

Recycling of modified polymers

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[3] Woods, R., Pikaev, A.: **Applied Radiation Chemistry: Radiation Processing**. New Jersey; A John Wiley & sons, inc. publ., 1994. 535p.

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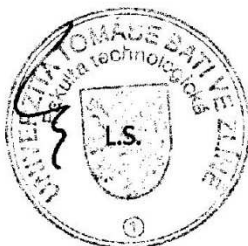
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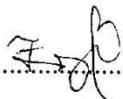
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ABSTRAKT

Tato diplomová práce se zabývá možností využití ozářených polyetylenů po skončení jejich životnosti. Po vystavení ionizačnímu záření, některé termoplasty síťují, čímž u nich dochází k chemickým změnám, které způsobí, že nemohou být znovu roztaveny. Díky tomu ztrácí ozářený polyetylén schopnost být recyklován konvenčními způsoby. Výzkum v této práci ukazuje možnost využití hadic a trubek z ozářeného HDPE i po skončení jejich životnosti, což by mohlo značným způsobem pomoci životnímu prostředí. Zkoumá změnu mechanických vlastností v závislosti na množství recyklátu použitým v čistém LDPE jako plnivo. Dále se výzkum zabývá vlivem typu a velikosti částic recyklátu na tyto mechanické vlastnosti a popisuje změnu tokových vlastností v závislosti na množství recyklátu ve směsi.

Klíčová slova: Polyetylén, Ozářený materiál, Recyklace, Tahová zkouška, Index toku taveniny

ABSTRACT

This Master Thesis deals with the potential use of irradiated polyethylene materials after the end of their lifetime. Some thermoplastic materials are cross-linked after exposure to ionizing radiation, i.e. their structure is chemically changed, and thus they cannot be remelted. Due to this, irradiated polyethylene loses the possibility to be recycled by conventional means. The research in this work shows the possibility of using pipes and hoses of irradiated HDPE even after their lifetime, which could significantly help to the environment. It examines the change of mechanical properties depending on the amount of recycled material used in the pure LDPE as filler. Furthermore, this work analyzes the influence of recycled particle size and type on the mechanical properties, and describes a change in flow properties of these mixtures depending on the amount of recycled material in the mixture.

Keywords: Polyethylene, Irradiated material, Recycling, Tensile test, Melt flow rate

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Motto

“
Není důležitá kvantita, ale kvalita
vědomostí. Je možné mít množství
vědomostí, ale neznat to
nejdůležitější.
”

“
What is important in knowledge is
not quantity, but quality. It is
important to know what knowledge
is significant, what is less so, and
what is trivial.
”

Lev Nikolayevich Tolstoy (*1828 - †1910)

I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

CONTENTS

INTRODUCTION	10
I THEORETICAL BACKGROUND	11
1 INTRODUCTION TO POLYMERS.....	12
1.1 MOLECULAR STRUCTURE OF POLYMERS.....	14
1.2 BASIC TYPES OF PLASTICS	17
2 POLYETHYLENES	18
2.1 LOW-DENSITY POLYETHYLENE.....	19
2.2 HIGH-DENSITY POLYETHYLENE.....	19
2.3 LINEAR LOW-DENSITY POLYETHYLENE.....	20
2.4 OTHER TYPES OF ETHYLENE	20
3 MODIFICATIONS OF PLASTICS	22
3.1 ADDITIVES – FILLERS	22
3.2 CROSSLINKING OF PLASTICS	23
3.2.1 Chemical crosslinking	24
3.2.2 Radiation crosslinking.....	25
4 RECYCLING OF PLASTIC WASTE	29
4.1 MECHANICAL RECYCLING	30
4.2 FEEDSTOCK RECYCLING (CHEMICAL RECYCLING).....	34
4.2.1 Chemical depolymerization	35
4.2.2 Gasification	35
4.2.3 Hydrogenation.....	36
4.2.4 Catalytic cracking.....	37
4.2.5 Pyrolysis.....	37
4.3 ENERGY RECOVERY.....	38
5 MATERIAL PROPERTIES TESTING.....	39
5.1 TENSILE TESTING.....	39
5.1.1 Testing specimens	40
5.1.2 Testing machines.....	41
5.1.3 Measured data	42
5.2 MELT FLOW RATE TEST	44
II ANALYSIS	47
6 OBJECTIVES OF MASTER THESIS.....	48
7 MACHINES AND DEVICE.....	49
7.1 ROTARY CUTTER MILL RAPID SK 2218	49
7.2 LABORATORY PNEUMATIC BLENDER	49
7.3 INJECTION MOLDING MACHINE ARBURG ALLROUNDER 420C	50
7.4 TENSILE TESTING MACHINE ZWICK 1456	51
7.5 DEVICE FOR MELT FLOW RATE MEASURING DYNISCO KAYENESS LMI 4003.....	52
7.6 VIBRATORY SIEVE SHAKER RETSCH AS 200 BASIC	53

8	MATERIALS AND PROCESSING	54
8.1	DOW LDPE 780E	54
8.2	SLOVNAFT HDPE TIPELIN PS 380-30/302	54
8.3	RECYCLATE PROCESSING.....	55
8.4	COMPOUND PREPARATION.....	56
9	EXPERIMENT	58
9.1	EVALUATION OF MEASURED DATA	58
9.2	SIEVING.....	60
9.3	MELT FLOW RATE.....	62
9.4	PRODUCTION OF TEST SPECIMENS.....	64
9.5	TENSILE TEST	65
9.5.1	Measured data for granules of LDPE and grit of recyclate.....	65
9.5.2	Measured data for granules of LDPE and powder of recyclate	77
9.5.3	Measured data for powder of LDPE and powder of recyclate.....	84
9.6	RESULTS DISCUSSION FOR TENSILE TEST	90

INTRODUCTION

Polymers are part of our everyday lives; they have penetrated into all sectors, from industry and transport to health care. However, with increasing consumption of these materials, there is a growing need of using these materials after the end of their life, because polymer waste needs decades to decompose in the nature. This problem has led to a growing effort of researchers all over the world to invent new and improve existing methods of recycling polymers, particularly plastic waste.

By modification of basic polymers we are able to obtain materials with excellent mechanical and other properties that are capable to replace traditional materials such as steel and wood in many areas. On the other hand, these modified polymers lose their ability to be easily and cheaply recycled. The modifications are carried out for decades, especially by adding specific additives, which serves to improve required properties, or in some cases to reduce price. In recent years, modification of plastics and elastomers by using ionizing radiation spread widely. This modification significantly changes properties of commodity and engineering plastics and allows their use in new applications.

This work investigates the possibility of using irradiated high-density polyethylene after the end of its lifetime. The main interest is to use this material as a filler for the other materials. Recycled material is processed to a different particle size and type and is added to the raw LDPE material in different concentrations. One section also examines the flow properties of prepared compounds. From the final compounds are prepared testing samples, which are then mechanically tested. Final compounds together with measured data are evaluated in corresponding chapters and compared and in the result discussion.

I. THEORETICAL BACKGROUND

1 INTRODUCTION TO POLYMERS

Polymers have become part of our everyday lives. They are materials with very high molecular weight and have various applications in our modern society. They are used extensively in food packaging, clothing, automotive industry, electronic and civil engineering, medical applications and so forth. [1]

Polymers in general can be divided into two large groups: natural and synthetic materials, or, from the point of view of their properties into plastics, thermoplastic elastomers and elastomers, as shown in Fig. 1. [1, 4]

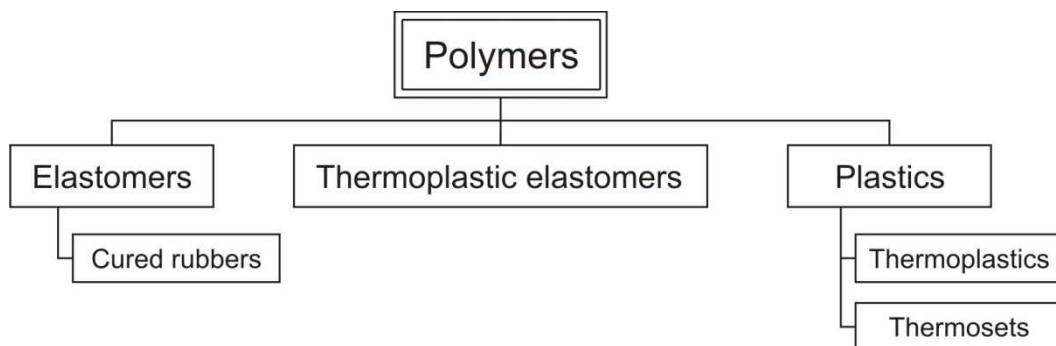


Fig. 1: Basic classification of polymers [4]

The difference in properties between the two basic groups is that elastomers are able to resume their original shape when a small deforming strain is removed, while plastics stay deformed even when the deforming force is removed. A special group of polymers are thermoplastic elastomers, which have the same properties as elastomers at room temperature, but they can be processed like thermoplastics. [4]

- **Thermoplastics** – solidify by simply cooling a polymer melt, on the other hand they soften upon heating and can be reshaped, i.e. undergo physical changes.
- **Thermosets** – are hardened by chemical reactions between various molecules and their shapes and properties are strictly set. After the reaction the structure is stable, i.e. after crosslinking they cannot be remelted and reshaped. [1]

As said before, plastics are widespread all over the world and their consumption is still increasing. The amount and proportions of plastics production is shown in Fig. 2. As can be seen, total world production of plastics in 2009 reached 230 million tonnes, where 55 million were produced in Europe. [14]

The largest producer of plastics in that year was North American Free Trade Agreement to which belong Canada, United States of America and Mexico. Market share of this company cover 23 % of total world production. [14]

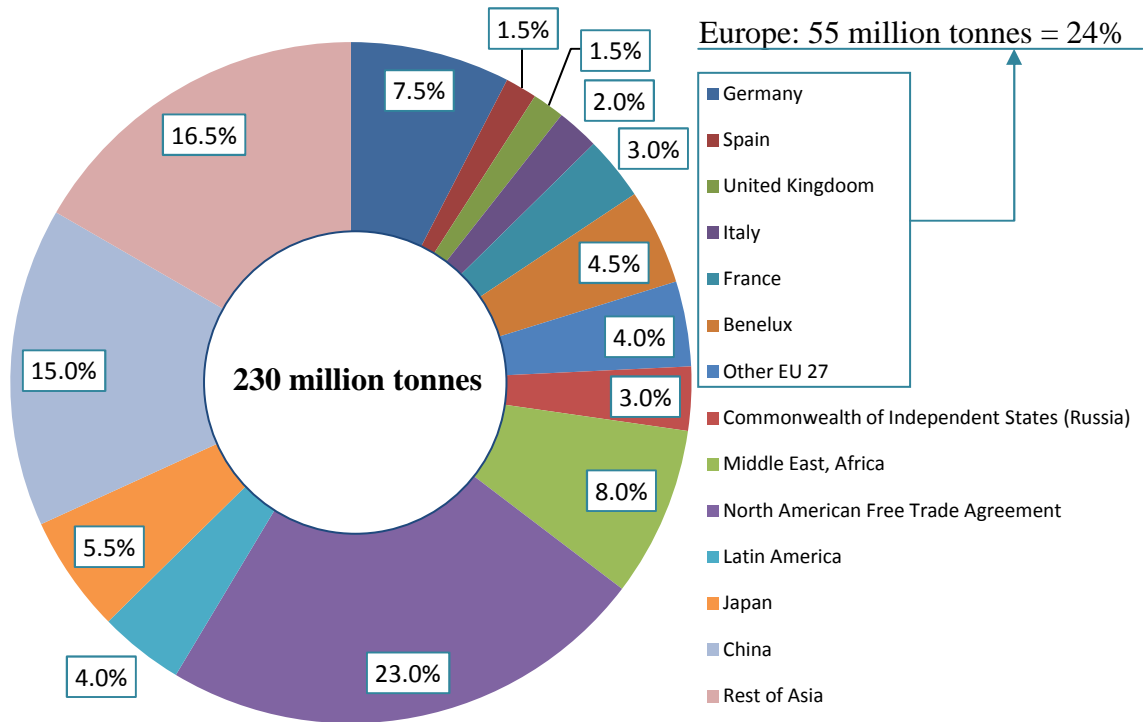


Fig. 2: World plastic production in 2009 [14]

Beside the division by properties, plastics can also be divided by their applications. There are:

- **Commodity plastics** – manufactured in great volumes, e.g. packing materials;
- **Engineering plastics** – with very good mechanical properties compared to the previous group. They have higher modulus of elasticity, impact strength or other properties and in some applications they can replace metals or precious materials;
- **High-performance plastics** – special types of engineering plastics with improved resistance to high temperatures. [1]

The dependence between the price and the volume of each category is demonstrated in Fig. 3.

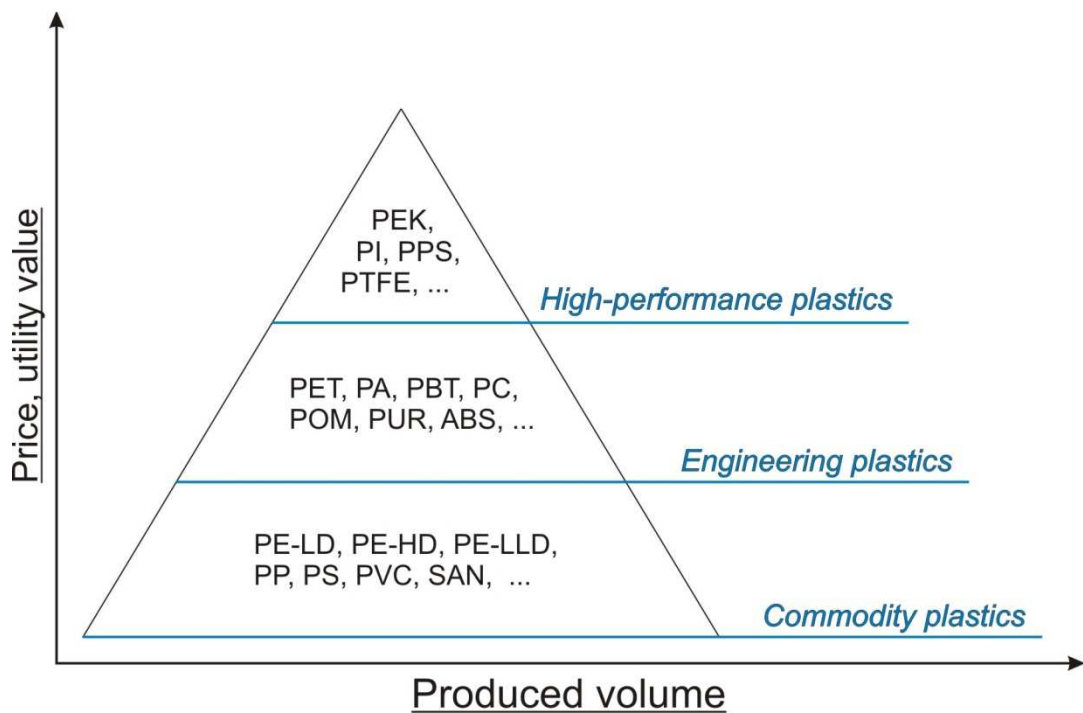


Fig. 3: Division of plastics according to price and applications [26]

1.1 Molecular structure of polymers

Polymers are materials with large molecules named macromolecules, which are obtained through chemical reactions of small molecule compounds called monomers. They usually contain atoms of carbon, hydrogen and oxygen, sometimes also nitrogen, chlorine or other elements. In addition we have prepolymers called oligomers that have higher molecular weight than monomers, but lower than polymers. Chemical reactions used to produce polymers are polymerization, polycondensation and polyaddition. An example of such a reaction is given in Fig. 4 for the simplest monomer - ethylene. [1]

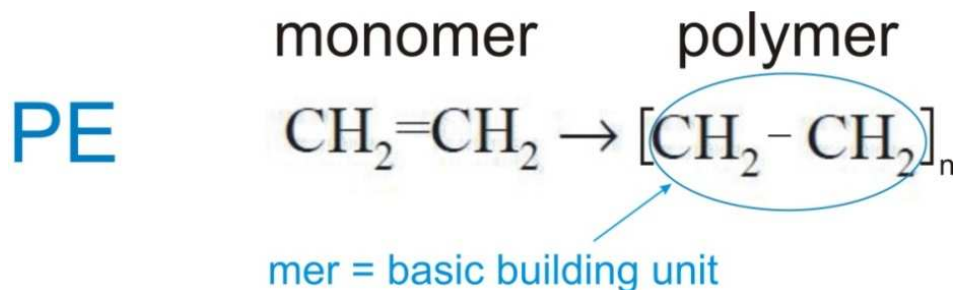


Fig. 4: Basic scheme of macromolecular substance [4]

As mentioned, polymers consist of large molecules formed in chains. According to the structure, the polymer could be:

- a) Linear
- b) Branched
- c) Cross-linked

as shown in Fig. 5. The structure affects properties of the polymer like fusibility, solubility, physical-mechanical properties, and so forth. [4]

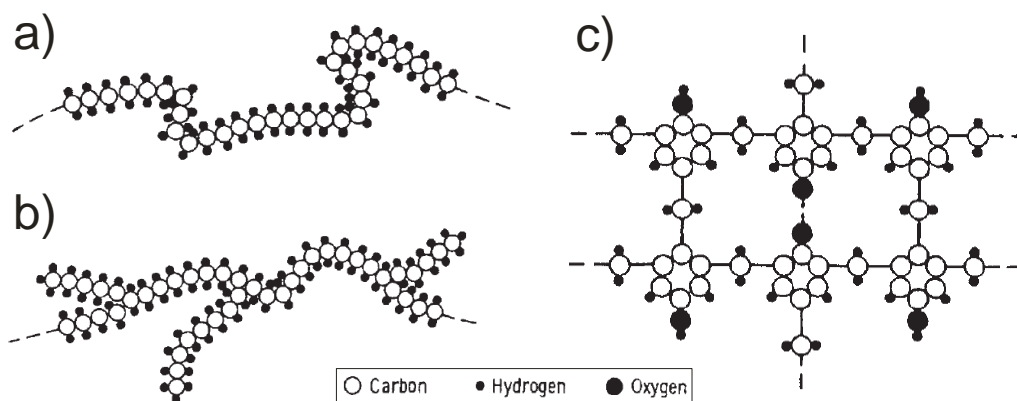


Fig. 5: Types of macromolecules [7]

If the polymer chain consists of two or more different repeated units, it is called copolymer. Copolymers are classified by the arrangement of monomeric units. As can be seen in Fig. 6, where A, and B are different monomeric units. In random copolymer they appear randomly, while in alternating copolymer they change regularly. On the other hand, block copolymer type A and B are arranged in larger blocks that can differ in length. Further, graft copolymers are formed when chains of one monomeric unit are attached to the backbone of the other. [2]

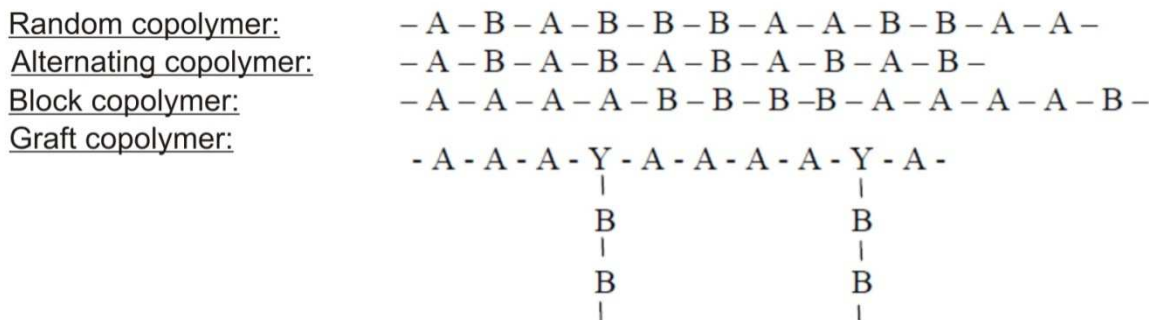


Fig. 6: Structure of copolymers [8]

Polymer structure can also differ in geometric features associated with the placement of successive repeated units in the polymer chain, which is called chain configuration. This can be applied to asymmetric molecules. The positions of two contiguous repeated units then can be “head-to-tail” or “head-to-head”, as demonstrated in Fig. 7:

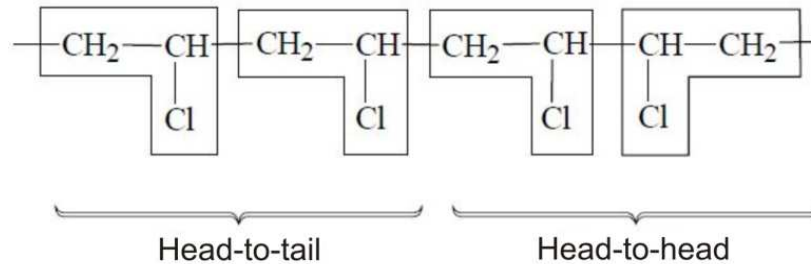


Fig. 7: Constitution of macromolecules [8]

The macromolecules of polymer materials may take form of highly ordered crystallites in a solid or viscous state or in a glassy solidified state as disordered amorphous regions between the crystallites. [9]

Amorphous state of polymeric materials is characterized by disorder of the individual macromolecules and the distance between them is also not constant. Amorphous polymers are transparent. The macromolecules of those polymers form coils in the melt after cooling into a solid state. These coils have about the same size. Macromolecules in the coils are entangled physically; however they may be chemically cross-linked. Those materials are characterized by high hardness, fragility, strength and modulus of elasticity. PMMA, PS and PC are typical representatives of this group. [9]

On the other hand, crystalline state of polymers is characterized by internal arrangement of macromolecules. Crystalline structure covers only a part of volume, while the rest is formed by amorphous state of polymer. Amount of crystalline state is expressed by degree of crystallinity in range from 30 to 80 percent. 100 % crystalline polymers do not exist, so polymers that contain both crystalline and amorphous regions are called semi-crystalline (or semi-rigid) polymers. To this group belong PE, PP, PA and POM. [9]

1.2 Basic types of plastics

Plastics can be grouped into several categories, depending on their chemical structure. The following provides an overview of the most important ones, where a blue arrow shows the group of main interest in this work. [1]

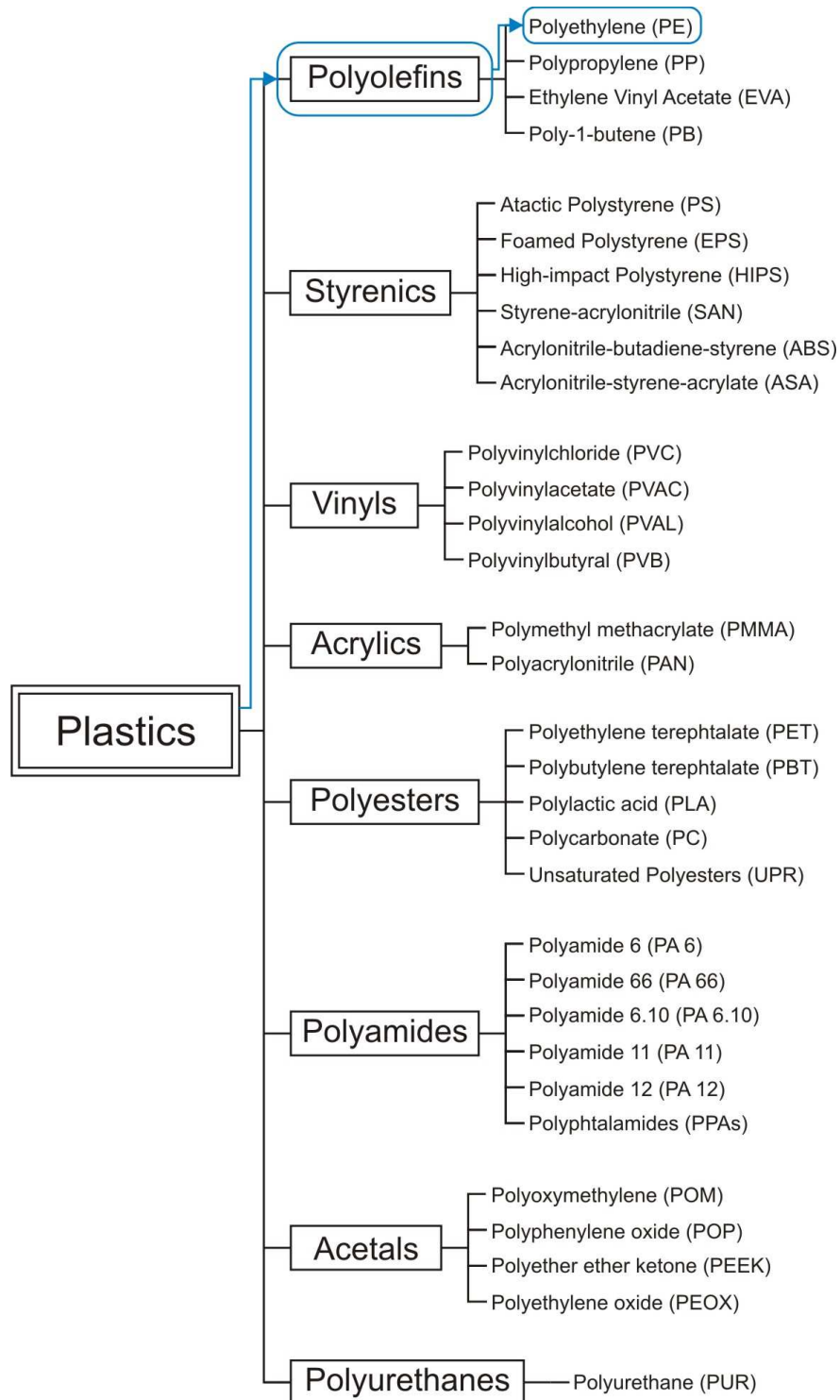


Fig. 8: Basic types of plastics [1]

2 POLYETHYLENES

As was described in the figure, polyethylenes belong to the group of polyolefins. They are polymers accrued from olefins. These are aliphatic or cycloaliphatic low-molecular-weight hydrocarbons, which consist of one or more reactive carbon-carbon double bonds. Olefins with one double bond in straight chain are alkenes or, in cyclic chain, cycloalkenes. Those with two carbon-carbon double bonds are called diolefins or dienes. The most important representatives of polyolefins are homopolymers and copolymers of ethylene, propylene and homopolymer of 1-butyne (ethylacetylene). [1, 4]

Polyethylenes used in practice consist of ethene homopolymers and copolymers with a small content of olefinic comonomers. Most of polyethylenes are more or less branched (Fig. 9), and branching affects the degree of crystallinity, which has a major influence on density and other properties. Another factor strongly affecting properties are molecular weight and configuration of molecules. [1, 4]

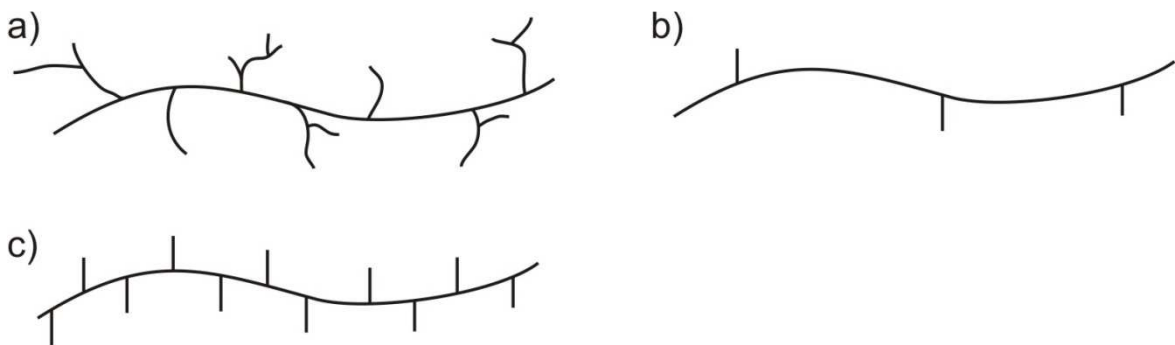


Fig. 9: Types of polyethylene according to branching [1]

{a) Low-density polyethylene, b) High-density polyethylene, c) Linear low-density polyethylene}

The common division of polyethylenes is shown in Tab. 1.

Tab. 1: Properties of different types of PE: [6]

Type of PE*	Density [g/cm ³]	Degree of crystallinity [%]	Melt temperature [°C]	Young's modulus [MPa]
ULDPE	0.890 – 0.915	/	/	/
LDPE	0.910 – 0.925	50 - 70	105 - 115	200 - 400
LLDPE	0.910 – 0.940	~ 50	125	250 - 700
MDPE	0.925 – 0.940	/	/	/
HDPE	0.940 – 0.965	60 - 95	125 - 136	600 - 1400

*VLDPE – Very low-density polyethylene

LDPE – Low-density polyethylene

LLDPE – Linear low-density polyethylene

MDPE – Medium-density polyethylene

HDPE – High-density polyethylene

In the following we are going to describe the most important categories in more detail.

2.1 Low-Density Polyethylene

Low density polyethylene LDPE was developed as the first from group of polyethylene. It was prepared by Imperial Chemical Industries in early 1930s in Britain. LDPE (and also MDPE) is obtained from oxygen or peroxide free-radical-polymerization. [1, 3]

This type of polyethylene is a semi-rigid and translucent material. The main molecular chain of LDPE consist relatively long branches. Its advantageous properties include toughness, flexibility, resistance to chemicals and low water absorption. It is resistant to organic solvents at room temperature, has a high impact resistance and excellent corrosion resistance. However, LDPE has a poor UV resistance, low strength and stiffness. Its maximum working temperature is also low and susceptibility to environmental stress cracking is observable. [5]

LDPE is used as a packaging film for food, shopping bags, coated paperboards and heavy-duty sacks. It can be also processed for products made by extrusion like wires, cables and pipes. [5]

2.2 High-Density Polyethylene

High-density polyethylene (HDPE) is prepared by insertion polymerizations with transition metal catalysts. Firstly it was produced by Karl Ziegler in Germany in 1954, and by Standard Oil and Phillips Petroleum in the United States. Its manufacture began in 1957 in Germany, Italy and the United States. [1]

This material possesses molecular weight below 300,000 g/mol. It has four times higher tensile strength than LDPE, the best impact strength from all available thermoplastics and is an excellent abrasion-resistant product. Other advantages are excellent machinability, self-lubricating characteristics and good chemical resistance to corrosives. In contrast, it is

prone to warpage because of its significant crystallinity. HDPE has also higher shrinkage than LDPE. Other disadvantages are poor UV resistance, lower stiffness and susceptibility to stress cracking. [5]

HDPE is processed into packaging containers, cans, split fibers, toys, wires and so forth. It is accepted by FDA requirements for direct food contact applications because of its non-toxic and non-standing. [1, 5]

2.3 Linear Low-Density Polyethylene

Linear low-density polyethylene (LLDPE) was developed by Phillips Petroleum in 1970's in the United States. LLDPEs are copolymers of ethene and 6 to 8 % of 1-butene, 1-hexene, or 1-octene, that are produced by insertion polymerization with transition metal catalysts in the gas phase, in solution, or in suspension. [1, 3]

LLDPE has more side branches compared to LDPE but they are comparatively shorter. The main advantages over LDPE are improved anti-tear properties, strength and stiffness.

LLDPE is commonly used in food packaging, industrial packaging and other applications of films. However, this material can also be used on tanks, drums, hoppers and bins. [5]

2.4 Other types of ethylene

Beside the above described categories, there are some more types of polyethylenes. Medium density polyethylene (MDPE) is obtained from mixture of LDPE and HDPE and its properties are between these two materials. It has good impact and drop resistance, but compared to HDPE its hardness and rigidity are lower. It is primarily used for pipes and fittings, carrier bags and packing films. [5]

Ultra-high-molecular-weight polyethylene (UHMWPE) is a type of polyethylene with molecular weight (M_r) greater than $3 \cdot 10^6$. It is a linear homopolymer that is yielded in the polymerization of ethylene gas in presence of a highly reactive organotitanite catalyst. This material was first produced by Karl Ziegler in early 1950s. Its characteristic properties are low weight, high tensile strength, self-lubrication ability and resistance to abrasion and corrosion. It exhibits the best sliding wear resistance and impact toughness of all polymers. The main disadvantage of this material is difficult processing. Due to this it is mainly used in medicine (joint replacements) and for parts in machinery products. [1, 5]

Ethylene vinyl acetate (EVA) is copolymer produced by free-radical initiation. EVA copolymers contain about 1 – 40 % of vinyl acetate. The low-vinyl-acetate copolymers show properties similar to LDPE, while high-vinyl-acetate types look more like gum rubber. These copolymers have low crystallinity because acetate branches interfere with crystallization. With increasing percentage of vinyl acetate tensile strength and toughness grow. EVA accepts high degree of filler loading without a physical properties drop. It is used for wrapping films, cork gaskets and glues, and can be found in medicine applications for example as disposable syringes. [1, 7]



Fig. 10: PE applications [39]

3 MODIFICATIONS OF PLASTICS

Modification of plastics is a very wide area that includes a large number of methods of physical and chemical transformations. Physical modifications are performed by mixing of different polymers or adding specific additives. Before additives were added to modify one specific property, nowadays many additives have more than one effect on a plastics compound. There are number of additives for plastics such us fillers, pigments and colorants, stabilizers, flame retardants, softeners, lubricants, blowing agents and many others. While chemical modifications are carried out through the chemical reactions of active substances with reactive groups of polymer chains. The most important chemical modification is polymer crosslinking. [4, 32]

Because the main objective of this work is to research the using of a recycled cross-linked HDPE as filler, following heading describes fillers and the cross-linking of plastics.

3.1 Additives – Fillers

Fillers are important additives that change specific properties. Firstly, basic low-performance materials such as clays and chalks were used as fillers especially for product price reduction. Nowadays, on modern market are offered fillers, which improve mechanical properties, UV or heat stability, thermal or electrical conductivity, or dimensional stability. Fillers are determined by its chemistry, and by physical aspects, such as size and geometry. Also weight of fillers is important. Mechanical properties, which fillers improve, are mainly strength, stiffness and hardness. [32]

By adding a filler, raw material becomes a composite and its recycling is then more complicated. Properties of final mixture and even the final product depend on the size of particles, on compound homogeneity and on dispersion of fillers in volume. The main disadvantage of fillers is that they tend to aggregate, which lead to irregular distribution in the compound. This bad distribution may cause processing problems, poor surface quality, and reduction in mechanical properties. Fillers may be in the form of powders, granules, short and long fibers, more such in the form of strips. [32, 33]

Most important types of fillers used in plastics shows following table:

Tab. 2: Important types of fillers: [6]

Type of filler	Characteristics/Main applications
Alumina trihydrate	Flame retardant and smoke suppressant
Barium sulphate	Increases specific gravity, frictional and chemical resistance
Boron fibres	Reinforcement: high tensile strength
Calcium	Extender: increases impact, tensile and compressive strengths
Carbon black	Pigment and antistatic agent
Carbon fibres	Reinforcement: high modulus and strength, conductive
Glass fibres	Reinforcement; increases dimensional stability and heat
Kaolin	Extender, Pigment
Metal fillers	Increases electrical and/or thermal conductivity, magnetic
Mica	Reinforcement; improves dielectric and thermal properties
Microspheres	Improves impact resistance and flow properties
Organic fillers	Extenders: (wood flour, nutshell, rice, corncobs, peanut hulls)
Polymeric Fillers	Reinforcement
Silica	Extender; Reinforcement
Talc	Extender; Reinforcement; improves stiffness and strength
Wollastonite	Improves strength, dimensional stability and electrical

3.2 Crosslinking of plastics

Crosslinking is a process in which polymer chains are associated through chemical bonds. Crosslinking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Crosslinking can appear on intramolecular (a) and intermolecular level (b), as shown in Fig. 10. In the former the bonds are created between individual polymer chains, in the other way are bonds created between molecules in the same chain. [10]

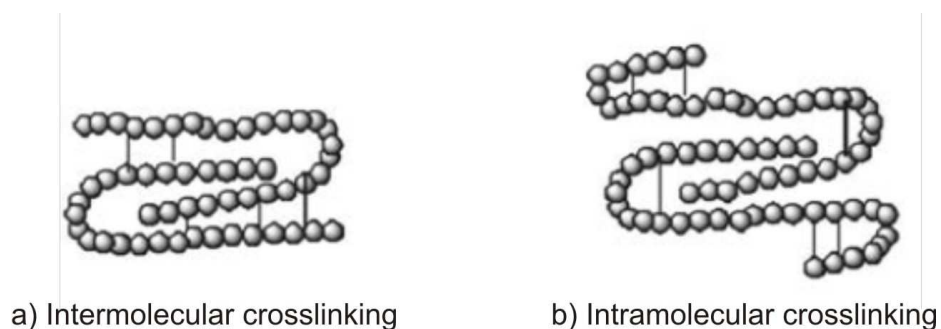


Fig. 11: Schematic diagram of possible crosslinking [10]

3.2.1 Chemical crosslinking

Chemical methods of crosslinking are accomplished at increased temperature, usually at about 125 °C, when most of polymer crystalline structure has turned to molten state. During cooling, recrystallization is blocked, therefore crystallinity is extensively reduced. [10]

Chemical crosslinking can be carried out with various chemicals, the most important of which are following:

❖ Peroxide crosslinking

Peroxide crosslinking (PEXa) starts with thermally initiated decomposition of peroxide (RO-OR). Produced RO* free radicals give rise in a further reaction to radical sites in the polymer chains. Recombination of radical sites in different chains leads to chain linking between carbon–carbon bonds. The mechanism of peroxide crosslinking is shown in Fig. 12. [12]

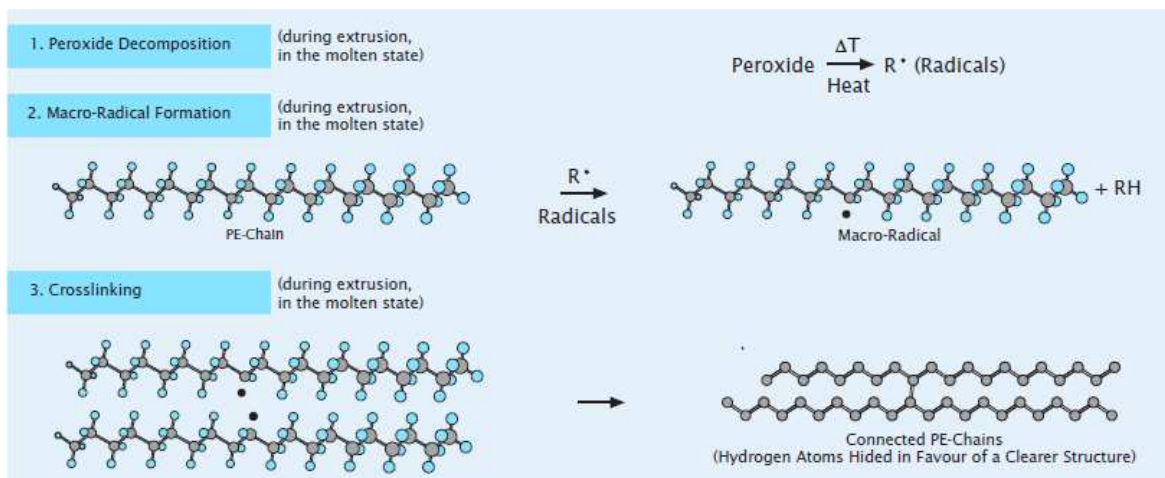


Fig. 12: Mechanism of peroxide crosslinking [12]

The type and quality of peroxide and other additives depend on the production process and on the basic material. In comparison to neat PE, products crosslinked by peroxides have lower density. PEXa serves for production of pipes by special extrusion process (named Engel after its inventor Thomas Engel). The minimum degree of crosslinking for PEXa is 70 %. [12]

❖ Silane crosslinking

Silane crosslinking (PEXb) reaction starts like the previous one. Peroxides are used to produce primary radical sites in polymer chains. Silane crosslinking is performed by silane

molecules (Trimethoxyvinylsilane), which are grafted on PE chains and act as linking agents. Crosslinking starts with addition of H₂O, which causes a reaction where Si – O – Si bridges are created. The reaction continues in the presence of a crosslinking catalyst and at a temperature of 80 °C up to 95 °C. [12]

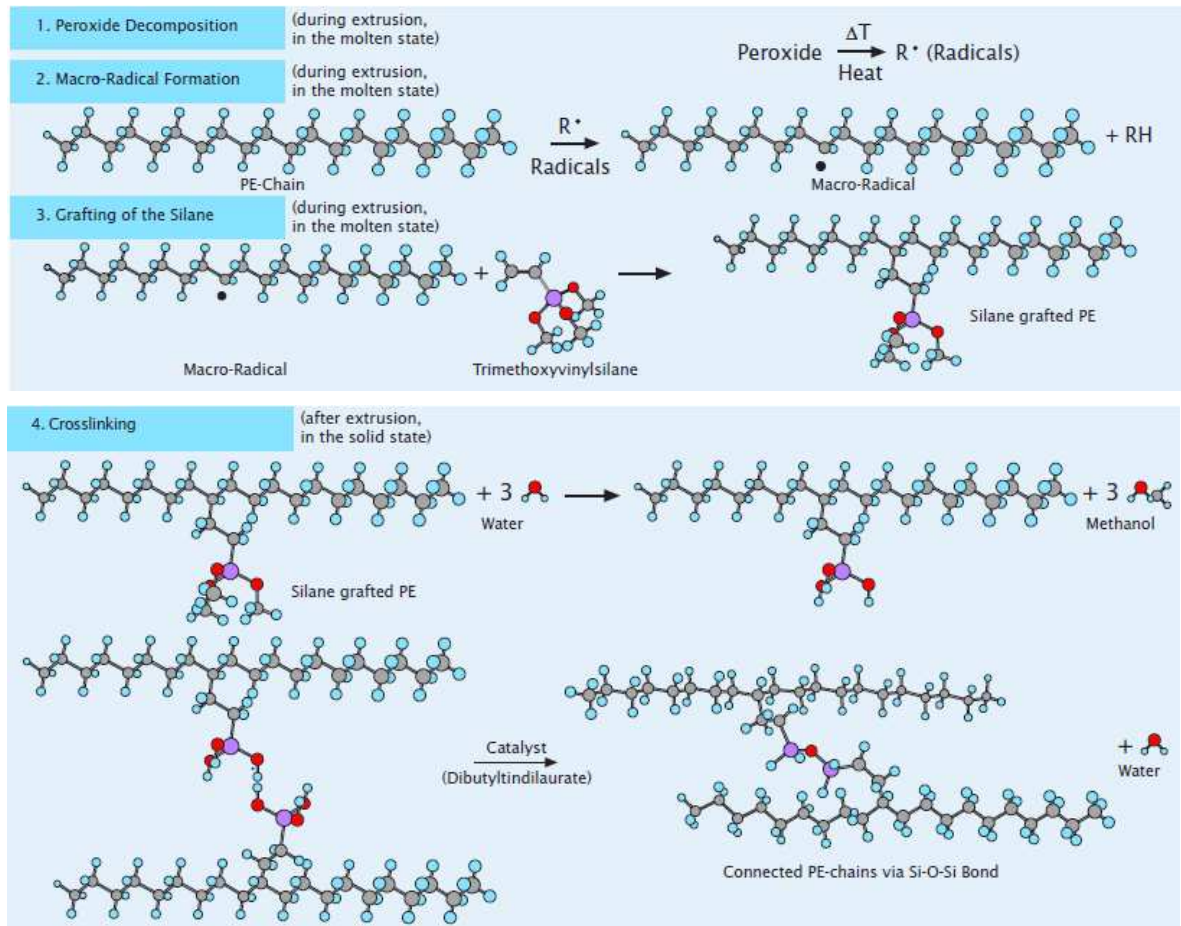


Fig. 13: Mechanism of silane crosslinking [12]

In industry, crosslinking of pipes is conducted in hot water or steam. Density of PE crosslinked by this way is essentially the same compared to the uncrosslinked base material. This method provides the degree of crosslinking at least 65 %. The main advantage of this method is that it can be carried out on conventional machinery. [12]

3.2.2 Radiation crosslinking

Radiation crosslinking (PEXc) is radiation-induced chemical change of the material that is carried out by the interaction of high energy radiation with matter. High energies used for the processing is greater than the ionization energies of atoms and molecules and are in kiloelectronvolts (keV) or megaelectronvolts (MeV). Radiation processing uses

electromagnetic (gamma) radiation from the radioisotopes of cobalt-60 and cesium-137, or electron beams generated by machines called electron accelerators. Energies used for commercial radiation processing are below 10 MeV to avoid any significant buildup of radioactive isotopes in the material. [13]

❖ Electron beams

Electron beams (β -rays) generated by accelerators are monoenergetic and the absorbed dose is greatest just below the surface of the irradiated material and falls rapidly at greater depths in the material (Fig. 14). The energy range of electron beams used in radiation processing is from 0.15 to 10 MeV. Compared with gamma irradiation, electron accelerators have advantages of higher power and directional beams. The time of irradiation by β -rays is in seconds. The limited penetrating power of electron beams means that they are mainly used for irradiating relatively thin objects like wires and cable insulation. [13, 34]

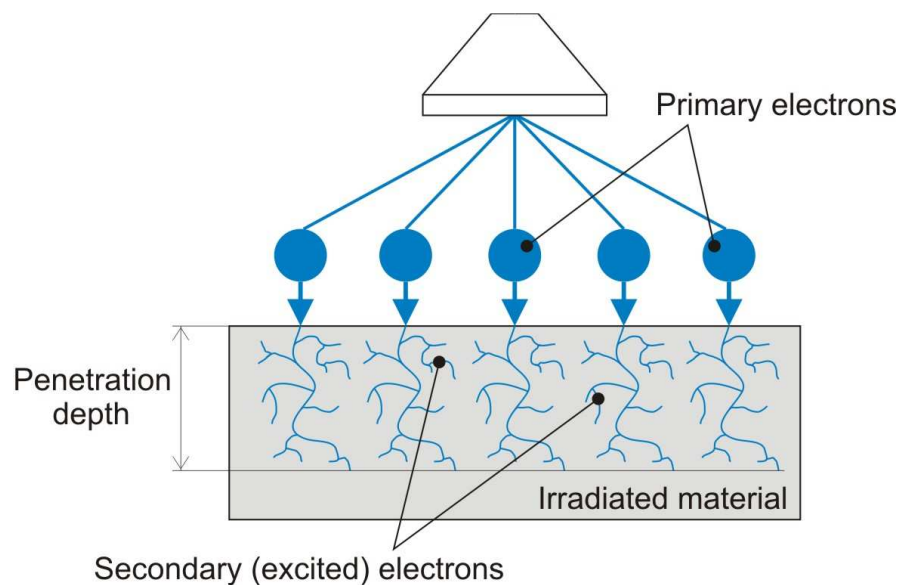


Fig. 14: Scheme of radiation crosslinking by electrons [34]

❖ Gamma rays

Gamma radiation has a high penetration capability at relatively low dose intensity as shown. The most used source of gamma rays (Fig. 15) is cobalt-60 (Co^{60}). The energy of emitted gamma rays is about 1.3 MeV. Conversely the electron accelerators, source of gamma rays cannot be turned off. Therefore the rays are sheltered, in most cases by water tank. Time of irradiation depends on dose intensity and reaches up to several hours. The gamma radiation is mainly used for radiation sterilization. [34]

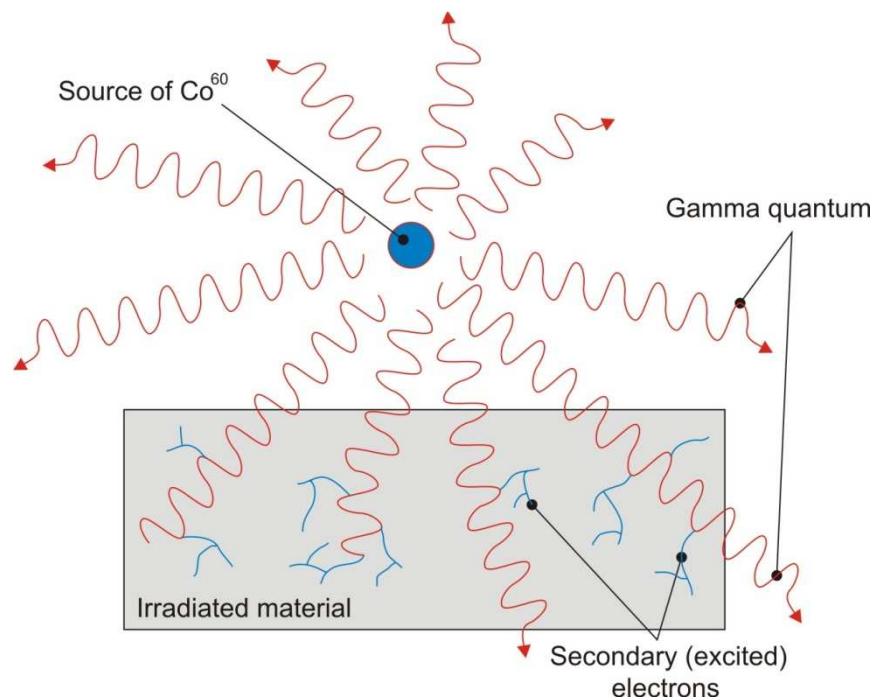


Fig. 15: Scheme of radiation crosslinking by gamma rays [34]

The mechanism of radiation-induced crosslinking will be explained on the crosslinking of polyethylene, the simplest polymer. High-energy radiation involves loss of two hydrogen atoms from adjoining chains and consequent bonding between the two carbon-centered free radical sites, leading to inter or intra chain bonding, as can be seen in Fig. 16. To reduce the dose required for crosslinking, crosslinking agents are used. [11]

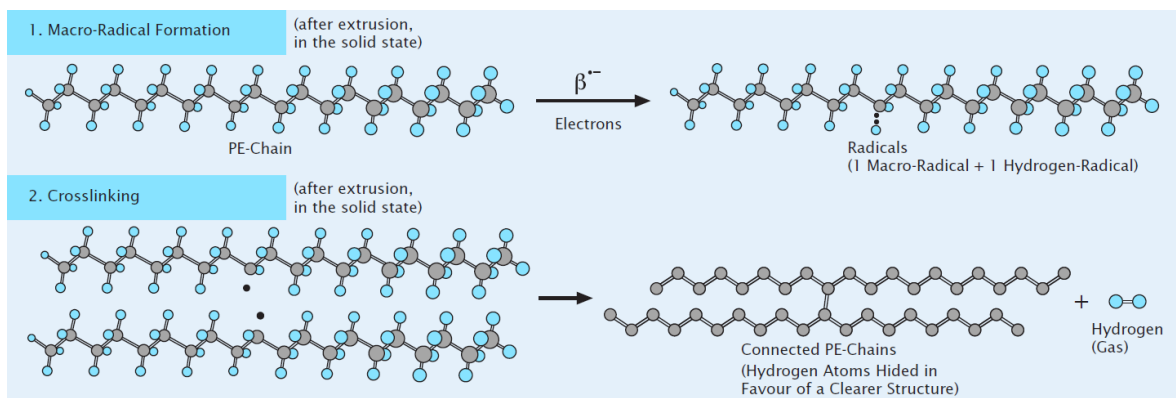


Fig. 16: Mechanism of radiation crosslinking [12]

Important quantities in radiation processing are the absorbed dose, which is the energy transferred from radiation to substrate, and radiation-chemical yield. The unit of absorbed dose of energy is the gray (Gy), where one gray is equal to energy absorption of one joule per kilogram. [13]

Changes in the structure induced by radiation crosslinking cause improvement in mechanical properties, mainly:

- Increase of Young's modulus
- Increase of strength
- Reduction of ductility and tensile creep
- Increase of weld line strength
- Improved hardness and resistance to abrasion. [34]

Not all plastics are crosslinked under the effect of ionizing radiation. Certain of them degrade. As was described before, crosslinking improve some mechanical properties and also increase molecular mass, thermal stability and lower solubility in organic solvents, while degradation has the opposite effect. The following table (Tab. 3) shows, which materials are predominantly crosslinked, conversely degrade. [13]

Tab. 3: Predominant radiation-induced change at plastics: [13, 34]

Plastics	Predominant radiation-induced change
Polyethylene	Crosslinking
Polypropylene	Crosslinking
Polymethyl acrylate	Crosslinking
Polyvinyl chloride	Crosslinking
Polyvinyl alcohol	Degradation
Polyvinyl acetate	Crosslinking
Polystyrene	Crosslinking
Polytetrafluoroethylene	Degradation
Polymethyl methacrylate	Degradation
Polyethylene terephthalate	Crosslinking
Polyamide	Crosslinking
Polyisobutylene	Degradation

The major industrial application of radiation crosslinking is for tubes, pipes, wire and cables, but also for foils, injected parts and composites. The products modified by radiation are not radioactive. [11, 34]

4 RECYCLING OF PLASTIC WASTE

The recycling of post-consumer materials is an important challenge for polymer industry. As a matter of annually increasing polymer production, the generation of polymer wastes has grown at a similar rate. The most effective waste management option is to reduce the source of plastic waste itself. It means to reduce a consumption of materials and products, followed by direct re-use. However, reduction of plastic materials consumption is very difficult, because they are widely used in practice to replace other materials. [15]

The factors that greatly limit plastic recycling are the small weight of plastic goods, and the fact that plastic wastes are mainly found in municipal solid waste, commingled with other materials such as soil, dirt, food remnants, paper labels, and so on. That was the main reason in history why the primary destinations of plastic wastes were landfill sites, where they remain for decades because of their slow degradation. In 1996 over 70 % of plastic wastes in Europe were disposed of in landfills, whereas in 2009 it was about 46 %. This reduction was achieved due to new development and improvement of recycling methods. [14, 22]

Following figure (Fig. 17) shows total recovery by country in Europe of post-consumer plastic waste in a given year. Recycling ability of different countries depends on strategy of waste management and on available technologies. [14, 19]

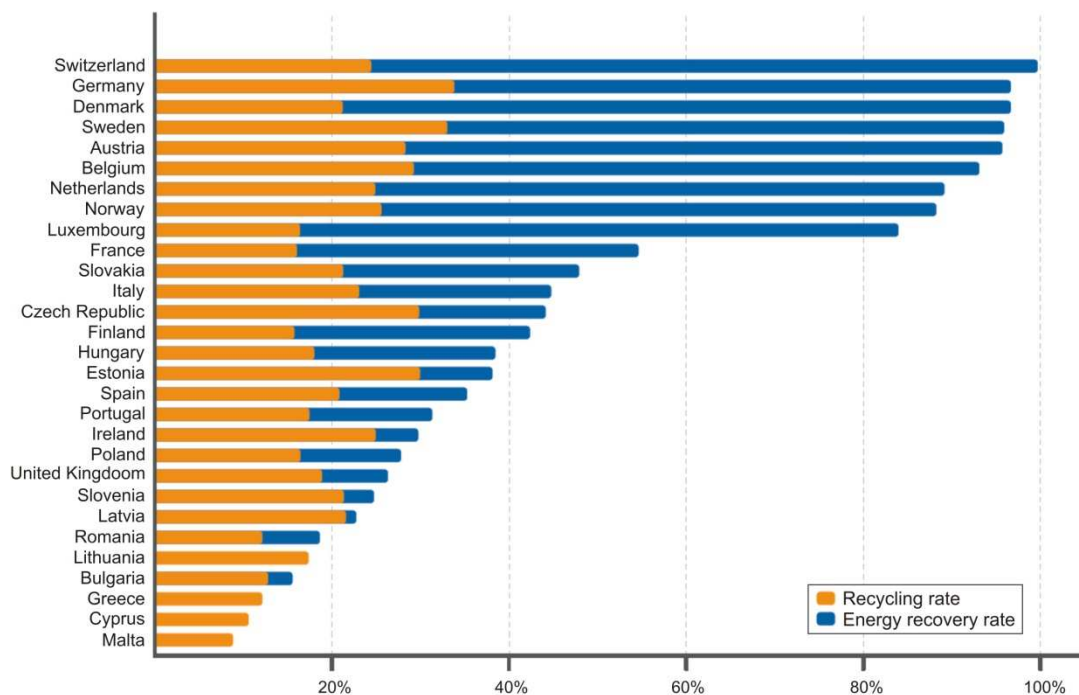


Fig. 17: Total recovery by country in Europe (2009) [14][19]

From total 55 million tonnes of plastics produced in Europe in 2009 was 45 million tonnes for processing industry. Post consumer waste from this production was 24.3 million tonnes, where 11.2 million tonnes were disposed of and rest was recovered, from which 5.5 million tonnes were recycled and 7.6 million tonnes were processed for energy recovery. [14, 19]

Plastic and overall polymer waste can be processed by 3 main ways, namely by mechanical recycling, feedstock recycling and incineration to recover energy from waste. The way is chosen according to degree of contamination, waste type and economical aspects. Fig. 18 shows a life cycle of plastic product from its inception, use, discarding and recycling.

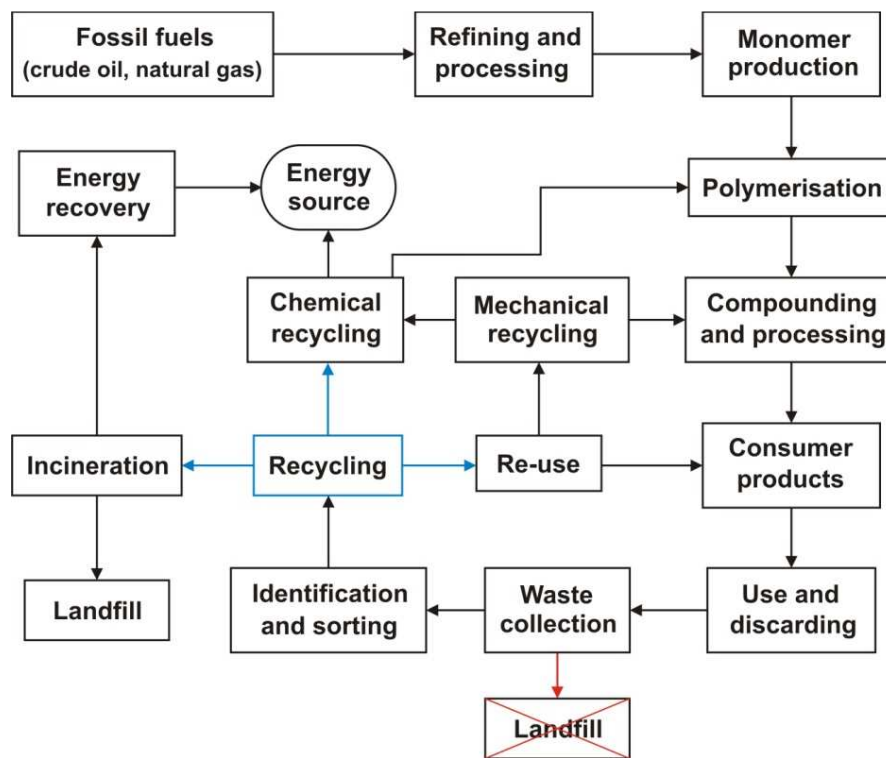


Fig. 18: Life cycle of plastic product [15]

4.1 Mechanical recycling

Mechanical or material recycling of plastics involves a number of treatment steps and operations, but compared to feedstock recycling it is still the most common method. Plastic wastes are physically pulverized back to a suitable size and reprocessed. In most cases, thermoplastics are pelletized or extruded into new products, while thermosets are ground up to be used as fillers. [15, 19]

Mechanical recycling can be divided into two types. Primary mechanical recycling allows reuse of the waste made during injection molding, extrusion and other processing operations. However, that waste cannot contain fillers or other additives and has to be a single material. This waste is collected directly in the workplace, reground and fed back into the production machine. The other type of mechanical recycling processes single or mixed plastic materials from external sources. Those wastes have to be sorted and cleaned because they contain contaminants. [15, 19]

The operations that mechanical recycling can contain (not always all of them) are described in Fig. 19 and these individual steps of recycling are described in the following text under this figure.

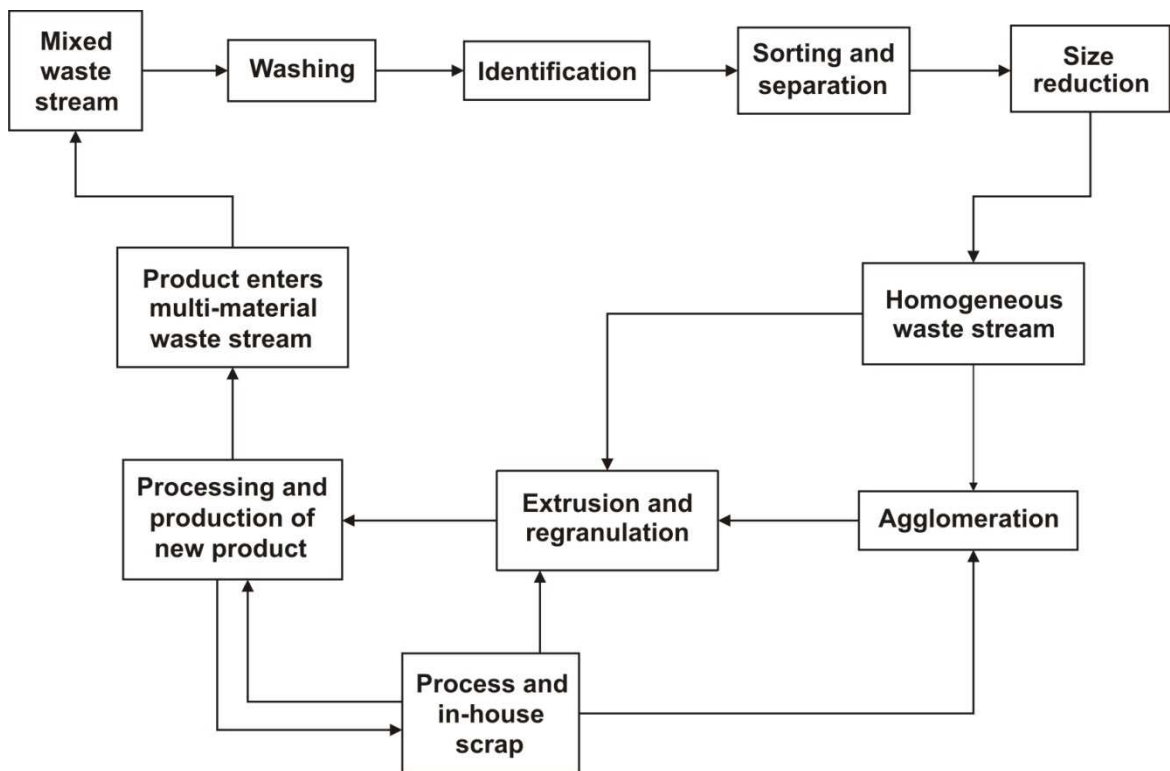


Fig. 19: Diagram of the operations in mechanical recycling [19]

❖ *Waste washing and contaminants removing:*

Washing is carried out primarily to remove dirt and other contaminants from the plastic waste. Contaminants can cause mechanical properties deterioration or can damage processing machinery, so it is important to remove them from the waste. They can include paints, labels, coatings, dust, wood, metals, glues or print inks. Washing increases the purity of the waste and can improve efficiency of other processes, e.g. sorting. [19]

The cleaning medium must remove the contaminants, labels and water soluble glues and must not affect the plastic material properties. Metals are removed from the waste by magnets, but non-magnetic metals are a big problem. One of the possibilities is to remove them by using a filter screen in further processing of the waste. This can be used if the level of other contaminants is low and the contaminants do not melt within the melting range of the plastic material. The filter screen consists of a very fine mesh that traps particles bigger than the holes in the sieve. These screens can be used in extruders or injection molding machines. [19]

❖ *Identification of Plastic wastes:*

Identification of plastic wastes is very important and influences effective recycling. Some plastics are relatively easy to identify such as PET bottles or foamed PS, but some plastics resemble one to another so it is very difficult to distinguish them. For this reason, Society of the Plastics Industry (SPI) in 1988 enforced a series of seven numbered classifications (Fig. 20) to help consumers classify different plastics. These symbols are minted in a mold forms or painted on the paper coat of plastic products. [15, 19]



Fig. 20: Recyclation codes by SPI [19]

Other methods that are used for plastic recognition are infrared spectroscopy or mass spectroscopy, which indicate specific chemical groups, thermal analysis (DSC) or nuclear magnetic resonance, which recognizes different molecular structures, opto-mechanical pattern recognition and X-ray fluorescence indicating the presence of metals or heteroatoms. However, all of these methods are very expensive and rarely used in recycling industry. [15]

❖ *Sorting and separation:*

Plastics are currently sorted and separated either manually or mechanically. Compared with mechanical sorting, manual sorting use simple devices, but purity of the resulting waste depend on the capabilities and experiences of the human operators. The main drawbacks of this method are bigger labor intensity and slow pace. Conversely, mechanical sorting utilizes differences in material properties. [15]

The most used way for plastics separation is based on their different densities. For example, all polyolefins (PP, LDPE, and HDPE) have densities below 1 g/cm^3 , so it allows a process called 'float-and-sink' (Fig. 21) to be used to distinguish them from other waste. This process uses water as a separation medium and is carried out in a flotation tank, where lighter polyolefin remains floating on the surface and denser particles sink. Other devices used for separation are hydrocyclones, which work on the same principle as static flotation tanks but allow better separation. Another way is to use compressed air for separation. New techniques used for separation are micronising, melt filtration, and separation of colored particles. The choice of particular sorting techniques depends on the composition of plastic waste and on economical aspects. [15, 19]

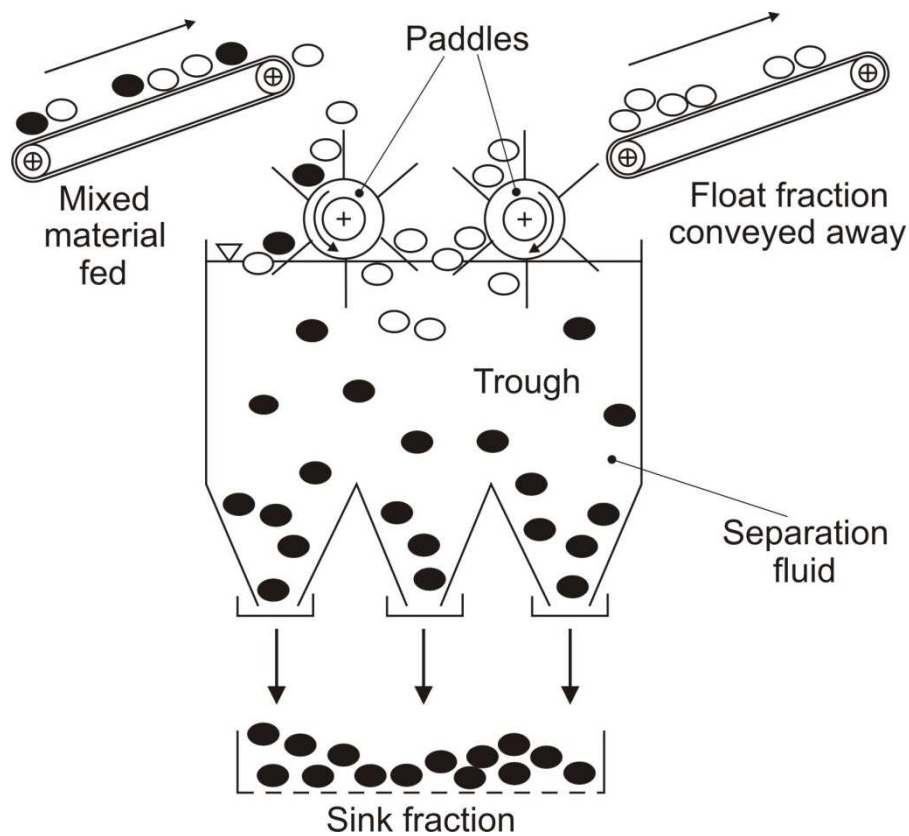


Fig. 21: 'Float-and-sink' separation [19]

❖ *Size reduction:*

The size of the material particles must be suitable for further processing. The size of particles is usually reduced in a two-stage process. In the first stage a shredder is used to get particles of about 25 – 50 mm. The second stage employs a rotary cutter, which represents a simple device consisting of the rotor with rotating knives, stator with stationary knives, the grinding chamber, and the screen. Plastic waste moves between the

stationary and rotating knives and is cut down to a certain size. This size corresponds to the mesh size of the screen, and is commonly around 5 mm. The heat generated from the shearing action of the blades must be taken away. It is carried out by an air extractor that also aids in moving reground material out of the chamber. The knives in device are rapidly worn, so it is necessary to replace or remove them for reshaping. [19]

❖ **Agglomeration:**

Agglomeration is carried out after the material is sorted into fairly homogeneous stream. Waste is agglomerated to increase the bulk density, which is necessary for good feeding of some plastication units. The principle is simple bonding of the flakes together at their surfaces. The surface of the particles is thermally stressed for a relatively short time and then they are pressed together by a small force. An example of plastic waste before and after agglomeration shows Fig. 22. [19]



Fig. 22: Particles thermally agglomerated [19]

4.2 Feedstock recycling (Chemical recycling)

This method is based on the decomposition of polymers by means of heat, chemical agents and catalysts to obtain a variety of products similar to the starting monomers, mixtures of compounds, mainly hydrocarbons, with possible applications as a source of chemicals or fuels. The products obtained from the plastic decomposition evince similar properties and quality to products prepared by conventional methods. [22]

The main disadvantage of this feedstock method is that it is almost completely restricted to the recycling of condensation polymers, so it has no use for the decomposition of most addition polymers. To condensation polymers, formed through a condensation reaction belong polyesters, polyamides, polycarbonates and polyacetals. [19]

Methods of feedstock recycling:

- ❖ *Chemical depolymerization*
- ❖ *Gasification*
- ❖ *Pyrolysis*
- ❖ *Catalytic cracking and reforming*
- ❖ *Hydrogenation*

4.2.1 Chemical depolymerization

Chemical depolymerization (chemolysis) is based on the breakdown of the polymer by reactions with certain chemical agents to yield the starting monomers. These monomers are the same as those used in the preparation of virgin polymers, thus the plastics prepared from both depolymerization and fresh monomers are expected to have similar properties and quality. This method is the most established method of plastic chemical recycling. Depending on the chemical agents, different depolymerization routes can be applied, such as glycolysis, methanolysis, hydrolysis and ammonolysis. Plastics, for which is this recycling method most frequently used are polyesters (PET), polyurethanes (PU) and polyamides (PA 6). [22]

4.2.2 Gasification

Gasification is based on effective degradation of polymer waste that yields synthesis gases such as CO and H₂ and a solid residue as the main products. This method uses partial combustion by different types of gases. These gases include oxygen in the form of air, steam, pure oxygen, oxygen-enriched air or carbon dioxide. The temperature required for this method depends on the type of gas and is generally in the range of 800 – 1600 °C and the pressures are between 15 and 30 MPa. Gasification can be divided into two general types: fixed-bed process and fluidized-bed process. In both processes, the waste is mixed with lignite and then fed to the gasifier. In fixed-bed process, gasification gas flows through the bed of carbonaceous fuel. In contrast, fluidized-bed process used fluidized fuel

distributed in oxygen or steam. Synthesis gas can be used for the preparation of methanol, ammonia, hydrocarbons and oxygenated compounds. Furthermore, this gas is used as a fuel gas. [15, 19, 22]

This technology was originally developed to be used for coal and oil. The major advantage of gasification is the possibility of treating complicated mixtures without any previous separation steps hence the plastics are gasified while mixed with other solid wastes. The main disadvantage is the need of downstream cleaning operations of the produced synthesis gas, which is then used for synthesis of various chemicals. [19, 22]

4.2.3 Hydrogenation

The hydrogenation process leads to the formation of highly saturated products by breaking down the polymer chains. It is necessary to avoid the presence of olefins in the liquid fractions, so that they can be used as fuels without further treatment. Another advantage is that hydrogen promotes the removal of heteroatoms (Cl, N and S) that may appear in the polymer wastes. On the other hand, hydrogenation main disadvantages are the cost of hydrogen and a fact that the reactions are carried out under high pressure, in many cases in the presence of solvents. Catalysts, which provides a cracking and hydrogen reactions are typically metal compounds (Fe, Mo, Ni, Co) supported on an acid porous matrix (alumina, amorphous silica-alumina, zeolites and sulfated zirconia). Hydrogenation is very expensive process, but the capital costs are quickly recovered through the high value of products like synthetic crude oil. [15, 22]

Plastic hydrogenation has been used for the conversion of various plastics like PE, PP, PS, PET and mixtures. The reactions are usually conducted in autoclaves at temperatures around 400 °C, under pressures of cold hydrogen up to 15.2 MPa, and in some cases in the presence of solvents. [22]

Degrading rubber wastes in hydrogen atmospheres is very suitable due to a high concentration of double bonds in the rubber backbone. Because used tires contain eminent amounts of sulfur, hydrogenation also allows the removal of this undesired element as H₂S, which enables production of oils with lower S content than in those derived from tire pyrolysis. [22]

4.2.4 Catalytic cracking

Catalytic cracking is based on contact of the polymer with a catalyst that promotes cleavage of the material. Due to combination of catalytic and thermal effects, the plastic degradation occurs. Catalytic cracking is similar to chemolysis, but there is no chemical agent incorporated to react directly with the polymer. The catalysts used to promote plastic degradation are acid solids (e.g. amorphous silica-alumina), different types of zeolites, and sulfated zirconia. Products yielded from this method are gases rich in C₃ and C₄ olefins and liquid hydrocarbons. The efficiency and speed of this method depend on the main catalyst properties, type, strength and concentration of active sites, available surface area, and average pore diameter as well as pore size distribution. The main advantages of catalytic cracking compared to simple thermal degradation are lower temperature of the process (about 400 °C) and shorter reaction times. This method is mainly applied to polyolefinic and polystyrene wastes, where the wastes must have relatively high purity. [22, 23]

4.2.5 Pyrolysis

Pyrolysis is a chemical degradation reaction that is caused by thermal energy in the absence of air and other gases. This process is capable to produce liquid fuels (or other useful chemicals like oils) and gases from thermoplastics and thermosets wastes. The products that can be obtained from plastic waste are gases rich in olefinic hydrocarbons and aromatic oils, and unlike from thermosets waste, oils rich in aromatic hydrocarbons and gases (CO, CH₄, H₂) can be obtained. [15, 23]

Pyrolysis is not the same as incineration because there is no oxygen in the system and no toxic or environmentally harmful emissions can be found. It can be carried out at various temperature levels, pressures, reaction times, and in the presence or absence of reactive gases or liquids, and of catalysts. Plastics pyrolysis is realized at low (<400 °C), medium (400–600 °C) or high temperatures (>600 °C). The major advantage of this technology is its ability to process unsorted, unwashed polymeric materials. Other normally hard-to-recycle plastics, such as laminates of incompatible polymers, multilayer films or polymer mixtures, can also be cracked by pyrolysis. [15, 23]

4.3 Energy recovery

Energy recovery is a method based on the energy recovering from the plastic waste, because this waste has a high calorific value. This process is used if other recycling method is not viable for some reason. Energy recovery is very difficult process, which consist of number of the operations as is shown Fig. 23. Hot water, steam or electricity is the form of energy that can be recovered from the plastic waste. The efficiency of energy recovery and the amount of emissions from combustion depends on the type of incinerator. The emissions are sensitive issue because the possible health and environmental problems. However, modern incinerators are able to reduce emissions to minimum if the right operating conditions are chosen according to the type and among of waste. In some cases, incineration is used not for energy recovery but to reduce the amount of waste. Actually, this is not a recycling but the wasting of valuable nonrenewable resources. [15]

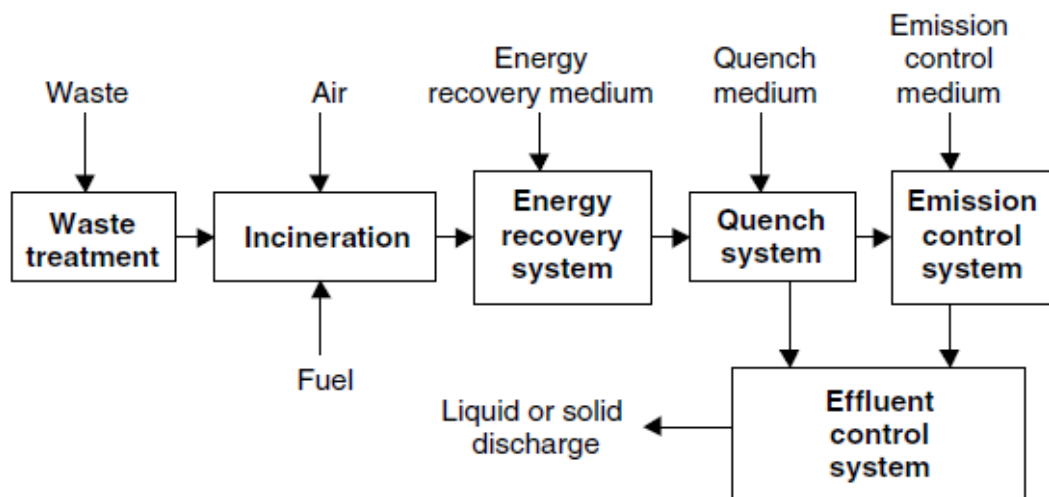


Fig. 23: Diagram of an incineration system [15]

There are three main types of incinerators, where individual devices differ in construction, efficiency and usage. Mechanical-stoker incinerator is used mainly for municipal solid waste. Other, Rotary kiln incinerator works on the same principle as conventional mechanical stoker but the combustion occurs in incline, rotating cylinder. This device is very expensive and suitable only for small applications. On the other hand, this device has large burning efficiency. Finally, Fluidised-bed incinerators use sand as the combustion zone. Sand is able to stand the high temperatures generated by the waste stream. The main advantages of this incinerator devices are easy control of the combustion, not complicated exhaust gas treatment and very good waste volume reduction. [15]

5 MATERIAL PROPERTIES TESTING

During processing and use materials are exposed to different types of stresses. That is the reason for measuring mechanical, rheological, thermal and other properties, which characterize suitability of the material for different applications. [17]

Among mechanical stresses belong tension, compression, bending, shear and torque, and they usually appear in combinations. Common methods do not test a part but a specimen made from the same material as the part itself. In most cases the testing specimen is strained by the force until it breaks. Rheological properties describe behavior of the polymer during its flow. Rheology deals with changes of flow at different temperature, pressure, time and so forth. These properties indicate the processability of the material. Thermal properties of plastics are equally important as mechanical properties. Unlike metals, plastics are extremely sensitive to temperature changes. Factors that affect thermal properties are crystallinity, molecular orientation, molecular weight and many others. [17, 18]

As the practical part of this thesis is devoted to the research of a mixture of recycled and pure material, which is then subjected to tension and flow testing, the next section will concentrate on these areas.

5.1 Tensile testing

Tensile testing belongs to the mechanical properties measurements. The results describe suitability of a certain material for engineering applications, tensile properties specify the quality of material, and can predict the behavior of the material under loading other than uniaxial tension. One of the most important properties is the strength of the material. The strength may be measured in terms of the stress necessary to cause appreciable plastic deformation or the maximum stress that the material can withstand. Tests run under standard conditions, which are the specimen size, preparation, conditioning, temperature, deformation speed and time (ISO standards). For measuring under elevated or lowered temperatures, special environmental chambers are needed. They contain automated systems for temperature control and are able to simulate vacuum or high-humidity environments. [1, 20]

5.1.1 Testing specimens

Testing specimens made of plastics are in most cases prepared by injection molding, where their shape (Fig. 24) and dimensions (Tab. 4) are given by the ISO standard. Intersection of these specimens is circular or rectangular. Their ends called shoulders have enlarged size or modified shape, because of their gripping to the testing machine. On gage length of the specimens, all deformations and fractures must occur. Testing specimen elongation is also measured on this length. [20]

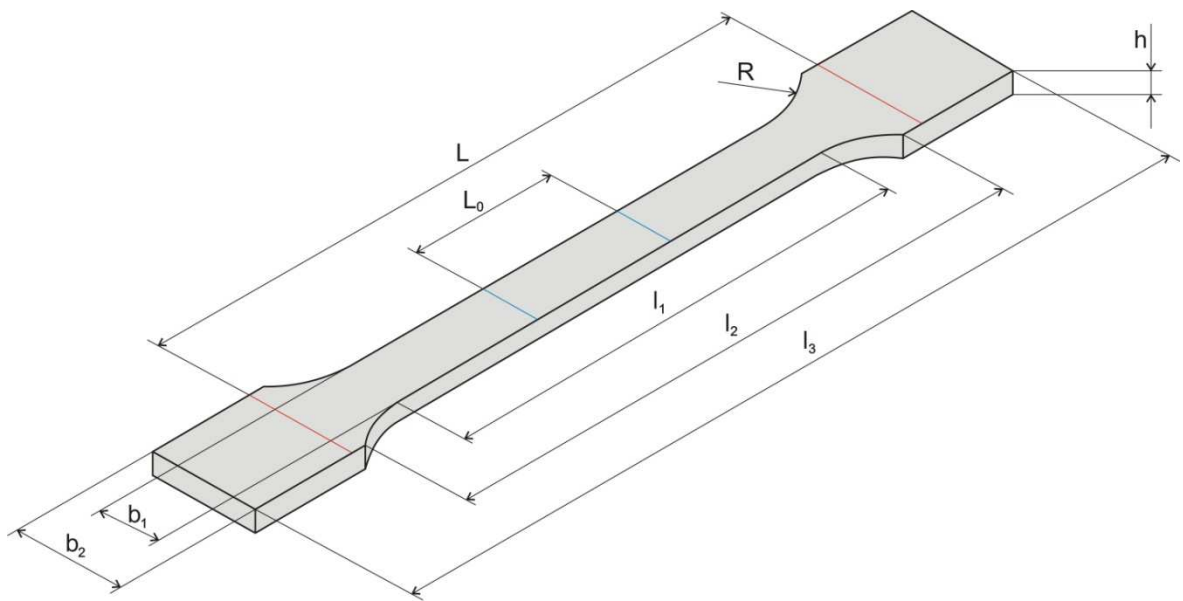


Fig. 24: Shape and dimensions of specimen [27]

Tab. 4: Dimensions of testing sample [27]

Dimensions of testing sample [mm]			
Dimension		Type 1A	Type 1B
b₁	Width of gage length	10 ± 0.2	
b₂	Width of gripping end	20 ± 0.2	
l₁	Length of gage length	80 ± 2	60 ± 0.5
l₂	Distance between gripping ends	104 - 113	106 - 120
l₃	Specimen length	≥ 150	
L₀	Distance of extensometers	30 ± 0.5	
L	Distance of grips	115 ± 1	$l_2 \begin{smallmatrix} +5 \\ 0 \end{smallmatrix}$
h	Specimen thickness	4 ± 0,2	
R	Radius	20 - 25	≥ 60

Fig. 25 shows different possibilities of testing specimens gripping considering their shape of their ends. The ends of specimen are enlarged and may be threaded or equipped with a hole for pin. The most widely used method is gripping to serrated wedges. The surface of the wedge, which is in the contact with the end of specimens, is fitted with a grooving. Tensile force must act in the axis of specimens and the gripping must withstand maximum load without a slippage or breakage of the specimens in this area. [20]

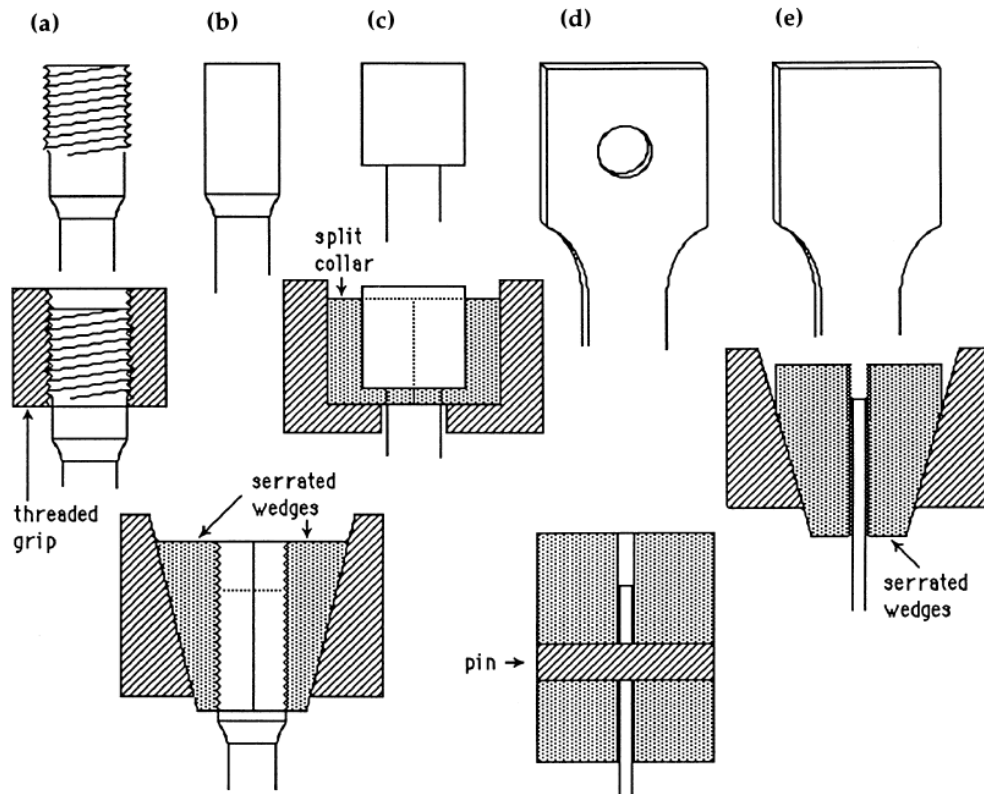


Fig. 25: Systems for gripping tensile specimens [20]

{ (a) – serrated wedges; (b) – butt end specimens, split collars constrained by a solid collar;
 (c) – sheet specimens gripped with pins; (d) – sheet specimens gripped by serrated
 wedges }

5.1.2 Testing machines

Common tensile tests are performed on universal machines that are able to test material in tension and also in compression or bending. Testing machines are either electromechanical or hydraulic. Electromechanical machines are based on a variable-speed electric motor and a gear reduction system. The crosshead, in which the specimen is gripped, is led on one, two or four screws. Its speed can be changed by modification of the speed of the motor. Second types, hydraulic machines, are based on a single or dual-action piston that moves the crosshead on the screws. [20]

In most cases, static hydraulic testing machines have a single action piston or ram. Hydraulic machines generate higher forces compared to electromechanical, but have a narrower range of test speeds and shorter crosshead displacements. [20]

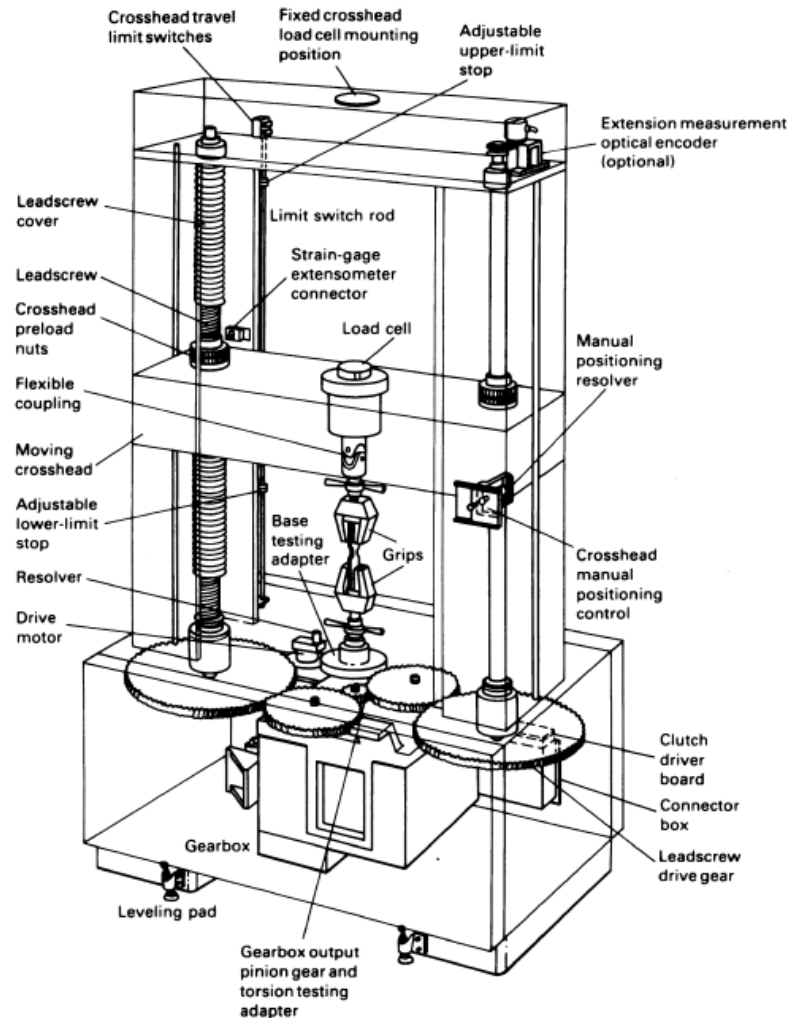


Fig. 26: Components of the electromechanical testing device [20]

5.1.3 Measured data

During the test, a computer records the course of the stress in dependence to the deformation and the data is plotted to the stress-strain curve. This curve contains some important points that represent specific stresses. Typical stress-strain diagram is shown in the Fig. 27. The initial proportion for most material is linear and is called area of Hooke's law validity. The slope of this linear part is called Young's or elastic modulus and as a constant, it is specific for given material. [20]

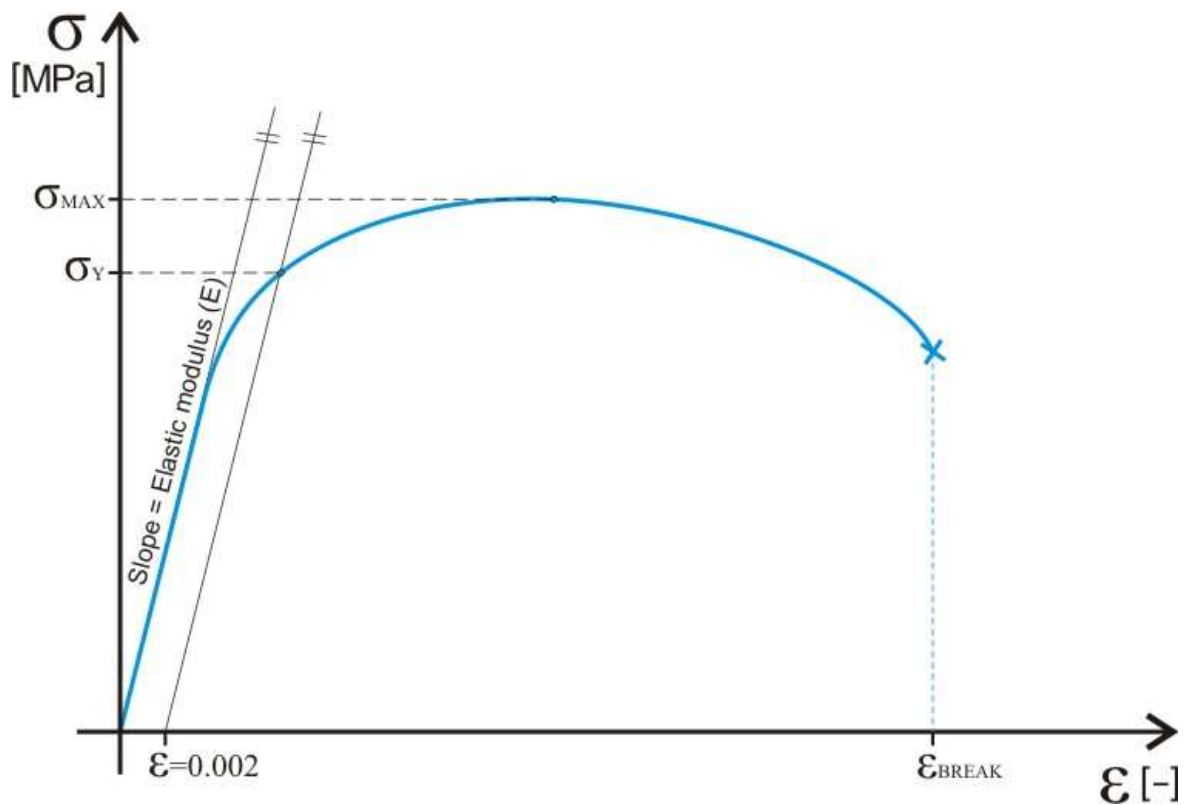


Fig. 27: Stress – strain diagram [16]

Hooke's law is defined as:

$$\sigma = E \cdot \varepsilon \quad [\text{MPa}] \quad (1)$$

where (σ) is the applied tensile stress, (ε) stands for the axial strain [-] and (E) means the Young' modulus [MPa]. [21]

Tensile strain or elongation is defined as the difference between the stretched (l) and the original (l_0) gage section length divided by the original length.

$$\varepsilon = \frac{l - l_0}{l_0} \quad [-] \quad (2)$$

A similar property is ductility, which is defined as elongation in percentage. Because an appreciable fraction of the plastic deformation will be concentrated in the necked region of the specimen, the value of the ductility depends on the gage length. [20]

$$\delta = \frac{l - l_0}{l_0} \cdot 100 \quad [\%] \quad (3)$$

The elongation caused by axial force in one direction, produce a contraction in the lateral direction. This contraction is perpendicular to the direction of the force. The ratio of lateral strain (ϵ_y) to longitudinal strain (ϵ_x) is called Poisson's ration (ν). [21]

$$\nu = -\frac{\epsilon_y}{\epsilon_x} \quad [-] \quad (4)$$

All measured stresses are called technical or engineering, because they are calculated to the original cross-section area. The tensile strength is the maximum load (F_{\max}) divided by the original cross-sectional area (S_0) of the specimen. [20]

$$Rm = \sigma_{MAX} = \frac{F_{MAX}}{S_0} \quad [\text{MPa}] \quad (5)$$

For a long time, tensile strength has been used for design of parts, but to compensate for the inaccuracy, it is reduced by the factor of safety. The current trend is to design parts on the base of yield strength. However, for brittle materials, the tensile strength is still a valid design criterion. [20]

Another term which appears in tensile testing is yield strength. It is the value of stress at which plastic deformation (yield) is observed. To set the point at which plastic deformations begins is very difficult. For easier definition, yield strength is classified as the offset stress from a linear part of the curve at a specific strain of 0.002. Many polymers have essentially no linear portion of their stress-strain curve. Thus, usual practice is to define the yield strength as the stress to produce some total strain, for example 0.005. [20]

$$\sigma_Y = \frac{F_{\epsilon=0.002}}{S_0} \quad [\text{MPa}] \quad (6)$$

5.2 Melt flow rate test

Melt flow rate (MFR), sometimes called Melt flow index (MFI), is a property that indicates liquidity of the polymer. Every thermoplastic material normally contains this information on the rheological data sheet. This test measures the extrusion rate of a molten material through a capillary of specified length and diameter under predefined conditions - temperature and load. [16, 17]

The MFR test is covered by ISO 1133 from 1966, where the test instrument is exactly specified with respect to dimensions, tolerances and temperature control. The die (capillary) has a diameter of 2.095 mm with tolerances ± 0.005 mm and is 8.000 mm long ± 0.025 mm. Basic section view of test instrument, is shown in the Fig. 28. The material is heated in the barrel under the piston and extruded by the pressure of the piston, while temperature is kept constant and measured by the thermometer. The result of this test is a number that indicates the amount of material in grams, which is extruded through the capillary in 10 min. [16, 18]

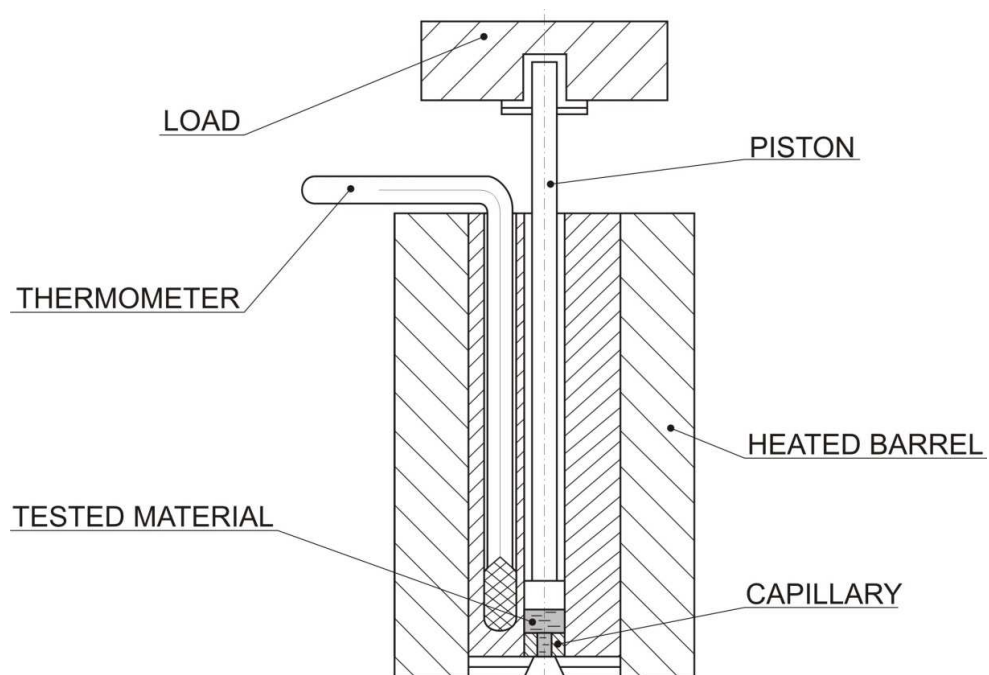


Fig. 28: Melt flow rate apparatus [18]

ISO standard 1033 describes two measuring methods. First of them, Method-A is based on cutting off the extrudate, which is then weighed. The cutoff time is specified between 5 to 240 s, depending on the viscosity of material. [18]

The formula used for MFR calculation for this method is:

$$\text{MFR} = \frac{t_{\text{ref}} \cdot m}{t} \quad [\text{g}/10\text{min}] \quad (7)$$

where m is average weight of material sample, t is the chosen time, after which is the sample cut and t_{ref} is time of extrusion equal to 10 min. [25]

Method-B is based on time measuring, for which the piston travels a distance from first point to the second. Then the material extruded during this time is weighed and the melt index is calculated by using the following formula:

$$\text{MFR} = \frac{427 \cdot L \cdot \rho}{t} \quad [\text{g}/10\text{min}] \quad (8)$$

where L is the length of calibrated piston travel [cm], ρ means the density of the polymer at the test temperature [g/cm^3] and t stands for time of extrusion, usually 10 min.

Density of the polymer at the test temperature is calculated from the weight of material m [g], extruded on a defined length l [cm]. [18, 25]

$$\rho = \frac{m}{0,711 \cdot l} \quad [\text{g}/\text{cm}^3] \quad (9)$$

Test results could be affected by several factors. The cylinder has to be preheated for a specified time, or nonuniformity in the melt flow can occur. Next, moisture in the material causes bubbles in the extrudate, which influence the weight of the extrudate. Finally, volume of the material put into the cylinder must be constant, or the heat input from the heated barrel to tested material will vary and results of repeated tests will be different. [18]

In general, a high-molecular weight material is more resistant to flow than a low-molecular weight material. Many plastic materials can have the same MFR, but different course of the flow curve, thus MFR alone is not enough for the prediction of material's properties. From this reason, the use of MFR as a measure of consistency is acceptable, but as a measure of processability it can be very misleading. The problem is that the shear rates of the test are much lower than typical shear rates in extrusion and injection molding. Consequently, the melt flow rate is mainly used to classify commercial materials according to their molecular weight. [16, 17]

II. ANALYSIS

6 OBJECTIVES OF MASTER THESIS

The aim of this Master Thesis is to examine the possibilities of use of irradiated HDPE products after the end of lifetime. The task is to determine the mechanical properties of LDPE after the addition of recycled HDPE as a filler in different concentrations and also compare the influence of the particles shape and form in which will recycled HDPE and raw LDPE occurred in the compound on these properties. Another task will be the measuring of melt flow rate of these compounds.

The main points for achieving the objectives:

- ❖ Preparation of recycled material for further processing
- ❖ Implementation of sieving
- ❖ Performance of melt flow rate test
- ❖ Preparation of test specimens
- ❖ Performance of tensile test
- ❖ Evaluation of measured data

7 MACHINES AND DEVICE

7.1 Rotary cutter mill RAPID SK 2218

Rotary cutter mill (Fig. 29) from company Maskin AB Rapid was used for the processing of recycle. This device contains a batching chamber, in which protecting sheet is placed that protects processed material against falling out. Material from this chamber goes directly on longitudinal knives of the mill, which crush the material on smaller particles. There is a sieve placed under the knives, which lets through a crushed material in size of 3-5 mm. Larger particles are pulled back by the knives and crushed again to an acceptable size.

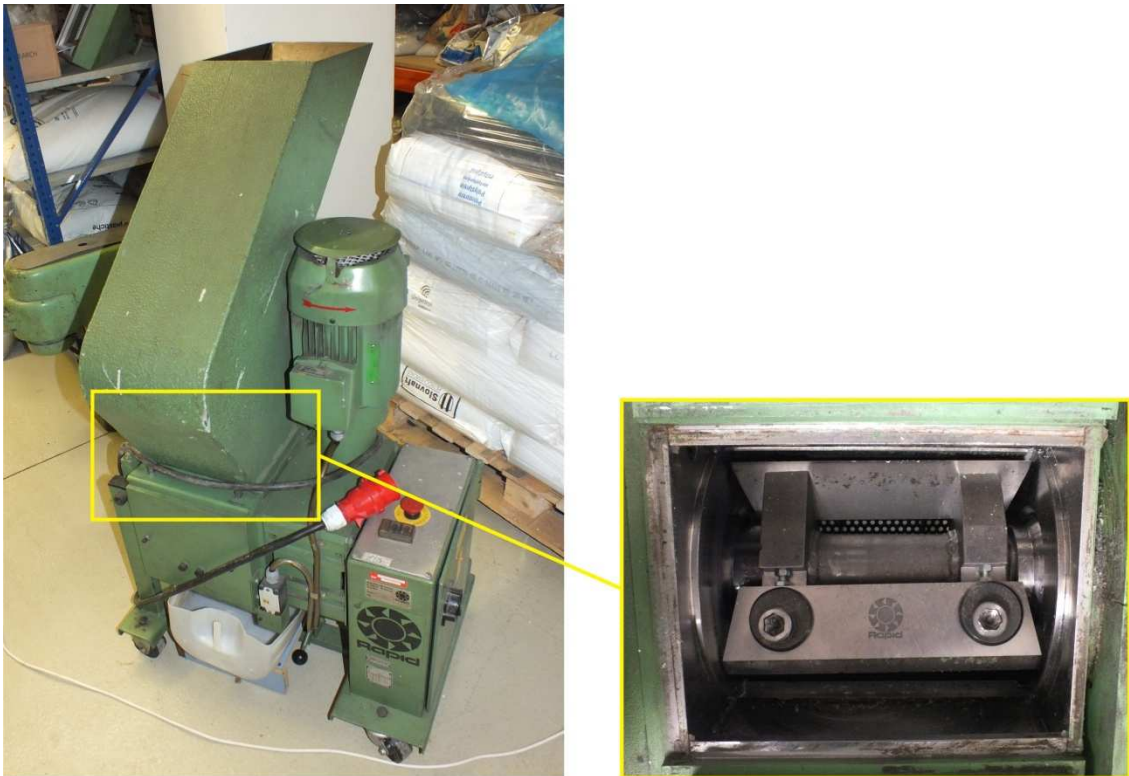


Fig. 29: Rotary cutter mill RAPID SK 2218

7.2 Laboratory pneumatic blender

Individual material were weighed and mixed to various compounds in appropriate concentrations. For the perfect mixing and uniform distribution of recycled material in raw LDPE, were compounds mixed in laboratory pneumatic blender (Fig. 30) available in department laboratories. It uses an air as a mixing element that is fed from the bottom of this device. The particles are lifted in the air, which leads to their perfect mixing.



Fig. 30: Laboratory pneumatic blender

7.3 Injection molding machine Arburg Allrounder 420C

For the production of standardized test specimens was used injection molding machine from Arburg Company marked Allrounder 420C. This machine is equipped with hydraulic clamping unit and uses SELOGICA control system for the monitoring of the injection process. Tillable terminal displays the progress of the injection cycle and the values of all set parameters.



Fig. 31: Injection molding machine Arburg Allrounder 420C [37]

7.4 Tensile testing machine ZWICK 1456

Tensile test of prepared specimens was performed on a universal tensile testing machine ZWICK Roell 1456 (Fig. 32). This testing machine is connected to a computer, which records measured data in program Test Expert Standard. The program is able to calculate basic statistical parameters, record a progress of the tensile curves in real time and measure Young's modulus using attached extensometers. Serrated wedges were used for specimens gripping, providing enough clamping force. The upper grip is movable and the lower is fixed to the machine frame. For measuring at elevated temperature (80 °C) was used temperature chamber ZWICK W91255. Construction and isolation of this chamber allows precise temperature setting and connection of extensometers.

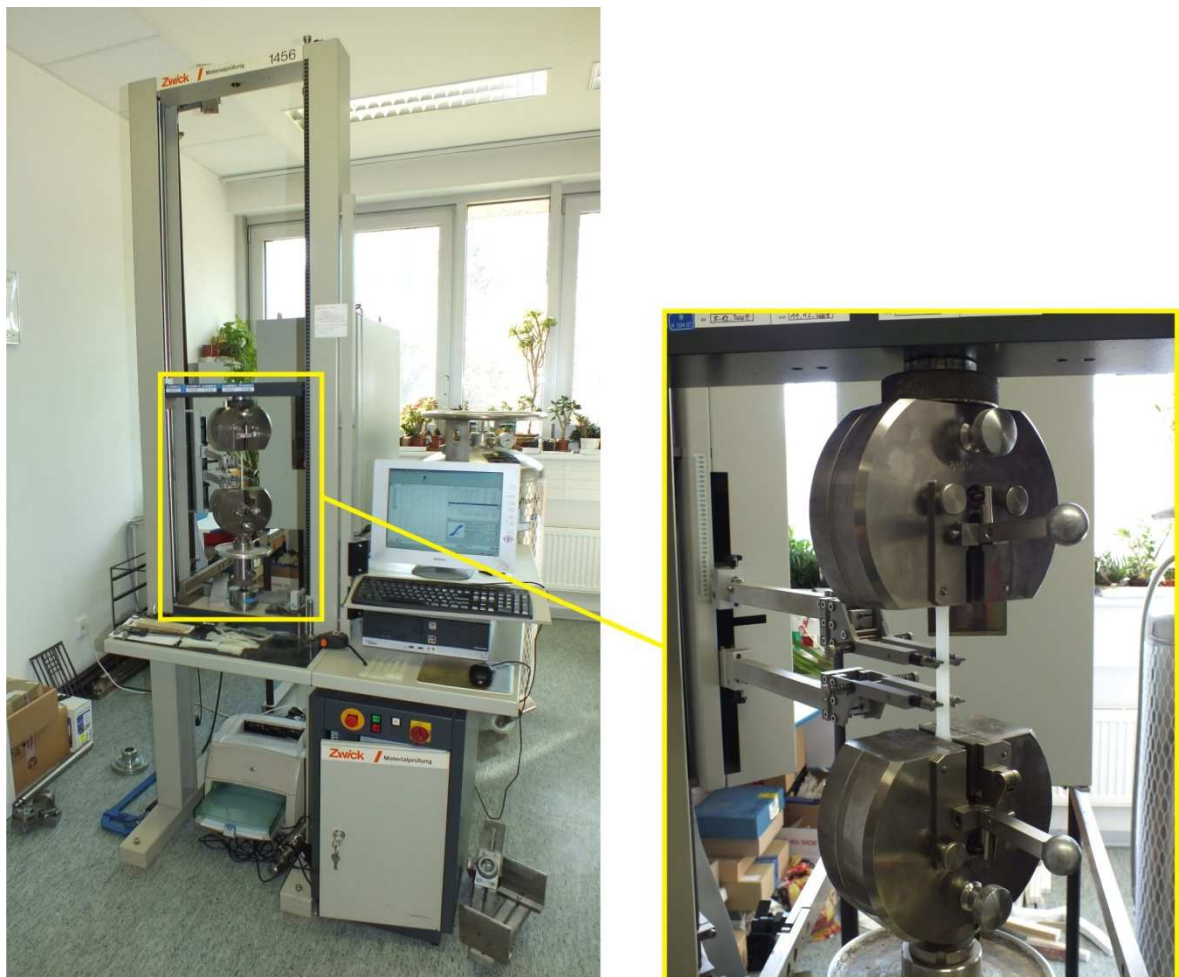


Fig. 32: Universal testing machine ZWICK 1456

7.5 Device for melt flow rate measuring Dynisco Kayeness LMI 4003

Testing device Dynisco Kayeness LMI 4003 is used for melt flow rate determination of thermoplastic materials. The heating chamber of this device is made of stainless steel and is heated by a pair of heating elements. The regulation of these elements is able to adjust temperature with an accuracy ± 0.1 °C. Extruding nozzle is made of tungsten steel, which provides high durability and resistance to abrasive materials. [38]



Fig. 33: Testing device for melt flow index Dynisco Kayeness LMI 4003

7.6 Vibratory sieve shaker RETSCH AS 200 Basic

Sieving device AS 200 Basic is testing device used for the particle size determination of sieved materials. It is equipped with a variable number of sieves with different mesh size, according to the needs of measurement. The device can sieve with amplitude from 1 to 100 mm and sieving time can be set from 1 - 60 minutes.



Fig. 34: Vibratory Sieve Shaker RETSCH AS 200 basic

8 MATERIALS AND PROCESSING

8.1 DOW LDPE 780E

Low-density polyethylene LDPE made by DOW called LDPE 780E was chosen as the basic material. This material is supplied by the manufacturer in the form of granules. Properties of this material guaranteed by the manufacturer are described in Tab. 5. The application and main advantages of LDPE are described in Chapter 2.

Tab. 5: Properties of DOW LDPE 780E [35]

Property	Value	Test method
Density	0.923 g/cm ³	ASTM D792
Melt Mass-Flow Rate (MFR) (190 °C, 2.16 kg)	20 g/10min	ISO 1133
Molding Shrinkage – Flow	2.3 %	ASTM D955
Molding Shrinkage - Across Flow	1.5 %	ASTM D955
Tensile Modulus (sample compression molded)	164 MPa	ISO 527-2
Tensile Stress - Yield (sample compression molded)	8.20 MPa	ISO 527-2
Tensile Stress - Break (sample compression molded)	10.5 MPa	ISO 527-2
Tensile Impact Strength	286 kJ/m ²	ISO 8256
Shore Hardness (Shore D)	49	ISO 868

8.2 Slovnaft HDPE TIPELIN PS 380-30/302

Irradiated material, which was used as a recyclate, was high-density polyethylene HDPE from the Slovnaft Company. Properties of this material guaranteed by the manufacturer are listed in following table (Tab. 6). Information about HDPE is also given in chapter 2.

Tab. 6: Properties of TIPELIN PS 380-30/302 [36]

Property	Value	Test method
Density	0.948 g/cm ³	ISO 1183-2
Melt Mass-Flow Rate (MFR) (190 °C, 5.0 kg)	0.95 g/10min	ISO 1133/B
Flexural Modulus	750 MPa	ISO 178
Tensile Strength - Yield	19.0 MPa	ISO 527-3
Tensile Strength	31.0 MPa	ISO 527-3
Izod Impact Strength	13 kJ/m ²	ISO 180
Shore Hardness (Shore D)	60.5	ISO 868

8.3 Recyclate processing

Recycled material was provided in the form of tubes, which served for floor heating. These tubes cannot be remelted after the end of lifetime, due to their modification by ionizing radiation. Therefore the recyclate was used as a filler. The tubes were irradiated by electron beams with energy of 10 MeV by total dose of 165 kGy. The recyclate was cleaned of all dirt and shortened into the suitable length for further processing. After these operations the material was crushed in a rotary cutter mill RAPID SK 2218 to a grit.

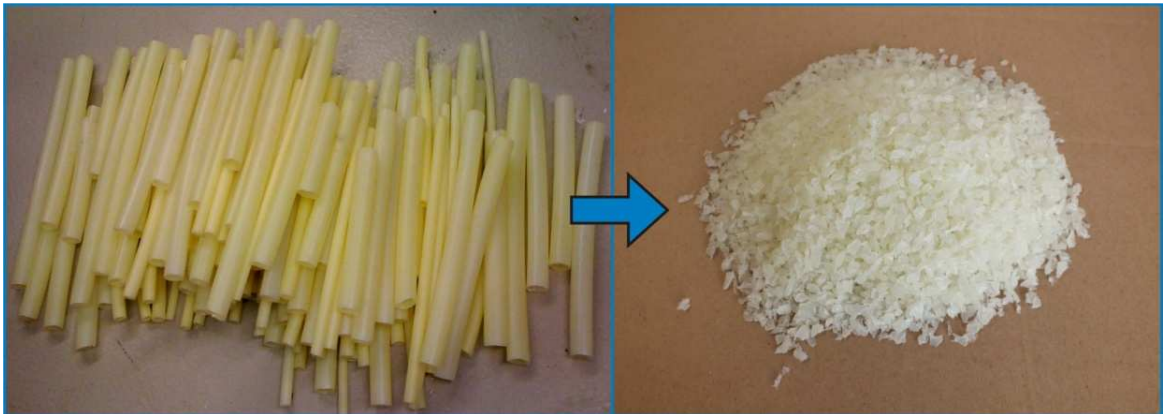


Fig. 35: Processed tubes

As was mentioned in chapter 7.1, particle size, which leaves the mill, is in the range from 3 to 5 mm. The diversity in shape and size of particles is shown in Fig. 36.



Fig. 36: Crushed particles size

8.4 Compound preparation

The mixtures were made by weighing of individual components, according to required concentrations, considering the total weight of the batch, which was 2100 g. Total weight of the batch, was calculated according to the required number of test specimens for tensile test. Compounds were mixed in the laboratory pneumatic blender. The initial pressure under which was air blown into the device, was 7.0 bar, then its value dropped to 5.6 bar at the end of mixing cycle. Mixing time was chosen with regard to the amount of material for 5 minutes. Individual compounds were prepared from various concentrations of raw LDPE and recyclate. There were prepared 3 types of compounds totally. The concentration of the first type compound, which contains of the recyclate in the form of grit and granules of LDPE, is shown in Tab. 7.

Tab. 7: Concentrations of reground recyclate with granules of LDPE

Mark of compound	Concentration
A1	100% LDPE + 0% HDPEr
A2	90% LDPE + 10% HDPEr
A3	80% LDPE + 20% HDPEr
A4	70% LDPE + 30% HDPEr
A5	60% LDPE + 40% HDPEr
A6	50% LDPE + 50% HDPEr
A7	40% LDPE + 60% HDPEr

The second compound was made of LDPE granules and HDPE powder, where the powder of recyclate was milled in the MEL-BAX company. Tab. 8 shows the amount of recycled material in the individual compounds

Tab. 8: Concentrations of powder recyclate with granules of LDPE

Mark of compound	Concentration
B1	100% LDPE + 0% HDPEr
B2	90% LDPE + 10% HDPEr
B3	80% LDPE + 20% HDPEr
B4	70% LDPE + 30% HDPEr
B5	60% LDPE + 40% HDPEr
B6	50% LDPE + 50% HDPEr
B7	40% LDPE + 60% HDPEr

Last compounds (Tab. 9) were made of powder recyclate, which was added to the raw LDPE that was also in the powder form, milled in MEL-BAX Company.

Tab. 9: Concentrations of powder recyclate with powder of LDPE

Mark of compound	Concentration
C1	100% LDPE + 0% HDPEr
C2	90% LDPE + 10% HDPEr
C3	80% LDPE + 20% HDPEr
C4	70% LDPE + 30% HDPEr
C5	60% LDPE + 40% HDPEr
C6	50% LDPE + 50% HDPEr
C7	40% LDPE + 60% HDPEr

9 EXPERIMENT

9.1 Evaluation of measured data

All measured data were evaluated in statistical program Minitab. Statistical quantities used for evaluation of the measured data were:

- **Arithmetic mean:**

The arithmetic mean (\bar{x}) is defined as the sum of values of variables (x_i) divided by the total number of variables (n). This quantity carries maximum information about entire set, but is very sensitive to distant values. [30]

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (10)$$

- **Standard deviation:**

Standard deviation (s) is calculated from the square root of variance. Variance is defined as the product of squared deviations of the measured values from the arithmetical mean divided by the total number of variables reduced by one. [30]

$$s = \sqrt{s^2} = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (11)$$

- **Standard error of the mean:**

Standard error of the mean (u_A) involves unknown causes of measurement errors. The condition for its determining is the number of measurements greater than 10 and ensured repeatability and independence of all measurements. [31]

$$u_A = s_{(y)} = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n \cdot (n - 1)}} = \frac{s}{\sqrt{n}} \quad (12)$$

- **Minimum and Maximum:**

These statistical parameters determine the minimum (MIN) or the maximum (MAX) value, which was measured in the entire set. [30]

- **First quartile:**

The first quartile (Q1) describes that 25 % of measured is less than this value and remaining 75 % is greater or equal to this quartile. [30]

- **Median:**

The second quartile (Q2), also called Median, divides the measured values on half, where 50 % is smaller and the other half is greater or equal to this parameter. [30]

- **Third quartile:**

The third quartile (Q3) divides measured data, where 75 % of all measured data is smaller than this quartile and the remaining 25 % is equal or greater than this value. [30]

- **Interquartile range:**

This parameter (IQR) shows the degree of variability of entire set and is defined as the distance between the first and third quartile (i.e. the difference between the third and the first quartile). [30]

For checking and graphical interpretation of the measured data were used box-plot diagrams, in which are displayed values of arithmetical mean, median, first and third quartile, MIN and MAX. Grey rectangle interprets the Interquartile range.

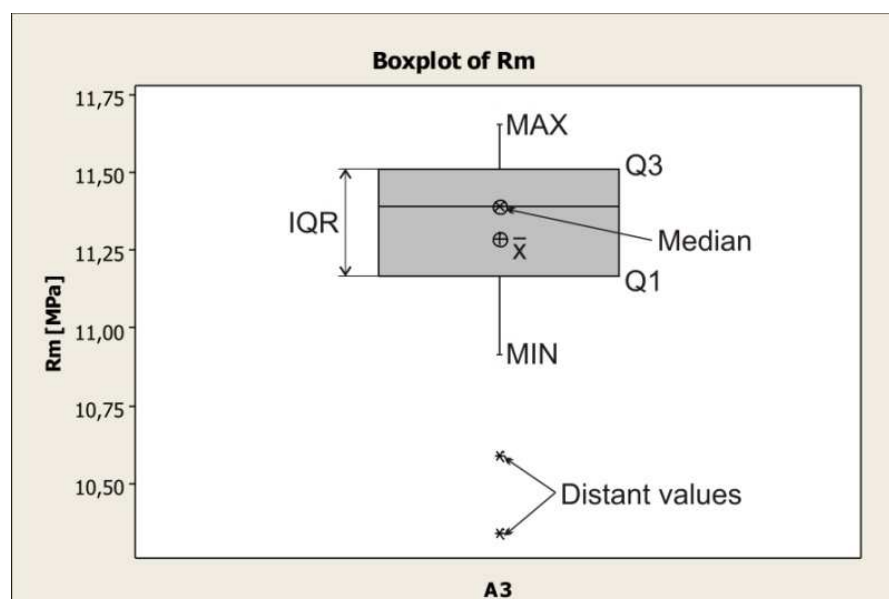


Fig. 37: Example of described box-plot diagram

Probable distant values are those measured data, which value is greater than $\frac{1}{2}$ interquartile range. The measured data can be considered as better as smaller is the IQR. Furthermore, closer the values of arithmetic mean and median are, the greater symmetry has the entire set.

9.2 Sieving

Sieving belongs to a narrow group of separation techniques of particle size analysis. The principle of this method is a gravitational transport of analyzed substance through a series of sieves with different mesh size. The size of mesh is gradually decreased from upper sieve to the bottom of device. Certain amount from total batch of a material remains on the individual sieves after the analysis. Therefore, the particles have a smaller size than the mesh size of upper sieve, but are larger than the mesh of sieve, on which they stayed. This part of total material batch is weighed and is defined, what range of dimensions this part have. [28]

Sieving was carried out on the Retsch AS 200 Basic, where totally 200 g of LDPE powder and recycled HDPE powder was sieved. Sieving time was set at 30 minutes and amplitude of vibration was set to 90 mm. Measured data are shown in following table (Tab. 10).

Tab. 10: Measured data from sieving

	LDPE		HDPEr	
Mesh size	Total batch - 200 g (100%)		Total batch - 200 g (100%)	
>500 μm	106.5 g	53.25 %	136.0 g	68.00 %
250 μm	72.0 g	36.00 %	49.0 g	24.50 %
125 μm	18.5 g	9.25 %	13.5 g	6.75 %
90 μm	2.5 g	1.25 %	1.5 g	0.75 %
63 μm	0.5 g	0.25 %	-	-

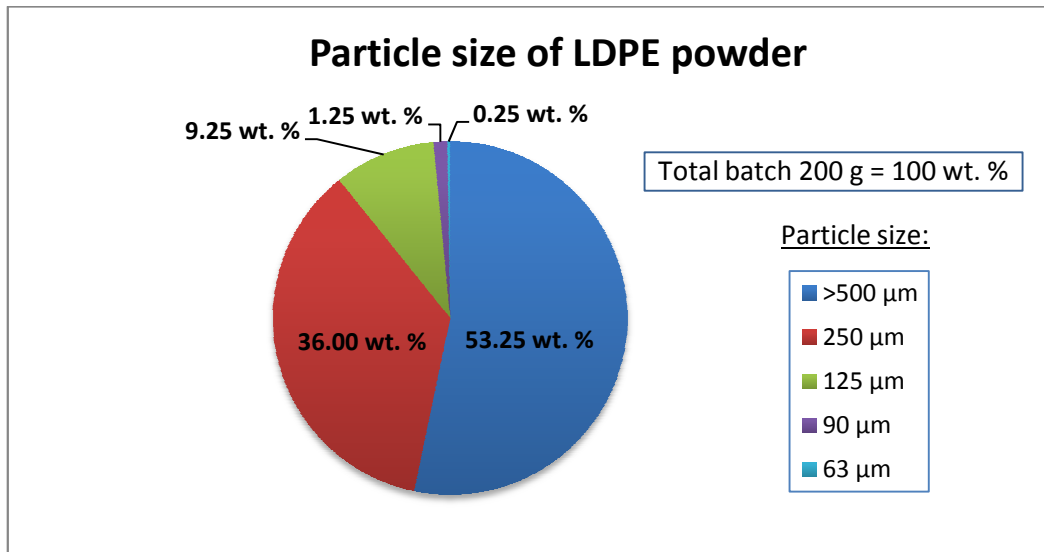


Fig. 38: Particle size of LDPE powder

The Fig. 38 shows that from the total 200 g of powder LDPE is 53.25 wt. % of particles larger than 500 μm, 36.00 wt. % of particles has a size ranging from 250 – 500 μm, another 9.25 wt. % is smaller than 250 μm and greater than 125 μm. Only 1.25 wt. % is larger than 90 μm and a slightly amount (0.25 wt. %) is in the range from 63 to 90 μm.

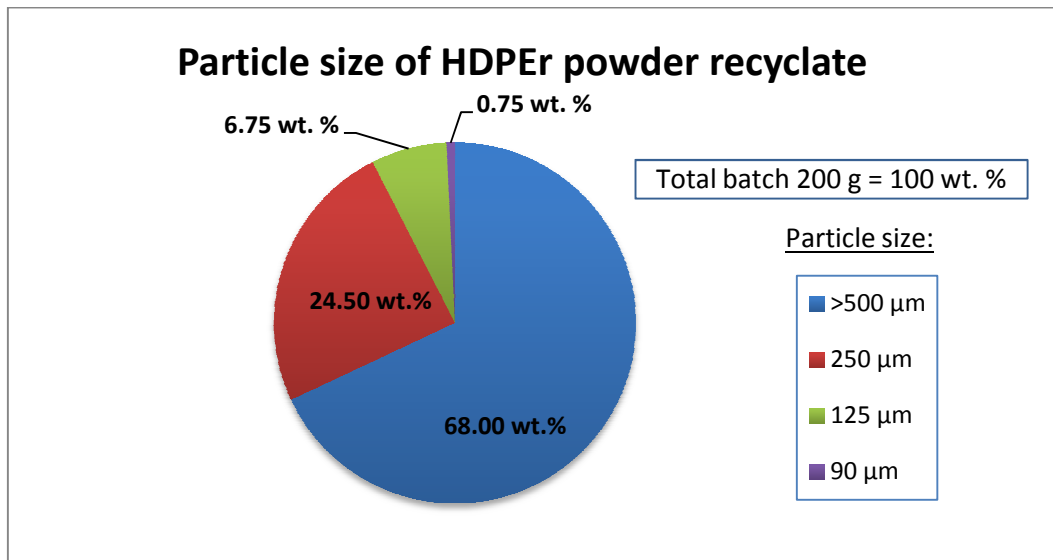


Fig. 39: Particle size of HPDEr powder recyclate

The chart above (Fig. 39) describes that 68.00 wt. % of powder recyclate is larger than 500 μm, another 24.50 wt. % has a size between 250 to 500 μm. Furthermore, there are 6.75 wt. % particles with size of 125 μm and smaller than 250 μm. Finally, only 0.75 wt. % from total batch is in the range from 90 to 125 μm.

9.3 Melt flow rate

Melt flow rate was measured on a Dynisco Kayeness LMI 4003. The sample of compound, which is needed for the test, was set according to the standard on 8 g. There were three measurements done for every concentration. The test was carried out according to EN ISO 1133, specifically method B, where is measured time, for which the piston traveled a specific distance from one point to another. The distance of these points was 2.6 cm. The material was heated in barrel for 240 seconds and the temperature at which test ran, was set to 190 °C. The weight, which extruded the compound through a capillary in device, weighted 2.16 kg.

Tab. 11: Melt flow rate of individual compounds

Type of compound	t [s]	MFR [g/10min]
A1 = B1	43.7	19.35
C1	42.0	20.31
C2	61.0	13.69
C3	82.0	10.37
C4	130.3	6.53
C5	248.0	3.44
C6	407.3	2.07
C7	1076.3	0.79

From all three types of compounds was melt flow rate measured only for compound of powder LDPE and the powder of recyclate, and for raw LDPE in the form of granules. The melt flow rate was calculated according to equations (8) and (9). Measured data (Tab. 11) showed that the melt flow rate decrease significantly with the growing content of recyclate in the compound. Already at 20 % content of recyclate the melt flow rate declined by nearly half from the value of 20.31 g/10min to 10.37 g/min. Additional decrease of MFR is shown in Fig. 40.

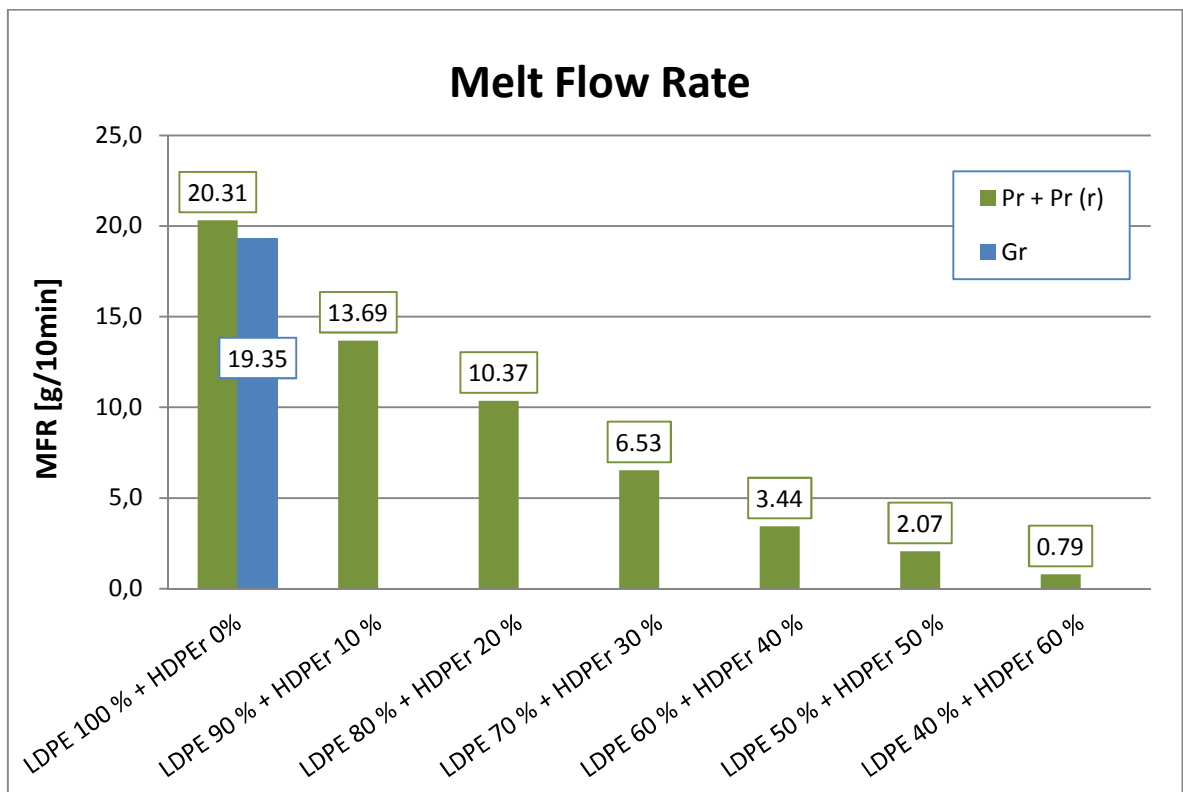


Fig. 40: Melt flow rate of Pr + Pr (r)

The compounds of granules LDPE and a grit recyclate were impossible to extrude through the capillary, because of the grit size. In contrast, another problem occurred in the compounds consisting of LDPE granules and a recyclate powder. The recyclate powder sedimented during weighing in the jar (Fig. 41), that caused a non-uniform dispersion of powder in the heated barrel. Due to this problem a granules of LDPE were firstly extruded and after then the recyclate powder.

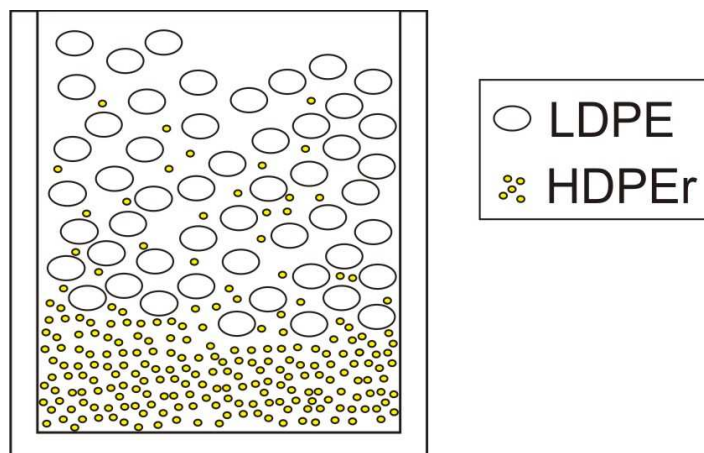


Fig. 41: Powder recyclate sedimentation during sample preparation

9.4 Production of test specimens

Test specimens for tensile test were made on injection molding machine Arburg Allrounder 420C. The shape of the specimens is given by the standard ISO 527 and specific dimensions as displayed in chapter 5.1.1. Process parameters, which were set on the injection molding machine, are shown in Tab. 12. Used injection mold was single cavity mold, thus during one injection cycle was produced only one specimen.

Tab. 12: 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	27.5mm
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 2	140 °C
Zone 3	150 °C
Zone 4	160 °C
Zone 5	180 °C
Temperature under the hopper	40 °C

Process parameters remained unchanged for lower concentration of recyclate, until the value of HDPEr in the compound reached 50 %. At this concentration the injection pressure was increased to 500 bar and holding pressure to 450 bar, while at 60 % of HDPEr in compound were both of these parameters increased to 550 bar. This increase was done because of sink marks on specimens and due to the problems with polymer fluidity. This change of process parameters was performed at all types of compounds.

9.5 Tensile test

As was mentioned before, tensile test was performed on ZWICK ROELL 1456 testing machine. The aim of this test was to measure the values of ultimate tensile strength, elongation and Young's modulus of the specimens for individual concentration of each compound type. The test was conducted at the ambient temperature of 24 °C and also at an elevated temperature of 80 °C in the temperature chamber. Totally, 20 specimens were measured for each temperature and concentration. Modulus of elasticity was measured after exceeding tensile strength of 5 N. Test speed was set on 50 mm/min and distance of extensometers, which was used for measuring of Young's modulus, was set to 30 mm. Under every table is given commentary about quality of measured data, followed by a box-plot diagram, in which are displayed measured values for appropriate parameter and temperature.

9.5.1 Measured data for granules of LDPE and grit of recyclate

Tab. 13: Young's modulus of Gr + Gr(r) at 24°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	231.37	1.91	8.53	215.89	227.04	231.07	236.65	251.61	9.61
A2	251.87	1.86	8.34	238.45	245.83	252.82	258.13	270.48	12.30
A3	288.75	4.79	21.43	242.83	274.39	292.35	308.19	316.30	33.79
A4	320.09	3.78	16.93	292.13	308.34	319.05	332.07	357.13	23.73
A5	372.37	6.60	29.51	301.24	352.72	378.04	390.74	423.64	38.02
A6	425.29	5.61	25.09	361.68	413.87	424.66	444.12	462.14	30.25
A7	453.57	6.47	28.93	396.11	433.80	451.40	479.75	497.95	45.94

The evaluated data, measured for the modulus of elasticity, show two probable distant values at the A1 and A6 concentrations as shown in Fig. 42. Furthermore, data for concentration A5 show a large variation range (MIN value is very far from MAX value). The highest quality shows the data measured for A1 and A2 concentrations.

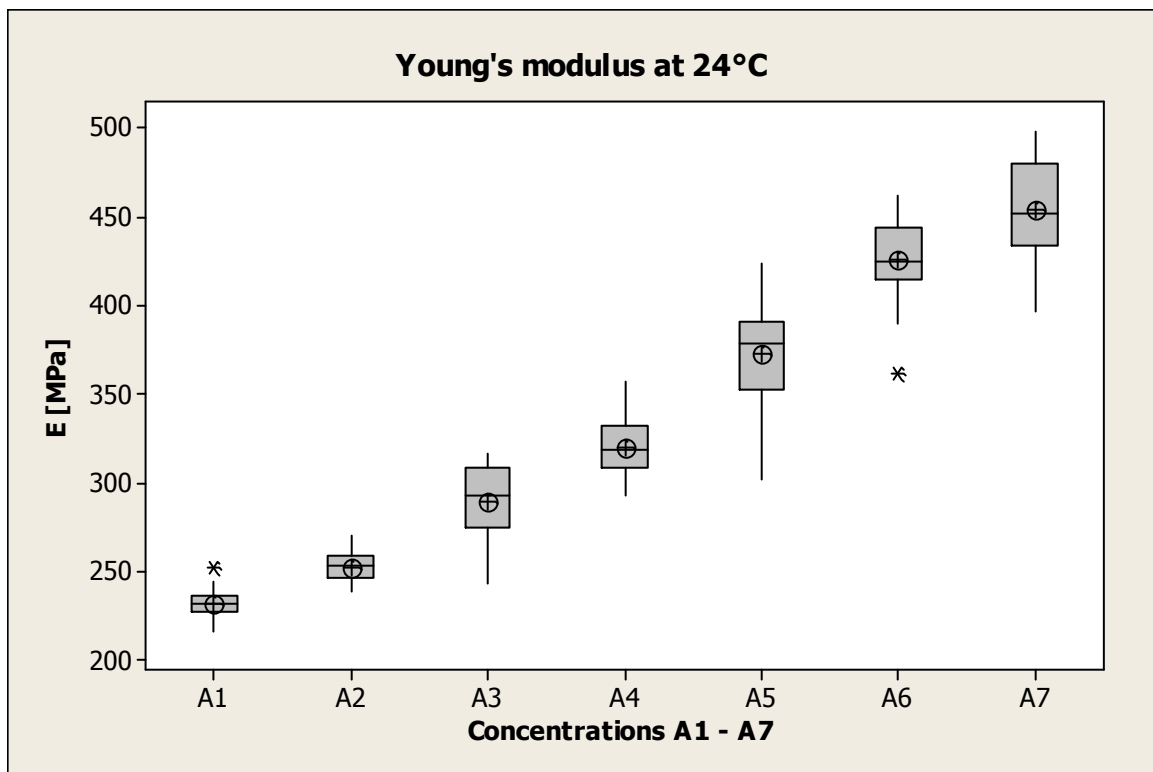


Fig. 42: Data quality of Young's modulus at 24°C (Gr + Gr(r))

Tab. 14: Nominal strain at Rm of Gr + Gr(r) (24°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	68.84	0.51	2.27	63.70	67.71	68.93	70.14	73.01	2.43
A2	45.30	2.36	10.56	26.18	34.10	49.36	53.57	58.14	19.48
A3	28.15	1.40	6.24	17.76	23.30	28.02	32.71	39.17	9.41
A4	20.54	0.82	3.68	14.93	18.03	20.19	22.70	28.34	4.68
A5	17.34	0.47	2.09	11.36	16.23	17.16	19.24	20.22	3.01
A6	13.32	0.35	1.56	10.64	12.08	13.44	14.82	15.65	2.74
A7	12.51	0.34	1.52	9.64	11.24	12.48	13.27	16.65	2.03

The values of nominal strain measured for A2 concentration show very large IQR, therefore the data are very diverse and more measured values would be necessary for evaluation with better quality. Moreover, arithmetic mean is quite far from the median. Totally three probable distant values were identified (Fig. 43).

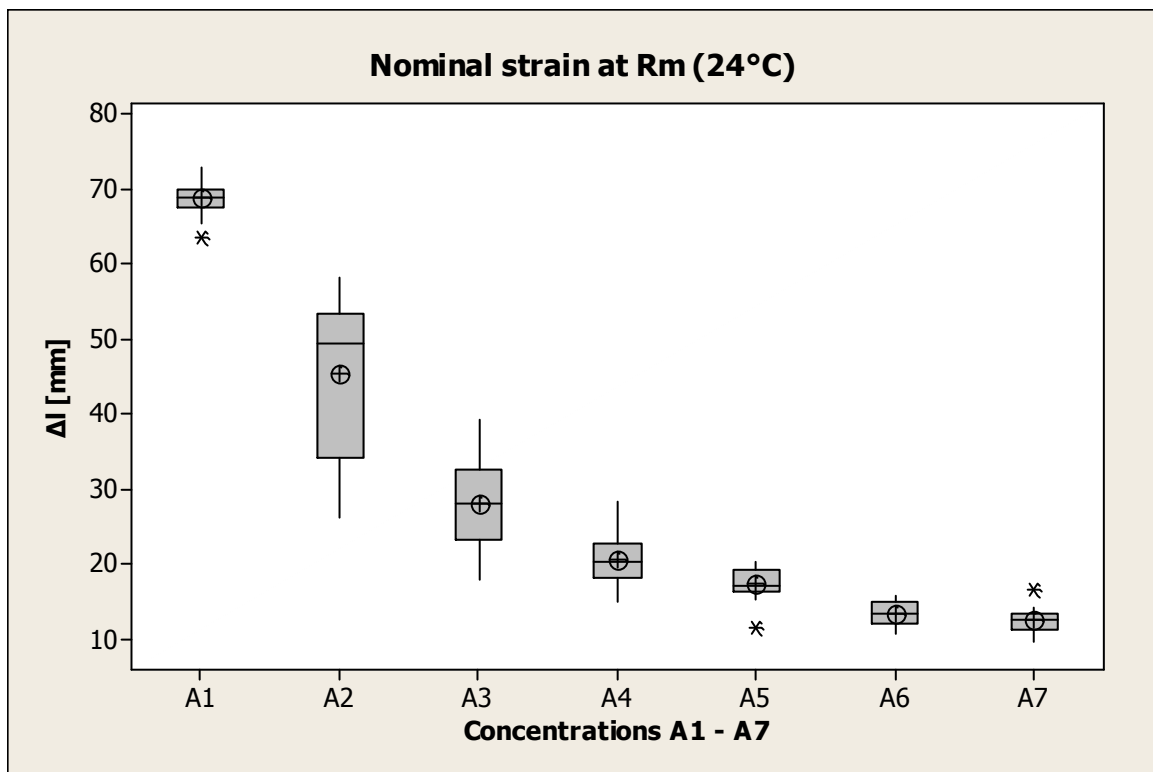


Fig. 43: Data quality of nominal strain at Rm of Gr + Gr(r) (24°C)

Tab. 15: Ultimate tensile strength of Gr + Gr(r) at 24°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	10.78	0.03	0.15	10.53	10.65	10.77	10.90	11.06	0.25
A2	10.83	0.05	0.22	10.34	10.62	10.89	10.96	11.18	0.34
A3	11.28	0.08	0.34	10.34	11.16	11.39	11.51	11.65	0.35
A4	11.85	0.05	0.23	11.27	11.76	11.88	12.02	12.19	0.26
A5	13.04	0.06	0.28	12.40	12.87	13.07	13.24	13.57	0.37
A6	14.01	0.13	0.57	13.10	13.52	14.03	14.49	14.98	0.97
A7	14.90	0.09	0.39	14.04	14.65	14.98	15.23	15.43	0.59

The values of arithmetic mean and median are quite far from each other at A2, A3 and A7 concentrations. In addition, A3 and A4 concentrations show two probable distant values each. A hypothesis testing is used to determine whether the marked values of data set are truly distant values. IQR evaluated for this data set are relatively narrow, hence it can be assumed that the results are representative.

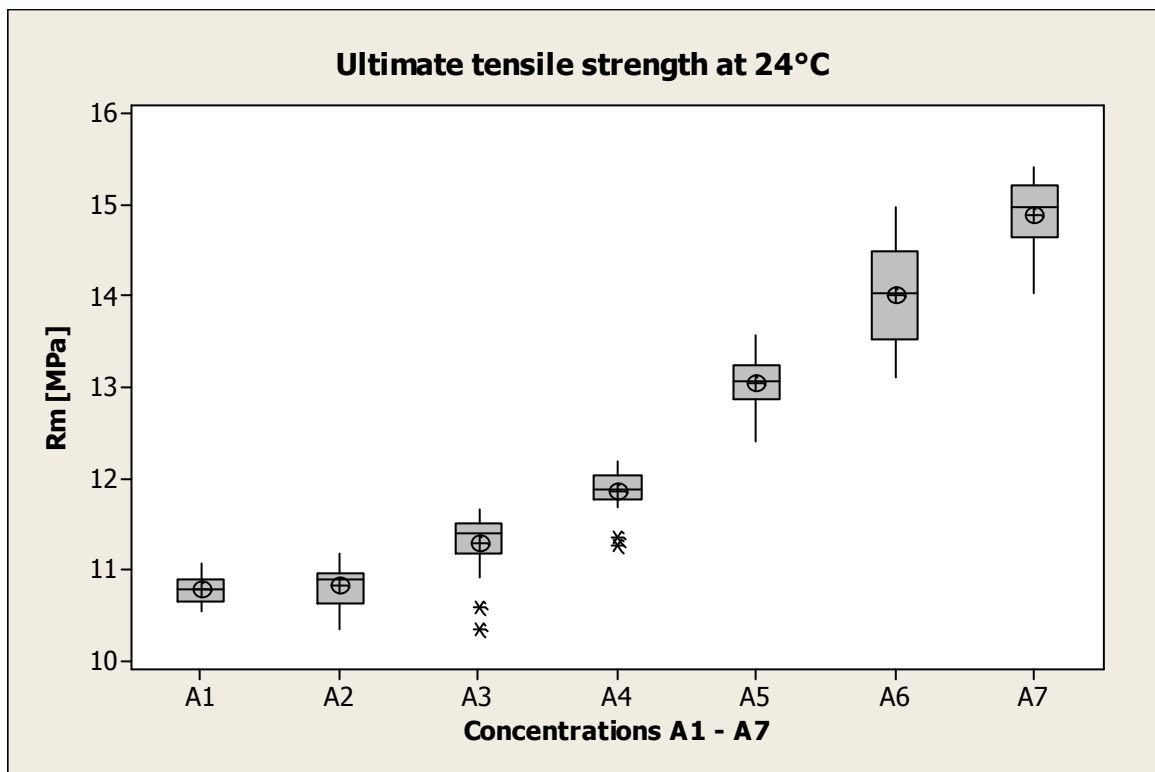


Fig. 44: Data quality of ultimate tensile strength at 24°C (Gr + Gr(r))

Tested samples show a gradual increase of elastic modulus with an increasing concentration of recyclate at ambient temperature equal to 24 °C. As the result of modulus increase, stiffness was improved. Young’s modulus of elasticity grown from the original 231.37 MPa for raw LDPE to 453.57 MPa for a compound with 60 % of recyclate. This increase is equal to 196 % compared to original value.

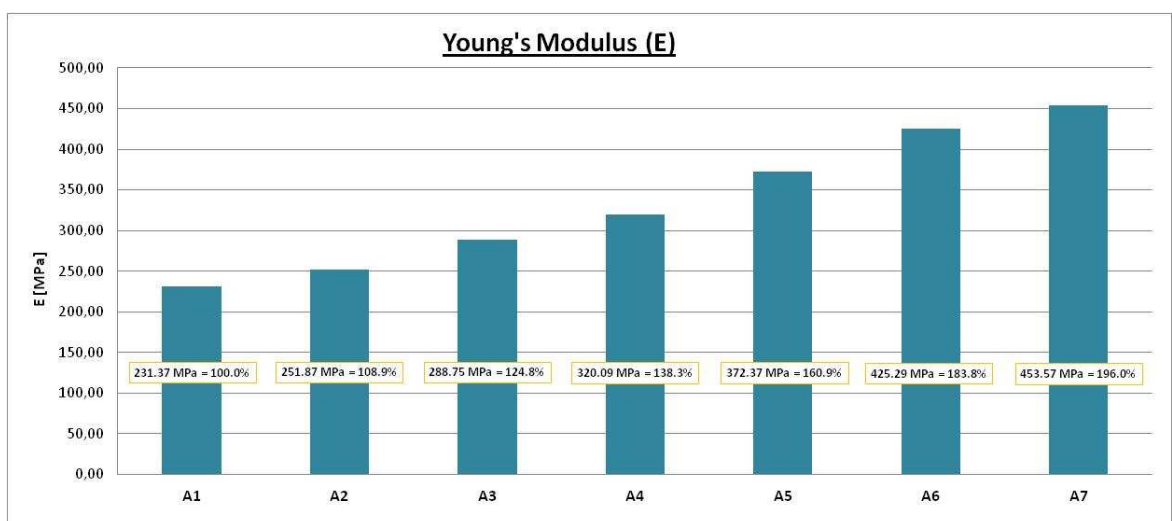


Fig. 45: Young’s modulus of Gr + Gr(r) at 24°C

The price for stiffness increase is a significant loss of ductility. Nominal strain at Rm decreased from the original value of 68.84 mm to 12.51 mm for the samples with highest recyclate concentration. This is nearly fivefold decrease. Expressing the nominal strain decrease in percentage, it is a drop to 18.2 % compared with original value for raw LDPE.

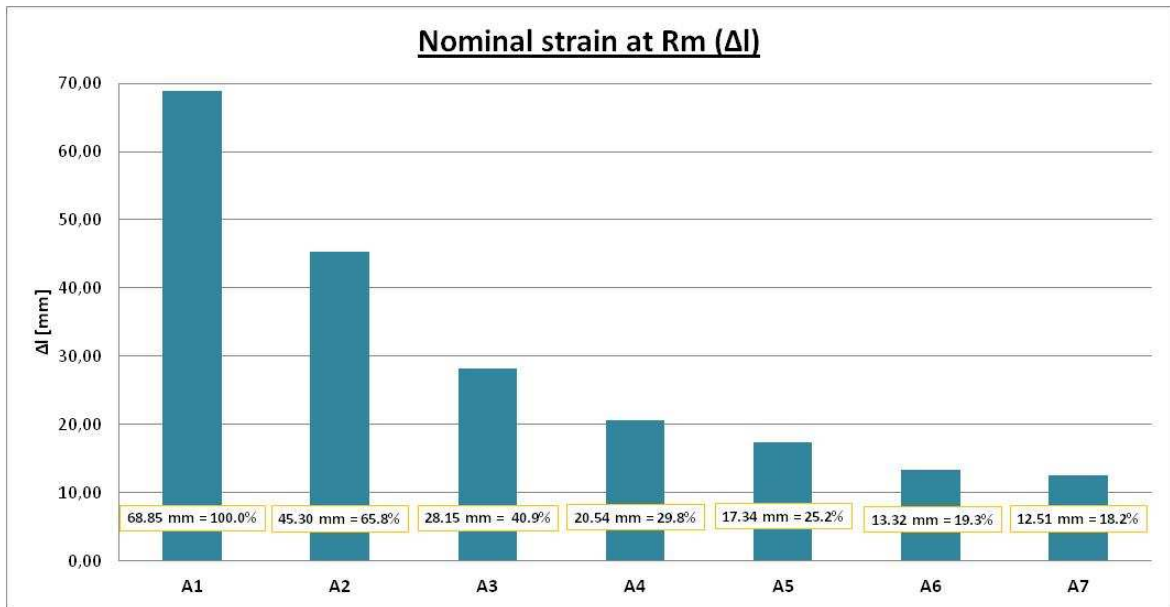


Fig. 46: Nominal strain at Rm of Gr + Gr(r) (24°C)

The ultimate tensile strength shows also a small increase (to 138.2 %), where it was increased from 10.78 MPa for raw LDPE to the value of 14.90 MPa equal for a compound with 60 % of recyclate. The progress of stress-strain curve is shown in Fig. 48.

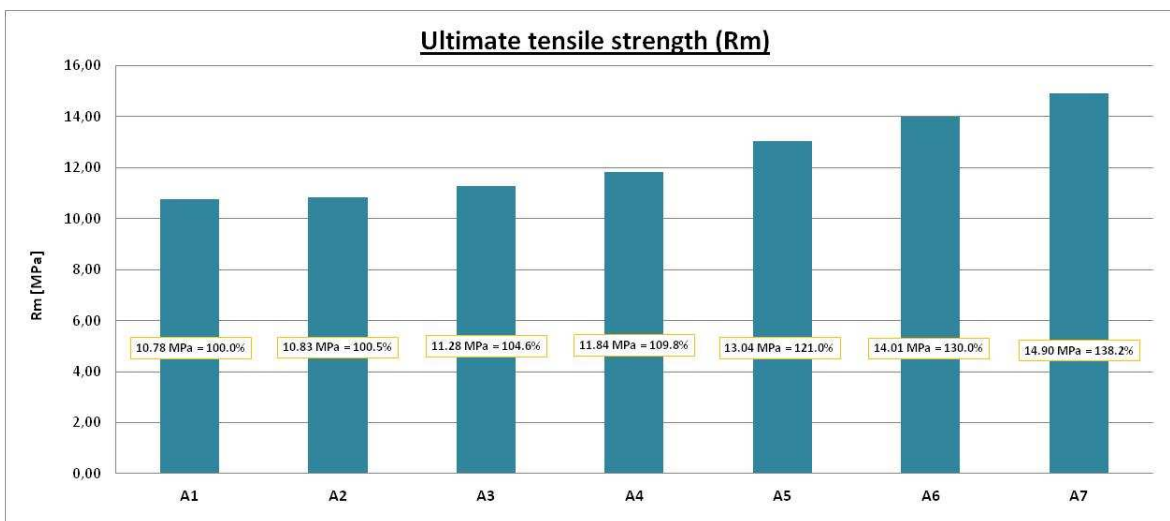


Fig. 47: Ultimate tensile strength of Gr + Gr(r) (24°C)

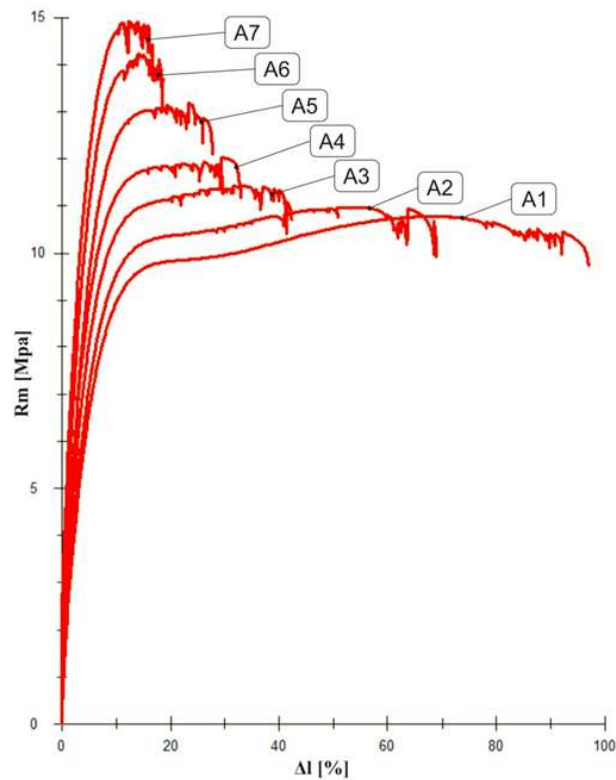


Fig. 48: Stress – strain curves for different concentrations of Gr + Gr(r) (24°C)

Tab. 16: Young’s modulus of Gr + Gr(r) at 80°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	36.87	0.47	2.11	33.21	35.35	36.74	39.08	40.13	3.73
A2	38.29	0.67	2.98	29.15	37.03	38.32	40.59	42.32	3.56
A3	41.57	0.53	2.38	36.44	39.87	41.52	43.43	45.45	3.56
A4	48.99	0.89	3.98	41.78	46.28	48.69	51.09	58.67	4.81
A5	53.35	1.20	5.37	45.03	49.20	53.36	56.78	66.68	7.58
A6	59.97	1.09	4.87	50.89	56.40	58.40	64.33	68.20	7.93
A7	69.27	1.30	5.83	57.17	64.93	68.78	73.91	82.08	8.97

The values measured for Young’s modulus at 80 °C show good quality, due to similar values of arithmetical mean and median. Only A6 concentration has the value of arithmetical mean far from the median. As can be seen in Fig. 49, there is an increase of interquartile range with growing concentration of recycle.

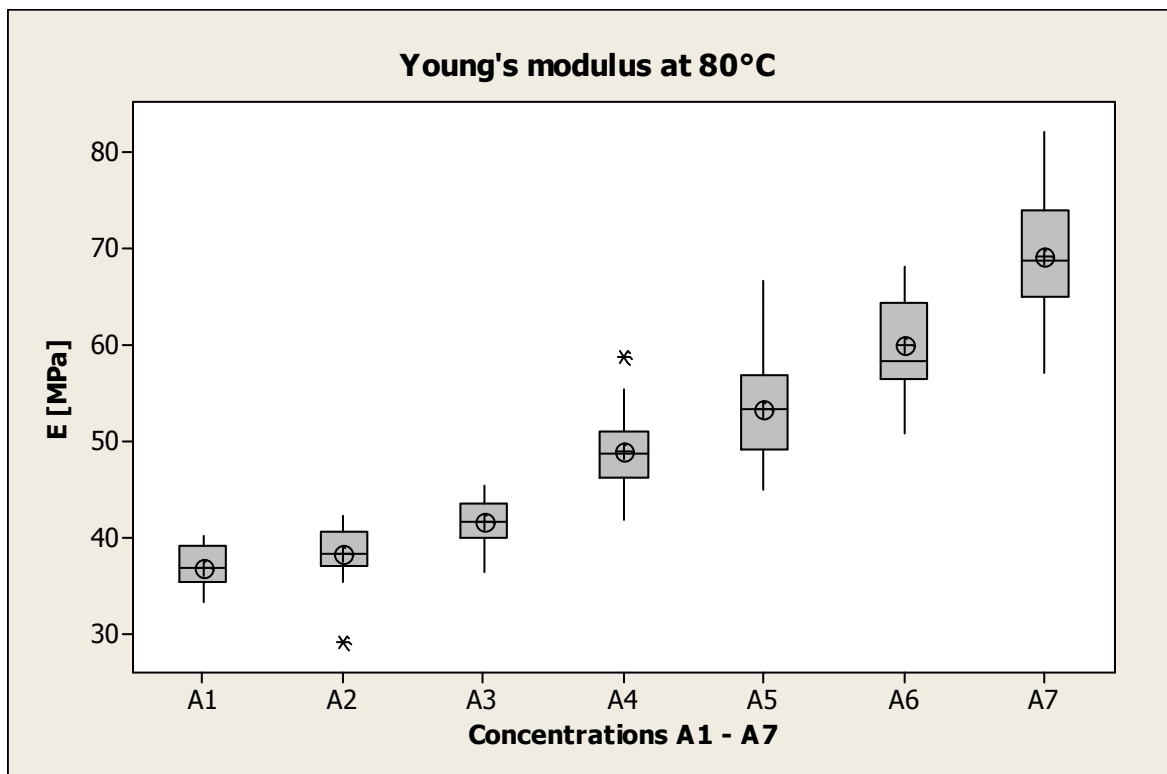


Fig. 49: Data quality of Young's modulus at 80°C (Gr + Gr(r))

Tab. 17: Nominal strain at Rm of Gr + Gr(r) (80°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	65.67	0.67	2.98	60.82	63.39	65.21	68.83	70.35	5.44
A2	43.81	1.71	7.66	27.85	38.86	44.14	50.21	55.27	11.35
A3	37.39	1.11	4.97	26.56	34.38	38.02	41.07	44.85	6.69
A4	29.40	1.15	5.13	17.95	24.97	30.77	33.24	36.51	8.28
A5	23.59	0.73	3.27	16.22	21.18	24.00	26.29	29.08	5.11
A6	20.10	0.50	2.21	16.31	18.75	20.31	20.93	25.76	2.19
A7	18.67	0.62	2.76	12.98	16.04	19.35	20.36	23.23	4.33

The values for nominal strain at elevated temperature have a relatively large IQR (especially A2 concentration) and almost every concentration have the value of arithmetic mean slightly far from median. The best quality of measured values seems to have an A6 concentration despite a probable distant value.

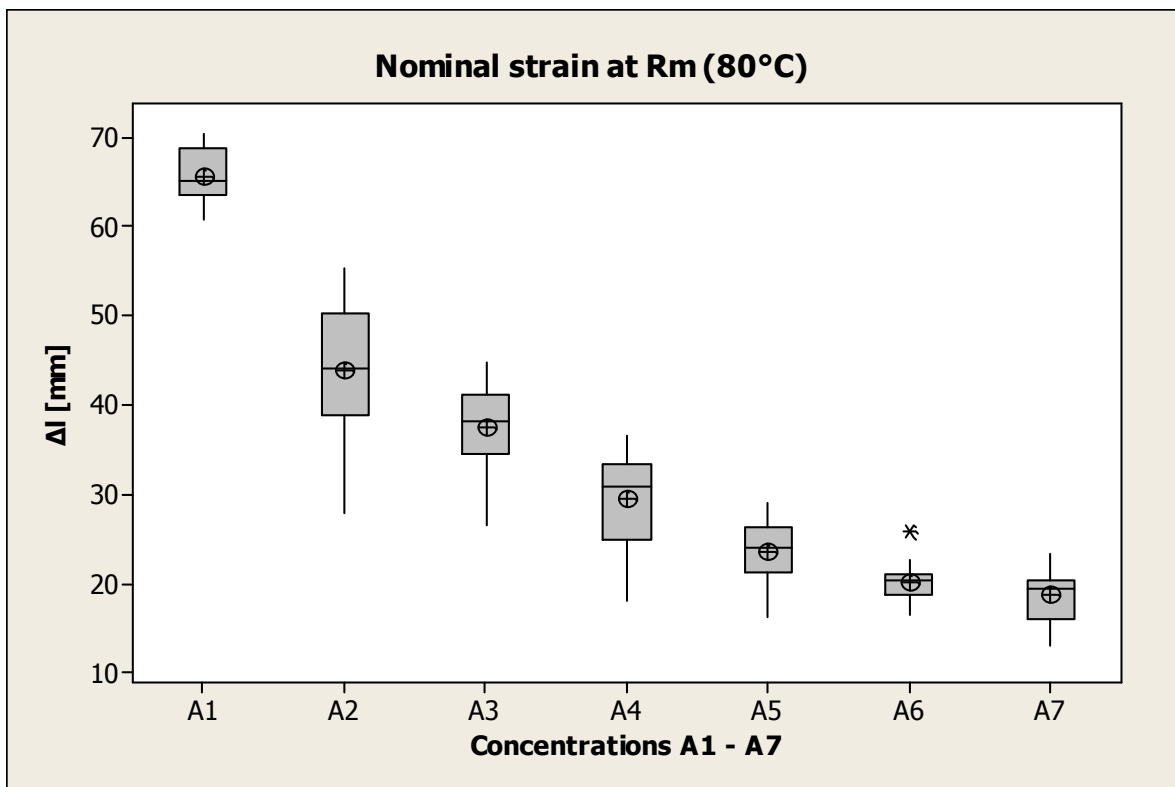


Fig. 50: Data quality of nominal strain at Rm of Gr + Gr(r) (80°C)

Tab. 18: Ultimate tensile strength of Gr + Gr(r) at 80°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
A1	4.64	0.04	0.17	4.35	4.51	4.63	4.79	4.90	0.28
A2	4.31	0.06	0.28	3.86	4.05	4.34	4.48	4.81	0.43
A3	4.40	0.04	0.16	4.07	4.26	4.42	4.53	4.66	0.27
A4	4.36	0.04	0.19	3.91	4.23	4.42	4.48	4.57	0.25
A5	4.49	0.10	0.44	3.87	4.28	4.44	4.57	6.09	0.29
A6	4.68	0.03	0.15	4.37	4.62	4.69	4.77	4.95	0.16
A7	5.08	0.05	0.21	4.55	4.92	5.12	5.23	5.40	0.31

The values for concentration A7 contain a distant value with high probability as can be seen in Fig. 51. Another distant value is probable identified at A6 concentration.

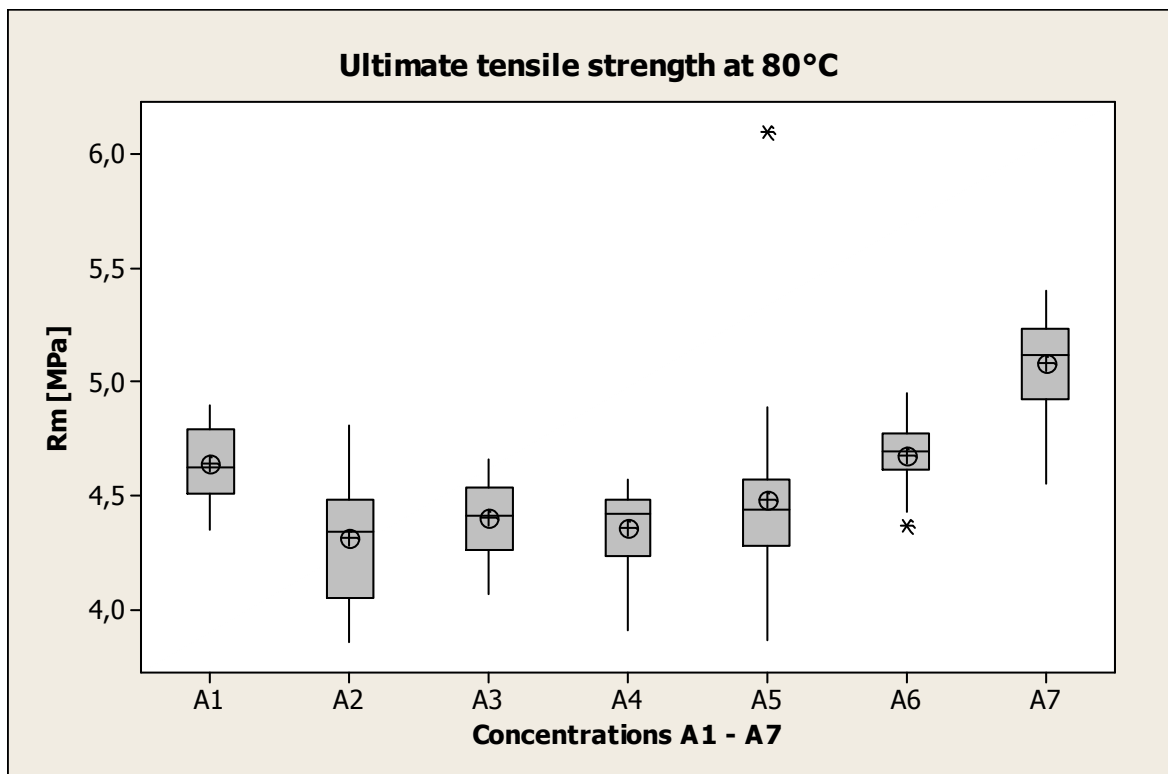


Fig. 51: Data quality of ultimate tensile strength at 80°C (Gr + Gr(r))

The following data are evaluated in the same sense, therefore for no other type of compound is given a detailed description of data quality and relevant box-plot diagrams are included in the Appendices. There are given only the relevant tables in which a data quality can be seen according to the above description.

At the temperature of 80 °C a significant decrease of all properties was measured at all concentrations. Thus, it was confirmed that the thermoplastics show a worse mechanical properties at an elevated temperature. The gradual addition of recyclate caused a grown of Young's modulus from original 36.87 MPa for the raw LDPE to 69.27 MPa for the highest concentration of recyclate in the compound. This increase corresponds to 187.9 %.

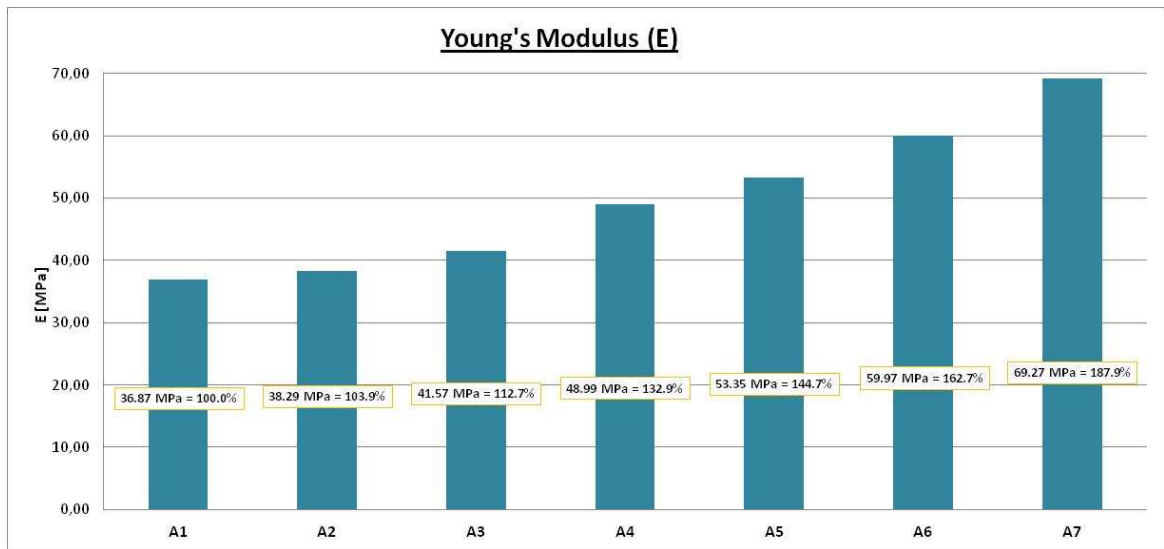


Fig. 52: Young's modulus of Gr + Gr(r) at 80°C

The strain at Rm of samples at temperature of 80 °C showed lower values first, where raw LDPE was extended by 65.67 mm, however at the content of recyclate equal to 20 % and higher, the specimens showed greater elongation compared to values measured for ambient temperature (24 °C). The total decrease to a value 18.67 mm for a recyclate content of 60 % was measured, which corresponds to 28.4 % of the initial elongation of raw LDPE.

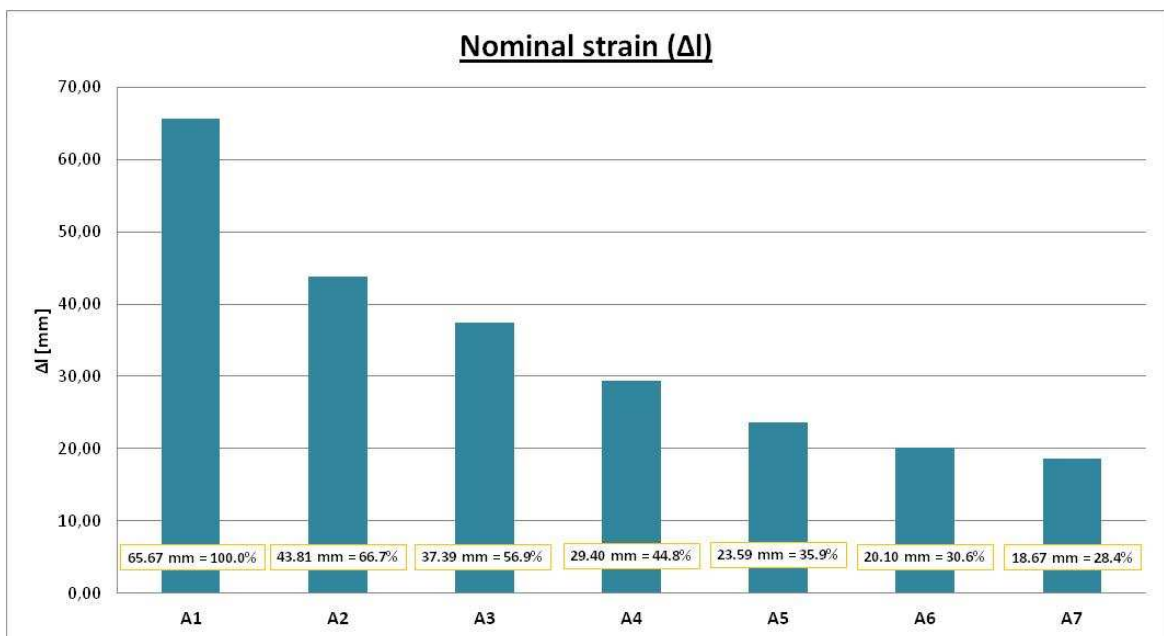


Fig. 53: Nominal strain at Rm of Gr + Gr(r) (80°C)

As can be seen in Fig. 54, the addition of recyclate caused a decrease of the ultimate strength to 4.31 MPa from the original 4.64 MPa. The ultimate strength stays almost constant at the content of 20 %, 30 % and 40 % recyclate. The increase occurs if the concentration of recyclate exceeds 50 %. The final increase to 109.5 % is seen at A7 concentration.

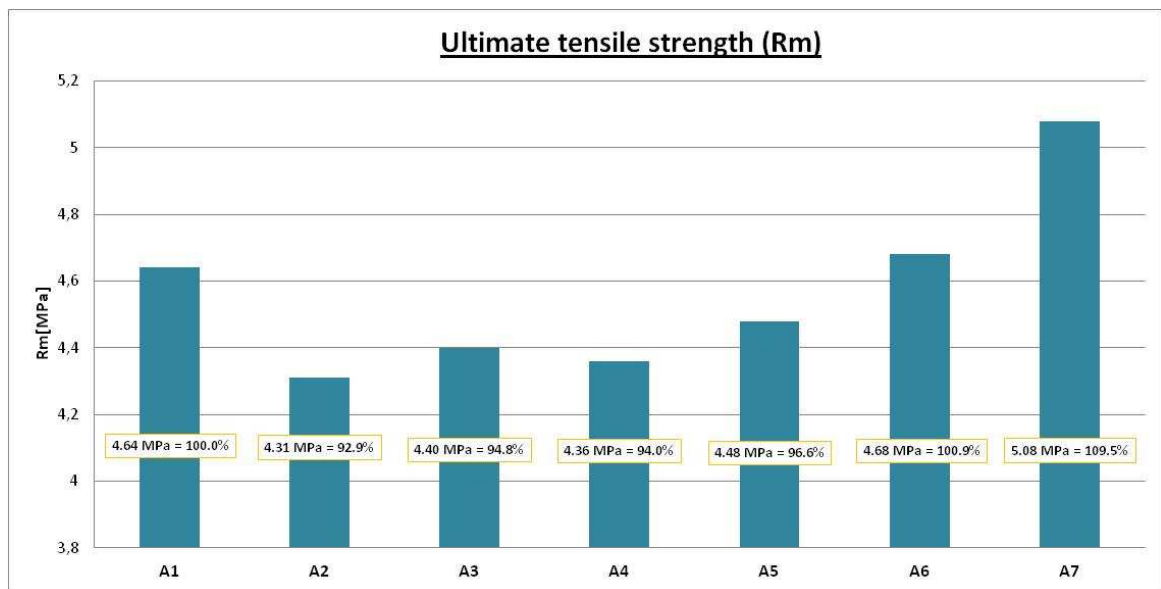


Fig. 54: Ultimate tensile strength of Gr + Gr(r) (80°C)

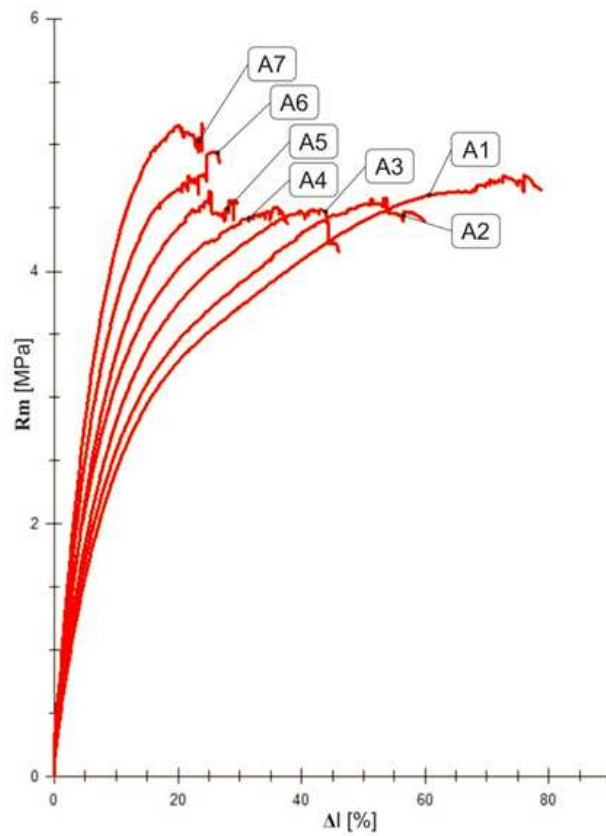


Fig. 55: Stress – strain curves for different concentrations of Gr + Gr(r) (80°C)

During the testing of this type of compounds, the damage of the specimen occurred always on the boundaries of the grit of recyclate. This fact is shown in Fig. 56.

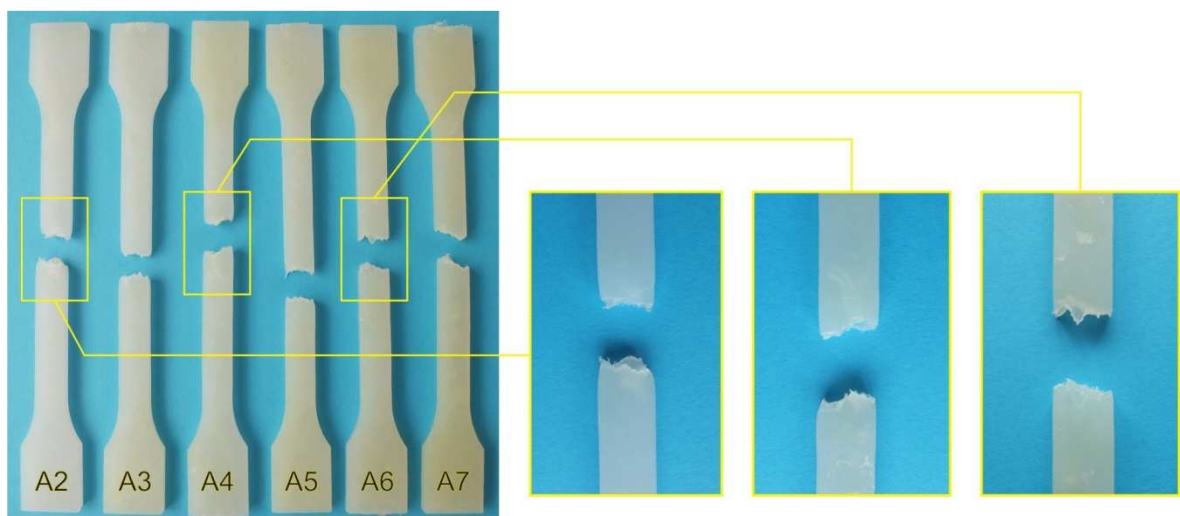


Fig. 56: Specimens after tensile testing

9.5.2 Measured data for granules of LDPE and powder of recyclate

Tab. 19: Young's modulus of Gr + Pr(r) at 24°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	231.37	1.91	8.53	215.89	227.04	231.07	236.65	251.61	9.61
B2	262.79	1.81	8.10	245.94	257.29	261.45	270.18	277.73	12.88
B3	291.25	2.45	10.94	274.64	281.12	291.31	299.11	315.40	18.00
B4	319.80	2.49	11.13	295.88	310.93	323.27	327.98	332.75	17.05
B5	371.50	1.95	8.72	355.23	364.65	373.55	378.20	390.57	13.55
B6	383.50	2.11	9.42	366.26	377.60	382.91	390.89	402.09	13.29
B7	428.09	3.09	13.83	401.93	420.57	428.44	441.70	446.82	21.13

Tab. 20: Nominal strain at Rm of Gr + Pr(r) (24°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	68.84	0.51	2.27	63.70	67.71	68.93	70.14	73.01	2.43
B2	54.32	0.41	1.83	52.08	52.72	53.72	55.22	58.14	2.50
B3	47.39	0.40	1.81	43.36	46.80	47.81	48.42	51.29	1.62
B4	38.99	0.34	1.53	37.42	37.62	38.40	40.90	41.39	3.28
B5	30.95	0.37	1.66	28.39	29.39	31.05	32.23	33.22	2.85
B6	26.97	0.36	1.60	23.17	26.19	27.05	28.32	29.43	2.14
B7	21.26	0.28	1.27	18.02	21.03	21.52	21.88	23.07	0.85

Tab. 21: Ultimate tensile strength of Gr + Pr(r) at 24°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	10.78	0.03	0.15	10.53	10.65	10.77	10.90	11.06	0.25
B2	11.23	0.03	0.15	10.90	11.15	11.22	11.33	11.63	0.18
B3	11.78	0.03	0.13	11.56	11.71	11.76	11.89	12.08	0.18
B4	12.45	0.02	0.09	12.29	12.36	12.46	12.50	12.58	0.14
B5	13.70	0.02	0.09	13.51	13.65	13.71	13.76	13.83	0.11
B6	14.12	0.05	0.22	13.86	13.94	14.06	14.31	14.55	0.37
B7	15.15	0.05	0.24	14.73	14.96	15.12	15.33	15.72	0.37

Compounds of LDPE granules and HDPEr powders showed again an increase of modulus of elasticity with growing concentration of recyclate. Young's modulus grew from the original value of 231.37 MPa to 428.09 MPa for B7 concentration. Thus, expressed in percentage, there was an increase of 185.0 %.

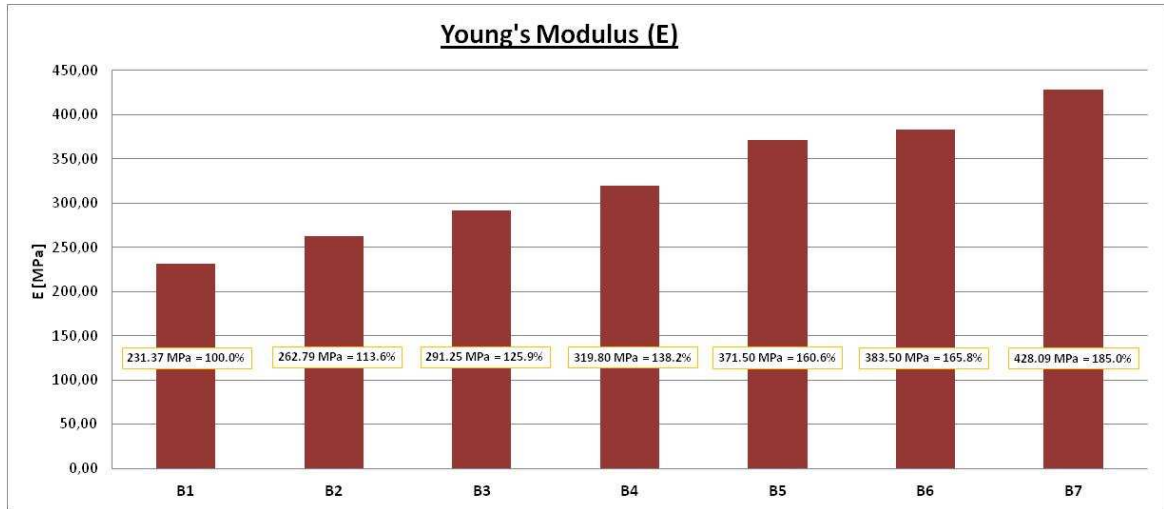


Fig. 57: Young's modulus of Gr + Pr(r) at 24°C

In the case of nominal strain of specimens at temperature of 24 °C was observed a minor decrease parallel as in the former type of compounds. Elongation decreased from the original 68.85 mm to 21.26 mm, which corresponds to 30.9 % compared to this original value.

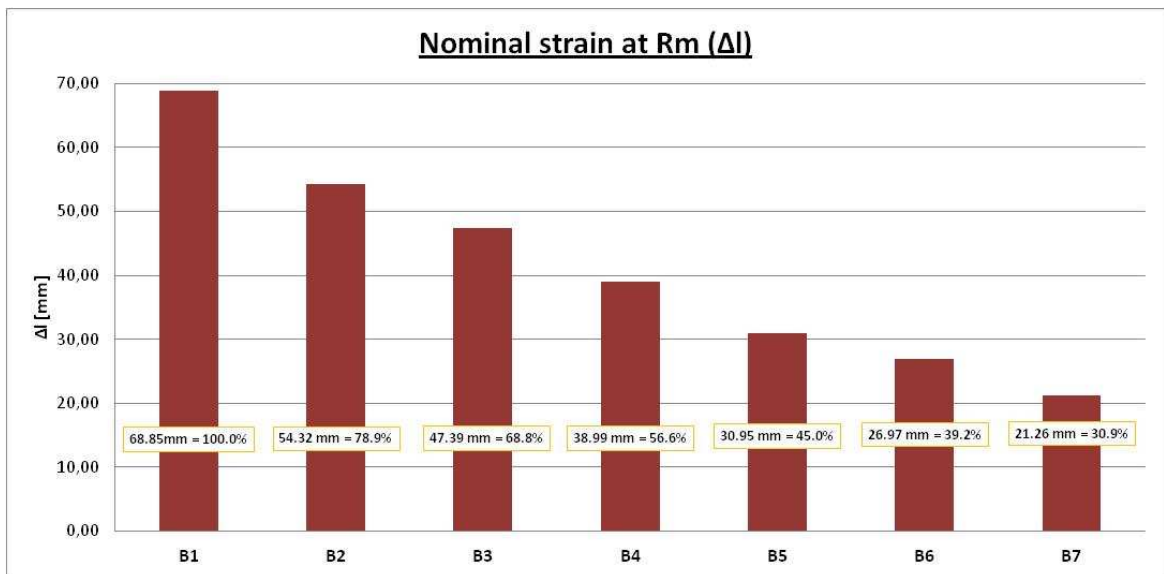


Fig. 58: Nominal strain at Rm of Gr + Pr(r) (24°C)

The ultimate tensile strength showed a gradual increase with growing content of recycle. Finally, this parameter has grown up to 140.6 % of original value in case of B7 concentration.

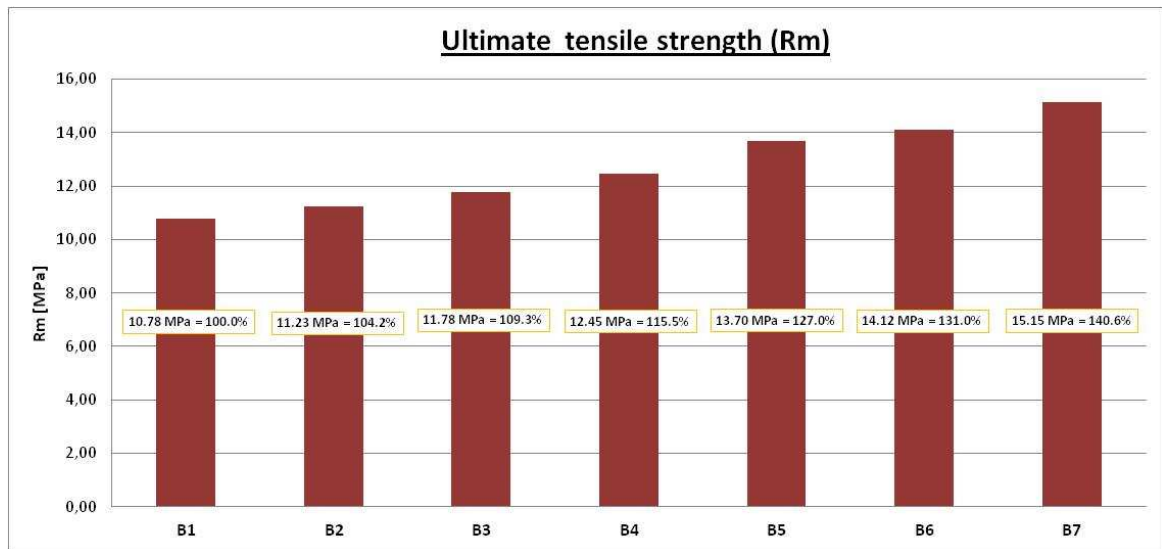


Fig. 59: Ultimate tensile strength of Gr + Pr(r) (24°C)

Fig. 60 shows the individual stress-strain curves. The curve for B1 concentration is not displayed because of its progress is identical to curve A1 in Fig. 48. Furthermore, smoother progress of individual curves without peaks can be seen compared to those displayed in Fig. 48. This fact can be mainly observed at lower concentrations.

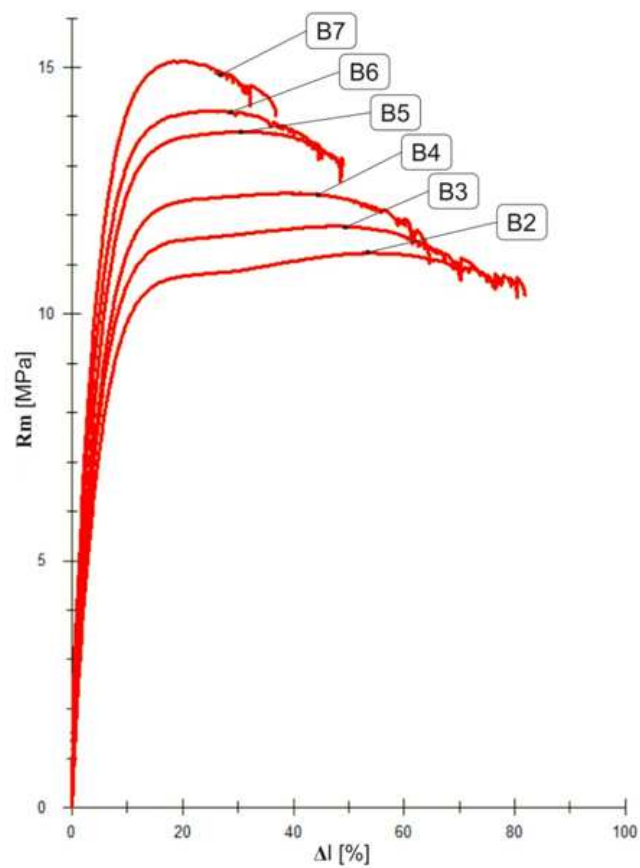


Fig. 60: Stress – strain curves for different concentrations of Gr + Pr(r) (80°C)

Tab. 22: Young’s modulus of Gr + Pr(r) at 80°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	36.87	0.47	2.11	33.21	35.34	36.73	39.08	40.13	3.73
B2	36.91	0.95	4.25	27.34	34.60	36.31	38.92	49.23	4.32
B3	40.04	0.78	3.50	33.06	36.99	40.16	43.06	44.89	6.06
B4	52.27	0.76	3.39	46.25	49.39	52.01	54.84	59.06	5.46
B5	57.11	1.01	4.54	48.39	53.12	56.83	60.81	63.81	7.68
B6	61.59	1.50	6.53	48.73	57.71	59.68	67.38	74.91	9.67
B7	71.07	1.12	4.90	63.53	66.86	71.51	76.01	79.12	9.15

Tab. 23: Nominal strain at Rm of Gr + Pr(r) (80°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	65.67	0.67	2.98	60.82	63.39	65.21	68.83	70.35	5.44
B2	56.96	0.51	2.30	53.17	54.33	57.52	58.00	62.39	3.67
B3	52.20	0.87	3.91	40.17	51.78	52.62	54.39	57.75	2.61
B4	46.47	0.85	3.81	36.95	44.86	47.53	48.76	53.05	3.90
B5	40.36	0.45	2.02	37.54	39.03	39.83	42.39	44.91	3.36
B6	36.91	0.62	2.68	32.17	34.73	37.41	38.18	42.74	3.45
B7	29.75	0.59	2.57	26.12	27.37	29.77	32.45	32.88	5.08

Tab. 24: Ultimate tensile strength of Gr + Pr(r) at 80°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
B1	4.64	0.04	0.17	4.35	4.51	4.63	4.79	4.90	0.28
B2	4.77	0.04	0.16	4.45	4.64	4.82	4.88	4.98	0.24
B3	4.94	0.05	0.21	4.42	4.80	4.91	5.12	5.23	0.31
B4	5.17	0.03	0.15	4.93	5.06	5.13	5.30	5.43	0.24
B5	5.61	0.05	0.22	5.13	5.50	5.61	5.76	5.97	0.27
B6	5.79	0.05	0.23	5.29	5.62	5.86	5.94	6.26	0.32
B7	6.04	0.04	0.19	5.74	5.90	5.97	6.15	6.51	0.25

The modulus of elasticity measured in the temperature chamber heated on 80 °C showed again a considerable decrease compared to values measured at the ambient temperature. Its value grew from 36.87 MPa to 71.07 MPa. Hence, there was a significant increase in the stiffness of the material equal to 192.8 % of original value.

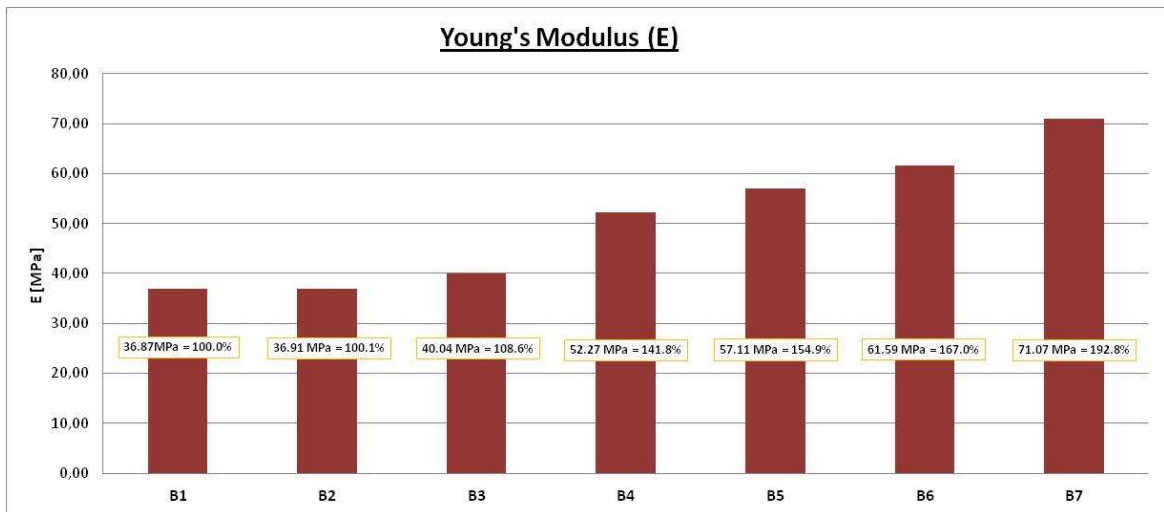


Fig. 61: Young's modulus of Gr + Pr(r) at 80°C

At the temperature of 80 °C the decrease of elongation as a result of filling is not so significant. Nominal strain at Rm decreased to 45.3 % of original value which corresponds to 29.76 mm.

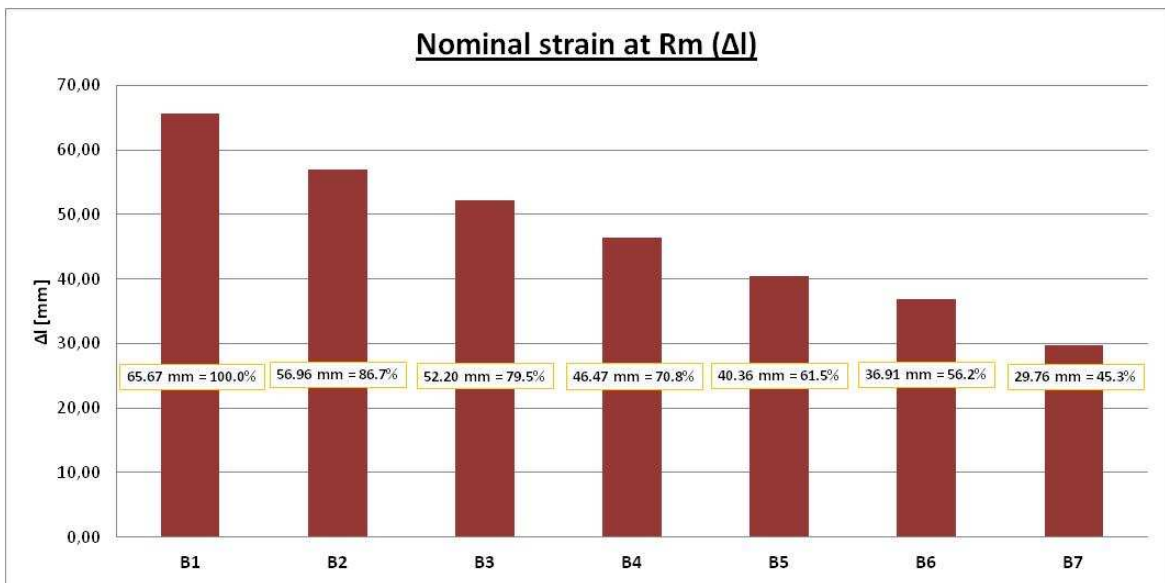


Fig. 62: Nominal strain at Rm of Gr + Pr(r) (80°C)

The ultimate tensile strength grows gradually again with increasing amount of recycle. Its value grows from 4.64 MPa to 6.04 MPa. This rise is equal to an increase of 130.1 %. The progress of stress-strain curves is shown in Fig. 64.

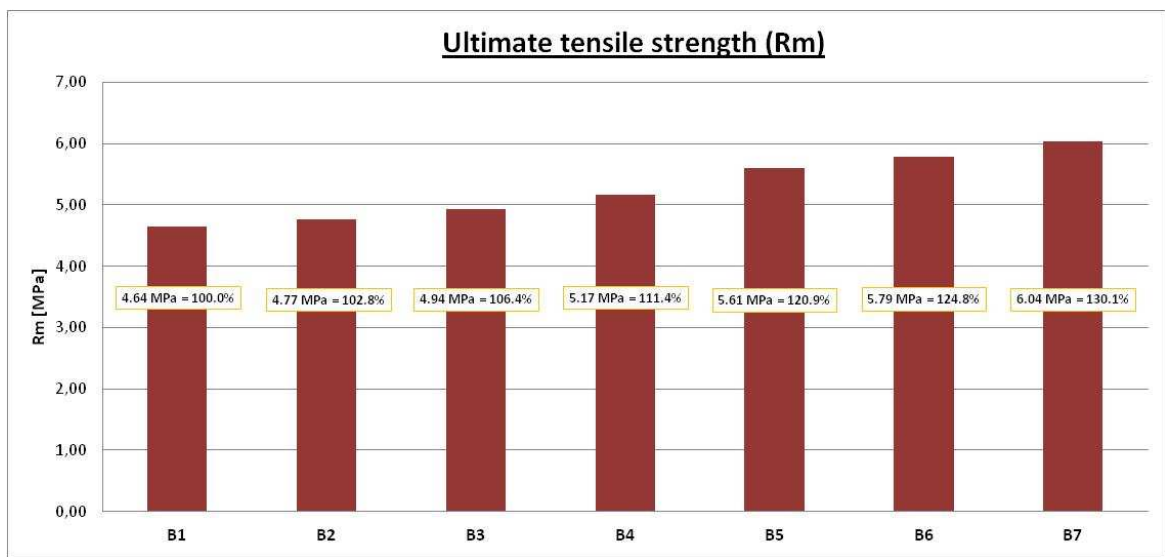


Fig. 63: Ultimate tensile strength of Gr + Pr(r) (80°C)

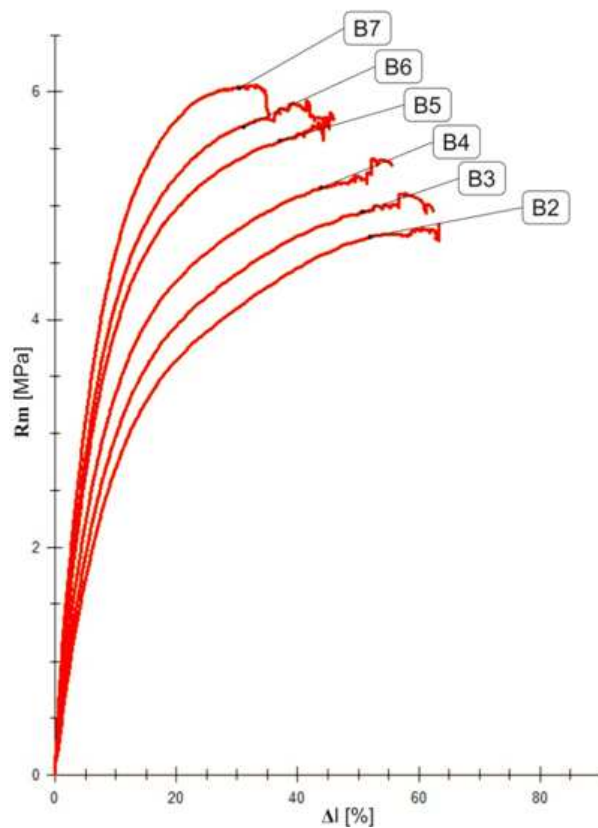


Fig. 64: Stress – strain curves for different concentrations of Gr + Pr(r) (80°C)

9.5.3 Measured data for powder of LDPE and powder of recycle

Tab. 25: Young's modulus of Pr + Pr(r) at 24°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	239.23	2.89	12.94	205.35	230.96	239.77	249.43	258.80	18.47
C2	253.85	1.51	6.77	240.77	249.47	252.38	259.87	265.31	10.40
C3	293.03	1.84	8.24	268.14	291.36	293.90	298.14	305.46	6.78
C4	339.01	2.27	10.14	320.08	332.81	337.52	348.75	355.18	15.94
C5	380.49	2.69	12.05	365.33	370.55	376.81	387.99	412.37	17.44
C6	418.53	3.09	13.84	404.90	408.86	415.85	421.12	463.05	12.26
C7	448.05	2.54	11.36	428.39	441.95	446.20	452.56	476.85	10.60

Tab. 26: Nominal strain at Rm of Pr + Pr(r) (24°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	62.82	0.38	1.69	58.78	62.11	62.91	63.97	65.26	1.86
C2	56.13	0.48	2.15	51.99	54.20	56.78	57.67	59.22	3.48
C3	46.97	0.40	1.78	43.34	45.39	47.34	48.19	50.11	2.81
C4	36.07	0.54	2.42	29.52	34.20	36.94	37.61	38.58	3.41
C5	25.74	0.38	1.71	22.71	23.87	26.34	26.98	28.70	3.11
C6	21.28	0.34	1.51	17.88	20.38	21.68	22.43	23.28	2.05
C7	18.53	0.32	1.42	16.01	17.23	18.66	19.56	20.84	2.33

Tab. 27: Ultimate tensile strength of Pr + Pr(r) at 24°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	10.53	0.03	0.14	10.40	10.45	10.48	10.56	10.99	0.11
C2	10.96	0.02	0.07	10.82	10.91	10.98	11.03	11.04	0.12
C3	11.79	0.02	0.07	11.60	11.76	11.80	11.82	11.93	0.06
C4	12.62	0.02	0.11	12.42	12.54	12.63	12.71	12.85	0.18
C5	13.64	0.02	0.08	13.43	13.61	13.66	13.70	13.81	0.09
C6	14.72	0.04	0.18	14.35	14.59	14.72	14.85	15.06	0.26
C7	15.49	0.04	0.18	15.21	15.38	15.46	15.61	15.87	0.24

Compounds made from the both material in the form of powder show the increase of stiffness from original value of 239.21 MPa for raw powder LDPE to 448.05 MPa for the compound with 60 % of powder recycle. Therefore, Young’s modulus was increased by 187.3 %.

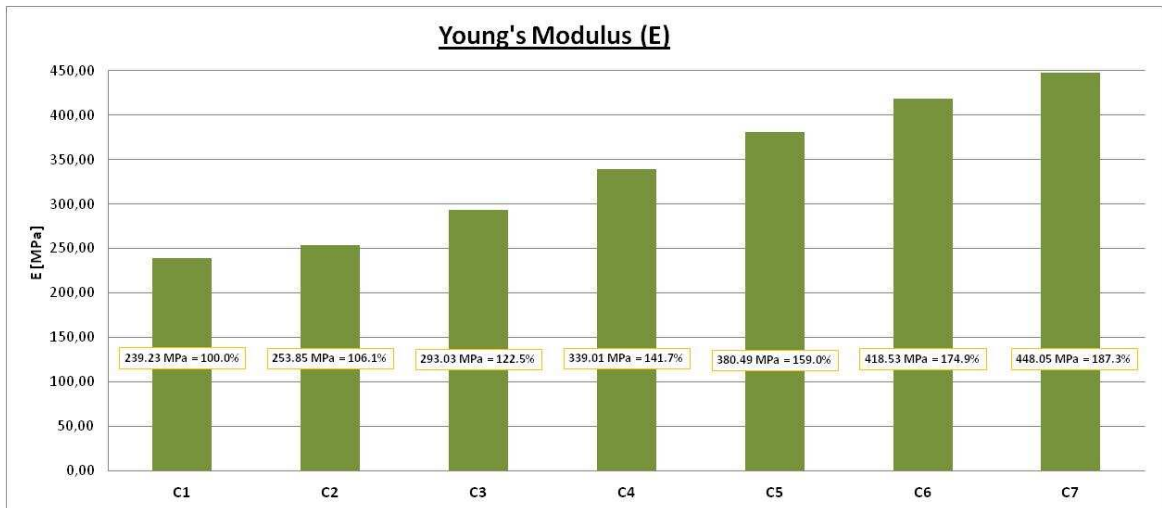


Fig. 65: Young’s modulus of Pr + Pr(r) at 24°C

The elongation of samples at the ambient temperature decreased again with a growing content of recycle in the compound. Total nominal strain at Rm of a compound with 60 % of recycle (C7) is equal to 18.53 mm, which corresponds to the 29.5 % of original value equal to 62.82 mm.

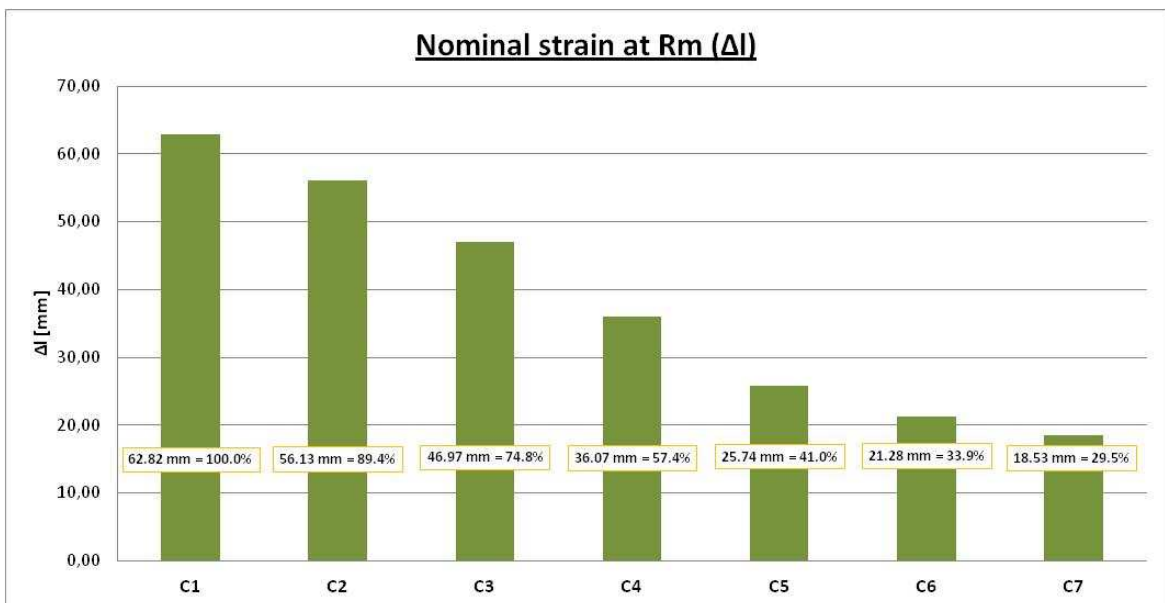


Fig. 66: Nominal strain at Rm of Pr + Pr(r) (24°C)

Ultimate tensile strength of powder compounds at temperature of 24 °C slowly grew from the original 10.53 MPa for raw powder of LDPE to a value of 15.49 MPa for concentration C7. Expressed in percentage an increase is equal to 147.1 %.

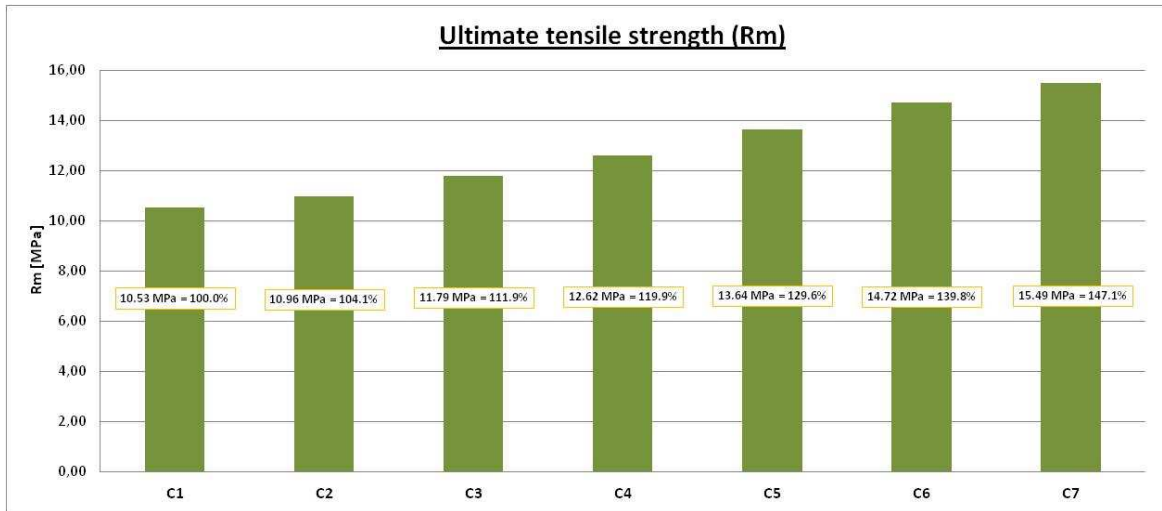


Fig. 67: Ultimate tensile strength of Pr + Pr(r) (24°C)

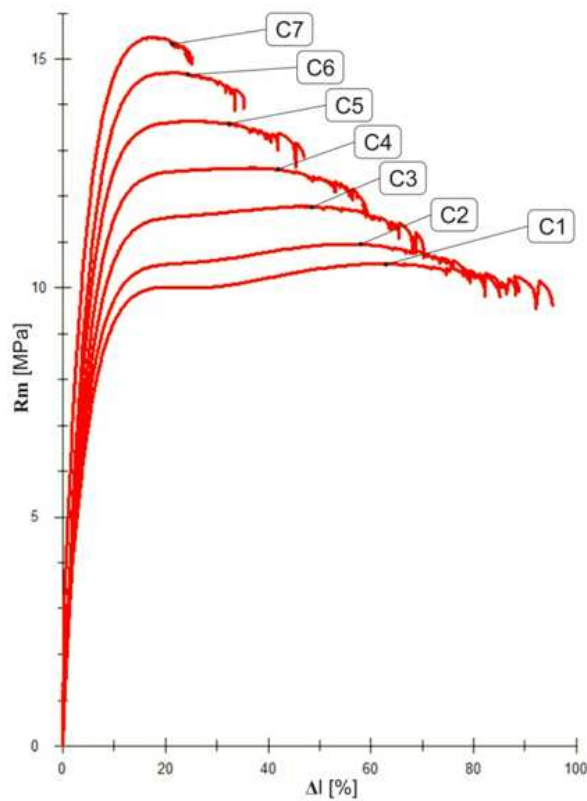


Fig. 68: Stress – strain curves for different concentrations of Pr + Pr(r) (24°C)

Tab. 28: Young's modulus of Pr + Pr(r) at 80°C - E [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	33.86	1.57	7.01	21.48	29.93	33.34	40.86	45.00	10.93
C2	31.80	1.00	4.49	24.05	28.77	30.73	35.65	41.83	6.88
C3	37.53	1.48	6.61	26.23	33.20	37.20	42.20	50.91	9.00
C4	50.93	0.80	3.59	42.04	48.86	51.72	53.35	56.43	4.50
C5	62.33	1.05	4.69	54.35	59.83	62.95	64.39	76.77	4.56
C6	70.47	1.24	5.55	61.72	66.49	70.50	73.73	86.62	7.25
C7	72.46	1.66	7.42	60.61	64.44	73.88	77.68	85.06	13.24

Tab. 29: Nominal strain at Rm of Pr + Pr(r) (80°C) - Δl [mm]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	61.31	0.64	2.84	56.57	58.28	62.49	63.92	64.72	5.64
C2	56.49	0.53	2.36	52.33	54.27	57.13	58.20	59.86	3.93
C3	51.81	0.78	3.51	39.87	51.25	52.23	52.84	58.26	1.60
C4	44.75	0.50	2.23	40.17	43.31	44.40	47.15	48.05	3.84
C5	34.93	0.59	2.66	29.50	33.17	34.31	37.65	39.35	4.48
C6	32.10	0.47	2.08	27.70	31.85	32.45	32.70	35.17	0.85
C7	27.85	0.76	3.39	22.84	24.91	27.14	31.27	33.63	6.37

Tab. 30: Ultimate tensile strength of Pr + Pr(r) at 80°C - Rm [MPa]

	\bar{x}	u_A	s	Min	Q1	Median	Q3	Max	IQR
C1	4.70	0.03	0.12	4.41	4.64	4.72	4.77	4.92	0.13
C2	4.73	0.02	0.10	4.53	4.69	4.72	4.78	4.95	0.09
C3	4.91	0.04	0.17	4.46	4.81	4.95	5.02	5.15	0.21
C4	5.13	0.04	0.16	4.88	5.01	5.14	5.20	5.43	0.19
C5	5.22	0.03	0.12	5.01	5.13	5.24	5.32	5.43	0.20
C6	5.45	0.04	0.17	5.15	5.34	5.42	5.60	5.73	0.27
C7	6.01	0.03	0.15	5.79	5.88	6.03	6.13	6.32	0.25

At elevated temperature was initially observed a decrease of modulus of elasticity at the compound with 10 % of recycle, from original 33.86 MPa to 31.80 MPa. This decrease is equal to 6.1 %. After that, an increase of modulus was measured with additional growth of recycle in the compound. C7 compound has a Young’s modulus equal to 72.46 MPa, which corresponds to 214.9 % of increase.

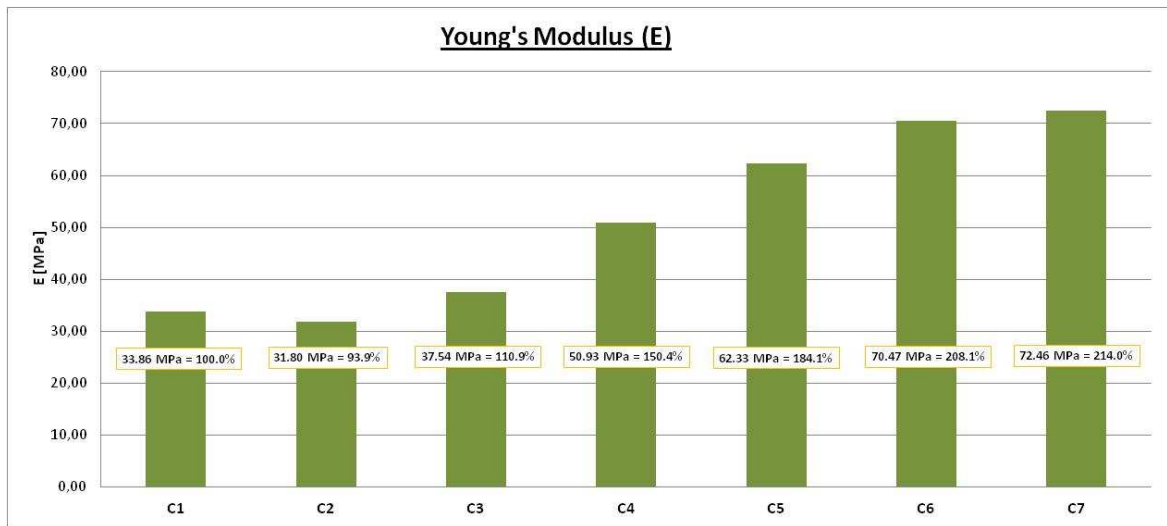


Fig. 69: Young’s modulus of Pr + Pr(r) at 80°C

The elongation of specimens declined very slowly at elevated temperature from the original 61.31 mm to 27.85 mm. That decrease corresponds to 45.4 % of original value.

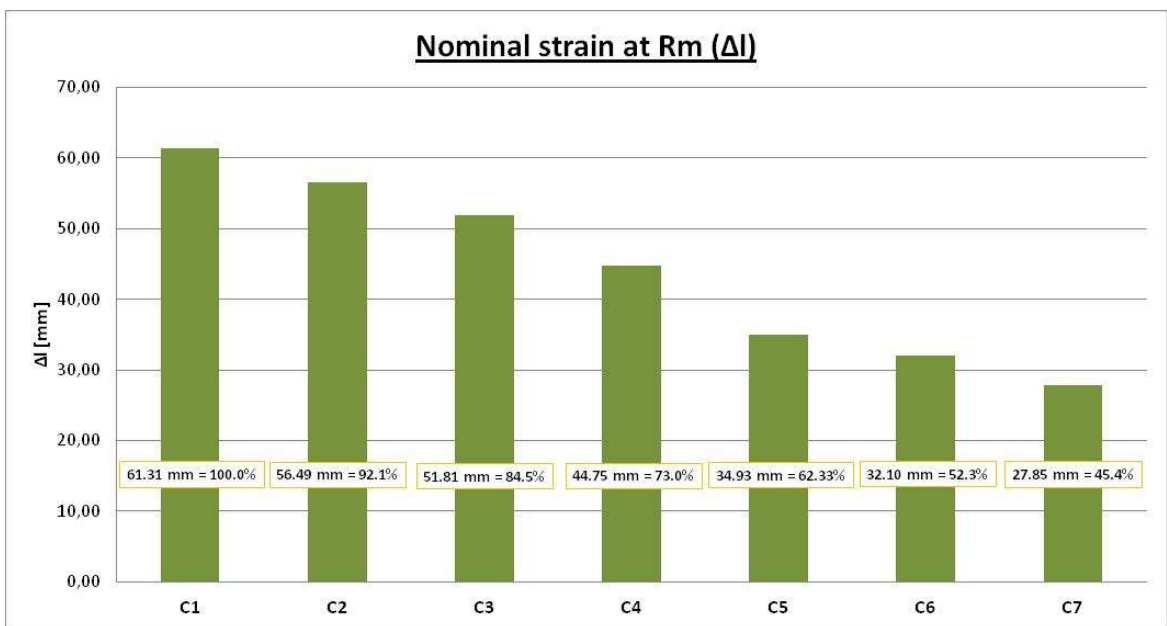


Fig. 70: Nominal strain at Rm of Pr + Pr(r) (80°C)

The ultimate tensile strength of powder mixtures grew very slowly. Last compound shows an increase of this parameter to 6.01 MPa. It is an increase to 128.1 % of original value for LDPE.

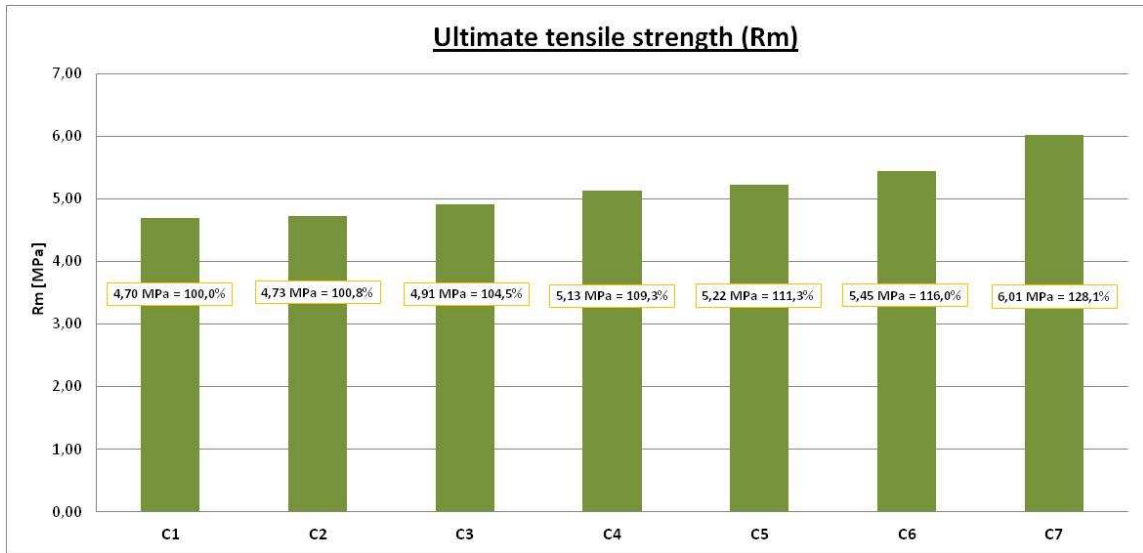


Fig. 71: Ultimate tensile strength of Pr + Pr(r) (80°C)

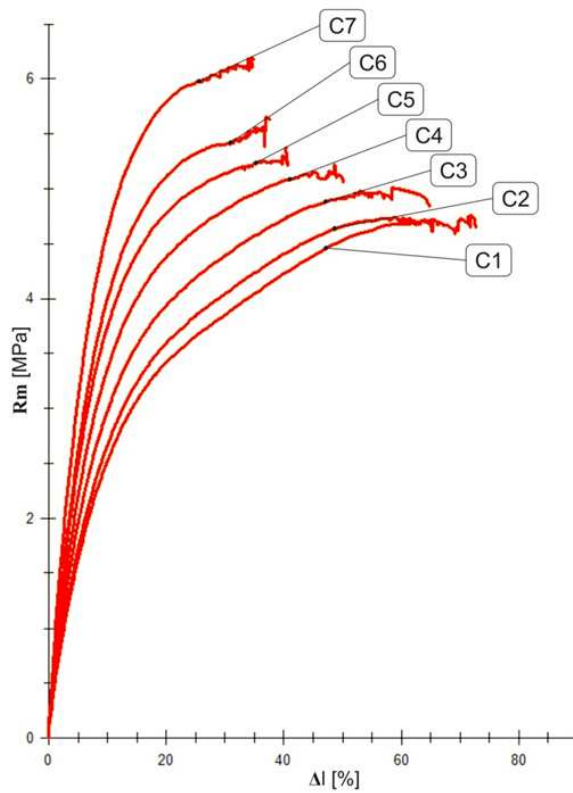


Fig. 72: Stress – strain curves for different concentrations of Pr + Pr(r) (80°C)

9.6 Results discussion for tensile test

Common bar charts of individual compounds were made for clearer comparison, showing all three measured mechanical properties for both temperatures.

❖ *Young's modulus at 24 °C*

When comparing the modulus of elasticity for all prepared compounds, at ambient temperature (Fig. 73) the highest values of this parameter had compounds consisting the grit of recyclate in the largest concentrations similarly as compounds prepared from the powder of both materials. Conversely, lower values showed at higher concentrations compounds of LDPE granules and powder recyclate. At lower concentrations are observed only minor differences in values.

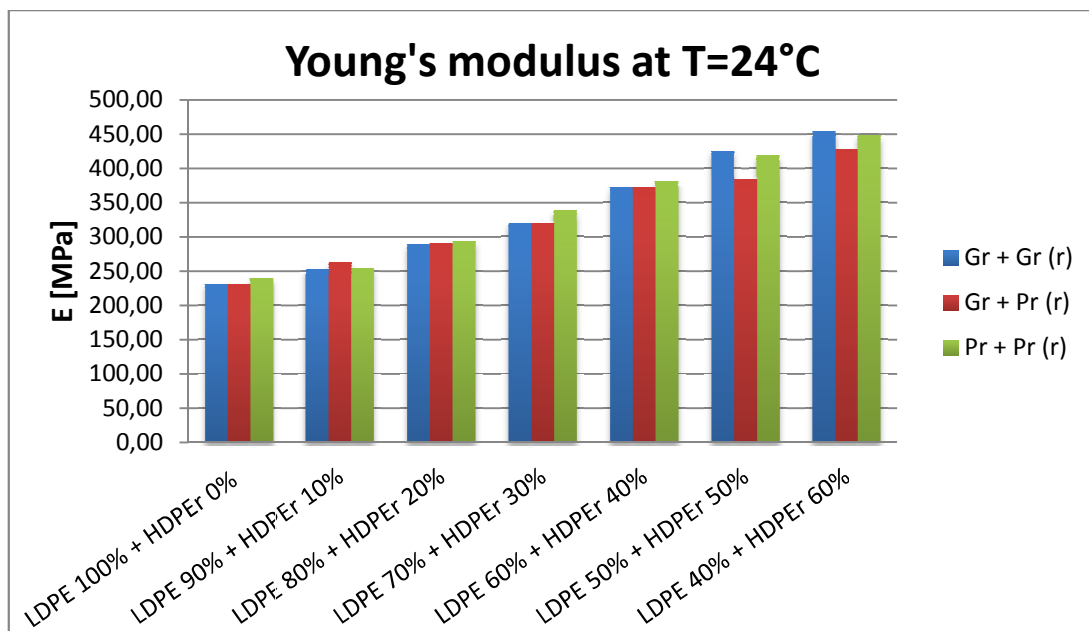


Fig. 73: Young's modulus for individual types of compounds (T=24°C)

❖ *Young's modulus at 80 °C*

Absolutely opposite case occurred at elevated temperature (Fig. 74), when compounds with a grit of recyclate exceeded the other types of compounds in lower concentrations. When the content of recyclate in the compounds was equal to 30 %, compounds of LDPE granules and powder recyclate showed the highest value of the Young's modulus of elasticity at elevated temperature. At higher concentration of recyclate excelled again compounds prepared from a powder of both materials. Another fact is that the basic material in the form of granules had at elevated temperature larger modulus than the material in the powder form and at ambient temperature it was contrary.

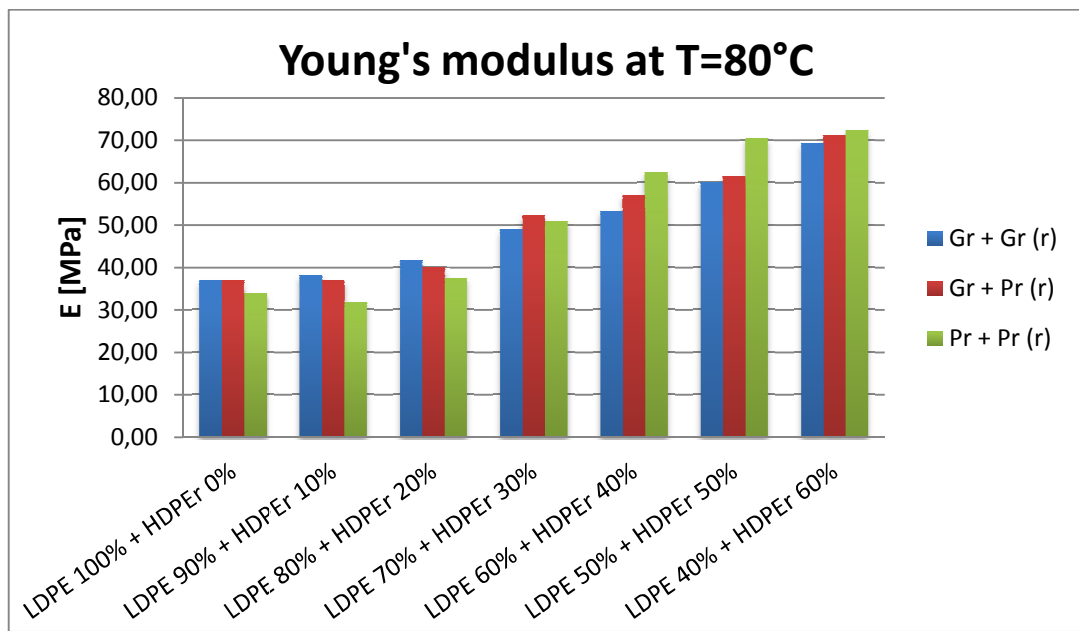


Fig. 74: Young's modulus for individual types of compounds (T=80°C)

❖ *Nominal strain at Rm for T=24 °C and T=80 °C*

Elongation of the test specimens decreased for all types of compounds (Fig. 75 and Fig. 76), where the larger drop at ambient and elevated temperature showed compounds of LDPE granules and recyclate grit. Overall, the lowest drop of ductility at both temperatures had compounds prepared from LDPE granules and recyclate powder.

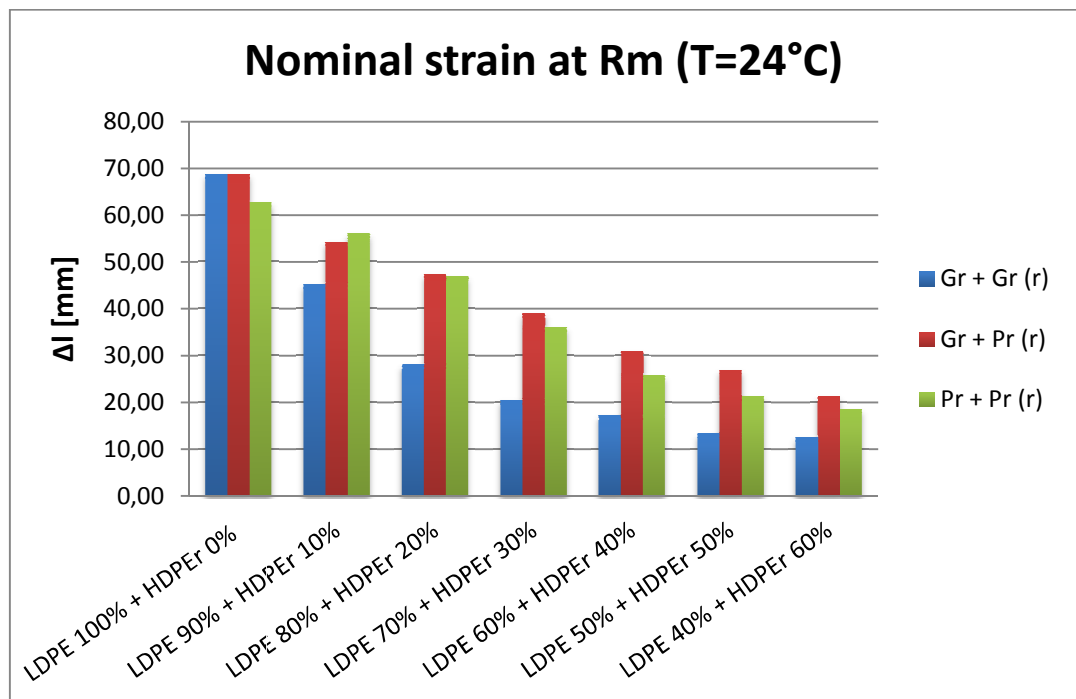


Fig. 75: Nominal strain at Rm for individual types of compounds (T=24°C)

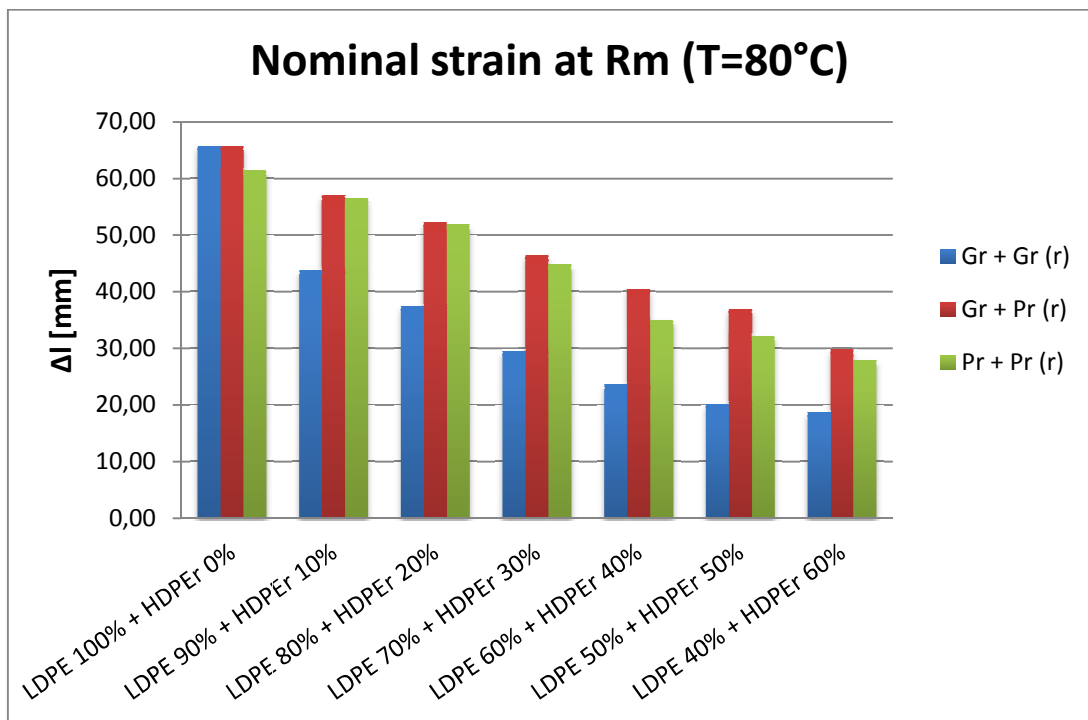


Fig. 76: Nominal strain at Rm for individual types of compounds (T=80°C)

The lowest values of elongation showed compounds containing a grit of recyclate apparently because the particles of grit in produced specimens are not quite evenly dispersed and also the shape and size of grit contributes to the creation of the crack and their subsequent propagation in the specimen. In contrast, the particles of recyclate are better dispersed in compounds, in which is recyclate in the form of powder. This dispersion and greater homogeneity certainly also affects the ultimate tensile strength. Furthermore, it is necessary to note that a basic material (LDPE) in the form of granules had the greater ductility than LDPE in the form of powder.

❖ *Ultimate tensile strength at 24 °C*

The lowest values of tensile strength at temperature of 24 °C (Fig. 77) showed compounds containing a grit of recyclate. This decrease was not any significant contrary to other types of compounds. The highest values of ultimate strength had in most cases compounds prepared from a powder of both materials. Only in a case, when a content of recyclate in a compound with granules of LDPE was equal to 10 %, this compound showed higher value of ultimate strength than other types.

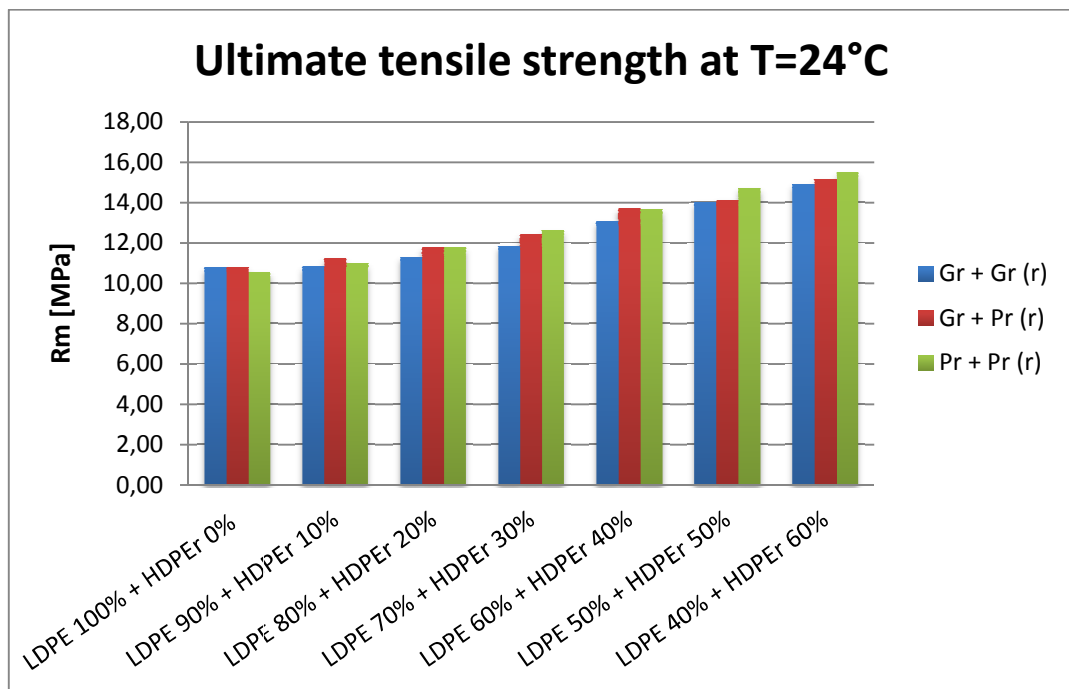


Fig. 77: Ultimate tensile strength for individual types of compounds (T=24°C)

❖ *Ultimate tensile strength at 80 °C*

At elevated temperature (Fig. 78) compounds prepared from the granules of LDPE and powder recyclate had the highest strength values in all cases. The lowest values showed again a compounds prepared from a grit of recyclate, where the value of the ultimate tensile strength of this compounds initially fell a then remained approximately constant.

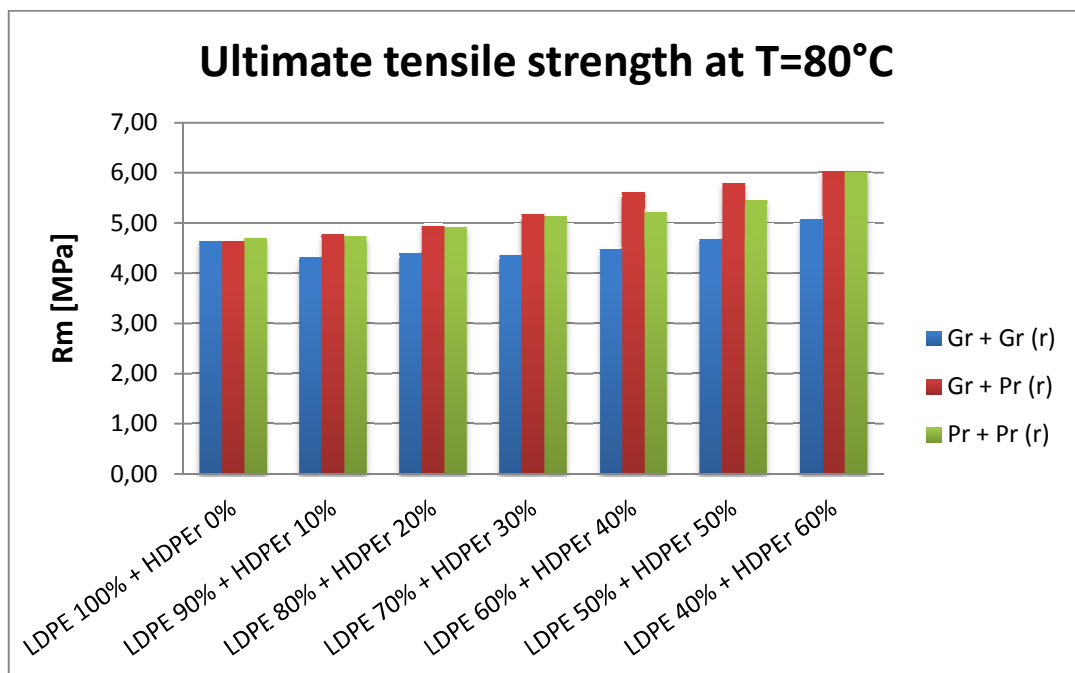


Fig. 78: Ultimate tensile strength for individual types of compounds (T=80°C)

CONCLUSION

The aim of this study was to explore the possibility of further use of irradiated material after the end of its lifetime. Recyclate was obtained from irradiated tubes, which were crushed to a grit and then grinded to a powder. From the recyclate were then prepared three types of compounds, in which recyclate and LDPE occurred in various forms. There was a sieving carried out before the preparation of powder compounds, which was used to determine the particle size of both powder materials.

In the production of testing specimens was observed gradual deterioration of the specimen's surface with growing content of recyclate in the compound. This deterioration resulted in the appearance of wrinkling and sink marks, especially for the compounds with a grit of recyclate. Other types of compounds had the same problems and also the problems with fluidity occurred. These problems were partially eliminated by adjustment of pressures and cooling times, but for the best surface quality of final product it would be necessary to optimize the process parameters.

The material was tested by tension at ambient and at elevated temperature. Individual results from the tests are commented in the relevant chapters and the overall comparison of the compounds according to the measured parameters is also commented in result discussion for tensile test. In the next section were measured flow properties for those compounds, for which it was possible according to the available measuring device. Further comments provides relevant chapter again.

Performed tests showed the possibilities of use of recycled material as a filler and also that it is possible to prepare the compounds of material, which will have improved mechanical properties compared to the raw material due to a filler recycled from irradiated HDPE. It is necessary to choose carefully the overall content of recyclate according to deterioration of flow properties with growing degree of filling.

Finally, it should be noted that the addition of recyclate changes the original color of material. Considering the measured data, the most advantageous is to use the powder recyclate as a filler, added to the basic material in the form of granules or powder.

On the other hand, recyclate processed into the form of grit is cheaper and can find application in hidden, less stressed and larger parts. The grit of recyclate has the main advantage that there is no next step in the processing of recycled material and its possible to use it without further modifications immediately after crushing in the rotary cutter mill. The main disadvantage of recyclate in the form of grit is bad dispersion of particles in the final product, especially at lower concentrations of recyclate.

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LIST OF ABBREVIATIONS

FDA	Food and Drug Administration
ISO	International Organization for Standardization
ASTM	American Society for Testing and Materials
MFR	Melt flow rate [g/10min]
E	Young's modulus of elasticity [MPa]
Rm	Ultimate tensile strength [MPa]
σ_Y	Yield strength [MPa]
Δl	Nominal strain at Rm [mm]
\bar{x}	Arithmetic mean [1]
s	Standard deviation [1]
u_A	Standard error of the mean [1]
Q1	First quartile [1]
Q3	Third quartile [1]
IQR	Interquartile range [1]
Gr	Granules of LDPE
Pr	Powder of LDPE
Gr(r)	Grit of recyclate
Pr(r)	Powder of recyclate
ν	Poisson's ratio [1]
ε	Elongation [%]
δ	Ductility [%]
PE	Polyethylene
PEXa	PE crosslinked by Peroxides
PEXb	PE crosslinked by Silanes
PEXc	PE crosslinked by radiation

LDPE	Low-density polyethylene
HDPE	High-density polyethylene
LLDPE	Linear low-density polyethylene
MDPE	Medium-density polyethylene
VLDPE	Very low-density polyethylene

LIST OF FIGURES

Fig. 1: Basic classification of polymers [4] 12

Fig. 2: World plastic production in 2009 [14] 13

Fig. 3: Division of plastics according to price and applications [26] 14

Fig. 4: Basic scheme of macromolecular substance [4]..... 14

Fig. 5: Types of macromolecules [7] 15

Fig. 6: Structure of copolymers [8]..... 15

Fig. 7: Constitution of macromolecules [8] 16

Fig. 8: Basic types of plastics [1]..... 17

Fig. 9: Types of polyethylene according to branching [1]..... 18

Fig. 10: PE applications [39] 21

Fig. 11: Schematic diagram of possible crosslinking [10]..... 23

Fig. 12: Mechanism of peroxide crosslinking [12]..... 24

Fig. 13: Mechanism of silane crosslinking [12] 25

Fig. 14: Scheme of radiation crosslinking by electrons [34] 26

Fig. 15: Scheme of radiation crosslinking by gamma rays [34] 27

Fig. 16: Mechanism of radiation crosslinking [12]..... 27

Fig. 17: Total recovery by country in Europe (2009) [14, 19] 29

Fig. 18: Life cycle of plastic product [15] 30

Fig. 19: Diagram of the operations in mechanical recycling [19] 31

Fig. 20: Recyclation codes by SPI [19] 32

Fig. 21: ‘Float-and-sink’ separation [19]..... 33

Fig. 22: Particles thermally agglomerated [19] 34

Fig. 23: Diagram of an incineration system [15] 38

Fig. 24: Shape and dimensions of specimen [27] 40

Fig. 25: Systems for gripping tensile specimens [20]..... 41

Fig. 26: Components of the electromechanical testing device [20]..... 42

Fig. 27: Stress – strain diagram [16]..... 43

Fig. 28: Melt flow rate apparatus [18] 45

Fig. 29: Rotary cutter mill RAPID SK 2218 49

Fig. 30: Laboratory pneumatic blender..... 50

Fig. 31: Injection molding machine Arburg Allrounder 420C [37] 50

Fig. 32: Universal testing machine ZWICK 1456 51

Fig. 33: Testing device for melt flow index Dynisco Kayeness LMI 4003.....	52
Fig. 34: Vibratory Sieve Shaker RETSCH AS 200 basic.....	53
Fig. 35: Processed tubes.....	55
Fig. 36: Crushed particles size.....	55
Fig. 37: Example of described box-plot diagram	59
Fig. 38: Particle size of LDPE powder	61
Fig. 39: Particle size of HPDEr powder recyclate	61
Fig. 40: Melt flow rate of Pr + Pr (r)	63
Fig. 41: Powder recyclate sedimentation during sample preparation.....	63
Fig. 42: Data quality of Young’s modulus at 24°C (Gr + Gr(r)).....	66
Fig. 43: Data quality of nominal strain at Rm of Gr + Gr(r) (24°C)	67
Fig. 44: Data quality of ultimate tensile strength at 24°C (Gr + Gr(r)).....	68
Fig. 45: Young’s modulus of Gr + Gr(r) at 24°C	68
Fig. 46: Nominal strain at Rm of Gr + Gr(r) (24°C)	69
Fig. 47: Ultimate tensile strength of Gr + Gr(r) (24°C).....	69
Fig. 48: Stress – strain curves for different concentrations of Gr + Gr(r) (24°C)	70
Fig. 49: Data quality of Young’s modulus at 80°C (Gr + Gr(r)).....	71
Fig. 50: Data quality of nominal strain at Rm of Gr + Gr(r) (80°C)	72
Fig. 51: Data quality of ultimate tensile strength at 80°C (Gr + Gr(r)).....	73
Fig. 52: Young’s modulus of Gr + Gr(r) at 80°C	74
Fig. 53: Nominal strain at Rm of Gr + Gr(r) (80°C)	74
Fig. 54: Ultimate tensile strength of Gr + Gr(r) (80°C).....	75
Fig. 55: Stress – strain curves for different concentrations of Gr + Gr(r) (80°C)	76
Fig. 56: Specimens after tensile testing	76
Fig. 57: Young’s modulus of Gr + Pr(r) at 24°C	78
Fig. 58: Nominal strain at Rm of Gr + Pr(r) (24°C)	78
Fig. 59: Ultimate tensile strength of Gr + Pr(r) (24°C)	79
Fig. 60: Stress – strain curves for different concentrations of Gr + Pr(r) (80°C).....	80
Fig. 61: Young’s modulus of Gr + Pr(r) at 80°C	82
Fig. 62: Nominal strain at Rm of Gr + Pr(r) (80°C)	82
Fig. 63: Ultimate tensile strength of Gr + Pr(r) (80°C)	83
Fig. 64: Stress – strain curves for different concentrations of Gr + Pr(r) (80°C).....	83
Fig. 65: Young’s modulus of Pr + Pr(r) at 24°C.....	85

Fig. 66: Nominal strain at Rm of Pr + Pr(r) (24°C).....	85
Fig. 67: Ultimate tensile strength of Pr + Pr(r) (24°C).....	86
Fig. 68: Stress – strain curves for different concentrations of Pr + Pr(r) (24°C).....	86
Fig. 69: Young’s modulus of Pr + Pr(r) at 80°C.....	88
Fig. 70: Nominal strain at Rm of Pr + Pr(r) (80°C).....	88
Fig. 71: Ultimate tensile strength of Pr + Pr(r) (80°C).....	89
Fig. 72: Stress – strain curves for different concentrations of Pr + Pr(r) (80°C).....	89
Fig. 73: Young’s modulus for individual types of compounds (T=24°C).....	90
Fig. 74: Young’s modulus for individual types of compounds (T=80°C).....	91
Fig. 75: Nominal strain at Rm for individual types of compounds (T=24°C).....	91
Fig. 76: Nominal strain at Rm for individual types of compounds (T=80°C).....	92
Fig. 77: Ultimate tensile strength for individual types of compounds (T=24°C).....	93
Fig. 78: Ultimate tensile strength for individual types of compounds (T=80°C).....	93

LIST OF TABLES

Tab. 1: Properties of different types of PE: [6].....	18
Tab. 2: Important types of fillers: [6]	23
Tab. 3: Predominant radiation-induced change at plastics: [13, 34]	28
Tab. 4: Dimensions of testing sample [27]	40
Tab. 5: Properties of DOW LDPE 780E [35].....	54
Tab. 6: Properties of TIPELIN PS 380-30/302 [36].....	54
Tab. 7: Concentrations of reground recyclate with granules of LDPE.....	56
Tab. 8: Concentrations of powder recyclate with granules of LDPE	56
Tab. 9: Concentrations of powder recyclate with powder of LDPE.....	57
Tab. 10: Measured data from sieving	60
Tab. 11: Melt flow rate of individual compounds	62
Tab. 12: Process parameters	64
Tab. 13: Young's modulus of Gr + Gr(r) at 24°C - E [MPa]	65
Tab. 14: Nominal strain at Rm of Gr + Gr(r) (24°C) - Δl [mm]	66
Tab. 15: Ultimate tensile strength of Gr + Gr(r) at 24°C - Rm [MPa]	67
Tab. 16: Young's modulus of Gr + Gr(r) at 80°C - E [MPa]	70
Tab. 17: Nominal strain at Rm of Gr + Gr(r) (80°C) - Δl [mm]	71
Tab. 18: Ultimate tensile strength of Gr + Gr(r) at 80°C - Rm [MPa]	72
Tab. 19: Young's modulus of Gr + Pr(r) at 24°C - E [MPa]	77
Tab. 20: Nominal strain at Rm of Gr + Pr(r) (24°C) - Δl [mm]	77
Tab. 21: Ultimate tensile strength of Gr + Pr(r) at 24°C - Rm [MPa]	77
Tab. 22: Young's modulus of Gr + Pr(r) at 80°C - E [MPa]	80
Tab. 23: Nominal strain at Rm of Gr + Pr(r) (80°C) - Δl [mm]	81
Tab. 24: Ultimate tensile strength of Gr + Pr(r) at 80°C - Rm [MPa]	81
Tab. 25: Young's modulus of Pr + Pr(r) at 24°C - E [MPa]	84
Tab. 26: Nominal strain at Rm of Pr + Pr(r) (24°C) - Δl [mm]	84
Tab. 27: Ultimate tensile strength of Pr + Pr(r) at 24°C - Rm [MPa]	84
Tab. 28: Young's modulus of Pr + Pr(r) at 80°C - E [MPa]	87
Tab. 29: Nominal strain at Rm of Pr + Pr(r) (80°C) - Δl [mm]	87
Tab. 30: Ultimate tensile strength of Pr + Pr(r) at 80°C - Rm [MPa]	87

APPENDICES

APPENDICE P I: Box-plot diagrams for Gr + Pr(r) at 24 °C

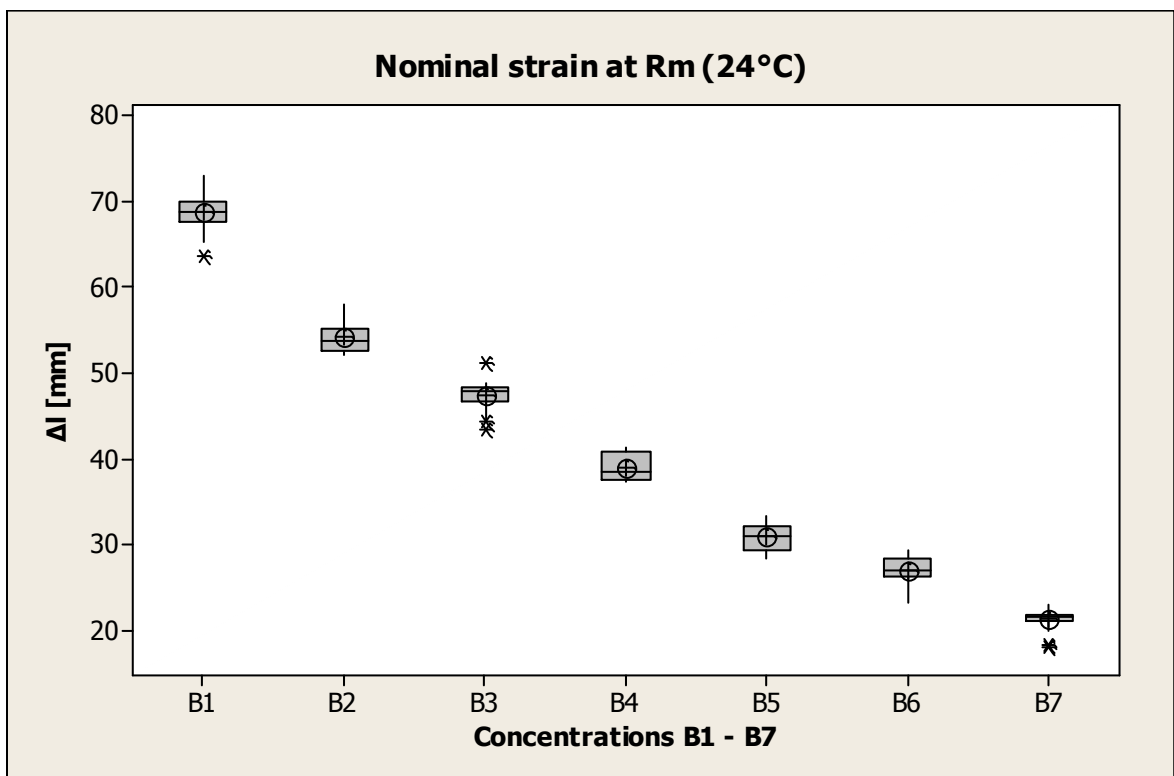
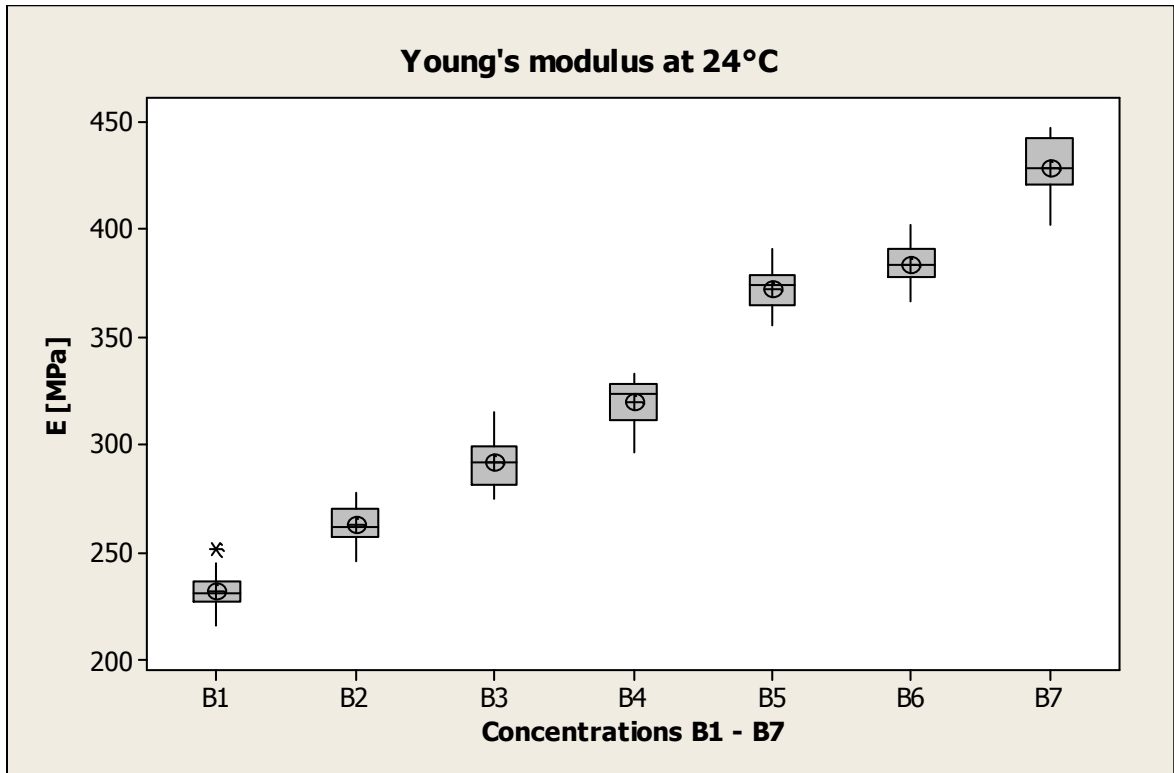
APPENDICE P II: Box-plot diagrams for Gr + Pr(r) at 80 °C

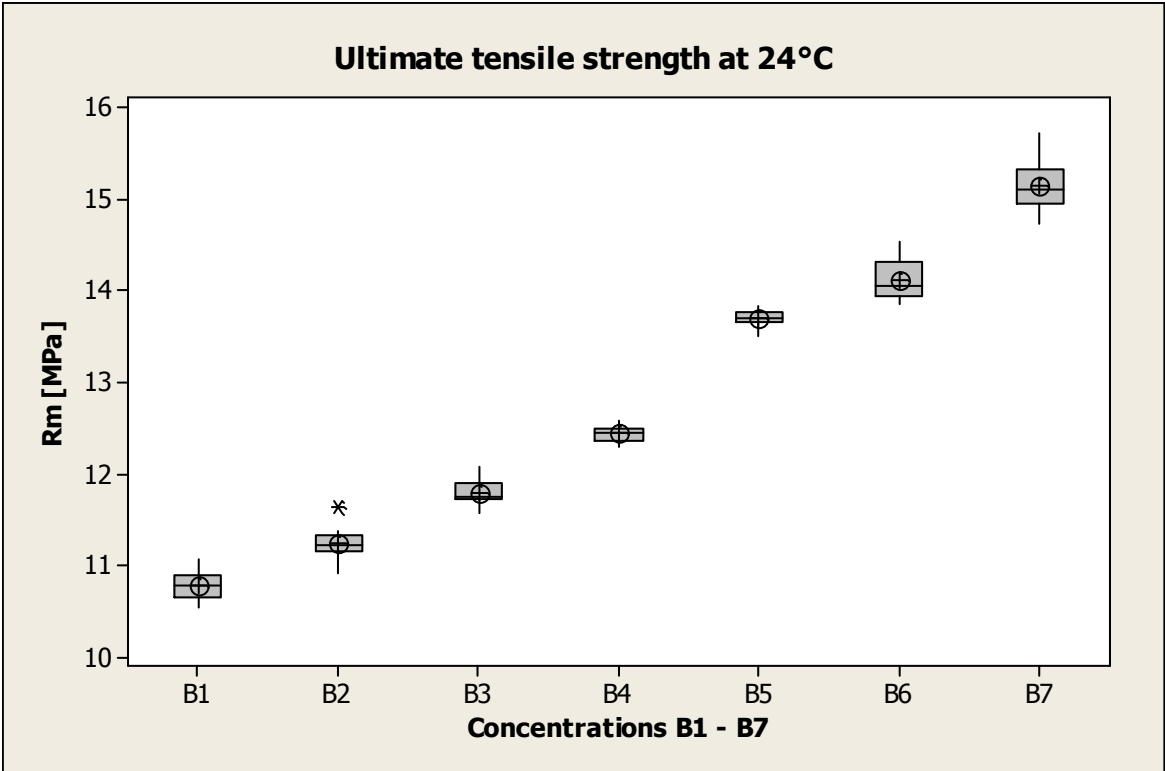
APPENDICE P III: Box-plot diagrams for Pr + Pr(r) at 24 °C

APPENDICE P IV: Box-plot diagrams for Pr + Pr(r) at 80 °C

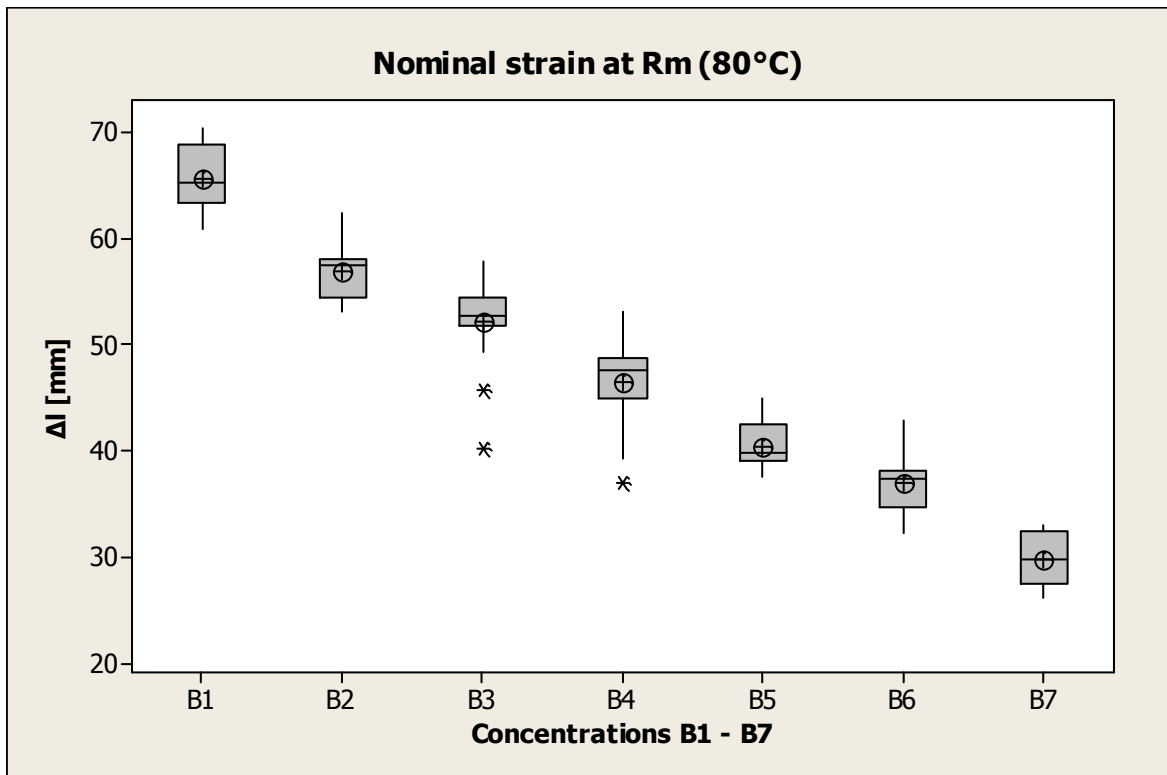
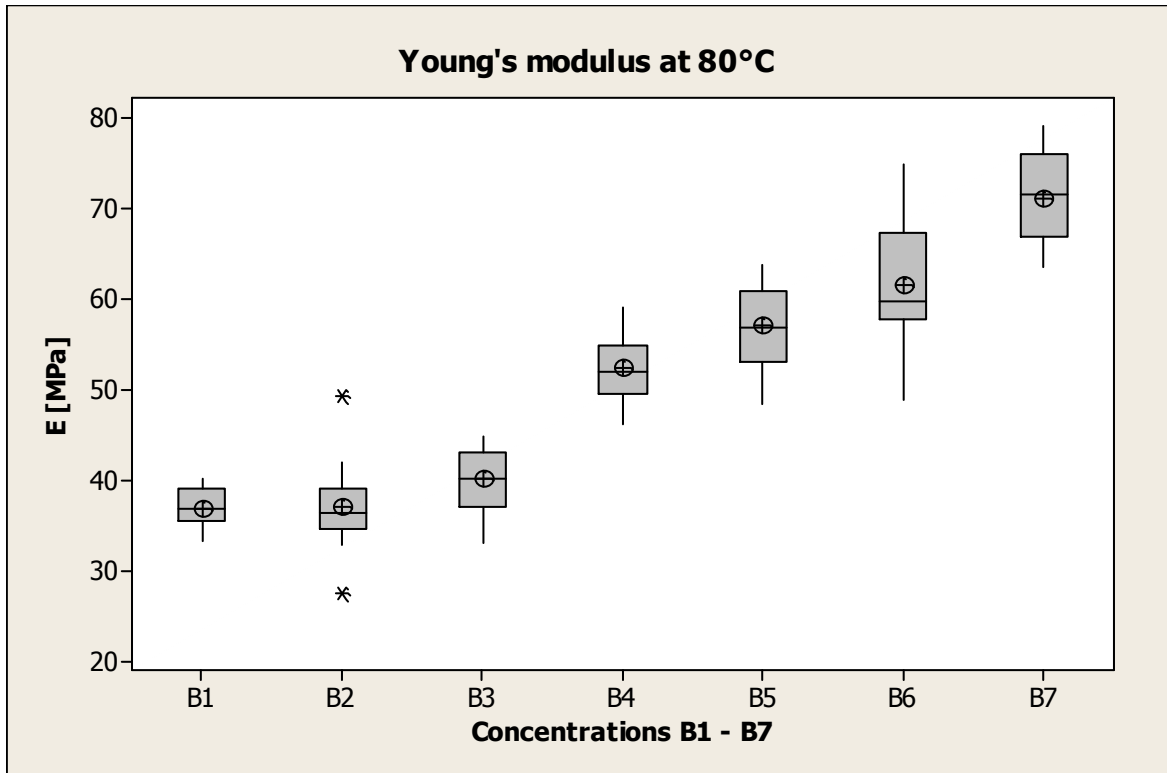
APPENDICE P V: CD-ROM

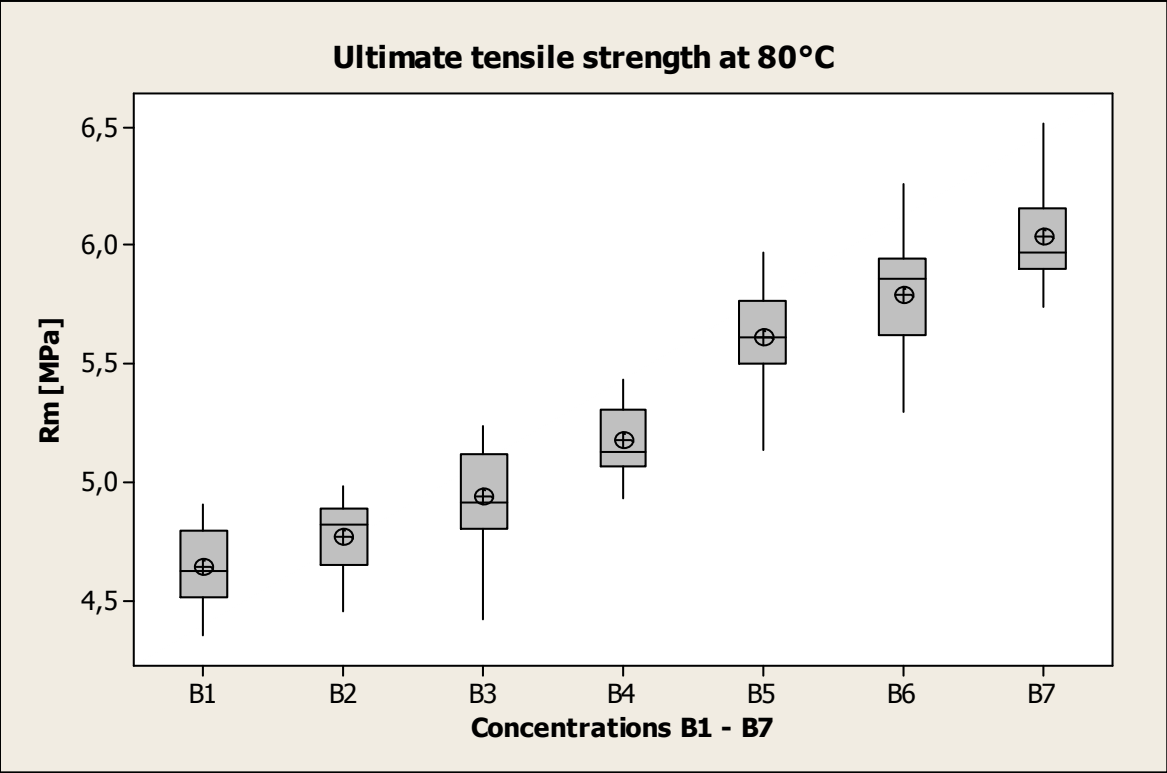
APPENDIX P I: BOX-PLOT DIAGRAMS FOR Gr + Pr(r) AT 24 °C



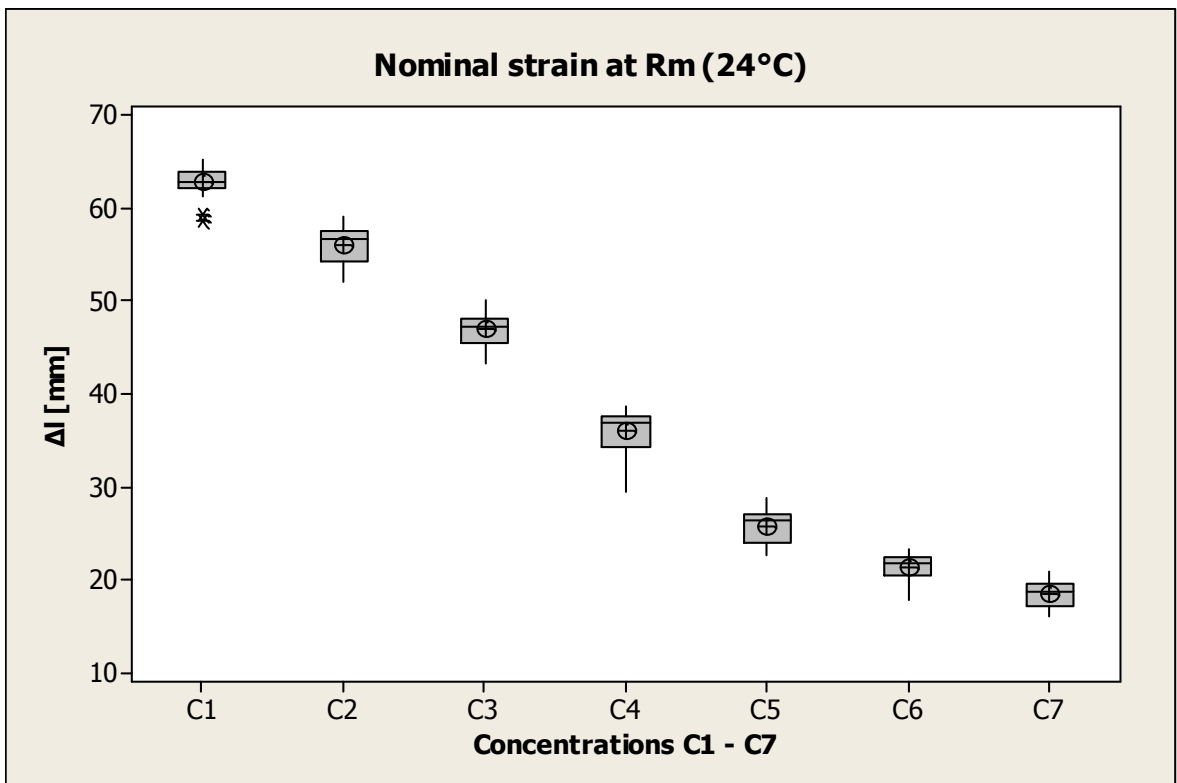
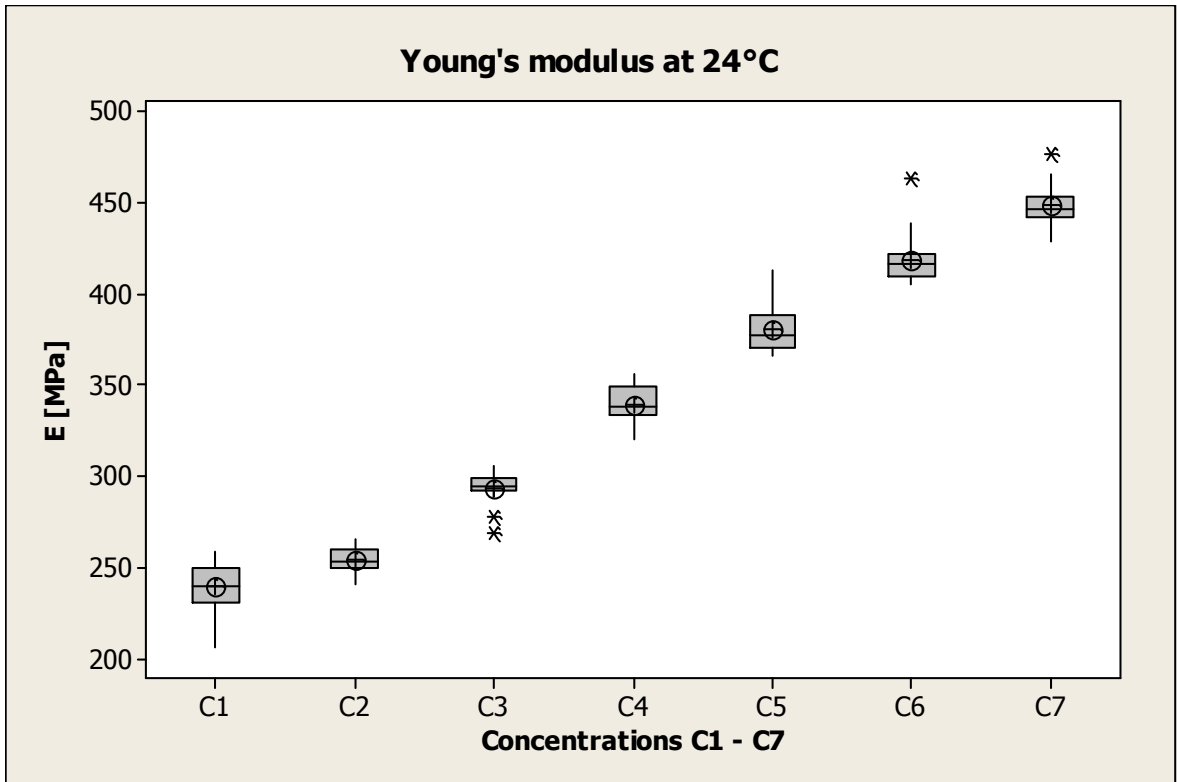


APPENDIX P II: BOX-PLOT DIAGRAMS FOR Gr + Pr(r) AT 80 °C

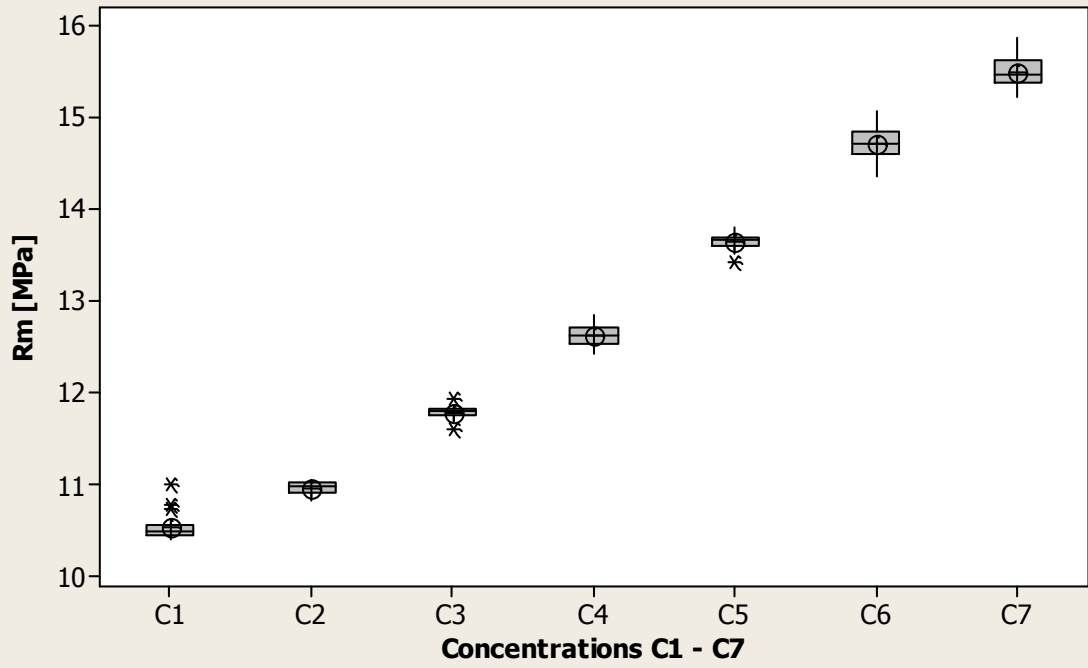




APPENDIX P III: BOX-PLOT DIAGRAMS FOR Pr + Pr(r) AT 24 °C



Ultimate tensile strength at 24°C



APPENDIX P IV: BOX-PLOT DIAGRAMS FOR Pr + Pr(r) AT 80 °C

