Temperature stability comparison of commodity and engineering thermoplastics after radiation cross-linking

Ales Mizera, Miroslav Manas, Zdenek Holik, David Manas, Michal Stanek, Jan Navratil, and Martin Bednarik

***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 selected thermoplastic tests showed significant changes of temperature stability after radiation cross-linking. From this point-of-view, new applications could also be seen in areas with service temperatures higher than their former melting point. The temperature stability comparison of irradiated and non-irradiated materials are presented in this paper.

***Keywords*—**Polymers, irradiation, cross-linking, temperature stability.

I. Introduction

POLYMERS rank among a construction materials which find use in industry branches the most. The advantage of polymers is a low weight together with the excellent mechanical properties, very good chemical resistance and other properties, which assign them for various applications. Disadvantage is mainly low temperature stability which significantly reduces usage of these polymers.

Every property improvement especially temperature stability helps to increase application possibilities. In addition, property modifications of standard polymers, which are relatively cheap products, give them advantage for another usage. One of the possibilities of improvement of polymers' properties is radiation cross-linking.

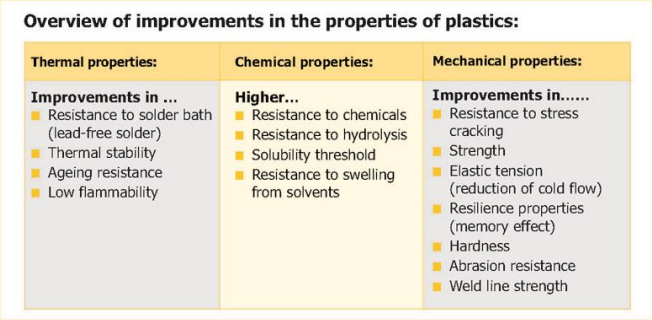

Fig. 1 Improved properties [2]

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

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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. 2). [1, 2]

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]

Radiation cross-linking of thermoplastic materials deals with creation of a cross-link among the macromolecular strings. Intermolecular forces are replaced by a covalent bond.

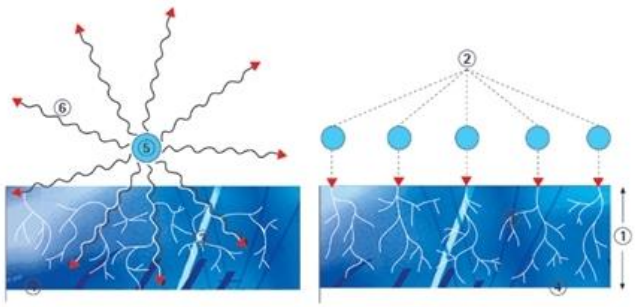

Fig. 2 Design of Gamma Rays (a) and Electron Rays (b),
1 – Penetration depth of an electron, 2 – Primary electron,
3 – Secondary electron, 4 – Irradiated material,
5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [2]

As a result, we can optimise properties of commodity and engineering polymers and impart them the properties of high performance polymers (Fig. 3). 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]

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 commodity polymers can be used in applications, which would be in term of temperature stability intended only to engineering thermoplastic polymers.

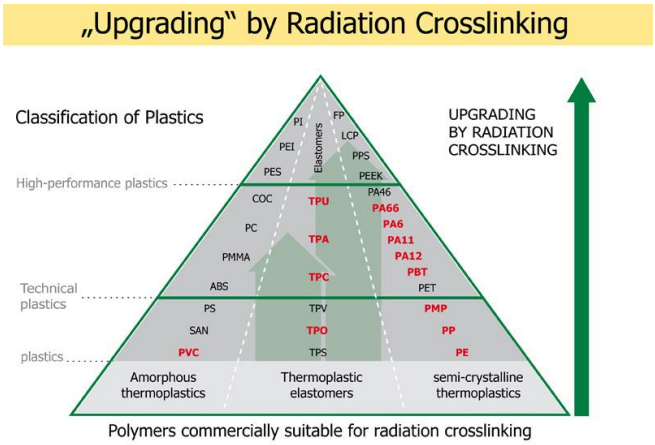

Fig. 3 Pyramid of Polymers [2]

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 thermoplastics were used:

- low density polyethylene (DOW LDPE 780E) made in DOW company,
- high density polyethylene (DOW HDPE 25055E), made in DOW company,
- thermoplastic elastomer (V-PTS-UNIFLEX-E25D/M* M800/20 natur) made in PTS company,
- polybutylene terephthalate (V-PTS-CREATEC-B3HZC* M800/25 natur) made in PTS company,
- polyamide 12 (V-PTS-CREAMID 12-AMN 0 TLD* M800/13 natur) made in PTS company,
- polyamide 11 (V-PTS-CREAMID-11T*M600/13 trans-parent) made in PTS company,
- polyamide 6 (PA6, FRISETTA, Frianyl B63 VN) made in NILIT Plastics company,
- polyamide 66 (PA66, FRISETTA, Frianyl A63 VN) made in NILIT Plastics 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 temperature stability of non-irradiated and irradiated selected polymers were tested after irradiation.

Fig. 4 Injection molding machine ARBURG Allrounder 420C [3]

B. Used Methods for the Testing

The thermo-mechanical properties and the temperature stability were measured. Perkin – Elmer Thermal Analyser TMA7 was used for the thermomechanical 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.

Fig. 5 Perkin Elmer DMA 7e [2]

III. Results and Discussion

The temperature behaviour of selected thermoplastics, before and after irradiation, was studied. The temperature stability was evaluated by TMA measurement and by visual observation.

A. Temperature stability

The temperature stability of selected thermoplastics 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 described the dose of radiation from 0 to 198 kGy.

1) Low density polyethylene (LDPE)

Irradiation affects the thermomechanical properties of the studied LDPE (Fig. 6). Non-irradiated sample is melted at the temperature 110°C. Irradiated LDPE samples with the dose of irradiation 33 and 66kGy are soften at the temperature 140°C. LDPE with the increased dose above 99kGy is not lost the temperature stability up to 160°C. Irradiated LDPE specimens above the dose of irradiation 165 kGy evince the significant improvement of temperature stability.

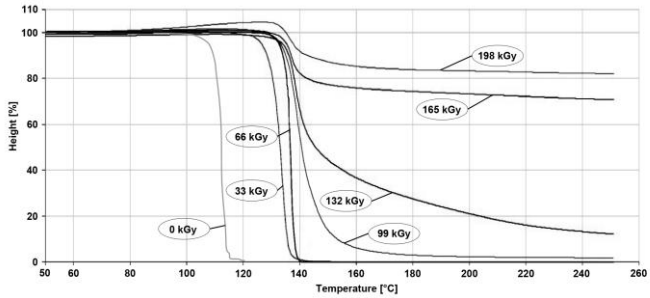

Fig. 6 LDPE thermomechanical analysis

The visual observation of sample behavior after two hours exposition at the temperature 220°C is given in Fig. 7. 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.

2) High density polyethylene (HDPE)

The Irradiation affects the thermomechanical properties of the studied HDPE (Fig. 8). Already small dose of radiation (up to 15kGy) move the softening point up to 170°C. HDPE irradiated by the dose of 198kGy evinces the significant improvement of temperature stability. There is 10% spike penetration into HDPE radiated by dose of 198kGy at 220°C.

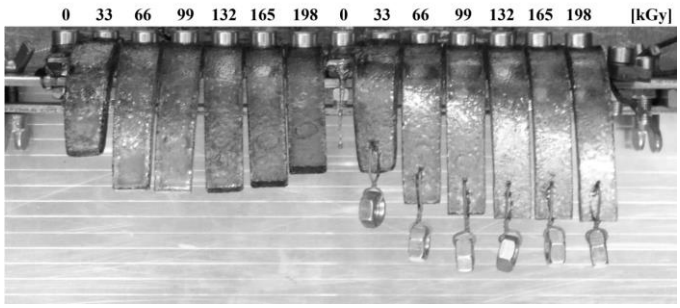

Fig. 7 LDPE specimen deformation after 2 hours temperature exposure 220°C

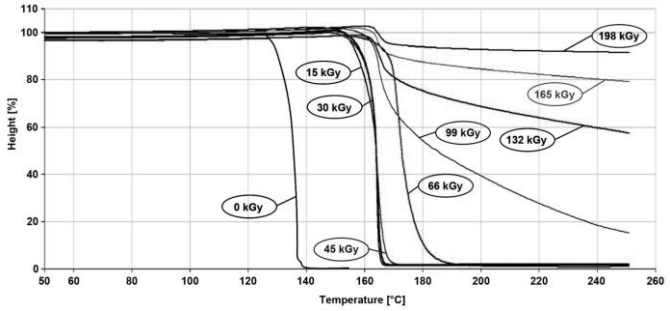

Fig. 8 HDPE thermomechanical analysis

The visual observation of sample behaviour after two hours exposition at 220°C is given on Fig. 9. 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. Specimen deformation is decreasing with increasing dose of radiation at elevated temperature. At 220°C the specimen from not irradiated HDPE 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.

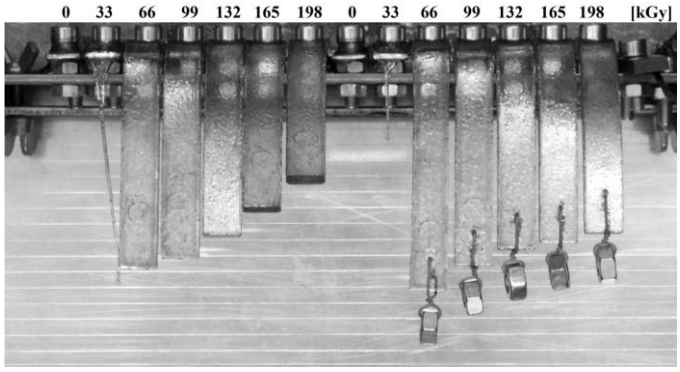

Fig. 9 HDPE specimen deformation after 2 hours temperature exposure 220°C

3) Thermoplastic elastomer (TPE)

Irradiation affects the thermomechanical properties of the studied TPE (Fig. 10). Already small dose of radiation (up to 33kGy) move the softening point up to 210°C. TPE irradiated by the dose of 198kGy evinces the significant improvement of the temperature stability. Irradiation TPE with the dose 198kGy holds temperature stability up to 360°C for short time.

The temperature stability of TPE was measured. The temperature stability was evaluated by visual observation in the temperature chamber. The visual observation of sample behaviour after two hours exposition at 220°C is given on Fig. 8.

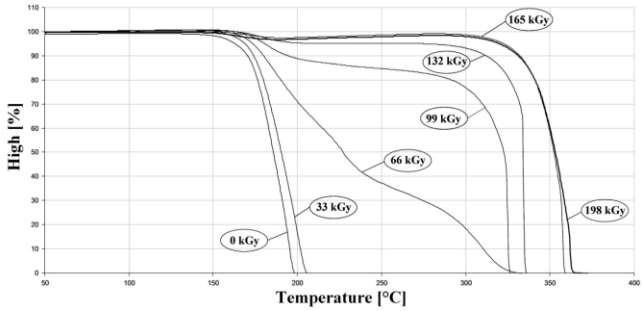

Fig. 10 TPE thermomechanical analysis

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. Specimen deformation is decreasing with increasing dose of radiation at elevated temperature (Fig. 11). At 220°C the specimen from not irradiated TPE 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.

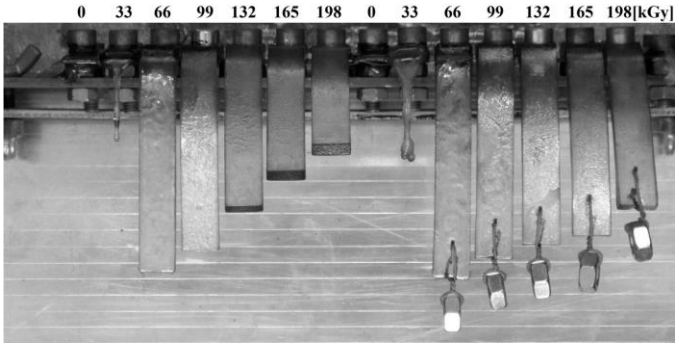

Fig. 11 TPE specimen deformation after 2 hours temperature exposure 220°C

4) Polybutylene terephthalate (PBT)

Irradiation affects the thermomechanical properties of the studied PBT (Fig. 12). Non-irradiated and irradiated PBT sample with the dose of irradiation 33 kGy are melted at the temperature 230°C. PBT with the increased dose above 132kGy is not lost the temperature stability up to 300°C. Irradiated PBT specimens above the dose of irradiation 132 kGy evince the significant improvement of temperature stability.

The visual observation of sample behaviour after one hour exposition at 250°C is given on Fig. 13. 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. Specimen deformation is decreasing with increasing dose of radiation at elevated temperature. At 250°C the specimen from not irradiated PBT 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.

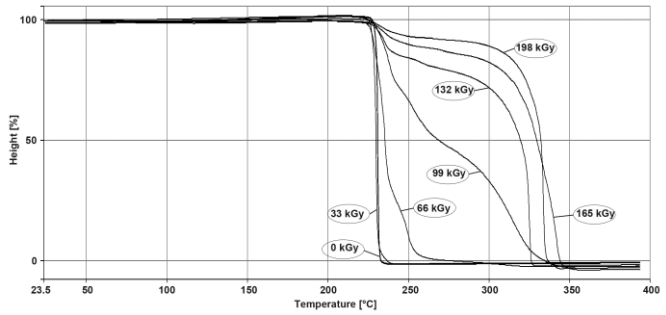

Fig. 12 PBT thermomechanical analysis

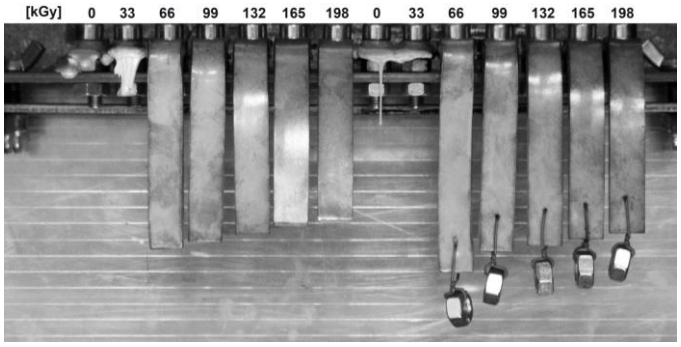

Fig. 13 PBT specimen deformation after 2 hours temperature exposure 250°C

5) Polyamide 12 (PA12)

Irradiation affects the thermomechanical properties of the studied PA12 (Fig. 14). Non-irradiated PA12 is melted at the temperature 190°C. Irradiated PA12 specimens have not lost the temperature stability up to 350°C. Irradiated PA12 specimens evince the significant improvement of temperature stability.

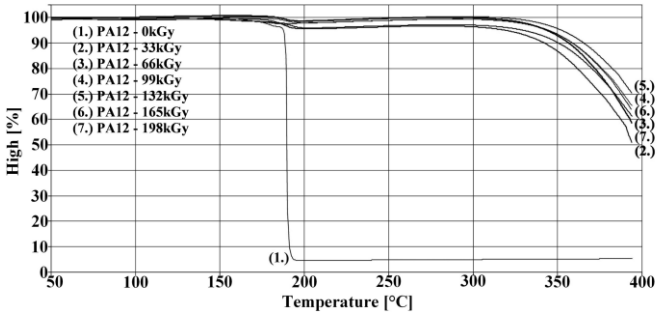

Fig. 14 PA12 thermomechanical analysis

The visual observation of sample behavior at 250°C is given on Fig. 15. 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.

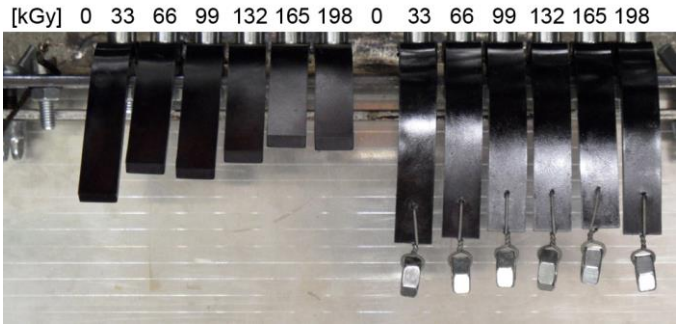

Fig. 15 PA12 specimen deformation after 2 hours temperature exposure 250°C

6) Polyamide 11 (PA11)

Irradiation affects the thermomechanical properties of the studied PA11 (Fig. 16). Non-irradiated PA11 is melted at the temperature 200°C. Irradiated PA11 at 33kGy is melted at the temperature 330°C. PA11with the increased dose above 66kGy have not lost the temperature stability up to 350°C. Irradiated PA11 specimens above the dose of irradiation 66 kGy evince the significant improvement of temperature stability.

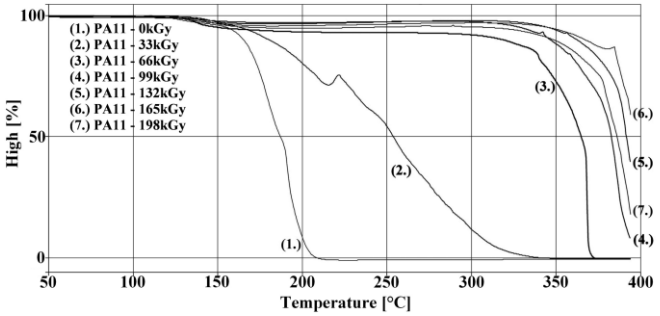

Fig. 16 PA11 thermomechanical analysis

The visual observation of sample behavior at 250°C is given on Fig. 17. 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.

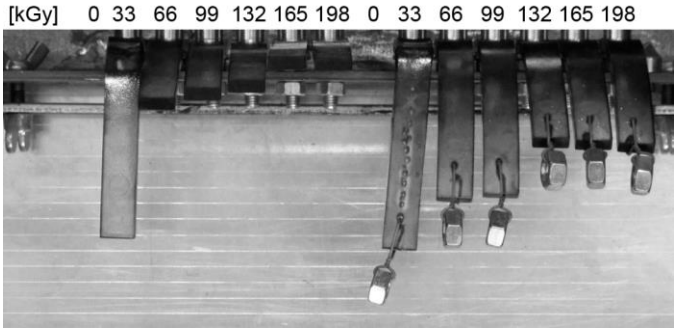

Fig. 17 PA11 specimen deformation after 2 hours temperature exposure 250°C

7) Polyamide 6 (PA6)

Irradiation affects the thermomechanical properties of the studied PA6 (Fig. 18). 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.

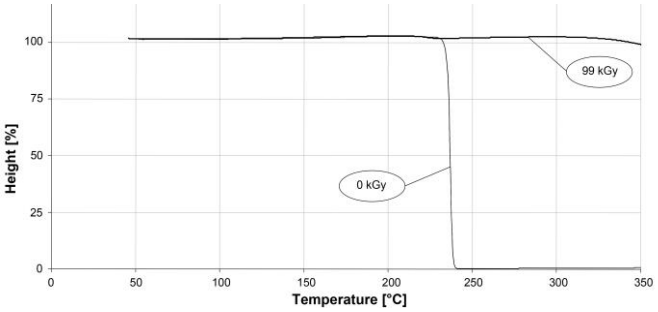

Fig. 18 PA6 thermomechanical analysis

The visual observation of sample behavior at 250°C is given on Fig. 19. Specimen deformation is decreasing slowly with increasing dose of radiation at elevated temperature. At 250°C the specimen from not irradiated PA6 is totally melted while the polymers with higher dose of irradiation keep their cross-section without changes, there are only deformation by their own weight.

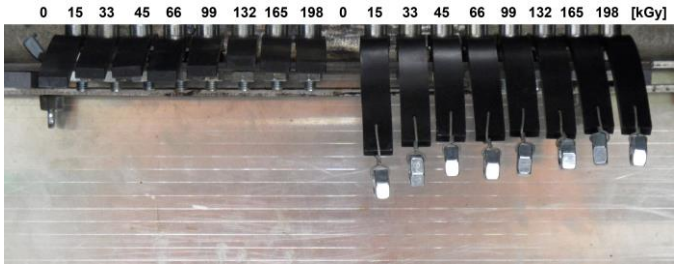

Fig. 19 PA6 specimen deformation after 2 hours temperature exposure 250°C

8) Polyamide 66 (PA66)

Irradiation affects the thermomechanical properties of the studied PA66 (Fig. 20). Non-irradiated PA66 was melted at 270°C. However, irradiated PA66 with the dose 99kGy moves the temperature stability for short time up to 350°C.

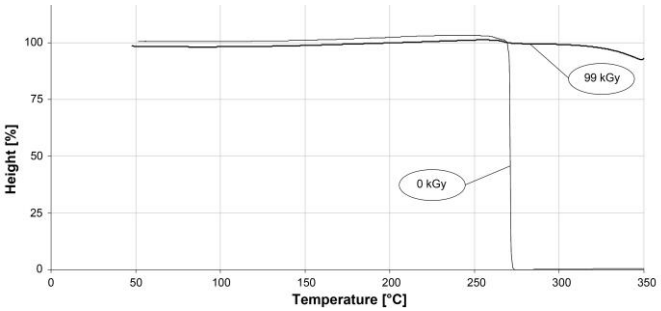

Fig. 20 PA66 thermomechanical analysis

The visual observation of sample behavior at 300°C is given on Fig. 21. Specimen deformation is decreasing slowly with increasing dose of radiation at elevated temperature. At 300°C the specimen from not irradiated PA66 is totally melted while the polymers with higher dose of irradiation keep their cross-section without changes, there are only deformation by their own weight.

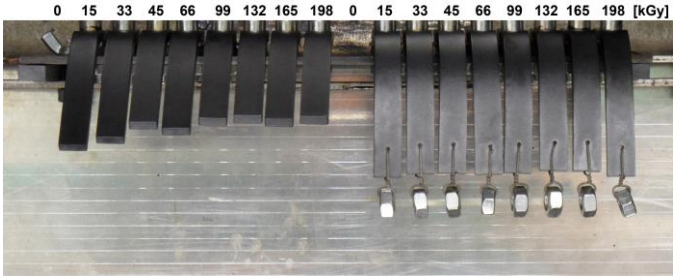

Fig. 21 PA66 specimen deformation after 2 hours temperature exposure 300°C

B. Thermal properties

It is useful knows the thermal properties of thermoplastics. When the thermal properties are used for prediction of temperature stability, the choice of materials for special applications is better. Thermal properties of commodity and engineering thermoplastic are given on Tab. 1 and Tab. 2. [10]

IV. Conclusion

Plastics are by far the largest group of polymeric materials being processed by electron beam irradiation. Cross-linking of construction polymers are a common practice. Radiation cross-linking of thermoplastics 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 selected thermoplastics after irradiation showed significant changes of their thermo-mechanical properties. A very important point is the improvement of the temperature stability, after irradiation. This significantly moves the application possibilities of the irradiated thermoplastics we tested to an area with service temperatures much higher than their former melting-point.

Acknowledgment

This paper is supported by the internal grant of TBU in Zlin No. IGA/FT/2014/016 funded from the resources of specific university research and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.

Tab. 1 Thermal properties of commodity thermoplastics and thermoplastic elastomer [10]

	Commodity thermoplastics		**Thermoplastic elastomer**
	LDPE	**HDPE**	**TPE**
Glass transition temperature [°C]	-130 to -100 / -30 to -10	-130 to -100	0 to 60
Melting temperature [°C]	100 to 115	125 to 135	190 to 230
Melting enthalpy [J/g]	(na)	293	30
Decomposition temperature [°C]	487 to 498	487 to 498	420 to 440
E-modulus [MPa]	200 to 400	600 to 1400	50 to 1000
Coefficient of linear thermal expansion [*10^6/K]	400	200 to 250	165 to 200
Specific heat capacity [J/(g.K)]	1,80 to 3,40	1,80 to 2,70	1,90 to 2,22
Thermal conductivity [W/(m.K)]	0,30 to 0,34	0,33 to 0,53	0,10 to 0,19
Density [g/cm^3]	0,91 to 0,93	0,94 to 0,96	1,00 to 1,20

Tab. 2 Thermal properties of engineering thermoplastics [10]

	Engineering thermoplastics				
	PBT	**PA12**	**PA11**	**PA6**	**PA66**
Glass transition temperature [°C]	40 to 60	40 to 50	40 to 55	45 to 80	65 to 90
Melting temperature [°C]	220 to 230	170 to 180	180 to 190	225 to 235	225 to 265
Melting enthalpy [J/g]	142	95	224	190	185
Decomposition temperature [°C]	408	464	430 to 450	435	430 to 473
E-modulus [MPa]	2500 to 2800	1400	1400	2800	3000
Coefficient of linear thermal expansion [*10^6/K]	80 to 100	120 to 140	85 to 120	80 to 90	35 to 45
Specific heat capacity [J/(g.K)]	1,30	1,17 to 1,26	1,26	1,59 to 1,70	1,67 to 1,70
Thermal conductivity [W/(m.K)]	0,25 to 0,29	0,22 to 0,24	0,23 to 0,28	0,22 to 0,33	0,24 to 0,33
Density [g/cm^3]	1,30 to 1,32	1,01 to 1,04	1,03 to 1,05	1,12 to 1,15	1,13 to 1,16

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