Mechanical Properties of Recycled Irradiated HDPE

J. Navratil, M. Stanek, M. Manas, D. Manas, K. Kyas, A. Skrobak, V. Senkerik

***Abstract*—**Irradiation of thermoplastics is a well-known modification used for improving cheap commodity plastics; however, little research was carried-out on recyclation of such modified materials. This research paper gives possible solution of utilization of recycled irradiated high-density polyethylene (HDPE). A powder of recycled irradiated HDPE was used as filler into a powder of pure low-density polyethylene (LDPE) and tensile test was performed. Materials were mixed together in concentrations from 10 to 60 % of the filler and injection molded to produce test specimens. Tensile test was performed at ambient - 23 °C and elevated - 80 °C temperatures. Among observed results were Young´s Modulus, Ultimate Tensile Strength and Nominal Strain to determine tensile behavior and to describe influence of the filler on this behavior. Measured results at ambient temperature show that there is significant rise of Young´s Modulus - from 239 MPa to 448 MPa, a growth of Ultimate Tensile Strength from 10 MPa to 15 MPa and on the contrary there is a drop in Nominal Strain from 62 % to 18 %. Similar trend is followed at elevated temperature; nevertheless, nominal values are lower. Findings of this research paper might help with possible utilization of irradiated materials after the end of their lifetime.

***Keywords*—**HDPE, Irradiation, LDPE, Radiation Crosslinking, Recyclation, Tensile Test, Toughness

I. Introduction

KNOWLEDGE of polymer irradiation has led to an increasing usage of cheap, commodity plastics in the areas where it was unthinkable before. There have been several studies investigating why there is such a boost in the spread of this technology and it has been found out that polymers exposed to the irradiation either degrade or crosslink. Those which crosslink have significantly improved mechanical, thermal and chemical properties which is taken advantage of. It allows us to use cheap commodity plastics, irradiate them and replace much more expensive engineering ones without any loss of desired behavior [15-24].

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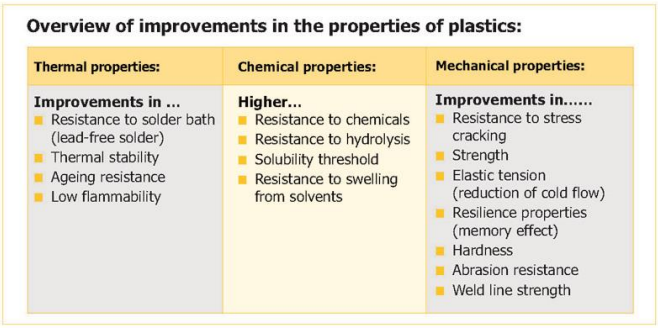

Fig. 1 Improved properties [27]

Three different responses to radiation occur regarding to the chemical structure of irradiated polymer. Polymers with more hydrogen atoms on the side of the chain tend to crosslink, polymers with a methyl group, di-substitutions or per-halogen substitutions on the side of the chain would degrade and aromatic polymers with benzene rings either in the main chain or on the side of the chain are usually radiation resistant [21-33].

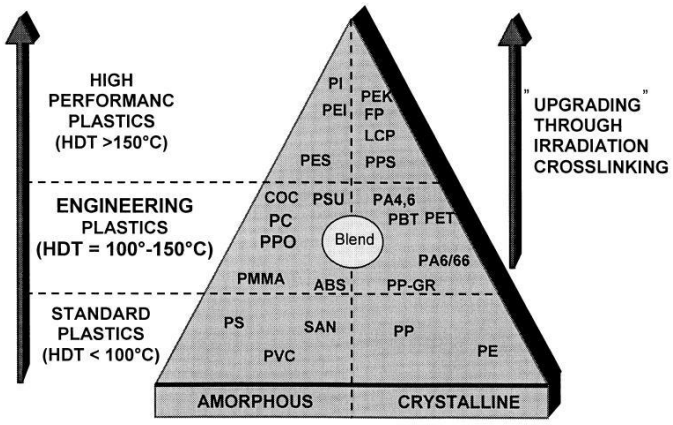

Fig. 2 Material classification [8]

Crosslinking, i.e. creation of a network in polymer structure occurs mainly in the amorphous regions of polymers. The degree of crosslinking is dependent on the radiation dose and energy [1-12].

Crosslinking is the intermolecular bond formation of polymer chains. The mechanism of crosslinking involves the

cleavage of a C-H bond on one polymer chain to form a hydrogen atom, followed by abstraction of a second hydrogen atom from a neighboring chain to produce molecular hydrogen. Then the two adjacent polymeric radicals combine to form a crosslink. The overall effect of crosslinking is that the molecular mass of the polymer steadily increases with radiation dose, leading to branched chains until a three-dimensional polymer network is formed when each polymer chain is linked to another chain [23-44].

The source of radiation may be an electron beam accelerator (beta radiation), which is a machine source of radiation, or a radioactive source such as Cobalt-60 (gamma radiation) [1-8, 19-29].

Electron beam accelerators (beta radiation) provide lower penetration depths and higher irradiation doses therefore they are used for commercial radiation modification of polymers. The energy of determines depth of penetration into the product [31-44].

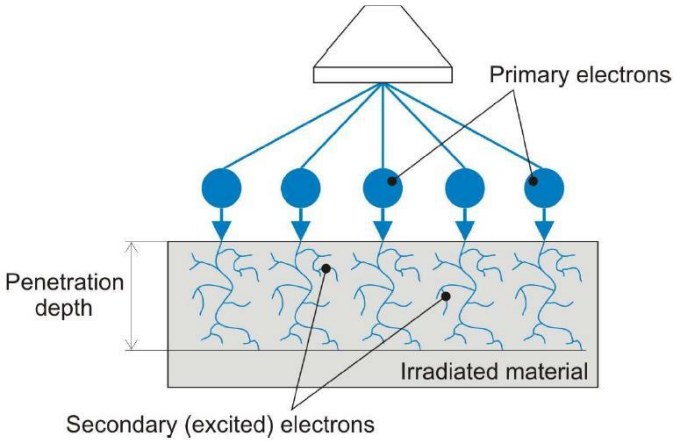

Fig. 3 Electron beam accelerator [34]

The Possible applications of this technology are for example:

- Cable insulations
- Pipes for surface heating
- Shrinkable products
- Corrugated piping
- Foamed materials
- Molded parts
- Packaging
- Automotive tires
- Contact lenses
- Teflon powder
- Adhesive tapes
- Cotton fibers
- Membranes
- Battery separators
- Wound dressing [11-22].

II. Experiment

The main goal of the experiment was to investigate possible utilization of a powder made from irradiated material after its service life and to determine its tensile behavior at two temperatures.

A. Materials

Two materials were tested. Pure low-density polyethylene (LDPE) and recycled irradiated high-density polyethylene (HDPE).

LDPE was used as a polymer matrix due to its advantageous combination of low price, processing properties, rigidity and availability; moreover, one of the main areas of application of this material is compounding. Supplier of this material was The Dow Chemical Company, type 780E. Its basic properties are shown in Table I. This material was supplied in the form of granules which had to be ground into the powder.

Table I LDPE material properties [26]

DOW LDPE 780E	
Density	0.923 [g/cm^2]
Mass-Flow Rate (190°C, 2.16kg)	20 [g/10min]
Molding Shrinkage (average)	1.9 [%]
Tensile Modulus	164 [MPa]
Tensile Stress at Break	10.5 [MPa]
Tensile Strain at Break	50 [%]
Tensile Impact Strength	286 [kJ/m^2]
Shore D Hardness	49
Vicat Softening Temperature	93 [°C]

Recycled material was provided in the form of tubes which served for surface heating. These tubes could not be remelted due to their modification by irradiation; therefore, they were used as filler. Irradiation was performed by electron beams (beta radiation) with energy 10 MeV by total dose of 165 kGy. This material was chosen for re-processing due to its growing usage for irradiation and thus increasing potential for recyclation after service life. Supplier of raw material was Slovnaft Petrochemicals, Inc., type TIPELIN PS 380-30/302. Basic properties of neat HDPE are shown in Table II; however, properties of irradiated HDPE differ.

Table II HDPE material properties [25]

Slovnaft TIPELIN PS 380-30/302	
Density	0.949 [g/cm^2]
Mass-Flow Rate (190°C, 5kg)	0.95 [g/10min]
Tensile Strength	31 [MPa]
Elongation at Break	1400 [%]
Flexural Modulus	750 [MPa]
Izod Impact Strength	13 [kJ/m^2]
Shore D Hardness	65

B. Specimens´ Preparation

Specimens' preparation was carried out in several steps. Firstly those tubes were cleaned and shortened to the suitable length and crushed in the rotary cutter mill to grit (Fig. 4).

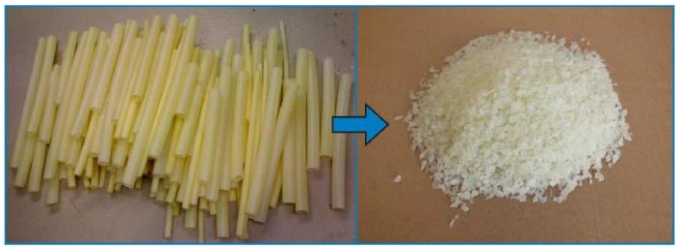

Fig. 4 Processed tubes

Particle size which leaves the mill varies between 3 to 5 mm. Diversity in shape and size is shown in Fig. 5.

Fig. 5 Particles shape and size

Thus prepared materials were then sent for grinding and resulting powder was used as filler/ polymer matrix. Before injection molding these materials underwent sieving to determine size of the particles. Sieving was carried out on the sieving machine where totally 200 g of powder was used. Sieving time was set to 30 minutes and amplitude of vibration was set to 90 mm. Measured data are shown in Fig. 6 and Fig. 7.

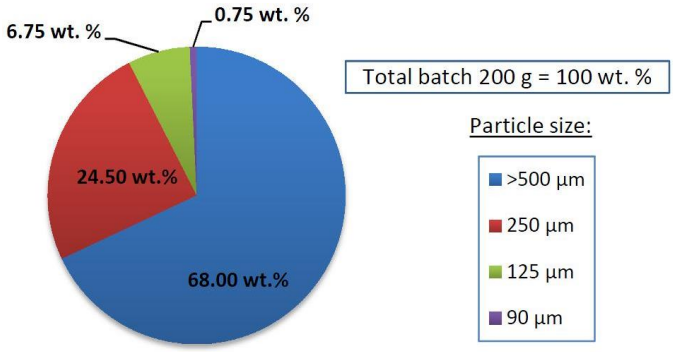

Fig. 6 HDPE particle size

As can be seen from the chart above (Fig. 6) there were 68 wt. % of particles greater than 500 µm, 24.5 wt. % varied between 250 µm and 500 µm, 6.75 wt. % was between 125 µm and 250 µm and finally 0.75 wt. % was from 90 µm to 125 µm.

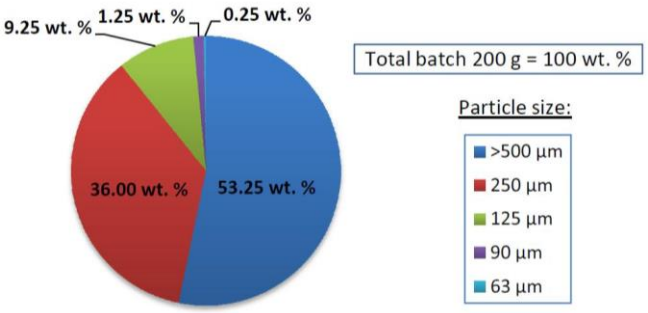

Fig. 7 LDPE particle size

In case of LDPE powder were 53.25 wt. % of particles greater than 500 µm, 36 wt. % varied between 250 µm and 500 µm, 9.25 wt. % was between 125 µm and 250 µm , 1.25 wt. % was from 90 µm to 125 µm and finally 0.25 wt. % was between 63 µm and 90 µm as is shown in Fig. 7.

Thus prepared raw material was mixed together in concentrations from 10 % to 60 %. Mixing was carried out in a "home-made" laboratory pneumatic blender. The initial pressure under which an air was blown into the device was 7 bar, time of mixing was chosen to be 5 minutes.

Resulting compound was injection molded in injection molding machine Arburg Allrounder 420C (Fig. 8) under process parameters shown in Table III; nevertheless, with increasing concentration of filler these process parameters had to be slightly changed. Therefore at 50 % concentration of filler was injection pressure increased to 500 bar and holding pressure to 450 bar. At 60 % concentration of this filler were both these parameters raised to 550 bar due to deteriorated

fluidity. To support this was MFR determined according to the standard ISO1133 (Fig. 8).

Fig. 8 Injection molding machine

Table III Process parameters

Process parameters	
Injection velocity	60 [mm/s]
Injection pressure	450 [bar]
Injection time	0.4 [s]
Cooling time	30 [s]
Mold temperature	40 [°C]
Feeding length	27.5 [mm]
Pressure at V/P	400 [bar]
Point of V/P	10 [mm]
Clamping force	950 [kN]
Feeding time	2.8 [s]
Packing phase	10.1 [s]
Packing	400 [bar]
Cycle time	55.5 [s]
Temperature zones of plastication unit	
Zone 1	135 [°C]
Zone 2	140 [°C]
Zone 3	150 [°C]
Zone 4	160 [°C]
Zone 5	180 [°C]
Temperature under the hopper	40 [°C]

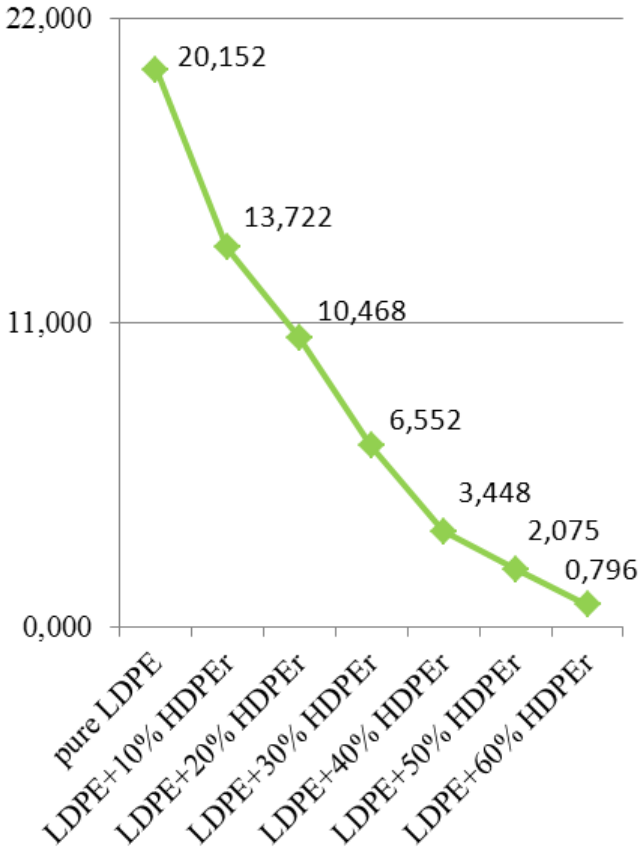

Fig. 9 Mass flow rate

Mass Flow Rate (MFR) decreased from 20.152 g/10min at non-filled pure LDPE to 0.796 g/10min at 60 % concentration of the filler. This equals to 96 % drop in compound fluidity. Both values are corresponding to the values from their datasheets and it can be seen that the more filler the lower fluidity; this finding justifies necessary changes in process settings.

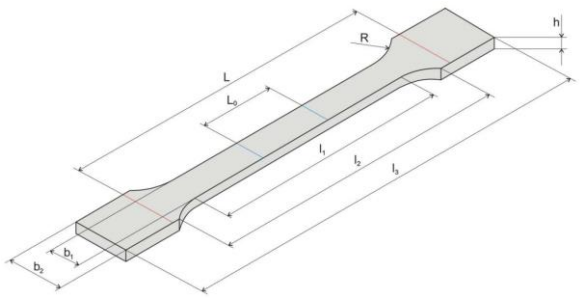

Fig. 10 Testing specimen [28]

Resulting test specimens had dimension and shape according to the standard ISO 527 (Fig. 10 and Table IV).

Table IV Testing specimen dimensions

Parameters	
b_1 - Width of Gage Length	10 ± 0.2 [mm]
b_2 - Width of Gripping End	20 ± 0.2 [mm]
l_1 - Length of gage Length	80 ± 2 [mm]
l_2 - Distance Between Gripping Ends	104 - 113 [mm]
l_3 - Specimen Length	≥ 150 [mm]
L_0 - Distance of Extensometers	30 ± 0.5 [mm]
L - Distance of Grips	115 ± 1 [mm]
h - Specimen Thickness	4 ± 0.2 [mm]
R - Radius	20 - 25 [mm]

III. Results

Testing testing machine was used for specimens´ testing. It was performed at two temperatures – ambient (23 °C) and increased (80 °C). Pipes of this irradiated HDPE were originally used for floor heating. Temperature of heating water had 80 °C therefore this temperature was chosen to determine tensile behavior under "real" conditions. Observed properties were Young´s Modulus, Ultimate Tensile Strength and Nominal Strain. All this properties give us complex description of examined tensile behavior; however, other properties have to be examined to fully understand and describe changes in properties.

A. Ambient Temperature (23 °C)

First observed result was Young´s Modulus – toughness of the material (Fig. 11). This material property grown rapidly with increasing amount of filler. Pure LDPE has Young´s Modulus 239.2 MPa and it grown up to 448 MPa at 60 % filled LDPE. Increase in this modulus is therefore 87 %.

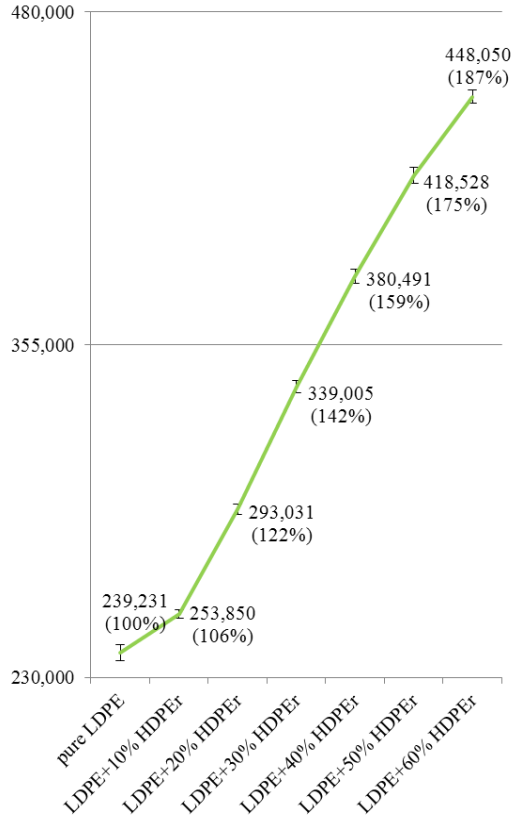

Fig. 11 Young´s modulus

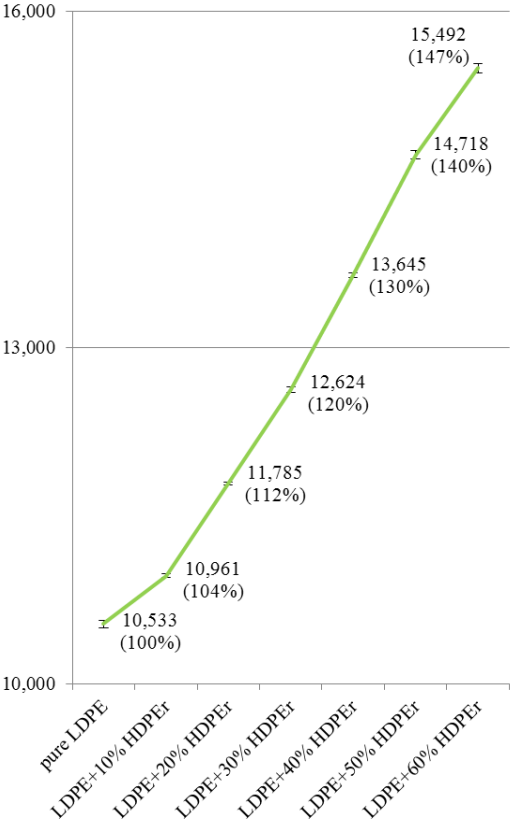

Fig. 12 Ultimate tensile strength

Ultimate Tensile Strength also grown rapidly with increasing concentration of filler; nevertheless, this growth was not so rapid. It grown only by 47 %. From 10.5 MPa to 15.5 MPa (Fig. 12).

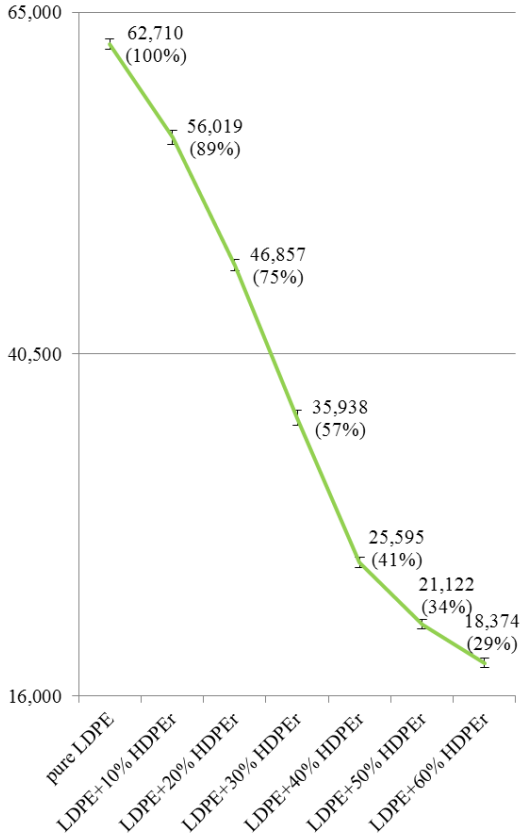

Fig. 13 Nominal strain

As a result of significant boost in Young´s Modulus and Ultimate Tensile Strength is a drop of elongation – Nominal Strain. It was reduced from 62.7 % to 18.4 % which represents 71 % drop in this particular material property. This can be seen in Fig. 13.

B. Elevated Temperature (80 °C)

Original purpose of these irradiated pipes was floor heating. Heating water had temperature 80 °C therefore was this temperature chosen to simulate real "working" conditions. All specimens were conditioned at this temperature for 30 minutes in heating chamber before testing.

Trend of Young´s Modulus is similar to the one at ambient temperature; however, nominal values were significantly lower due to the weakened intermolecular forces. Pure LDPE has modulus 33.9 MPa then it slightly decreased at 10 % of filler to 31.8 MPa and furthermore it grown rapidly up to 72.5 MPa at 60 % concentration. This small drop in Young´s Modulus is most probably caused only due to the error in measurement therefore it does not have any importance. However, overall result is that Young´s Modulus grown by 114 % which is even more than at ambient temperature (Fig. 14).

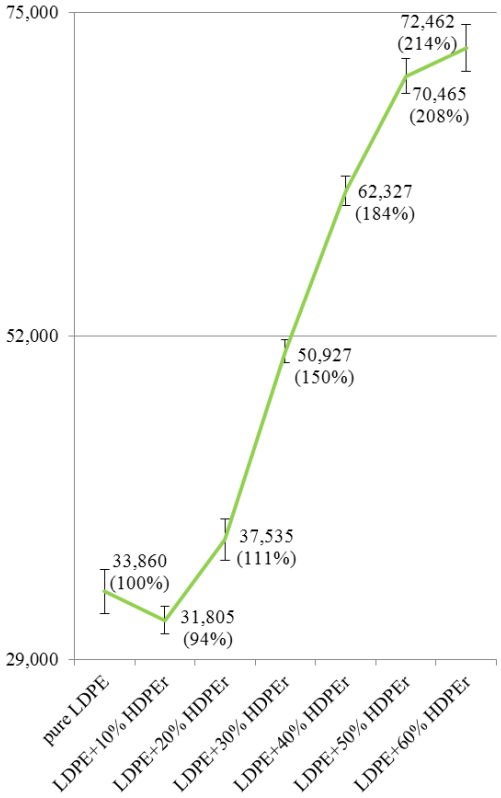

Fig. 14 Young´s modulus

Another observed result was Ultimate Tensile Strength (Fig. 15).

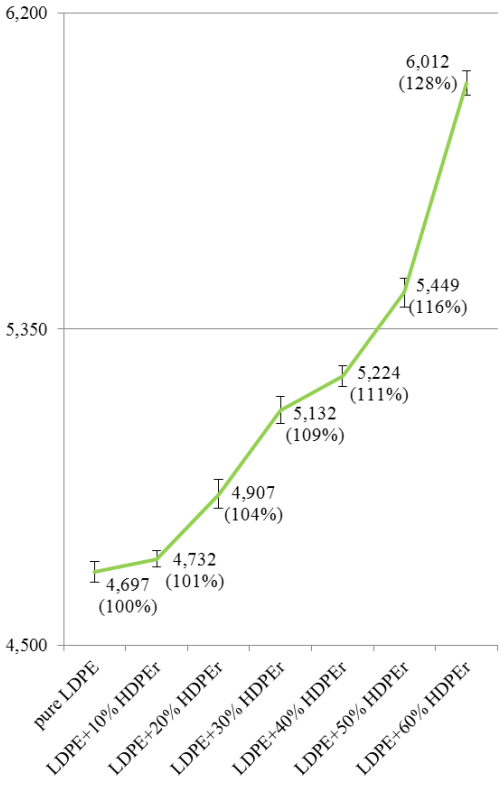

Fig. 15 Ultimate tensile strength

An upturn in Ultimate Tensile Strength was also observed. It boosted from 4.7 MPa to 6 MPa at the highest concentration of the filler. Difference between the lowest and the highest value is 28 % which comparable to the difference measured at ambient temperature (Fig. 15).

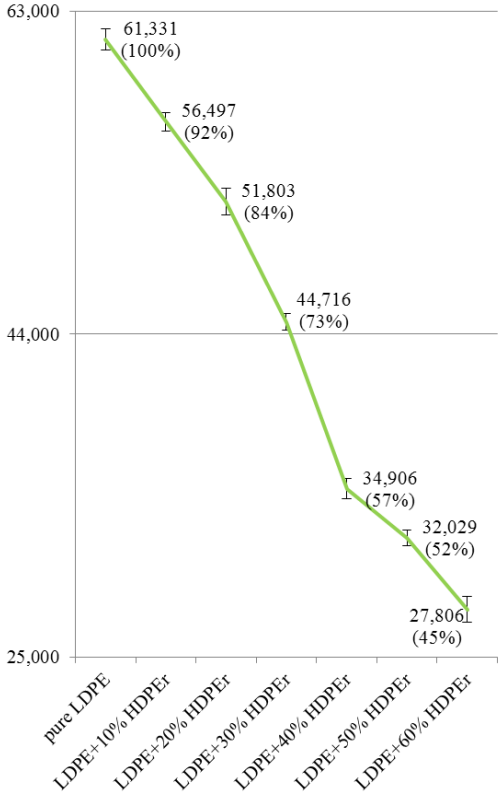

Fig. 16 Nominal strain

Last observed variable was Nominal Strain at 80 °C (Fig. 16). Nominal Strain declined from 61.3 % to 27.8 % which means that elongation at elevated temperature is lower than at ambient temperature. This result denies all the theory saying that with increasing temperature increases elasticity as well therefore much more detailed investigation is needed.

IV. Discussion

It can be observed that recycled irradiated material can be utilized after the end of its service life and as an added value there is also significant improvement in Young´s Modulus – toughness of the material and in Ultimate Tensile Strength – strength of the material. As a result of this there is a significant decrease in Nominal Strain – elongation of the material.

The fact that plastic materials exposed to the radiation have improved properties is discussed in the introduction. But according to this research paper it can be taken advantage of this improvement even after the service life of such irradiated materials when using them as filler.

The best results are achieved at materials with the highest concentration of the filler but their processability are worsen therefore higher concentrations than 60 % are not recommended.

Comparing results at ambient and elevated temperature show that the trend remains unchanged at all three observed variables even the differences are almost the same but the nominal values are lower at the elevated temperature. Courses of the tensile curves are depicted in Fig. 17 and Fig. 18.

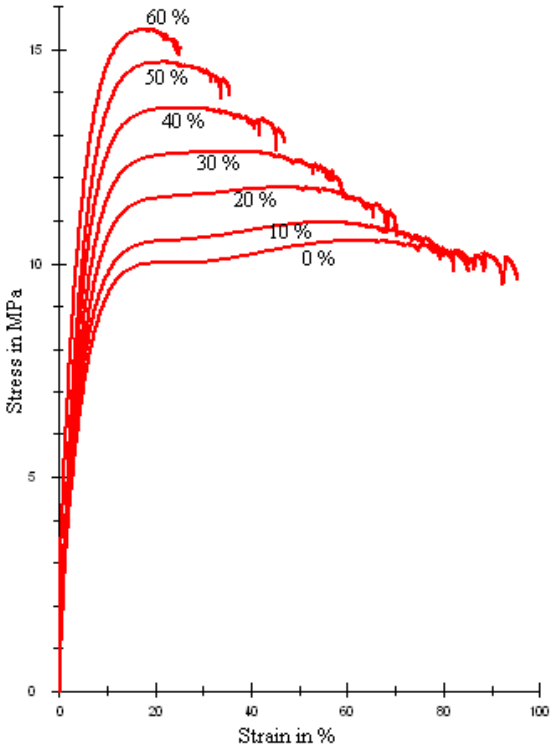

Fig. 17 Ambient temperature – 23 °C

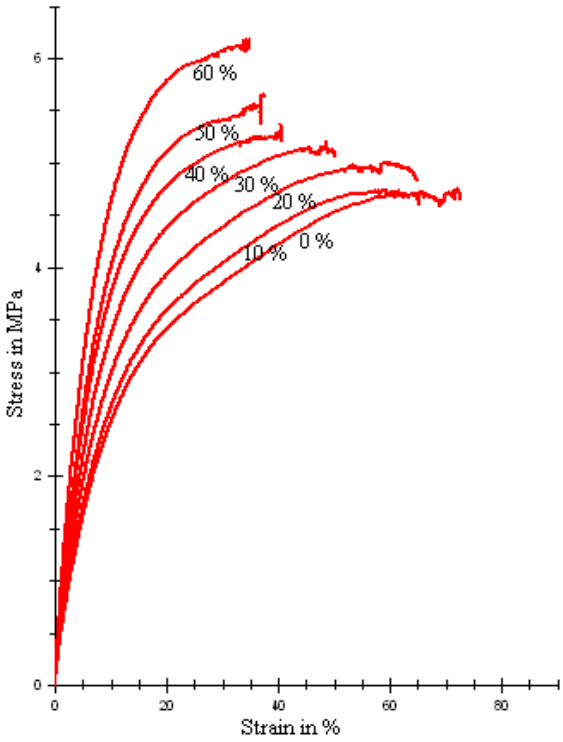

Fig. 18 Elevated temperature – 80 °C

V. Conclusion

The main goal of this research paper was to investigate possible utilization of irradiated high-density polyethylene after the end of its lifetime.

A powder of recycled irradiated HDPE was used as filler into powder of pure LDPE in several concentrations. Results of observed mechanical properties indicate that there is an increase in this properties and that this might be a possible way of usage of such materials; however, this study only concentrated on changes in mechanical properties and therefore other properties as well as structure are to be investigated to confirm or deny this findings and to fully understand the interaction between polymer matrix and filler.

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References

[1] J. Gehring, A. Zyball, Radiation Crosslinking of Polymers - Status, Current Issues, Trends and Challenges, *Radiation Physics and Chemistry*, Vol.46, No.4-6, 1995, pp. 931-936.

[2] S. Rouif, Radiation Cross-Linked Polymers: Recent Developments and New Applications, *Nuclear Instruments and Methods in Physics Research B*, Vol.236, No.1-4, 2005, pp. 68-72.

[3] D.R. Kerluke, S. Cheng, Radiation Processing for Modification of Polymers, *ANTEC 2003 Conference Proceedings*, 2003, pp. 2694-2699.

[4] D.R. Kerluke, S. Cheng, Radiation Processing of Polymers: The Current Status and Prospects for the Future, *ANTEC 2004 Conference Proceedings*, 2004, pp. 3738-3739.

[5] S. Bhatt, R. Hoffman, Outgassing Behavior of E-Beam Irradiated HDPE and ETFE, *ANTEC 2006 Conference Proceedings*, 2006, pp. 1540-1543.

[6] J. Chen, M. Czayka, R.M. Uribe, Effects of Electron Beam Irradiations on the Structure and Mechanical Properties of Polycarbonate, *Radiation Physics and Chemistry*, Vol.74, No.1, 2005, pp. 31-35.

[7] R. Feulner et al., The Effects of E-Beam Irradiation Induced Cross Linking on the Friction and Wear of Polyamide 66 in Sliding Contact, *Wear*, Vol.268, No.7-8, 2010, pp. 905-910.

[8] J. Gehring, With Radiation Crosslinking of Engineering Plastics into the Next Millennium, *Radiation Physics and Chemistry*, Vol.57, No.3-6, 2000, pp. 361-365.

[9] S. Machi, Radiation Technology for Sustainable Development, *Radiation Physics and Chemistry*, Vol.46, No.4-6, 1995, pp. 399-410.

[10] A. Bhattacharya, Radiation and Industrial Polymers, *Progress in Polymer Science*, Vol.25, No.3, 2000, pp. 371-401.

[11] M. Stanek et al., Optimization of Injection molding process, *International Journal of Mathematics and Computers in Simulation*, Vol.5, 2011, pp. 413-421.

[12] M. Stanek et al., Simulation of Injection Molding Process, *International Journal of Mathematics and Computers in Simulation*, Vol.5, No.5, 2011, pp. 413-421.

[13] D. Manas et al., Thermal Effects on Steels at Different Methods of Separation, *Chemicke Listy S*, Vol.105, No.s5, 2011, pp. 713-716.

[14] M. Manas et al., Improvement of Mechanical Properties of TPE by Irradiation, *Chemicke Listy S*, Vol.105, No.s5, 2011, pp. 828-829.

[15] J. Javorik, M. Stanek, The Shape Optimization of the Pneumatic Valve Diaphragms, *International Journal of Mathematics and Computers in Simulation*, Vol.5, No.4, 2011, pp. 361-369.

[16] M. Stanek et al., Influence of Surface Roughness on Fluidity of Thermoplastics Materials, *Chemicke Listy*, Vol.103, No.1, 2009, pp. 91-95.

[17] A. Mizera et al., Properties of Selected Polymers after Radiation Cross-Linking, *International Journal of Mathematics and Computers in Simulation*, Vol.6, No.6, 2012, pp. 592-599.

[18] M. Manas et al., Modification of Polyamides Properties by Irradiation, *Chemicke Listy S*, Vol.103, No.s1, 2009, pp. 24-28.

[19] D. Manas et al., Wear of Multipurpose Tire Treads, *Chemicke Listy*, Vol.103, No.13, 2009, pp. 72-76.

[20] A. Mizera et al., Properties of HDPE after Radiation Cross-Linking, *International Journal of Mathematics and Computers in Simulation*, Vol.6, No.6, 2012, pp. 584-591.

[21] M. Stanek et al., Plastics Parts Design Supported by Reverse Engineering and Rapid Prototyping, *Chemicke Listy*, Vol.103, No.1, 2009, pp. 88-91.

[22] M. Stanek et al., Simulation of Injection Molding Process by Cadmould Rubber, *International Journal of Mathematics and Computers in Simulation*, Vol.5, No.5, 2011, pp. 422-429.

[23] M. Stanek et al., How the Filler Influence the Fluidity of Polymer, *Chemicke Listy S*, Vol.105, No.s15, 2011, pp. 303-305.

[24] K. Kyas et al., Simulation of Rubber Injection Molding Process, *Chemicke Listy S*, Vol.105, No.s15, 2011, pp. 354-356.

[25] HDPE TIPELIN PS 380-30/302, *Material Datasheet*, Slovnaft.

[26] LDPE DOW 780E, Material Datasheet, Dow.

[27] BGS - Beta Gamma Service, *website*, http://www.bgs.eu/.

[28] ČSN EN ISO 527-2, *Czech Technical Standard.*

[29] K. Kyas et al., Rubber Product Properties Influenced by Runners Trajectory, *International Journal of Mathematics and Computers in Simulation*, Vol.7, No.1, 2013, pp. 1-8.

[30] K. Kyas et al., Temperature Influence of Rubber Testing Samples During Its Preparation, *Chemicke Listy S*, Vol.107, No.s1, 2013, pp. 59-61.

[31] M. Bednarik et al., Strength of Bonded Joints of LDPE After Surface Treatment Beta Radiation, *Chemicke Listy S*, Vol.107, No.s1, 2013, pp. 103-105.

[32] A. Mizera et al., Properties of LDPE After Radiation Cross-Linking, *Chemicke Listy S*, Vol.107, No.s1, 2013, pp. 150-152.

[33] J. Navratil et al., Recyclation of Irradiated HDPE - Influence on Material Hardness, *Chemicke Listy S*, Vol.107, No.s1, 2013, pp. 155-157.

[34] A. Mizera et al., Temperature Stability of Modified TPE-E by Radiation Cross-Linking, *Chemicke Listy S*, Vol.107, No.s1, 2013, pp. 152-155.

[35] A. Mizera et al., Temperature Stability of Radiation Cross-Linked Polyehtylenes, *Plasty a Kaucuk - Special*, Vol.49, 2012, pp. 21-23.

[36] J. Cerny et al., Modern Method of Design of Ergonomic Parts, *Plasty a Kaucuk - Special*, Vol.49, 2012, pp. 6-8.

[37] J. Cerny et al., Wear of Heavy Industry Tires, *International Journal of Mathematics and Computers in Simulation*, Vol.7, No.1, 2013, pp. 1-8.

[38] V. Senkerik et al., Influence of Temperature and Amount of Recycled Material to PC Properties, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 235-238, 2013

[39] A. Mizera et al., Properties of PA12 after Radiation Cross-Linking, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 209-212, 2013

[40] A. Mizera et al., Properties of PA11 after Radiation Cross-Linking, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 201-204, 2013

[41] M. Stanek et al., Polymer Fluidity Influenced by Amount of Talc, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 181-185, 2013

[42] D. Manas et al., Effect of Beta Low Irradiation Doses on the Microhardness of PA 66, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 190-195, 2013

[43] D. Manas et al., Effect of Beta Low Irradiation Doses on the Microhardness of PC, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 196-200, 2013

[44] K. Kyas et al., Effect of Type of Runner on Curing Rate during Injection Molding of Rubber Compound, *Recent Advances in Systems Science – Proceedings of the 17th International Conference on Systems*, Rhodes Island, pp. 221-225, 2013