Comparison of Properties between Irradiated PA11 and PA12 by Accelerated Electrons

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***Abstract*—**Radiation processing involves the use of natural or manmade sources of high energy radiation on an industrial scale. The principle of radiation processing is the ability of high energy radiation to produce reactive cations, anions and free radicals in materials. The industrial applications of the radiation processing of plastics and composites include polymerization, cross-linking, degradation and grafting. Radiation processing mainly involves the use of either electron beams from electron accelerators or gamma radiation from Cobalt-60 sources. The PA11 polyamide 11 and the PA12 polyamide 12 tested showed significant changes of temperature stability and mechanical properties after irradiation. From this point of view, new applications could also be seen in areas with service temperatures higher than their former melting point. The comparison of the temperature stability and mechanical properties of irradiated and non-irradiated PA11 and 12 are presented in this paper.

***Keywords*—**Polyamide 11, polyamide 12, irradiation, properties, temperature stability.

I. Introduction

THE cross-linking of rubbers and thermoplastic polymers is a well-proven process for the improvement of thermal properties. The chemical cross-linking or rubber vulcanization is normally induced by the effect of heating after processing with the presence of a curing agent. The cross-linking process for thermosets is very similar. In thermosets, the polymer molecules are also chemically linked due to heat after processing. Cross-linked rubbers have a wide-meshed molecular network that keeps them soft and their properties change only slightly on a wide temperature scale. On the other hand, thermosets are characterized by a very narrow-meshed network. Due to this fact, they hardly change their high level of stiffness on a wide temperature scale at all. The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) is performed separately, after processing. Generally, ionizing radiation includes accelerated electrons, gamma rays and X-rays. [1]

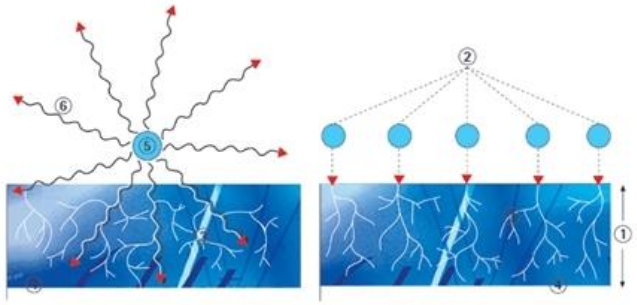

Fig. 1 Design of Gamma Rays (a) and Electron Rays (b),
1 – Penetration depth of an electron, 2 – Primary electron,
3 – Secondary electron, 4 – Irradiated material,
5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [2]

Radiation processing with an electron beam offers several distinct advantages when compared with other radiation sources, particularly γ-rays and x-rays. The process is very fast, clean and can be controlled with much precision. There is not permanent radioactivity since the machine can be switched off. In contrast to γ-rays and x-rays, the electron beam can be steered relatively easily, thus allowing irradiation of a variety of physical shapes. The electron beam radiation process is practically free of waste products and therefore is no serious environmental hazard. These are not only capable of converting monomeric and oligomeric liquids, but also can produce, due to cross-linking, major changes in the properties of solid polymers. The cross-linking level can be adjusted by the irradiation dosage. The absorbed dosage means the value of energy of ionizing radiation absorbed by a unit of mass of the processed material. The unit of absorbed dose is 1 Gray (1 Gy = 1J/kg). The main difference between beta and gamma rays is in their different abilities to penetrate the irradiated material. Gamma rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons. Due to electron accelerators, the required dosage can be applied within seconds, whereas several hours are required in the gamma radiation plant (Fig. 1). [1, 2]

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Beta and gamma rays can be used for the irradiation of polyolefines, polyesters, halogen polymers and polyamides from the thermoplastics group, elastomers and thermoplastic elastomers. Some of them need the addition of a cross-linking agent. Polymers can be classified into two groups according to their response to ionizing radiation. One group exhibits predominant cross-linking, the other predominant chain scission. [1, 2]

Irradiation cross-linking of thermoplastic materials deals with creation of a cross-link among the macromolecular strings. Intermolecular forces are replaced by a covalent bond. As a result, we can optimise properties of standard and engineering polymers and impart them the properties of high performance polymers (Fig. 2). Irradiation of polymers turned out to be interesting because of economic reasons, production costs and a life time of products. However, these benefits depend on the type of irradiated polymer and the radiation dosage. Behaviour of each material is different after irradiation. We cannot expect the improvement in all areas (in mechanical, thermal and chemical). Most of polymers are not suitable for irradiation because of degradation and deterioration of their properties. [8]

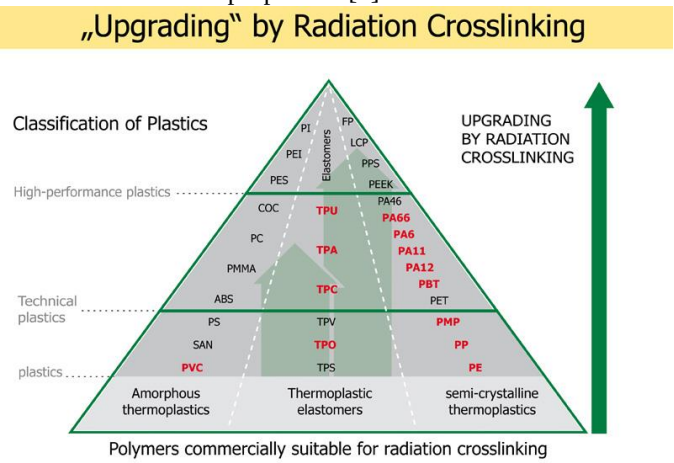

Fig. 2 Pyramid of Polymers [2]

Radiation cross-linking usually improves strength, reduces creep, contributes to chemical resistance improvement and in many cases improves tribological properties. Effect of radiation cross-linking significantly improves temperature stability. Because of that, materials which belong to group of standard polymers can be used in applications, which would be in term of temperature stability intended only to constructive thermoplastic polymers.

In comparison with other construction / engineering materials, mainly metals; polymers including TPE, PE and PAs have limited levels of both mechanical and thermal properties. These limitations significantly reduce the applicability of polymers. Every improvement of these properties, of course, makes their applicability wider. Irradiation of thermoplastics is an important way to change their thermal properties. From the usage point-of-view, it is mainly the temperature stability which is a very important factor. Polymers can be irradiated in many forms, such as pellets and powder, films, extruded and molded parts or as wire and cable insulation [1]. Plastic parts suitable for radiation cross-linking are extruded products like tubes, pipes and profiles as well as injection-moulded parts.

II. Material and Methods

A. Material Preparation

As the basic polymer material were used Polyamide 11 (V-PTS-CREAMID-11T*M600/13transparent) and Polyamide 12 (V-PTS-CREAMID 12-AMN 0 TLD*M800/13 natur), both of them were produced in PTS Plastic-Technologie-Service. An ARBURG Allrounder 420C Advance Injection molding machine was used for sample preparation, with the processing conditional to comply with the each polymers producer's recommendations. Irradiation of tested polymers were performed with the kind help of BGS Germany, in the BGS Wiehl plant using accelerated electrons with a dosage range of 0 to 198kGy. The mechanical properties and the temperature stability of non-irradiated and irradiated selected polymers were tested after irradiation.

B. Used Methods for the Testing

The mechanical properties of selected polymers were measured. Tensile test was carried out on tensile test machine ZWICK 1456, according to standard CSN EN ISO 527-1, 527-2 with used rate 50mm/min. Test data was processed by Test Expert Standard software and modulus (E [MPa]) and tensile stress (σ_t [MPa]) were determined. The hardness was measured using a HPE – D Berreiss hardness tester type, and the Shore D Method. The shape and the dimensions of the testing samples were in accord with the CSN 621431 standard. Lastly were measured the thermo-mechanical properties and the temperature stability. Perkin – Elmer Thermal Analyser TMA7 was used for the thermo-mechanical analysis, heated from 50°C to 400°C at 20°C/min, hold for 1 min at 50°C. Temperature stability was determined the visual observation in the temperature chamber.

III. Results and Discussion

The mechanical and temperature behaviour of polyamide 11 (PA11) and polyamide 12 (PA12), before and after irradiation, were studied. For easier of evaluation of the measured data, and the comparison of the irradiated polymer with a non-irradiated one, the changes of measured were used in some graphs. The property of the non-irradiated polymer had the value of 100%, while others were expressed in % as the ratio of measured property of irradiated polymers to the same property of non-irradiated polymer.

A. Tensile Test and Hardness

Irradiation affects the mechanical properties of the PA11 and PA12 were studied at the ambient temperature for hardness and at 23°C and 80°C for tensile test.

1) Tensile Strength and E-modulus

Irradiation affects the tensile strength of the PA11 studied at the ambient temperature (Fig. 3).

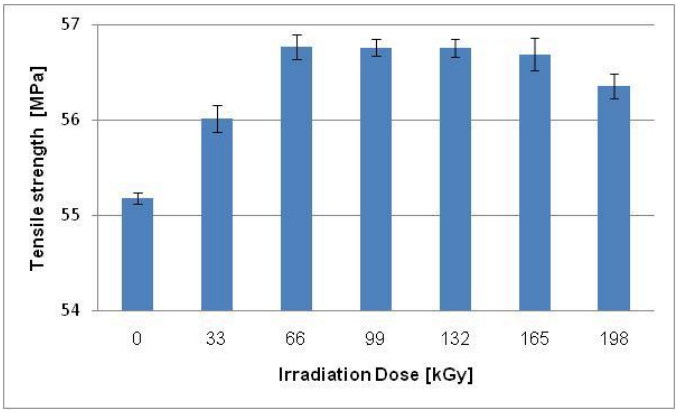

Fig. 3 PA11 Tensile strength at the temperature 23°C

At the ambient temperature tensile strength of irradiation PA11 with a dosage of 66kGy, was increased about 1,2 MPa compared to non-irradiated PA11.

Irradiation affects the tensile strength of the PA12 studied at the ambient temperature (Fig. 4).

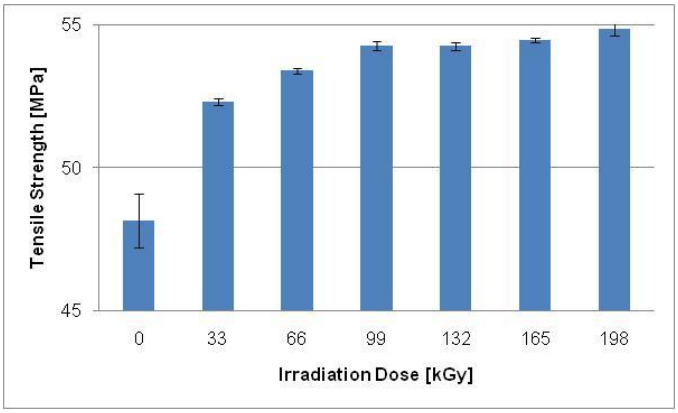

Fig. 4 PA12 Tensile strength at the temperature 23°C

At the ambient temperature tensile strength of irradiation PA12 with a dosage of 66kGy, was increased about 7 MPa compared to non-irradiated PA12.

In the Fig. 5 is displayed the dependence of irradiation dose on the change of tensile strength for PA11 and PA12 at 23°C. The tensile strength is rather constant for PA11. The maximal rise is 3% for PA11 with the 66kGy dose of irradiation. Unlike this the tensile strength of PA 12 rise rapidly with the dose of irradiation up to 99 kGy and then with the increased dose of irradiation the tensile strength stay nearly constant. The maximal rise is 14% for PA12 with the 198kGy dose of irradiation.

In the Fig. 6 can be seen irradiation affects the tensile strength of the PA11 studied at 80°C. At 80°C tensile strength of irradiation PA11 with a dosage of 99kGy was increased about 1,9 MPa compared to non-irradiated PA11.

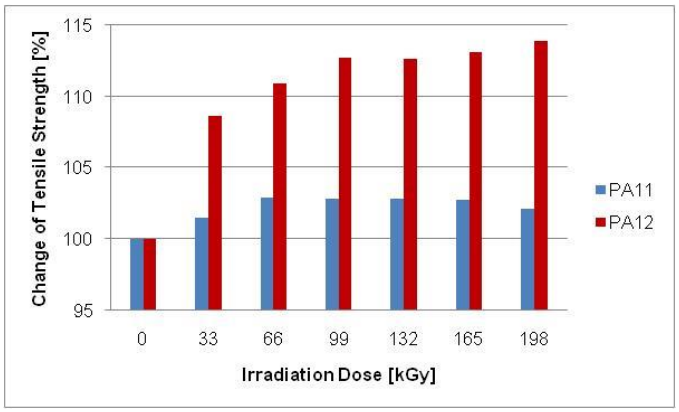

Fig. 5 Comparison of tensile strength of PA11 and PA12 at 23°C

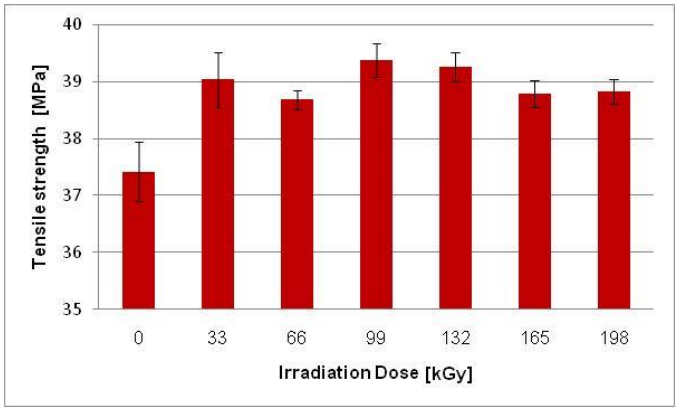

Fig. 6 PA11 Tensile strength at the temperature 80°C

In the Fig. 7 can be seen irradiation affects the tensile strength of the PA12 studied at 80°C.

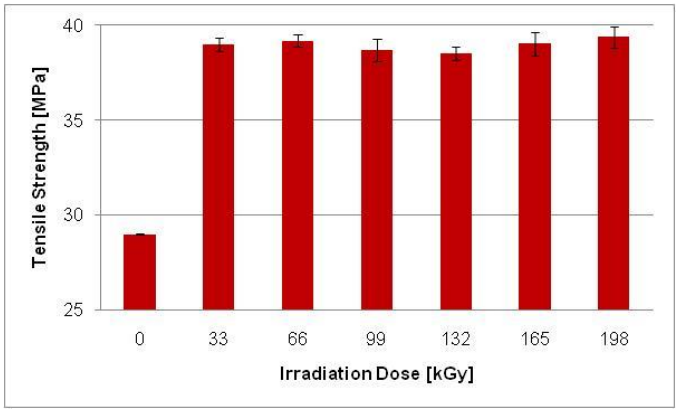

Fig. 7 PA12 Tensile strength at the temperature 80°C

At 80°C tensile strength of irradiated PA12 specimens were increased about 10 MPa compared to non-irradiated PA12.

In the Fig. 8 it is shown the dependence of irradiation dose on the change of tensile strength for PA11 and PA12 at 80°C. The tensile strength is rather constant for PA11. The maximal rise is 5% for PA11 with the 99kGy dose of irradiation. The PA12 tensile strength rises sharply at 33kGy and then it stays with the increased doses of irradiation is tensile strength constant. The maximal rise is 35% for PA12 with the 66kGy dose of irradiation.

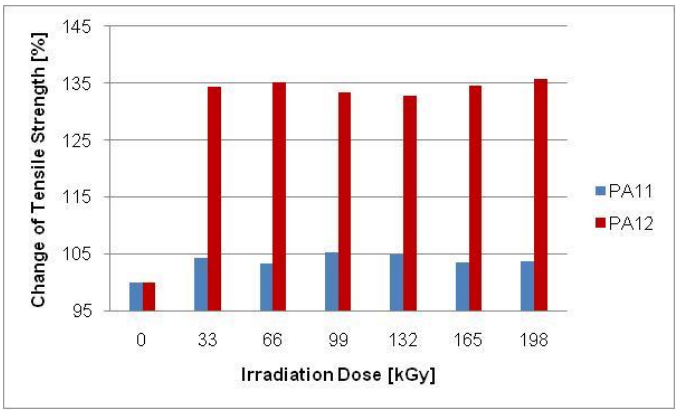

Fig. 8 Comparison of tensile strength of PA11 and PA12 at 80°C

Irradiation affects the E-modulus of the PA11 studied at both the ambient (Fig. 9) and increased temperature.

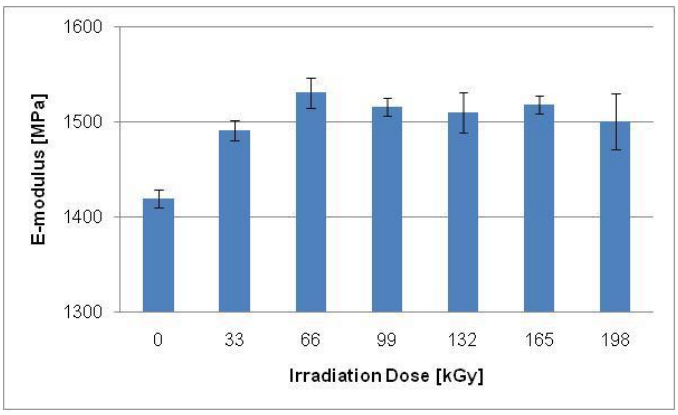

Fig. 9 PA11 E-modulus at the temperature 23°C

At the ambient temperature PA11 E-modulus is increased up to 66kGy and then it is begun to decrease with increased irradiation dose.

Irradiation affects the E-modulus of the PA12 studied at both the ambient (Fig. 10) and increased temperature.

At the ambient temperature PA12 E-modulus is increased sharply at 33kGy about 500MPa and then it is increased slightly along the irradiation doses.

In the Fig. 11 is displayed the dependence of irradiation dose on the change of E-modulus for PA11 and PA12 at 23°C. The E-modulus is rather constant for PA11. The maximal rise is 9% for PA11 with the 66kGy dose of irradiation. The PA12 E-modulus rises sharply at 33kGy and then with the increased doses of irradiation tensile strength steadily increases. The maximal rise is 74% for PA12 with the 198kGy dose of irradiation.

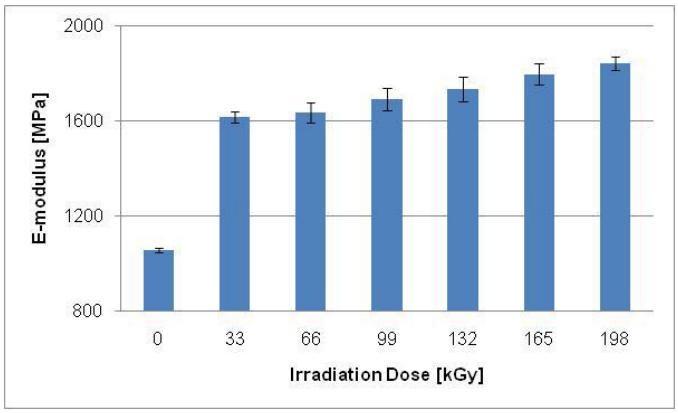

Fig. 10 PA12 E-modulus at the temperature 23°C

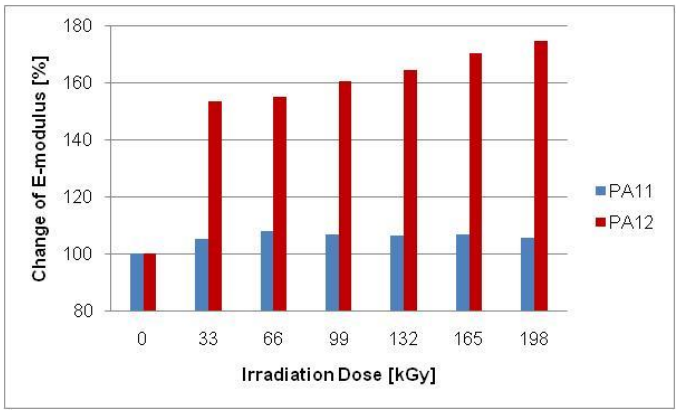

Fig. 11 Comparison of E-modulus of PA11 and PA12 at 23°C

Irradiation affects the E-modulus of the PA11 studied at 80°C (Fig. 12).

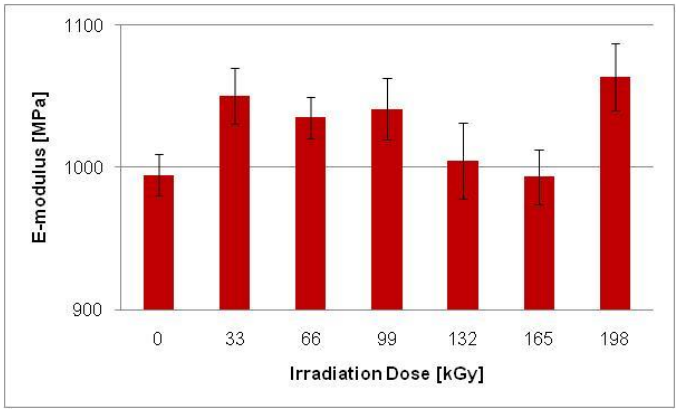

Fig. 12 PA11 E-modulus at the temperature 80°C

PA11 E-modulus at 80°C is increased up to 33kGy and then it is begun to decrease with irradiated dose up to 165kGy then there is increasing about 70MPa at 198kGy.

Irradiation affects the E-modulus of the PA12 studied at 80°C (Fig. 13). Irradiated PA12 with the irradiation dose of 165kGy is increased about 100MPa compared to non-irradiated PA12.

In the Fig. 14 is shown the dependence of irradiation dose on the change of E-modulus for PA11 and PA12 at 80°C. The PA11 E-modulus changes minimally along with increased

irradiation dose. The maximal rise is 7% for PA11 with the 198kGy dose of irradiation. The PA12 E-modulus rises by 11% at 33kGy and then with the increased doses of irradiation is E-modulus rather constant up to 99kGy and then E-modulus of 165kGy irradiated PA12 rises by 29% against non-irradiated PA12.

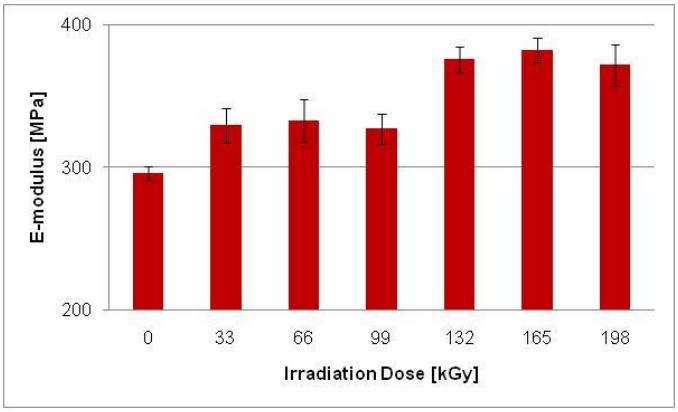

Fig. 13 PA12 E-modulus at the temperature 80°C

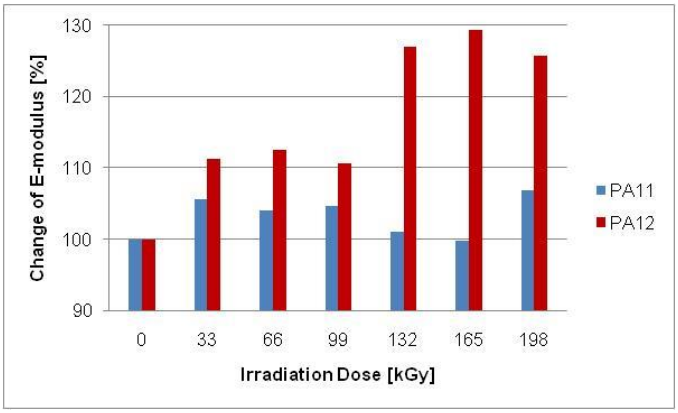

Fig. 14 Comparison of E-modulus of PA11 and PA12 at 80°C

2) Hardness

Irradiation affects the hardness of PA11 and PA12 were studied at the ambient temperature. In the Fig. 15 it is possible to see the changes of hardness of PA11 at the ambient temperature.

At the ambient temperature PA11 Shore D hardness is slightly increased with the increase irradiation dose. The Shore D hardness of irradiated PA11is increased by 2 Shore D compared to non-irradiated PA11 at 165kGy.

In the Fig. 16 it is possible to see the changes of hardness of PA12 at the ambient temperature.

At the ambient temperature PA12 Shore D harness is increased with the increase irradiation dose up to 165kGy. The Shore D hardness of irradiated PA12 is increased about 3,2 Shore D compared to non-irradiated PA12 at 165kGy.

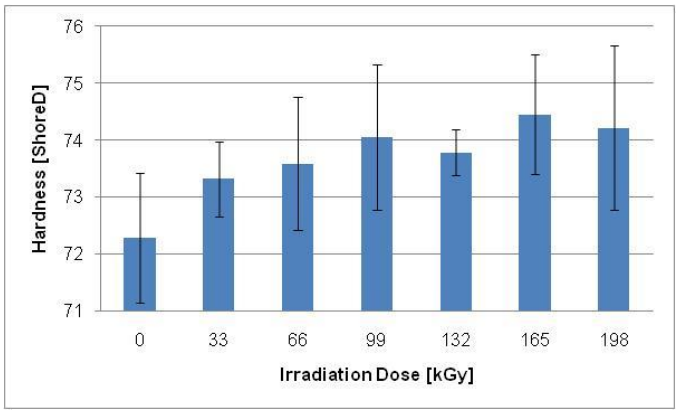

Fig. 15 PA11 Hardness at the temperature 23°C

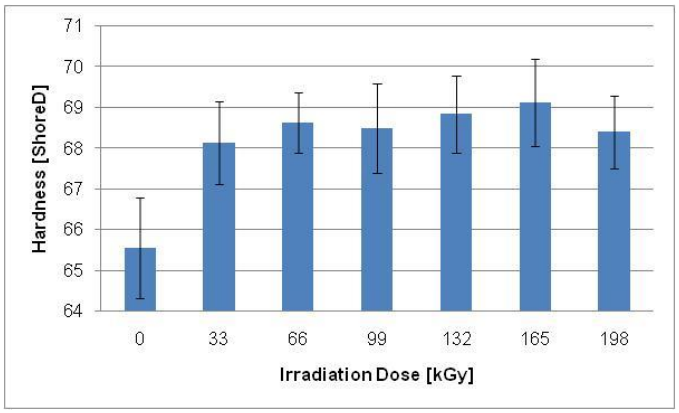

Fig. 16 PA12 Hardness at the temperature 23°C

In the Fig. 17 is shown the dependence of irradiation dose on the change of hardness for PA11 and PA12 at 23°C.

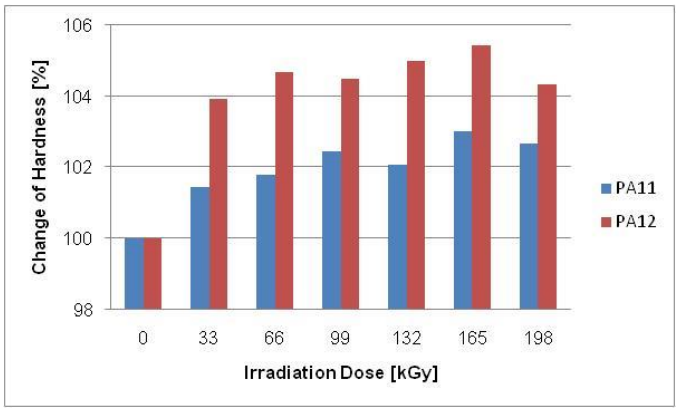

Fig. 17 Comparison of hardness of PA11 and PA12 at 23°C

No significant changes of hardness were found after the irradiation on the PA11 and PA12 sample. A maximum increase of PA11 hardness (i.e. about 3%) was measured after the irradiation dosage of 165kGy. Higher doses of irradiation had no significant effect on the PA11 Shore D Hardness. A maximum increase of PA12 hardness (i.e. about 5%) was measured after the irradiation dosage of 132kGy. Higher doses of irradiation had no significant effect on the PA12 Shore D Hardness.

B. Temperature Stability

The temperature stability of selected polymers was measured. The temperature stability was evaluated by TMA measurement and by visual observation. The graphical depiction of TMA results and description of a test record of the temperature stability inside a temperature chamber are numerically distinguished according to the dose of radiation. Specimens are numbered from 1 to 7 according to the dose of irradiation (number 1 means non-irradiated polymer – 0kGy, number 7 the specimen with the highest dose – 198kGy).

1) Thermo-mechanical analysis

Irradiation affects the thermo-mechanical properties of the studied PA11 (Fig. 18).

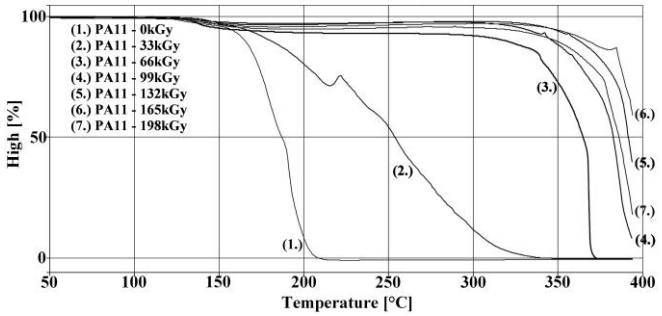

Fig. 18 Thermo-mechanical analysis of PA11

Non-irradiated PA11 is melted at the temperature 200°C. Irradiated PA11 at 33kGy is melted at the temperature 330°C. PA11with the increased doses above 66kGy have not lost the temperature stability up to 350°C (Fig. 18). Irradiated PA11 specimens above the dose of irradiation 66 kGy evince the significant improvement of temperature stability.

Irradiation affects the thermo-mechanical properties of the studied PA12 (Fig. 19).

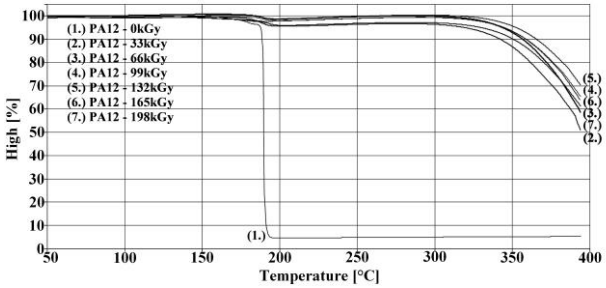

Fig. 19 Thermo-mechanical analysis of PA12

Non-irradiated PA12 is melted at the temperature 190°C. Irradiated PA12 specimens have not lost the temperature stability up to 350°C (Fig. 19). Irradiated PA12 specimens evince the significant improvement of temperature stability.

2) Visual Observation of Selected Polymers in the Temperature Chamber

The visual observation of sample behavior at the temperature is given in the next pictures.

Specimens are fitted horizontally in the temperature chamber and loaded by the bending moment both form its own weight and the weight on the end of specimen.

The visual observation of PA11 sample behaviour at 150°C is given on Fig. 20. Non-irradiated PA11 start to deform at the temperature 150°C. Higher irradiated PA11 are not deformed. The surface quality and the colour of polymer is the same like before the exam.

The visual observation of PA12 sample behaviour at 150°C is given on Fig. 21. All PA12 specimens are not deformed. The surface quality and the colour of polymer is the same like before the exam.

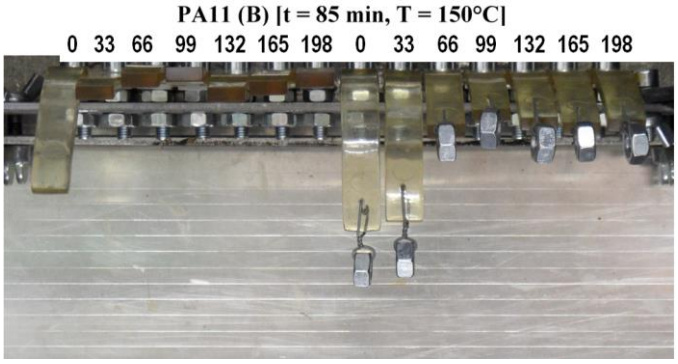

Fig. 20 PA11 specimen deformation at 150°C

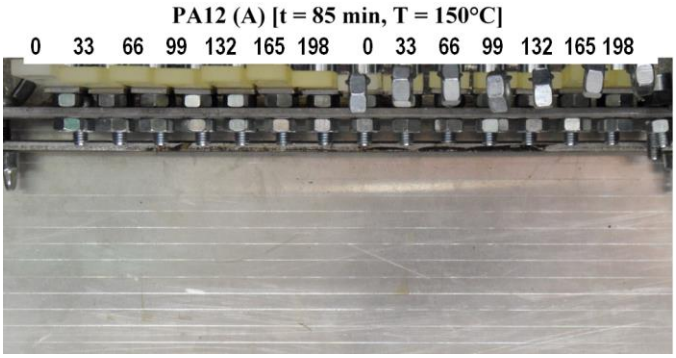

Fig. 21 PA12 specimen deformation at 150°C

The visual observation of PA11 sample behavior at 220°C is given on Fig. 22. At 220°C the non-irradiated PA11 specimen is totally melted while the polymer irradiated by the dose of 198kGy keeps its cross-section without changes, there is only deformation by its own weight. The surface quality of polymer is the same like before the exam.

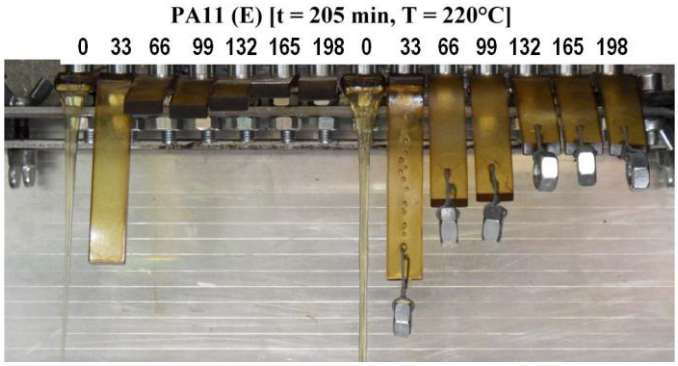

Fig. 22 PA11 specimen deformation at 220°C

The visual observation of PA12 sample behavior at 220°C is given on Fig. 23. At 220°C the non-irradiated PA12 specimen is totally melted while the polymer irradiated by the dose of 198kGy keeps its cross-section without changes, there is only deformation by its own weight. The surface quality and the colour of polymer start to deteriorate.

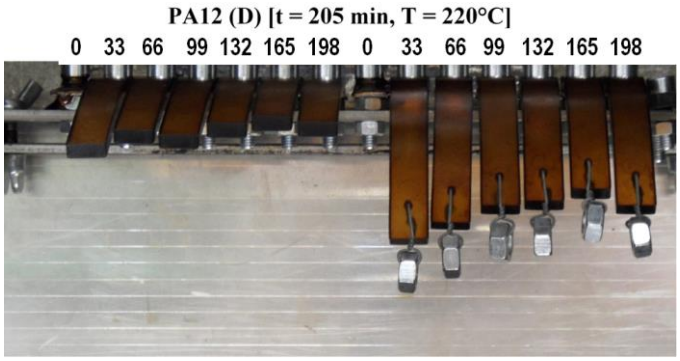

Fig. 23 PA12 specimen deformation at 220°C

The visual observation of sample behavior at 250°C is given on Fig. 24. The irradiated PA11 by the dose of 198kGy keeps its cross-section without changes; there is only deformation by its own weight. The surface quality and the colour of polymer start to deteriorate.

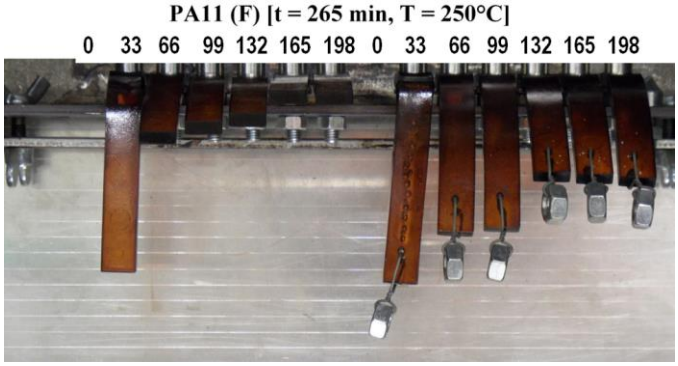

Fig. 24 PA11 specimen deformation at 250°C

The visual observation of sample behavior at 250°C is given on Fig. 25. Specimen deformation is decreasing with increasing dose of radiation at elevated temperature. At 250°C the specimen from not irradiated PA12 is totally melted while the polymer irradiated by the dose of 198kGy keeps its cross-section without changes, there is only deformation by its own weight. The surface quality worsens and the colour of polymer specimen change due to thermo-oxidation.

The temperature stability of polymers is very low in comparison with other construction materials. Experiments done in this project showed that irradiation cross-linking markedly affected the temperature stability of the studied selected polymers. The higher irradiation dosage, the better the temperature stability of these polymers is. The tested specimens remained without dimensional changes at the higher temperatures after irradiation. The same specimen, at higher temperatures, creates changes of colour due to thermal oxidation - but its dimension/cross-section remains without change. Their better temperature stability make possible to use the studied selected polymers even at service temperatures higher than their former melting point.

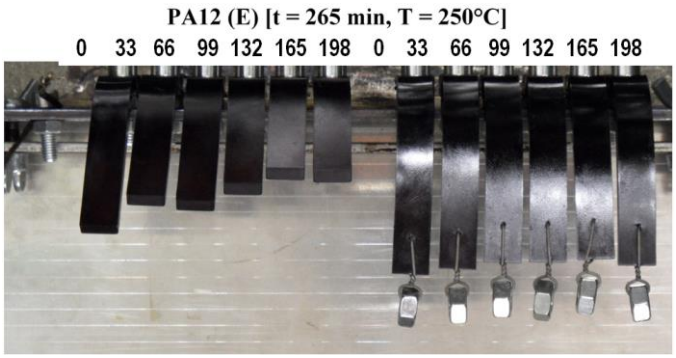

Fig. 25 PA12 specimen deformation at 250°C

IV. Conclusion

Plastics are by far the largest group of polymeric materials being processed by electron beam irradiation. Cross-linking of polyolefins, PVC, polyesters, polyurethanes, fluoropolymers and fiber-reinforced composites are a common practice. Radiation cross-linking of PE requires considerably less overall energy and space, and is faster, more efficient and more environmentally acceptable. The disadvantage of electron beam cross-linking is a more or less nonuniform dose distribution. This can happen, particularly in thicker objects, due to intrinsic dose-depth profiles of electron beams. Another problem can be a nonuniformity of rotation of cylindrical objects as they traverse a scanned electron beam. However, the mechanical properties often depend on the mean cross-link density. [1]

The results of the measurements of PA11and PA12 after irradiation showed significant changes of their mechanical and thermo-mechanical properties. The irradiated PA11 mechanical properties are changed minimally at both temperatures 23°C and 80°C, the increase is only about 5%. Unlike irradiated PA12 where mechanical properties are changed significantly. The tensile strength of PA12 with dose of irradiation 66kGy is higher than non-irradiated PA12 by 35% at 80°C. The E-modulus of PA12 with the doses of irradiation 198kGy is higher than non-irradiated PA12 by 70%. A very important point is the improvement of the PA11 and PA12's temperature stability, after irradiation. This significantly moves the application possibilities of the PA11 and PA12s which we tested to areas with much higher service temperatures than their former melting-point. The future measurements of PA11 and PA12will show if these materials are acceptable for radiation technology.

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