Kaunas University of Technology
Faculty of Mechanical Engineering and Design

Creation and Investigation of Polyolefins and Nanoclays Composites

Master’s Final Degree Project

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Prof. Virginija Jankauskaite
Supervisor

Kaunas, 2020

Kaunas University of Technology

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Industrial Engineering and Management (6211EX018)

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Declaration of Academic Integrity

I confirm that the final project of mine, Hemanth Raju Sundar, on the topic „Creation and Investigation of Polyolefins and Nanoclays Composites“ is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

I fully and completely understand that any discovery of any manifestations/case/facts of dishonesty inevitably results in me incurring a penalty according to the procedure(s) effective at Kaunas University of Technology.

(name and surname filled in by hand) (signature)

Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Task of the Master's final degree project

Given to the student – Hemanth Raju Sundar

1) **Title of the project –**

Creation and Investigation of Polyolefins and Nanoclays Composites

(In English)

Poliolefinų ir nanomolio kompozitų kūrimas ir tyrimas

(In Lithuanian)

2) **Aim and tasks of the project –**

To investigate the polyolefin and nanoclay composites structure and properties and compare their behaviour with microparticle filled polyolefin.

Tasks:

1) to study the morphology of the nanoclay particles before and after modification with quaternary ammonium salts;
2) to determine the influence of filler type and amount on the mechanical properties of polyolefin composites;
3) to investigate the structure of composites and interaction mechanism between filler particles and polymer matrix;
4) to compare the structure and properties of polyolefins with nanometric and micrometric filler particles;
5) to analyse the environmental impact of the composite and perform a cost analysis of filled polyolefin composition products;

3) **Initial data of the project –**

N/A

4) **Main requirements and conditions –**

1) Plastics- Determination of tensile properties- Part1- General principles LST EN ISO 527-1.
2) Plastics- Determination of tensile properties- Part2- Test conditions for moulding and extrusion plastics LST EN ISO 527-2.
3) Equipment for structural and mechanical investigation of nanocomposites.

Project author	Hemanth Raju Sundar		
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Supervisor	Virginija Jankauskaite		
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Hemanth Raju Sundar. Creation and Investigation of Polyolefins and Nanoclays Composites. Master's Final Degree Project, supervisor Prof. Virginija Jankauskaite; Faculty of Mechanical Engineering and Design, Kaunas University of Technology.
Study field and area (study field group): Production and Manufacturing Engineering (E10), Engineering Sciences (E).

Keywords: polyolefins, nanoclays, microfiller, modifier, structure, mechanical properties.

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Summary

The goal of this study was to create and investigate polyolefins and nanoclay composite, investigate their morphology and mechanical properties and also compare with microfilled polypropylene composite. The montmorillonite clay (MMT) was used as nanofiller. It was organically modified with quaternary ammonium salts of different structure and influence of modification on the morphology of MMT was investigated. Two polyolefins, such as linear low-density polyethylene (LLDPE) and propylene (PP), were used for investigation. Because all fillers to be used disrupted microstructure of LLDPE, hence only PP was used for further investigation. The PP composites filled with MMT and shale ash (waste) were prepared and their morphology and properties have been investigated. It was shown that the morphology and mechanical properties of the PP composites are dependent on the filler nature and content. However, low adhesion interaction at the interface between filler and polymer matrix was observed in both MMT and shale ash addition cases. Therefore, in further studies it is necessary to compatibilize filler and polyolefin. The environmental impact of created PP composites was analysed and approximate life cost estimation of the PP composite products for packaging film and the automotive panel was carried out. It was shown that the PP composites were profitable in use for the automotive panel comparing to conventional products. The research carried out in the master’s final degree project is devoted to solve one of the task of the project no. J05-LVPA-K-04-0045 “Development of Innovative Plastic and Other Additive Composites with Distinctive Physical and Chemical Properties”, which is funded by European Regional Development Fund according to the 2014–2020 ‘Operational Program for the European Union Funds Investments’ under measure No. J05-LVPA-K “Intellect Joint Science-Business Projects” (coordinator UAB Vilkritis, period of implementation 28-02-2019—27-02-2021).

Hemanth Raju Sundar. Poliolefinų ir nanomolio kompozitų kūrimas ir tyrimas. Magistro baigiamasis projektas, vadovė Prof. Virginija Jankauskaitė; Kauno technologijos universitetas, Mechanikos inžinerijos ir dizaino fakultetas.

Studijų kryptis ir sritis (studijų krypčių grupė): Gamybos inžinerija (E10), Inžinerijos mokslai (E).

Reikšminiai žodžiai: poliolefinai, nanomolis, mikroužpildas, modifikatorius, struktūra, mechaninės savybės.

Kaunas, 2020. 54 psl.

Santrauka

Darbo tikslas – sukurti ir ištirti poliolefinų ir nanomolio kompozitus, įvertinti jų morfologiją ir mechanines savybes bei palyginti su mikrodalelėmis užpildytu polipropileno kompozitu. Montmorilonito molis (MMT) buvo naudojamas kaip nanoužpildas, kuris buvo organiškai modifikuotas skirtingos struktūros ketvirtinėmis amonio druskomis. Ištirta modifikacijos įtaka MMT morfologijai. Tyrimams buvo naudojami dviejų tipų poliolefinai: linijinis mažo tankio polietilenas (LLDPE) ir propilenas (PP). Kadangi buvo nustatyta, kad užpildai suardo LLDPE mikrostruktūrą, todėl tolesniems tyrimams buvo naudojamas tik PP. Darbe PP kompozitai buvo užpildyti MMT ir skalūnų pelenais (atliekomis), ištirta jų morfologija, mechaninės savybės. Parodyta, kad PP kompozitų morfologija ir savybės priklauso nuo užpildo prigimties ir kiekio. Tačiau tiek MMT, tiek skalūnų pelenų įmaišymo atvejais pastebėta maža adhezinė sąveika tarp užpildo dalelių ir polimerinės matricos. Todėl tolimesniuose tyrimuose būtina padidinti suderinamumą tarp užpildo ir polimero. Buvo išanalizuotas sukurtų PP kompozitų rinkos analizė, atliktas sukurtų PP kompozitų panaudojimo pakavimo plėvelėms ir automobilių skydeliams gamybai išlaidų įvertinimas. Parodyta, kad ekonomiškai naudinga naudoti PP kompozitus automobilių skydelių gamybai. Magistro baigiamajame projekte atlikti tyrimai skirti ES struktūrinių fondų projekto Nr. J05-LVPA-K-04-0045 „Inovatyvių plastiko ir kitų priedų kompozitų, pasižyminčių išskirtinėmis fizinėmis ir cheminėmis savybėmis, kūrimas“, kuris finansuojamas Europos regioninės plėtros fondo lėšomis pagal 2014–2020 m. Europos Sąjungos fondų investicijų veiksmų programos priemonę Nr. J05-LVPA-K „Intelektas. Bendri mokslo–verslo projektai“ (koordinatorius UAB „Vilkritis“, įgyvendinimo laikotarpis 2019-02-28 – 2021-02-27) vienam iš uždavinių spręsti.

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List of abbreviations

PP – polypropylene;
PE – polyethylene;
MAgPP – maleic anhydride grafted polypropylene;
BN – boron nitride;
T_g – glass transition temperature;
DMBHT – dimethyl benzyl dihydrogenated tallow ammonium chloride;
SEM – scanning electron microscopy;
TGA – thermogravimetric analysis;
LDPE – low-density polyethylene;
PLS – polymer layered silicate;
PET – polyethylene terephthalate;
PPCNs – polypropylene clay nanocomposites;
FTIR – Fourier transform infrared spectroscopy;
LLDPE – linear low-density polyethylene;
OMMT – organic modified montmorillonite;
MMT – montmorillonite;
OMHT – organically modified hectorite;
MICA – amino silane treated phlogopite;
MBA – methylene bissaniline;
DSC – differential scanning calorimetry;
TPO – thermoplastic polyolefins;
MFI – melt flow index;
HDT – heat distortion temperature;
M_W – molecular weight;
DTG– derivative thermogravimetry;
HDPE – high-density polyethylene;
NR – natural rubber;
MMT-Na^+ – sodium montmorillonite;
TPS – thermoplastic starch;
DMDHT – dimethyl dihydrogenated tallow ammonium chloride;
TEM – transmission electron microscopy;
MALDPE – maleic anhydride grafted low-density polyethylene;
XRD – X-ray diffraction;

Introduction

Polyolefins are the class of carbon chain thermoplastics and elastomers and are the biggest class of synthetic polymer made. Because of the high chemical resistance, less cost of preparation and fewer weight polyolefins are broadly used in today's world. Among all polyolefins, polypropylene and polyethylene are the most commonly used materials. Polypropylene and polyethylene as neat material exhibit low properties, such as low impact strength, poor adhesion due to hydrophilic reactive groups of PP and PE chain. However, disperse fillers and nanofillers can improve the properties and polyolefin composites with enhanced properties and cost-saving possibility can be obtained. Even Composite materials can be characterized as the consolidation of two or more materials that gives a different property than the neat ones.

In recent years there are many types of research works towards polymer-based nanocomposites for various end applications. Montmorillonite clay is widely used for polymers modification, because of its compatibility with the polymers. Clay contains aluminosilicate mineral as well as sodium ions presence between the layers of clay. The nature of the clay, its content and reciprocal action between the fillers and the polymer matrix have a greater influence on the extent of enhancement of the nanocomposites. The main reason for obtaining the nanocomposites is based on the view they exhibit better properties than microfilled composites. However, the mixing of the particles is not simple. Henceforth there is a requirement of modification for the nanoclay to be used as filler for preparation of the nanocomposites. It is also seen that only a limited quantity of nanofiller is enough to change the characteristics of the matrix. Even waste of shale has compatibility with polyolefins and to produce different properties of the composites, this leads to the research interest.

In the view of obtaining improved properties of the composite materials then the composite materials can be used for various end applications rather than using conventional polyolefin material.

The aim of this work is to investigate the polyolefin and nanoclay composites structure and properties and compare their behaviour with microparticle filled polyolefin.

The tasks of the work are:

1. to study the morphology of the nano clay particles before and after modification with quaternary ammonium salts.
2. to determine the influence of filler type and amount on the mechanical properties of polyolefin composites.
3. to investigate the structure of composites and interaction mechanism between filler particles and the polymer matrix.
4. to compare the structure and properties of polyolefins with nanometric and micrometric filler particles.
5. to analyse the environmental impact of the composite and perform a cost analysis of filled polyolefin composition products.

The master's final degree project is devoted to the project no. J05-LVPA-K-04-0045 "Development of Innovative Plastic and Other Additive Composites with Distinctive Physical and Chemical Properties", funded by European Regional Development Fund according to the 2014–2020 ‘Operational Program for the European Union Funds Investments’ under measure No. J05-LVPA-K “Intellect Joint Science-Business Projects” (Annex 1).

1. Relevance of research

Polyolefins structural properties and uses. Polyolefins are also named as polyalkenes and they are the biggest class of commodity thermoplastics. These are uncomplicated alkenes including ethylene's, propylene 's, butanes and pentenes and copolymers. PE and PP are better essential polyolefins. Using very easy approaches such as injection moulding, extrusion and thermoforming, blow-moulding, also by using standard thermoplastic equipment PP and PE can be processed. These are the most popular resins because of their easy processability, low price in consolidation with their excellent chemical and physical properties.

Polypropylene has a molecular formula (C3H6)n, as like everything the crystalline polymers have a pyramid structure. Its equities are resolved by the different criteria of this complex and the maximum influential being the crystallinity, crystal adjustment, lamella thickness, the number of tie molecules and spherulite size. The second one which is most widely used is a thermoplastic polymer, because of the large availability, average rate, good properties and simple to produce is PP. Thermoplastic polymers are the consolidation of propylene monomers, it is used in functions like packaging, household areas, electrical equipment manufacturing and in transportation sectors. Following are different types of PP:

- Atactic PP (aPP): methyl groups are anyhow placed on the main chain and they are completely amorphous, and they don't have melting temperature rather they just soften upon heating and flow like an adhering liquid.
- Syndiotactic polypropylene (sPP): methyl troops are preferably adapted and located along the main chain and these are semicrystalline polymers.
- Isotactic PP (iPP): The methyl groups are placed on one part of the structure that makes the PP homogenous, stable, these are called semicrystalline polymers and have of crystallinity of high degree.

Polypropylene has a molecular formula (C3H6)n. it is produced by chain-growth polymerization of propene (Fig. 1).

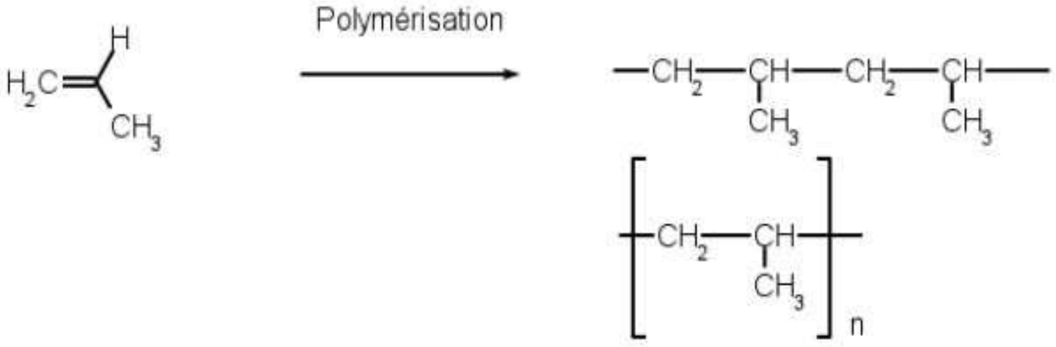
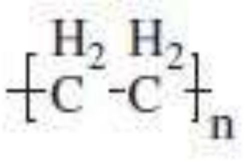


Fig. 1. Structure of PP [1]

Polyethylene, Ethylene is the single monomer constituent, PE is a semicrystalline thermoplastic POE and is extensively used in-universe. The complexion of PE decides the application of PE. Based on molecular-weight, crystallinity (density) and branching. A special variety of different grades are commercially available. The mechanical properties and melt flow behaviour of PE varies on the amount of the branching of polymer and the polymer molecular weight. It is brittle if PE of higher molecular weight is without branching. The highest volume of grades is:

- High-density PE (HDPE): The Lower degree of branching than LDPE. HDPE has a crystallinity of the highest degree and is different among every Pes. HDPE is more stable than PE, i.e the chain packs into crystal structure very well. These are less permeable, more rigid and much denser. It harder and stronger than LDPE but has less toughness, flexibility and lower stress crack resistance. When high strength and rigidity also high chemical resistance is needed there HDPE is used.
- Low-density PE (LDPE): They have a high form of chain branching, as a result, they are ductile, flexible material and have a unique flow property. However, they have a lower tensile strength, heat deflection temperature and melting point than HDPE.
- Linear low-density PE (LLDPE): They are useful in film applications, as they have a fine structure with a very large short branches, they have similar strength as HDPE and have increased tensile strength than LDPE and greater puncture resistance compared to LDPE [2].

The (C2H4)n, is the chemical formula for polytethylene, the pair of methylene group is connected to each other as shown in the structure in Fig. 2.



$$\left[\overset{H_2}{C}-\overset{H_2}{C}\right]_n$$

Fig. 2. Structure of polyethylene [3]

The advantages of polyolefins, PE and LDPE are one of the most widely used polyolefins polymers possessing major advantages like low density, great stiffness, great softening temperature, very great chemical inertness and most importantly they are cheap, easy to process and more economical to for producing new polymeric materials [4]. PP has good profitability, high detention and rigidity. Polyolefins have benefits over polyamide use for those applications, it as lower pot life, lower application temperature and better adhesion to olefinic substrates [5].

The few disadvantages of polyolefins are they have difficulty to bond, the impact strength is poor, they have oxidative degrading and lower grades are available as their inflammable. With high thermal expansion their flammable as well, very less temperature capacity, they tend to stress cracking with poor weathering.

Nanoclays are in demand for preparation of polymer/layered silicate, they have a similar family of 2:1 phyllosilicate. The formation is of four bonds coordinated atoms of silicon having the octahedral magnesium hydroxide. The density is approximately 1nm. The alkali and the alkaline earth cations are been balanced by the anions. This type of counterbalance process is called CEC and is represented as mequiv/100g [6].

The most common silicates are bentonite, hectorite and saponite. They are different kinds of arrangements one is tetrahedral- replaced where the negative ions are situated upon the surface and are easier for the reaction of polymer matrices than the other octahedrally substituted material.They are the layers of silicates consisting of platelets of nanosized thickness which are connected by forces of van der Waals.

Nanocalys are usually incorporated with polymers in order to enhance their properties. The four major bands of nanoclays are kaolinite, montmorillonite, illite and chlorite. MMT has attracted more in the field of composites as they are cost-effective, easily available, processability is simple and has significant improvement in the performance. Natural MMT has hydrophilic properties because of the positive ions on their area and henceforth the consolidation with polymers are not effective. Hence modification of them is required which is done with organic compounds through intercalation and grafting. Colosite, Garamite are organically modified nanoclays, they have very good interlayer spacing, hydrophobic surface and better interaction with polyolefins. MMT is the most widely used as a nanofiller for creating nanocomposites.

Nanoclays are commonly used as nanofillers are bidimensional platelets and have a thickness around 1nm. The interaction with nanoclays and polymers produces two types of nanocomposites, intercalated and exfoliated nanocomposites which has extensive polymer penetration. Nanoclay is blended into TPS to increase the mechanical equity also the thermal capability and water resistance. Very commonly layered silicates that were used are montmorillonite, hectorite and saponite. They have two structures: tetrahedra-substituted and octahedral substituted. Polymer interacts much immediately with tetrahedral than octahedrally substituted material [7].

To have the nanoclay render with the polymers, the silicate layer should be organophilic which can be completed by CEC method with positive ions surfactants. This is possible for primary, secondary, tertiary and quaternary alkylammonium or alkyl phosphonium positively charged ions as well [6]. They have the feature of rising the characteristics of the polymer matrix by rending or creating characteristically behaviour and to increase the property the interaction mechanism should be good and is obtained by CEC which again is decided based on the preparation technique of the composite and their structural characteristics.

The barrier properties of the nanocomposites are increased in terms of nanofillers, they increase the properties of the composites and render enhanced characteristics and properties. They have dimension less than ten square nanometer one of the dimensions and because of its nano dimensions they render high interface, strong interaction between the particles and form good interfacial reactions between the composite particles and give better improved properties than the conventional material. The type interaction depends upon the modifier used and the length of the chain so that there is enough increased space for the composite particles to settle in the mixture and form a good interaction. Also, the addition of the compatibilizers also tends to increase the reaction of the between the polymers and nanoclays, with consideration of the operational conditions, the way the materials are mixed.

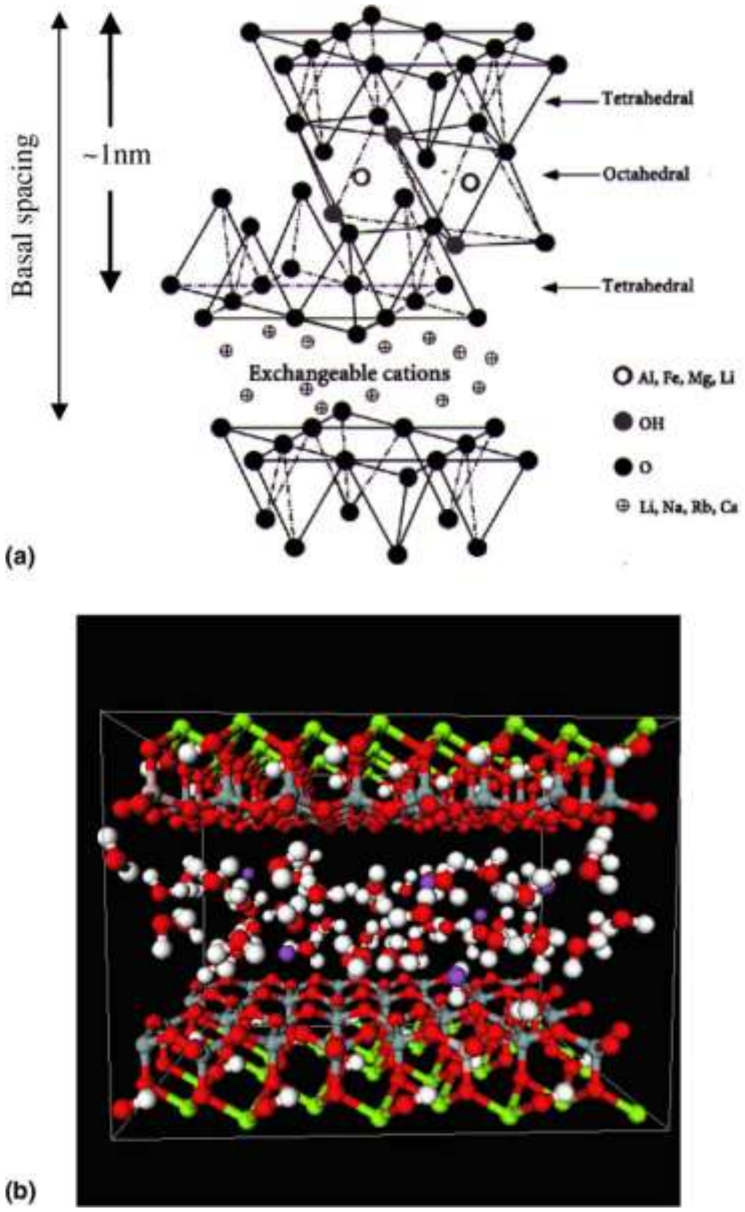


Fig. 3. Idealised structure of 2:1 layered silicate (a), 3D crystal image of MMT (b) [1]

The advantages of nanoclays on addition with the polyolefins always develop the mechanical properties of the composite and permeability of gases can be reduced. They also improve the thermal capability of composite material. The easy opportunity of getting the clay from the nature and easy production make nanoclay a significant material for research, industry and technology.

The obstacle properties of nanocomposites are improved when they are used as a nanofillers. It improves the mechanical enforcement, detention of chloride penetration, self-covenant equity and reduces permeability and shrinkage of the concrete. The nanocomposite has a particle size less than ten square nm in one of the aspects. Nanocomposites possess unique properties than macro- or micro-composite counterparts because of their interaction mechanism, large interface area and of nanoscale effect, hence has lots of opening in high technology [8]. Nanocomposites have a big outer area to size ratios in nanostructures. Aside from the properties of the individual component, interfaces perform an important act of developing or undeveloping all properties of the system [9].

The peeling and diffusion of the nanoclays lean on various factors like alters used, their interaction mechanism, their interlayer spacing, if compatibilizer used, the atomic density of the polymer model and definitely the preparation or operational method and conditions(rpm, temperature, configurations of extruders, etc) [10].

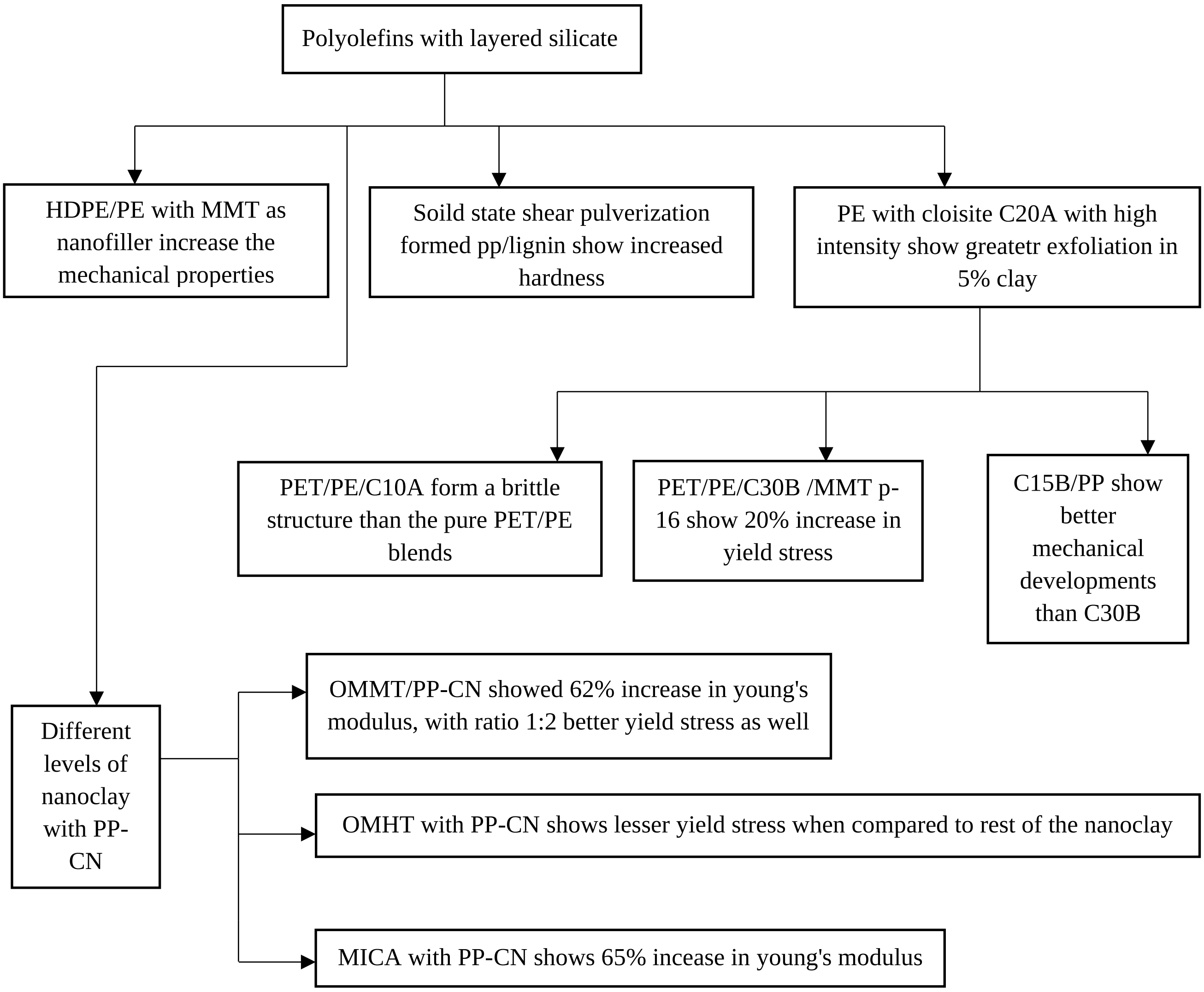


Fig. 4. Schematic diagram of composite with layered silicate

Mechanical properties of polyolefins and nanoclay composites PP, and PE have different characteristics and concludes in terms of mechanical properties when individually tested but when these to are bought together they exhibit enhanced property results, because of their compatibility with each other.

Tensile strength of PP/PE blends: When individually tested the strength of PP was found be a minimal value of 35mpa and that of HDPE was 22mpa but when PP reinforced to HDPE (50PP/50HDPE), it had an increase in the flexural strength due to formation of polyblends and it has a maximum value of 146 Mpa tensile modulus. Increase in HDPE to PP reduces the flexible strength but the small inclusion of di lauroyl peroxide rise the mechanical values of the sample.

Flexural strength: The dispersion of the PP in HDPE also increases the flexural as same with tensile strength as above. Hence the combination of these type of polyolefins results in better mechanical properties

Impact strength: Although the impact strength cannot be matched to tensile strength with this reinforcement of polyolefins. But better impact strength can achieve with the nanofiller to these polyolefins.

Even though polyolefins composites have a very wide application in engineering and polymer industries, they have few drawbacks in the performance of their materials such as low mechanical properties like tensile strength and stiffness. In order to overcome this, fillers are required i.e adding nanoclay as fillers would compensate the drawback.

Nanoclay MMT, in particular, are most widely used reinforcement fillers in polymers owing to large availability, unique properties and low cost [11]. Henceforth the nanofillers have a very important presence in the improvement of the mechanical characteristics. This mechanical property is one of the major factors to be studied when it comes to composites materials. Here are few composites having different variation in their mechanical properties and it could be understood from this for further progression of the materials for required applications [6,12].

PET/PE blends were done with melt-extrusion, later were compatibilized by the inclusion of modified Nano clays montmorillonites Cloisite 10A and 30B. The mechanical behaviour of this blends using and without using OMMT was defined by uniaxial tensile assessments. There was a negative effect with the addition of C10A in the outputs stress and expansion at the break, PET/PE/C10A is brittle where pure PET/PE is ductile. Whereas on adding C30B and MMT-P16 is showed the opposite effect of the previous the yield increased by approximately by 10% and 20% correlated to PET/PE. Studies show that the expansion at the break and the repercussion detention decreases upon an increase in accumulation of the clay of PET/C30B nanocomposites [13].

Lignin is an outgrowth of the paper and pulp industries. Here polypropylene or lignin composites were prepared through melt process and had a higher Young's modulus but had a drastic decline in flexural property and break at young's modulus. But the composite made up of rock state shear pulverization (SSSP) had a good effect on the material, in this method LDPE, PP with lignin were used. Here 81%, 62% rise for 30 wt % lignin in LDPE and PP compare to the new polymer [14].The SSSP-formed with 70/30 wt % PP/lignin combination represents the big increment in hardness hybrids and are nearing the values of polycarbonate.

Here the PP clay nanocomposites (PP-CNs) is mixed with various nano clays using Injection melt compounding with a specially devised hyperbolical nozzle for better mechanical properties. Here the PP-CNs were produced with the 4 different levels of nano clays organically modified montmorillonite (OMMT), Montmorillonite (MMT), organically modified hectorite (OMHT), amino silane treated phlogopite (MICA) in 3 distinct nanoclay ratios (1:2,1:1,2:1). Statistical analysis reveals that comparing to other PPCNs mica-phlogopite is superior.
It was seen a sudden escalation in stiffness with the included nanoclays. MICA stationed PP-CN showed 65 % topmost elevation in young's Modulus. Also, the clay platelets were assigned, ordered and inconstant disturbed was shown by its structure.

There was also 62% of sudden escalation in stiffness for the PP-CN positioned OMMT nanoclay. Also, an escalation in yield stress was seen related to the original Polypropylene in PP-CNs OMMT when nanocaly ratio was 1:2. It is apparently clear that with the nano clays in more quantity displayed better yield stress. This kind of response was only seen when OMMT and MICA were chosen as nanoclays. Better mechanical and thermal properties are seen when OMMT nano clays are selected for PP-CNs manufacturing [15].

Preparatory methods are (i) intercalation of polymers, (ii) situ method, (iii) melt interaction method. These techniques have shown better mechanical and material qualities than conventional material. The improvements have high modulus, increased tensile strength and elongational strength, increased thermal properties and so forth.

The main reason for better properties of the composite is the formation the particles, that is their interaction with each other, the polymer and nanoclay, there are usually two types of formation formed first is the intercalation, where a crystallographic structure is formed and the second one is the exfoliated nanocomposite where there is a polymer and layered silicate is divided with an average distance (Fig .5).

Intercalating polymers into silicate galleries is one of the successful methods to produce polymer/layered silicate nanocomposite. Intercalated polymer and silicate layer usually happens by either adding monomers into silicate layers or by direct addition of polymer into silicate layer by using the solution or melt methods [6].

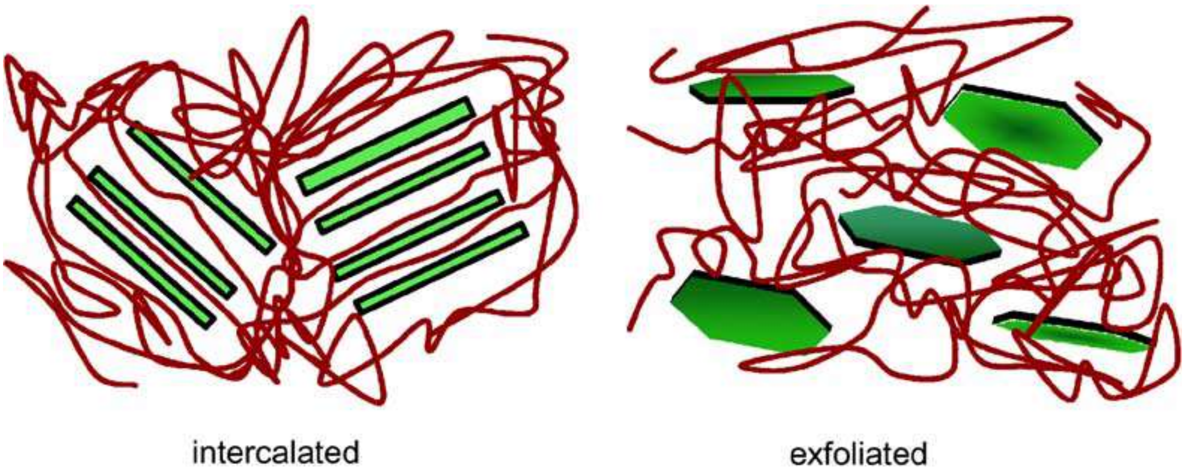


Fig. 5. Schematic illustration of two different types of thermodynamically achievable polymer/layered silicate nanocomposites [6].

To have proper interaction between the composites there must be conversions of silicate surface of hydrophilic into organophilic, so that there will be endurance for the particle to interact and form structure of intercalation and exfoliation.

The formation and development of PP-nano clay composite are been studied here. The reinforced nanoclay polypropylene composites were done by melt processing and there is an overview here. To develop this composite of nanoclay and nanoclay matrix, three different nano clays, two different coupling agents of maleic-anhydride-grated Polypropylene and 2 distinct mixing methods were done. Some of the properties like tensile, flexural strength, and modulus, their significant improvements were achieved with C-15A nanoclay (Dimethyl di hydrogenated tallow) and it was characterized by coupling agent of larger molecular weight with small grafting content and development was accompanied by raise in Izod significance strength. Similarly, another nanoclay Cloisite® 30B (Methyl, tallow, bis-2-hydroxyethyl) with smaller molecular weight and larger grafting content was used but the improvements were not pronounced. But there was greater thermal instability for this nanoclay than Cloisite® 15A.

The moduli, durability, and heat resistance can be increased and decreases gas passability and flammability with the presence of nano-reinforcement in nanocomposites. The nano-reinforcements, nano clays are of lesser cost with their availability of easily accessible, and their non-isometric structure have gained much attention in the world of material engineering, which is derivate from the big aspect ratio, that boosts the strengthening result in fields of thermal, mechanical properties.

For proper interaction of nanoclay and PP chain/matrix, the coupling agent is important, and the procedure used for the interaction. Here two coupling agents of MAgPP were used that is one of them with the lesser molecular weight but, higher graft and one more with the higher molecular weight but, smaller graft content. There are two processes carried out for interaction these nano clays, coupling agent and PP matrix, one is direct method and the second is masterbatch procedure [6].

Preparation of composite materials include various factors and each factor plays an essential role for change of typical features of the material and thermal instability is one of the important concerns in composites materials [16].

Some of the methods are used for biodegradable polymers and silicate composites. Here smectite-type layered silicates Montmorillonite and hectorite are used for the development of the nanocomposites. These are the most usually used silicates nano clays.

The development methods used for this biodegradable polymer and silicate composites are

(i) Interrelation of polymers and prepolymers in solution.

This is solvent placed on a scheme, the polymers are immersible and nanoclay is immersible, where the nanoclay is dissolved in a solvent like H_2O and after the polymer and nanoclay solution is blended and thereafter on removal of the solvent the interrelated structure is same, and a polymer-nano clay (PLS) nanocomposite is formed.

(ii) In subinterval active polymerization

Here, the nanoclay is bloated in the liquid monomer or a monomer explication, as a result, there is a polymer formed in between the sheets. Polymerization is started with heat or radiation or catalyst established over cation exchange method.

(iii) Melt intercalation method

In this technique above the melting point annealing of polymer, a combination compound of the polymer layered silicate is done. All along with hardening, the polymer chains enter the gallery of nanoclays. Intercalation and exfoliation of the nanocomposites can be said with the amount of penetration of polymers in the nanoclay galleries.

Biodegradable nanocomposites have many advantages:

(a) The compounding in nanocomposites takes place in 2D rather than 1D because of this they have enhanced mechanical properties in solid and semi-liquid states and no other treatment is necessary to exfoliate the composites.

(b) Due to the creation of a cross path with the of nano clay in the nanocomposites they have enhanced resistance qualities for the gas like, e.g. O_2, H_2O, CO_2, etc.

(c) Thermal stability of biodegradable polymers escalates the inclusive property related to the temperature of the composites as the clay behaves as a heating resistor.

(d) The biodegradability of clay and the degeneration rate of some polymers can be controlled. It can be enhanced after nanocomposite is combined with organical nanoclay.

(e) Melt viscosity is enhanced in nanocomposites formation, which helps for future processing.
These properties are low at very less nano clay content ($\leq$5 wt%) and the nanocomposites have lots of applications and further research and modification are required and the properties can be easily changed according to the users [6].

Thermal properties play a vital role in term of scientific approach where they give information about the performance of the material at an increased temperature and based upon this the materials can be selected for the suitable application and lead the way for creating materials with needed properties.

The addition of MMT ion in the polymer gives an outcome of increased polymer composites. Here the nanocomposite was set by melt compounding method, where the MMT clay is naturally altered with 4,4'-methylenebisa (MBA) from 1.5 to 5 wt%. The exfoliation of these composites was observed by XRD, while the thermal capability of the clay and the nanocomposites was analyzed by DSC and TG. Polymer matrix used was polypropylene (PP) and polyethylene (PE).

The complete exfoliation of the nano clay had taken place and the structure of the nanocomposite material was formed for all new materials and it was clear from the spacing between clay, which was observed from the diffraction peak.

The thermal capability of polyethylene and polypropylene/clay nanocomposites is opposed by two functions, one is the barrier result that improves thermal capabilities, other is the catalyst, tending towards low thermal capability. It was found that the melting property of such material is highly enhanced because the creation of the clay enhanced defensive character on the time of the combustion but is suitable in case of weight above 5 wt%. The melting temperature of nanocomposites was increased than the unmodified polyolefins and it was shown in the Differential scanning calorimetry (DSC) results and every nanocomposites regarding with PE shows a very lesser glass transition temperature (Tg) with respect to unmodified PE [17].

One of the nanoclay(cationic) sodium montmorillonite (MMT-Na^+), it is a hydrated aluminium silicate, which has Na^+ as dominating changing cation. The crushed which has particle size lesser than 2 µm, for CEC modification it was used with ILs. To check the results of IL structure and the length of chain of the positive ions on the expansion of the clay distribution, intercalation and thermal stability the process was done with different structure of cations and anions.

The lower molecular weight such as, 1-ethyl-3-methylimidazolium bromide, 1-hexyl-3-methylimidazolium chloride and N-ethyl pyridinium tetrafluoroborate are used. Trihexyltetradecyl phosphonium, decanoate trihexyltetradecyl phosphonium tetrafluoroborate are ILs with high molecular weight which was used. Basal spacing expanded comparably to dimensions and type of cations but even if it's increased also it was yet lower than the commercial MMT that has a large amount of long-chain quaternary ammonium modifiers. Later on, it gave some changes after the melt compounding of modified clays in polypropylene. Even though organoclays have long chain ammonium cations they showed lower thermal resistance than the modified clays and had good dispersion characteristics in polyolefins matrix which was same as the thermal stability of the PP with phosphonium clays [18].

Masterbatch dilution and melt compounding cause change in the characteristics of the melt PP and HDPE nanocomposites regarding young modulus and impact strength of the materials but there was no change in terms thermal stability by the processing techniques.

The longer the dwelling time, the extruder gives lots of active period for the exfoliation of clay particles and allows high polymer penetration between nanoclay platelets and also have higher adhesion activity. Changes were commendable in the case of PP than in PE [19].

The stress-strain behaviour with five various hyperplastic continuous models having second-order polynomial, Yeoh, third-order versus practical information for NR/EPDM,/nanoclays composites was investigated, due to varying different loadings of nanoclay's (1,3,5,7 wt%) and many different composition's, the mechanical Properties were increased with clay loading in comparing with NR/EPDM. The tensile modulus, compression set, and strength and the thermal stability were increased with more EPDM content. Based on the results it was seen that the second order polynomials, third order and marlow model's were possible to find the behaviour of the materials at different amounts in tension as well as compression states in the σ-ε curve of samples. Due to more deviation from the experimental data the Arruda, Yeoh models must be handled with care as nanoclay content decreases or EPDM samples increases and they have a good amount of degree of applicable in confining situation and strain [20].

The increase in the properties of the composite sometimes increase with the addition the clay percentage at the same time it might decrease with further addition of the clay percentage, this depends on various factors like length of the chain that is gap in the polymers matrices for the nanoclay's to render in, to form the structure as mentioned above in the formation sector. The technique used for the preparation of the composite, the type of clay used and mainly the clay should be able to render a with the polymer matrix and have organophilic nature, sometimes content of grafting is done for more interaction between the particles. The compatibilizing agents are used as well for better gap creation and better bonding with the clay particles and the polymer matrix. The nanoclay are very powerful in terms of action as in only small amount nanoclay is enough to vary the properties of the nanocomposites and very interactive the polymers are in the extensive used in the recent years.

Greater grafting content was increased with greater MA content and good ultrasonic energy. On the other side, the grafting frequency becomes less as the MA content becomes high. With high-intensity ultrasound irradiation, highest level of dispersion that is exfoliation was seen in 5 %- clay and 0.6 %-

MA nanocomposites. Tensile modulus was developed with applied ultrasound intensity and elongation decreased but with the increase in MA content modulus decreased [21].

There are different techniques to study characteristics of the nano particle composites, their state of morphology of the nanoparticles studied using XRD and TEM because it is easily available. There are few other techniques used to see the compatibility of nanocomposites.

(i) TEM: It gives a quality image of the structure of internal views, its spatial distribution of particles and dispersion of nanoparticles, and defects in the structure can be seen.
(ii) XRD: It is one of the easiest techniques of finding the space between the interlayers of silicate and in the intercalated nanocomposites. They have a clear understanding of the particle’s behaviour like if intercalation or exfoliation and give clear understanding of basal distance.
(iii) SEM: In this, the electron beams produced from the microscope helps to produce the image of the surface of the sample. The information about the surface morphology and composition of sample is known from the signals produced from the electrons by interacting with the atoms. They help to give the image for the focused points and helps in determining the changes occurred there.
(iv) FTIR: Infrared spectroscopy helps in collecting high spectral intent data for a large spectral range, which can be used for the gas, solid or liquid absorption or emission [6].

It was noted that the for microfiller Al_2O_3, TiO_2 and fly ash showed a decrease in their flexural strength with increasing filler ratio, whereas the tensile modulus increased with the increase in their content [22].

Application of polyolefins films and composites. Nanocomposites have very wide applications in the field of injection moulding, like in fields of automobile, architecture, electrical, etc. They have very good application in the future life, through reinforcements there can be new dimensions in polymer technology, where carbon-carbon are very expensive, and the replacement for that can be the composite materials [23]. They also have a wide scope in food packaging.
To receive a film of good depilation also a barrier and mechanical properties, polypropylene, and polyethylene films with nanoparticles are used. The polypropylene which was selected is a copolymer of the transational-high fluidity, and LDPE (ALCUDIA 017) are used. In getting the exfoliated film, nanoparticle feed position has the main importance in a double screw extruder. With Masterbatch method, the LDPE and polypropylene were processed. In Masterbatch polypropylene, the polypropylene and the polypropylene adjusted with the MAPP and Cloisite 15A are in same percentages. Also, in Masterbatch, low-density polyethylene that has polyethylene and low-density polyethylene adjusted with MALDPE and Cloisite 15A are in same parts. In extruder 170°C for polypropylene, and 130°C for polyethylene are the temperature used. To enhance affinity to montmorillonite used, a compatibilizer is required as nanocomposites of PP and PE are hydrophobic. Hence polypropylene and ethylene were adjusted by maleic anhydride. The maleic anhydride, which was used in both, was in the range of 0.5% - 1%. IR spectrum consisting of the nano-compounds of the PP and LDPE shows the additives of C15A nanoparticles in polymetric matrix. By using the XRD spectrum, the distance that was increased between the interplanar spaces and nano compounds. The Cloisite 15A have the property of enhancing the quality of the packed food as they possess railing properties. The study of nanocomposites and their impact on packaging are of great importance [24].
The nanocomposites materials also shine in the automotive industry for its material saving and cost reduction compared to the conventional materials.

To conclude, composite materials, have different properties under different circumstances including right from the compounding method adopted to the nanoclay choose to compound with the polyolefins under different ratios of mixture. Different studies of these scientific papers are used for further development of various properties of the polyolefins and nano clays composites in terms of their mechanical properties. A very small amount of nanofiller is enough to increase the properties of the polymer.

All though many previous studies showed different improved properties and morphology of polyolefin composite using nanoclay and microfiller, but there was grafting of compatibilizers with the polyolefin matrix, this enthusiast's to study further the composites using polyolefin matrix without compatibilizers and use of different nanoclay material Dellite67G, XDS and microfiller shale ash (waste), study their morphological changes and properties compared to conventional polyolefins.

2. Materials and Methods

2.1. Materials

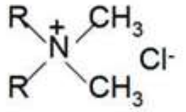
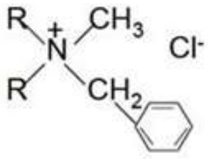
Polyolefins: Two grades of homopolymers were used:

- linear low-density polyethylene LLDPE M200026 (GAP polymer, Saudi Arabia) having application in injection moulding with a fine molecular weight and has a melting point T_m = 121^{o}C.
- polypropylene PPH HV 50 46 (Plastimex Sp. z.o.o., Poland) with a melting point of T_m = 160^{o}C.

Fillers: Mineral nanoparticles and microparticles were applied for polyolefine properties modification.

- The nanofiller to be used is based on MMT clay, an abundant natural smectite clay material derived from bentonite ore. MMT was altered with quaternary ammonium salts and organically modified MMT (OMMT) was obtained. The characteristics of MMT are shown in Table 1.

Table 1. Characterization of montmorillonite clays

Montmorillonite type*	**Modifier**	**Structure parameters**	**Properties**
Unmodified montmorillonite Dellite LVF (sodium bentonite)	–	Sodium bentonite (Na, Ca)0.33(Al, Mg)2(Si4O10) (OH)2 nH2O	- CEC = 105 meq/100g
Modified montmorillonite Dellite 67G**	 dimethyl dihydrogenated tallow ammonium chloride (DMDHT)	Hydrogenated DMDHT ≈ 65% C18H37, 30% C16H33, 5% C14H29	- particle size – 7-9 nm; - specific weight – 1.7 g/cm3; - bulk density – 0.45 g/cm3; - d001 ≈ 3.37 nm - CEC = 115 meq/100 g
Modified montmorillonite Viscogel XDS**	 dimethyl benzyl dihydrogenated tallow ammonium chloride (DMBHT)	Hydrogenated DMBHT ≈ 65% C18H37, 30% C16H33 and 5% C14H29	- bulk density – 0.4 – 0.6 g/cm3; - moisture content – 3%; - d001 ≈ 3.90 nm - CEC = 115 meq/100 g

Note: *All montmorillonites were purchased from Laviosa Chimica Mineraria S.p.A (Livrono, Italy).

**High modifier content.

2.2. Modification procedure

- Firstly, MMT suspension (4 wt.% of MMT in distilled water) was stirred 2h at a constant rate of 120 min^{-1}.
- Required modifier content (calculated according to CEC) was added in MMT suspension and was stirred 2h at a constant rate of 180 min^{-1} and temperature of 60 ^{o}C.
- Organically modified OMMT was washed until secondary products of the reaction were removed.

The ion exchange reaction is done mainly to have an increased layered distance in order to fill the polymers and surface organophilic and also to increase the wetting between the polymers and nanoclays [8]. After modification, all MMT interlayer Na+ ions were replaced by cations of quaternary ammonium salt (Fig. 6).

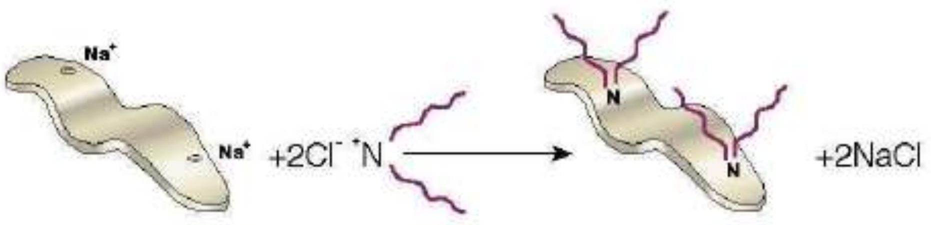


Fig. 6. Scheme of montmorillonite (sodium bentonite) modification with quaternium ammonium salts [1]

Platelets of nanoclays have submicron dimensions, excepting their thickness, which is only about 1 nm. Amount of nanofiller in polyolefin compositions was 1 – 2 %.

- The microfiller used is based on shale ash – solid substance (waste) that remains in the burning of shale. The shale ash of grade Kukermite 8F – D7 (Estonia Energy) was used, which composition and properties presented in Table 2.

Table 2. Shale ash of Kukermite 8F – D7 grade composition and properties

Appearance	**Composition**	**Properties**
Slightly brownish fine powder	CaO – 34 % SiO_2 – 34 % MgO – 6% Al_2O_3 – 8% Fe_2O_3 – 5%	Particle size – 4μm - 7μm Specific surface area – 3800m^2/kg Density – 2.7g/cm^3 Moisture – 0.2% Melting point range – 1100 ^{o}C Decomposition temperature – >700 ^{o}C Odour – odourless

The amount of microfiller in polyolefin compositions were 2 – 20 %.

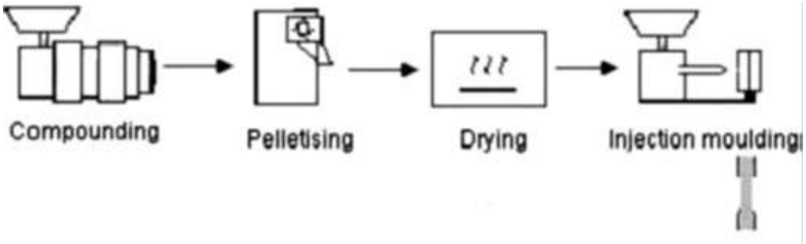
2.3. Test specimen’s preparation and mechanical testing

The test specimens for mechanical testing were prepared at Vilkritis UAB, Vilnius. The company is well known for sales in plastic production processes, their consultancies in potential applications, specialisation in distribution and production of new materials.

At first, the polyolefins compositions were obtained by mixing required compounds in the twin-screw extruder (MP Extruder, Greece):

- polyolefin (PE, PP)
- filler (shale ash, nanoclay.)
- antioxidant SONGNOX™ 21B (mix of phosphite antioxidant:phenolic antioxidant = 2:1)

After compounding moulded plastic strings were pelletised and obtained pellets dried at 75 ºC for 2h in a desiccant dryer. Dog-bone tensile test specimens were moulded using an injection moulding machine ENGEL ES 80/45 HL-Pro Series (Fig. 7).



(a)

(b)

Fig. 7. Compounding and test specimens for mechanical testing preparation scheme (a), equipment’s used for sample preparation (b)

The test specimens of the type 1A with the dimensions according to the requirements of standard LST EN ISO 527-2 were used (Fig. 8, Table 3).

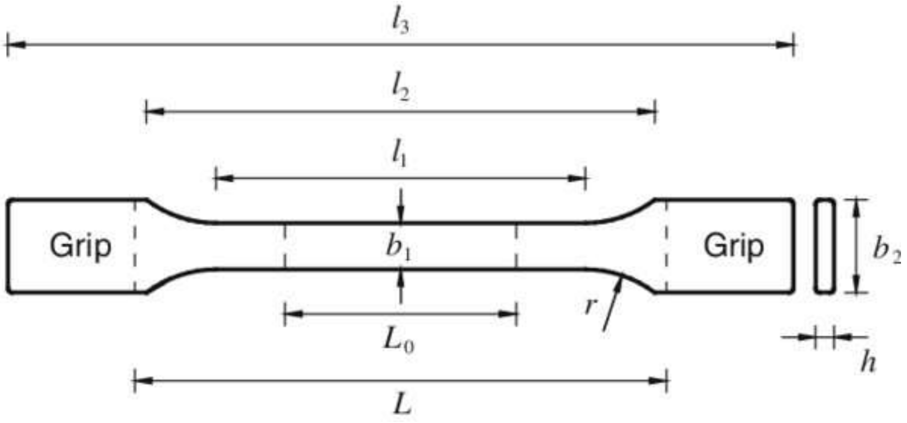


Fig. 8. Type 1A test specimens [25]

The universal testing machine H2KT having a load cell of 1 kN at room temperature was used to perform the tensile test (Tinius Olsen, Rehill, England). Measurements were done at room temperature for 5 test pieces for each set of samples and the mean values were calculated.

Table 3. Dimensions of type 1A specimen

	Specimen type	**1A dimensions**
l_3	Overall length of specimen	170
l_1	Length of narrow parallel and sided portion of specimen	80 ± 2
r	Radius of specimen	24 ± 1
l_2	Distance between broad parallel-sided portions of specimen	109.3 ± 3.2
b_2	Width at ends of specimen	20.0 ± 2
b_1	Width at narrow portion of specimen	10.0 ± 0.2
L_0	Gauge length of specimen	75.0 ± 0.5
L	Initial distance between grips of specimen	115 ± 1

2.4. Methods for structure characterization

Scanning electron spectroscopy (SEM) using SEM ZEISS EVO MA10 having an accelerating voltage-30 kV and with a resolution of 3.5 nm was used to determine the surface morphology of the sample, where in the samples were made into small amount in the form of dried powder's, placed on carbon tape's, coated with a thin conductive layer of gold.

Transmission electron microscopy (TEM) using the TEM Tecnai G2 F20 X-TWIN (FEI) with a emission electron gun having an accelerating voltage-200 kV the micrographs were captured, with the samples prepared by mixing the filler in ethanol, sonification was done for 10 min and drop of solution was placed on Lacey carbon grid for proper imagining.

X-ray diffraction analysis (XRD) of samples were done on the D8 Advanced diffractometer (Bruker AXS, Karlsruhe, Germany). The diffractometer was operated at a voltage-40 kV and tube current of 40 mA. The CuK_α wavelength was selected by filtering the X-ray beam with Ni 0.02 mm filter. Bragg-Brentano geometry was used to record the diffraction pattern which consisted of a fast counting silicon strip-based technology detector Bruker LynxEye. Using coupled two theta scans type the specimens of nanoclays were examined over the range $2\theta = 1\text{-}70^\circ$ and speed of 6° min^{-1}.

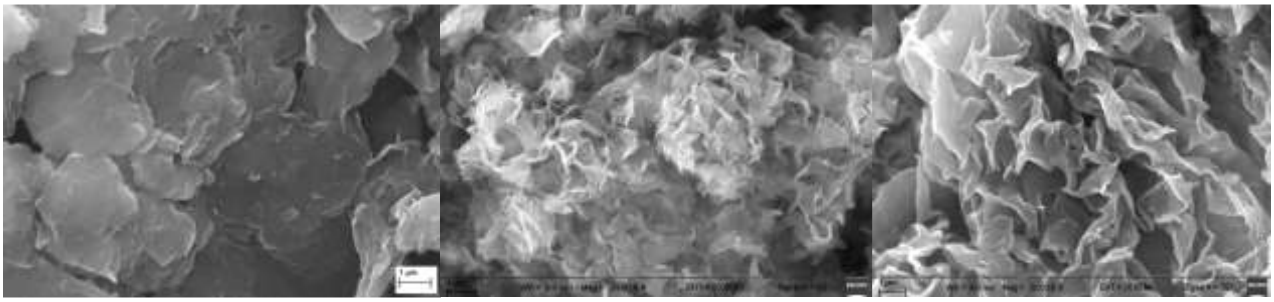
Thermogravimetric analysis (TGA) and differential scanning colorimetry (DSC) were carried out using a Linseis STA PT1600 DTA–TG/DSC. The heating of fine ground samples was done in Pt crucible (25 – 900 °C) weighing 15-17 mg at a heating rate of 15 °C/min under 100 ml/min flow of inert nitrogen gas. The heat was measured using thermocouple type S, consisting of Pt/Rh with one rod of 10% Rh and the other 100% Pt.

The textural parameters of the samples were determined with the help of Quantachrome Autosorb-iQ-KR/MP gas absorption analyst by nitrogen adsorption-desorption isotherms at −196 ºC (77 K). Prior to the analysis, the powder specimen was outgassed covered by desolation at 95 ºC for 12h. The S_{BET} were found using the BET (Brunauer– Emmett–Teller) equation. Calculation of S_{BET} was done using the relative pressure(P/P_o) (0.05-0.35). The density functional theory (DFT) was used for finding the pore size distribution at transition kernel of 77K using N_2 carbon equilibrium transition. The total pore volume was measured from adsorption isotherm by the uptake of nitrogen at a relative pressure of $P/P_0=0.99$. All calculations were performed by ASiQwin (Version 2.0) program developed by Quantachrome Instrument.)

3. Results and Discussion

3.1. Influence of modification on montmorillonite clay structure

SEM micrographs of surface morphology of unmodified MMT and organically modified OMMT particles are shown in Fig. 9. Unmodified MMT particles are blocky, irregular shape with small curvature and larger anisotropy. The MMT acted with quaternary ammonium salts resulted different morphology. The OMMTs showed exfoliated structures that is the peeling was seen with the formation of loose sheets further with the increase in the alkyl chain length of the quaternary ammonium salt it further showed more exfoliation forming a sheet structure. Therefore, the morphology of Dellite 67G differs from Viscogel XDS.



(a) (b) (c)

Fig. 9. SEM image of unmodified MMT (a), DMDHT modified Dellite 67G (b), DMBHT modified Viscogel XDS (c)

Surface morphology studies of modified montmorillonite were performed using the TEM method (Fig. 10). The TEM image of the OMMT shows a nano dispersion morphology developed. The dark region represents dispersed layers of OMMT, while light region represents the modifier used. The plate structure is observed, and silicate layers have a varying length of 100 nm upto 1000 nm and a thickness of ~ 10 nm. After modification, the distance between the silicate layers is extended – in this case, up to 2.39 nm.

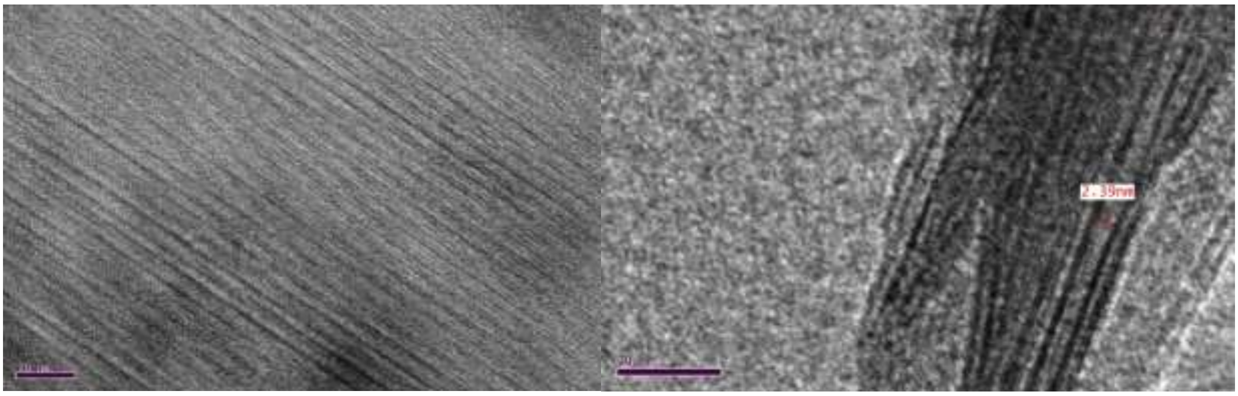


Fig. 10. TEM images of modified OMMT of various magnifications

The changes in modified OMMT structure were studied by XRD. using the Bragg equation the distance between the layers was calculated.

$$2d\sin\theta=n\lambda \quad (1)$$

d - the average distance between layers;
θ - the diffraction angle;
λ - the inlet x-ray wavelength (0.154 nm);
n - the diffraction number.

As it is seen from Fig. 11, in the case of unmodified MMT the distance between MMT layers is 1.20 nm according to the calculation at angle 2θ=7.3°. After modification with quaternary ammonium salt diffraction maximum in XRD curve shifts to the lower 2θ value (2θ= 2.3°) and interplanetary distance between nanoclay layers increases up to 3.83 nm due to intervene of the modifier molecules. It suggests the modifier as completely immersed in the MMT gallery. After the modification, the quaternary ammonium salts replaced the hydrophobic inorganic exchangeable cations of Na^+, resulting in the interlayer expansion. After modification, it easy to mechanically separate (exfoliate) of silicate layers and forming nanometric particles occurs.

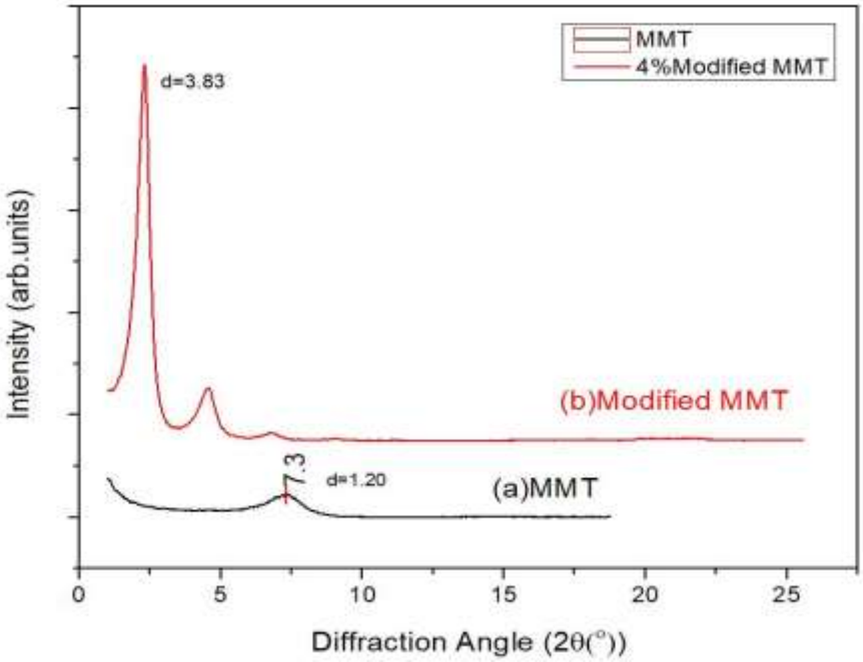


Fig. 11. XRD curves of MMT (a) and OMMT (b)

Thermal analysis for the material was performed in the nitrogen atmosphere and the TG curves of neat MMT, OMMT, and modifier were obtained (Fig. 12). The MMT remains stable up to 630 °C. Modifier DMDHT shows two steps of weight loss at 180 °C and 401 °C. The first step seen corresponds to water elimination and the second corresponds to aluminium silicate dehydroxylation. Complete destruction of modifier occurs at 450°C. The TG curve of DMDHT modified OMMT is like that of modifier, however, nanostructured additive shows higher thermal stability because of its higher onset temperature than the modifier and this behaviour is in agreement with partially exfoliated structure. This shows that there is partial exfoliation taken place with the modifiers and clays. The amount of residues formed for the modifier and OMMT is 2% and 52%, respectively.

The DTG curves for the MMT, OMMT and modifier are shown in Fig. 13. In the DTG curve of OMMT, peaks at 197 ºC (start 155 ºC, end 229 ºC), 340 ºC (start 305 ºC, end 358 ºC) and 403 ºC (start 372 ºC, end 436 ºC) are observed. It can be assumed that decomposition of modifier DMDHT occurs at 197 ºC and is related to water evaporation or moisture with weight loss 6-9% [26]–[28]. The second at 340 ºC was related to breaking of ester bonds of modifier. The main organic degradation took place from 400 ºC to 500 ºC which split the modifier molecules attached to the montmorillonite layers.

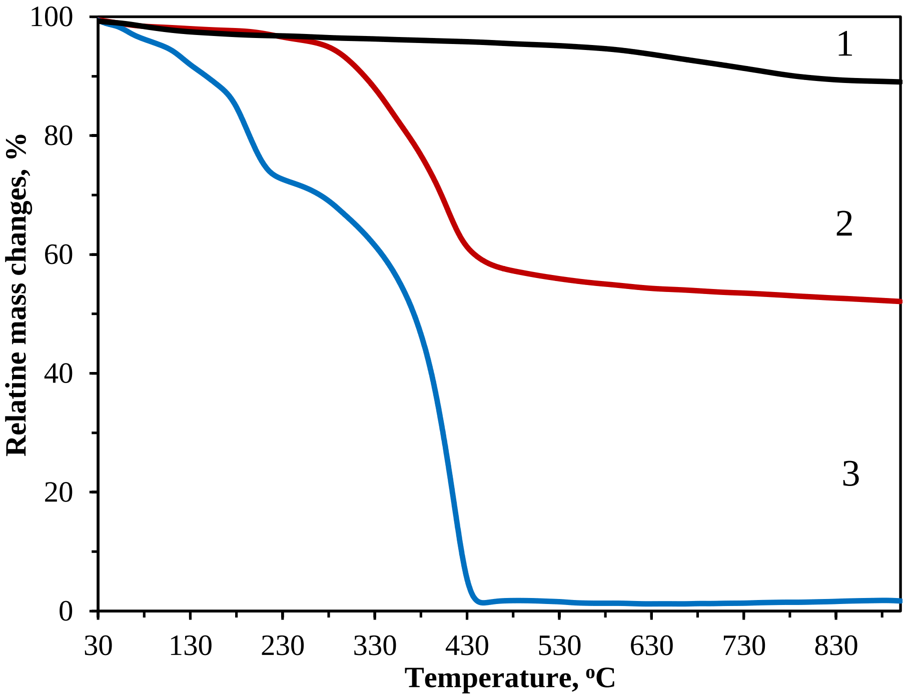


Fig. 12. TG curves of unmodified MMT (1), OMMT Viscogel XDS (2) and modifier DMDHT (3)

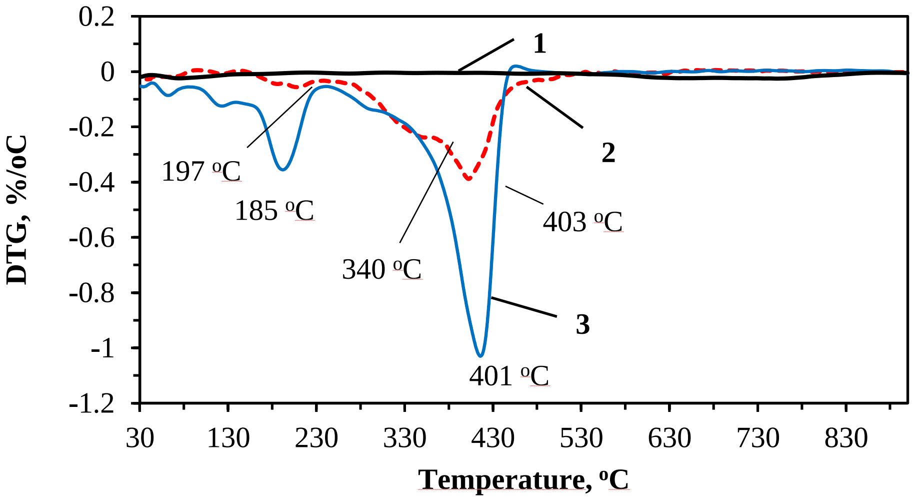


Fig. 13. DTG curve of MMT (1), OMMT Viscogel XDS (2) and modifier DMDHT(3)

The DSC curves for MMT and OMMT is shown in Fig. 14. Curve for OMMT is similar to that of unmodified one and exhibits a heat flow exothermic peaks at 100 ºC – 150 ºC showing transition temperature and at 380 ºC – 410 ºC showing the melting of the material much higher than the modifier due to the thermal stability of MMT. The oxidation takes place around 840ºC – 900 ºC and the decomposition of the material happens [32,33].

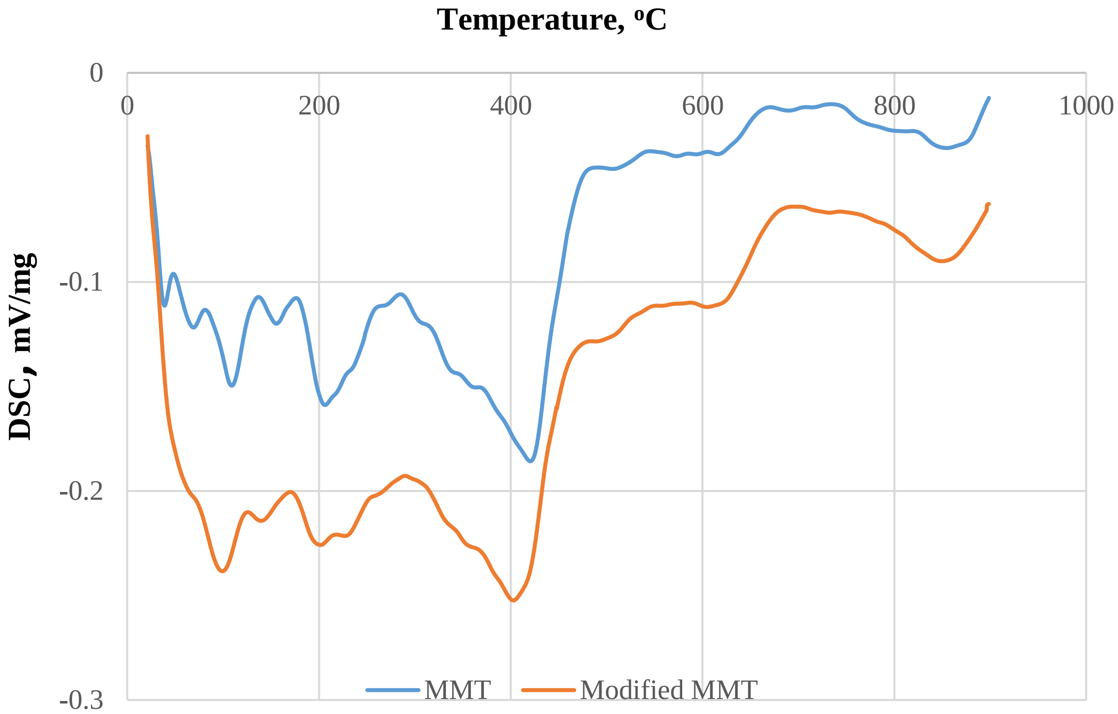
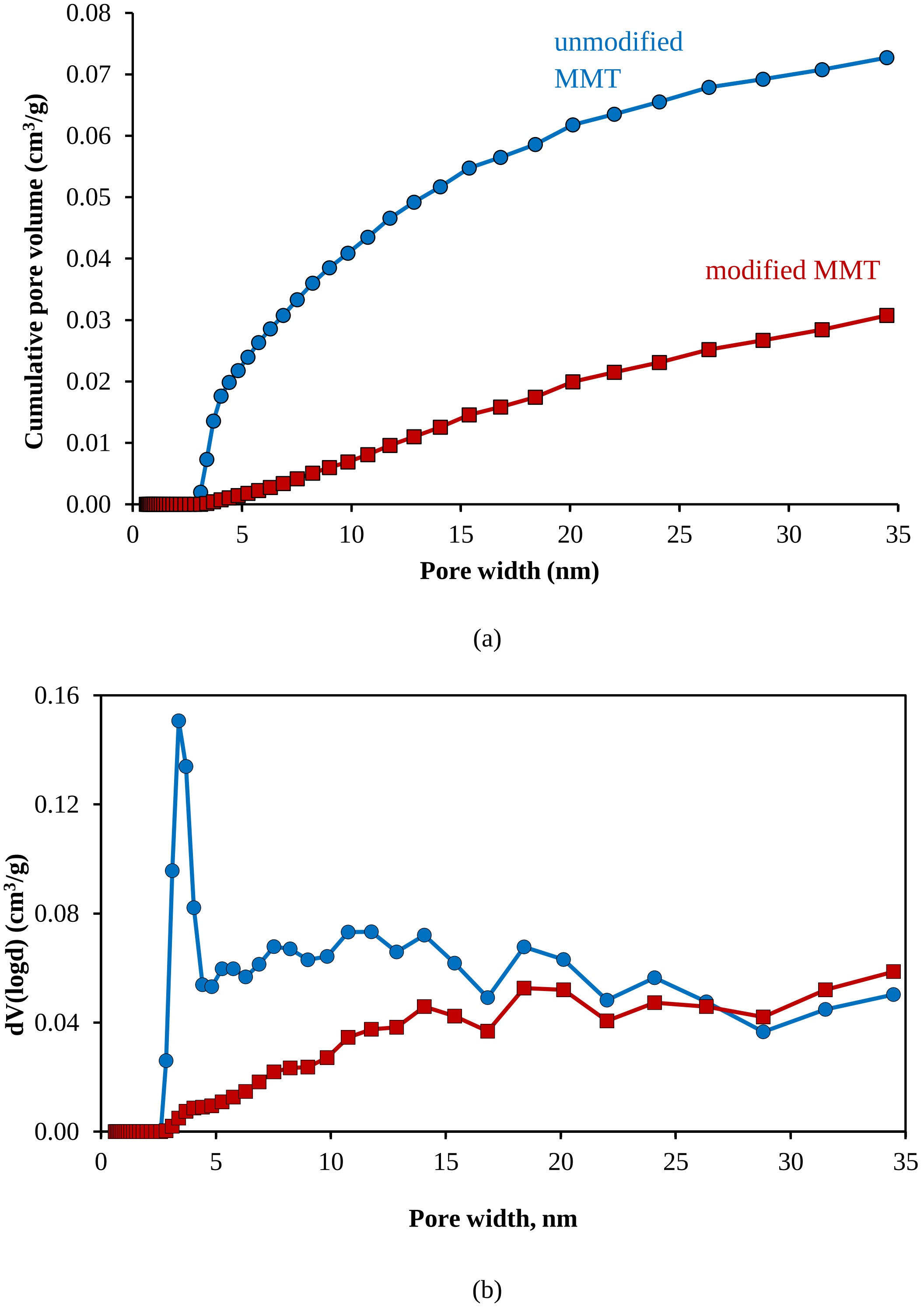


Fig. 14. DSC curve of MMT and OMMT

Further, N_2 adsorption-desorption studies of modified OMMT were performed, the specific surface area SBET, pore size Vp and their distribution D were calculated (Fig. 15, Table 4). The relatively low specific surface area value (SBET = 21 m^2/g) of the unmodified MMT confirms that the silicate interlayer is filled with Na^+ ions, which prevent N_2 molecules penetrating between the tetrahedral layers of silicates. The decrease of SBET for modified OMMT specimens to 6.4 m^2/g proves that the modifier ions (quaternary ammonium ions) intervene between the aluminosilicate layers, fill gaps and prevent the diffusion of nitrogen molecules into the interlayer. The pore distribution curves suggest that pores of 3.3 nm size are predominated.



(a)

(b)

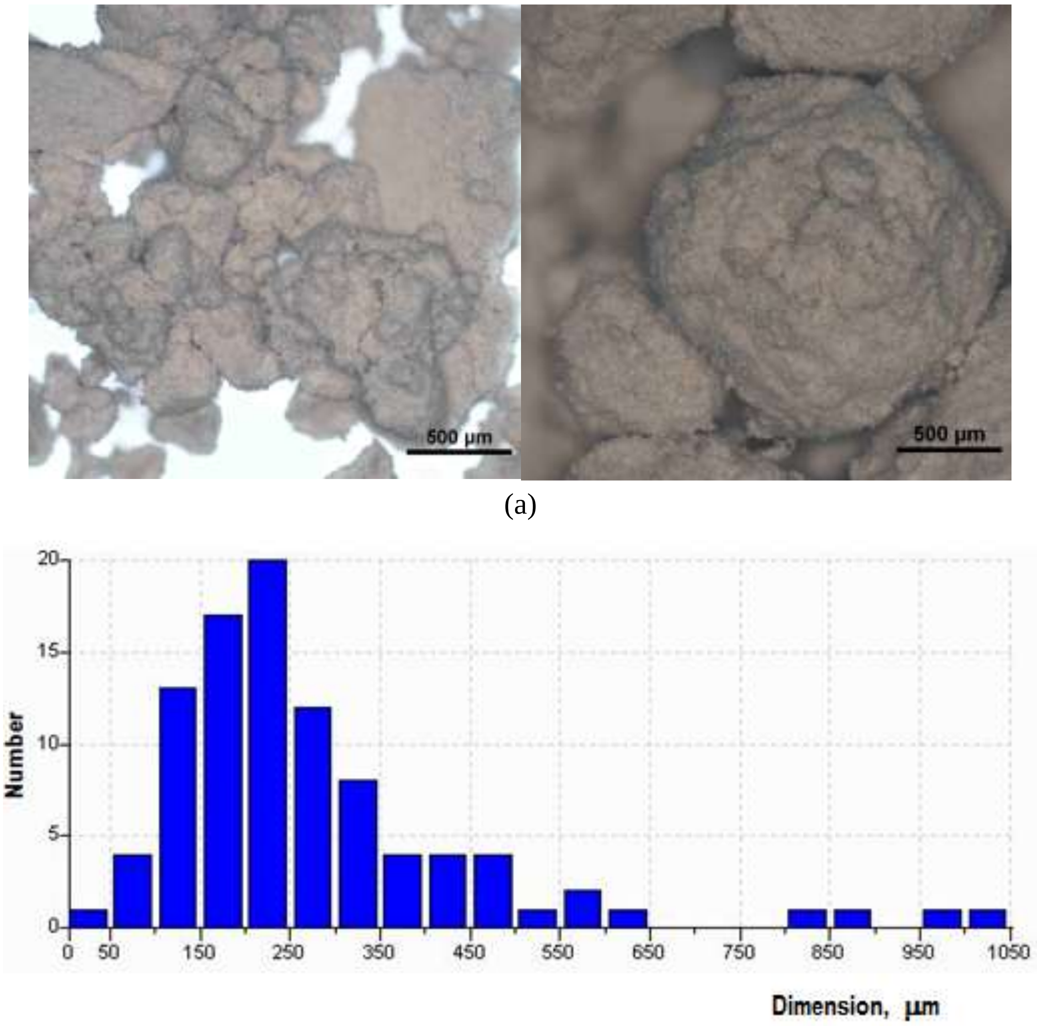
Fig. 15. Pore volume (a) and pore size distribution (b), MMT and OMMT

Table 4. Porosity parameters of unmodified MMT and modified OMMT

Sample	**Surface area S_{BET}, m^3/g**	**Pore volume V_p, cm^3/g**	**Pore diameter D(DFT), nm**	**Basal distance d_{001}, nm**
MMT	21.0	0.0073	3.2	1.23
OMMT	6.4	0.0031	34.5	3.91

3.2. Shale ash particles structure investigation

The structure of shale ash particles, were investigated using optical microscopy (OP) and SEM which are obtained as waste after burning of shale. As can be seen from OM micrographs (Fig.16(a)), shale ash particles tend to agglomerate and high size derivatives with main diameters of 150 – 250 μm are formed (Fig. 16(b)). From these micrographs, it is practically impossible to determine shale ash particles shape. Therefore, SEM investigation was performed.

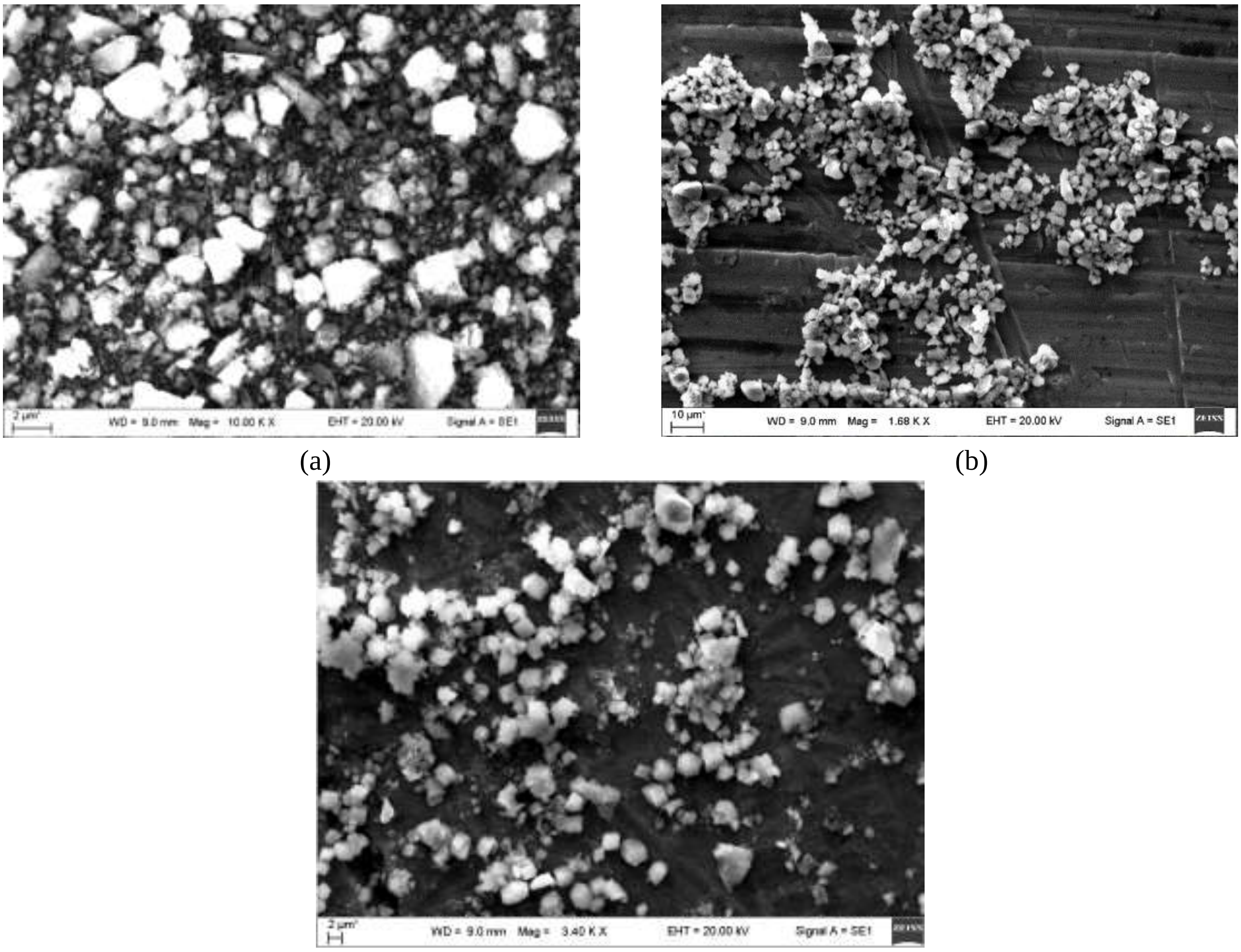


(a)

(b)

Fig. 16. Optical microscopy image of shale ash particles (a), ant size distribution histogram (b)

SEM image of microsized shale ash particles is shown in the Fig. 17. Tendency of these particles to agglomerate is observed in the SEM images also (Fig. 17(a)). Therefore, shale ash particles suspension was sonified before testing to estimate main particle size. After sonification, the degree of agglomeration decreases. As it is evident from Fig. 17(c), the ash particles have sharp angles, the shape of most of them is close to a square with main dimension in the range 2 – 4 μm.



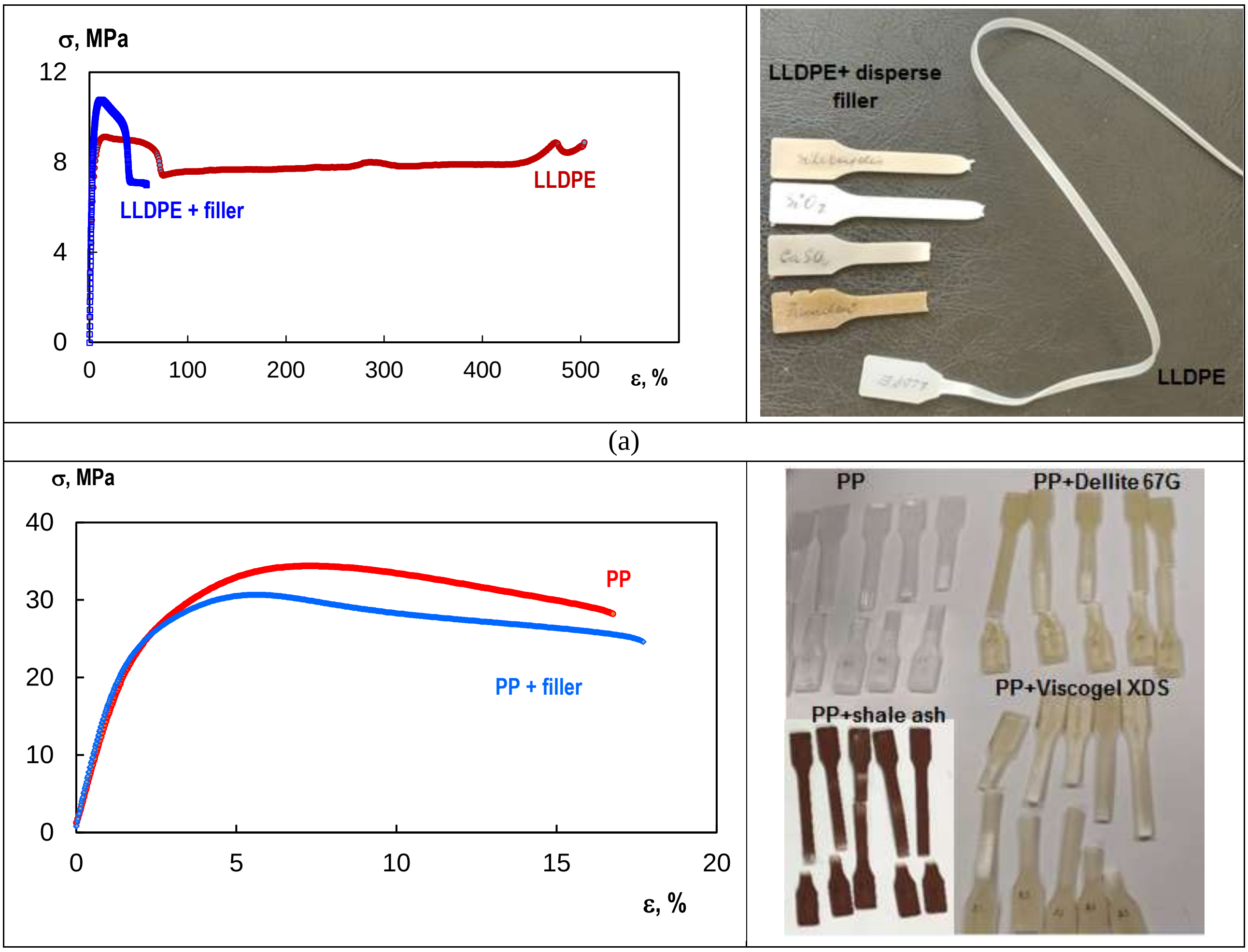
(a) (b)

(c)

Fig. 17. SEM image of shale ash particles before dispersion (a) and after sonification in ultrasonic bath (b) and with ultrasound probe (c)

3.3. Polyolefin composites mechanical properties and structure

The disperse filler influence on the behaviour of polyolefins at tension are seen in Fig. 18. The stress σ – strain ε dependence of LLDPE and PP homopolymers significantly differs. For LLDPE homopolymer it is characteristic low strength values (i.e., yield point – <10 MPa), but high deformation properties – elongation at break reaches more than 500% (Fig. 18(a)). On the other hand, PP homopolymers has unpronounced yield point and maximal strength value is >35 MPa, but elongation at break – only <15% (Fig. 18(b)). PP composite σ–ε behaviour is close to that of homopolymer, while incorporation of filler significantly changes LLDPE properties at tension – deformation ability decreases drastically, probably, due to the destroying polymer microstructure. Therefore, for further investigations, only one polyolefin – PP was chosen.

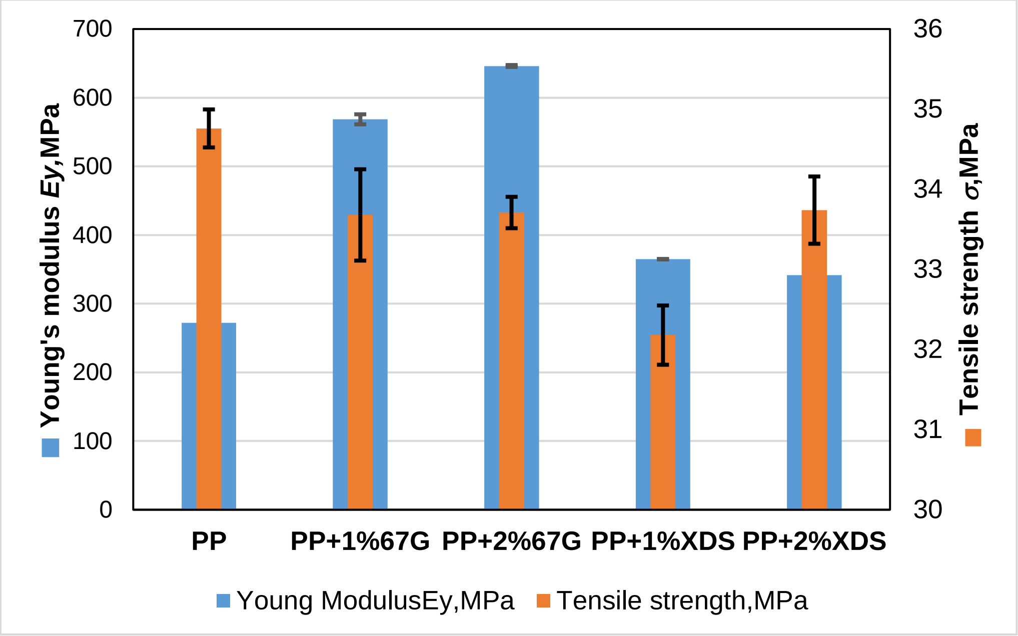


(a)

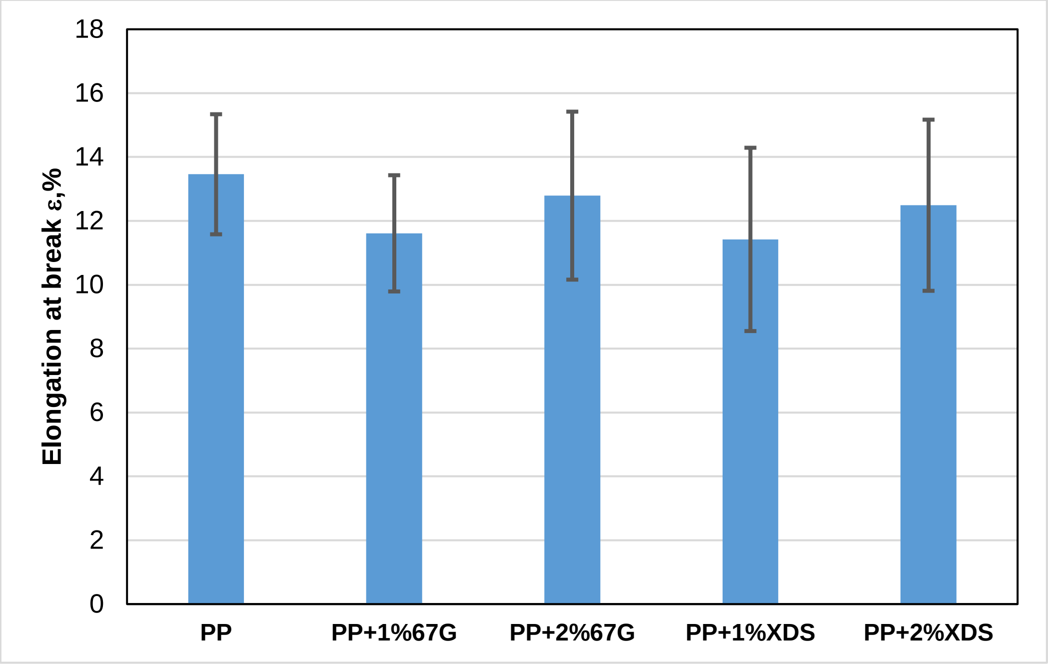
(b)

Fig. 18. $\sigma - \varepsilon$ curves and test samples view after tension of polyolefin homopolymers and their composites with disperse filler particles: LLDPE (a), PP (b)

The effect of content of nanoclay in the PP matrix on E_Y, tensile strength (σ) and elongation at break (ε) are shown in Fig. 19. Young's modulus (E_Y) increases more than 2-times as 1–2 % of nanoclay Dellite 67G is added into PP matrix (from 272 MPa to 568–646 MPa). In the case of Viscogel XDS E_Y increase degree is lower, but its values are greater than the pure PP, as it can be seen in Fig. 19(a), incorporation of 1wt% of Dellite 67G leads to increase of 52% of E_Y, while with 2wt% of Dellite 67G leads increase of 57% E_Y. Similarly, for Viscogel XDS, E_Y increases by 33% for loading of 1wt% of nanoclay and 25% – for 2 wt%. The changes of E_Y value for Viscogel XDS occur within the confidence interval. The tensile strength of PP/Dellite 67G nanocomposite shows lower values compare to that of pure PP. While for PP/Viscogel XDS nanocomposites the tensile strength decreases by 3–7% depending on the nanoclay amount. As shown from Fig. 19(b), the values of elongation break for the PP/Dellite 67G and PP/Viscogel XDS nanocomposites are similar to that of pure PP within the confidence interval. Annex 2 represents the summary of mechanical properties of the PP/Dellite 67G and PP/Viscogel XDS composites.



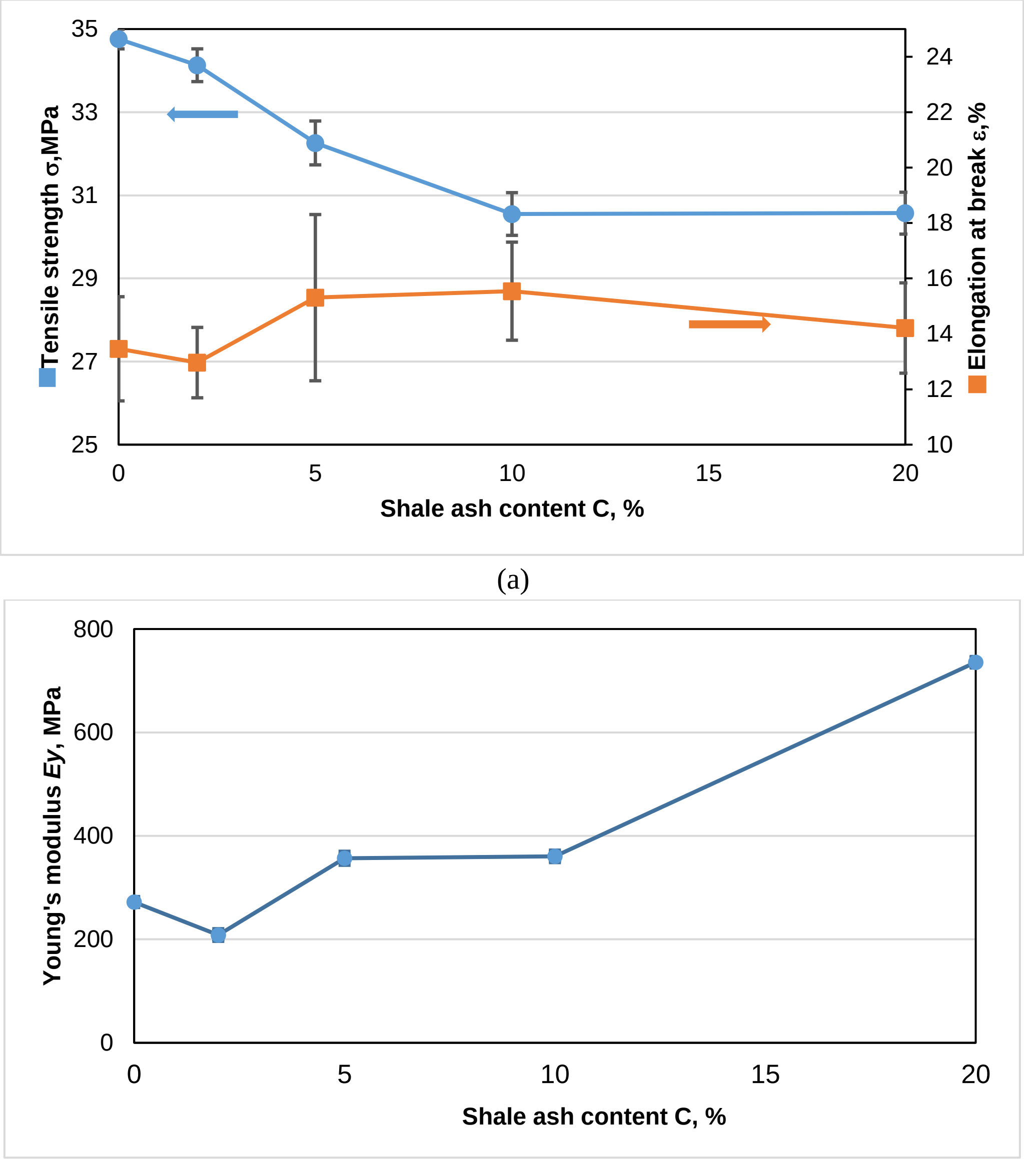
(a)



(b)

Fig. 19. Dependence of mechanical properties of PP/OMMT composites: Young's modulus and tensile strength (a), elongation at break (b)

The Fig. 20 represents the mechanical properties of PP/shale ash composite with one of the waste microparticles – shale ash. It is clear that the tensile strength of the ash-filled PP composite decreases with addition in the filler loading up to 20wt%. The elongation at break almost is independent on the filler amount content and is close to that of PP homopolymer. Shale ash of higher amount than 5 % increases Young's modulus E_Y values – it shows 63% increase in the case of 20wt% of shale ash in PP composition. The incorporation of filler markedly increases stiffness of PP composite. Annex 2 presents the summary of mechanical properties of PP/shale ash composites.



(a)

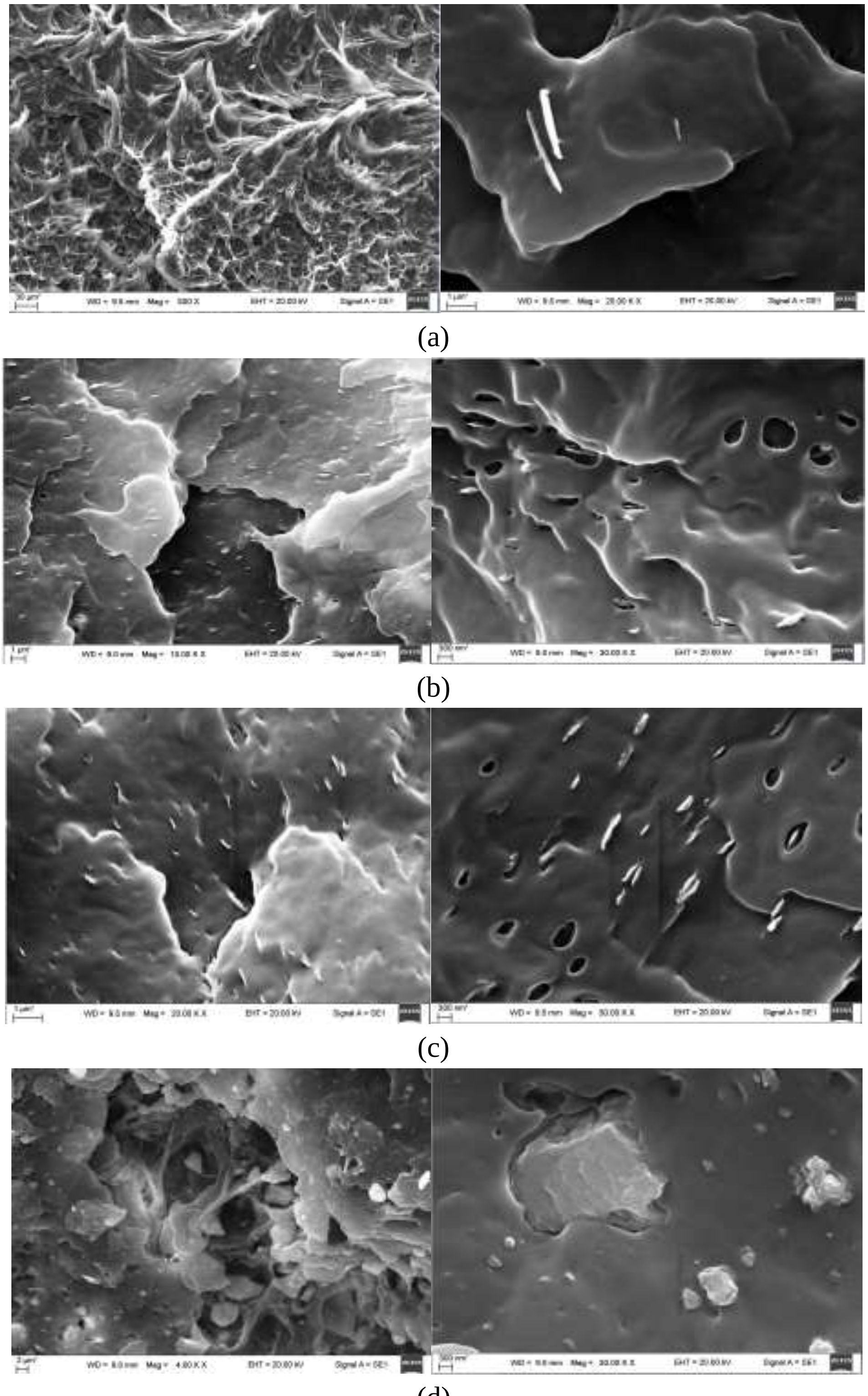
(b)

Fig. 20. Dependence of mechanical properties of PP/shale ash composites: tensile strength and elongation at break (a), Young 's modulus (b)

SEM micrographs of fracture surface of PP composites with nano and micro fillers were studied to understand the failure mechanism under loading and interface reaction between components of composite. The fractured surface images of pure PP and its composites are shown in Fig. 21.

In the SEM micrographs of PP homopolymer show fractured surface, some pollutions can be observed (Fig. 21(a)). In the composition of PP/2wt% Dellite 67G, it can be observed practically homogenous distribution of OMMT particles (Fig. 21(b)). However, at higher magnification, it can be seen a large number of holes with pull out of the particles from the matrix, where OMMT particles were located before fracture. Also, voids can be seen around the OMMT particles, which indicate that there is poor adhesion interaction between OMMT and PP matrix at the interface. Similar results can be seen for PP/2wt% Viscogel XDS nanocomposite, as shown in Fig. 21(c). Interaction at the interface of nanocomposites components greatly influences on their mechanical properties [31].

Also, low adhesion interaction between PP matrix and the shale ash particles are observed in the case of PP/20 wt% shale ash (Fig. 21(d)) but no pull-out particles are visible. Thus, the decrease of tensile strength of composite can be explained by improper adhesion interaction between filler particles and the PP matrix [32]. Besides, the shale ash particles tend to form agglomerates, additionally reducing the mechanical properties of the composite.



(a)

(b)

(c)

(d)

Fig. 21. SEM micrographs of pure PP (a), PP+2 wt% Dillite 67G (b), PP+2 wt% Viscogel XDS (c), PP+20wt% shale ash (d) at different magnification

Thermal investigation shows that fillers increase PP composites thermal characteristics (Fig. 22). The temperature loss of 10% by weight for pure PP sample is at 347.8 ºC, while for PP/2% Dellite 67G nanocomposite it increases up to 419.3 ºC and for PP/10% shale ash up to 421.8 ºC. It is seen that the destruction temperature's of PP composite sample is greater than that of pure PP. Likewise, the residual at 550 ºC is highest in the case of PP/10% shale ash and reaches 10.1%. For PP and PP/2% Dellite 67G nanocomposite, the residue at 550 ºC is the same 2.4%.

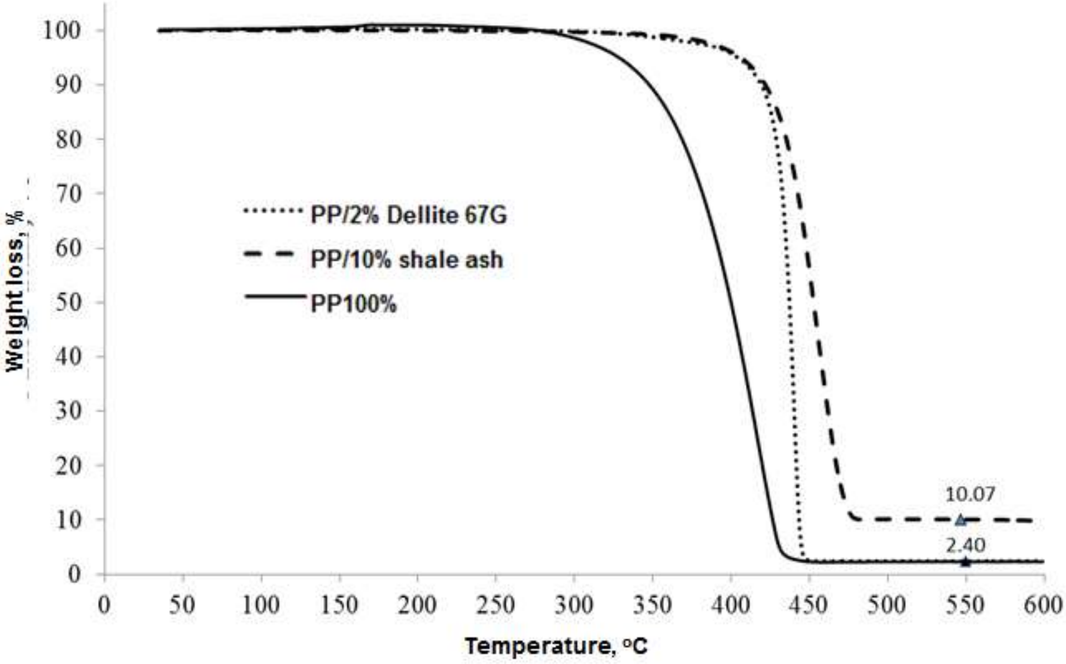


Fig. 22. TGA thermograms of PP and its composites

To determine polyolefin and OMMT composite structure the XRD investigation was performed. The XRD graph for pure PP, composites with 2wt% of Dellite 67G and Viscogel XDS is shown in Fig. 23. In the curves of PP nanocomposites at the region of small diffraction angles ($2\theta = 1 - 9^o$) three diffraction maxima – (001), (002), and (003) are visible. They are attributed to the organically modified OMMT and are reflected the distance between the SiO_4-tetrahedral and AlO_6-octahedral layers of Dellite 67 G and Viscogel XDS. It shows that during mixing nanoparticles of both montmorillonites are not exfoliated in PP matrix. In the case of exfoliation, the diffraction maxima disappear, suggesting that the tetrahedral and octahedral layers no longer form a common crystalline lattice and OMMT is properly dispersed in PP.

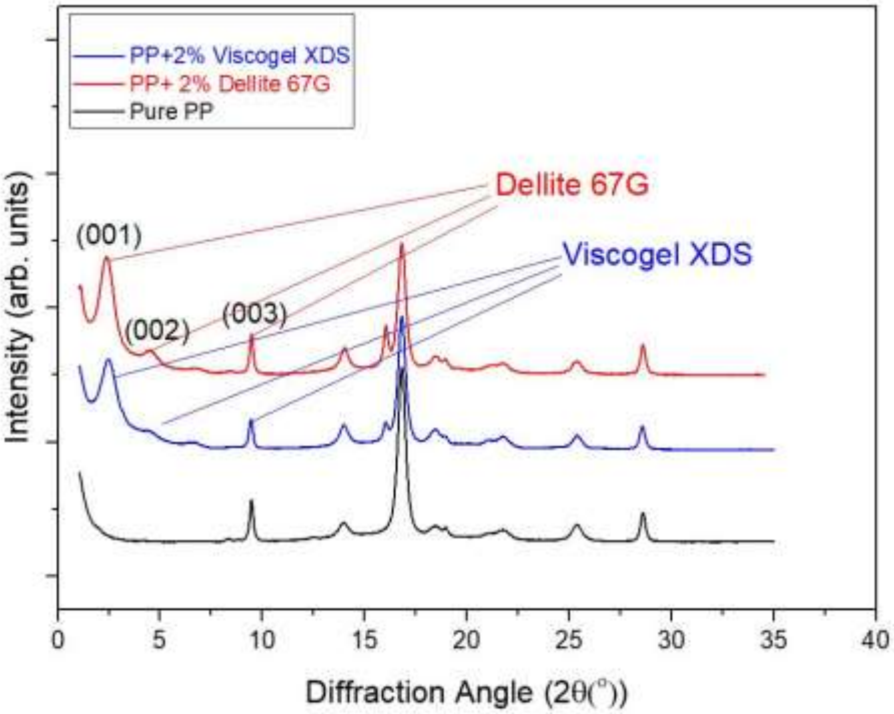


Fig. 23. XRD curve of PP and its composites

It is clear from the result that the incorporation of nanofiller resulted in a decrease in tensile strength and elongation at break, because montmorillonites are not exfoliated in PP matrix and weak adhesion [22]. In the case of shale ash nonhomogeneous particles distributed in the matrix and particles agglomeration leads to the reduced strength. Besides, the decrease in tensile strength with increase in filler content might be due to the weak adhesion between blend components. Loading of nano or micro fillers increased Young’s modulus and stiffness of composites arised in several times. Stress-strain behaviour of PP composites was close to that of homopolymer, while in the case of LLDPE filling drastically changed stress-strain behaviour.

In comparison to other research works, this study showed some improvement in mechanical properties of organically modified OMMT PP. Most of the studies are done using nanoclay Dellite 72T in various polymers with the addition of compatibilizer (i.e., maleic anhydride). Only few works are attributed to the studies with OMMT of Dellite 67G and Viscogel XDS type. However, when compared with previously studied organically modified OMMT, Dellite 67G and Viscogel XDS showed higher stiffness and resistance to temperature than other organic nanoclays, such as C20A, C15B [4-7] .

4. Managerial recommendations of polyolefin composite materials

The polyolefin PP and PE due to their versatile property have many applications. The major reason for the composition of these polyolefin would be either to improve their properties or in the involvement of reduction of material. Here in this work nanoclay was used as a filler to PP matrix to form a nanocomposite with higher the mechanical properties and micro filler shale ash for reduction of material for same functionality. Their environmental impact and market review were analysed. Since PP have a wide application, their application in the field of packaging film and injection mould automotive panels for cars is consider and compared with the conventional method in terms of cost and material reduction and environmental disadvantages or advantages.

4.1. Environmental impact

The sustainability throughout the product lifecycle using PP has been appreciable, as PP is the one by- product having lower usage of energy and lower emission of greenhouse gas with lower environmental effect compared to rest of the fibre resins and a simple lifecycle of PP with its effects on environment can be seen in the Fig. 24.

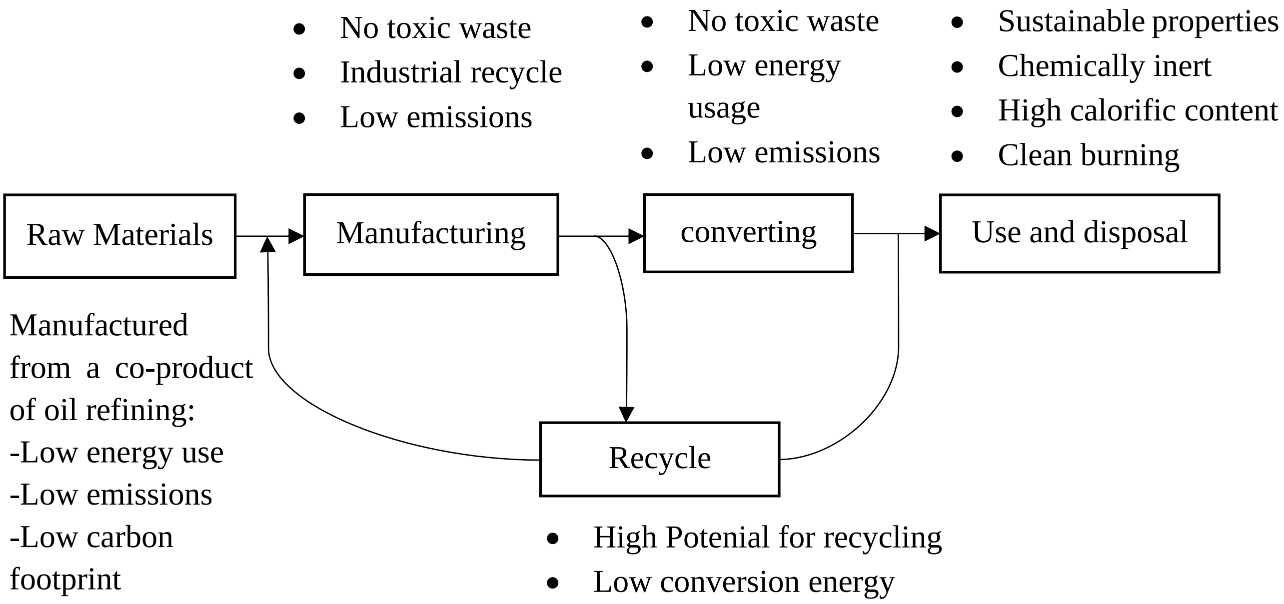


Fig. 24. Lifecycle of PP with its effects on environment

Manufacturing PP fibre has a very low effect on the surroundings with no toxic waste, no toxic emission, no halogens or no fluorocarbons they are absolute toxic-free. The products made out of PP have a low melting point and they result in low impact on the surroundings and the energy required to create the product is reduced, waste from converting operations is recyclable in manufacturing operation and there is no emission toxic gases or wastes. PP contributes to the sustainable energy as they possess versatile property, they are chemically inert and hence very less effect on health and environment, because of its low density very less amount of it required to make products, the durability is longer and helps the product have a long life and doesn't require immediate replacement, can be easily cleaned without high energy or environmentally unfriendly methods. PP fibre has a very high calorific value, it provides a high energy value for the amount of CO_2 emitted, it is incinerated as part of a mixed waste stream.

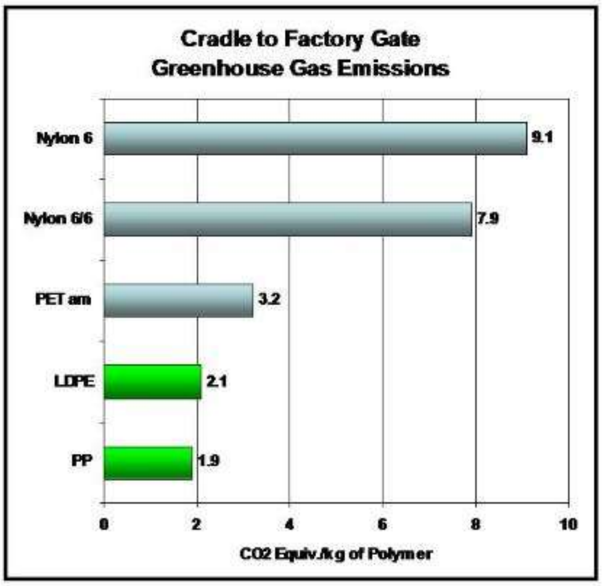


Fig. 25. Gas emissions rate [33]

All though nanoclay may cause a difference in the environment they are of less important as low loading is used. The polyolefin nanocomposite doesn't produce many effects on the environment as the percentage of nanoclay used is very less and are negligible.

4.2. Market view on polyolefin composite materials

The polyolefin composite has a wide market aspect based on its property and applications. The global polyolefin composite market is expected to reach a CAGR (compound annual growth) around 8.1% during the year 2017- 2027. The global polyolefin composite market is anticipated to a value at USD 387.09 Bn by 2027 [34]. The market division depends on the product type, application and end-user. By region, North America is one of the market segmentations, similarly, the market is divided into different regions Asia -Pacific for its cheap resources, Europe for its competitional fact, Middle East for its natural availability of resources and Africa. The most predicted is Asia that is expected to dominate the global market for the polyolefin composite due to availability of many composite manufacturers in the region. Moreover, high availability of low-cost materials in Asia- Pacific region are compelling manufacturers in Europe and North America to set up a manufacturing plant in the region. The PP/nanoclay and PP/shale ash have demanded requirement in the field of automotive, packaging, garments. The composites provide structural and cost benefits in automotive interiors and widely used for industrial applications. The cost-effective physical properties of the composite is major support for the demand of the global polyolefin market from the industrial applications, especially in automotive industry.

4.3. Material reduction and cost estimation of composite product

The addition of nanoclay or microfiller not only increases the mechanical properties but also its barrier and fire-resistant. There is a possibility of reduction of materials due to improved mechanical properties in fields of films and structural elements. This reduction in material is going to affect the total cost of the nanocomposite product as well. The analysis for packaging film was done only with PP/nanoclay composite and not shale ash as it was considered not suitable for packaging of food. Cost analysis and weight reduction for two products were investigated, film for packaging and

injection moulded automotive panels for cars in accordance with life cycle assessment and life cycle costing.
It is important to consider functional unit and it was defined for each product with the reference to paper [35].

For the packaging film, 1,000 bags of ‘Fruitfante’ candies was chosen as a functional unit with a weight of 200g, it was produced by a company named by schuttelaar B.V. located in waddinxsveen, in Netherlands. The conventional material used for making such bags were pure PP. The weight of one bag was 3.66 E-03kg and the requirement of film for one functional unit was 3.66 kg. Based on the thickness, length, width of bag and density of PP the weight of the film was estimated.

For the automotive panel, functional unit was chosen as low weight family car that runs for an average of 150,000 km for its whole life and the conventional material used for this was PP-glass fibre composite.
Panel requirement for functional unit: 20kg.
To estimate the material reduction Ashby material indices for different product indices was used.

Packaging film: $M = \sigma/\rho$ (2)
Assumptions:
Few assumptions were made that the strength was limited, the material shouldn’t tear, and tearing was due to parallel force to that of the surface of the film.

Automotive panels: $M = E_y^{1/3}/\rho$ (3)
Assumptions:
The assumption made for automotive panel was that there is limited stiffness so that the material should not bend.
Where, M is material indices; E_y is Young’s modulus; σ is tensile strength; ρ is density.

Ashby’s material indices, according to this if there is a higher index then material required for the same function is less and they exhibit inverse relationship.
For packaging film, weight saving percentage was determined using:

$$\text{Change of weight (\%)} = \left(\frac{\sigma/\rho[\text{conv}]}{\sigma/\rho[\text{pp/filler}]} - 1\right)*100 \qquad (4)$$

similarly, for automotive panel,

$$\text{Chang of weight (\%)} = \left(\frac{E^{1/3}/\rho[\text{conv}]}{E^{1/3}/\rho[\text{pp/filler}]} - 1\right)*100 \qquad (5)$$

The values of tensile strength (σ), young modulus (Ey) and specific weight are listed in Table 5. Substituting these values in Eqs. 2-5 gave the results for estimates of weight saving and is listed in Table 6. The stiffness value or PP/GF composite was taken from source [35]. The weight of the product using PP/ filler composite was determined using the weight reduction formula with respect to the conventional material for a functional unit. It was seen that there was reduction of weight for PP/nanoclay and PP/shale ash composite for the case of automobile panel but there was increase of weight in case of packaging film. The change of weight percentage depends on their mechanical properties value.

Table 5. Parameter values

Parameter	**Value**	**Unit**
σ-PP	34.76	MPa
σ- PP/nanocomposite, 2% clay	33.71	MPa
σ- PP/shale ash composite, 5%filler (automotive panels)	32.26	MPa
Ey - PP	272.20	MPa
Ey- PP/nanocomposite, 2%clay	646.22	MPa
Ey-PP/GF composite, (30% GF)	576	MPa
Ey-PP/shale ash, 5%filler	356.80	MPa
ρ -pp	0.91	t/m3
ρ- PP/nanocomposite, 2%clay	0.9280	t/m3
ρ- PP/shale ash,5%filler	0.940	t/m3
ρ- PP/GF composite	1.4020	t/m3

Table 6. Estimation of weight-saving when PP composite were used

	Weight of functional unit with conventional material	**Weight saving (%)**		**Formula used**	**Weight of functional unit with PP/filler composite**	
		PP/nanoclay	PP/shale ash		PP/nanoclay	PP/shale ash
Packaging film, based on mechanical properties	3.660 kg	4.9	-	Eq. 4	3.830 kg	-
Automotive panels	20 kg	–36.3	–21.3	Eq. 5	12.74 kg	15.74 kg

The cost for manufacturing the products where consider estimating market prices of all materials and energy input. The accordant inputs are shown in Table 7. The life cycle cost was determined from material, energy input and their cost. The price for nanoclay, PP and shale ash was obtained from the company Vilkritis UAB, Vilnius. The costs for the production method of the product and price estimates for the energy inputs was used from source [35] are given in Table 8 and Table 9. It has to be noted that price consideration varies with different source, year and geographical outlets. A very rough estimation was done considering these factors. However, to a large extent, the uncertainty has been nullified because the comparative assessment was done. The conventional and PP/filler composite was processed in the same way.

The polyolefin PP, MMT nanoclay and shale ash were used at different weight percentage and 2wt% of nanoclay and 5wt% of shale ash is considered for further estimations.

1. Bentonite sodium (nonmodified nanoclay) – 69.90 Eur/2500 g
2. Modifier – quaternary ammonium salt – 28 Eur/250 g

and the modification ratio was 100 g Bentonite sodium: 55 g quaternary ammonium salt and these data of price was obtained from the industry.

Table 10, shows that in the case of PP/nanoclay product for packaging film the life cycle cost was higher than the conventional products. While for the automotive panel the PP/filler composite showed lesser life cycle cost than the conventional and this can be told by the fact that the reduction of weight for both the composite was higher for automotive panel composite.

Table 7. Energy and material inputs (f.u: functional unit, conv: conventional material)

Input	**Unit**	**Packaging film**		**Automotive panel**		
		PP/nanoclay f.u: 3.83 kg	Conv f.u: 3.66 kg	PP/nanoclay f.u:12.74 kg	PP/shale ash f.u: 15.74 kg	Conv f.u: 20 kg
PP	kg	3.75	3.66	12.48	14.9	
PP/GF composite	kg	-	-	-	-	20
Filler	kg	0.08	-	0.25	0.78	
Electricity for nanoclay modification production	MJ	2.12	-	21.01	-	-
Electricity for PP/filler composite	MJ	9.1	-	57.2	57.2	-

Table 8. Price estimation for material and energy inputs in the life cycle of the products

Material	**Price (Euro)**	**Unit**	**Source**
Nanoclay	27.96	€/kg	Industry
polypropylene	787	€/tonne	Industry
Shale ash	330	€/ tonne	[36]
PP/GF composite	1550	€/tonne	[35]
Electricity	18.3	€/tonne	[35]
Incineration	100	€/tonne	[35]

Table 9. Cost estimates of product forming methods

Production Method	**Costs (€/tonne)**
Film Extrusion	870.00
Injection moulding for panel	420.00

Table 10. Results life cycle costing

	Life cycle costs conventional product (€/functional unit)	**Life cycle cost PP/filler product (€/functional unit)**		**Difference (%)**	
		PP/nanoclay	PP/shale ash	PP/nanoclay	PP/shale ash
Packaging film	6.49	8.93	-	37.5	-
Automotive panel	42	24	20	–42.8	–52.3

It can be seen that the PP/nanoclay composite is not compatible or not profitable in case packaging film product as the weight saving percentage was less that is no weight reduction, this can be due to dependence of the tensile strength as well density of the composite and also the life cycle cost was higher for this composite, this can be reduced if with lower cost of nanoclay. There was a profitable life cost for the PP/nanoclay and PP/shale ash for automotive panel product.

5. Recommendations

The interaction mechanism and properties of the composite could be increased using the compatibilizers, which would increase interaction between polyolefin and filler particles. In this case coupling agents, such as maleic anhydride grafted polyolefins can be used. Such functionalized polypropylene or polyethylene can increase dispersal ability, act as compatibilizing agents and adhesion promoter. Coupling agent minimizes phase separation between polar fillers and nonpolar polymers. Therefore, the mechanical properties of polyolefins can be increased.

Conclusions

1. The morphological features of montmorillonite modified with quaternary ammonium salts were changed. The exfoliation was seen with an increase in the silicate layer distance up to 3.83 nm and thermal characteristics was changed with increase of thermal stability showing higher destruction temperature than unmodified montmorillonite. The surface area of organic modified montmorillonite was reduced to 6.4 m^3/g proving proper intervene of quaternary ammonium ions into montmorillonite layers.
2. Nano and micro filler have changed mechanical properties of polyolefin composite at tension:
    - Young’s modulus (stiffness) of polypropylene/nanoclay composite was increased by 1.3 – 2 times depending on the nanofiller type. The tensile strength decreased by 3–7% for polypropylene/nanocaly. The elongation at break for the polypropylene composites was similar to that of homopolymer.
    - Fillers drastically changes stress-strain behaviour of linear low-density polyethylene due to the destruction of composite microstructure.
    - Shale ash increases Young’s modulus (stiffness). In the case of 20wt% of shale ash stiffness of polypropylene composite increases by 63%. Tensile strength decreases with the increased in shale ash content, but elongation at break is independent of shale ash content and is close to homopolymer.
3. The filling changes polypropylene morphology. During mixing nanoparticles of montmorillonite are not exfoliated in the matrix. Besides, weak adhesion between blend components is characteristic for both polypropylene/nanoclay and polypropylene/shale ash composites and voids, pull out of particles are visible at the interface. Additionally, shale ash particles tend to agglomeration leading to the low mechanical properties at tension of composite materials.
4. The thermal properties for both polypropylene/nanoclay and polypropylene/shale ash composites are increased. The temperature loss for composites was increased by 20-21% and higher destruction temperature is observed for composites than in the case of unfilled polypropylene.
5. Polypropylene composites have lesser impact on environment than other polymer composite and the weight reduction of composite material for automotive panel product was higher up to 36% in case polypropylene/nanoclay composite and 21% for polypropylene/shale ash, these composite also showed approximate higher life cycle cost saving of 42% and 52% for polypropylene/nanoclay and polypropylene/shale ash respectively.

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Annexures

Annex 1. Development of innovative plastic and other additive composites with distinctive physical and chemical properties

Development of Innovative Plastic and Other Additive Composites with Distinctive Physical and Chemical Properties

Project no.: J05-LVPA-K-04-0045
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Project coordinator: Joint stock company "Vilkritis"

Project partners: Kaunas University of Technology

Annex 2. Mechanical properties of PP composites

A.2.1. Mechanical properties of PP/MMT composites

MMT content *C*, %	**Tensile strength *σ*, MPa**	**Elongation at break *ε*, %**	**Young 's modulus E_Y, MPa**
PP			
0	34.76 ± 0.23	13.46 ± 1.88	272.203 ± 0.18
Dellite 67G			
1	33.68 ± 0.57	11.61 ± 1.82	568.55 ± 7.3
2	33.71 ± 0.19	12.79 ± 2.63	646.22 ± 1.38
Viscogel XDS			
1	32.18 ± 0.37	11.42 ± 2.87	364.87 ± 15.64
2	33.74 ± 0.42	12.49 ± 2.68	341.47 ± 5.475

A.2.2. Mechanical properties of PP/shale ash composites

Shale ash content *C*, %	**Tensile strength *σ*, MPa**	**Elongation at break *ε*, %**	**Young 's modulus E_Y, MPa**
PP			
0	34.76 ± 0.23	13.46 ± 1.88	272.20 ± 0.18
Shale ash			
2	34.13 ± 0.39	12.96 ± 1.27	208.39 ± 1.81
5	32.26 ± 0.52	15.30 ± 3.00	356.80 ± 3.17
10	30.55 ± 0.51	15.54 ± 1.77	360.44 ± 1.69
20	30.57 ± 0.50	14.21 ± 1.63	735.70 ± 0.72