Properties of Selected Polymers after Radiation Cross-linking

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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 TPE-E thermoplastic elastomer, LDPE low density polyethylene and PA6 polyamide 6 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 TPE-E, LDPE and PA6 are presented in this paper.

***Keywords*—**Polymers, irradiation, cross-linking, 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]

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]

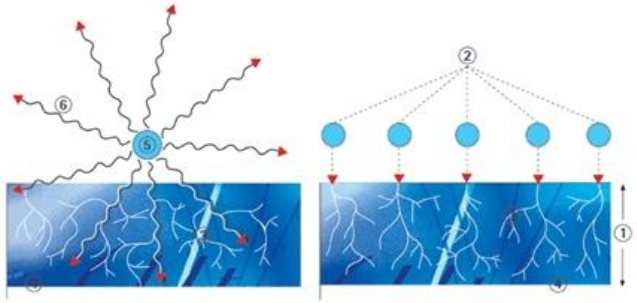

Fig. 1 Design of Gamma Rays (a) and Electron Rays (b),
1 – Penetration depth of an electron, 2 – Primary electron,
3 – Secondary electron, 4 – Irradiated material,
5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [2]

Beta and gamma rays can be used for the irradiation of

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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]

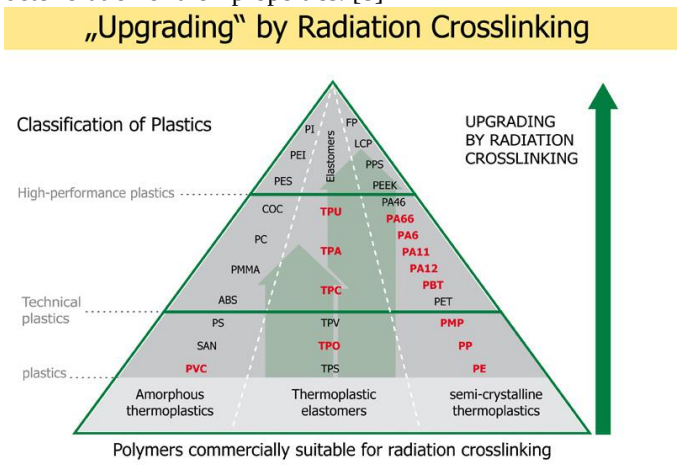

Fig. 2 Pyramid of Polymers [2]

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 materials were used Thermoplastic Elastomer (TPE-E, V-PTS-UNIFLEX-E25D/M*M800/20 natural) made in PTS company, Low Density Polyethylene (LDPE, BRALÉN, VA 20-60) made in Slovnaft Petrochemicals Company and Polyamide 6 (PA6, FRISETTA, Frianyl B63 VN) made in PTS company. 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 thermal stability of non-irradiated and irradiated selected polymers were tested after irradiation.

B. Used Methods for the Testing

Firstly, was determined the degree of cross-linking by gel measurements (gel content), according to the standard EN ISO 579. Then the mechanical properties were measured. Tensile test was carried out on tensile test machine ZWICK 1456 for LDPE and PA6, according to standard CSN EN ISO 527-1, 527-2 with used rate 50mm/min. Tensile test was carried out on tensile machine Alpha Technologies T2000 for TPE-E, according to standard CSN ISO 37 with used rate 500mm/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 gel content, mechanical and thermal behaviour of selected polymers (TPE-E, LDPE and PA6), before and after irradiation, was studied. For easy of evaluation of the measured data reasons, and the comparison of the irradiated polymer with a non-irradiated one, dimensionless values (-) were used in some cases. The property of the non-irradiated polymer had the dimensionless value of 1, while others were expressed as the ratio of measured property of irradiated polymers to the same property of non-irradiated polymer.

A. *Gel Content*

The results of the gel content measurements of TPE-E after irradiation showed Table 1. and Fig. 3.

Table 1 Gel Content of TPE-E after irradiation

Irradiation Dose (kGy)	Gel Content (%)
0	0
66	65,9
99	72,8
132	77,6
165	76,4
198	86,3

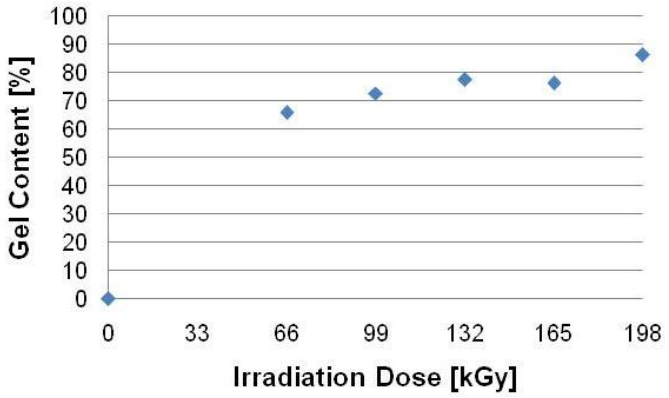

Fig. 3 Gel Content of TPE-E after irradiation

The highest gel content was measured by the TPE-E with the doses 198kGy.

The results of the gel content measurements of LDPE after irradiation showed Table 2. and Fig. 4.

Table 2 Gel Content of LDPE after irradiation

Irradiation Dose (kGy)	Gel Content (%)
0,0	0,0
15,3	0,0
30,3	0,0
45,8	0,0
73,2	29,0
111,4	55,0
146,2	57,1
183,9	56,2
219,6	67,3

At lower doses of radiation zero LDPE gel content was measured, but from the results of the tensile tests, we can observe an improving trend even at these low doses. This is due to the formation of microgels which build elastically active network chains and can transmit the tension. During the gel content determining, these microgels are filtered simultaneously with soluble parts - sol. Accuracy of the test depends on the size of the sieve's mesh.

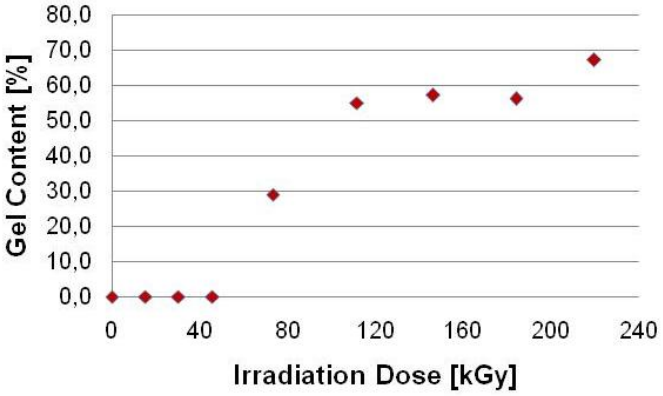

Fig. 4 Gel Content of LDPE after irradiation

PA6 gel content was measured only at the dose 99kGy. Irradiation PA6 with the dose 99kGy contains 67,4% gel content.

The results of all measurements are given in the Fig. 5.

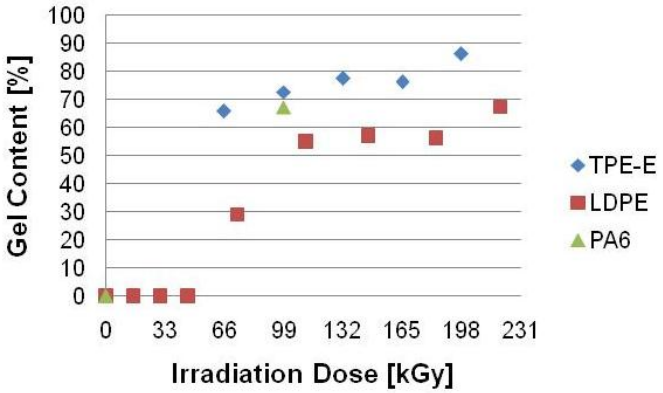

Fig. 5 Gel Content of the studied polymers

B. *Tensile Test and Hardness*

Irradiation affects the mechanical properties (tensile test and hardness) of the selected polymers (TPE-E, LDPE and PA6) studied at the ambient temperature.

1) *Tensile Strength, Elongation and E-modulus*

Irradiation affects the tensile strength of the TPE-E studied at the ambient temperature (Fig. 6).

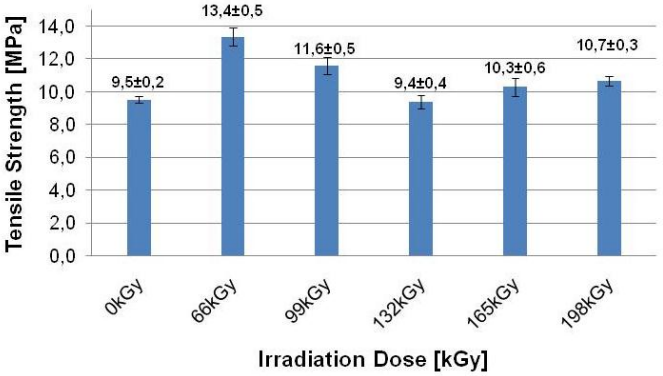

Fig. 6 TPE-E Tensile Strength at the ambient temperature

The TPE-E tensile strength rises more than 35% after irradiation with a dosage of 66 kGy. Although the gel content rises with the dose of irradiation, the tensile strength goes down with dosages higher than 66 kGy. Then, with a dosage of 132 kGy and higher, the value of the tensile strength oscillates around the value of the non-irradiated polymer. From the point-of-view of its TPE-E tensile strength a dosage of irradiation of 66 kGy would seem to be optimal (Fig. 6).

Irradiation affects the tensile strength of the LDPE studied at the ambient temperature (Fig. 7).

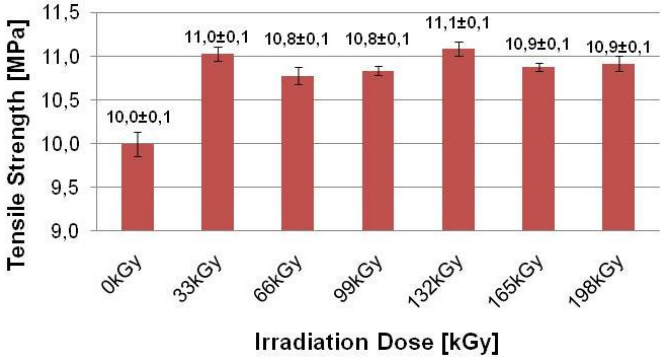

Fig. 7 LDPE Tensile Strength at the ambient temperature

At the ambient temperature the tensile strength of irradiation LDPE with a dosage of 132kGy, was increased about 1,1 MPa compared to non-irradiated LDPE.

Irradiation affects the tensile strength of the PA6 studied at the ambient temperature (Fig. 8).

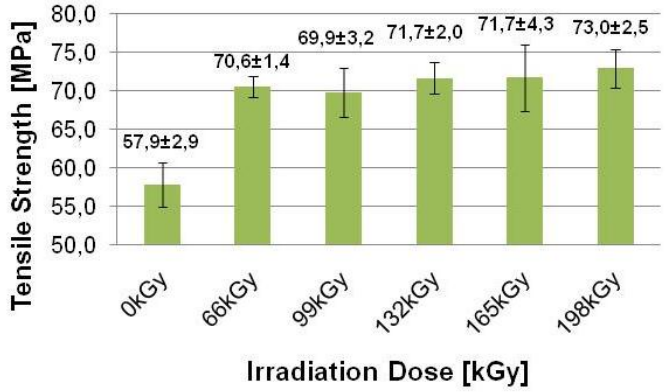

Fig. 8 PA6 Tensile Strength at the ambient temperature

At the ambient temperature the tensile strength of irradiation PA6 with a dosage of 198kGy, was increased about 15,1 MPa compared to non-irradiated PA6.

In the Fig. 9 it is possible to see the changes of tensile strength of selected polymers at the ambient temperature.

The TPE-E tensile strength rises by 40% after irradiation with a dosage of 66 kGy at the ambient temperature, but the PA6 tensile strength rises only 27% after irradiation with a dosage of 198 kGy. From the point-of-view of its tensile strength, the dosage of irradiation 66 kGy would seem to be optimal for TPE-E, 132kGy for LDPE and 198 for PA6 (Fig. 9).

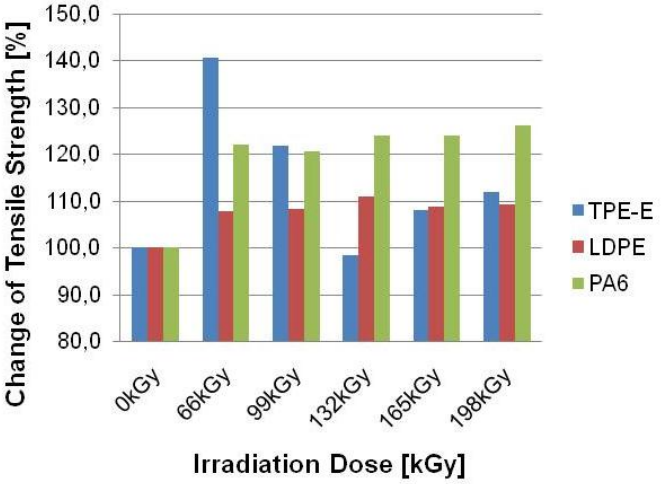

Fig. 9 Comparison of Tensile Strength of selected polymers in percentage

Irradiation affects the elongation of the TPE-E studied at the ambient temperature (Fig. 10).

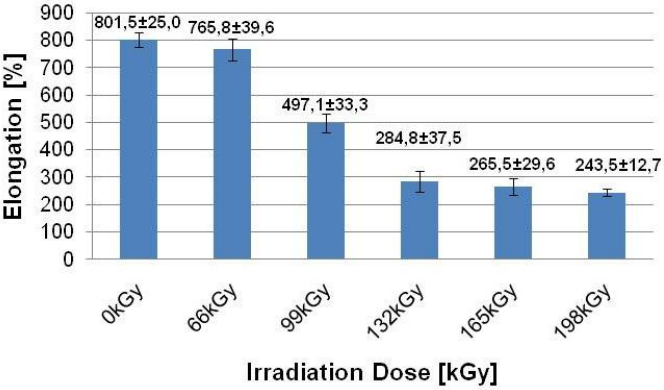

Fig. 10 TPE-E Elongation at the ambient temperature

Elongation of the TPE-E goes down continually in line with the irradiation dosage. At the highest applied dosage of irradiation (i.e. 198 kGy), the elongation is only 25% of the former (non-irradiated) polymer. Due to irradiation, the studied TPE-E significantly loses its flexibility.

Irradiation affects the elongation of the LDPE studied at the ambient temperature (Fig. 11).

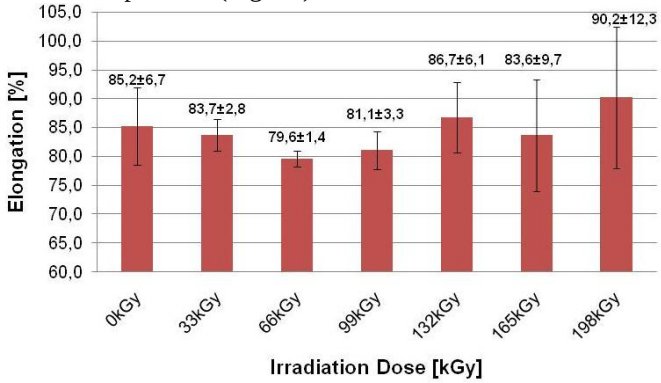

Fig. 11 LDPE Elongation at the ambient temperature

At the ambient temperature the elongation of irradiated LDPE with a dosage of 198kGy, was increased about 5 MPa compared to non-irradiated LDPE.

Irradiation affects the elongation of the PA6 studied at the ambient temperature (Fig. 12).

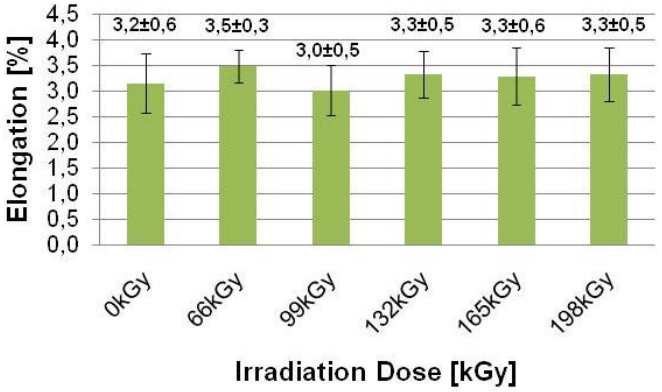

Fig. 12 PA6 Elongation at the ambient temperature

At the ambient temperature the elongation of irradiated PA6 was not changed compared to non-irradiated PA6.

In the Fig. 13 it is possible to see the changes of elongation of selected polymers at the ambient temperature.

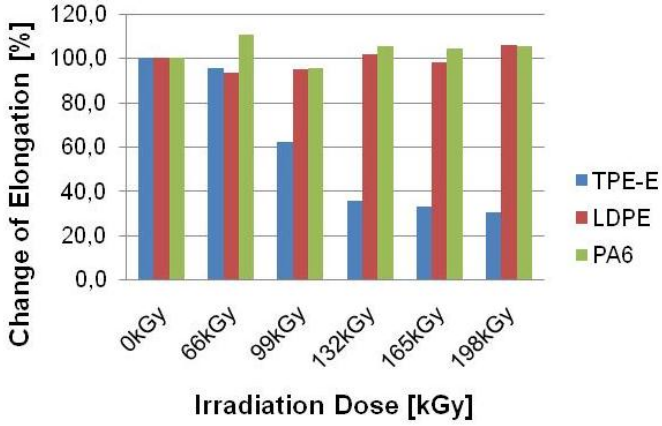

Fig. 13 Comparison of Elongation of selected polymers in percentage

Elongation of the TPE-E goes down continually in line with the irradiation dosage. No significant changes of elongation were found after the irradiation of the sample LDPE and PA6.

Irradiation affects the E-modulus of the TPE-E studied at the ambient temperature (Fig. 14).

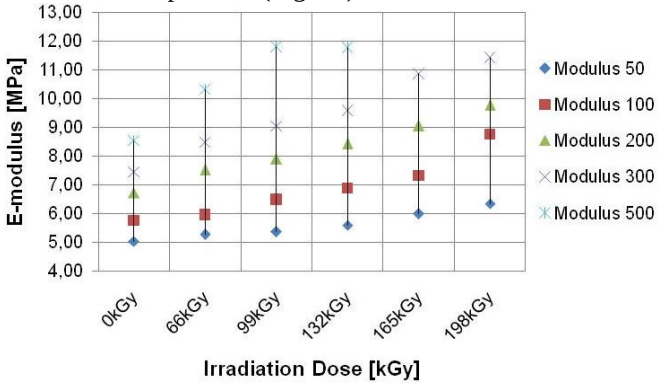

Fig. 14 TPE-E E-modulus at the ambient temperature

The modulus of Elasticity rises gradually in line with the dosage of irradiation. The Modulus 100 is higher by 25% and the modulus 300 is more than 50% higher after irradiation with a dosage of 198kGy (Fig. 14).

Irradiation affects the E-modulus of the LDPE studied at the ambient temperature (Fig. 15).

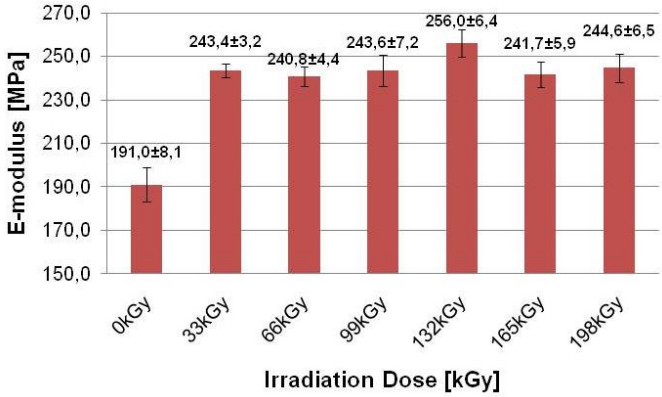

Fig. 15 LDPE E-modulus at the ambient temperature

At the ambient temperature the E-modulus of irradiated LDPE with a dosage of 132kGy, was increased about 65 MPa compared to non-irradiated LDPE.

Irradiation affects the E-modulus of the PA6 studied at the ambient temperature (Fig. 16).

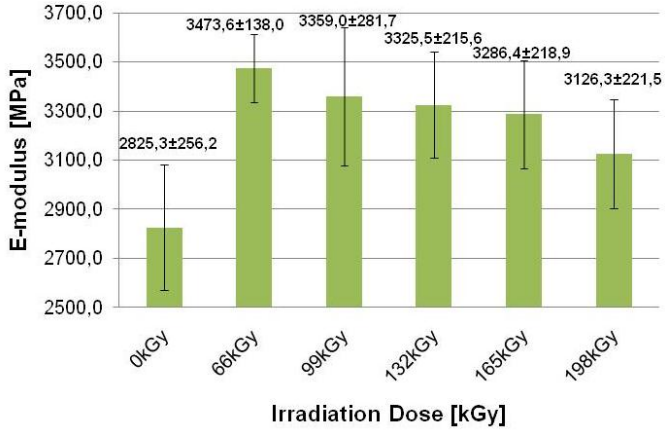

Fig. 16 PA6 E-modulus at the ambient temperature

At the ambient temperature the E-modulus of irradiated PA6 with a dosage of 66kGy, was increased about 648 MPa compared to non-irradiated PA6.

In the Fig. 17 it is possible to see the changes of E-modulus of selected polymers at the ambient temperature.

The TPE-E E-modulus rises more than 50% after irradiation with a dosage of 198 kGy at the ambient temperature, but at the same temperature the PA6 E-modulus rises only 20% after irradiation with a dosage of 66 kGy. From the point-of-view of its elastic modulus, the dosage of irradiation 198 kGy would seem to be optimal for TPE-E, 132kGy for LDPE and 66kGy for PA6.

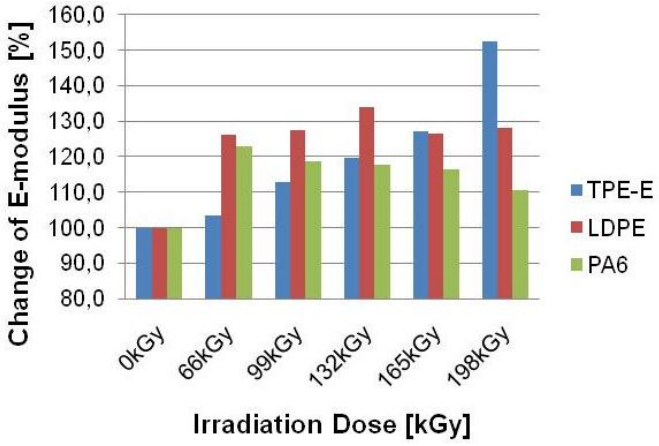

Fig. 17 Comparison of E-modulus of selected polymers in percentage

2) Hardness

Irradiation affects the hardness of selected polymers studied at the ambient temperature. In the Fig. 18 it is possible to see the changes of hardness of selected polymers at the ambient temperature.

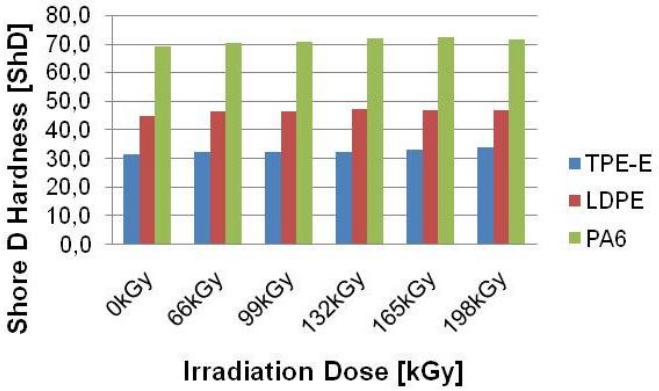

Fig. 18 Comparison of Hardness of selected polymers

At the ambient temperature the Shore D hardness of irradiated PA6 with a dosage of 165kGy, is higher about 40 MPa than irradiated TPE-E with a dosage of 165kGy.

In the Fig. 19 it is possible to see the changes of hardness of selected polymers at the ambient temperature.

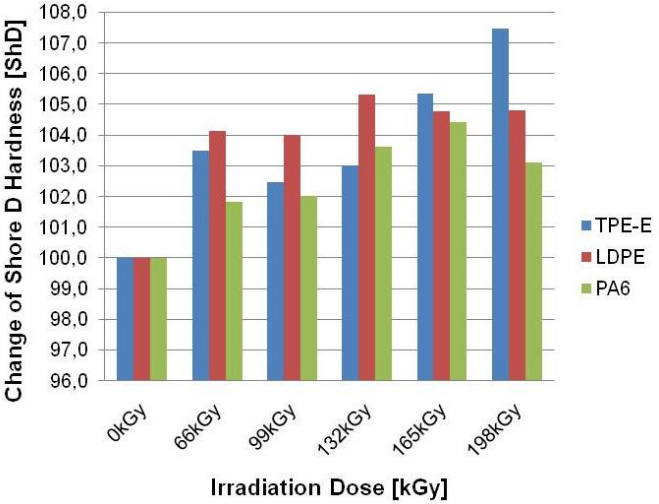

Fig. 19 Comparison of Hardness of selected polymers in percentage

No significant changes of hardness were found after the irradiation on the selected polymer samples. A maximum increase of TPE-E hardness (i.e. about 8%) was measured after the irradiation dosage of 198kGy.

C. 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 and colorfully 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 TPE-E (Fig. 20).

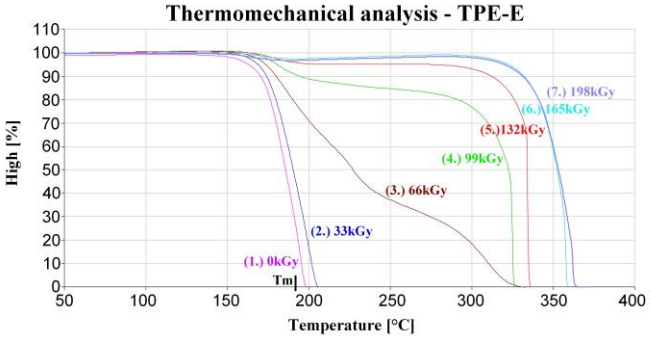

Fig. 20 Thermo-mechanical Analysis of TPE-E

Already small dose of radiation (up to 33kGy) move the softening point up to 210°C. TPE-E irradiated by the dose of 198kGy evinces the significant improvement of the temperature stability. Irradiation TPE-E with the dose 198kGy holds temperature stability up to 360°C for short time.

Irradiation affects the thermo-mechanical properties of the studied LDPE (Fig. 21).

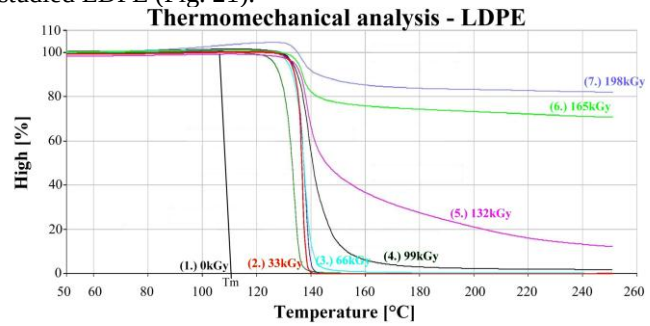

Fig. 21 Thermo-mechanical Analysis of LDPE

Already small dose of radiation (up to 33kGy) move the softening point up to 140°C. LDPE irradiated by the dose of 198kGy evince the significant improvement of the temperature stability. There is 20% spike penetration into LDPE radiated by dose of 198kGy at 220°C.

Irradiation affects the thermo-mechanical properties of the studied PA6 (Fig. 22).

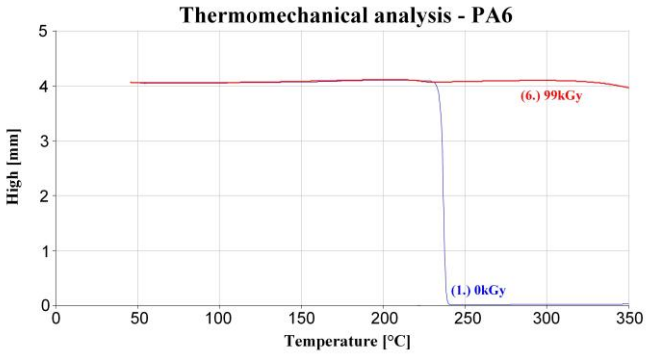

Fig. 22 Thermo-mechanical Analysis of PA6

Non-irradiated PA6 was melted at 240°C. However, irradiated PA6 with the dose 99kGy moves the temperature stability for short time up to 350°C.

2) Visual Observation of Selected Polymers in the Temperature Chamber

The visual observation of sample behavior at the temperature is given in Fig. 23, 24 and 25.

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 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.

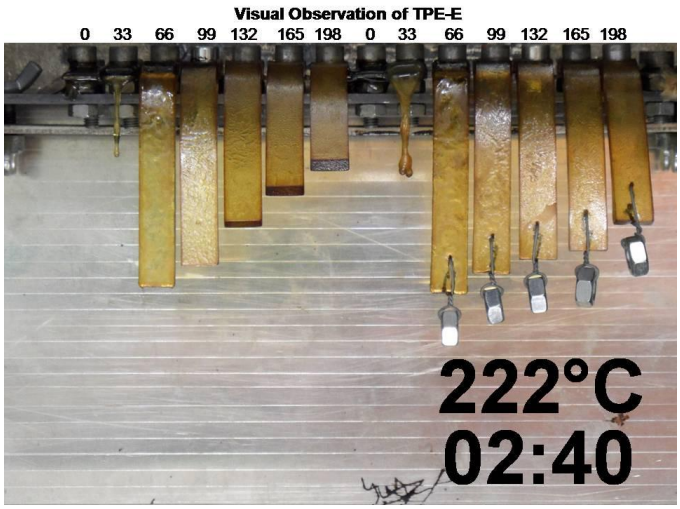

Fig. 23 TPE-E specimen deformation at 222°C

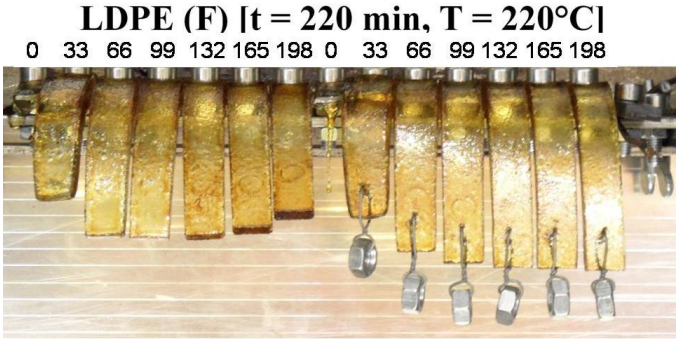

Fig. 24 LDPE specimen deformation at 220°C

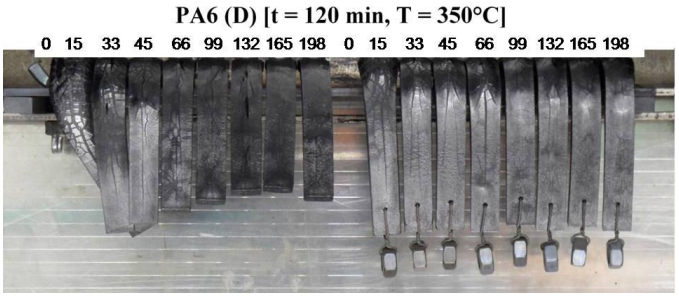

Fig. 25 LDPE specimen deformation at 220°C

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 TPE-E, LDPE and PA6 after irradiation showed significant changes of its mechanical and thermo-mechanical properties. The tensile strength rises for all measured materials, after irradiation with a dosage of kGy. The E –modulus rises gradually in line with the dose of irradiation. The maximum difference (about 50%) between irradiated and non-irradiated TPE-E was measured after irradiation with a dosage of 198 kGy. A very important point is the improvement of the TPE-E, LDPE, PA6's thermal stability, after irradiation. This significantly moves the application possibilities of the TPE-E, LDPE, PA6s we tested to an area with service temperatures much higher than their former melting-point.

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