TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

STUDY OF COMPOSITES MATERIALS FILLED WITH OIL SHALE ASH

UURING PÕLEVKIVI TUHAGA TÄIDETUD KOMPOSIITMATERJALIDEST

MASTER THESIS

Üliõpilane:	Faisal Nadeem
Üliõpilaskood:	184638KVEM
Juhendaja:	Dr. Illia Krasnou, Research Scientist

Tallinn 2020

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Department of Materials and Environmental Technology

STUDY OF COMPOSITES MATERIALS FILLED WITH OIL SHALE ASH

Student: Faisal Nadeem, 184638KVEM
Study programme: KVEM12/18, Technology of Wood, Plastic and Textile
main speciality: Plastic
Supervisor(s): Dr. Illia Krasnou, Research Scientist, 58389514
Consultants: …………………………………………………………….(name, position)
……………………………………………………………………………… (company, phone, e-mail)
Thesis topic: ′′Study of Composites Materials Filled with Oil Shale Ash′′
′′ Uuring põlevkivi tuhaga täidetud komposiitmaterjalidest′′

Thesis main objectives:

1. To study the composites of Low-Density Polyethylene and oil shale ashes for the application of injection moulding.
2. To investigate the influence of filler content on to the processing conditions, mechanical and thermal properties.
3. To find an alternative filler for the polymers in comparison with the other mineral fillers (Calcium Carbonate).

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Mixing, Compounding and Injection Molding of the Low Density Polyethylene (LDPE) compounds with oil shale and coal ash.	May 2019
2.	Testing of the LDPE and ash compounds.	Nov 2019
3.	Mixing, Compounding and Injection Molding of the Low Density Polyethylene (LDPE) compounds with Calcium Carbonate.	Feb 2020
4.	Testing of the LDPE and Calcium Carbonate compounds	March 2020

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PREFACE

The basic idea of this research is to explore the prospective of power plant fly ashes application as filler for thermoplastics. The use of energy production waste as raw material is expected to be cost reducing and environmentally friendly. This study focused on the development of novel composite material by application of ash powders as reinforcement filler for low density polyethylene (LDPE) matrix, as well as to determination of the optimal injection molding parameters. In this work, compounds of LDPE with BOS (Burnt oil shale) ash, Coal ash and calcium carbonate were produced by using single screw extruder and then processed by injection moulding machine to produce bone shape samples. The effect of different filler load (10–30 wt.%) on the mechanical and physical properties is investigated. The morphology and structural properties were studied by scanning electron microscopy infrared spectroscopy and differential scanning calorimetry. It was found that the effect of ash content on the mechanical properties (such as tensile and impact strength) is similar to $CaCO_3$ in low range of load. At filler load more than 20wt.% the LDPE composite properties significantly decrease by adding of fly ash filler. At the same time ash filled composite processing conditions require negligible modification in comparison to neat polymer or $CaCO_3$ filled polymer. All the work was done under the supervision of the research scientist Dr. Illia Krasnou in the department of materials and environmental technology at Tallinn Technical University.

Keywords: Oil shale ash, Coal ash, polymer composite, processing, mechanical properties

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List of abbreviations and symbols

BOS	Burnt Oil Shale
LDPE	Low Density Polyethylene
$CaCO_3$	Calcium Carbonate
HDPE	High density polyethylene
PP	Polypropylene
LDPE	Low density polyethylene
LLDPE	Linear low-density polyethylene
PET	Polyethylene terephthalate
PTT	Polytrimethylene terephthalate
PC	Polycarbonate
PE	Polyethylene
PVC	Polyvinyl chloride
GCC	Ground calcium carbonate
PCC	Precipitated calcium carbonate
MFI	Melt Flow Index
Tm	Melting Temperature

INTRODUCTION

Over the last few decades, polymers not only prospered but have become the most dominant and alternative materials to the conventional materials like metals and wood in the global market. As the supply and demand increased, manufacturers started to look for the ideas of cost reduction and to improve the properties of plastic materials. Fillers were introduced because they were easy to incorporate into plastics and offer countless options for product improvement (Kutz, 2011). Many researchers have investigated the usage of natural and synthetic fillers for polymers like PVC, PE and PP. In terms of mineral fillers for thermoplastics, calcium carbonate is the most extensively used filler because of low cost and distinguished mechanical properties such as flexural, tensile and impact strength of calcium carbonate filled polymers (U. Atikler et al., 2006). According to (Wypych, 2016) $CaCO_3$ is a mineral filler which can be seen as an accumulation in sedimentary rocks and it can be obtained from rocks and minerals which have an excessive concentration of Calcium carbonate.

Similarly, oil shale is also a type of sedimentary rock which comprises organic matters that can fetch valuable amount of oil and gas only after destructive extraction (Dyni, 2006). There are mainly two types of ashes, burnt oil shale ash which is high in calcium content and harmless for the environment is a by-product of burning oil shale for the process of power generation. It is produced from the combustion zone together with smoke gases. Basically, fly ash obtained from the smoke removal systems of the furnaces which accumulate the ash in the electro-static filters. On the other hand, the coal fly ash is produced by the combustion of coal with exhaustion of smoky gases from the furnace which leads to trap the ash powder in the electro-static or filter bags. The darkest color of the coal fly ash represents the higher residual content of coke (Anti Viikna, 2012).

The use of fly ash as a particulate filler for polymer composites have been studied by many researchers. For instance, (D. G. Hundiwale et al., 2002) reported an increase in mechanical properties of natural rubber filled with fly ash along with an economic benefit. Similarly, (H.V. Ramakrishna et al, 2006) suggested that the incorporation of fly ash into polybutylene terepthalate-toughened epoxy resin significantly improves the mechanical properties. Also, (Iftekhar Ahmad, 2010) studied the mechanical properties of fly ash filled HDPE and reported a 25% increase in flexural strength, an 80% increase in flexural modulus and a 22% increase in tensile strength. On a similar note, (Suryasarathi Bose, 2004) investigated the fly ash filled nylon 6 and reported an increase in HDT, rigidity, heat resistance and dimension stability. Fly ash has been employed in many polymer composites but a major drawback is the formation of agglomerates in the polymer matrix because of high particle-to-particle interaction between hydroxyl groups on the surface of the ash particles (T. Chaowasakoo, 2007). With respect to the studies and results obtained by different researchers for ash-filled polymer composites, a common conclusion can be concluded that fly ash and other types of ashes can be formulated with polymers. The content of ash in polymer composites have a positive effect on mechanical properties and chemical resistance, however, exceeding the ash content can lead to negative effects on the properties of composites. (Andrzej Garbacz, 2013)

In the present study, attempts have been made to utilize the burnt oil shale ash and coal ash as a filler for LDPE composites. As both, the ashes are a waste product with an availability of 7 million tons per annum in Estonia. It is also reported that drying and processing of fly ash are not essential as compared to the $CaCO_3$ and chalk which required these steps after extraction. (Mariliis Beger, 2018), so, their probable applications will be an environmental and economic advantage. This research work is composed of the three main parts, compounding, moulding and testing.

In the first phase, compounds of LDPE with coal ash, burnt oil shale ash and calcium carbonate were prepared at single screw extruder. It is important to mention that coal and BOS ashes were available in three different particle fractions such as fine, medium and coarse particle sizes. For that reason, three samples from each ash type were prepared with filler load of 10, 20 and 30 wt. % with LDPE. In the second phase, LDPE filled with ash and calcium compounds were processed on injection moulding machine to get the bone shape samples. Finally, testing phase started to analyse the morphology, mechanical, structure and thermal properties of ash filled LDPE composites in comparison with calcium carbonate and neat LDPE.

1. LITERATURE REVIEW

1.1 Oil shale

As discussed earlier, oil shale is a type sedimentary rock which contains a heavy amount of organic matter such as Kerogen. Because of that organic matter, a remarkable proportion of shale oil and combustible gas can be extracted by different means of destructive distillation. Oil shales can be further divided into three categories that are of terrestrial origin, lacustrine (lake) origin, and marine origin. These categories are totally dependent on the environment of the deposition. The phrase oil shale is inapplicable, neither the shale holds the oil not it is a shale. The shale which is a hard rock is called as marl while the organic material is usually kerogen. With the appropriate processing of Kerogen, it can transform into a stuff like petroleum or liquid hydrocarbon by heating up to a high temperature. This process transforms the kerogen into a liquid which is known as shale oil and it is required to be treated and refined into petroleum product. In comparison with normal and regular rocks oil shale has quite higher organic content. A thermal treatment is required to extract hydrocarbons from the oil shale which is scientifically known as destructive distillation.("Hydrocarbons in Basement Formations," 2018).

1.1.1 Chemical composition of oil shale

Generally, the mineral elemental composition oil shale consists of silicon, calcium, aluminum, magnesium, iron, sodium, potassium, carbon, oxygen and sulfur. The chemical composition of oil shale comprises of complex organic molecules such as hydrogen and carbon along with different quantities of heteroatomic compounds with; oxygen, nitrogen and sulfur. The properties of the oil extracted from the shales are heavily influenced by the heteroatomic compounds and regions. For example, oil shale from Estonia is oxygen-rich and oil shale from saline lake environments, such as from USA is rich in nitrogen. (Atwater, 2020).

1.1.2 Oil shale resources

There are more than 600 familiar deposits of the oil shale in the world. The largest oil shale resources are in the USA which accounts for the 72% of the world’s oil shale reserves. Other largest reserves are in Brazil, Jordan, Russia and in Morocco. There are 2.8-3.3 trillion-barrel oil which is recoverable in the deposits of the oil shale. In comparison to conventional crude oil, oil shale reserves are three times larger worldwide. (Pawan R. Ingole, 2014)

1.2 Composites

Composites are those materials that are produced by the combination of two or more materials with different properties and composition. The composite materials form together a stronger product, but they do not mix or blend or lose their original character. (Williams, 2015).

Composites and blends differ from each other, in the blends, the two components or materials cannot be identified separately while the blend has been formed in composites can be distinguished. These different components of the composites combine to get the required properties or strength. Basically, composites consist of two or more distinct phases such as matrix phase and dispersed phase. The primary phase which is mostly flexible and less rigid phase with an uninterrupted character is knows is as matrix phase. The main purpose of the matrix phase is to hold the dispersed phase and share the load. Dispersed phase is normally known as secondary phase because it is harder than matrix, for that reason, it is often known as reinforcing phase. Based on the phases of matrix, composites can be categorized into three categories, metal matrix composites, ceramic matrix composites and polymer matrix composites. Out of these, polymer matrix composites are popular because of their simple methods of manufacturing and low cost. The most common materials in this category are polyester, vinyl ester, epoxy, phenolic, polyamide, polypropylene and polyether ether ketone (PEEK). Fibers are the most common reinforcement materials, but common ground minerals can also be used. Moreover, composites can offer following benefits. (Sabu Thomas, 2012)

a) High tensile strength
b) High specific stiffness
c) High fracture resistance
d) Good abrasion resistance
e) Good impact resistance
f) Good corrosion resistance
g) Good fatigue resistance
h) Low cost.

Applications of the composites are not limited to one sector of the industry; composites are employed in almost all major engineering items. The major applications include aerospace structures, marine structures, automotive, sports goods, electrical applications, biomedical applications, civil infrastructures and chemical processing equipment (Sabu Thomas, 2012).

1.2.1 Recent developments in composites

Fibre-reinforced polymer (FRP) composites are widely used in the industry and the usage of FRP composites is increasing day by day. The main reason behind this growing trend is the advanced forms of FRP such as high-performance resin system and new styles of reinforcements like carbon nanotubes and nano particles. FRPs and other similar materials are not environmentally friendly and difficult to recycle as well. Therefore, natural fibres from plants like hemp, jute, bamboo and sisal can be used as fibre from these plants are readily available from a renewable source with biodegradability. However, natural fibres are hydrophilic with high moisture content which leads to a weak interface between fibre and hydrophobic matrix. To improve the interfacial adhesion, the surface of both fibres and matrix must be properly wetted. In Europe, natural fibres have become an important part of the materials for automobile industry for the exterior and interior of the cars (Sabu Thomas, 2012).

1.2.2 Polymer composites with mineral & natural fillers

The main purpose of using mineral fillers in composites is to lower the cost and improve the mechanical and thermal properties. Moreover, mineral fillers are also vital for the stiffness of the matrix, to decrease the thermal expansion coefficients and to decrease the volume shrinkage. Furthermore, it has also been noticed that the mineral filler reduces the chemical and thermal shrinkage of the matrix material. Hence mineral fillers improve the dimensional changes and formation of the residual stresses in the composites. (Stig-Goran, 1995).

From the last few years, mineral fillers such as talc, kaolin, wollastonite, mica and calcium carbonate have been employed widely to reinforce the thermoplastic composites. These fillers have the potential to improve the mechanical properties, heat deflection temperature (HDT), melt flow index (MFI), flame retardancy, dimensional stability and crystallinity for thermoplastic matrices. For instance, talc-filled thermoplastics showed better stiffness, dimensional stability and crystallinity. Similarly, kaolin-filled epoxy and PP tends to have better toughness with other mechanical properties. (Jang, 2016). It is also noticed that the incompatibility between hydrophilic fillers and hydrophobic polymer matrix is the major problem in polymer composites. The incompatibility between filler and matrix is the main reason behind the poor adhesion which also leads to the poor load transfer between matrix and filler. To solve this problem, numerous coupling agents are being used to improve the adhesion between filler and matrix. Silane coupling agents are the best for the improvement in mechanical properties for fillers like fly ash, cellulose-based fibers or zeolite with matrix materials like High-density polyethylene (HDPE), Polypropylene (PP) and Low-density polyethylene (LDPE). In terms of mineral fillers for thermoplastics, calcium carbonate is the most extensively used filler because of low cost and distinguished mechanical properties such as flexural, tensile and impact strength of calcium carbonate filled HDPE, PP, LDPE and LLDPE composites. (Tihminlioğlu, 2006).

Different types of ashes from natural sources have been also considered by researchers as a potential material for polymer composites, for instance, (Zhi Cao et al., 2016) studied the effect of surface-treated peat ash on the properties of neat HDPE and a grafted HDPE. According to the study, they used stearic acid for the surface treatment of peat ash before incorporation with neat HDPE and grafted HDPE (g-maleic anhydride). The results of their study show that peat ash improves the tensile and flexural strength of the composites, but impact strength was reduced significantly along with MFI. Similar study from (Qingfa Zhang et al., 2020) suggests the incorporation of biochar from rice husk with HDPE up to 50 wt. % to get the improved mechanical properties and flame retardancy of the composites.

Another study by (A.H.Awad, 2019) assessed the mechanical and physical properties of LDPE filled with marble dust which is just like any other mineral filler. They found that incorporation of marble dust with LDPE increases the flexural and compression strength, hardness, wear and thermal resistance. The only drawback is the shape of the particle which are not uniform.

1.2.3 Fly Ash-filled polymer composites

It is a common practice in polymer industry to use fillers either for cost saving or to enhance the mechanical properties of the final product. Fly ash which has a high calcium content can be utilized commercially in plastics industry as an alternative to other mineral fillers like alumina, calcium carbonate, talc and clay, titanium dioxide, kaolin and aluminum trihydrate. Over the last few decades, composites filled with mineral fillers gained confidence in the market as a strength enhancers and cost reducers. The use of fly ash as a particulate filler for polymer composites is not common, however, results of previous studies suggests that oil shale ash is a ready-made mineral filler for plastics. In comparison with commercial mineral fillers, fly ash has few drawbacks like large particle size and smooth spherical inert surface. Many researchers reported that fly ash can be used as a filler in composites, but it can lead to lower mechanical properties due to poor adhesion between polymer and filler. However, it can be improved by the surface modification of the ash by chemical activation or by mechanical activation which is also known as physical modification. Mechanical milling is the process which can not only reduce the size of coarser particles into fine or nano level but makes the filler surface more reactive with improvement in the surface properties like surface energy, surface area and roughness. (Sateesh Bonda, 2014). According to (K. Thomas Paul, 2007) mechanical milling of the fly ash tends to reduce the particle size from micro to nano level which helps to improve the surface area and shape of the ash particles tremendously. Moreover, results from the research of (Sateesh Bonda, 2014) suggest that surface modification of fly ash by milling showed an improvement in surface reactivity with the formation of rough and irregular surfaces of fly ash. Composites of modified fly ash with polypropylene also demonstrated the improved mechanical properties.

Fly ash is also a potential candidate as a filler for structural parts, concrete industry and recycled thermoplastic matrices. For instance, it is reported that incorporation of fly ash into recycled PET improves the compression strength of the final product. (Yadong Li a, 1998). Moreover, the use of coupling agents have been studied extensively, for instance (Esteban Igarza et al., 2014) reported an improvement in adhesion and dispersion between fly ash and PP due to the addition of a coupling agent (Maleic anhydride- 1 wt.%) and improvement in tensile strength of the composites as well. Also, (Sukanya Satapathy et al., 2010) incorporated fly ash (60-100um particle size) into the blends of waste polyethylene and reclaimed rubber with silane coupling agents for surface treatment and to improve the filler-rubber interaction, adhesion and dispersion. They reported, improved tensile and flexural strength along with better thermal stability. Furthermore, (Nikolai Zaichenko, 2018) reported from their research that fly ash without any surface modification gave impressive results with recycled PET matrix. But surface treatment of the fly ash with sulfuric acid improved its adhesion characteristics with recycled PET matrix and enhance the mechanical properties like compression strength. It is also noted that fly ash turned out to be an effective reinforcement agent for the composites of recycled rubber and plastics (HDPE and PTT). A small amount of fly ash (0.25 %) incorporated into the recycled rubber and plastics composites not only increases the compression strength but it also acts as a nucleation center and supports the self-assembly of the composite components. This type of composite materials is recommended for developing outdoor products like anti-shock carpet for parks and pavement slabs because of their non-wetting behavior with a dense structure. (Anca Duta, 2011). Another research on the usage of fly ash with the waste PE and PVC to produce extruded pipes. According to (China Patent No. CN1110773A, 1994) fly coal ash with the particle size of 200 to 300 mesh size were used with the waste PE and PVC for kneading, mixing and extrusion to produce the cost effective pipe of same specifications and mechanical properties of other materials and fillers.

Polymer compounds containing fly ash can be a viable solution for the industry. As claimed by (Estonia Patent No. WO2017182043A1, 2017) extruded pellets of fly ash-filled polymer composites can be produced by the process of extrusion containing 70 to 90 wt. % of fly ash with 10 to 30 wt. % of polymer (PP, PE, PC). These extruded pellets can be used as an additive or filler in the polymer composites matrices (PP, PE, PC) to improve the strength, to reduce the cost and to provide the reinforcement. As per the claim, automotive industry, building and construction industry and packaging industry has tested the fly ash mineral granules and proved its high quality and efficiency.

1.2.4 Calcium carbonate-filled polymer composites

In the earth's crust, calcium carbonates are one of the most plentiful materials. Calcium carbonates are formed from fossils, marbles and from the metamorphosis of sedimentary rock and they exist in the form of limestone and chalk. Generally, these materials are very soft in nature and white in color and they contain up to 98% of calcium carbonate with trace amounts of magnesium carbonate, iron oxide and aluminum silicates. Calcium carbonate is the most extensively used filler for plastics as it is cheaper and can be used in higher quantities. In general, calcium carbonate is a popular cost reducing filler for plastics manufacturers, but it can also be used to improve stiffness and impact strength, mainly with fine particle grades. (Maier & Calafut, 1998).

Calcium carbonate is normally used in its natural form which is also known as ground calcium carbonate (GCC) and the synthetic form which have very fine particles is called as precipitated calcium carbonate (PCC). Both GCC and PCC are widely used in polymer industry but GCCs are the main fillers for Polyolefins, unsaturated polyesters and for PVC while PCC is mostly used in PVC compounds. (Gilbert, 2017). Also, there are various types of Calcium carbonate for different applications of plastics. For example, Fine calcined clays which are suitable for high optical properties, $CaCO_3$ treated with vinyl functional silane for high voltage rubber cable insulations, high whiteness calcium carbonate which is derived from the pure Italian marbles for the applications of PVC, masterbatches and paint emulsions and fined calcite which is available in different form like microcrystalline, crystalline with surface modification with stearic acid. Microcrystalline calcites are normally in good colour with high quality of fine particle size which is good for PVC compounds. (Murphy, 2001). Calcite is also a popular functional filler for PP because of its thermodynamic stability. Calcite-filled PP can increase toughness and shows a superb balance of stiffness and impact strength. (Thriveni Thenepalli, 2015)

Calcium carbonate filled polymers tend to have improved certain properties. For instance, calcium carbonate filled PP have a flexural modulus of about 3000 MPa but other mechanical properties like compression strength, elongation and tensile strength can be reduced with an increased dosage of $CaCO_3$ filler. (Maier & Calafut, 1998). As stated by (Pardeep Kumar, 2015), with an increase in the filler content (up to 40 wt. %) in the PP-$CaCO_3$ composites, tensile strength and impact strength decreased but with the filler content of 25 wt. % tensile strength increased because of good filler and matrix interaction which helps more stress transfer from matrix to filler. But once the filler content increased it enables the poor interfacial bonding between matrix and filler which tends to decrease the tensile strength. For LDPE- calcium carbonate composites (with 10 wt % of CaCO3), the analysis showed significant variations in the mechanical and rheological properties that occur like an increase in the viscosity with an increase in the elastic modulus but with a reduction in tensile strength and elongation at break. It is also noted that an increase of processing time from 4 to 9 minutes can improve the filler dispersion in the matrix. (Francesco Paolo La Mantia, 2012). According to (Yung Ngothai, 2009) particle size of calcium carbonate plays an important role in a composite matrix. The reduction in tensile and flexural properties is due to the large particles who detach themselves from the matrix. However, smaller the particle size of the calcium carbonate, greater the tensile strength of the composite as the dispersion will not be affected in the matrix.

Furthermore, incorporation of $CaCO_3$ also improves brightness and glossiness. It is also reported that calcium carbonate can reduce the cost up to 50% of expensive pigments for white colour like titanium dioxide in a formulation. (Maier & Calafut, 1998). Calcium carbonate also enhance the processing, in the barrel minerals acts as a heat conductor to aid the processing and reduce the cycle time. Also, it revamps the cooling time by improving the mould productivity. Compounds of $CaCO_3$ filled polymers with high content of calcium carbonate (90 wt. % and 10 wt. % Polyolefin) are also available in the form of pellets which can be incorporated directly in the hopper with other materials. (Murphy, 2001).

1.3 Low density polyethylene (LDPE)

In 1933 at Imperial chemical industries, Fawcett and Gibson were researching the high-pressure and high-temperature reactions of ethylene and benzaldehyde and unexpectedly found LDPE as a waxy solid powdery substance. After months of experimentation, researchers at ICI came to know that under the high pressure, the presence of oxygen is essential to initiate the conversion process of ethylene monomer to PE. In other words, oxygen presence helps the formation of free radical initiators which eventually break up to start the free-radical addition polymerization of LDPE. The long-chain branching and short-chain branching in the LDPE resins is because of the process of free radical polymerization. The pressure and temperature in the reactor control the density of the LDPE. Because of the limited range of pressure and temperature in the reactor, commercially LDPE can be produced with a density of about 0.915 to 0.935 g/cm^3 (Spalding & Chatterjee, 2017).

The reason for low density in LDPE is the considerable number of branches that obstruct the process of crystallization which results in lower densities. These branches mainly contain ethyl and butyl groups which are clustered together along with some long chain branches. A simple structure of LDPE branches can be seen in figure 1.1 (Peacock A. J., 2000)

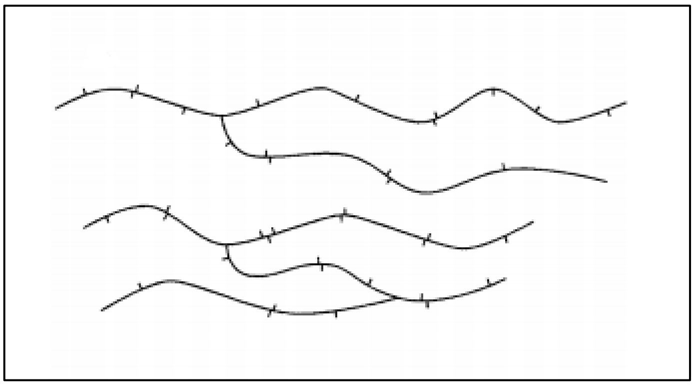

Figure 1. Schematic representation of LDPE structure (Peacock A. , 2000)

1.3.1 Properties of LDPE

LDPE is tough, flexible, semi-rigid and translucent material. It can be easily processed at normal operating temperatures by conventional methods of plastics production. LDPE is low in cost and has good resistance to chemicals, weather, organic solvents at room temperature along with low water absorption. It also has low working temperatures, low moisture permeability, low tensile strength and a soft surface with excellent corrosion resistance. On the other hand, there are certain disadvantages of LDPE also, such as low strength, flammability, poor UV resistance, stiffness, susceptibility to environmental stress cracking. (Cornelia Vasile, 2005)

The thermal and mechanical properties of LDPE are totally dependent on crystallinity, molecular weight distribution, structure and the type of comonomer. In the structure of LDPE, long-chain branches are important. It has two branches per hundred carbon atoms and a crystallinity of 50%, however, polymerization conditions can change the degree of branching and crystallinity can be varied as well from 35 to 75%. In comparison to LLDPE, long-chain branches helps to produce more amorphous LDPE with high clarity and a lower melting point. (Cornelia Vasile, 2005). Other properties of LDPE can be find in Table 1.

Table 1. Properties of LDPE (Wypych, Handbook of Polymers (2nd Edition), 2016)

Property	**Value**
Mechanical & Rheological	
Tensile strength (MPa)	10-20
Tensile modulus (MPa)	96-262
Tensile elongation at yield (%)	200-600
Flexural strength (MPa)	7.5
Flexural modulus (MPa)	230-495
Charpy impact strength, unnotched, 23°C (KJ m^{-2})	18.2
Toughness, Izod notched impact at room temperature (J m^{-1})	999
Shrinkage (%)	2.4
Melt index (g/10 min)	0.25-55
Physical	
Density at 20 °C (g cm^{-3})	0.915- 0.930
Melting temperature (°C)	105-115
Glass transition temperature (°C)	-103 to -133
Heat deflection temperature at 1.8 MPa (°C)	36-40
Vicat temperature (°C)	76-109

1.3.2 Applications of LDPE

LDPE is the most widely used polymer in the industry. Because of its reduced degree of crystallinity, flexibility and low melting point, LDPE is one of the most suitable materials for the blown film. It accounts for more than half of all its usage for blown film products. LDPE films are soft, transparent and are unsuitable for high load applications. Major use of LDPE films are commercial and retail packaging, diaper backing, garbage bags, shrink wraps, agricultural cover films, greenhouse skin films and moisture barrier films for the construction industry. Another major application of LDPE films in packaging as a coating layer in the tetra pack for milks and juices. Thin films from LDPE can be coated directly onto the cardboard which makes it waterproof and heat-sealable. (Peacock A. J., 2000) Applications of LDPE is not only limited to films but there are plenty of other items like insulation of wire and cables, disposable goods, gloves, lids, bowls, toys, squeeze bottles, heat seal films for metals, thermoformed products, vacuum formed products, shower curtains, chemical tanks linings and many more (Cornelia Vasile, 2005).

1.4 Aim and objectives

The main aim of this research work is to investigate the effect of fly ash on processing conditions and on thermal and mechanical properties of LDPE and to compare the results with other mineral fillers like calcium carbonate, in order to find an alternative mineral filler with a lower price.

1.4.1 Objectives

Following are the objectives.

- Mixing and compounding of BOS, coal and calcium carbonate fillers with LDPE (10,20 and 30 wt. %) of filler content.
- Injection molding of the compounds with a bone shape mold.
- To investigate the influence of filler content (10-30 wt. %) on the processing conditions of injection molding.
- To analyse the composites by Testing.
    - Charpy Impact test and tensile test for mechanical properties.
    - Scanning electron microscope for morphology.
    - Melt flow index and differential scanning calorimetry (DSC) for thermal and structural properties.
    - Fourier transform infrared spectroscopy (FTIR) for chemical and structural properties.
- To compare the results with other common mineral filler like calcium carbonate, in order to find an alternative mineral filler for thermoplastics with a lower price.

2. EXPERIMENTAL WORK

2.1 Materials

2.1.1 Polymer matrix

The low-density polyethylene granules with MFI = 1.10 g/10 min. and Tm = 117°C was chosen for the compounding. Unfortunatley, due to the scarcity of the LDPE granules we had to use another grade of LDPE material (MFI = 1.98 g/10 min.) for the last few samples. Therefore, term LDPE I and LDPE II has been used to differentiate both materials.

2.1.2 Fillers

A fine calcium carbonate powder with the average particle size of 1.3 um was used for the compounding with LDPE to analyze and compare the $CaCO_3$ filled LDPE along with the LDPE-ash composites.

Two types of ashes supplied by Eesti Energia, BOS and coal ashes were prepared by sieving and differentiated by average particle size: BOS fine (30um), BOS medium (59 um), and BOS coarse (81), Coal fine (25 um), Coal medium (111 um), Coal coarse (128 um). For experimental work, 26 samples were prepared in total with each type of ash along with neat LDPE. For example, Fine BOS ash has three samples (10, 20 and 30 wt. %) with pure LDPE and same sequence were followed for other types of ashes. Table 2 represents the sample plan which was followed during this work.

Table 2. Sample plan

S No.	Sample	wt.%			
1	LDPE I	100			
2	LDPE I + Fine BOS ash		10	20	30
3	LDPE I + Medium BOS ash		10	20	30
4	LDPE I + Coarse BOS ash		10	20	30
5	LDPE I + Fine Coal ash		10	20	30
6	LDPE I + Medium Coal ash		10	20	30
7	LDPE II + Coarse Coal ash		10	20	30
8	LDPE I + Calcium Carbonate		10	20	30
9	LDPE II	100			
10	LDPE II + Calcium Carbonate		10	20	30

2.2 Compounding

The basic idea of making compounds was the ease of injection moulding process as it is quite difficult to control the feeding of the material with different particle sizes and densities (filler powder could stick on the walls of the hopper and separate from the polymer). Firstly, we made a sample production plan (Table 2) as per two types of ashes and with respect to their particle size. Mixing of the compounds was done by a lab-scale barrel - mixer for 15 minutes with 50 rpm to get a homogenous mixture, the load of each sample was 1000 grams. Composites with BOS and Coal ashes as well as $CaCO_3$ were compounded with three different filler load: 10, 20, and 30 wt.%.

Composites were prepared by compounding at a single-screw Lab scale ‘Brabender Plasti corder’ (PLE 651). The parameters of compounder were kept the same for all materials and the processing temperatures were chosen between 160°C to 180°C. The compounder feeding zone temperature was 160°C and the compression zone was set on to 175°C while metering and forming zone temperatures were 180°C respectively. Mixed powders of LDPE and fillers were fed into the compounder manually in small portions. Screw rotational speed was kept at 35 rpm and electric motor torque (acting on the screw compounder) at below 100 Nm. As feed was not continuous, torque varied between 50 – 80 Nm. The extruded filament had been continuously deposited on a moving belt and cooled by vigorous airflow then chilled filament chopped into pellets of 5 mm size by blade cutter.

Figure 2. Figure 2. Brabender compouder Plasti corder (PLE 651)

2.3 Injection molding of compounds

The bone-shaped specimens were prepared by injection molding according to standard ISO 527-2. For Injection molding; a Battenfeld BA230E machine with a clamping force of 230 kN was used. The mould used was a bone shape mould producing standard samples for the purpose of testing. The mould temperature was maintained between 45 – 50°C with the help of an external mold temperature controller. The sampling process was started with pure LDPE samples which were a reference sample to compare with the ash and $CaCO_3$ compounds. The process of pure LDPE samples and LDPE + 10% Fine BOS ash were smooth and processed quickly on injection molding with nominal process parameters of the polyethylene. However, it was noticed that as the ash content increased, short shot appeared (Figure 4.) and required some process adjustments. For instance, barrel temperature, injection speed, injection pressure, holding pressure and holding time increased to avoid short shots and to improve the flow of the material. Technological parameters variation is represented in Table 3.

Figure 3. Injection molding machine Battenfeld BA230E

Table 3. Process Parameters of LDPE+ ASH and $CaCO_3$ compounds.

S No.	Polymer (wt. %)	Filler (wt. %)	Cycle time (sec.)	Injection Pressure (bar)	Injection Speed (rpm)
1	LDPE I 100	_	17.6	65	7
2	LDPE I 90 %	Fine BOS Ash 10 %	17.2	65	7
3	LDPE I 80 %	Fine BOS Ash 20%	17.6	99	9
4	LDPE I 70 %	Fine BOS Ash 30%	25.1	99	13
5	LDPE I 90 %	Medium BOS Ash 10%	21.1	70	13
6	LDPE I 80 %	Medium BOS Ash 20%	21.1	70	9
7	LDPE I 70 %	Medium BOS Ash 30%	25.1	80	13
8	LDPE I 90 %	Coarse BOS Ash 10%	21.1	70	13
9	LDPE I 80 %	Coarse BOS Ash 20%	21.1	83	9
10	LDPE I 70 %	Coarse BOS Ash 30%	21.1	81	13
11	LDPE I 90 %	Fine Coal Ash 10%	25.1	72	13
12	LDPE I 90 %	Fine Coal Ash 20%	25.1	72	13
13	LDPE I 70 %	Fine Coal Ash 30%	25.1	72	13
14	LDPE I 90 %	Medium Coal Ash 10%	21.1	70	13
15	LDPE I 80 %	Medium Coal Ash 20%	21.1	70	13
16	LDPE I 70 %	Medium Coal Ash 30%	25.1	72	13
17	LDPE II 90%	Coarse Coal Ash 10%	21.1	70	13
18	LDPE II 80%	Coarse Coal Ash 20%	21.1	81	9
19	LDPE II 70%	Coarse Coal Ash 30%	21.1	81	13
20	LDPE I 90%	$CaCO_3$ 10%	17.6	65	9
21	LDPE I 80%	$CaCO_3$ 20%	21.1	80	9
22	LDPE I 70%	$CaCO_3$ 30%	21.1	80	9
23	LDPE II 100%	_	26.6	73	11
24	LDPE II 90%	$CaCO_3$ 10%	26.6	73	11
25	LDPE II 80%	$CaCO_3$ 20%	26.6	75	11
26	LDPE II 70%	$CaCO_3$ 30%	26.6	75	11

Figure 4. Appearance of short shots during injection moulding with an increment in ash content (before the optimization of process parameters)

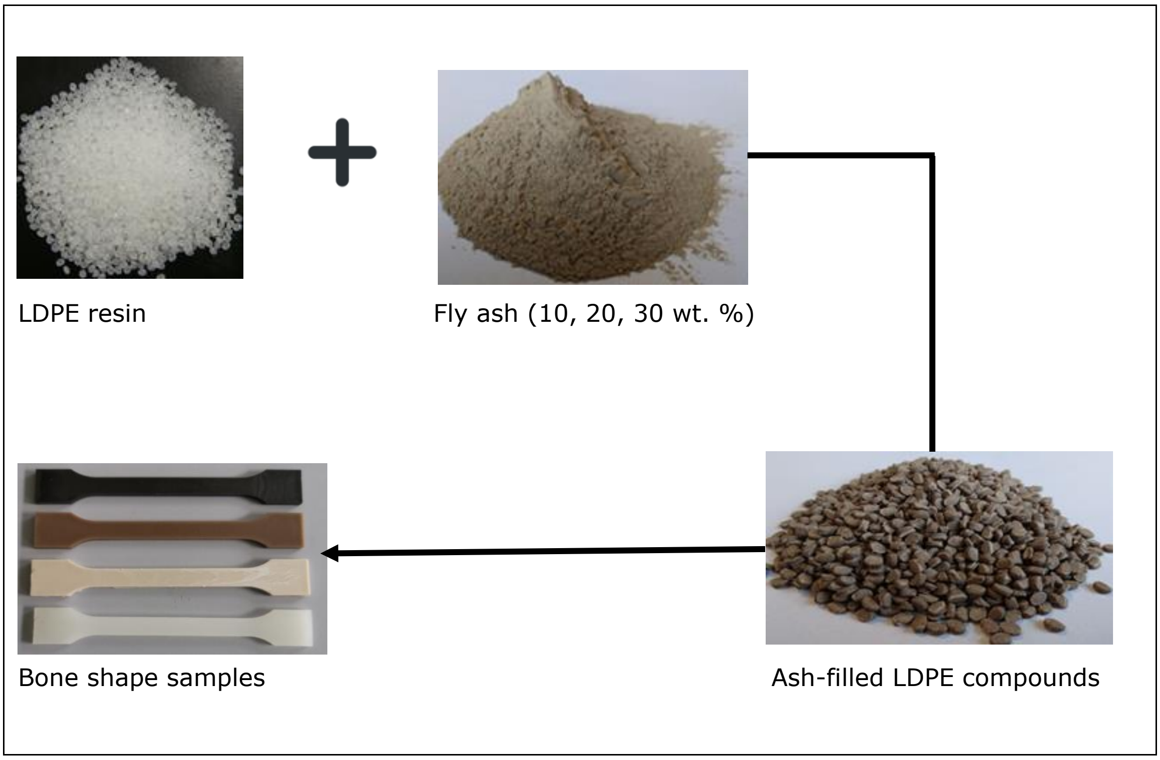

Figure 5. Overview of the process of compounding and injection molding to get the bone shape samples.

2.4 Testing of composites

2.4.1. Ash characterization

Analysis of ashes chemical and mineral composition was done by X-ray fluorescence method (EDXRF) according to standard EN 196-2:2013 using HE XEPOS spectrometer (Spectro Analytical Systems) in He atmosphere. Spectrometer was equipped with 50W tungsten end-window tube (60kV, 2mA) and silicone drift detector. Mo, Al_2O_3, Co and Pd(L) targets where used for signal optimization. Mineral composition was determined by pre-calibrated geological software package for semi-quantitative analysis. All specimen were analyzed in powder form (dried and ball mill ground), powders were placed in XRF sampling cup with 4µm prolene foil (Chemplex).

2.4.2 Polymer matrix characterization

Melt flow index (MFI) test was conducted by Ceast Melt flow Junior (figure 6) according to ASTM D1238 to analyze the melt flow of ash-filled LDPE compounds and to check the effect of the ash content on the melt flow. MFI test was done at 190°C with 2.16 kg load, ten specimens per samples were tested in 10 minutes to calculate the average melt flow rate.

Figure 6. Melt Flow Tester

Thermal and structural properties including melt temperatures and degree of crystallinity were determined by differential scanning calorimetry (DSC) using Perkin Elmer DSC 7 calorimeter. All experiments performed under the 20 ml/h N_2 gas flow and heating rate of 20 °C/min. The degree of crystallinity X_c calculated as:

$$X_c = 1/(1 - w_f)\ (\Delta H_m)/(\Delta H_m^0) \times 100\% \qquad (2.4.2)$$

Where ΔH_m – enthalpy of fusion,
ΔH_m^0 – 100% crystalline polyethylene theoretically calculated enthalpy of fusion provided by Perkin Elmer DSC analysis software
w_f – PE content in composite.

2.4.3 Composite materials characterization

Fourier transform infrared spectroscopy (FTIR) was done by means of Interspec 200-C instrument with attenuated total reflection (ATR) attachment to analyze the changes in chemical composition of the composite materials with respect to the ash content.

2.4.4 Mechanical properties

Tensile testing was done in compliance with ISO 527-2 and on a universal testing machine Instron 5866. The basic aim of the tensile testing was to see the impact of ash content on modulus of elasticity and tensile strength. For this test, 10 specimens were tested for one sample at a speed of 50 mm/min. with a load cell of 50 KN. Also, to calculate the tensile properties, blue hill software was used which gathered the data and generated the curves for each specimen automatically.

Charpy impact test was carried out according to ISO 179 by using Zwick 5102 pendulum impact tester to verify the impact strength of the compounds with respect to ash content. The samples were notched prior to the testing and were placed horizontally on the machine to be struck by a hammer. Ten specimens were tested for one batch to get the average results. Charpy impact strength was calculated using the following formula.

Charpy impact strength: $KJ/m^2 = \frac{W}{h \times b_N} \times 10^3$ (2.4.3)

where W - energy in joules absorbed by the specimen

b_N - width of the specimen from the notch base (8 mm)

h - thickness of the specimen (4 mm)

Figure 7. Charpy impact tester

2.4.5 The morphology

(SEM) was done with a tabletop microscope supplied by Hitachi TM-1000 to examine the morphology of ash particles in LDPE composites and how well the ash particles dispersed with the polymer matrix with respect to their particle size. For morphological studies we prepared specimens of composites frozen in liquid nitrogen and then fractured. The samples were placed on double sided carbon tape and then fixed on a sputter. The surface morphology of the composites was analyzed at different magnifications.

2.5 Results

2.5.1 Melt flow index (MFI)

The results of MFI tests indicate that there is no significant change in the melt flow of the compounds upon increasing of the ash content up to 30 wt.% but general trendline is decreasing. For instance, pure LDPE-I had an MFI of 1.1 g/10 min. and loading of LDPE-I with 30 wt. % of fine BOS ash decrease MFI to 0.7 g/10 minutes. This result shows that processing parameters for ash-filled LDPE compounds could be similar to pure polymer and does not demand significant adjustment of the processing parameter as well as the energy consumption of equipment. The decrease in the melt flow index could be attributed to the agglomeration of the ash particles which results in small restriction of flow.

Similary, for drax coal ash, we noticed a slight decrease in the MFI due to the filler content of drax ash. For example, loading of LDPE-I with drax coal fine ash up to 30 wt. % did not decrease the MFI at all but with the filler content of 30 wt.% for drax coal medium ash with LDPE-I, MFI decreased to 0.7 g/10 min. On similar notes, LDPE-II had an MFI of 1.98 g/10 min. and loading of LDPE-II with drax coarse ash of 30 wt. % shows a slight decrease in MFI up to 1.70 g/10 min.

On the other hand, compounds of LDPE filled with $CaCO_3$ showed an increase of MFI upon increasing the content of $CaCO_3$. For example, LDPE with 10wt.% of $CaCO_3$ had the MFI of 1.3 g/10 min. but LDPE with 30 wt. % of $CaCO_3$ showed almost double increment up to 2.30 g/10 minutes. Calcium carbonate is often used to improve lubricity and wetting characteristics of polymer resin, which typically lead to a decrease in mixing viscosity, better filler dispersion and, thus to increase the plasticity and processability of the polymer. Table 2.3 shows the MFI values of the LDPE composites while figures 8 and 9 shows the change in MFI due to the effect of the filler content.

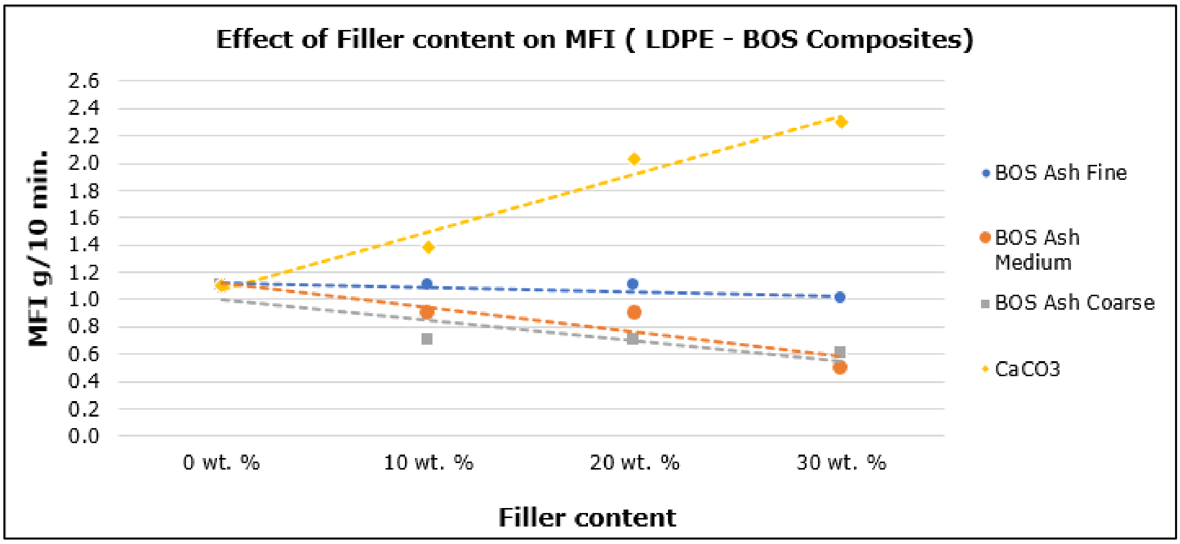

Figure 8. Change in MFI due to the filler content (LDPE-BOS ash composites)

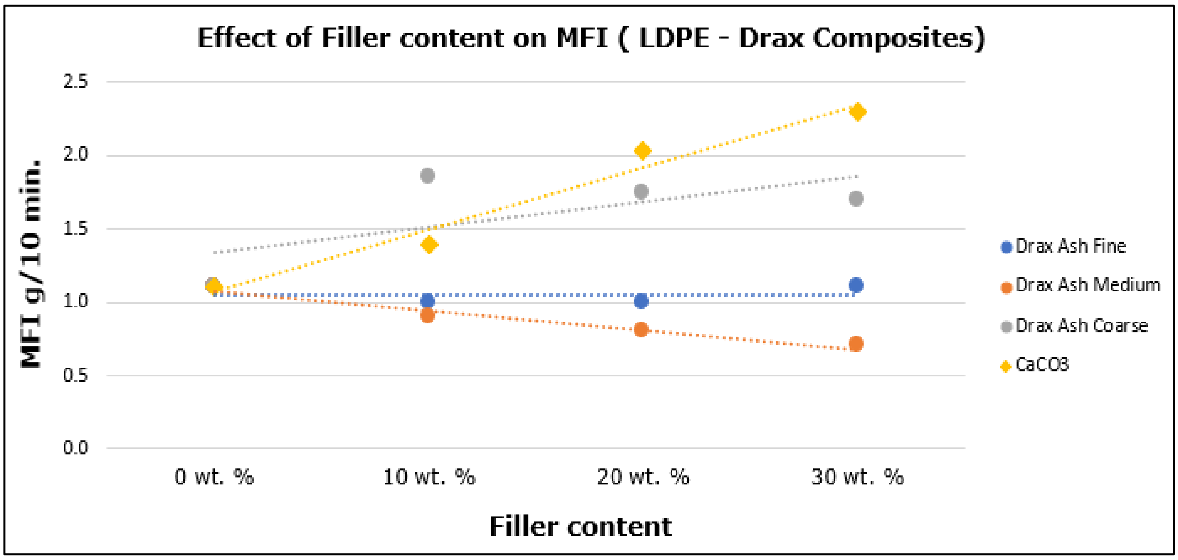

Figure 9. Change in MFI due to the filler content (LDPE-drax ash composites)

2.5.2 Mechanical properties

Impact test

The results of impact test suggest that the ash content is directly proportional to the impact strength of the composites, with the increase of the ash content the impact strength decreases significantly. For example, composites of BOS ashes with LDPE-I showed an almost 50% decrease in the impact strength with filler loading of 30 wt.%.

Similarly, composites filled with Drax coal medium and Drax coal coarse ashes, showed a decreased up to 50 and 70 % with an exception for Coal Fine Ash which showed a significant stability up to 30 wt.% of the ash with the LDPE-I (Figure 10).

On the other hand, the addition of calcium carbonate filler up to 20 wt.% with LDPE-I showed a 10 % improvement in the impact strength while LDPE-I with 30 wt. % of CaCO3 remained stable and did not cause a much decrease in the impact strength. However, composites of CaCO3 filled with LDPE-II showed an almost 50% decrease in the impact strength. Results of LDPE composites with CaCO3 show that the impact strength is also dependent on the matrix polymer, different matrix polymer with the same filler of CaCO3 may have different results. Overall results of the impact strength gave an indication that the addition of the ash filler load increased the brittleness of the composites.

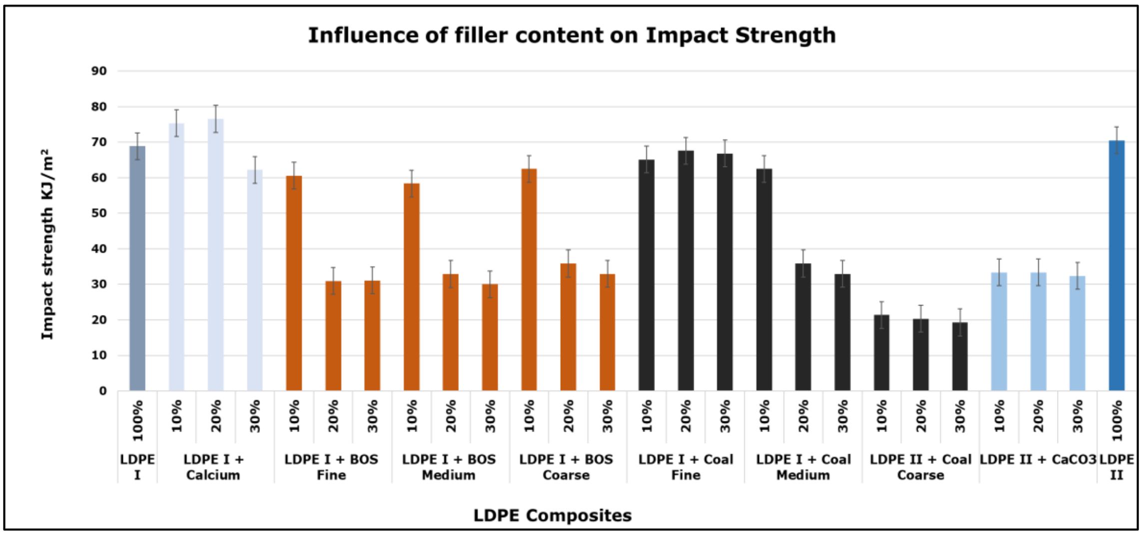

Figure 10. Influence of filler content on impact strength

Tensile Test The results of tensile tests gave clear indication that there is no significant change in the tensile strength of the composites was found up to 30 wt.% filler load in comparison with the neat LDPE. For instance, LDPE-I filled with 30 wt. % of BOS fine ash showed a 21% decrease in tensile strength. Similarly, LDPE-II filled with 30 wt.% of coal coarse ash showed a 36% decrease. At the same time, increase in the ash content showed a slight improvement in the modulus of elasticity (Figure 12) in some compounds such as LDPE filled with 30 wt.% of BOS fine ash and LDPE-II filled with coal coarse ash got an extraordinary increase in it. Similarly, composites of LDPE with $CaCO_3$ showed stability in tensile strength in comparison to neat LDPE and ashes. Mechanical properties of composite materials are represented in Table 4.

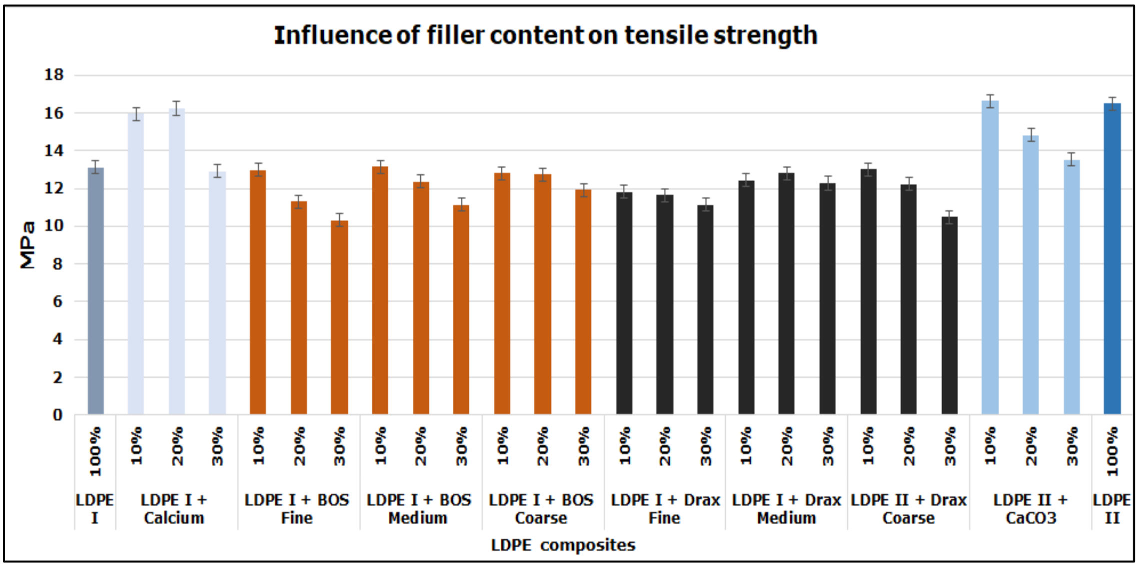

Figure 11. Influence of filler content on Tensile strength

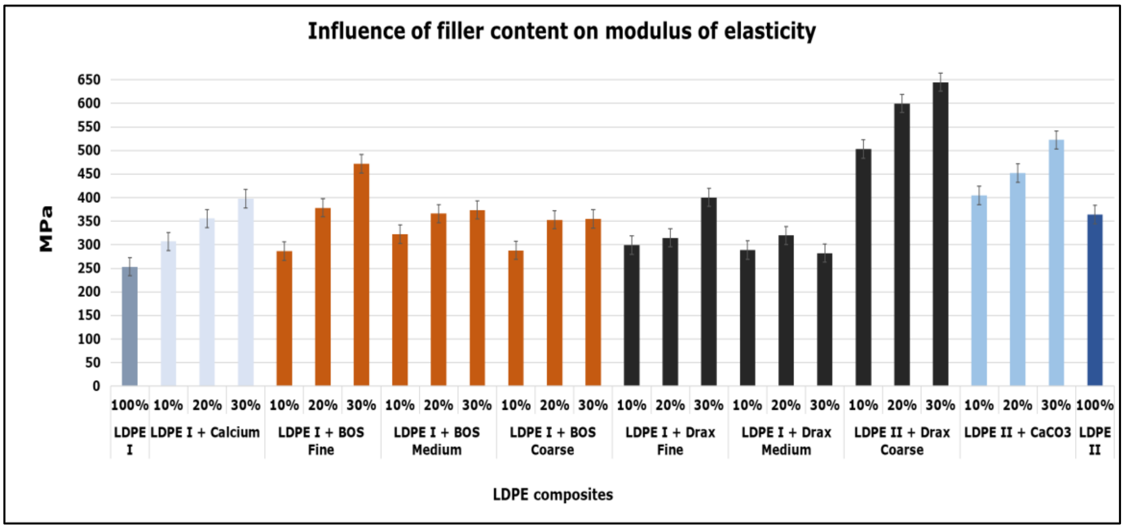

Figure 12. Influence of filler content on modulus of elasticity

Table 4. Mechanical and thermal properties of LDPE + BOS, DRAX and $CaCO_3$ compounds

S No.	Polymer (wt. %)	Filler (wt. %)	MFI g/10 min.	Impact strength (KJ/m^2)	Tensile strength (MPa)	Modulus of elasticity (MPa)
1	LDPE I 100	–	1.10	68.88	13.13	253.30
2	LDPE I 90 %	Fine BOS Ash 10 %	1.10	60.60	12.97	286.44
3	LDPE I 80 %	Fine BOS Ash 20%	0.90	30.96	11.29	378.56
4	LDPE I 70 %	Fine BOS Ash 30%	0.70	31.08	10.33	471.55
5	LDPE I 90 %	Medium BOS Ash 10%	1.10	58.40	13.14	322.49
6	LDPE I 80 %	Medium BOS Ash 20%	0.90	32.90	12.38	365.94
7	LDPE I 70 %	Medium BOS Ash 30%	0.70	30.05	11.13	373.96
8	LDPE I 90 %	Coarse BOS Ash 10%	1.00	62.48	12.81	288.13
9	LDPE I 80 %	Coarse BOS Ash 20%	0.50	35.89	12.73	352.96
10	LDPE I 70 %	Coarse BOS Ash 30%	0.60	32.93	11.91	354.9
11	LDPE I 90 %	Fine Drax Ash 10%	1.00	65.14	11.83	299.18
12	LDPE I 90 %	Fine Drax Ash 20%	1.00	67.69	11.65	314.73
13	LDPE I 70 %	Fine Drax Ash 30%	1.10	66.80	11.13	400.60
14	LDPE I 90 %	Medium Drax Ash 10%	0.90	55.94	12.44	288.67
15	LDPE I 80 %	Medium Drax Ash 20%	0.80	35.73	12.81	319.78
16	LDPE I 70 %	Medium Drax Ash 30%	0.70	26.69	12.28	282.31
17	LDPE II 90%	Coarse Drax Ash 10%	1.85	21.40	13.02	503.45
18	LDPE II 80%	Coarse Drax Ash 20%	1.75	20.32	12.22	599.84
19	LDPE II 70%	Coarse Drax Ash 30%	1.70	19.30	10.48	644.94
20	LDPE I 90%	$CaCO_3$ 10%	1.39	75.31	15.95	306.95
21	LDPE I 80%	$CaCO_3$ 20%	2.03	76.56	16.24	355.61

Table 4 continue

Table 5. Mechanical and thermal properties of LDPE + BOS, DRAX and $CaCO_3$ compounds

S No .	Polymer (wt. %)	Filler (wt. %)	MFI g/10 min.	Impact strength (KJ/m²)	Tensile strength (MPa)	Modulus of elasticity (MPa)
22	LDPE I 70%	$CaCO_3$ 30%	2.30	62.18	12.91	397.88
23	LDPE II 100%	_	1.98	70.49	16.50	364.41
24	LDPE II 90%	$CaCO_3$ 10%	1.90	33.40	16.62	404.49
25	LDPE II 80%	$CaCO_3$ 20%	2.31	33.40	14.81	452.02
26	LDPE II 70%	$CaCO_3$ 30%	2.45	32.40	13.54	522.50

2.5.3 Composite materials characterization

Infrared spectroscopy (ATR-FTIR) spectra of all tested in this work types LDPE composites gave clear indications that there are no chemical reactions that happened between the fillers and the matrix polymer (see Figure 13).

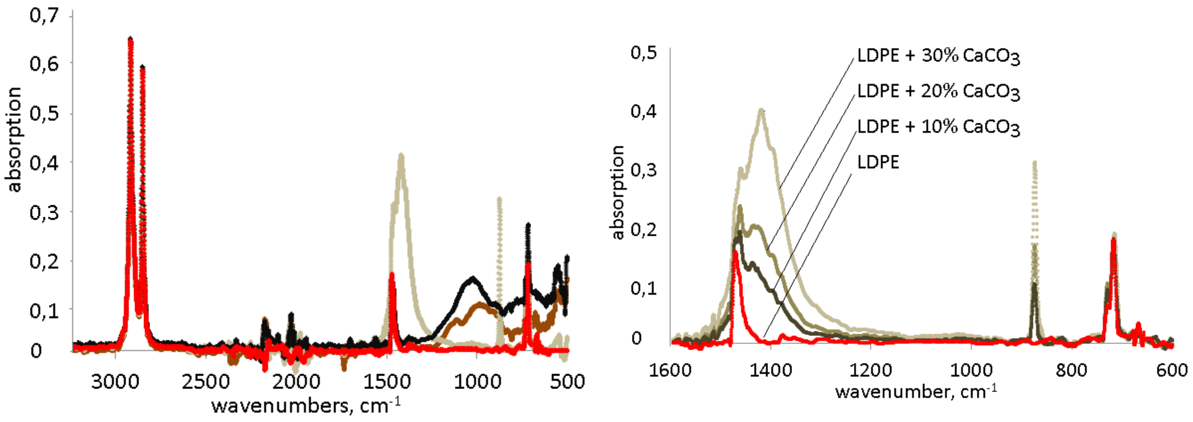

Figure 13. Infrared spectra of neat LDPE-I (red) and LDPE-I filled with 30% fine BOS (brown), 30% fine DRAX (black) and 30% $CaCO_3$ (gray) (left graph). Infrared spectra of LDPE-I filled with different load of CaCO3 (right graph)

As could be seen from figure 13 (left) absorption bands characteristic to LDPE undergo no changes for all the studied composites. Two peaks specific to amorphous phase: at 716 cm^{-1} corresponding to $–CH_2–$ methylene group rocking and at 2913 cm^{-1} to $–CH_2–$ asymmetric stretching remains the same. No variation in these absorption bands evidences any changes in crystallinity of polymer. No changes found in bands 1467 cm^{1} corresponding to C–H bending and at 2847 cm^{-1} to $–CH_2–$ symmetric stretching in both amorphous and crystalline phases. (Daniel Joséda Silva, 2017) LDPE in solid state can contain three types of crystals with different lattice parameters; unfortunately, it is not possible to distinguish between the crystalline phases from the FTIR spectra. (Peacock A. , 2000)

According to the literature different calcium carbonate phases could be recognized by FTIR, due to the difference in absorption of two groups: carbonate group CO_3 out-of-plane deformation (v_2 band) and in-plane deformation (v_4 band). (Ming Ni, 2008) A calcite polymorph phase has characteristic v_2 band at 872 cm^{-1} and v_4 band at 713 cm^{-1}; amorphous phase of $CaCO_3$ has characteristic split v_3 band at 1461 cm^{-1} (asymmetric stretching) and 1437 cm^{-1} (symmetric stretching). (Qiang Shen, 2006) No shift of these peaks after compounding with LDPE evidences structural stability of $CaCO_3$ filler at compounding conditions, as well as no chemical reaction with polymer matrix. As well absorption intensity rises upon increase of $CaCO_3$ content in composite. (see figure 13 right).

Table 5 represents EDXRF data for both types of ashes: as could be expected DRAX have higher the total organic carbon content between 3.7-4.7 % compare to BOS 0.1-0.3 %. At the same time the loss on ignition (unburnt carbon content) of BOS equals to 3.5% is in similar range as DRAX 4.5%. It was interesting to compare chemical composition of ashes analyzed by X-ray fluorescence with chemical composition of composites analyzed by infrared spectroscopy.

FTIR spectra of ash filled composites are represented in figure 14, one could see gradual increase of light absorption by filler in wavenumber range from 1200 to 700 cm^{1}, which could be attributed to different oxide groups. Bands: 1017 cm^{-1} assigned to Si-O stretching for kaolinite and 795 cm^{-1} for quartz, 873 cm^{-1} to C-O for calcite (Clara Jeyageetha .J, 2013), the broad extending band in the range of 800–700 cm^{-1} and lower assigned to the Al_2O_3 amorphous structure and 1070 cm^{-1} to Al-O stretching for tetrahedron crystalline phases (K. Djebaili, 2015). From the comparison of EDXRF and FTIR data (figure 14 and table 5) good correlations between x-ray fluorescence and IR absorption of ashes is found. BOS show well distinguished absorption at 1114 cm^{-1} of Si-O-Si stretching for quartz upon which 38,99% of the BOS composition, similar band for DRAX is strongly overlapped, despite of even higher content (52,31%) in composition. DRAX show clear absorption at 1070 cm^{-1} from Al_2O_3 which take 25,53% of ash composition. Most of oxides identified by EDXRF have characteristic IR absorption bands in range below 700 cm^{-1} down to 400 cm^{-1}, but in case of studied composites these peaks strongly overlapped by absorption of matrix polymer.

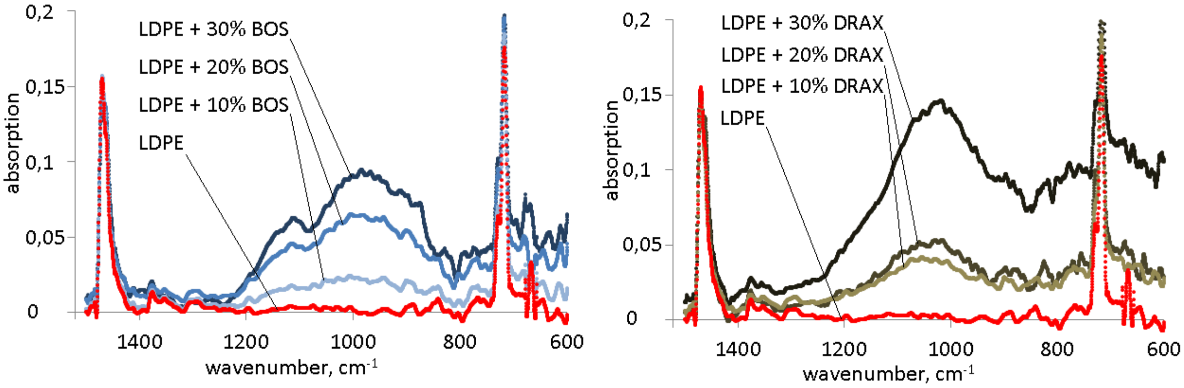

Figure 14. Infrared spectra of LDPE filled with different load of BOS fine and Drax fine ash

Table 5. Chemical composition of ashes according to EDXRF

	BOS ash	**Drax ash**
Oxide	**wt.%**	**wt.%**
Al_2O_3	11,69	25,53
CaO	26,25	2,27
K_2O	5,12	3,35
MgO	4,4	1,7
Mn_2O_3	0,05	0,08
Na_2O	0,15	1,4
P_2O_5	0,17	0,28
SiO_2	38,99	52,31
TiO_2	0,57	1,01
SO_3	4,53	0,46
Na_2O-eq.	3,52	3,46

2.5.4 Thermal Properties

Thermal and structural properties were analyzed by DSC and are represented in table 6 which shows that there is no significant change in the melting temperature of the composites neither when polymer is filled with the ash nor $CaCO_3$. Also, the degree of crystallinity did not increase much which means there is no interaction between polymer matrix and filler particles which could induce crystallization of polymer chains.

Table 6.Thermal and structural properties of LDPE+BOS, DRAX and CaCO3 compounds.

S No.	Polymer (wt. %)	Filler (wt. %)	Melting Temperature T_m (°C)	Degree of Crystallinity (%)
1	LDPE I 100	_	117	32
2	LDPE I 90 %	Fine BOS Ash 10 %	115.9	19
3	LDPE I 80 %	Fine BOS Ash 20%	113.5	25
4	LDPE I 70 %	Fine BOS Ash 30%	114.2	19
5	LDPE I 90 %	Medium BOS Ash 10%	114.5	24
6	LDPE I 80 %	Medium BOS Ash 20%	115.5	17
7	LDPE I 70 %	Medium BOS Ash 30%	114.5	18
8	LDPE I 90 %	Coarse BOS Ash 10%	116.5	20
9	LDPE I 80 %	Coarse BOS Ash 20%	115.2	20
10	LDPE I 70 %	Coarse BOS Ash 30%	113.8	16
11	LDPE I 90 %	Fine Drax Ash 10%	114.5	38
12	LDPE I 90 %	Fine Drax Ash 20%	115.2	20
13	LDPE I 70 %	Fine Drax Ash 30%	115.2	07
14	LDPE I 90 %	Medium Drax Ash 10%	116.8	25
15	LDPE I 80 %	Medium Drax Ash 20%	115.8	19
16	LDPE I 70 %	Medium Drax Ash 30%	115.5	11
17	LDPE II 90%	Coarse Drax Ash 10%	131.9	45
18	LDPE II 80%	Coarse Drax Ash 20%	128.9	10
19	LDPE II 70%	Coarse Drax Ash 30%	129.2	16
20	LDPE I 90%	$CaCO_3$ 10%	115.6	24
21	LDPE I 80%	$CaCO_3$ 20%	116.6	20
22	LDPE I 70%	$CaCO_3$ 30%	116.9	08

2.5.5 Morphology

SEM images of fractured specimens' surfaces gave an insight into how well the particles of the ashes dispersed into the polymer matrix. For instance, if to compare the finer fractions of BOS and coal ashes, it appears that the drax coal ash particles have a perfect spherical shape which improves the distribution of the particles in polymer matrix while particles of BOS ashes are not in uniform shape and are capable for agglomeration (see Figure 15 and 17). The higher modulus of elasticity of LDPE II with drax coarse ash could also be attributed to the fact that LDPE II is in powder form and drax coal ash is also in good spherical shape (see figure 16 and 18) which prevents the formation of agglomerates and improve the dispersion of ash into the polymer matrix thus resulting a stiffer material. Moreover, it appears that $CaCO_3$ has the best dispersion within the LDPE matrix (see Figure 19).

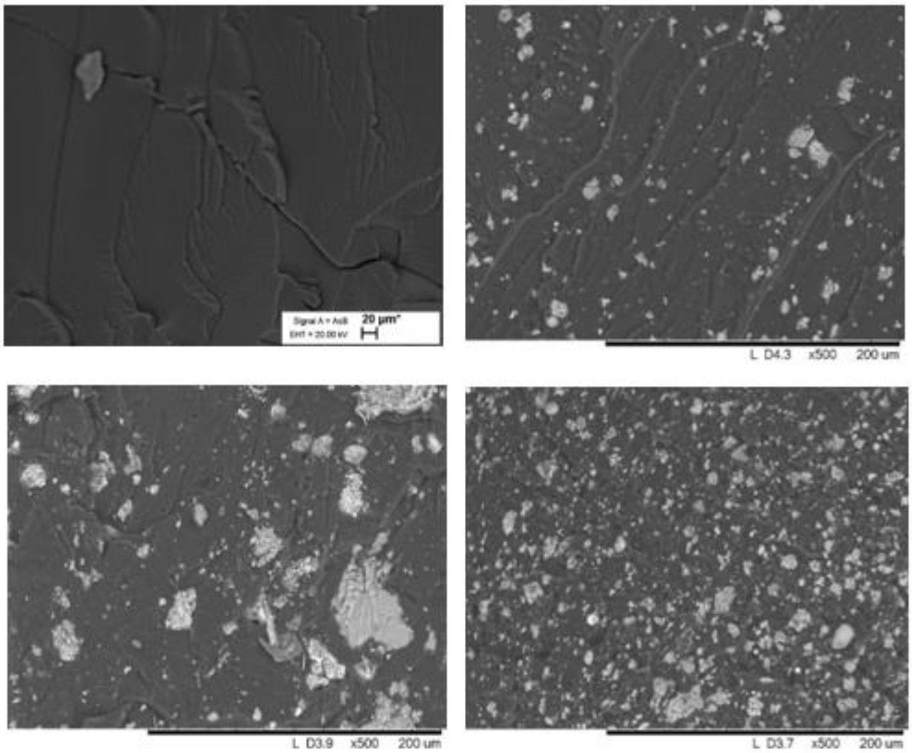

Figure 15. SEM image of neat LDPE I (top left), LDPE I+ BOS Fine 10 wt.% (top right), LDPE I+ BOS Fine 20 wt.% (bottom left) and LDPE I+ BOS Fine 30 wt.% (bottom right)

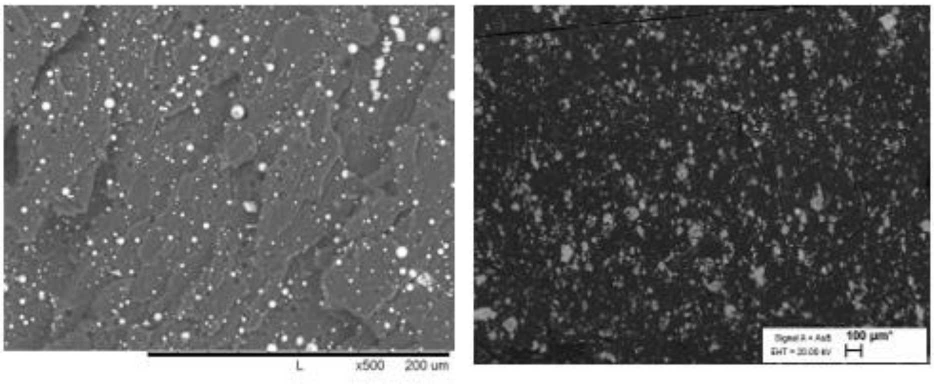

Figure 16. SEM image of LDPE II + Drax coarse 20 wt.% (left) and LDPE I + BOS Coarse 20 wt.% (right)

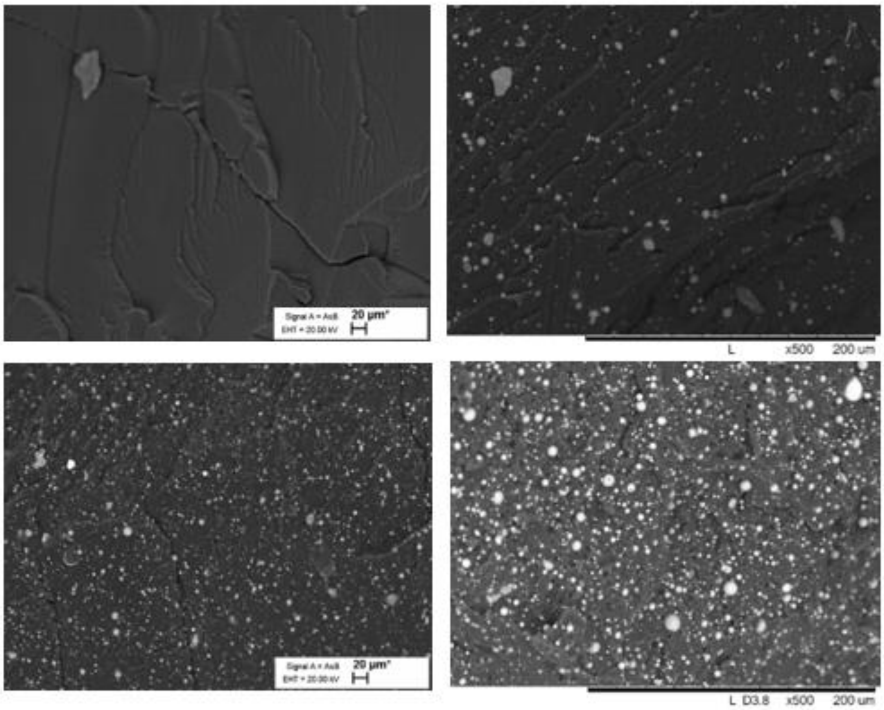

Figure 17. SEM image of neat LDPE I (top left), LDPE I+ drax Fine 10 wt.% (top right), LDPE I+ drax Fine 20 wt.% (bottom left) and LDPE I+ drax Fine 30 wt.% (bottom right)

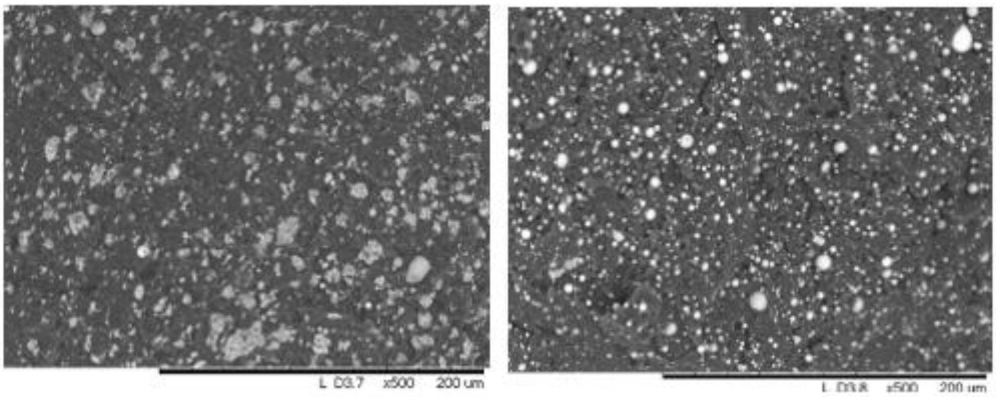

Figure 18. SEM image of LDPE+BOS fine 30 wt.% (left) and LDPE+ DRAX fine 30wt.% (right)

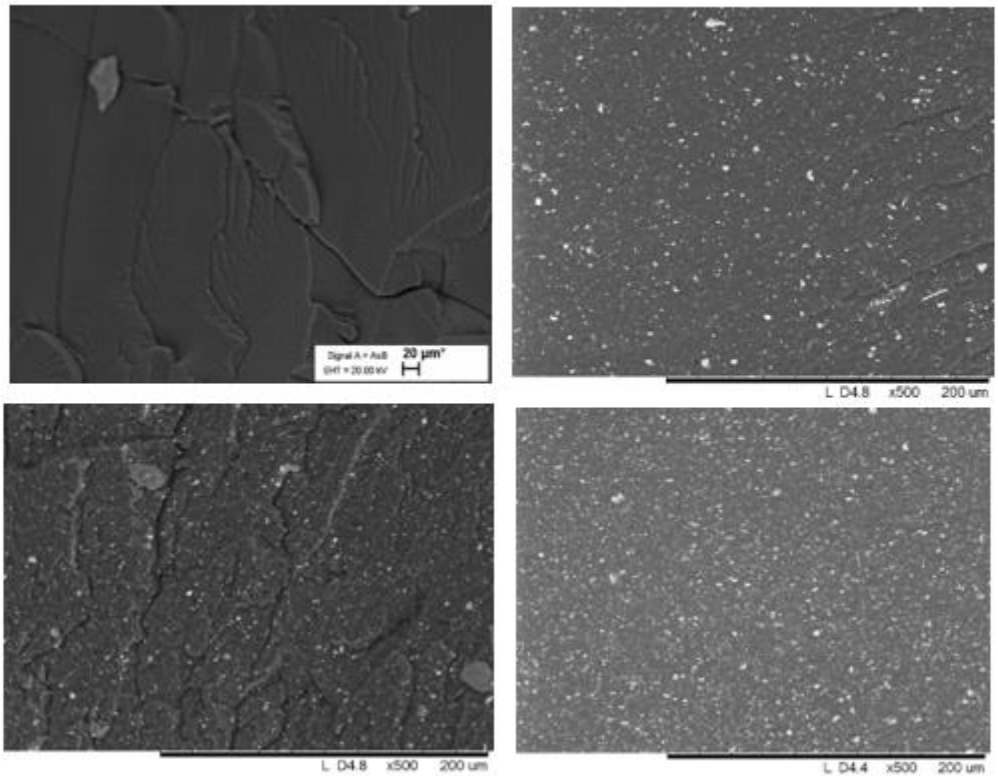

Figure 19. SEM image of LDPE I (top left), LDPE I+ CaCO3 10 wt.% (top right), LDPE I+ CaCO3 20 wt.% (bottom left) and LDPE I+ CaCO3 30 wt.% (bottom right)

3. SUMMARY

Composite materials made of LDPE filled with BOS ashes show a decrease in the impact strength upon the increase in the content of the ash. Also, the modulus of elasticity increased as well with an increment in the content of ash filler which led to an excessive stiffness of the material. Similarly, upon increasing the ash content, MFI of the material decreased which led to a change of the injection molding processing parameters. Overall, BOS fine Ash with 10wt.% showed the best results if to compare with 20 and 30wt.% load. One should notice that composites filled with ash have a dark - brown color.

Composite materials made of LDPE filled with fine coal ashes show a similar range of impact strength as of pure LDPE, but LDPE filled with larger fractions of coal ashes shows a decrease in the impact strength with respect to the content of the filler. As the content of the coal ash increased, stiffness also increased which led to modify the process parameters of the injection molding as MFI of the compounds got decreased a bit. In a nutshell, fine coal ash showed the best results in comparison to coal medium and coarse ash as well as to BOS ashes. In addition, coal ash has a black color that gives black color to the final product.

One should notice that negligible modifications in processing parameters were required for the preparation of BOS and coal ash compounds in comparison to neat polymer and polymer filled with $CaCO_3$. In comparison with ashes, compounds of LDPE with CaCO3 show a stable performance in terms of impact strength which did not decrease as the content of calcium carbonate increased but the stiffness of the final product increased as well with the dosage of 30% wt. of $CaCO_3$.

With reference to the above-mentioned data, it can be concluded that BOS and coal ashes can be used as fillers for thermoplastics and processed by conventional methods such as extruder compounding and injection molding. Moreover, it seems so that products from BOS and coal ash compounds can be used in the applications where impact strength is not required or negligible. However, these ashes cannot be used to produce lighter color products because of their natural dark color. On the other hand, in comparison with calcium carbonate, BOS ash can be a handy alternative as a cost reduction filler because it is waste material in countries where oil shale is locally available.

4. CONCLUSION

1. Composites with load of ash up to 30 wt. % could be compounded and injection moulded at similar conditions and processing parameters same as neat polymers.
2. Ash load slightly decreases impact strength of composite, makes it brittle.
3. Ash load has negligible effect on tensile strength of composite, keeps it tough.
4. Ash load slightly increase Young's modulus of composite, makes it stiff.
5. BOS ash could work as brown pigment, DRAX ash could work as black pigment.
6. Ashes are twice cheaper than widely used $CaCO_3$ filler.
7. Ashes found to be perspective fillers for manufacturing of compression and injection moulded boards, panels and other construction elements.

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