Recyclation of Modified HDPE

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***Abstract*—**Little research was done to investigate possible utilization of the irradiated materials after the end of their lifetime despite the growing potential of modification by irradiation. This research paper deals with usage of this recycled material as filler into non-recycled one. A powder or a grit of recycled irradiated high-density polyethylene was used as filler into non-irradiated powder or granules of low-density polyethylene. Three types of compounds were prepared – each with the same concentrations. These were from 0 % to 60 %. Notched Charpy Impact Test was then performed at ambient conditions and influence of this filler was tested. Two parameters were observed – Maximum Force (force needed for breakage of the material) and Impact Toughness (describing impact behavior of the material). Measured results show minimum influence on Maximum Force in cases of powder filler – it varied around 280 N. In case of grit filler it grew rapidly with increasing concentration – from 286 N to 348 N. Results of Impact Toughness are much more consistent because all three compounds show similar trend. In all cases was this trend decreasing – the higher filling level the lower Impact Toughness. These findings are showing the way of possible re-use of irradiated materials.

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

I. INTRODUCTION

MODIFICATION of of plastics by irradiation has been used for 50 years. Original purpose was sterilization but since a positive effect on plastic materials was discovered it is used in plastic industry as well. Irradiated materials 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. In Table I are depicted some of improved properties [5-21, 29-33].

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Table I Improved properties [1-6]

Thermal properties	Chemical Properties	Mechanical Properties
Dimensional Stability	Solubility Reduction	Modules Increase
Deformation	Swelling Resistance	Strength Increase
Aging Resistance	Stress Cracking Resistance	Elongation Decrease
Heat Distortion Temperature	Hydrolysis Resistance	Hardness Increase
Flame Resistance	Aggressive Agents Resistance	Abrasion Resistance
Glow Wire Resistance		Creep Resistance

Irradiation takes place at ambient conditions and on the final product thus processability is not influenced; however, not every material undergoing irradiation has improved properties. 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 [1-9].

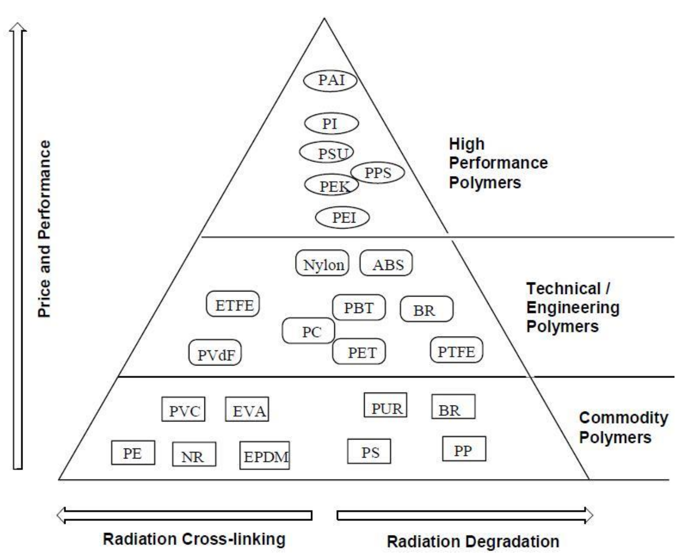

Fig. 1 Material classification [3]

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 [19-31]

The source of radiation may be an electron beam accelerator (beta radiation) or a radioactive source such as Cobalt-60 (gamma radiation) [3-15].

Electron beams (beta radiation) generated by accelerators are monoenergetic and the absorbed dose is highest just below the surface of the irradiated material and falls rapidly at higher penetration depths. The energy range of electron beams used in radiation processing is from 0.15 to 10 MeV. Electron beams are mainly used for irradiation of relatively thin objects such as wires and cable insulations [30-37].

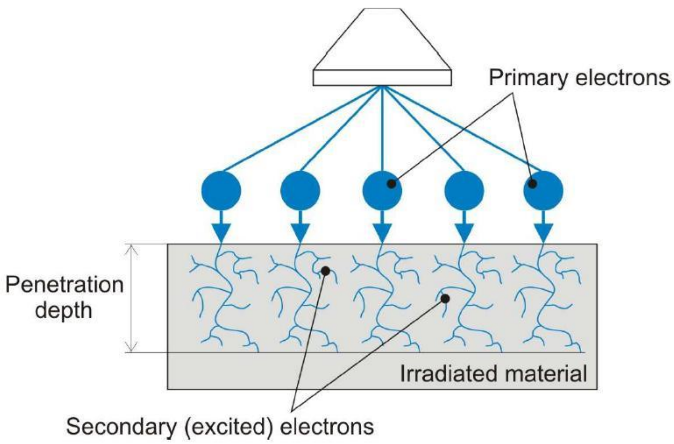

Fig. 2 Beta radiation [32]

Gamma radiation has a high penetration capability at relatively low dose intensity. The most used source of this radiation is Cobalt-60 which emits energy of about 1.3 MeV. Source of gamma radiation cannot be turned off, unlike source of beta radiation; therefore it has to be shielded all the time. The gamma rays are mainly used for sterilization [21-27].

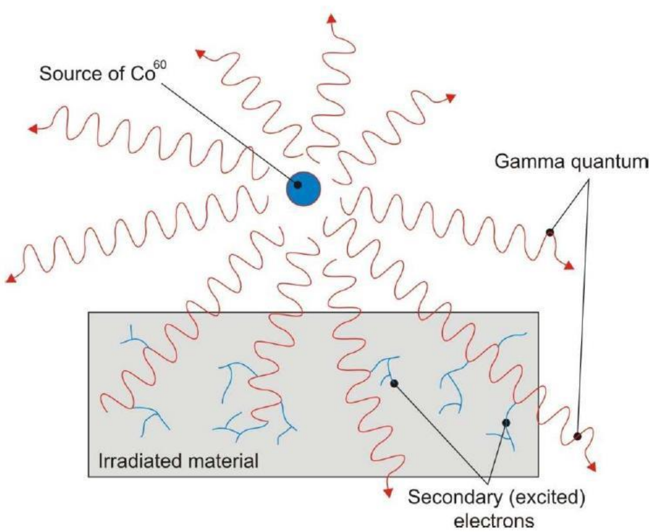

Fig. 3 Gamma radiation [32]

Comparing both sources, beta radiation provides shorter irradiation times (seconds), higher doses, directional beams but lower penetration depths. Gamma radiation on the other hand provides higher penetration depths but lower doses and longer irradiation times (hours) [22-37].

II. Experiment

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

A. Materials

Two materials were tested. Neat low-density polyethylene (LDPE) and recycled irradiated high-density polyethylene (HDPE). Three combinations of these materials were then prepared:

- LDPE powder/HDPEr powder
- LDPE granules/HDPEr powder
- LDPE granules/HDPEr grit

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 II. This material was provided in the form of granules.

Table II 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 III; however, properties of irradiated HDPE differ.

Table III 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
Vicat Softening Temperature	120 [°C]

B. Preparation of the Specimens

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 and Fig. 5).

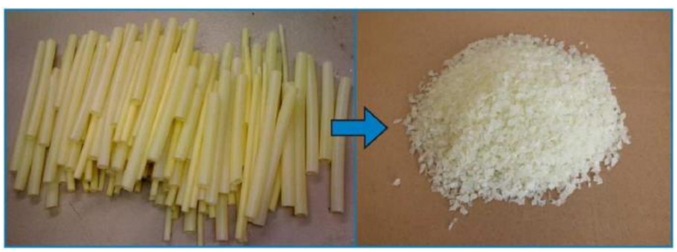

Fig. 4 Processed tubes

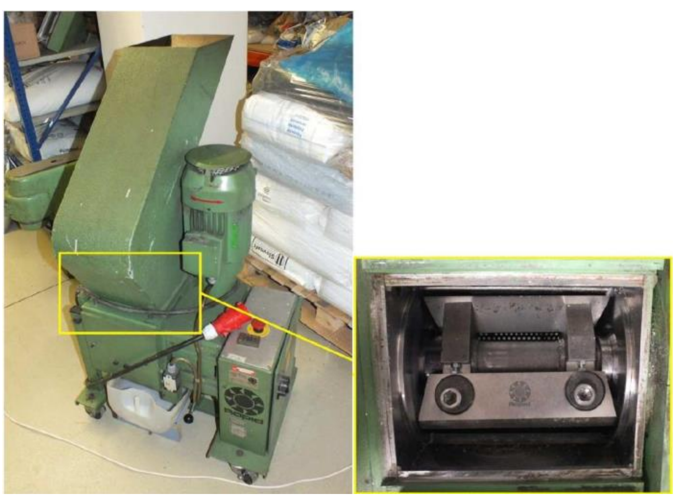

Fig. 5 Rotary cutter mill

Particle size which leaves the mill varies between 3 to 5 mm. Diversity in shape and size is shown in Fig. 6.

Thus prepared materials were then sent for grinding. Size of the particles of the resulting powder had to be determined. Therefore these powders underwent sieving, which was carried out on the special sieving machine. Total batch of 200 g was used. Parameters of the sieving were set to 30 minutes and amplitude of vibration was set to 90 mm. Measured data are shown in Fig. 7 and Fig. 8.

Fig. 6 Particles shape and size

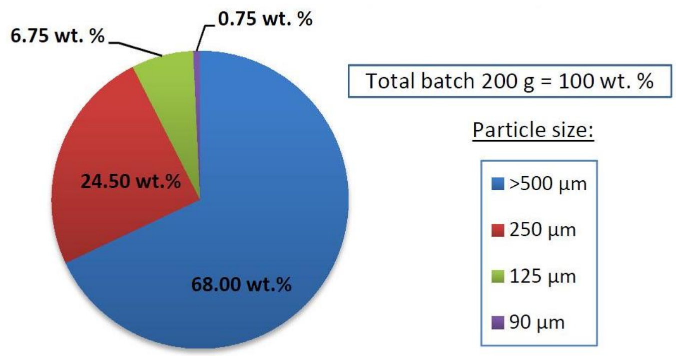

Fig. 7 HDPE particle size

As can be seen from the chart above (Fig. 7) 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.

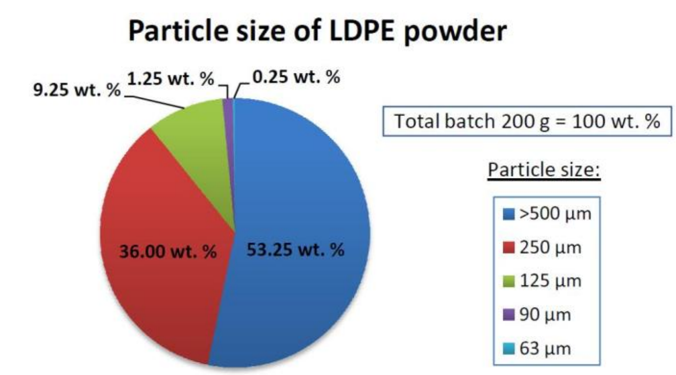

Fig. 8 LDPE particle size

In 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 (Fig. 8).

Thus prepared raw materials were mixed together in concentrations from 10 % to 60 %. Mixing was carried out in a “home-made” laboratory pneumatic blender (Fig. 9). 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. 9 Pneumatic blender

Resulting compound was injection molded in injection molding machine Arburg Allrounder 420C under process parameters shown in Table IV; 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.

Table IV 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. 10 and Table V).

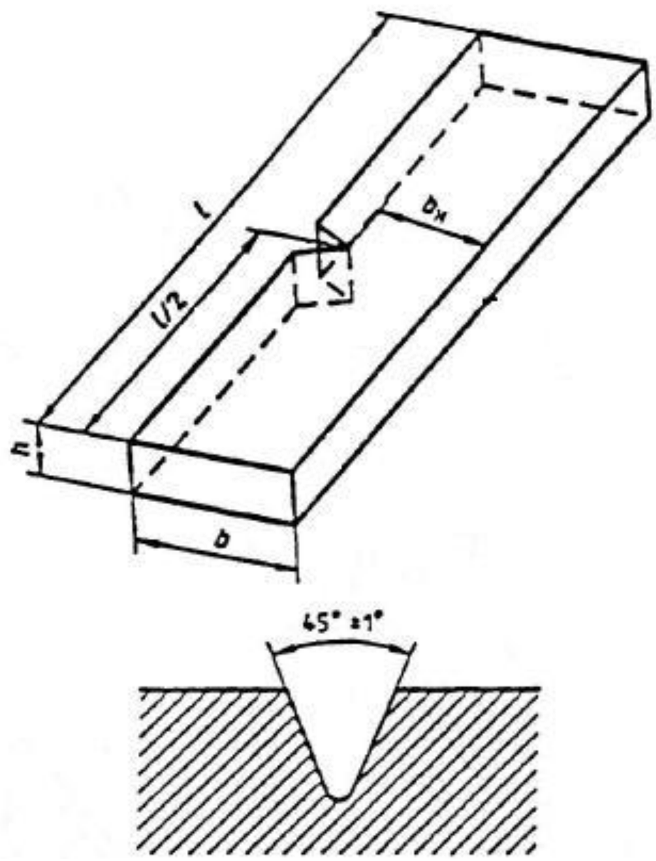

Fig. 10 Testing specimen [28]

Table V Specimen dimension [28]

Test Specimen Parameters	
b - Width of Specimen	10 ± 0.2 [mm]
h - Thickness of Specimen	4 ± 0.2 [mm]
l - Length of Specimen	80 ± 2 [mm]
b_N - Notched Width of Specimen	8 ± 0.2 [mm]
R - Radius of Notch	0.25 ± 0.05 [mm]
Parameters of Test	
Weight of Hammer	2.192 [kg]
Length of Arm	0.5 [m]
Angle of Arm	40 [°]
Impact Energy	2.51 [J]

III. Results

Testing Charpy V-notched test was carried out on Resil Impactor Junior testing machine at ambient temperature (23 °C). Observed properties were Impact Toughness (Am) and Maximum Force (Fm).

A. Powder/Powder Combination

First observed result was Maximum Force necessary for breakage of the specimen.

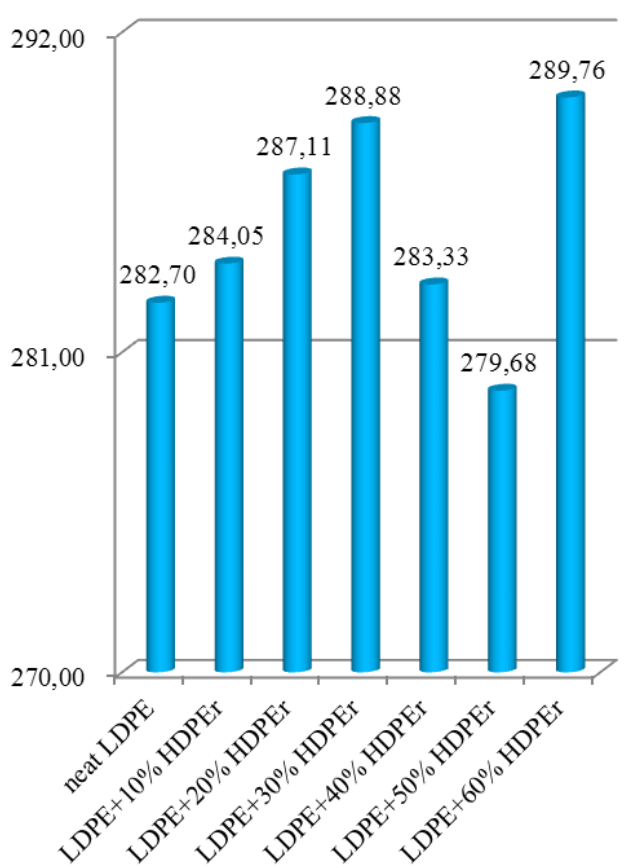

Fig. 11 Maximum force

As can be seen from Fig. 11 there is an upward trend with an increasing amount of the filler until 40% concentration. It increases from 282.7 N to 288.9 N then there is a drop up to 279.7 N and a hike again at highest concentration to 289.7 N. However values of Maximum Force vary about 280 N and therefore the influence of the filler on this variable is negligible.

In Fig. 12 is shown influence of the filler on Impact Toughness and there is observed decreasing trend with increasing amount of the filler. This means that the more filler the higher brittleness. Impact toughness dropped from 21.7 kJ/m^2 to 7.8 kJ/m^2. There is almost threefold drop in this parameter.

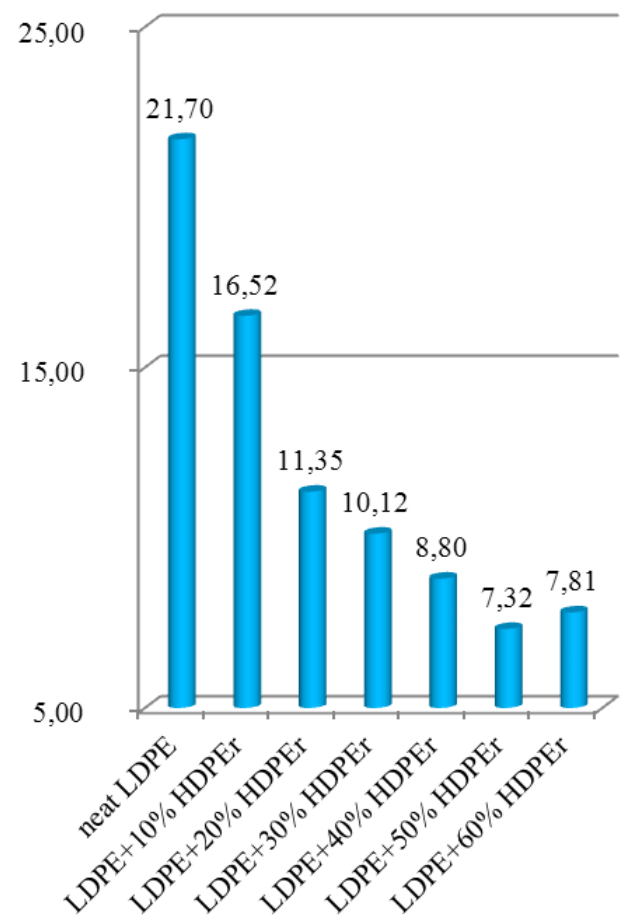

Fig. 12 Impact toughness

B. Granules/Powder Combination

Results of granules/powder compounds are depicted in following figures where Maximum Force and Impact Toughness are compared.

The highest value of Maximum Force was achieved at non-filled specimen – 286.1 N and the lowest value was 279.3 N at 30% concentration of filling. It is observed that influence of the filler is insignificant too because it varies around 280 N. Variation might be caused by an error in measurement (Fig. 13).

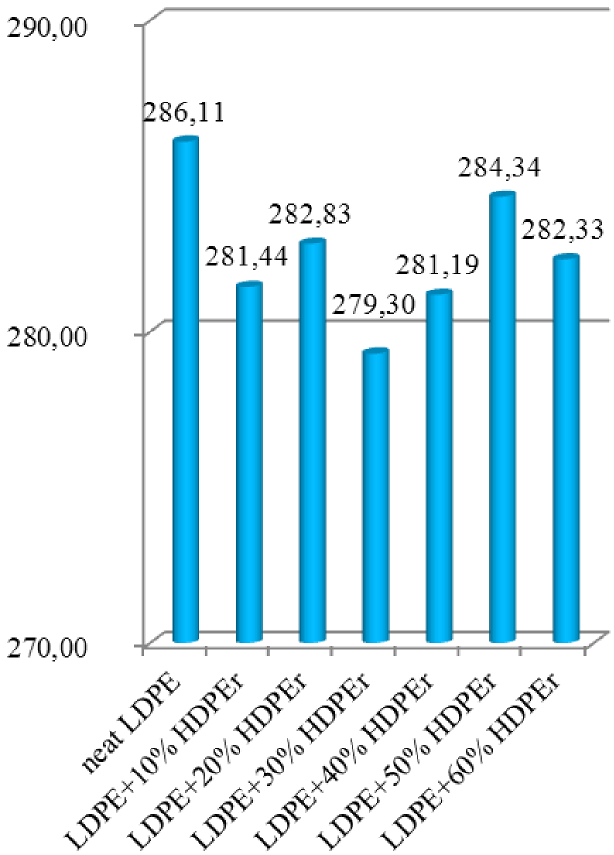

Fig. 13 Maximum force

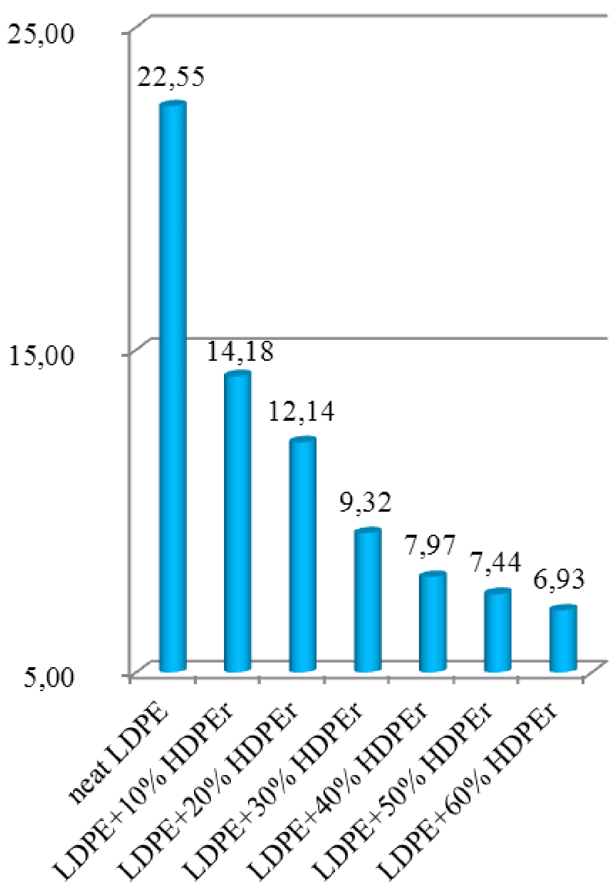

Fig. 14 Impact toughness

Impact Toughness (Fig. 14) has similar trend to the previous compound. The highest value – 22.5 kJ/m^2 was observed at non-filled material and the lowest – 6.9 kJ/m^2 was achieved at 60% concentration therefore the brittleness grown as well. The difference between highest filling and neat LDPE is even higher than in previous case, it might be caused by more random dispersion of the powder particles.

C. Granules/Grit Combination

Last combination of materials was LDPE granules mixed with HDPE grit.

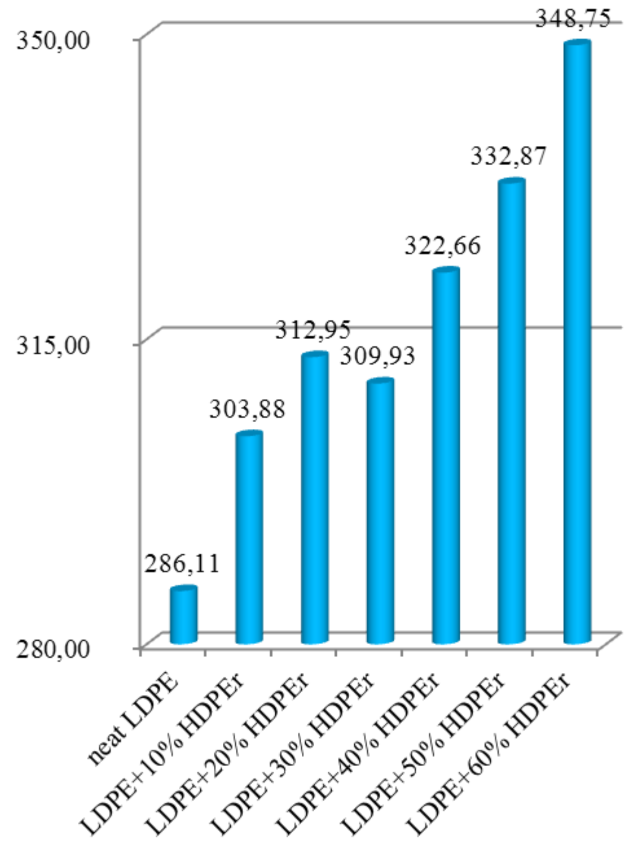

Fig. 15 Maximum force

Granules/grit combination shows different behavior compared to other combinations. As can be seen in Fig. 15 Maximum Force grows rapidly with increasing amount of the filler from 286.1 N at non-filled LDPE to 348.8 N at LDPE with 60% concentration of the filler. This different behavior might be caused by different particle size of the filler which is much bigger than in case of powder.

In Fig. 16 is depicted Impact Toughness of the last compound and trend is comparable to the previous ones; however, the fall is not so significant. It dropped from 22.5 kJ/m^2 to 14.24 kJ/m^2. This drop represents almost 37 % decrease in toughness of the material.

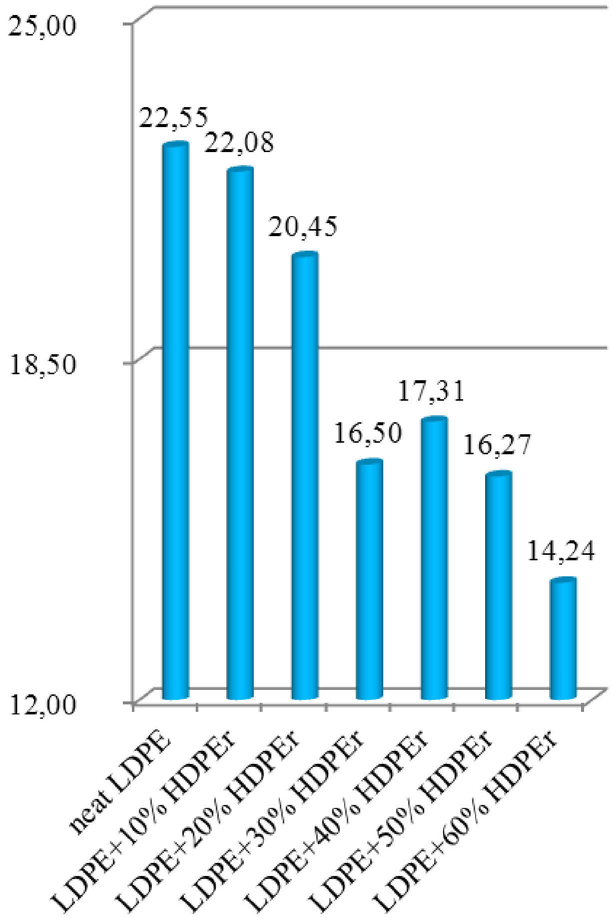

Fig. 16 Impact toughness

IV. Discussion

Measured results show that there was found desirable utilization of recycled irradiated HDPE after its service life. However using such materials as fillers has influence on their behavior – in this case on the Maximum breakage Force and Impact Toughness.

It can be seen that force necessary for breakage of the specimen is influenced only negligibly in cases where the filler was in powder form. In case where the filler was grit the force grown rapidly. Most probable explanation is that the force is dependent also on particle size and thus grit has much different results comparing to powder.

It cannot be determined which result is the best because it depends on possible application.

For comparison purposes was also neat HDPE and irradiated HDPEx tested and it might be observed that Maximum Force is two times higher than in case of LDPE with HDPE filler and that irradiation causes increase of this force (Fig. 17). Impact Toughness of neat HDPE is lower than neat LDPE – material is more brittle. Irradiation on the other hand makes HDPE more ductile – Impact Toughness grows almost twofold (Fig. 18).

Fig. 17 Maximum force

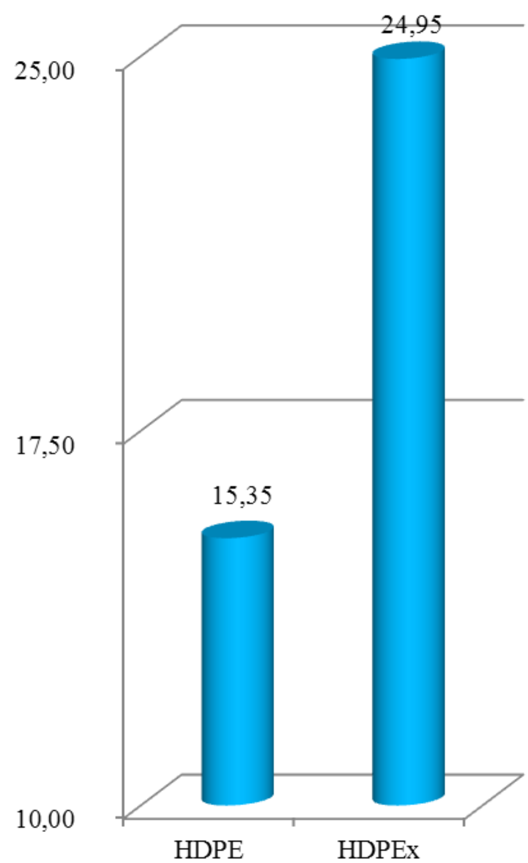

Fig. 18 Impact toughness

V. Conclusion

The main goal of this paper was to examine possible utilization of irradiated materials after the end of their lifetime. Recycled irradiated HDPE was used in two forms – powder and grit and it was mixed with non-irradiated LDPE which was also in two forms – granules and powder. Three types of compounds were prepared and Charpy V-notched Impact Test was performed. Results indicate that there is an influence of the filler on the impact toughness; however, further research is necessary to provide more "in depth" look into the material structure and to explain such behavior.

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