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Radiation Effects in Polyamides

Mária Porubská

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Abstract

Polyamides (PAs) are largely used either as engineering materials in virgin form or as composites and a component of polymer blends. Various processes have been used to modify some properties of polymers to improve their utility. For this purpose, radiation technologies present clear, one-step procedures and offer improvement to the performance of PA materials. Irradiation by accelerated electron beams, γ-rays, and accelerated protons is applied on PAs, particularly PA-6, as well as PA composites. Variations of important characteristics, such as chemical structure, supermolecular structure, mechanical properties, thermal resistance, water absorption, and other parameters, are analyzed involving results obtained by other authors. The application of irradiation on incompatible polymer blends involving PA is presented as well. The selection of radiation treatment of PAs has to be considered to obtain optimal results.

Keywords: Polyamide, Properties, Electron beam, γ-rays, Proton beam

1. Introduction

Polyamides (PAs) are linear semicrystalline polymers containing amide groups -CO-NH- in the chains. The nomenclature applied for PA uses numbers to describe the number of carbons between acid and amine function groups including the carbon of the carboxylic acid. Two types of polyreactions are used for their preparation. The first, polyaddition, is based on a lactam as the starting reactant. After opening the lactam ring breaking peptide bond, the created end groups -C(O)- and -N(H)- are coupled with -N(H)- and -C(O)- groups originating from other cleaved molecules of the lactam. This is the case of PA-6 when ε-caprolactam is used.

$$n\left[(CH_2)_5 - CO - NH\right] \overset{H_2O}{\rightarrow} \left[-HN - (CH_2)_5 - CO -\right]_n \tag{1}$$
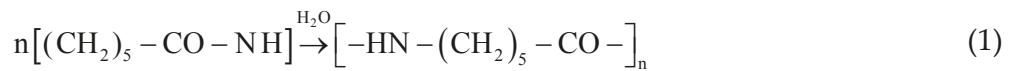
The same result can be reached using the corresponding amino acid. However, the cleavage of water molecules is required, which is the characteristic for a polycondensation mechanism. Therefore, polycondensation is the second polyreaction used to prepare PAs. The most commonly applied reaction is the polycondensation of dicarboxylic acids with diamines (e.g., adipic acid with hexamethylene diamine giving PA-66).

$$H_2N - (CH_2)_6 - NH_2 + HOOC - (CH_2)_4 - COOH \rightarrow \left[-HN - (CH_2)_6 - NH - OC - (CH_2)_4 - CO-\right]_n \tag{2}$$
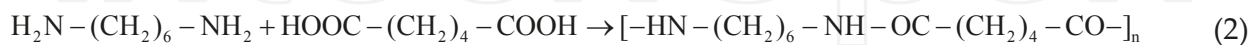
In such a case, the structure of the PA corresponds to the repetition of structure unit consisting of one of each monomer, so that they alternate in the chain unlike for a PA chain synthesized from a monomer as single starting reactant. Many demanding applications require a careful control of the synthesis as well as processing conditions considering the resulting molecular mass.

Variation of the starting reactants enables a large scale of PAs differing in properties from hard and tough PA to soft and flexible to be acquired. Depending on the type, PAs absorb different amounts of moisture, which affect the mechanical as well as dimensional characteristics. In general, PAs are characterized by high rigidity, hardness, abrasion resistance, thermal stability, good sliding properties, stress cracking resistance, barrier properties against oxygen, smells, and oils. The disadvantages of PA types involve a weak stability in the presence of UV radiation, oxidizing agents, strong acids, and bases, high shrinkage in molten section, degradation in electrical and mechanical properties due to high moisture absorptivity, and high notch sensitivity. The various particular properties of PAs enable various PAs to be processed into various items. They are most frequently used in the textile industry, electrotechnics, and automotive industry as engineering plastics either virgin or composites with modifying fillers. Depending on the type of the product application, the manufacturers can adjust the properties of initial materials to some extent. Besides physical modification, involving admixture of proper additives, the chemical modification of PA can also be applied. According to PA type, a high melting temperature within 170°C up to 290°C occurs. Therefore, the homogenous admixture of intended agents into the melt is possible only for sufficiently thermally stable substances. When the chemical modification of PA requires the generation of radicals (e.g., grafting various functional groups or crosslinking initiated by organic peroxides), then this modification cannot be always carried out in melt due to a weak thermal stability of some substances participating in the process. In particular, peroxides will be thermally destroyed well before the PA is melted. This handicap can be overcome using a proper radiation technology enabling such a modifying process in the solid state. Presenting a technology of one step, the radiation technologies have been largely applied during the last decades and have brought a wider spectrum of properties or design variations.

Because PA-6 and PA-66 comprise most of the world's market (~80%) [1], the effects of radiation modification involving them have been frequently investigated. Concerning some conflicting reports on electron beam effect on polymers found in scientific sources, in general, it could be said that variations in gel content in PAs irradiated with identical doses may not be the same. The reason is that the competing reactions, chain scission and recombination, can be affected by several factors, among others polymer type with its molecular characteristics. However, under irradiation, the most decisive factors are time and dose rate. The presence of oxygen provokes some side reactions and the consequence is a complex process. The oxygen effect can be hardly eliminated completely even if the irradiation is carried out in an inert atmosphere. Within the simultaneous process of recombination and scission macroradicals, the most important factor is the stationary concentration of the macroradicals.

Therefore, although the doses are the same, the results may differ if different electron beam sources and PA types are used. From this aspect, every comparison can be of framing character only. The same can be said regarding γ or proton exposure.

2. Electron beam irradiation of PAs

The effect of electron beam on PAs depends on several factors, such as installed parameters of the accelerator, absorbed dose, rate of the dose, environment of irradiation, geometry of irradiated object, temperature, and postradiation treatment. Concerning the environment, air is used mostly and an inert atmosphere is less common but more thrifty towards the polymer. Under irradiation of polymers, free radicals are created. Subsequently, two main actions take place, that is, recombination of the radicals resulting in crosslinking and oxidation resulting in polymer degradation. Both processes run in parallel [2], competing mutually, and the results depend on concrete conditions.

What exactly occurs when a PA is irradiated with an electron beam? An interaction occurs primarily in hydrocarbon sequences (R). The complete action involves three basic steps: initiation (generation of free radicals), propagation, and termination. In general, the following scheme can describe such processes.

Initiation:

$$R \rightsquigarrow R^* \rightarrow R^\circ + H^\circ \tag{3}$$

Propagation:

$$R^\circ + O_2 \rightarrow ROO^\circ \tag{4}$$

$$ROO^\circ + RH \rightarrow R^\circ + ROOH \tag{5}$$

$$\text{ROOH} \overset{\Delta}{\rightarrow} \text{RO}^\circ + \text{HO}^\circ \qquad\qquad (6)$$

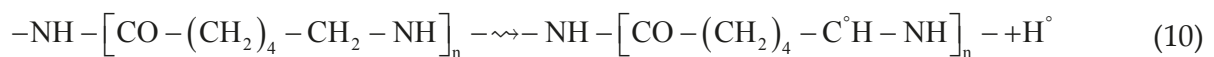$$\text{ROOR} \overset{\Delta}{\rightarrow} 2\text{RO}^\circ \qquad\qquad (7)$$

The generated radicals can take part in the destruction of the next hydrocarbon sequences, and hydroperoxides start the formation of new radicals and intermediates. In the presence of oxygen, the creation of carbonyl and aldehyde groups is significant as well.
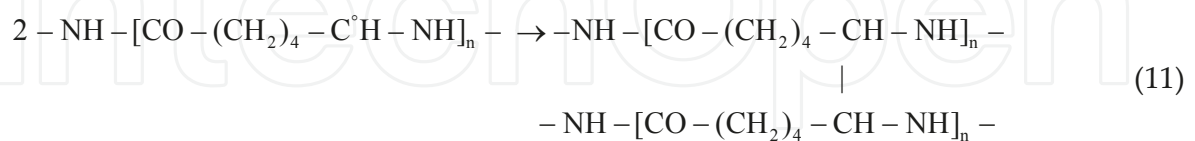
Termination:

$$\text{ROO}^\circ + \text{H}^\circ \rightarrow \text{ROOH} \qquad\qquad (8)$$

$$\text{ROO}^\circ + \text{R}^\circ \rightarrow \text{ROOR} \qquad\qquad (9)$$

In the case of PA-6, the splitting of H^0 from ethylene group occurs most probably in the vicinity of the –NH–CO– sequence:

$$-\text{NH} - \left[\text{CO} - (\text{CH}_2)_4 - \text{CH}_2 - \text{NH} \right]_n - \rightsquigarrow - \text{NH} - \left[\text{CO} - (\text{CH}_2)_4 - \overset{\circ}{\text{C}}\text{H} - \text{NH} \right]_n - + \text{H}^\circ \qquad (10)$$
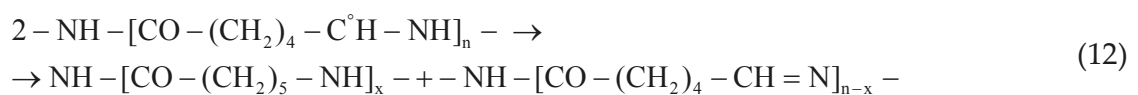
However, abstraction of hydrogen can occur in any other place within the hydrocarbon sequence as well.

Propagation takes place according to the above-mentioned steps. Termination of the radicals can occur as follows:
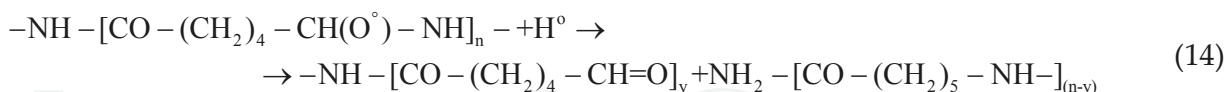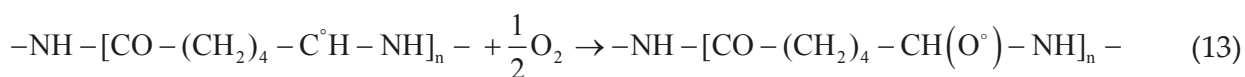
a) Crosslinking:

$$2 - \text{NH} - [\text{CO} - (\text{CH}_2)_4 - \overset{\circ}{\text{C}}\text{H} - \text{NH}]_n - \rightarrow - \text{NH} - [\text{CO} - (\text{CH}_2)_4 - \text{CH} - \text{NH}]_n -$$
$$| \qquad\qquad (11)$$
$$- \text{NH} - [\text{CO} - (\text{CH}_2)_4 - \text{CH} - \text{NH}]_n -$$

b) Disproportionation:

$$2 - \text{NH} - [\text{CO} - (\text{CH}_2)_4 - \overset{\circ}{\text{C}}\text{H} - \text{NH}]_n - \rightarrow$$
$$\rightarrow \text{NH} - [\text{CO} - (\text{CH}_2)_5 - \text{NH}]_x - + - \text{NH} - [\text{CO} - (\text{CH}_2)_4 - \text{CH} = \text{N}]_{n-x} - \qquad (12)$$

c) Oxidation and following degradation:

$$-NH-[CO-(CH_2)_4-\overset{\circ}{C}H-NH]_n-\ +\frac{1}{2}O_2\ \rightarrow -NH-[CO-(CH_2)_4-CH\left(O^\circ\right)-NH]_n-\qquad (13)$$

$$-NH-[CO-(CH_2)_4-CH(O^\circ)-NH]_n-\ +H^\circ \rightarrow$$
$$\rightarrow -NH-[CO-(CH_2)_4-CH{=}O]_y+NH_2-[CO-(CH_2)_5-NH{-}]_{(n\text{-}y)}\qquad (14)$$

Besides the above-mentioned irradiation conditions, the formation of intermediates and final products can be affected by the polymer structure, so that the products can be variable because of some side reactions.

2.1. Variations in chemical structure

In general, the modification of semicrystalline polymers by energetic radiation in the solid phase below the melting temperature of the crystallites is characterized by changes proceeding preferentially or, in many cases, almost exclusively in the amorphous phase [3,4]. Within the pre-crosslinking phase, there is the branching in the polymer [5] as revealed by the solution viscosity measurement for PA-6 [6,7] and glass fiber-reinforced PA-6 (PA-6/GF) with 30% GF [7], indicating an increase in the molecular weight due to the recombination of macroradicals at the polymer chain centers (**Figure 1**). Consequently also, viscosity increases in normal cases.
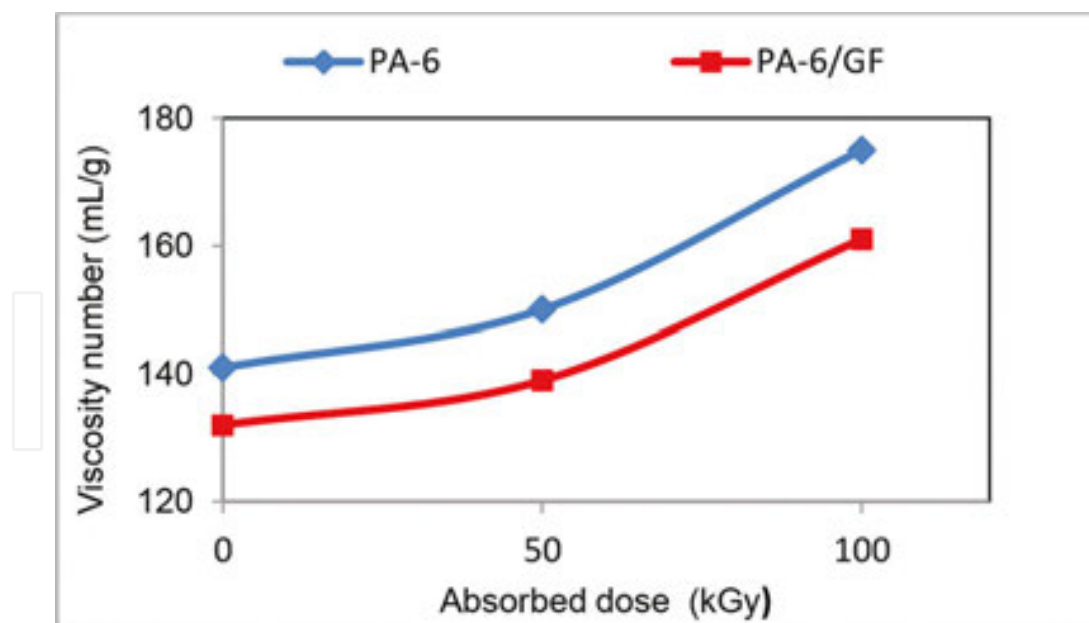

Figure 1. Dependence of viscosity number for virgin PA-6 and PA-6 in PA-6/GF on electron beam absorbed dose. Adapted from Porubská et al. [7].

A measurable portion of insoluble gel occurs at approximately 200 kGy (gel point) when the irradiation is conducted in air (**Figure 2**).
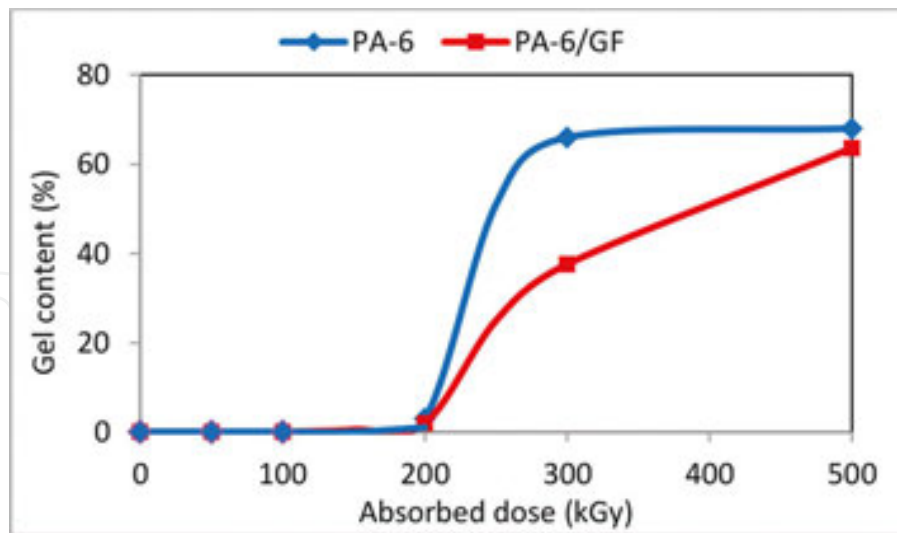
Figure 2. Dependence of gel content on absorbed electron beam dose for virgin PA-6 and PA-6/GF (30%) composite [7]. With permission of Elsevier.

This gel point is confirmed in several studies [7–10], although a low gel content for PA-6 was measured under the 150 kGy dose as well [11,12]. Some specific results in experiments with electron beam irradiation of PA-6 and PA-6,6 tyre cords and calendered fabrics are published by Aytaç et al. [13] when, contrariwise, some decrease in limiting viscosity number with increasing dose was observed within doses of 0 to 75 kGy. The measured data are explained by sufficient time for oxygen to diffuse into the samples during the foregoing calendering as well as by a low dose rate (25 Gy/pass). Under those conditions, radiolytic and oxidative degradation occur. The following strength testing confirmed the objectivity of the results.

Irradiation temperature	p_0/q_0	G_s	G_c	G_s/G_c
RT	0.63	0.49	0.39	1.3
50°C	0.60	0.61	0.50	1.2
70°C	0.49	0.46	0.50	0.91
80°C	0.29	0.23	0.40	0.58

Table 1. Radiochemical G_s scission yield and G_c crosslinking yield of PA-6 irradiated at different temperatures [10]. With permission of Elsevier.

Besides dose, temperature at the irradiation site also plays a role. As study [10] demonstrated that the crosslinking effect grows with increasing dose and temperature. Corresponding experiments with PA-6 film irradiated over a range of 15 to 1200 kGy (and at a dose rate of 4.48 kGy/min) were carried out at different temperatures from room temperature (RT) to 80°C involving the glass transition temperature (T_g) of approximately 50°C. Although the PA-6 gel point for all samples was observed more or less at 200 kGy, the gel content increased with temperature and the highest value (75%) was observed for a temperature of 80°C and dose of

800 kGy. The crosslinking rates of PA-6 irradiated above T_g are higher than those samples irradiated at temperatures below T_g. The increasing tendency in crosslinking with increasing temperature is attributed to the enhanced mobility of the PA-6 molecules above T_g; therefore, the probability of radical recombination is higher. The radiochemical yields of crosslinking and degradation determined according to the Charlesby-Pinner equation [14] are given in **Table 1**.

The ratio p_0/q_0 [(ration of main chain fractures to chain units)/(units crosslinked to chain units)] for PA-6 decreases with the increase in radiation temperature of the samples. This is a consequence of higher mobility of the chains and the recombination of radicals generated by the main chain scission as well as by the release of hydrogen radicals due to electron beam energy [Eq. (3)], indicating that crosslinking is the predominant process at temperatures above T_g. In contrast, the scission prevails at RT, below T_g [10,11]. Compared to the G_s/G_c values reported for PA-66, the scission dominates more in PA-66 than in PA-6 [8,9,15,16]. This demonstrates that a small difference in PA structure can play a role.

The final amount of the gel in polymer is limited. Generally, in virgin PA, the gel portion grows dramatically beyond the gel point and, in a certain phase, becomes stabilized. The reason is that a balance between the scission and recombination occurs, as the increasing viscosity in the matrix due to crosslinks breaks the mobility of the radicals to recombine. Although the gel content remains the same, the decrease of the swelling [17] or molecular weight between crossbonds [10] with increasing doses indicates that the network becomes denser [7] as seen in **Table 2**.

Dose (kGy)	RT	50°C	70°C	80°C
300	41,000	31,500	31,900	40,300
400	30,800	23,600	23,900	30,250
600	20,500	15,700	15,900	20,100
800	15,400	11,800	11,900	15,100
1000	12,300	9500	9500	12,100

Table 2. Average molecular weight between crosslinks (Mc) in PA-6 samples irradiated at different temperatures and doses [10]. With permission of Elsevier.

Irradiation experiments were also conducted in an inert (nitrogen) atmosphere and also with the annealing what led to lower chain scission and increased crosslinking reaction [18].

The crosslinking agents for polymers, including PAs, are molecules that contain two or more double bonds per molecule, such as triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), and trimethylolpropane trimethacrylate (TMPTMA). The energy of electron beam easily cleaves them into radicals formatting cross-bonds. Then, the crosslinking agent can increase the crosslinking rate and shift the gel point to a much lower absorbed dose [6] because of the higher efficiency of free radical production. The presence of a filler (e.g., GF reinforcement) in the PA matrix can also modify the crosslinking rate, even if contrarily [7] in comparison to the

crosslinking agents. The filler increases the viscosity of the matrix, which leads to a retardation of the cross-bond formation when compared to virgin PA due to slower macroradical recombination, leaving more time for disproportionation.

Concerning gel formation, the application of electron beam irradiation on incompatible polymeric blends or layers in laminates to generate free radicals and the following interaction, the grafting, between the components to improve their compatibility, can vary from case to case. Gel point shifts depending on the character of the polymeric components as well as possible crosslinking agent addition are shown in several works involving PA-6 [19–21]. Rare data on electron beam effect on gel creation in PA-12 can be found for ethylene propylene diene monomer (EPDM)/PA-12/maleated EPDM blend and these do not show any PA-in origin gel up to 200 kGy [22].

It is worth mentioning that crosslinking becomes easier as the number of methylene groups between the amide groups increases [23,24]. This finding is based on the gel measurement on PA-6, PA-610, and PA-12 irradiated under the same conditions. This conclusion is understandable because, as mentioned above, the initiation starts through a hydrocarbon sequence. The longer the hydrocarbon sequence, the more probable the hydrogen abstraction occurs.

2.2. Thermal properties related to supermolecular structure

Differential scanning calorimetry (DSC) is a useful tool to examine the structural variations in irradiated polymeric materials. Two basic types of data can be obtained from DSC curves, melting or crystallization temperature (T_m or T_c) and melting or crystallization enthalpy (ΔH_m or ΔH_c). The former is connected with the size of the crystalline units, whereas the last corresponds to the crystalline portion. The larger the crystalline unit, the higher T_m observed. Similarly, the more the crystalline phase in the polymer, the higher the melting enthalpy measured. In general, for most polymers fully or partially crosslinkable by electron beam irradiation, the dependences of both melting temperature and melting enthalpy on the dose measured from the first DSC heating reflect immediate changes in the original crystalline structure occurring during irradiation. The data from the second melting demonstrates the overall changes particularly due to irradiation-induced crosslinking and partial degradation, both occurring during irradiation mainly in the amorphous phase. The original crystalline structure melts within first heating. The following cooling leads to the crystallization of the melt of the irradiated polymer, so that the effect is related to the overall degree of crosslinking, representing defects hindering the crystalline structure formation after melting during the first heating [2]. The kinetic parameters of processes linked to the heat exchange can be determined as well.

Because PAs are semicrystalline polymers, DSC is used often to characterize them. As mentioned previously, the crosslinking mainly occurs in the amorphous phase. The effects of dose on the T_m determined for virgin PA-6 in the first and second runs (melting T_{m1} and remelting T_{m2}) are displayed in **Figure 3**, whereas **Figure 4** shows the dependence of melting and remelting enthalpies. A monotonous decrease in the T_m is observed over the 0 to 500 kGy dose range and the second run (T_{m2}) is lower than the first run (T_{m1}) [7,16].
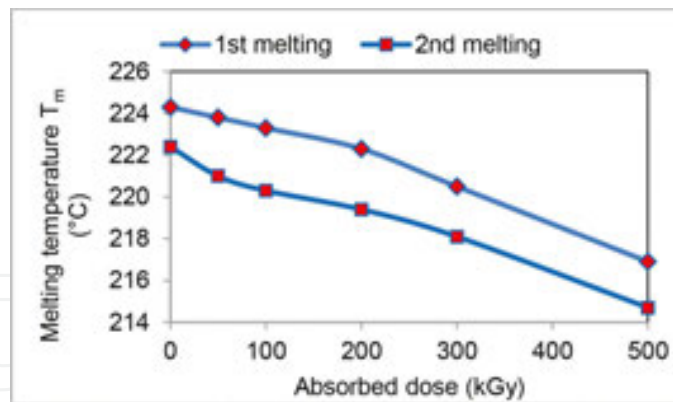
Figure 3. Variation of the first and second melting temperatures with absorbed electron beam dose for virgin PA-6 [7]. With permission of Elsevier.
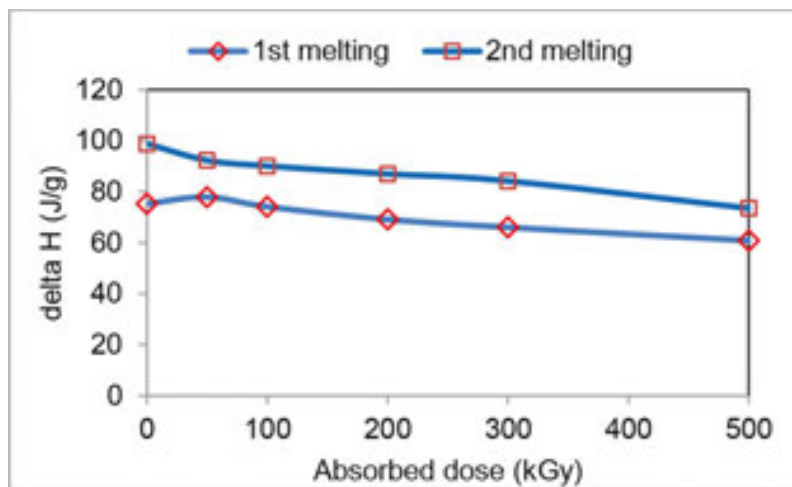

Figure 4. Variation of the first and second melting enthalpy with absorbed electron beam dose for virgin PA-6 [7]. With permission of Elsevier.

Such behavior is typical for the second run of irradiated crosslinkable polymers after melting and following the crystallization of a previously crosslinked material. The decrease of T_{m1} points to the thinning of the lamellae as a consequence of crystalline phase disruption within irradiation. The decrease in ΔH_1 indicates this fact, too. Consequently, it can be implicated that, during irradiation also, a considerable degradation occurs along with crosslinking. Similar facts are observed, irradiating PA-6 at temperatures above T_g with doses of 0 to 1200 kGy. T_m decreased from 224°C for 0 kGy up to 213°C for 1000 kGy. However, irradiation at RT leads to a decrease of T_m up to 600 kGy only with a subsequent mild increase [10]. One possible explanation may be the formation of larger crystallites due to a higher generation of smaller fragments from PA chains at higher doses and those being more mobile incorporate into existing crystallites more easy. This suggestion is in compliance with the finding that the samples irradiated above T_g showed a predominance of the crosslinking over scission (Section 2.1).

The effect of irradiation on crystallinity is linked with the values of the melting enthalpy directly proportionally, and some decrease is observed for virgin PA-6 with rising dose (**Figure 4**). The higher value of ΔH_{m2} than ΔH_{m1} for PA-6 (**Figure 4**) is a consequence of different cooling rates between cooling the testing specimens after preparation by injection molding (using a higher initial cooling rate from the processing temperature of ~290°C) and cooling of the sample after first heating in the DSC cell (applied cooling rate of 10°C/min). Therefore, a lower crystalline portion is the result for rapidly cooled materials. The irradiation effect on PA-6 is also observable on the shape of the DSC melting curves (**Figure 5**).
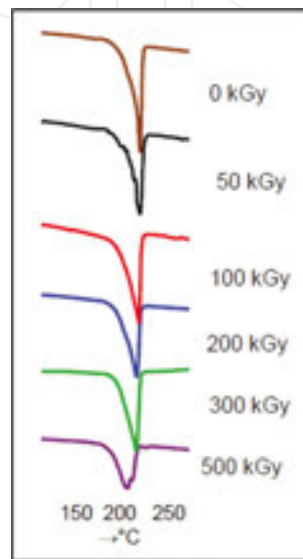
Figure 5. DSC melting endotherms of first melting (150–250°C) for PA-6 irradiated with electron beam.

The endotherms of irradiated samples become wider with increasing dose as a consequence of the progressive lamella thinning and amorphization that took place under electron beam irradiation. Additionally, the enlargement in the peaks indicates that the distribution of crystallite size becomes broader while the unit endotherm surface (ΔH_m) decreases.

PA-6 included in a multilayer film and irradiated in nitrogen applying a dose in the range of 0 to 150 kGy shows only a small total decrease in melting temperature at approximately 1°C and the crystallinity is diminished from 25.3% to 21.5% [18].

The influence of the crosslinking agent TAC on PA-6 irradiated with relatively low doses up to 100 kGy demonstrates a more pronounced effect on T_m and crystallinity than present in virgin PA-6. The decrease in both T_m and crystallinity for the doped PA is clearly observable already for the 40 kGy dose, whereas, for the virgin PA-6, the decrease is moderate, if any. The decrease in T_m seems to be dependent on TAC content (the more TAC, the lower the T_m), but the measure of the decrease in crystallinity is not affected by TAC content in the range of 1% to 3% [6].

The development of thermal characteristics with dose can somewhat vary when PA is part of a blend or composite. PAs are often used as reinforced composites or filled with various fillers,

with GF being the most common reinforcing additive. There is not much information on the crosslinking of reinforced PAs (PA/GF) in the scientific literature. Concerning the changes in the melting temperature (**Figure 6**) and enthalpy of PA-6/GF (**Figure 7**) with rising dose, they are much less pronounced for PA-6/GF composite compared to virgin PA-6 (Figures **3** and **4**), indicating that the presence of GF partially eliminates the irradiation effects on PA. This conclusion arises from the dependences in **Figure 2** as well.
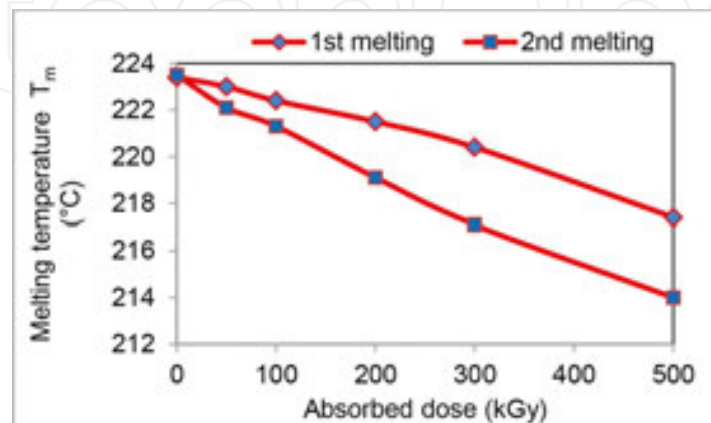
Figure 6. Variation of the first and second melting temperatures with absorbed electron beam dose for PA-6/GF(30%) composite [7]. With permission of Elsevier.
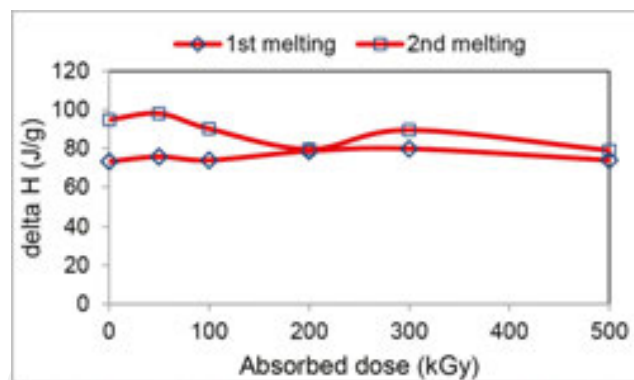

Figure 7. Variation of the first and second melting enthalpy with absorbed electron beam dose for PA-6/GF (30%) composite [7]. With permission of Elsevier.

The examination of (PP/PA-6+talc) composite with or without a compatibilizer or a crosslinking agent TAIC, applying a dose in range of 0 to 200 kGy [25], reveals a decrease in T_m for PA-6 component only when doses 50 and 100 kGy are used. A dose of 200 kGy provokes already a minor T_m growth and that is evident for the formulation containing TAIC. However, all T_ms are lower than the T_ms for the corresponding unexposed composite. Concerning the degree of PA-6 crystallinity, the percentage for (PP/PA-6+talc) formulation varies mildly being lower for the initial crystallinity; for the formulation involving the compatibilizer and TAIC, the decrease is definite.

The behavior of PA-66 is similar to PA-6 in principle. Injection-molded PA-66 samples irradiated with 200 and 500 kGy doses show the decrease in initial T_m regardless of the addition of TAC or the exposure at RT or 120°C. Nor does the water annealing affect this tendency, but the decrease for the samples with no TAC irradiated at RT is a little less when compared to the others. The same can be said about the crystallinity [15]. Thus, the dependences of the crystallinity on dose for PA-66 films [8] and for the injection-molded pieces are the same essentially regardless of the mode of sample preparation.

Data on PA-12 melting characteristics are found for EPDM/PA-12/maleated EPDM blend after being irradiated with 25 to 100 kGy doses [22]. Melting temperature does not show any change and the crystallinity is more or less also the same. However, such a narrow dose range does not allow the estimation of further development under higher doses.

2.3. Mechanical properties

The molecular and supermolecular structure of a polymer determines its properties. When any variation occurs in the structure, it should manifest itself in some changes of the properties. Electron beam activates significant structural changes, namely, scission and crosslinking as well as oxidative degradation if irradiated in air. Each particular property of a polymer is unequally sensitive towards the structural modification; therefore, it is important for examination to be focused exactly. Tensile properties, such as Young's modulus, strength at yield or break, elongation at yield or break, and flexural and impact parameters, reflect these variations well.

In general, when virgin PA is irradiated, the development of the tensile parameters follows the general framework that modulus and stress at yield are progressive, whereas stress at break and elongation are regressive. The scale of measured values is a question of the quality of the irradiated PA. The shape of stress-strain curves for the same PA remains similar irrespective of the absorbed dose [16].

The dimensional stability on load, the stiffness, is one important parameter for design engineers. In thermoplastics, the shape stability is affected by the crystallinity content to a great extent. Within the tensile properties, Young's modulus is the corresponding testing parameter for stiffness. As mentioned in Section 2.1, electron beam irradiation in the solid state results in crosslink formation primarily in the amorphous phase or at the crystal boundaries [3,4]. In addition, for thermoplastics, an observable increase in the strength parameters occurs when the gel content is at or more than 50 wt% [4]. Thus, unless the crystalline phase is substantially degraded, notable changes in the modulus will not occur as evident from the dependences of Young's modulus for virgin PA-6 and PA-6/GF composite (**Figure 8**).

In reality, regarding a large fluctuation in the standard deviation (brought on by GF dispersion within the PA matrix) for the composite, any variations of Young's modulus are statistically nonsignificant to be presented. Concerning virgin PA-6, the increase in the modulus is evident at 500 kGy dose when the gel content is more than 50%. In another study [11], a steady increase in the modulus of virgin PA-6 is measured within the dose range of 100 to 500 kGy. However, in this case, the gel point is measureable already at approximately 100 kGy and 50% growth
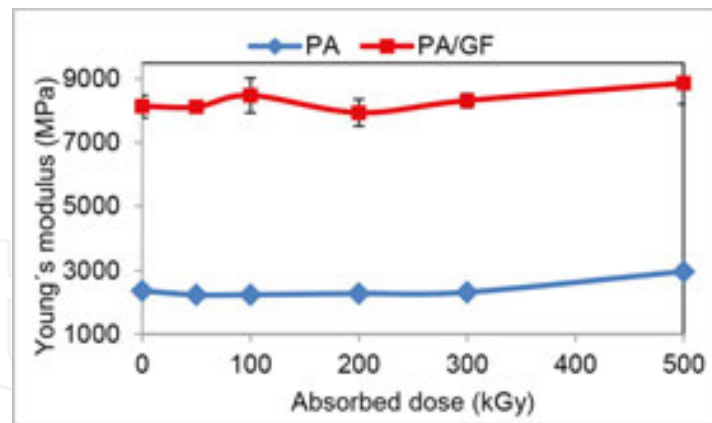
Figure 8. Variation of Young's modulus with absorbed electron beam dose for virgin PA-6 and PA-6/GF (30%) composite [7]. With permission of Elsevier.

in the gel content can be estimated at approximately 150 kGy. The relative increase in the modulus at a 500 kGy dose is approximately the same (28% over the initial rate) as the above-mentioned result. When the crosslinking agent is added to the polymer to increase the gel formation, the limit of 50% gel is achieved earlier. Therefore, the higher modulus is observed when compared to the virgin polymer [11], as the crystalline phase, being not yet impaired, is supported by the sufficient gel portion.

The modulus and yield tensile strength of injection-molded PA-66 irradiated in the range of 0 to 500 kGy are found to increase over the unexposed samples with dose but displays a maximum at 200 kGy. Similar results are obtained in the elongation development; however, beyond 200 kGy, the elongation is reduced below the initial value [15] due to crosslinking.

The influence of the crosslinking agent can also be demonstrated on tensile strength and elongation of PA-6 exposed to irradiation within the range of 0 to 100 kGy. These characteristics are kept the same [6], because this dose range does not involve the gel point yet. However, the addition of the crosslinking agent increases the tensile strength and a decrease in the elongation immediately from 40 kGy, indicating that the corresponding gel point is lower than 40 kGy in this case. The higher the crosslinking agent concentration, the greater the effect is found.

The importance of the selection of the crosslinking agent is reflected by the experiment where PA-66 is doped with 1% TAC, TAIC, or TMPTMA when irradiated with doses up to 600 kGy [12] in air. The tensile strength for virgin PA-66 and PA-66 with TAC exhibits a similar pattern of initial rise up to 200 kGy followed by a gradual reduction up to 600 kGy. In the case of PA with TMPTMA, the tensile strength reduces continually. In the case of TAIC, in contrast, the strength rises throughout the whole range of irradiation. The elongation of PA-66 virgin as well as PA-66 with TAC or TMPTMA reduces displaying a sharp decrease at 100 kGy for the PA containing the agents and a more moderate decrease for virgin PA-66 up to 300 kGy. Beyond these doses, the corresponding values change negligibly. The elongation of PA-66 with TAIC follows a completely different course. It gradually drops over the entire range of dosage and the resulting elongation is the highest when compared to others (**Figure 9**). This possibly

indicates that, despite having the highest gel content, the network is less dense, with TAIC saving more elasticity compared to others.
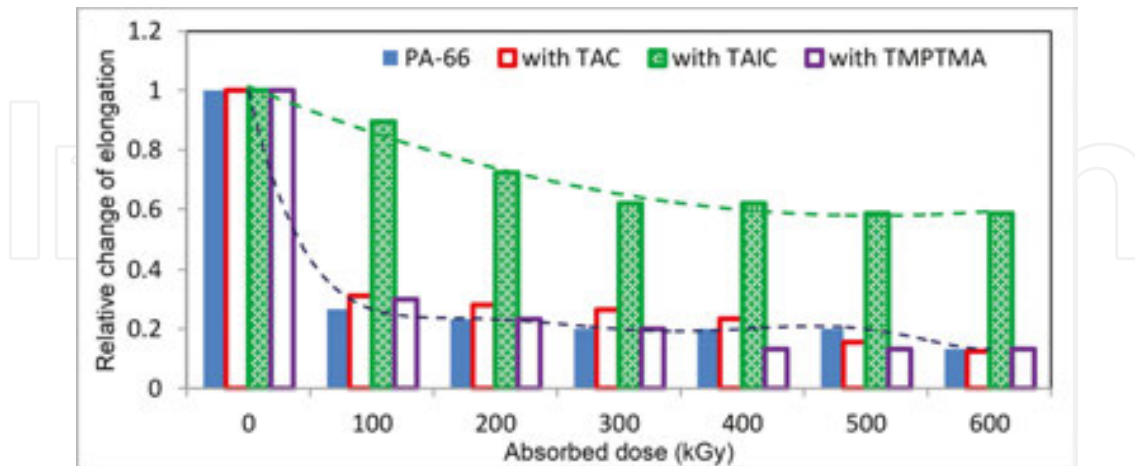

Figure 9. Relative variation of elongation of PA-66 with and without crosslinking agents with dose of e-beam. Adapted from Pramanik et al. [12].

Concerning the modulus (**Figure 10**), this increases beyond 200 kGy sharply for virgin PA-66 in compliance with the above-mentioned finding that at least 50% gel is needed to contribute towards the modulus increase [4].
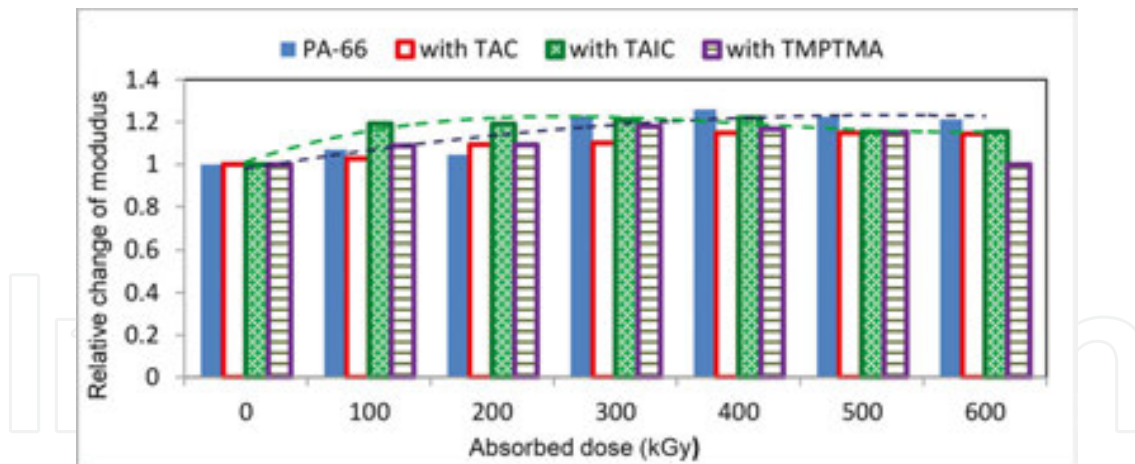

Figure 10 Relative variation of tensile modulus of PA-66 with and without crosslinking agents with dose of e-beam. Adapted from Pramanik et al. [12].

The addition of the crosslinking agents increases the modulus over the virgin PA-66 in the order of TAIC>TAC>TMPTMA, although the dependences follow individual courses. The crosslinking efficacy of the agents in PA-66 is of the same order as well.

The effect of another agent, glycidyl methacrylate (GMA), is similar [21]. PA-6 doped and then irradiated with a dose in the range of 0 to 200 kGy in nitrogen to condensate mutually shows

a modulus at 100 and 200 kGy, which is 36% and 45%, respectively, above the unexposed virgin PA-6. At the same time, the corresponding tensile strength is determined to be approximately 15% over the virgin PA-6.

Radiation technology is used in an effort to improve the deficient compatibility of different polymers in blends or composites and to model the resulting properties to a certain extent due to the binding of each other through free radicals generated in the components. PA-6 and linear low-density polyethylene (LLDPE) are typical immiscible polymers. The morphologic examination of the mixture of the PA-6/LLDPE/GMA exposed to electron beam under nitrogen atmosphere within the range of 5 to 200 kGy displays a reduced diameter of the dispersion particles and an increase in the interfacial adhesion. The elongation at break of the blend irradiated at 100 kGy is approximately four times higher than that of the virgin PA-6. This parameter is strongly reduced when the blend is irradiated at 200 kGy, which is supposed to be the crosslinking of LLDPE [20]. The tensile strength and modulus increase with rising irradiation dose nonlinearly.

Electron beam irradiation of multilayer film LDPE/PA-6/LDPE with doses up to 125 kGy in nitrogen results in the increase of the tensile strength and the decrease of the elongation [18].The growth is more rapid up to 50 kGy and then is more moderate. In contrast, the elongation decreases presenting a mirror curve to the strength. This phenomenon is explained by the formation of carbonyl groups in LDPE in the case of the low doses, which facilitate the miscibility of the LDPE with PA-6. On the contrary, at high doses, the presence of crosslinked LDPE would most likely introduce microregions of immiscibility with the PA-6.

The preparation of a thermoplastic elastomer from an immiscible blend consisting of the EPDM, maleated EPDM, and PA-12 is another demonstration of the utility of electron beam irradiation [22]. The irradiation was conducted up to 100 kGy in nitrogen so that PA-12 chain scission occurred generating free radicals but no crosslinking and led to a mutual link of the components and from disastrous mechanical properties to desired ones. The increase is quoted for Young's modulus, tensile strength, and elongation; in addition, the recyclability of the thermoplastic elastomer is gained for three cycles at least.

Waste polymers can be used again when they are combined with other appropriate components. Therefore, waste PA copolymer PA-66/PA-6 blended with acrylonitrile butadiene rubber and subjected to electron beam irradiation shows tensile strength and elongation, depending on dose and composition, at levels between the parameters of those individual components. The obtained compatibility matches with scanning electron microscopy (SEM) images [26].

A composite consisting of ethylene-vinyl acetate copolymer (EVA) flame retarded by a combination of cellulose acetate butyrate microencapsulated ammonium polyphosphate, PA-6, and TAIC reveals a drastic increase in tensile strength by 62% over the initial value at 160 kGy. Beyond this dose, the tensile strength falls, whereas the elongation at break decreases continually from the beginning [27].

Adhesive joints in composite items often involve PAs. Polycarbonate (PC) sheet covered with PA-6 being irradiated with dose of 43 to 432 kGy [28] displays variation in the fracture stress

and elasticity of the joint as dependence on dose differing from the neat components. Whereas the fracture stress for the composite increases up to approximately 120 kGy and levels beyond this, the strain falls with rising dose up to 220 kGy and then increases. Some optimum in the characteristics could be found according to topical design requirements.

Young's modulus of composite (PP/PA-6+talc) with or without a compatibilizer or crosslinking agent TAIC, applying a dose of 0 to 200 kGy [25], gives the dependence on dose with composition. Whereas the modulus of the mixture containing all components accounts for only 73% (PP/PA-6+talc) before irradiation, it exceeds the other mixtures after 200 kGy irradiation. Qualitatively, the same tendency is observed for tensile strength, too. These results indicate that, with a combination of suitable composition and electron irradiation, materials could be designed with the desired properties.

Further research in this field is open and not all efforts lead to desired results. For example, experiments with composites of monomer casting PA-6 containing 2% nanofillers as particle carbon or silicon carbide or carbon shortcut fibers with no crosslinking agent give only 6% increase in tensile strength and Young's modulus when irradiated by electron beam with 20 kGy dose [29].

The weakness of PAs as semicrystalline materials is quantified for a low impact strength or toughness. After virgin PA-6 is electron irradiated, a considerable deterioration of these parameters is found. The Izod impact strength falls sharply with the rising dose, and after absorbing 600 kGy, the impact strength retains 31% of the initial level only. The addition of the crosslinking agents changes this uniformly decreasing behavior. According to the agent type, the dependence of Izod impact strength on dose is of variable character, reaching a maximum at 400 kGy followed by a sharp decline beyond this dose [11]. However, the net result is a decrease when compared to the nonirradiated sample. A rather different situation occurs for PA-66 [12]. The Izod impact strength of virgin PA-66 is reduced at 100 kGy to 68% of the initial value and then displays a leveling effect up to 300 kGy, and beyond this dose, a sharp decrease is followed by no significant change at higher doses. Again, the crosslinking agents have a variable influence and result in a dependence including smaller fluctuations in comparison to the virgin PA-66. An observation of the fracture surface leads to the finding that both virgin and crosslinker-doped PA-66 irradiated up to 300 kGy show ductile failure, whereas the materials irradiated with doses of 400 to 600 kGy indicate brittle failure. One of the several reasons why electron irradiation lowers the impact strength may be a certain obstruction in the dissipation of the impact energy when the initial amorphous phase is progressively crosslinked and restricted in the chain motion and relaxation. The contribution of oxidative degradation becomes more evident in the reduction at higher doses.

The flexural characteristics for PA-6 reveal an analogous behavior with the corresponding tensile strength and tensile modulus (i.e., they increase with dose) [11]. The increase in the flexural modulus at 500 kGy is 13% over the initial level and the flexural strength 20%, respectively. The addition of effective crosslinking agents TAIC and TAC raises these values. In the case of PA-66, the flexural modulus increases up to 400 kGy by 40% and then it falls sharply, remaining still at an increase of 20% over the initial level [12]. The same crosslinking

agents as in the PA-6 increase the flexural modulus, almost copying the behavior of virgin PA-66 at a higher level.

The irradiation of composite (PP/PA-6+talc) with 0 to 200 kGy doses leads to an increase in flexural strength by 18%; when the composite contains also the compatibilizer and crosslinking agent TAIC, the increase is higher by 137%. Both corresponding flexural moduli are increased by 24% and 200%, respectively [25].

It can be concluded that, besides irradiation conditions, the mechanical properties in blends of PA with other polymers or modifiers are dependent on the character of all components and the interactions between them induced by the irradiation.

2.4. Thermal resistance

The thermal resistance of polymers is usually measured by heat deflection temperature (HDT) and Vicat softening temperature. There are other specific tests adjusted to the factual requirements of manufacturers. However, they are used by narrow groups of design engineers and in the framework of quality testing.

The HDT (or heat distortion temperature) is the temperature at which a polymer sample deforms under a specified load. It might be expected that parameter HDT will increase with rising dose. In fact, for PA-6 irradiated within 0 to 500 kGy, it is found that there is a progressive growth up by 9°C at 500 kGy. All the related values appear near 50°C, the T_g of PA-6 [7]. The HDT increase with increasing dose reflects the progressive restriction of the chain mobility in the amorphous phase as a consequence of the network structure formation and the lower deformability (**Figure 11**).
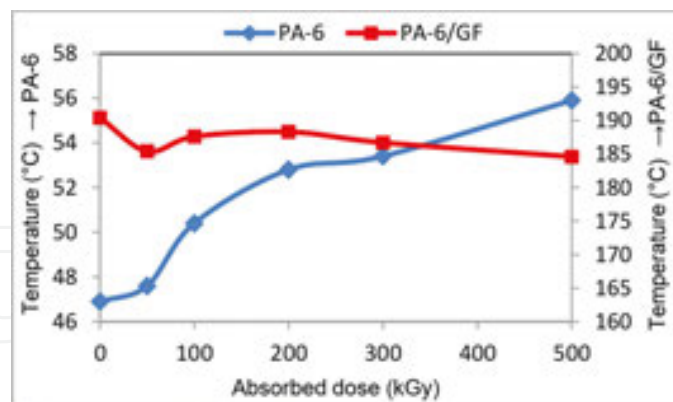

Figure 11. Variation of HDT with absorbed electron beam dose for virgin PA-6 and PA-6/GF (30%) composite. Adapted from Porubská et al. [7].

A different situation is in GF-reinforced PA-6. The presence of GF restrains the segmental motion of the polymer chains, and therefore, the initial HDT (190°C) observed for the composite PA-6/GF is much higher than virgin PA-6 (47°C). Unlike the virgin PA, the HDT values for PA-6/GF decreases in response to irradiation, with a decrease of 6°C at the highest dose [7]. Analogous results can be assumed for other composites as well.

How much crosslinking can affect HDT for PA-6 is seen from the electron beam irradiation of PA-6 containing 2% TAC. Whereas the HDT before exposure is 120°C, after absorbing 80 kGy dose, this figure increases up to 170°C [6] due to ~96% gel content (**Figure 12**).
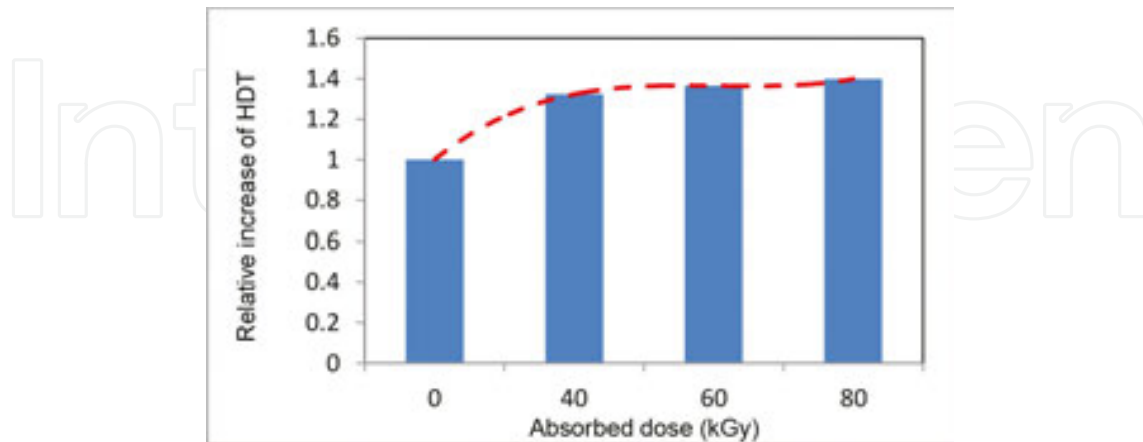

Figure 12. Variation of HDT with absorbed dose for PA-6 at 2% TAC level. Adapted from Dadbin et al. [6].

The irradiation of composite (PP/PA-6+talc) in the range of 0 to 200 kGy displays the rise in HDT depending on the dose from 63°C for the nonirradiated sample to 72°C for that irradiated with 200 kGy. However, when compatibilizer and crosslinking agent TAIC is incorporated in the composite, the HDT gives value of 84°C [25].

The Vicat softening temperature (or Vicat hardness) is taken as the temperature at which the specimen is penetrated to a depth of 1 mm by a flat-ended needle with a 1 mm^2 cross-section. There is not much information on the effect of electron irradiation on the Vicat softening temperature for PAs in the scientific sources. Unlike the HDT, the Vicat temperature for virgin PA-6 (186°C) reaches a maximum (190°C) at the lowest dose of 50 kGy and then decreases with increasing dose nearly returning to its original level (187°C) [7]. The mentioned increase is possibly related to the release of physical entanglements due to the supplied energy from the electron radiation. That enables the involvement of some released segments in amorphous phase into the crystalline phase and its enlargement. A moderate increase in the melting enthalpy/crystallinity at 50 kGy dose corresponds to this. The decrease in the Vicat temperature at a higher dose is assigned to the progressive disruption of the surface structure and the thinning of the lamellae what is obvious also from the lower melting onset (**Figure 3**). The softening temperature for PA-6/GF composite is less pronounced, with a total decrease of only 2°C (**Figure 6**). This observation corresponds to the different crystallinities of both materials (PA-6/GF > PA-6).

2.5. Water absorption

Generally, PAs tend to absorb water due to the nonbinding interactions of water molecules with polar groups in the matrix. The water present in PA acts as a plasticizer. The water absorption affects the dimensional stability and mechanical properties of the polymers,

whereas humidity in PA matrix can support hydrolytic destruction and can also be a source of oxygen when PAs are processed or irradiated accelerating the polymer oxidative degradation. Therefore, water absorptivity is one of the crucial parameters affecting the PA properties. That is why the comparison of some characteristic values for various PAs requires a standard conditioning (temperature, humidity, and time) before the PA is tested.

The entry of water molecules into a PA matrix is controlled by diffusion. The penetration of the matrix by water molecules requires enough space inside the matrix for the translation motion of water molecules. The space is formed by vacancies due to the rotating movement of segments of macromolecule chains. The fewer the restrictions of motion in the polymer segments, the more vacancies are created. Because the crosslinking shortens the chain sequences between the cross-points and thus restricts the segmental rotation, water molecule mobility in the polymer should be more difficult suppressing water diffusion. This supposition is confirmed empirically. Water absorption in PA-6 irradiated in range of 0 to 600 kGy decreases throughout all doses from 2.3% to 1.7% at the highest dose [11]. As expected, the decline is greater with the incorporation of the crosslinking agents TAIC or TAC (**Figure 13**).
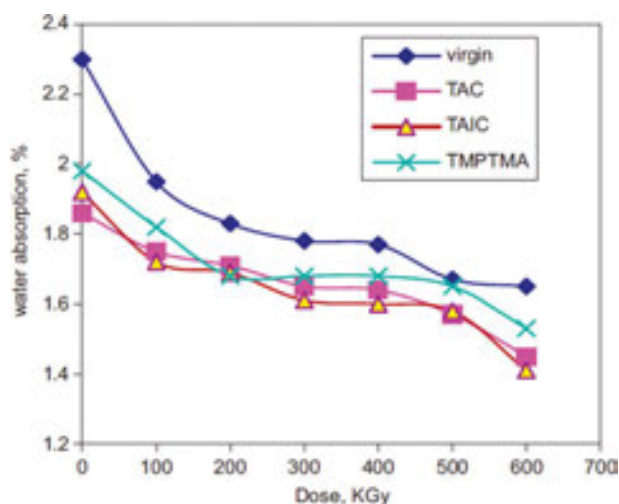

Figure 13. Variation of water absorption for PA-6 without and with 1% crosslinking agents with dose of e-beam radiation [11]. With permission of Elsevier.

Because the concentration of the effective crosslinking agent affects the gel content, it is expected to influence water absorption in the PA correspondingly. Such an example is shown in PA-6 doped with 1%, 2%, and 3% TAC [6]. The measured data confirmed this supposition and the largest decrease at 80 kGy is read for PA-6 with 3%>2%>1% TAC. The decline of water absorption compared to virgin PA-6 irradiated within 0 to 200 kGy occurs also after adding approximately 3% GMA under identical conditions [21]. Similarly, injection-molded PA-66 reveals a lowering of water absorption when irradiated in the range of 0 to 500 kGy, but the PA-66 dipped in TAC solution before the irradiation shows a further decrease in this parameter [15].

3. γ-Irradiation of PAs

In polymer chemistry, as for electron irradiation, γ-irradiation is employed to initiate chemical reactions also in the solid phase without the addition of initiator. The purpose can be to initiate the crosslinking of individual polymers or the grafting of various monomers onto PA chains. Basically with γ-irradiation of PAs, the same processes run as those with electron irradiation. However, some differences occur due to variable conditions.

3.1. Variations in chemical structure

γ-Ray radiation differs from electron beam mainly by a much slower rate of dose due to γ-rays being always of less energy than 10 MeV. Therefore, γ-irradiation requires a longer period to supply the same dose as an electron beam. When a polymer is γ-irradiated in air, enough time is available for generated radicals to react with oxygen. Therefore, considerable oxidative degradation can be expected along with crosslinking. In contrast, an inert atmosphere during irradiation as well as after the irradiation suppresses oxidative degradation and supports crosslinking. However, the oxidative degradation cannot be excluded absolutely due to some portion of oxygen (and possibly also humidity) present in the polar PA matrix. These antici-pations were confirmed and both chain scission and crosslinking are observed to occur in PA-6 under γ-irradiation in either air or inert atmosphere, with chain scission prevailing over crosslinking if irradiation proceeds in air [30].

A thorough comparison is provided by a recent study [31] examining PA-6 and GF-reinforced PA-6 (30% GF) irradiated with different γ-ray doses in the range of 0 to 500 kGy in either air or inert atmosphere. As displayed in **Figure 14**, it can be seen that the irradiation in air generates a small amount of gel in PA-6 only, whereas no gel is found in the PA-6/GF composite.
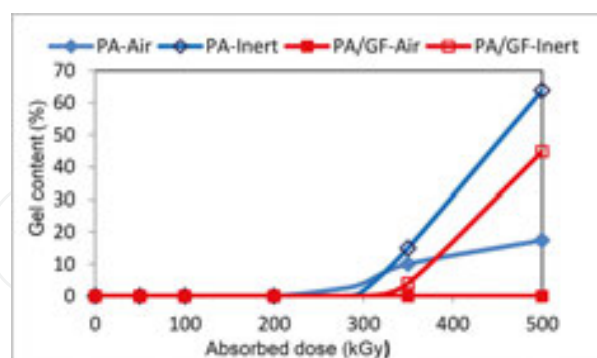

Figure 14. Dependence of gel content in PA-6 and PA-6/GF composite on absorbed dose when γ-irradiated in air or inert atmosphere.

In the PA-6, the crosslinked portion irradiated in air increases slightly with the rising absorbed dose. Concerning the gel point, a calculation following the Charlesby-Pinner equation [14] using the experimental data and taking into consideration the experimental errors gives an estimation that the gel point is to be in the vicinity of a dose of 300 kGy for the PA-6 irradiated in both atmospheres. Such gel point is somewhat higher compared to 200 kGy dose value

determined for the same materials irradiated with electron beam in air [7]. The irradiation of PA-6 in argon atmosphere produced considerably more gel in comparison to exposure in air. It demonstrates oxygen influence. The absence of oxygen (or low content of it) affords better facilities to form crosslinks from generated macroradicals because the macroradicals are not attacked. In argon atmosphere, the gel point for PA-6 as well as PA-6/GF is observed to be approximately 300 kGy. However, also in inert atmosphere, PA-6 shows more gel (65%) than PA-6/GF (45%) for the ultimate dose of 500 kGy. The lower gel content in the composite confirms the retarding action of the filler on the networking of the PA matrix. Simultaneously measured solution viscosity for PA-6 increases up to 200 kGy, and above this dose, the viscosity could not already be measured correctly due to the incomplete dissolution of the PA-6 polymer indicating incoming gel point. The increase of the PA-6 solution viscosity below 200 kGy indicates growth in the molecular mass via the recombination of the secondary macroradicals formed on PA-6 chains, which leads to branching as pre-crosslinking stage up to the gel point [5,6]. Whereas the irradiation of PA-6/GF in air did not generate any gel within the applied dose, viscosity increased (see **Table 3**), illustrating some recombination of the macroradicals and relating growth in molecular mass. The solubility of the PA-6/GF matrix was observed within all doses corresponding with no gel content. The reduction of the viscosity beyond 350 kGy is attributed to the continuing branching of already branched chains. A consequence is that the amount of the particles and the corresponding gyration radius of the macromolecules decrease, reducing the viscosity.

Dose (kGy)	Viscosity number (mL/g)	
	PA-6	PA-6/GF
0	143	130
50	146	131
100	154	133
350	—	212
500	—	180

Table 3. Viscosity number of PA-6 and PA-6/GF irradiated with γ-rays in air (solvent formic acid, dose rate of 9.5 kGy/h).

Gupta and Pandey [30] presented a similar fact when, irradiating in air, the chain scission of PA-6 prevailed over crosslinking. Because γ-irradiation took a longer time (from 5 to 52 h), during this period, oxygen could attack the produced macroradicals. The result was the overbalance of scission due to oxidation over crosslinking. In addition, the presence of GF hindered the diffusion of the macroradicals in the matrix, so that the branching was supported and crosslinking was suppressed.

An opposite effect can occur as reported by Aytaç et al. [13] for PA-6 and PA-6,6 tyre cords being calendered and then γ-irradiated within 0 to 75 kGy in air. As already mentioned about the electron exposure of those materials (Section 2.1), also the γ-irradiation of those PAs led to the reduction of the limiting viscosity number with increasing dose. This demonstrates how

any pretreatment of material subsequently subjected to the irradiation can be important. In general, calendering itself can start mechano-oxidative degradation leading to the decrease in molecular mass as well as in the corresponding viscosity. In addition, during the calendering, the diffusion of oxygen into the PAs is more facile, as the molecular movement in matrix is increased at higher temperature. From this point of view, the decrease in the limiting viscosity number is expected. The decrease is larger than that under comparable exposure to electron beam, indicating more deteriorative effect of γ-irradiation in comparison to electron beam. Corresponding dependences of the breaking strength on dose show a lower strength, too, in conformity with the viscosity results.

PAs are combined with other polymers in various microfiltration membranes especially to enhance the mechanical properties. The membranes are exposed to γ-irradiation to be sterilized. Such a membrane involving PA-66 as reinforcing part was put in Pyrex glass, purged with argon, and, after adding deionized water again, purged with argon and sealed. The glass with the membrane was γ-irradiated in the range of 0 to 100 kGy and then several character- istics were tested [32]. At first sight, this is different from the PA-6 and PA-6,6 cords mentioned previously [13]. However, also in this case, the reduced viscosity as a function of dose displays a decrease with dose (**Figure 15**).
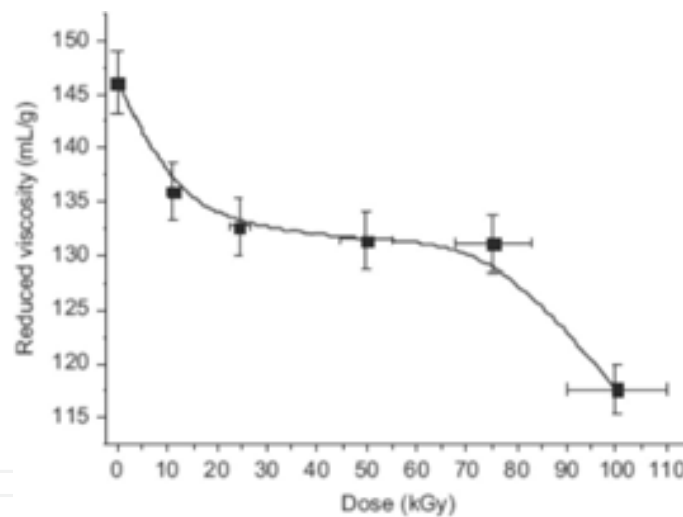

Figure 15. Evolution of reduced viscosity of PA-66 as a function of γ-irradiation doses [32]. With permission of Elsevi- er.

The downward trend of the reduced viscosity indicates the decrease in molecular mass due to chain scission despite the exposure being conducted in argon purged deionized water. The authors [32] suggested that the viscosity reduction could be due to the chains connecting different lamellae. However, the water medium is a rich source of oxygen and could be the main reason in supporting oxidative degradation. Free radicals generated by γ-rays induce the cleavage of water molecules. In addition, water penetrates PA relatively easy acting as a plasticizer, and the applied dose within 10 to 100 kGy is sufficient to attain the dissociation energy for water producing oxygen (HO-H ~498 kJ mol^{-1} and O-H ~428 kJ mol^{-1}) and that is

comparable to the dissociation energy for H-C cleavage (H-C ~339 kJ mol^{-1}, H-CH ~452 kJ mol^{-1}, and H-CH$_2$ ~473 kJ mol^{-1}) [33]. That is why corresponding tensile properties (Young's modulus, stress at break, elongation, and energy at break) [32] mirrors the course of the decreasing viscosity.

Radicals generated during irradiation are capable of surviving in the polymer matrix for a long time as found by Menchaca et al. [34,35] after 6 years from exposure of PA-6,12 crystalline fibers with applied low dose of 1 to 25 kGy at ambient conditions. The survival of frozen free radicals in the matrix demonstrated itself by the changes in some properties as thermal and morphology characteristics; the melting temperature decreased and the crystallinity increased with the period of storing. It indicates that formed shorter chains generated thinner lamellae and integrated into the crystalline phase.

Applying γ-irradiation can also lead to an improvement in the compatibilization of immiscible polymers in a blend. An example is the blend of PA-6 with LDPE either irradiated or nonir-radiated [36]. The structure and properties of the blends with γ-irradiated LDPE differ significantly compared to PA-6 blends with the nonirradiated materials. The difference was ascribed to the formation of functionalized groups on the polyethylene chain during irradia-tion in air and these interact with PA. However, when analogous blends of LDPE/PA-6 are irradiated in vacuum [37], crosslinking is achieved mainly in the PE component, whereas the main effect on PA-6 is chain branching.

3.2. Thermal properties related to supermolecular structure

A comparison of DSC characteristics for PA-6 and composite PA-6/GF after being γ-irradiated in air or in inert [31] within 0 to 500 kGy can provide some framework observations. Similar to Section 2.2, both first and second heating runs give complementary information. First, the effect of irradiation dose on T_{m1} for PA-6 is qualitatively the same if irradiated in air or inert atmosphere; however, the absolute values for each particular dose indicate lower T_{m1} values for samples irradiated in air (**Figure 16**).
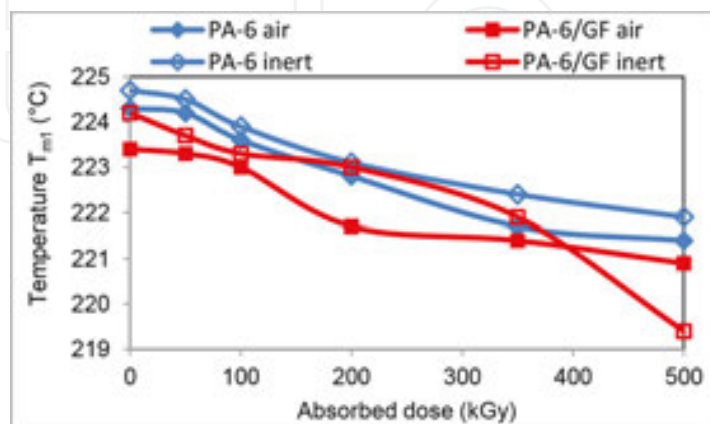

Figure 16. Variation of the first melting temperature of PA-6 and composite PA-6/GF (30%) with absorbed dose of γ-irradiation in air and inert atmosphere. Adapted from Porubská et al. [31].

The effect of GF presence consists of a certain soft increase of sensitivity towards irradiation, which is in certain contradiction with lower gel formation. It may mean that the presence of GF can act as a nucleating agent. If so, the crystallites are formed especially around the fiber surface. However, during exposure, the fiber surface is more heated than the matrix and some destruction in crystalline portion occurs in this area. That is why the noticeable decrease in T_{m1} is observed for the composite irradiated in inert atmosphere.

The figures of melting heat ΔH_1 (**Figure 17**), directly proportional to crystallinity, do not show any tendency with increasing dose in air, changing only within variance of the experimental results.
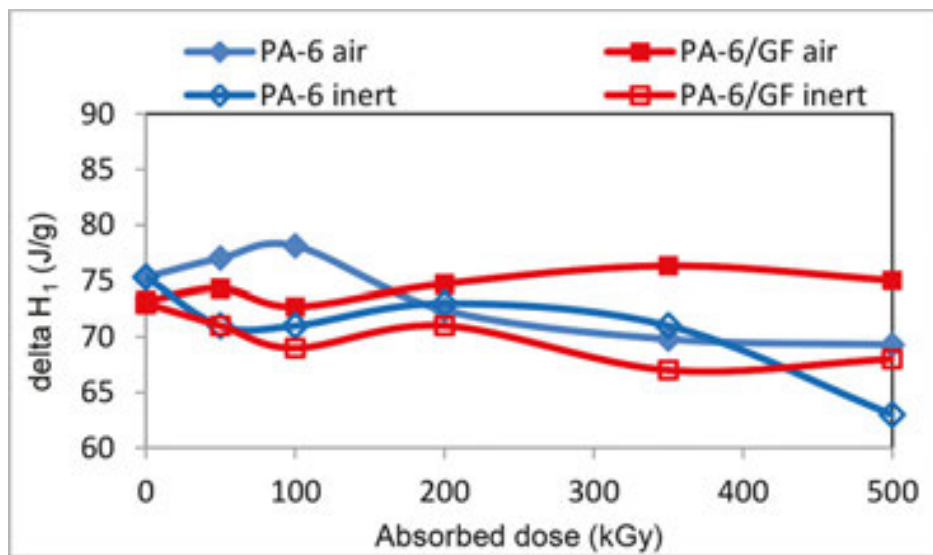

Figure 17. Variation of the first melting enthalpy of PA-6 and composite PA-6/GF (30%) with absorbed dose of γ-irradiation in air and inert atmosphere. Adapted from Porubská et al. [31].

It can be seen that the values of ΔH of both PA-6 and composite PA-6/GF samples irradiated in air are higher compared to those irradiated in inert atmosphere. The course of changes of ΔH measured in the second DSC run, ΔH_2 (**Figure 18**), depending on the absorbed dose is in conformity with expectation, consisting of a gradual decrease of ΔH_2 values with rising dose. Irradiation in air results in higher melting heat values than irradiation in inert atmosphere. In this case, perhaps the important role consists of heating the samples during irradiation and the extent of heating depends on the absorbed dose.

All samples show a decrease in remelting temperature T_{m2} with rising dose (**Figure 19**), which is conformable with expectation. The reason is that the crystallization of polymer remelted after being irradiated is hindered due to the defects generated in polymer within irradiation. However, the same decrease in T_{m1} would not be expected if the irradiation impose structural changes in amorphous phase first. Because T_m and ΔH vary, the crystalline phase also is affected by irradiation, inducing the lamellae thinning. It is evident that the process runs already from the beginning of irradiation.
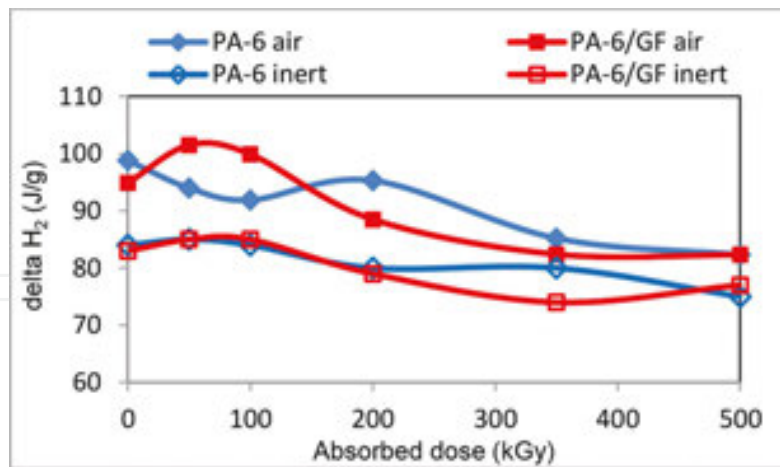
Figure 18. Variation of the second melting enthalpy of PA-6 and composite PA-6/GF (30%) with absorbed dose of γ-irradiation in air and inert atmosphere. Adapted from Porubská et al. [31].
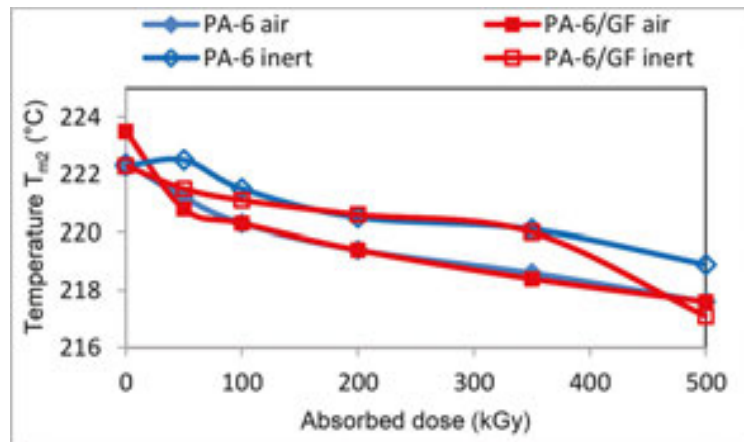

Figure 19. Variation of the second melting temperature of PA-6 and composite PA-6/GF (30%) with absorbed dose of γ-irradiation in air and inert atmosphere. Adapted from Porubská et al. [31].

Similar to electron beam irradiation, the presence of crosslinking agents can modify the crystallinity of γ-irradiated PAs, too. Electrospun PA-66 fibers exposed in nitrogen atmosphere with 20 and 50 kGy dose do not display any change in crystallinity, whereas the addition of TAC raises the crystallinity and this increases with applied dose [38]. This fact is interpreted as the consequence of a TAC-induced crosslinking and formation of a tighter network. Thermal stability measured as weight loss depending on temperature is lower with TAC than without it. After irradiation, the stability with TAC improves, however, without achievement of stability for nonadditive PA-66, whereby the dose of 20 kGy provides better result than 50 kGy.

The exposure of PA-66 to various doses of γ-rays ranging from 100 to 1250 kGy shows an increase in the crystalline nature of the polymer at higher doses as a result of significant decrease in the peak width of X-ray diffraction (XRD) patterns [39]. Higher doses induce more macromolecular fragments of higher mobility and these can integrate easily into crystalline phase modifying supermolecular structure.

Waste PA finds exploitation in various material combinations. Hassan et al. [40] studied the effect of γ-irradiation on blends containing waste PA-6/PA-66 copolymer and ground rubber from tires with various ratios of these incompatible components. The blends irradiated in the range of 0 to 200 kGy give the melting temperature and crystallinity decreasing with increasing dose due to the crosslinking at interphase. The visible side shoulder in the endotherm for 100 kGy is missing in the 200 kGy endotherm and microphotographs show a relatively smooth fracture surface. Thermal stability measured by thermogravimetry is a little worse after irradiation. Montmorillonite clay is then added into the blend to formulate nanocomposite [41]. The composite after being γ-irradiated between 0 and 200 kGy obtains a markedly magnified thermal stability. When 12% montmorillonite is present in the mixture, the DSC data indicate the increase in the melting temperature with dose with reverse order of the onset in melting endotherm. The crystallinity is observed to be highest for the 100 kGy dose and the corresponding endotherm outlines multiplicity. The increase of montmorillonite portion to 18% leads to a decrease in the melting temperature. Also, the temperature onset falls. In this case, the highest crystallinity belongs to the nonirradiated composite and is followed by the 200 kGy dose. The dose of 100 kGy corresponds to the lowest crystallinity with the most structured melting endotherm. The multiplicity of the endotherm indicates a new element in the supermolecular structure as a consequence of γ-irradiation. Another composite consisting of the same polymer components PA-6/PA-6,6 copolymer and ground rubber but with added carbon black was examined by the same authors [42], applying the same doses of 0 to 200 kGy. As reported, the content of carbon black within 6% to 24% improves the thermal stability in both cases without and with γ-irradiation. The melting temperature and crystallinity of the composite with 12% carbon black decrease with rising dose slightly more when compared to 18%. The melting endotherm becomes smoother and the composite irradiated with 200 kGy presents a homogeneous fracture surface. Such studies are useful in optimizing a filler portion regarding other required properties. Usually, some compromise is necessary.

3.3. Mechanical properties

The development of mechanical properties of PAs irradiated with γ-rays is, as usual, linked to changes in the molecular and supermolecular characteristics. Evaluating the behavior of PA-6 and composite PA-6/GF γ-irradiated in air [31] concludes that the Young's modulus of PA-6 is soft decreasing with rising irradiation dose, whereas, for the nonirradiated composite PA-6/GF, the values are almost identical with the material irradiated with the highest dose (**Figure 20**).

For both materials, the dependencies exhibit a shallow minimum around the gel point as a result of the superposition of the two opposite effects, namely, branching, chain scission, and cross-bond formation. These effects are more evident for PA-6 in comparison to the composite PA-6/GF. At first sight, it seems to be a misinterpretation. However, one has to take into consideration generally lower figures for PA-6 modulus and a small variation leads to a larger relative variation than in the case of the composite. Overall marginal variations of modulus are linked to a low gel content for PA-6 and no gel for PA-6/GF (Section 3.1) as well as small changes in crystallinity (Section 3.2). Because the level of crystallinity and crosslinking
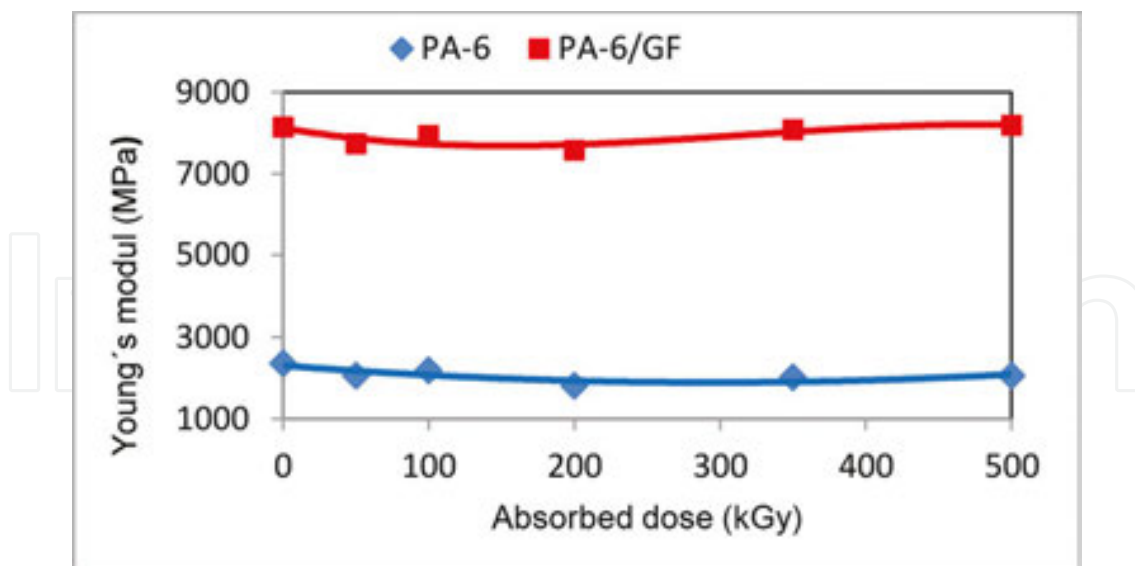
Figure 20 Variations of Young's modulus for virgin PA-6 and composite PA-6/GF γ-irradiated in air.

determines the modulus value, a significant variation of the modulus values should not be expected as demonstrated in **Figure 20**.

Testing tensile strength reveals that yield point can be observed only for PA-6, and the composite PA-6/GF exhibits brittle behavior without signs of yielding. A considerable decrease of yield stress from 71 to 51 MPa is observed already at the lowest dose of 50 kGy and then the curve leveled off up to the highest dose of 500 kGy. The tensile strength at break for PA-6 does not vary considerably with rising irradiation dose. This result is attributed to the gel content (Section 3.1), which contributes to retain the strength at break with no significant variation in the whole dose range compensating the strength decrease induced by degradative influence of γ-irradiation in air. In contrast to PA-6, all exposed PA-6/GF samples showed a little reduction in tensile strength at break. The reason is the different gel formation; whereas no gel was measured in the composite, a certain amount of gel was determined in PA-6 beyond gel point. Therefore, zero gel in PA-6/GF could not compensate the decrease in the strength due to the degradation of the polymer matrix.

Variations in elongation at yield for PA-6 as well as for the composite are negligible and this parameter for PA-6/GF is identical with the elongation at break. For PA-6, the starting elongation at break at ~147% increased to 240% already at 50 kGy without any change for the other doses. Such mild increase in the elongation at break is caused by the minor decrease of crystalline portion as well as the lamellae thinning as a result of oxidative degradation with the consequence of easier plastic deformation. In addition, at low gel content (maximum ~17%), shorter recombined chains act in the matrix as plasticizers and increase its deformability. The effect is not observed for the composite PA-6/GF, as it is overlapped by enhanced brittleness of the material due to the presence of the anisotropic GF.

Concerning irradiation in an inert argon atmosphere, a comparison of effect on the moduli is demonstrated in **Figure 21**.
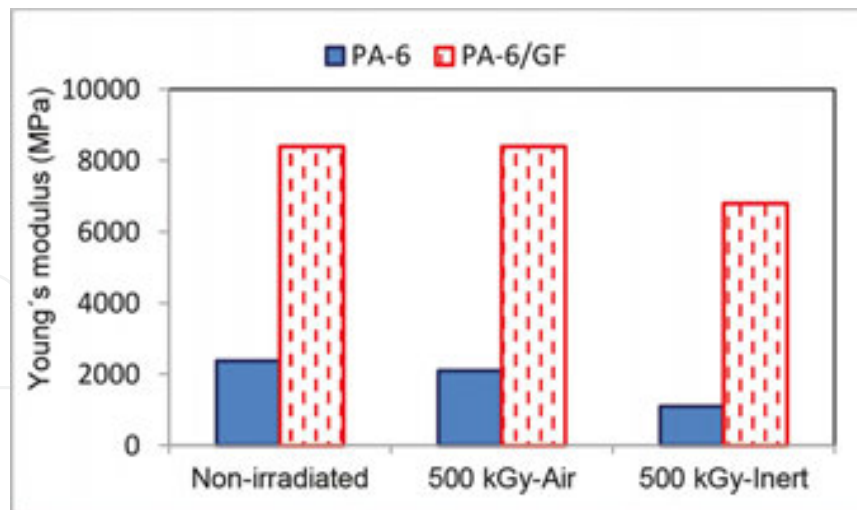
Figure 21. Comparison of variations of Young's modulus for virgin PA-6 and composite PA-6/GF γ-irradiated by 500 kGy dose.

When PA-6 and PA-6/GF were irradiated in inert atmosphere, the relevant moduli showed lower values in comparison to the materials exposed to γ-irradiation in air. In consideration of the marginally changing results of Δ*H* in the first DSC run and so also the minor changes in crystallinity, the most probable reason consists of the lamellae thinning as a result of irradiation, demonstrated by the lowering in the melting temperature. It is known that the stiffness of the material may decrease if crystallites are smaller even when crystallinity does not change [4].

The reduction of tensile strength for both samples is more enhanced when irradiated in inert atmosphere. As displayed in **Figure 22**, the changes are rather small, except for yield, where the extent of changes is close to the values for Young's modulus.
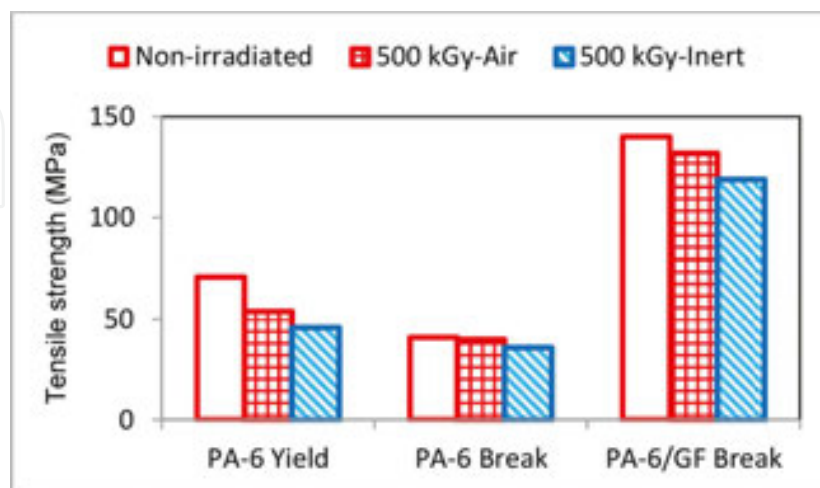

Figure 22. Comparison of variations of tensile strength for virgin PA-6 and composite PA-6/GF γ-irradiated by 500 kGy dose.

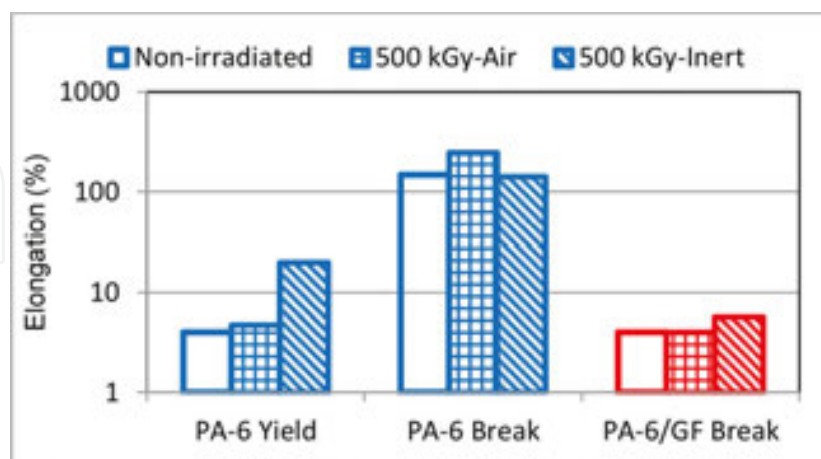The changes in elongation at break and at yield (in the latter case only for PA-6) are shown in **Figure 23**.

Figure 23. Comparison of variations of elongation for virgin PA-6 and composite PA-6/GF γ-irradiated by 500 kGy dose.

The elongation at yield for PA-6 irradiated with 500 kGy in inert atmosphere increased for up to quintuple value, whereas irradiation in air led to negligible change. In contrast, the elongation at break is higher after irradiation in air when compared to irradiation of PA-6 in inert atmosphere, and this is lower than for the unexposed sample. Irradiation of PA-6/GF in air led to the elongation at break with no change, whereas a little increase is observed when irradiated in inert atmosphere. This indicates some increase of the matrix deformability due to a low crosslinking level.

Concerning exposure in inert atmosphere, similar data are given for electrospun PA-66 fibers irradiated in nitrogen atmosphere with 20 and 50 kGy dose. Tensile stress lowers with dose, whereas an increase is observed after adding the crosslinking agent TAC [38]. The same is reported for Young's modulus.

Notched impact strength of PAs is often unfavorable property. An examination of this aspect was demonstrated by Charpy notched impact test being carried out for both PA-6 and PA-6/GF irradiated within 0 to 500 kGy in air [31]. The dependence of the impact strength on dose reveals a different behavior. The PA-6 curve shows a maximum at 50 kGy. The corresponding impact strength is 80% higher compared to the initial value. This can be attributed to the perturbation of initial physical nodes in amorphous phase and branching, which facilitates more elastic dissipation of impact energy and supports a deceleration of crack propagation. Higher doses form a network, although not a dense one, but it supports the absorbing impact because of its elasticity. Whereas oxidation-degradation occurs simultaneously, the result represents a superposition of the positive contribution of elasticity and a negative oxidation-degradation under irradiation. At 500 kGy, the final impact strength for PA-6 is 1.5 times higher than the starting value. However, an opposite trend is observed for the PA-6/GF composite. In this case, the impact strength decreases mildly with rising dose up

to 82% of the initial value linking the zero gel observed (**Figure 14**) and more or less constant crystallinity (Figures **17** and **18**). As evidenced by SEM photos, although easier GF dewetting in nonirradiated composite may act as an obstacle for crack propagation at impact, after irradiation, higher GF adhesion makes the material more compact and less resistant to impact failure.

Blends containing waste PA-6/PA-66 copolymer and ground rubber from tires irradiated within 0 to 200 kGy in air show lower values in tensile strength and elongation compared to the unexposed sample, whereas elastic modulus is changed little. All the variations are a function of the component ratio [40]. When montmorillonite clay is involved in the blend, formulating a nanocomposite, a decrease in tensile strength, and an elongation at break is observed for each dose in comparison to the starting material. However, the courses of both parameters are a function of the montmorillonite portion, indicating an optimum for 12% clay. Concerning modulus, a decrease is measured regardless of dose, but the differences between the compositions are not large [41]. The same doses of 0 to 200 kGy were applied on the mixture of the above-mentioned polymer components PA-6/PA-66 copolymer and ground rubber with the addition of carbon black [42]. The tensile strength of nonirradiated sample is observed to be higher than the irradiated samples, except the dose of 50 kGy being above the initial material. However, irradiation led to a decrease in elongation for all doses compared to that unexposed. For the latter case, the addition of carbon black increased elongation significantly; for others, there was a slower increase. In both tensile characteristics, the differences between doses 100 and 200 kGy are marginal, whereas the variations are more profound for the dose of 50 kGy. The dependences of the parameters on carbon black portion within 6% to 24% are almost flat.

γ-Rays are applied in the field of flame retardation of polymers, too. The recent study of Sonnier et al. [43] demonstrates for blend PP/PA-6/crosslinking agent that, depending on the type of retardation, the best flame-retarded blend before irradiation can become the worst one after irradiation at a higher dose. In this case, a dose up to 100 kGy was used. Testing of the dependence of Young's modulus on temperature provided results similar for all blends at RT for whatever the dose, and these decreased slowly when the temperature increased. Above 150°C, the decrease was faster. Heat distortion of the blends accelerated with rising dose, whereas the distortion was not observed for nonirradiated blend. It is concluded that, if heat shielding effect is applied to provide the flame retardation, the top protective layer can be disrupted and heat release rate will increase to a considerable extent. In such case, the barrier layer is not capable to prevent the subsequent transfer of heat.

3.4. Sterilization of PA materials by γ-radiation

Low doses of γ-radiation are often used for the sterilization of food packaging. Polymers used to package food intended for irradiation must receive relevant approvals. Evaluation of e-beam, γ- and X-ray treatment on the chemistry and safety of polymers used with prepackaged irradiated foods showed that the three forms of irradiation have virtually indistinguishable effects on polymers irradiated in vacuum [44]. However, γ-irradiation in air results in

facilitated damage due to slow dose rate providing enough time to oxidative degradation. It is accepted, in general, that the foods in contact with irradiated polymeric materials should not be endangered by radiolytic products with adverse impact on health.

PAs are governed by excellent barrier performance. That is why several works are devoted to the issue of food packaging involving PAs. An examination of various plastic multilayer PA-6 films, used for meat and cheese, after being irradiated (up to 12 kGy) reveals that the release of ε-caprolactam from exposed PA-6 is of a much higher extent compared to that of nonirradiated samples, indicating chain scission [45]. Félix et al. [46] conducted a migration assay at 40°C for 10 days focusing on the effect of γ-irradiation with 12 kGy dose on ε-caprolactam migration from multilayer PA-6 films into food simulants. The results revealed that the irradiation caused almost no changes in ε-caprolactam levels, with the exception of olive oil, which showed an increase in the caprolactam level. However, all the tested films were within the legislation and did not exceed limits for ε-caprolactam migration. Park et al. [47] reported that 5 kGy γ-irradiation significantly increased the formation of ε-caprolactam in PA-6 from 70.76 to 164.10 ppm. The formation of ε-caprolactam ranged between 122 and 164 ppm in the dose range of 5 to 200 kGy.

Barrier five-layer food packaging films, consisting of two outer PA-6 layers (~15%) and a middle LDPE layer (50%), after being irradiated with a larger range of doses of 5 to 60 kGy were analyzed focusing on volatile and nonvolatile radiolytic products and sensory changes [48]. The data show that a large number of radiolytic products are produced such as hydrocarbons, alcohols, carbonyl compounds, and carboxylic acid but also amide type of products. These substances are detected even at the lower doses of 5 and 10 kGy. Most of the substances are assumed to come from LDPE because that is used also as recycled. The type and concentration of radiolytic products increase progressively with the absorbed dose. In addition, irradiation dose appears to influence the sensory properties of table water in contact with the films being classified according to stricter requirements.

In another study [49], the authors analyzed 13 different multilayer polymeric materials for food used before and after their exposure to γ-radiation regarding the profile of volatile compounds released from the polymeric materials. Thermosealed bags of different materials were filled with either air or nitrogen to evaluate the oxygen influence. One third of the samples were analyzed without irradiation, whereas the rest were irradiated at 15 and 25 kGy. Half of the samples were processed just after preparation and the other half was stored for 8 months at RT before analysis. Significant differences between nonirradiated and irradiated bags were found. Sixty to 80 compounds were released and identified per sample. Independent of the filling gas, the results of nonirradiated materials were almost identical. In contrast, the chromatographic profile and the odor of irradiated bags filled with nitrogen were completely different from those filled with air. The migration of compounds from irradiated materials to the vapor phase was much lower than the limits established in the relevant EU Commission Regulation.

4. Proton irradiation of PAs

Compared to electron and γ-irradiation, there is far less information on proton beam irradiation in the scientific sources. One possible reason is that proton irradiation is used mostly in the medical domain for therapy and production of isotope-labeled pharmaceutical preparations.

Currently, proton beam is used as a direct writing method using focused proton beam to decorate resistant polymers at the nanolevel. In comparison to electron beam, the proton writing offers a unique advantage consisting of the fact that proton penetrates materials more deeply, maintains a straight line, and makes three-dimensional structures with vertical and smooth walls as well as low roughness. This advantage is a consequence of a greater proton mass when compared to electron.

Unlike PAs, some works dealing with other polymers (PMMA, PDMS, fluorinated PI, PP, PTFE, PS, LDPE, PP, PET, and PVC) can be found. Semicrystalline PAs are not typical materials for optical or decorative purposes because of their nontransparency. Maybe this is why studies on PAs irradiated with proton beam are rare if not missing.
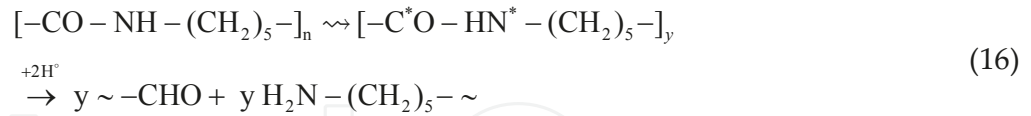
Concerning polymers, it is known that also protons affect the polymers mainly through scission and crosslinking of macromolecule chains. Solitary data on PA-6 irradiated by proton beam in air can be found in the paper dealing with Fourier transform infrared (FTIR) spectroscopy comparison of electron with proton beam impact [50]. When irradiating the same PA-6 with an equal dose of 500 kGy, the proton beam generates less gel (57.5%) than the electron beam (67.6%). Therefore, the first DSC melting temperature is a little higher for a proton-irradiated sample (217.6°C) than for an electron-irradiated one (216.9°C). Accordingly, the crystallinity for proton-irradiated PA-6 is slightly higher when compared to the corresponding electron-irradiated PA-6, but the difference in the mentioned thermal characteristics is marginal. FTIR spectroscopy shows some differences in the postirradiation species related to nonidentical gel formation. The proton beam irradiation results in a finer structure of some absorption bands, particularly in the range of 400 to 1650 cm^{-1}, indicating the generation of structures that are more varied. The consequence is that the cleavage of PA-6 macromolecules by the proton beam produces fragments containing amine groups and terminal methyl groups, whereas the increase in concentration of these groups in electron-irradiated PA-6 appears to be insignificant in comparison to virgin PA-6. Based on the finding, besides crosslinking [Equation (11)] and oxidation degradation [Equations (13) and (14)], a possible parallel scenario can occur when proton beam interacts with PA:
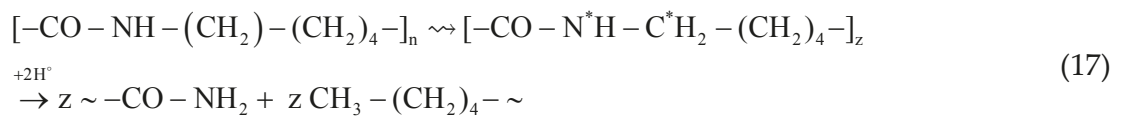
a) Unsaturated structures formation:

$$[-CO-NH-(CH_2)_5-]_n \xrightarrow{-2H^\circ} [-CO-NH-CH_2-CH=CH-CH_2-CH_2-]_x \qquad (15)$$
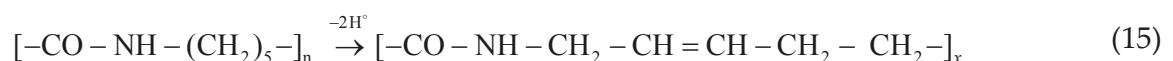
The double bond can occur between any carbons within the ethylene segments.

b) Amine species formation:

$$[-CO-NH-(CH_2)_5-]_n \rightsquigarrow [-C^*O-HN^*-(CH_2)_5-]_y$$
$$\xrightarrow{+2H^\circ} y \sim -CHO + y\, H_2N-(CH_2)_5-\sim \tag{16}$$

c) Both methyl-ended and shorter amide chain formation:

$$[-CO-NH-(CH_2)-(CH_2)_4-]_n \rightsquigarrow [-CO-N^*H-C^*H_2-(CH_2)_4-]_z$$
$$\xrightarrow{+2H^\circ} z \sim -CO-NH_2 + z\, CH_3-(CH_2)_4-\sim \tag{17}$$

The processes reflect some differences also in tensile properties as seen in **Table 4**.

Tensile property	Relative change after 500 kGy dose	
	PA-6/EB	**PA-6/PB**
Young's modulus	1.256	1.167
Tensile strength at break	1.582	1.398
Elongation at yield	1.075	2.077

Table 4. Relative changes of selected tensile properties for PA-6 irradiated by electron (PA-6/EB) and proton (PA-6/PB) beams in air towards properties of nonirradiated PA-6.

A thorough comparison of the advantages versus disadvantages of the proton beam irradiation in comparison to other radiation technologies in the domain of PAs cannot be concluded unless more data are available.

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