

Properties of HDPE 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 HDPE high density polyethylene 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 HDPE is presented in this paper.

Keywords—High density polyethylene, irradiation, cross-linking, temperature stability.

I. INTRODUCTION

POLYMERS belong to constructive materials which find use at the most industry branches. The advantage 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 properties improvement especially temperature stability helps to increase application possibilities. In addition, properties modification of standard polymers, which are relatively cheap products, gives them advantage for another usage. One of the possibilities of polymers properties

improvement is their radiation cross-linking.

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. 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 no 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]

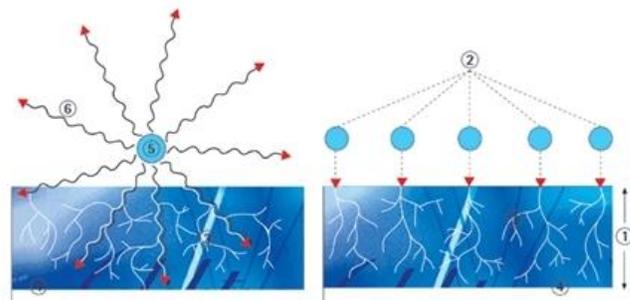


Fig. 1 Design of Gamma Rays (a) and Electron Rays (b), 1 – Penetration depth of an electron, 2 – Primary electron, 3 – Secondary electron, 4 – Irradiated material, 5 – Encapsulated Co – 60 Radiation source, 6 – Gamma Rays [2]

Beta and gamma rays can be used for the irradiation of polyolefines, polyesters, halogen polymers and polyamides

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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 of polyolefins, particularly the family of polyethylenes, represents an important segment of the radiation processing. Polyolefins can be irradiated in many forms, such as pellets and powder, films, extruded and molded parts or as wire and cable insulation. [1]

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.

II. MATERIAL AND METHODS

A. Material Preparation

As the basic polymer material was used High Density Polyethylene (HDPE 25055E) made in DOW Chemical Company. An ARBURG Allrounder 420C Advance Injection molding machine was used for sample preparation, with the processing conditional to comply with the HDPE producer's recommendations. Irradiation of tested HDPE polymer was 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 high density polyethylene 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 machine ZWICK 1456, according to standard CSN EN ISO 527-1, 527-2. 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, the flammability 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. The flammability was measured with hot fire test loop, according to standard CSN EN 60695-2. The temperature stability was determined by visual observation in the temperature chamber.

III. RESULTS AND DISCUSSION

The gel content, mechanical and thermal behaviour of high density polyethylene (HDPE), 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 HDPE after irradiation showed Table 1. and Fig. 2.

Table 1 Gel Content of HDPE after irradiation

Irradiation Dose (kGy)	Gel Content (%)
0	0
15,3	0
30,3	0
45,8	0
73,2	0
111,4	54,8
146,2	56,4
183,9	59,7
219,6	65,3

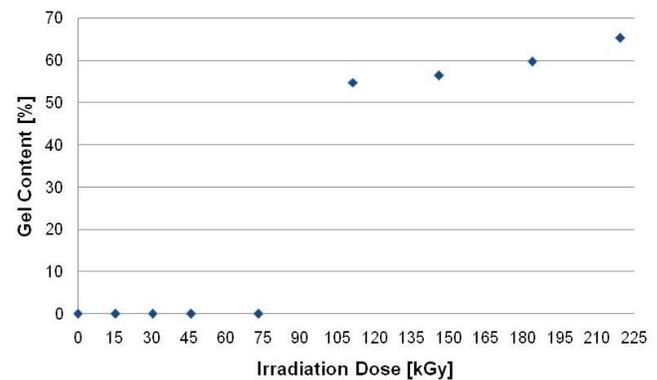


Fig. 2 Gel Content of HDPE after irradiation

At lower doses of radiation zero HDPE gel content was measured, but from the results of 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.

B. Tensile Test and Hardness

Irradiation affects the mechanical properties of the HDPE studied at the ambient temperature for hardness and at 23°C and 100°C for tensile test.

1) Tensile Strength and E-modulus

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

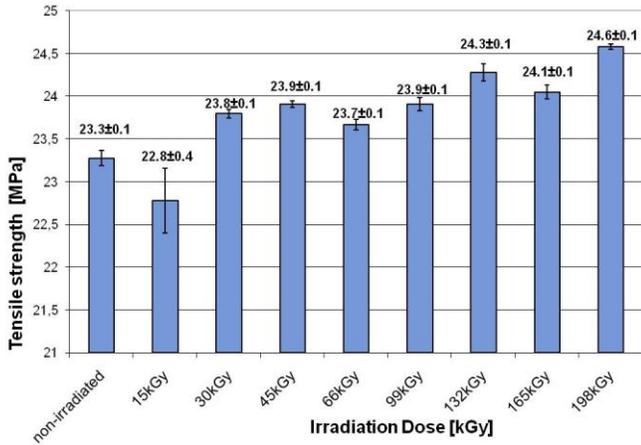


Fig. 3 HDPE Tensile Strength at the ambient temperature

At the ambient temperature tensile strength of irradiation HDPE with a dosage of 198kGy, was increased about 1,3 MPa compared to non-irradiated HDPE.

Irradiation affects the tensile strength of the HDPE studied at 100°C (Fig. 4).

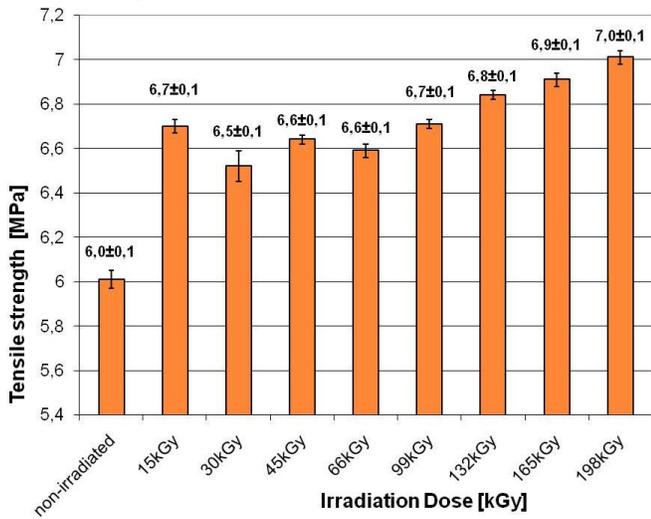


Fig. 4 HDPE Tensile Strength at 100°C

At 100°C tensile strength of irradiation HDPE with a dosage of 198kGy was increased about 1 MPa compared to non-irradiated HDPE.

In the Fig. 5 it is possible to see comparison of HDPE tensile strength in percentage at the ambient temperature and 100°C.

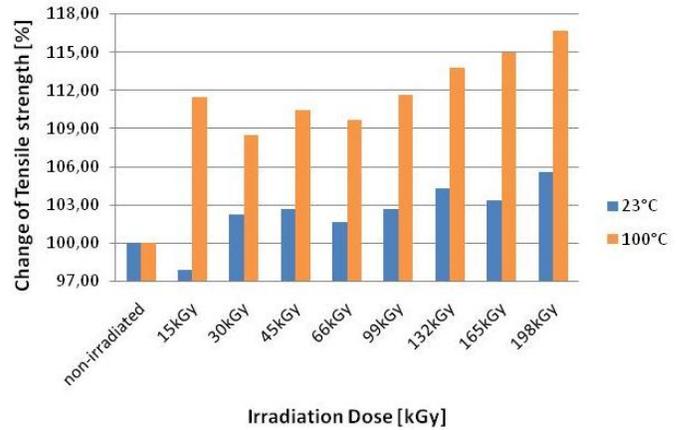


Fig. 5 HDPE Tensile Strength at 23°C and 100°C

The tensile strength rises by 5% after irradiation with a dosage of 198 kGy at 23°C but at 100°C the tensile strength rises more than 15% after irradiation with a dosage of 198 kGy. From the point-of-view of its tensile strength a dosage of irradiation of 198 kGy would seem to be optimal (Fig. 5).

Irradiation affects the E-modulus of the HDPE studied at both the ambient and increased temperature (Fig. 6).

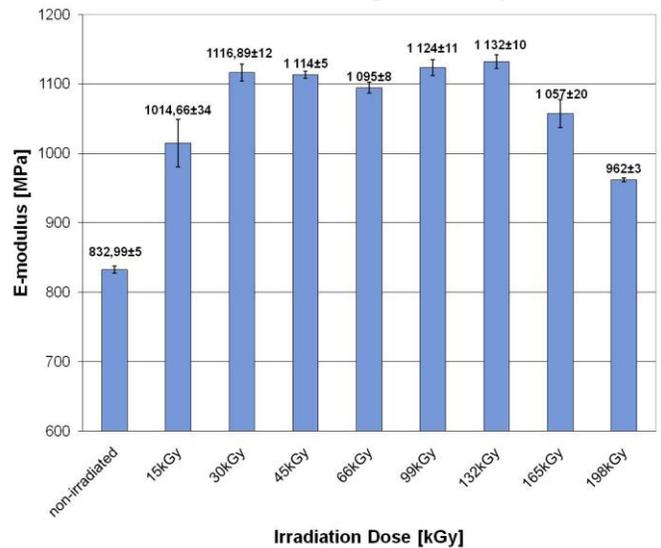


Fig. 6 HDPE E-modulus at the ambient temperature

At the ambient temperature HDPE E-modulus increased up to 30kGy. It is stable up to 165kGy and then it begins to decrease.

Irradiation affects the E-modulus of the HDPE studied at 100°C (Fig. 7).

In the Fig. 7 it is possible to see the changes of HDPE E-modulus at 100°C where the dose of irradiation above 66kGy causes increased of E-modulus about 10MPa.

In the Fig. 8 it is possible to see comparison of HDPE E-modulus in percentage at the ambient temperature and 100°C.

The E-modulus rises more than 35% after irradiation with a dosage of 132 kGy at 23°C but at 100°C the E-modulus rises only 13% after irradiation with a dosage of 132 kGy. From the point-of-view of its elastic modulus a dosage of irradiation of 132 kGy would seem to be optimal (Fig. 8).

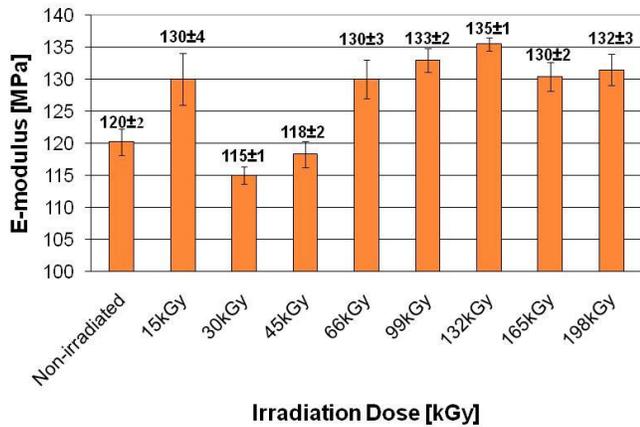


Fig. 7 HDPE E-modulus at 100°C

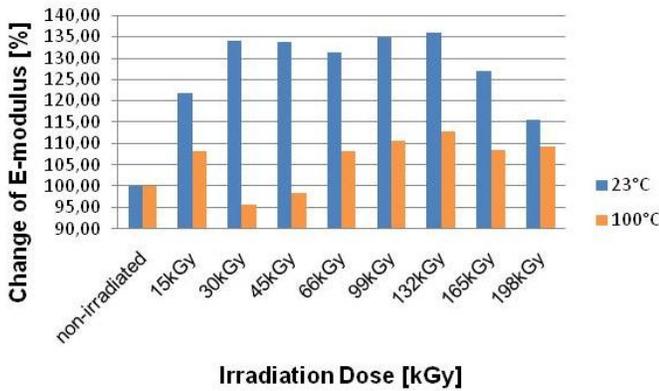


Fig. 8 HDPE E-modulus at 23°C and 100°C

2) Hardness

Irradiation affects the hardness of the HDPE studied at the ambient temperature (Fig. 9).

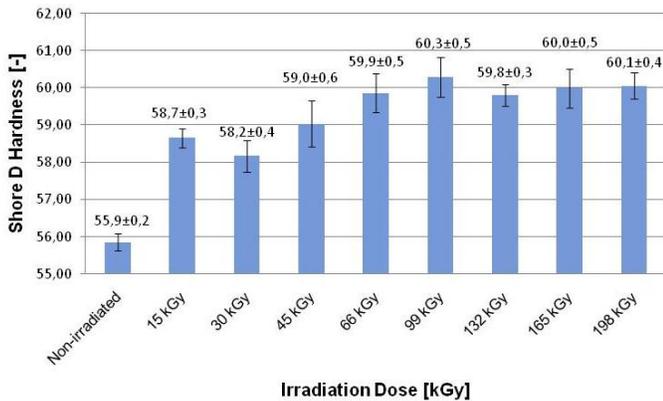


Fig. 9 HDPE Hardness at the ambient temperature

At the ambient temperature Shore D hardness of irradiation HDPE with a dosage of 99kGy was increased about 4 Shore D compared to non-irradiated HDPE.

In the Fig. 10 it is possible to see comparison of HDPE Shore D hardness in percentage at the ambient temperature.

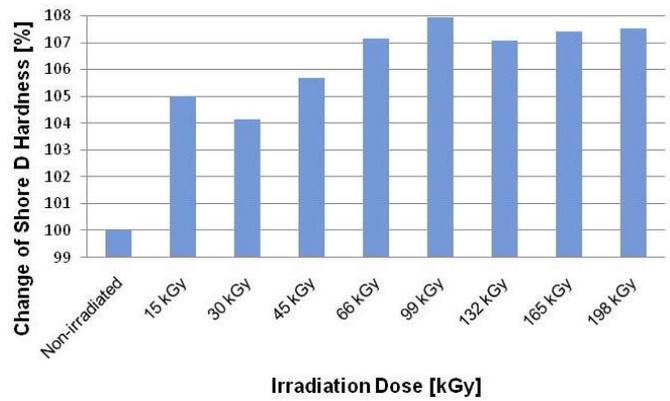


Fig. 10 Comparison of HDPE Hardness

No significant changes of hardness were found after the irradiation on the HDPE sample. A maximum increase of hardness (i.e. about 8%) was measured after the irradiation dosage of 99kGy. Higher doses of irradiation had no significant effect on the Shore D Hardness. From the point-of-view of its Shore D hardness a dosage of irradiation of 99 kGy would seem to be optimal (Fig. 10).

C. Temperature Stability

The temperature stability of HDPE 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 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 HDPE (Fig. 11).

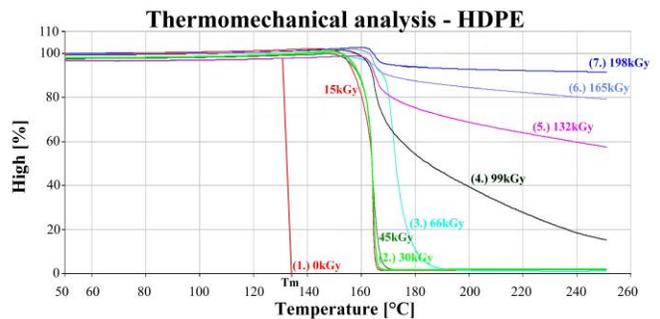


Fig. 11 Thermo-mechanical Analysis of HDPE

Already small dose of radiation (up to 33kGy) 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. 11).

2) Hot Wire Test

At observed non irradiated (but also irradiated) material HDPE, there was a short time inflammation at the higher temperatures during the contact with hot wire loop, then the

flame expired and after some time it inflamed again. After that there was melted material dropping, including fiber formation. After removing the specimen from the loop spike, the flames did not expired at the limit set. At 700°C all needed criteria were satisfied (ČSN EN 60695-2-12:2000) and flammability index value was written down - **GWFI: 700/0,8**.

Conditions of flammability index (ČSN EN 60695-2-13:2000) were satisfied at the same temperature and measured index (temperature) of flammability of this material was determined - **GWIT: 725/0,8**.

During the testing, all of the irradiated specimens showed lower ability to resist the temperature stability in comparison to non irradiated specimens. Value of indexes GWFI and GWIT become stabilized in values **GWFI: 650/0,8** a **GWIT: 650/0,8**.

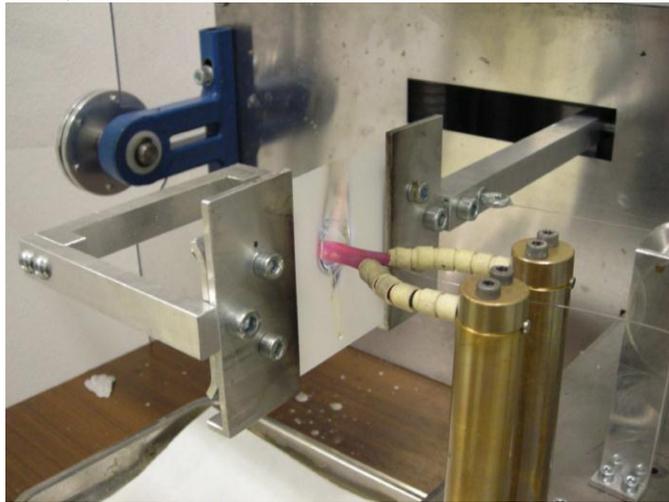


Fig. 12 Non irradiated burning specimen from HDPE at 850°C, 132 kGy

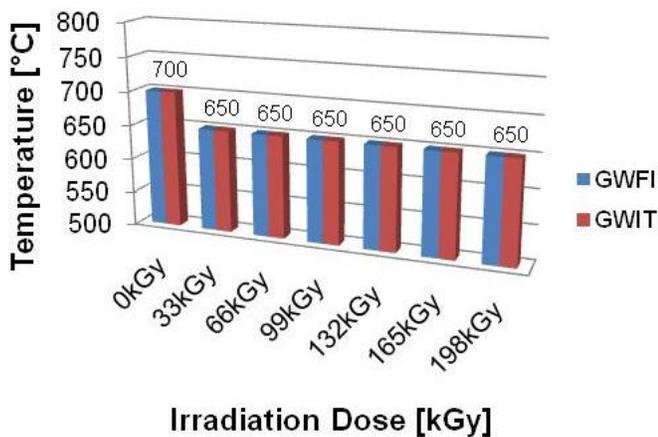


Fig. 13 Resulting graph HDPE for the test GWFI and GWIT

In this case, the material irradiation, in point of increasing the temperature stability, is not eligible.

Non irradiated material indicated higher temperature stability. At irradiated specimens were observed lower tendency of material melting in contact area of the hot wire loop and the specimen. This resulted in higher thermal energy accumulation in this area and so to the higher flammability.

Time value (elapsed time from the beginning of hot wire loop spike activity until specimen or specified material inflammation) was gradually increasing. Up to a temperature of 650 °C the specimen did not inflamed at all.

The flame length was moving from 50mm (at low temperatures) up to 80mm (at higher temperatures) independently on the dose of irradiation.

3) Visual Observation of HDPE in the Temperature Chamber

The visual observation of sample behaviour at 125°C is given on Fig. 14. Specimens are fitted horizontally in the temperature chamber and loaded by the bending moment both from its own weight and the weight on the end of specimen. Specimens are not deformed. The surface quality and the colour of polymer is the same like before the exam.

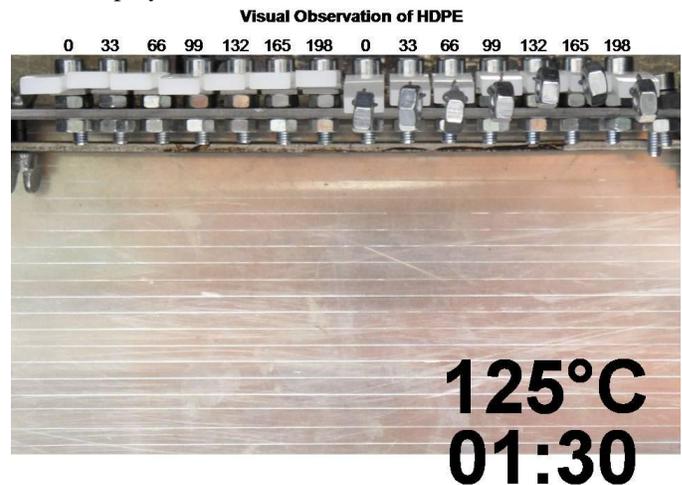
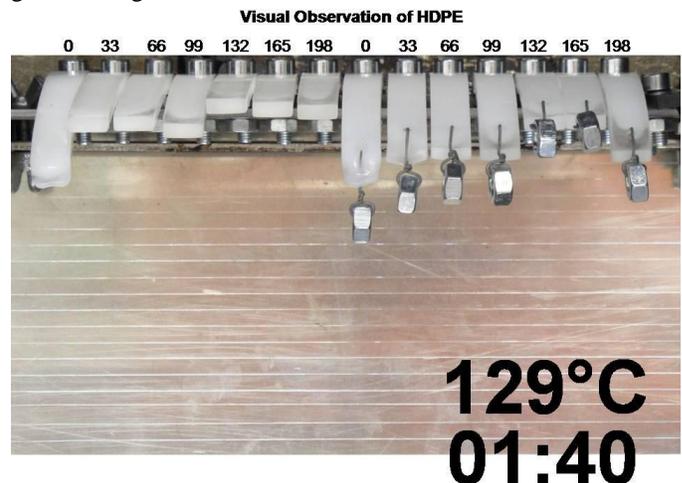


Fig. 14 HDPE specimen deformation at 125°C

The visual observation of sample behaviour at 129°C is given on Fig. 15.



The visual observation of sample behavior at 138°C is given on Fig. 16. At 138°C the specimen from non-irradiated HDPE is totally destroyed (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 is the same like before the exam.

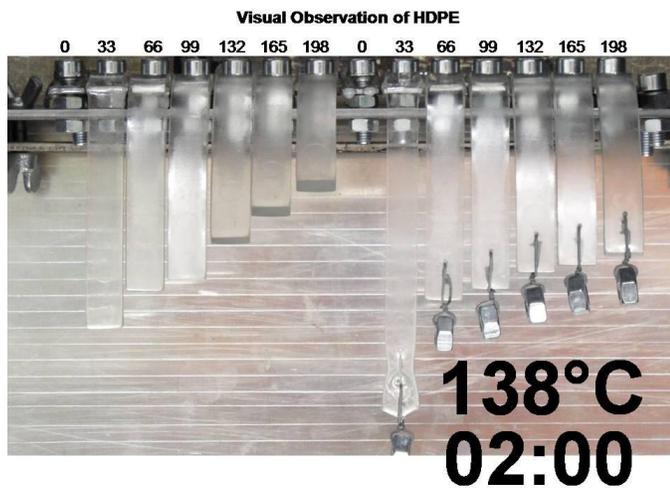


Fig. 16 HDPE specimen deformation at 138°C

The visual observation of sample behavior at 157°C is given on Fig. 17. At 157°C the HDPE irradiated specimen with the doses 33kGy is totally destroyed (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 is the same like before the exam.

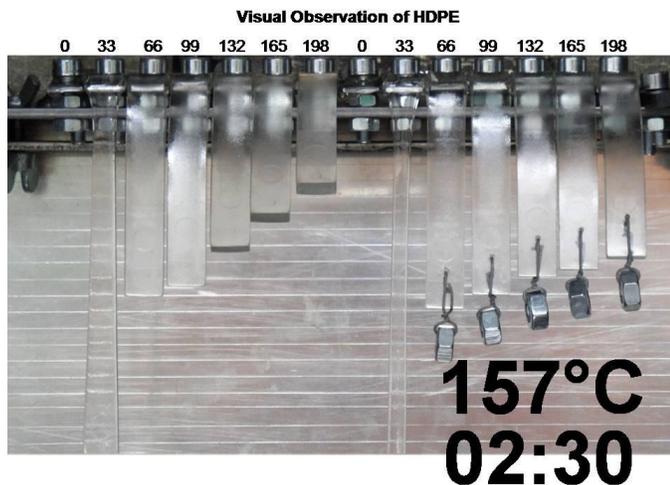


Fig. 17 HDPE specimen deformation at 157°C

The visual observation of sample behavior at 182°C is given on Fig. 18. The irradiated HDPE 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.

The visual observation of sample behavior at 207°C is given on Fig. 19. The irradiated HDPE 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 are visibly damaged.

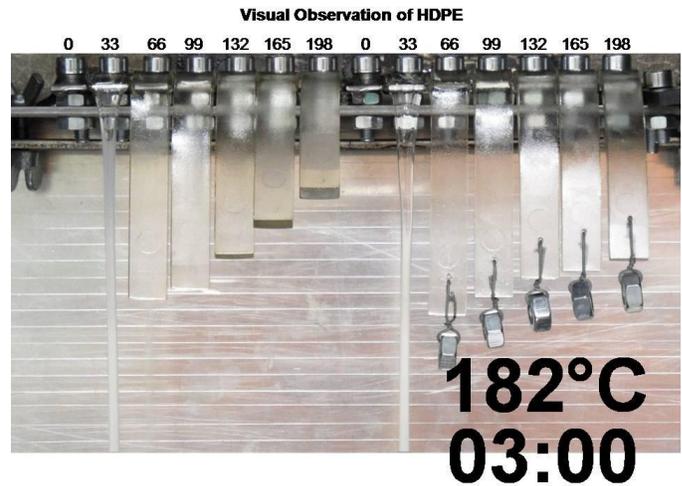


Fig. 18 HDPE specimen deformation at 182°C

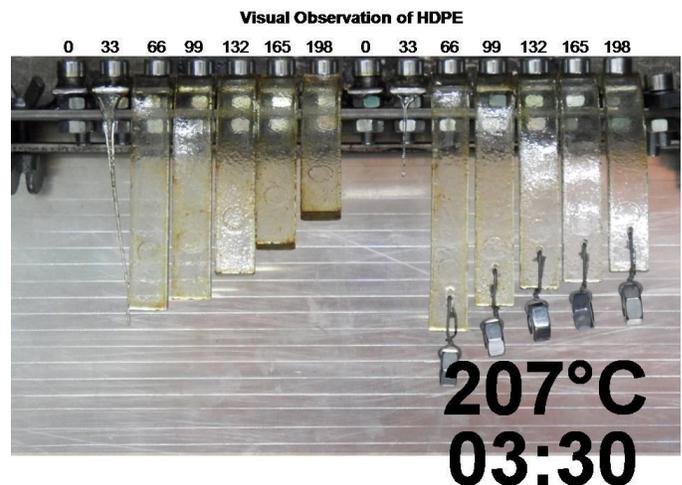


Fig. 19 HDPE specimen deformation at 207°C

The visual observation of sample behavior at elevated temperature is given on Fig. 20. Specimen deformation is decreasing with increasing dose of radiation at elevated temperature. At 218°C the specimen from not irradiated HDPE is totally destroyed (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 HDPE studied. The higher the irradiation dosage, the better is the temperature stability of studied polymers. The tested specimen remained without dimensional changes at 140°C, after irradiation with a dosage of more than 132 kGy. The same specimen, at temperatures higher than 220°C, creates colour changes due to thermal oxidation - but its dimension/cross-section remains without change. Its better temperature stability

makes possible to use this polymer - even at service temperatures higher than its former melting point.

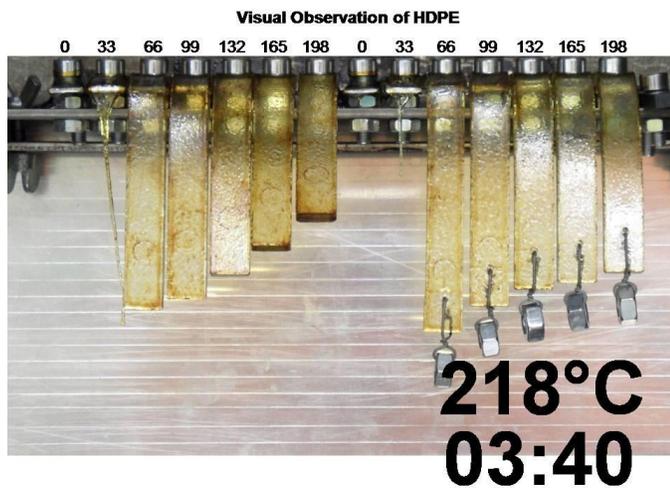


Fig. 20 HDPE specimen deformation at 218°C

D. Summary of Measured Results

The results of the measurements of HDPE after irradiation showed Table 2.

Table 2 Summary of measured results

Measured Values	Irradiation Dose [kGy]								
	0	15	30	45	66	99	132	165	198
Rm 23°C [%]	0	-2	2	3	2	3	4	3	6
Rm 100°C [%]	0	11	8	10	10	12	14	15	17
E-modulus 23°C [%]	0	22	34	34	31	35	36	27	15
E-modulus 100°C [%]	0	8	-4	-2	8	11	13	8	9
Shore D [%]	0	5	4	6	7	8	7	7	8
Temperature Stability at 200°C	x	-	x	-	≠	≠	≡	≡	≡

Rm ... Tensile Strength, x ... Melted, - ... Non-tested, ≠ ... Change of cross-section, ≡ ... Without cross-section change.

The result from the measured tensile test is that the better effect has irradiation with higher temperatures (100°C) when the tensile strength is increased by 14% for irradiated HDPE with the dose 132kGy.

With increasing temperature we can observe decreasing effect of irradiation to the E-modulus. At 23°C is the E-modulus increased by 36%, but at 100°C only by 13%, for irradiated HDPE with the dose 132kGy.

Effect of irradiation on hardness is not significant (about 7%).

The biggest effect of irradiation is the improvement of temperature stability, when HDPE irradiated by dose higher than 132kGy is for a short time capable to resist up to 200°C.

Measured results show that optimal irradiation dose is 132kGy.

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]

As can be seen from the tests results, the irradiation cross-linking improves the HDPE mechanical properties. The improvement is more considerable in case of higher temperature (100 °C), as a consequence of creation of cross-link (during irradiation cross-linking) resulting in protraction of macromolecular chain, which is thus more flexible during thermal load than individual shorter macromolecular chains.

Irradiation improves the thermal properties of polymer. Tested polymer (HDPE) shows better temperature stability after irradiation. Irradiation significantly extends the application area of polymers. The service temperature can be higher than the melting point of not irradiated polymers.

The results of the measurements of HDPE after irradiation showed significant changes of its mechanical and thermo-mechanical properties. The tensile strength rises by 5%, after irradiation with a dosage of 198 kGy at the temperature 23°C and at the temperature 100°C the tensile strength rises by 15%, after irradiation with a dosage of 198kGy. The E –modulus rises gradually in line with the dose of irradiation to the dosage 99kGy then the E-modulus declines. A very important point is the improvement of the HDPE's thermal stability, after irradiation. The tested polymer, when irradiated by a dosage of 198 kGy showed no dimensional changes - even at a temperature of 220°C. This significantly moves the application possibilities of the HDPEs we tested to an area with service temperatures much higher than their former melting-point. The measurements of hardness showed that irradiation also partly affects the HDPE hardness. Irradiation is also a method which reduces the creep behaviour of the studied polymer. The resistance to creep of cross-linked HDPEs, increases with the irradiation dose.

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REFERENCES

- [1] Drobny, J.G., *Radiation Technology for Polymers*, Boca Raton: CRC Press, 2003, ISBN 1-58716-108-7.
- [2] BGS – Beta Gama Service. [online]. www: <<http://bgs.eu>>
- [3] Brocka, Z., *Werkstoff- und Einsatzpotential strahlenvernetzter Thermoplaste*, Lehrstuhl für Kunststofftechnik (LKT), Nürnberg, 2008.
- [4] Woods, R. J., *Applied radiation chemistry: radiation processing*, A Wiley-Interscience publication, New York, 1994, ISBN 0-471-54452-3.
- [5] Drobny, J.G., *Handbook of Thermoplastic Elastomers*, William Andrew Publishing, Norwich, NY, 2007, ISBN: 978-0-8155-1549-4
- [6] Manas, M., Stanek, M., Manas, D. at all: *Temperature stability of irradiated polymers*. Chemicke listy, 105(S), p254-256, ISSN 0009-2770.
- [7] Holik, Z., Danek, M., Manas, M., at all: *Effect of irradiation cross-linking on mechanical properties of selected types of polymer*. Chemicke listy, 105(S), p269-271, ISSN 0009-2770.
- [8] Z. Holik, M. Danek, M. Manas, J. Cerny, “The Influence of Cross-linking Agent on Mechanical Properties of Polyamide Modified by Irradiation Cross-linking”, in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Spain, 2011, pp.222-225.
- [9] Z. Holik, K. Kyas, M. Krupal, J. Cerny, M. Danek, “Improvement of Polypropylene Properties”, *21st International DAAAM Symposium*, 2010, Zadar, Croatia, p. 1191-1192.
- [10] H. Vaskova, V. Kresalek, „Raman Spectroscopy of Epoxy Resin Crosslinking“, in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Canary Islands 2011, p.357-360.
- [11] M. Manas et al., *Improvement of Mechanical Properties of the TPE by Irradiation*, Chemicke Listy, Vol.105, 2011, pp. 828-829.
- [12] M. Manas et al., *Modification of Polyamides Properties by Irradiation*, Chemicke Listy, Vol.103, 2009, pp. 24-26.
- [13] D. Mañas, M. Mañas, M. Stanek, T. Drga, *Influence of Radiation on Polymer Properties*, Chemicke listy, Vol. 101, 2007, pp. 27-28.
- [14] D. Manas et al., *Thermal Effects on Steels at Different Methods of Separation*, Chemicke Listy, Vol.105, 2011, pp. 713-715.
- [15] D. Manas et al., *Influence of Mechanical Properties on Wear of Heavily Stressed Rubber Parts, KGK – Kautschuk Gummi Kunststoffe*, Vol.62, 2009, pp. 240-245.
- [16] D. Manas et al., *Wear of Multipurpose Tire Treads*, Chemicke Listy, Vol.103, 2009, pp. 72-74.
- [17] D. Manas, M. Stanek, M. Manas, “Workability and Wear of Rubber Parts”, Chapter 54 in *DAAAM International Scientific Book 2007*, Published by DAAAM International, DAAAM International, Vienna, Austria, p.611-626
- [18] M. Stanek et al., Optimization of Injection molding process, *International Journal of Mathematics and Computers in Simulation*, Vol.5, 2011, pp. 413-421.
- [19] M. Stanek et al., Simulation of Injection Molding Process by Cadmould Rubber, *International Journal of Mathematics and Computers in Simulation*, Vol.5, 2011, pp. 422-429.
- [20] M. Stanek et al., *Influence of Surface Roughness on Fluidity of Thermoplastics Materials*, Chemicke Listy, Vol.103, 2009, pp. 91-95.
- [21] M. Stanek et al., *Plastics Parts Design Supported by Reverse Engineering and Rapid Prototyping*, Chemicke Listy, Vol.103, 2009, pp. 88-91.
- [22] M. Stanek et al., *How the Filler Influence the Fluidity of Polymer*, Chemicke Listy, Vol.105, 2011, pp. 303-305.
- [23] M. Stanek, D. Manas, M. Manas, J. Javorik, “Simulation of Injection Molding Process,” in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, p.231-234.
- [24] M. Stanek, D. Manas, M. Manas, O. Suba, “Optimization of Injection Molding Process by MPX,” in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, p.212-216.
- [25] M. Stanek, M. Manas, T. Drga, D. Manas, “Testing Injection Molds for Polymer Fluidity Evaluation”, *17th DAAAM International Symposium: Intelligent Manufacturing & Automation: Focus on Mechatronics and Robotics*, Vienna, Austria, 2006, p.397-398.
- [26] S. Sanda et al., *Injection Mold Cooling System by DMLS*, Chemicke Listy, Vol.103, 2009, pp. 140-142.
- [27] S. Sanda et al., *Gate Effect on Quality of Injected Part*, Chemicke Listy, Vol.105, 2011, pp. 301-303.
- [28] V. Pata et al., *Visualization of the Wear Test of Rubber Materials*, Chemicke Listy, Vol.105, 2011, pp. 290-292.
- [29] V. Pata et al., *Visualization of the Wear Test of Rubber Materials*, Chemicke Listy, Vol.105, 2011, pp. 290-292.
- [30] K. Kyas, M. Stanek, Manas, M. Stanek, M. Krupal, Z. Holik, *Simulation of rubber injection holding process*, 2011, Chemicke listy, Volume 105, Issue 15, pp. S354-S356
- [31] Ovsik, M. – Manas, D. – Stanek, M. – Manas, M. – Cerny, J. – Bednarik, M. – Mizera, A.: Microhardness of Modified Thermoplastics, *Annals of DAAAM for 2011 & Proceedings of the 22nd International DAAAM Symposium*, 23-26th November 2011, Vienna, Austria, ISSN 1726-9679, ISBN 978-3-901509-83-4, p. 1187-1188, Published by DAAAM International Vienna, Vienna
- [32] Navtatil, J. – Stanek, M. – Manas, M. – Manas, D. – Bednarik, M. – Mizera, A.: Utilization of DMLS in Injestion Mold Design, *Annals of DAAAM for 2011 & Proceedings of the 22nd International DAAAM Symposium*, 23-26th November 2011, Vienna, Austria, ISSN 1726-9679, ISBN 978-3-901509-83-4, p. 1507-1508, Published by DAAAM International Vienna, Vienna
- [33] J. Javorik et al., The Shape Optimization of the Pneumatic Valve Diaphragms, *International Journal of Mathematics and Computers in Simulation*, Vol.5, 2011, pp. 361-369.
- [34] J. Javorik, M. Stanek, “The Numerical Simulation of the Rubber Diaphragm Behavior,” in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Spain, 2011, pp. 117-120.
- [35] J. Javorik, D. Manas, “The Specimen Optimization for the Equibiaxial Test of Elastomers,” in *Proc. 13th WSEAS International Conference on Automatic Control, Modelling & Simulation*, Lanzarote, Spain, 2011, pp. 121-124.
- [36] MIZERA, A., MAÑAS, M., HOLÍK, Z., DANĚK, M. Teplotní odolnost radiačně síťovaných polymerů *8th ITC – Tools 2011 = VIII. ITC 2011 – Nástroje 2011* [CD-ROM], Zlín : FT UTB ve Zlíně. Ústav výrobního inženýrství, 2011 [cit. 2011 -07-14]. Adresář: \ITC2011\ITC2011_31.pdf. ISBN 978-80-7454-026-4.
- [37] HOLÍK, Z. - MAÑAS, M. – DANĚK, M. – MACOUREK, J. .:Improvement of Mechanical and Thermomechanical Properties of Polyethylene by Irradiation Crosslinking. Chemicke listy. Volume 103, 2009, s.60-63, ISSN 0009-2770 (IF: 0,593 MF: 1,256)
- [38] *PTS - Plastic Technology Service* [online]. 2009 [cit. 2009-12-22]. WWW: <<http://www.pts-marketing.de/>>