Tensile Toughness of Irradiated HDPE

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

***Abstract*—**Although irradiation of plastics is a well-recognized modification, little research has been undertaken on the possible re-use of such modified materials. In this research paper their possible utilization as fillers into non-irradiated materials is investigated. A powder of recycled irradiated high-density polyethylene (HDPE) was used as filler and granules of non-irradiated neat low-density polyethylene (LDPE) were used as a polymer matrix. Both materials were mixed together in seven concentrations (from 0 % to 60 % of the filler) and test specimens were prepared from the resulting compound by an injection molding technology. Tensile test at two temperatures (ambient – 23 °C and elevated – 80 °C) was performed and influence of the filler on strength, toughness and elasticity was observed. According to measured results there is significant growth of, strength (up to 41 %) and toughness (up to 85 %) and on the contrary significant loss of elasticity (up to 69 %), similar trend is observed at elevated temperature as well. These findings indicate that it is possible to re-use irradiated polymer material after the end of its service life, while taking advantage of the improvement in the resulting mechanical properties.

***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 improved mainly mechanical (elastic modulus, hardness, yield strength), thermal (stability, expansion) and also chemical (solubility threshold) properties [1-10, 30-37].

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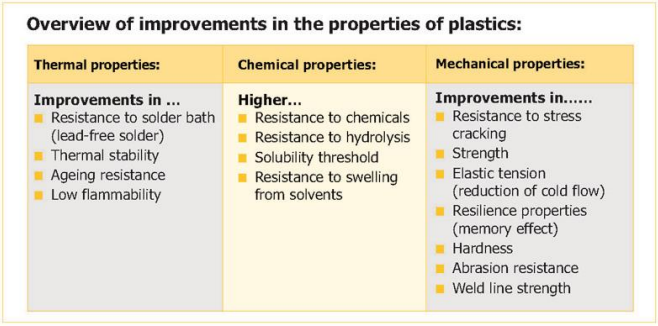

Fig. 1 Improved properties [27]

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 [9-18].

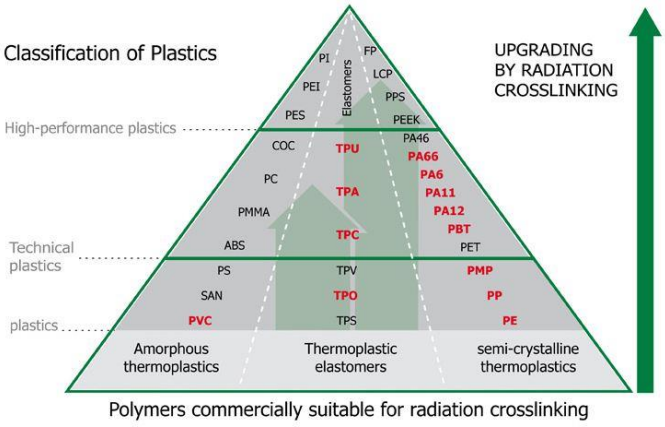

Fig. 2 Material classification [27]

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 [1-15, 19-27].

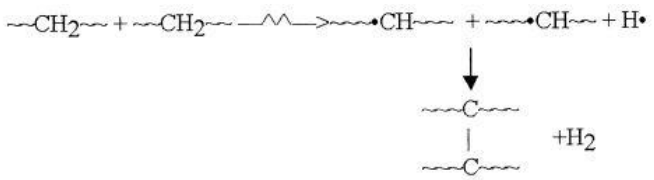

Fig. 3 Crosslinking mechanism [10]

The crosslinking mainly occurs in the amorphous regions of polymers. The degree of crosslinking is proportional to the radiation dose which can be controlled by dose rate and conveyor speed [2-5, 28-30].

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) [14-22].

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 [2-12].

Cobalt-60 (gamma radiation) on the other hand offers higher penetration depths and lower irradiation doses and unlike beta radiation it takes several hours to irradiate products. Gamma radiation is due to the above mentioned reasons used mainly for radiation sterilization [1, 25-36].

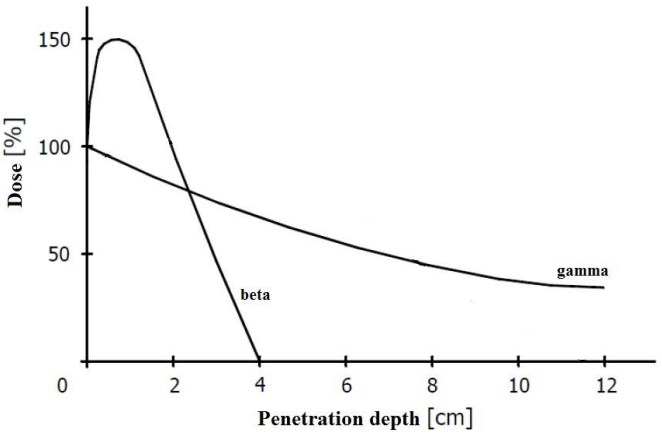

Fig. 4 Radiation sources comparison [32]

Radiation crosslinking is utilized for irradiation of many industrial products such as:

- wires and cables
- foamed polyethylene
- contact lenses
- composites
- pipes
- heat shrinkable tubing and sheets [8-23].

II. Experiment

The main goal of the experiment was to determine possible utilization of a powder made from irradiated material after its service life and to examine its influence on tensile toughness.

A. Materials

Two materials were tested. Neat 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 1. This material was supplied in the form of granules.

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 floor heating. These tubes could not be remelted due to their modification by beta radiation; 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 2; 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	49
Vicat Softening Temperature	120 [°C]

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. 5 and Fig. 6).

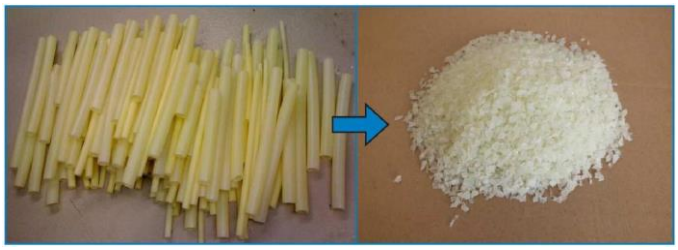

Fig. 5 Processed tubes

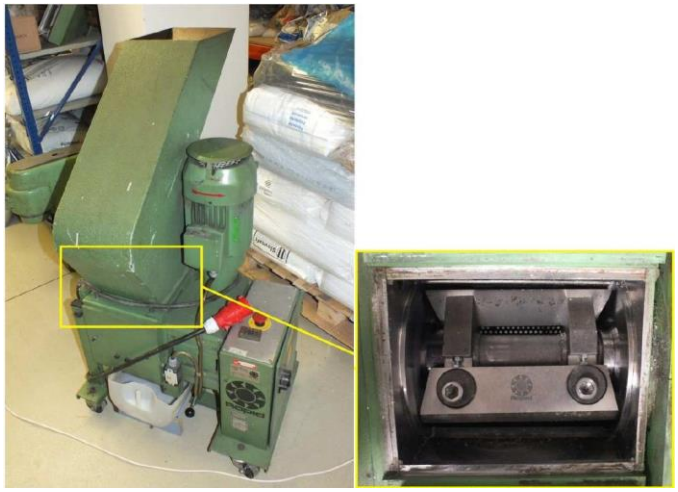

Fig. 6 Rotary cutter mill

Particle size which leaves the mill varies between 3 to 5 mm. Diversity in shape and size is shown in Fig. 7.

Fig. 7 Particles shape and size

Thus prepared material was then sent for grinding and resulting powder was used as filler; nevertheless, before compounding this powder underwent sieving to determine size of the particles. Sieving was carried out on the sieving machine (Fig. 8) where totally 200 g of recycled HDPE powder was sieved. Sieving time was set to 30 minutes and amplitude of vibration was set to 90 mm. Measured data are shown in Fig. 9.

Fig. 8 Sieving device

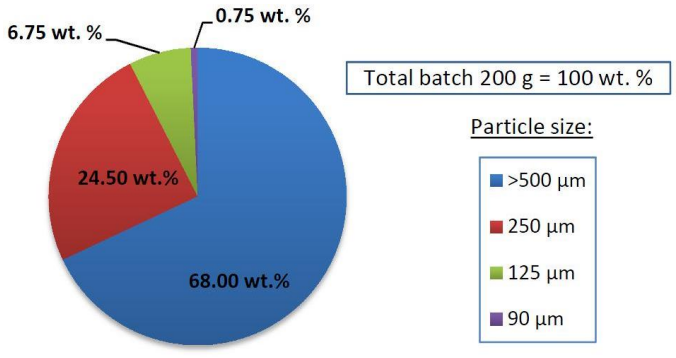

Fig. 9 HDPE particle size

As can be seen from the chart above (Fig. 9) 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.

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

Fig. 10 Pneumatic blender

Resulting compound was injection molded in injection molding machine Arburg Allrounder 420C under process parameters shown in Table 3; however, with increasing concentration of filler this 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 the deteriorated fluidity. This might be caused by changing the ratio of matrix/filler in favor of filler.

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]

Resulting test specimens had dimension and shape according to the standard ISO 527 (Fig. 11 and Table 4).

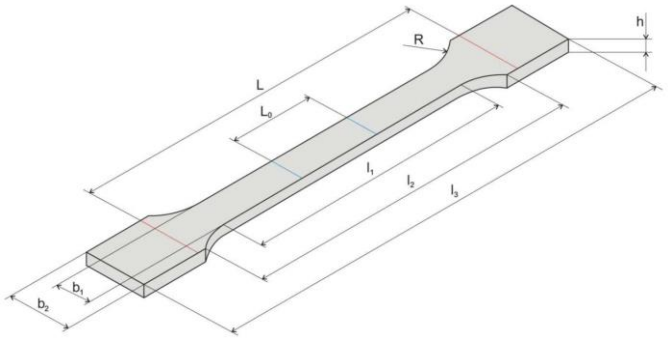

Fig. 11 Testing specimen [28]

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 was carried out on tensile testing machine at two temperatures – ambient (23 °C) and elevated (80 °C). Elevated temperature was chosen due to the original purpose of the pipes which was hot water transportation. Observed properties were toughness (Young´s Modulus – E), strength (Ultimate Tensile Strength – Rm) and elasticity (Nominal Strain at Rm – ε).

A. Ambient Temperature (23 °C)

First observed result was Young´s Modulus – toughness of the material.

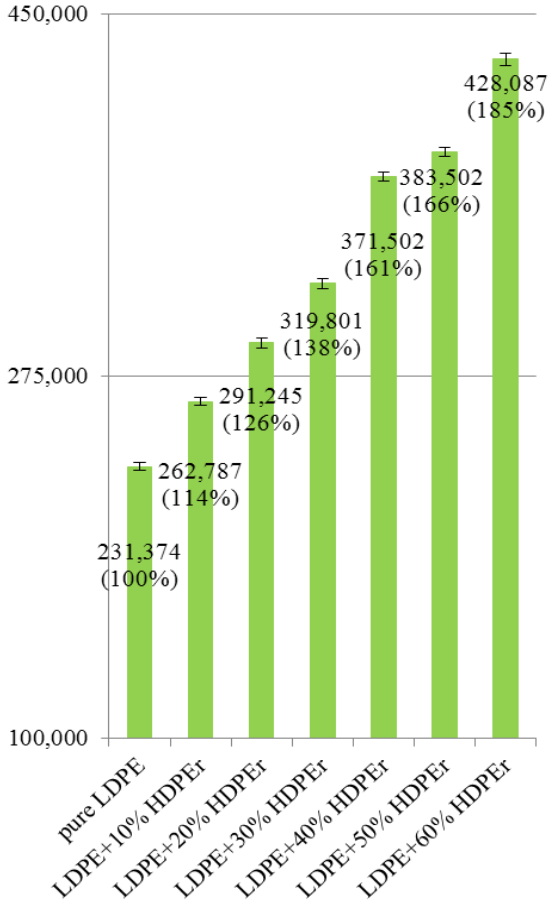

Fig. 12 Young´s modulus

As can be seen from Fig. 12 there is an upward trend with an increasing amount of the filler. It grown from 231 MPa at non-filled neat LDPE to 428 MPa at 60 % filled LDPE which means that the toughness grown almost twice.

In Fig. 13 is shown influence of the filler on Ultimate Tensile Strength and the trend is similar to the Young´s Modulus one. Only the hike is not so significant because it risen from 11 MPa at non-filled neat LDPE to 15 MPa at 60 % filled LDPE. That means that strength grown by 41 %.

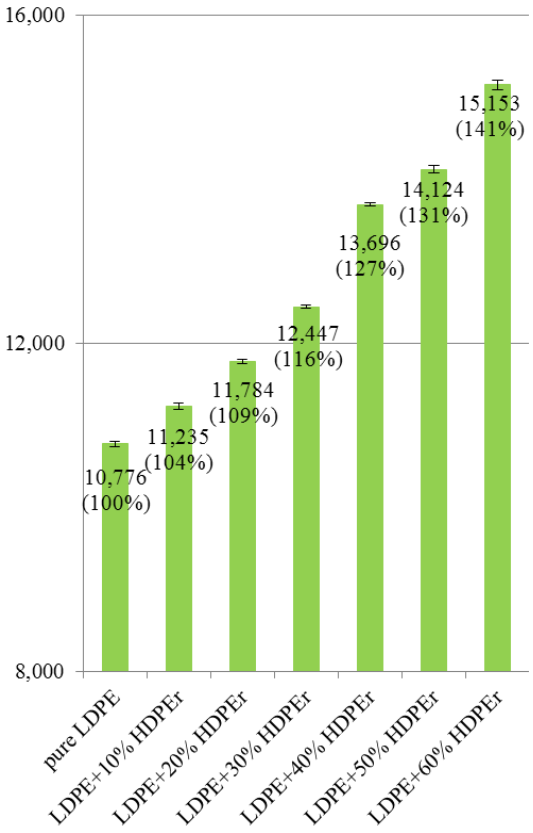

Fig. 13 Ultimate tensile strength

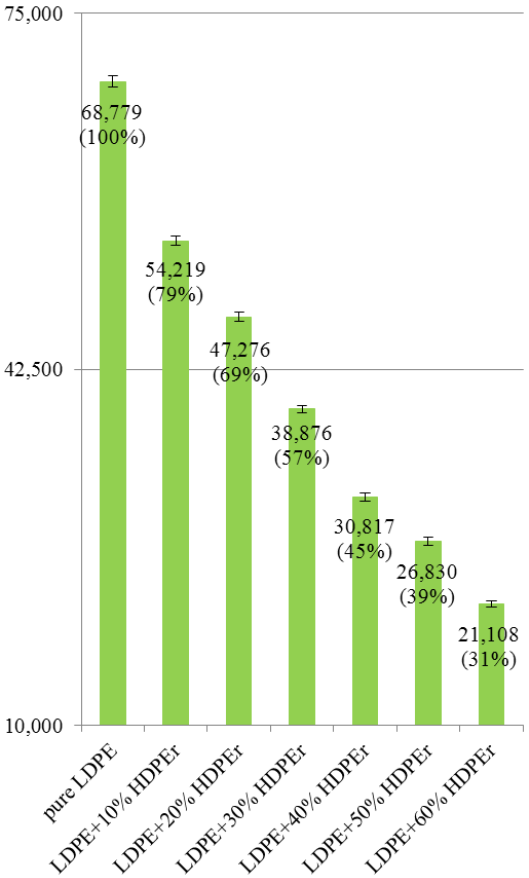

Fig. 14 Nominal strain at Rm

Significant loss of elasticity is a result of increased Young´s Modulus and Ultimate Tensile Strength (Fig. 14). Nominal Strain at Rm fallen from the original value 69 % to 21 % for the sample with the highest recyclate concentration.

B. *Elevated Temperature (80 °C)*

Temperature 80 °C was chosen deliberately due to the original purpose of these irradiated pipes. They served as a floor heating and the flowing water had up to 80 °C.

Trend of increasing Young´s Modulus is comparable to the one at ambient temperature; however, this increase is not gradual but sharp. The most significant change is among concentrations 20 % and 30 % of the filler (from 40 MPa to 52 MPa). Nevertheless, overall upturn is also almost twofold because it grown from 37 MPa at non-filled neat LDPE to 71 MPa at 60 % filled LDPE. This trend can be seen in Fig. 15.

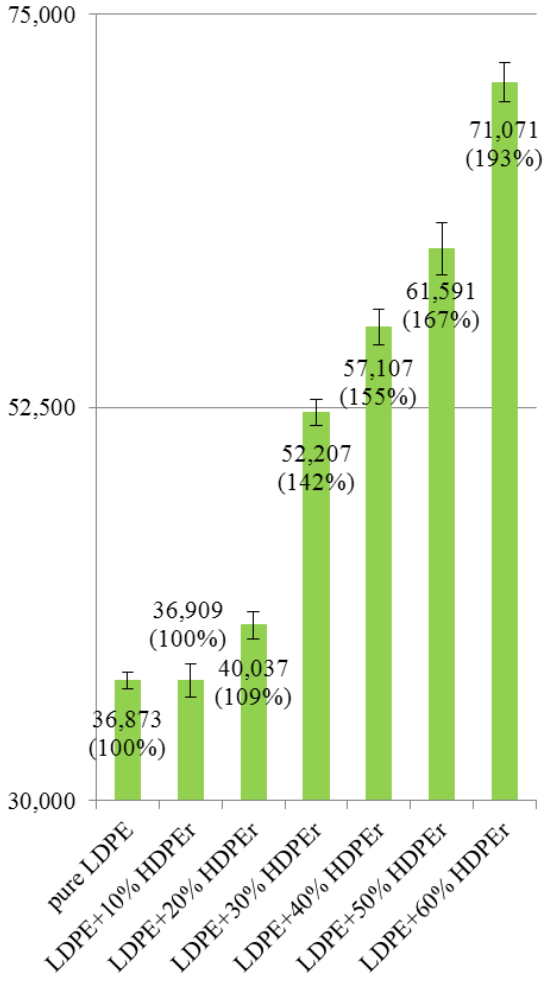

Fig 15. Young´s modulus

Another observed result was Ultimate Tensile Strength (Fig. 16). Ultimate Tensile Strength boosted from 4.6 MPa to 6 MPa. This corresponds to 30 % rise and to the previous results measured at ambient temperature – 23 °C. We might observe that the positive effect of the filler remains unchanged even at elevated temperature.

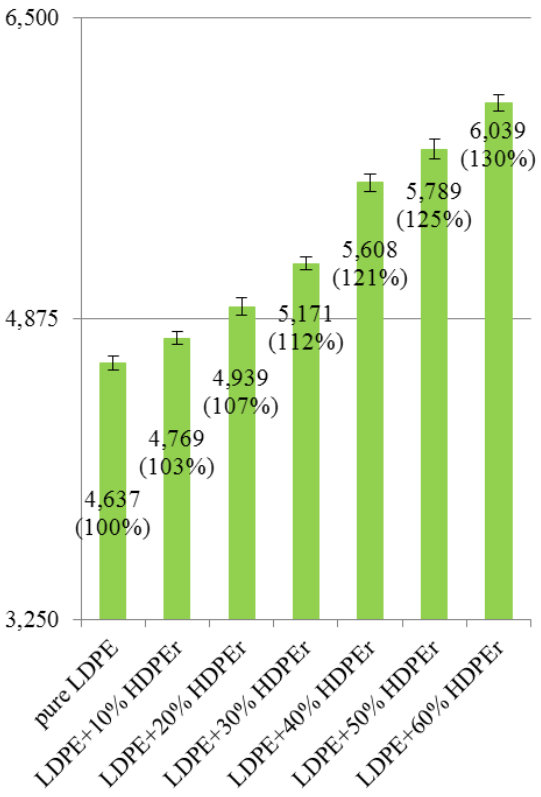

Fig. 16 Ultimate tensile strength

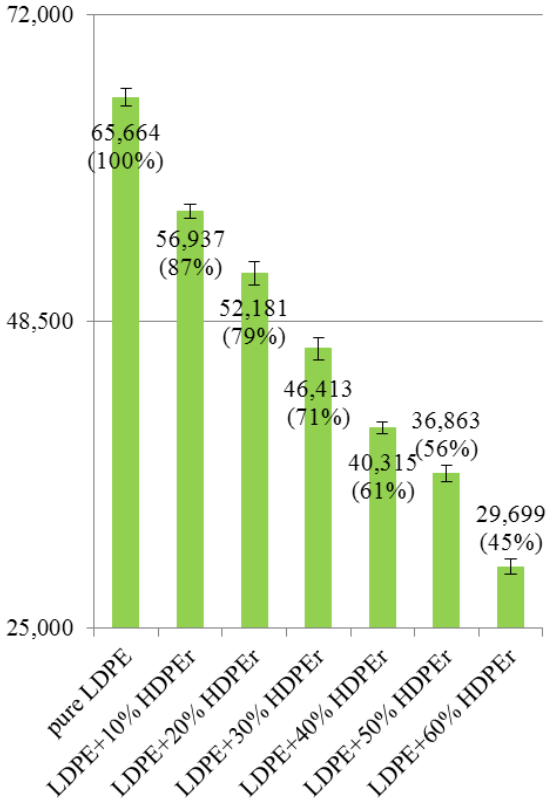

Fig. 17 Nominal strain at Rm

Last observed variable is Nominal Strain at Rm at 80 °C (Fig. 17). Elongation decreased from 66 % to 30 % which are

almost the same values as at the ambient conditions. This result denies all the theory saying that with increasing temperature increases elasticity as well therefore much more detailed investigation is needed.

IV. Discussion

Measured results show that there is not only desirable utilization of recycled material but also significant property improvements. 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.

It can be seen that strength and toughness grow with increasing amount of the filler and elasticity decreases on the other hand. This is just confirmation of the well-known fact that the higher stiffness the lower elasticity but it is quite surprising that it was possible to achieve such behavior even at plastic to plastic interaction.

The best results have materials with the highest concentration of the filler but their processability are worsen therefore higher concentrations 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 due to the weakened intermolecular forces. Courses of curves are depicted in Fig. 18 and Fig. 19.

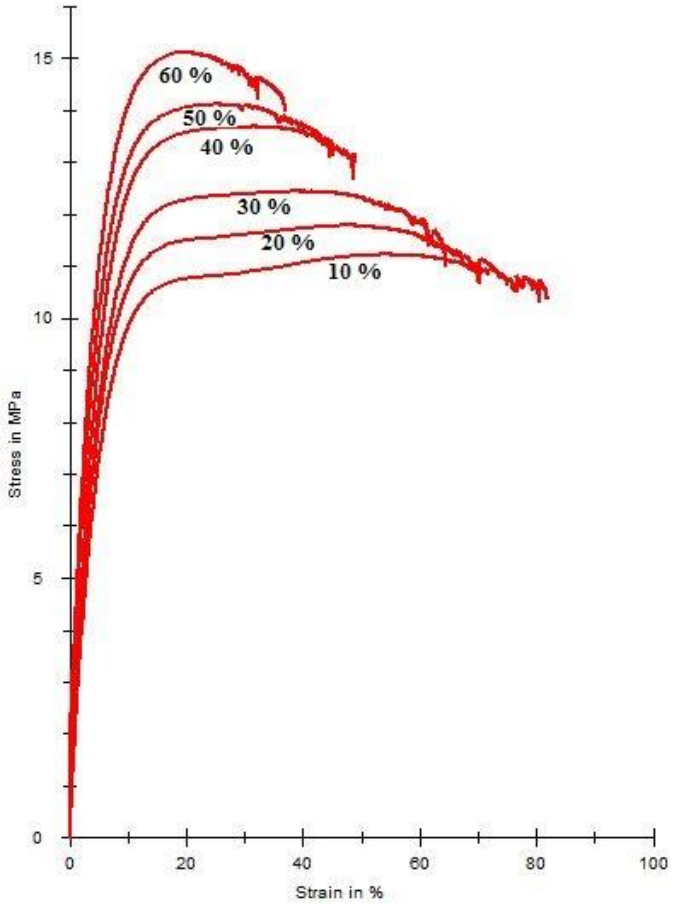

Fig. 18 Ambient temperature – 23 °C

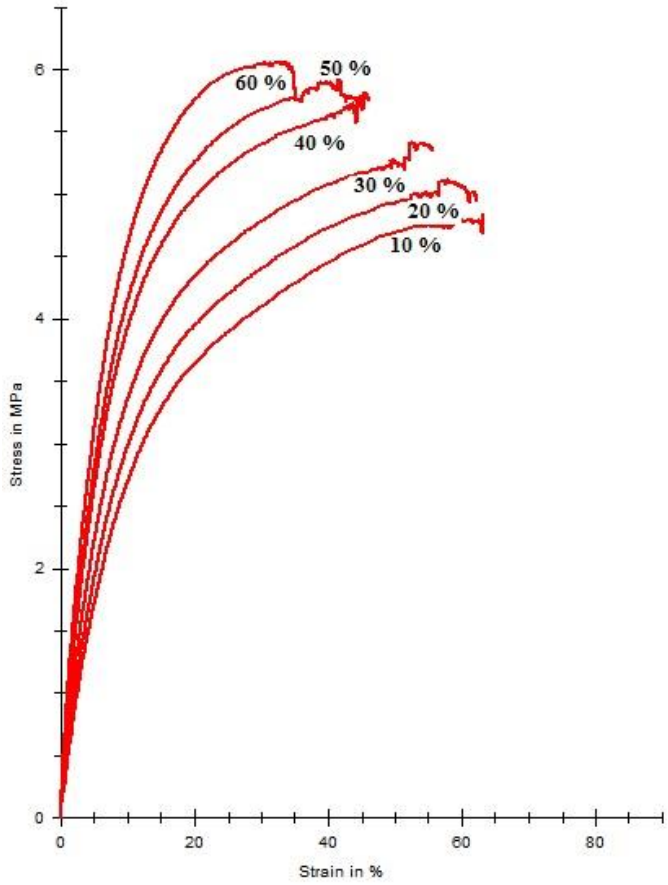

Fig. 19 Elevated temperature – 80 °C

V. Conclusion

The main purpose of this paper was to investigate possible usage of irradiated materials after the end of their lifetime. A powder of recycled irradiated HDPE was used as filler into granules 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 utilization such materials; however, this study only concentrated on changes in the 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 its filler.

Acknowledgment

This paper is supported by the internal grant of TBU in Zlin No. IGA/FT/2013/020 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 and Technology Agency of the Czech Republic as a part of the project called TA03010724 AV and EV LED luminaire with a higher degree of protection.

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