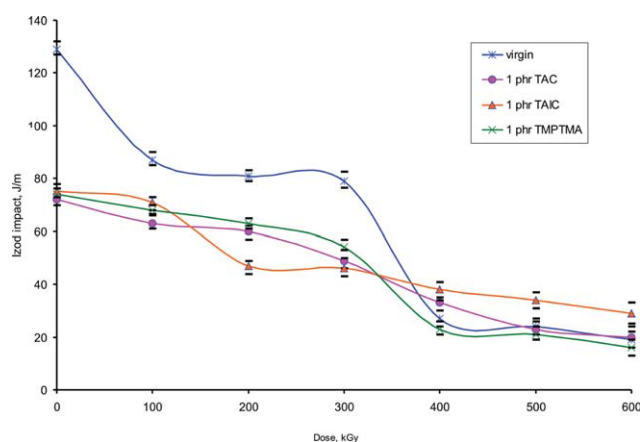


Figure 5 Variation of Izod impact strength with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as a successful material for many rigid applications where tensile strength is more critical than the impact strength.

Flexural modulus of nylon 66 is found to increase with increasing dose of irradiation till 400 kGy, where an increase of 40% flexural modulus is observed, followed by sharp fall through 600 kGy dose. However, the increase of flexural modulus with dose of irradiation is far more remarkable when some specific crosslinkers are added into the system. At 400 kGy radiation for TAC blended nylon 66, flexural modulus has increased by 48%, whereas for TAIC, it is 52%, followed by a sharp decrease with further increase of dose. The behavior of the third crosslinker, TMPTMA, with the increasing dose of e-beam is almost similar to that exhibited by virgin nylon 66 with 40% increase of flexural modulus at 400 kGy e-beam (Fig. 6). Mode of deformation in the flexure of virgin nylon 66 was yielding-type indicative of ductile failure at lower doses of e-beam, and the extent of yielding decreased with the increasing dose of e-beam showing brittle failure at 400 kGy and more. However, when crosslinkers were added, the deformation remained ductile throughout the entire range of doses applied.

The most significant achievement in this study is the decrease of water absorption of nylon 66 with increasing irradiation dose. This is very much desirable as far as the performance property of nylon 66 is concerned. Percent water absorption of all nylon 66 samples, with or without crosslinker, has gradually fallen with the increasing dose of irradiation through out the experiment. Percent water absorption of virgin nylon 66 has been reduced by 24% at 600 kGy, whereas a maximum of 35% reduction at the same radiation dose has been observed while TAIC is incorporated as a crosslinker (Fig. 7). In the study of e-beam irradiation of nylon 66 film, Sengupta and coworkers⁸ also found that water

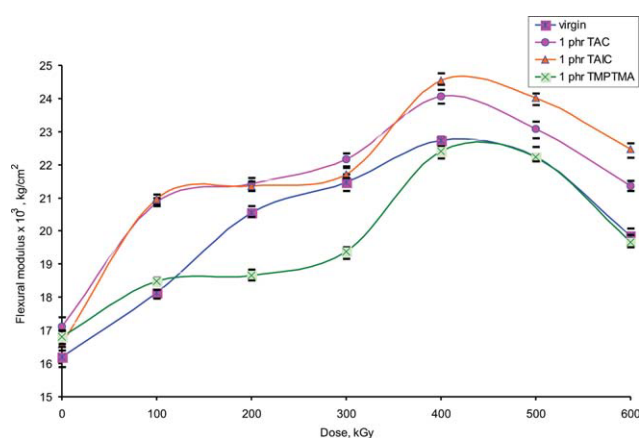


Figure 6 Variation of flexural modulus with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

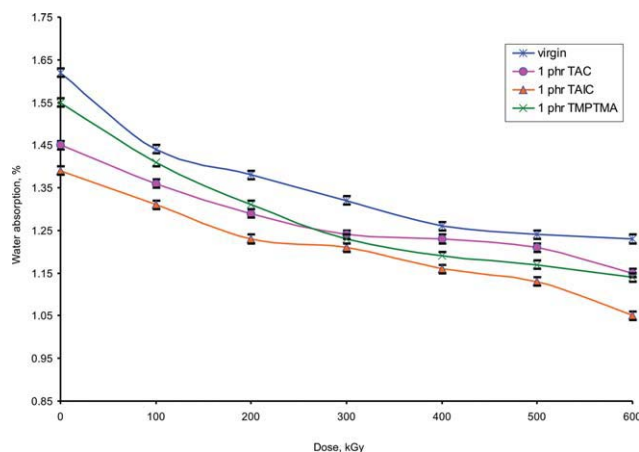


Figure 7 Variation of water absorption with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uptake was less for the films that received a radiation dose of 200 and 500 kGy than the unirradiated film. Reduction of water absorption may be attributed to the crosslinking of polyamide molecules in nylon 66. This is further clear from the fact that melt mixing of crosslinkers with nylon 66 leads to its thermal crosslinking resulting a maximum of 14% reduction of water absorption in the case of TAIC, even when it is not irradiated with e-beam.

Improvement of mechanical properties and reduction of water absorption of nylon 66, when irradiated by e-beam, is due to the crosslinking of polyamide molecules in the presence of high energy radiation. Increase of crosslinking of nylon 66 with increasing e-beam dose may be verified by the increase of gel content in nylon 66 as the dose of e-beam increases. In case of virgin Nylon 66, there is no gel formation till 100 kGy, followed by 60% gel formation at 300 kGy, and thereafter a gradual increase to 70% at 600 kGy. TAC and TAIC-blended

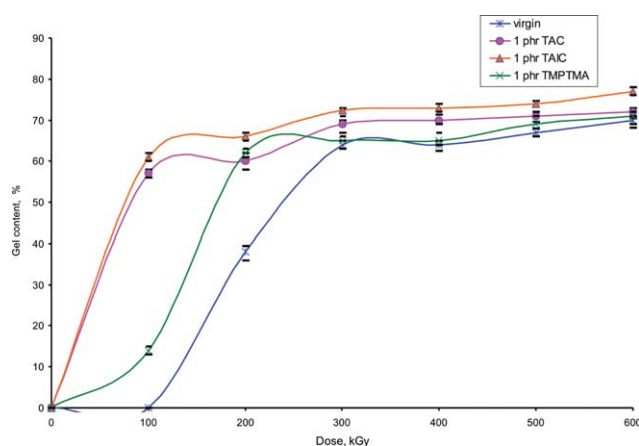


Figure 8 Variation of gel content with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nylon 66, on the other hand, have shown 57% (TAC) and 61% (TAIC) gel formation at 100 kGy, followed by a gradual increase to 72% (TAC) and 77% (TAIC) at 600 kGy. In the presence of TMPTMA, nylon 66 has shown 14% gel formation at 100 kGy, 58% at 200 kGy, and 68% at 600 kGy (Fig. 8).

$G(s)/G(x)$ value of virgin nylon 66 is determined from Charlesby–Pinner plot as 1.40, while it has decreased to 1.36 for TAC, 1.32 for TAIC, and 1.38 for TMPTMA (Table II). This is indicative of the occurrence of more crosslinking while crosslinkers are incorporated into nylon 66. Crosslinkers have played very important role by accelerating the process of crosslinking through the generation of free radicals during irradiation by e-beam. The decrease of the value of $G(s)/G(x)$ ratio in nylon 66 with the incorporation of various crosslinkers has been correlated with the change in mechanical as well as physical properties in Table III. The more the decrease of $G(s)/G(x)$ value, the better is the efficiency of the crosslinker to enhance the properties of nylon 66 through intermolecular crosslinking of the polyamide chains. Thus, TAIC is found to be the best crosslinker so far as improvement of physicomaterial properties of nylon 66 is concerned.

It is interesting to note that when a crosslinker is blended with nylon 66 by melt mixing, the mechanical properties of nylon 66 are much affected, even if it is not irradiated by e-beam. TAIC-blended nylon 66 has shown an increase of 2% hardness and 16% tensile strength, a decrease of 6% elongation percent and 42% impact strength, and a reduction of 14% water absorption at zero dose of e-beam when compared with the corresponding values of virgin nylon 66 (Figs. 1, 3–5, and 7). The change in mechanical properties and water absorption of nylon 66 at zero irradiation when crosslinker is incorporated into it by melt mixing may be attributed to the thermal crosslinking and/or postpolymerization of polyamide molecules occurred during melt mixing. Occurrence of crosslinking/polymerization has been verified in this study by the increase of gel content in nylon 66 with increasing dose of e-beam. In the case of virgin nylon 66, there is no gel formation till 100 kGy (Fig. 8). This is because the extent of thermal crosslinking/polymerization of polyamide molecules during melt mixing is not enough to form

TABLE II
 $G(S)/G(X)$ Values of Nylon 66 from Charlesby–Pinner Plot

Serial No.	Particulars	p_0/q_0	$G(S)/G(X)$
1.	PA 66	0.70	1.40
2.	PA 66 + 1 % TAC	0.68	1.36
3.	PA 66 + 1 % TAIC	0.66	1.32
4.	PA 66 + 1 % TMPTMA	0.69	1.38

TABLE III
Variation of Properties of Nylon 66 with Different Crosslinkers

Properties of Nylon 66	Virgin nylon 66	TMPTMA/ nylon 66	TAC/ nylon 66	TAIC/ nylon 66
G(s)/G(x) ratio	1.40	1.38	1.36	1.32
Decrease in water absorption at 400 kGy (%)	24	27	29	35
Increase in tensile strength at 400 kGy (kg/cm ²)	-19	-19	5	22
Increase of flexural modulus at 400 kGy (kg/cm ²)	40	40	48	52
Gel at 400 kGy (%)	62	64	69	72

insoluble and infusible mass of nylon 66 gel. This is, however, advantageous as far as the processability of nylon 66 is concerned as its processing is not affected by the thermal crosslinking/polymerization during its melt mixing with crosslinker.

It has been observed in this study that the improvement of most of the properties up to 200 kGy e-beam dose is much significant than that observed beyond 200 kGy. Table IV shows that when nylon 66 is irradiated at 0–200 kGy dose, there is an increase of hardness by 4 U, tensile strength by 50 kg/cm², gel content by 38%, and a decrease of elongation by 17%, impact strength by 48 J/m, and water absorption by 0.25%. On the other hand, the corresponding values at 200–600 kGy dose are observed as an increase of four unit of hardness, decrease of 131 kg/cm² of tensile strength, increase of 32% gel content, and a decrease of 10% elongation, 62% impact strength, and 0.15% water absorption. Similarly in TAC or TAIC mixed nylon 66, enhancement of most of the properties in 0–200 kGy dose range is much better and significant than that observed in 200–600 kGy dose. The major improvement of properties and performance of nylon 66 at lower doses of e-beam will undoubtedly emphasize on more industrial acceptance of radiation processing of this polymer over its conventional processing techniques.

DSC thermograms of TAIC blended nylon 66 as presented in Figure 9(a–c) reveal that crystalline melting temperature (T_m) and crystallization temperature (T_c) of nylon 66 have decreased gradually with increase of e-beam dose. T_m of nylon 66 has been reduced from 263 to 247°C while T_c decreased from 234 to 212°C, when irradiated from 0 to 600 kGy

dose. The decrease of melting and crystallization temperatures with increasing dose of e-beam is due to the reduction of crystallinity of nylon 66 in the presence of high energy radiation. The reduction of crystallinity of nylon 66 has been verified by the plot of percent crystallinity versus e-beam dose as shown in Figure 10. Sengupta and coworkers¹¹ studied on injection-molded nylon 66, where specimens were dipped in TAC solution before ambient temperature irradiation by e-beam and found that crystallinity decreased with increasing radiation dose. The decrease of percent crystallinity is indicative of the development of more amorphous nature in nylon 66 when irradiated by e-beam. Reduction of percent crystallinity of nylon 66 with increasing doses can be correlated with the decrease of water absorption and increase of gel content as shown in Figure 11. This indicates that as the dose of e-beam increases, there occur more crosslinking resulting in increased gel formation, which is responsible for the increase in amorphousness and decrease in hygroscopicity of irradiated nylon 66.

TGA thermograms of nylon 66 in the presence and absence of TAIC are shown in Figure 12(a,b). The temperature corresponding to maximum rate of degradation (T_{max}) has been increased from 440 to 450°C for nylon 66 virgin and to 460°C for TAIC-blended nylon 66 when irradiated through 300 kGy e-beam. Rate of degradation (dw/dT) has been decreased from 1.697 to 1.504%/°C for virgin nylon 66 and to 1.489%/°C for TAIC mixed nylon 66 at 300 kGy dose (Table V) indicating clearly that the thermal stability of nylon 66 has increased at higher doses of e-beam in the presence of crosslinker. Sengupta and coworkers¹⁵ also showed that nylon 66

TABLE IV
Change of Properties of Nylon 66 at 0–200 kGy Dose Range when Compared with 200–600 kGy Dose Range

Properties of Nylon 66	Virgin Nylon 66		TAIC-Nylon 66		TAC-Nylon 66	
	0–200 kGy	200–600 kGy	0–200 kGy	200–600 kGy	0–200 kGy	200–600 kGy
Increase in tensile strength (kg/cm ²)	50	-131	142	29	33	-104
Increase of Rockwell hardness	4	4	9	2	8	4
Decrease in percent elongation	17	10	10	4	22	5
Decrease in impact strength (J/m)	48	62	82	18	69	40
Decrease in water absorption (%)	0.25	0.15	0.39	0.18	0.33	0.14
Increase in gel content (%)	38	32	60	12	58	13

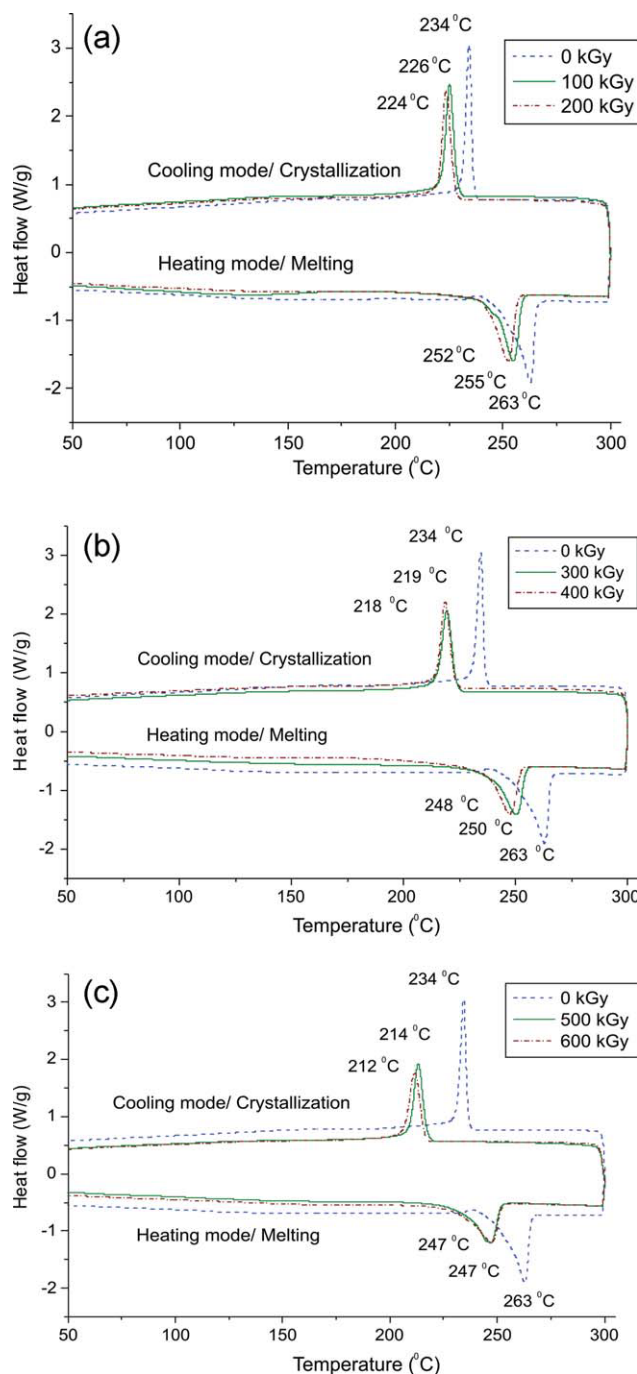


Figure 9 (a) DSC thermograms for TAIC mixed nylon 66 at 0, 100, and 200 kGy. (b) DSC thermograms for TAIC mixed nylon 66 at 0, 300, and 400 kGy. (c) DSC thermograms for TAIC mixed nylon 66 at 0, 500, and 600 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film specimens, which received an irradiation dose of 200 kGy e-beam in air, had a higher thermal stability than the neat nylon 66. Improved thermal stability of irradiated nylon 66 may be attributed to three-dimensional network developed by crosslinking of the polyamide chains on irradiation by e-beam. Improvement of thermal stability due to crosslinking

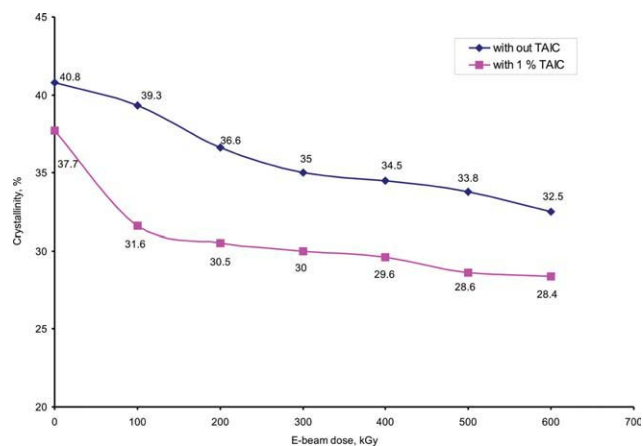


Figure 10 Percent crystallinity with dose of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is further confirmed by higher values of maximum degradation temperature and lower rates of degradation of TAIC mixed nylon 66 specimens than those of virgin nylon 66.

CONCLUSIONS

Nylon 66 when treated with e-beam in air at ambient temperature improved performances and properties are observed in comparison with those obtained from unirradiated nylon 66. The development of e-beam-irradiated crosslinked structures in nylon 66 has improved its many physicochemical properties to remarkably higher level. Changes in mechanical properties could be attributed to both increased crosslinking and reduced crystallinity in presence of high energy radiation. The e-beam-crosslinked nylon 66 may be useful for making rigid and

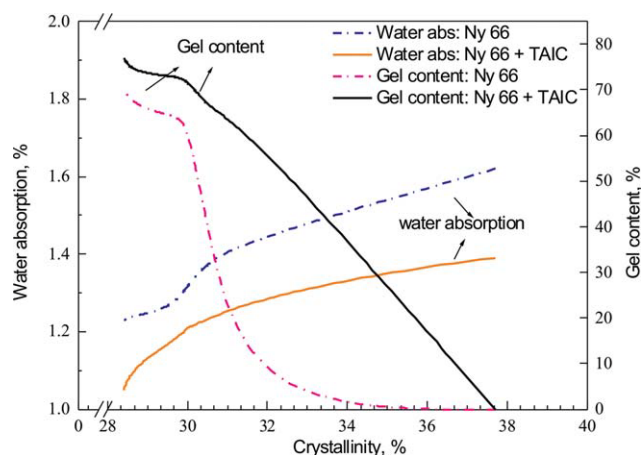


Figure 11 Variation of water absorption and gel content with percent crystallinity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

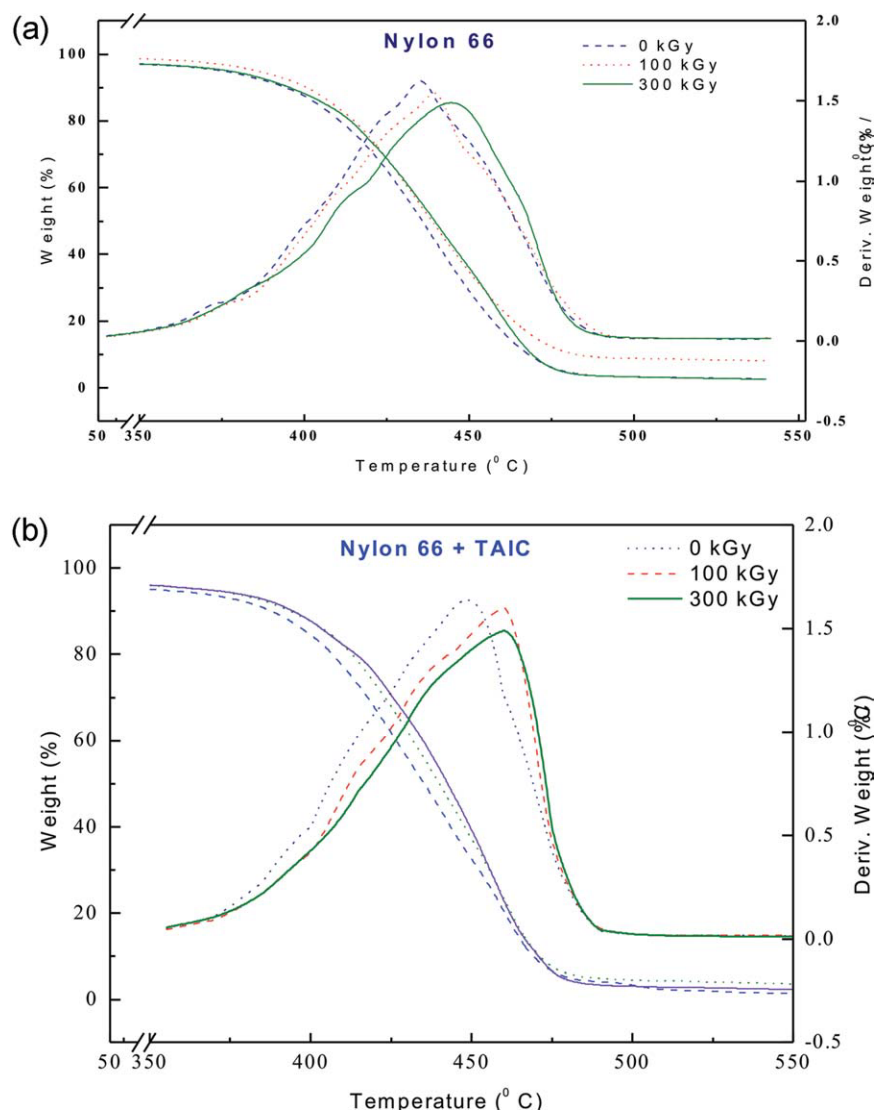


Figure 12 (a) TGA thermograms of nylon 66 at various doses of e-beam. (b) TGA thermograms of TAIC mixed nylon 66 at various doses of e-beam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dimensionally stable articles with superior mechanical properties and improved serviceability.

Hardness, tensile strength and modulus, and flexural strength and modulus of nylon 66 have improved largely when injection-molded test specimens are irradiated by e-beam up to a certain dose level. Crosslinker plays an important role during e-beam irradiation of nylon 66 resulting in larger improvement of properties than is found with virgin

nylon 66. TAIC is found to be the best crosslinker as it has caused maximum improvement of properties at a particular e-beam dose. The 200 kGy e-beam radiation is found to be the workable dose where a combination of all the best properties of nylon 66 has been observed.

Percent water absorption of nylon 66 has been found to decrease markedly with the increasing dose of e-beam. Decrease of water absorption at higher

TABLE V
 T_{\max} and Rate of Degradation at T_{\max} for Various Nylon 66 Specimens

Thermal parameters	Nylon 66			Nylon 66 + TAIC		
	0 kGy	100 kGy	300 kGy	0 kGy	100 kGy	300 kGy
T_{\max} (°C)	440	445	450	450	455	460
dw/dT (%/°C)	1.697	1.620	1.504	1.678	1.560	1.489

dose of e-beam reduces the inherent hygroscopicity of nylon 66 resulting in improved dimensionally stable articles made out of this material. Improved mechanical properties blended with enhanced dimensional stability by e-beam irradiation of nylon 66 would make this material certainly more attractive in designing intricate components out of it.

Improvement of mechanical properties and reduction of water absorption of nylon 66 by e-beam irradiation are due to the radiation-induced crosslinking/postpolymerization of the polyamide molecules in nylon 66. Formation of radiation induced chain branching in nylon 66 has been reported earlier by Dadbin et al.¹⁶ when irradiated by e-beam at 40–150 kGy doses. Development of crosslinked structure in irradiated nylon 66 has been evidenced by the formation of infusible and insoluble gel in irradiated samples. It is further verified by the increase of gel content in irradiated nylon 66 with increasing dose of e-beam. Presence of crosslinker has decreased $G(S)/G(X)$ value in irradiated nylon 66 indicating more crosslinking in irradiated samples than that occurred in virgin nylon 66.

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