

Characterization of aluminosilicate nanoparticles as a reinforcement in composite materials based on polymeric matrix

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Materials

ABSTRACT

Purpose: of this paper is to characterised MMT particles as a reinforcement in polyethylene based composite material and determine its influence on the mechanical properties of obtained materials.

Design/methodology/approach: Within the framework of experiment there has been produced composite materials based on polyethylene with 1 wt%, 3 wt% and 5 wt% content of montmorillonite using injection moulding method.

Findings: Influence of the montmorillonite additive on polyethylene properties.

Research limitations/implications: Presented method of composite preparation leads to microcomposite materials, it does not enable intercalation or exfoliation of silicate nanofiller.

Originality/value: The obtained investigation results confirm the relation between amount of introduced montmorillonite and hardness as well as strength properties of composites. Properties are better up to some content, strictly defined and equal to 4-5 wt%, and then get worse.

Keywords: Polymer-aluminosilicate composites; Injection moulding; Microstructure; Mechanical properties

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1. Introduction

In the time of the rapid technological development, materials characterized by better and better properties are intensively searched. The materials that have been used are displaced by

modern and intelligent materials, that are individually matched up with possible application. Conventional materials are interchanged with its new equivalent, and examples may be composite materials displaced by modern nanocomposite materials. The adventure of nanocomposite materials is that even small amount of nanofillers (1-5%) significantly improves

mechanical or physical and chemical properties of manufactured material, what is directly related to development of the group of materials like polymeric nanocomposites. Very important group of nanofillers applied in polymeric nanocomposites are aluminosilicates, and among them especially montmorillonite (MMT) is commonly used [1-5].

Alumino-silicates are characterized by many various structures. This diversity is determined by varied possibilities of cross-linking of silicon oxide groups with anionic complexes as well as diversify configuration of anions (their size and varied composition of alumino-silicates and silicates).

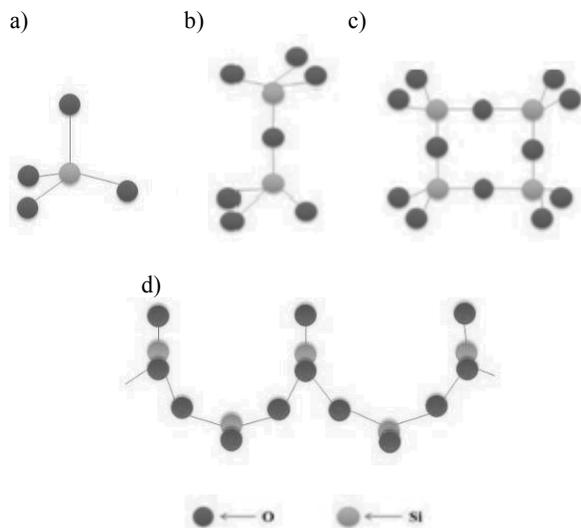


Fig. 1. Examples of silicates structures: a) single tetrahedrons, b) double tetrahedrons, c) rings, d) single and double chains

Taking into consideration structure of silicates and alumina-silicates, they can be divided into following subclasses (Fig. 1) [6]:

- Nesosilicates (single tetrahedrons);
- Sorosilicates (double tetrahedrons);
- Inosilicates (single and double chains);
- Cyclosilicates (rings);
- Phyllosilicates (sheets);
- Tectosilicates (frameworks).

The main cations usually present in silicates and alumino-silicates are potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), iron (Fe) and aluminium (Al). Aluminium occurs in silicates in both forms as cation and as a part of anion.

Montmorillonite is the main constituent of the volcanic ash weathering product, bentonite. This mineral is yellow, green, grey or white coloured. It was discovered in 1896 by WC. Knight in Montmorillon in France. The particles of montmorillonite are plate-shape and they consist of three layers - two silica tetrahedral sheets sandwiching a central alumina octahedral sheet. The oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets. The chemical formula and the atomic structure is shown on Fig. 2 [7-9].

Polymer based nanocomposite materials with montmorillonite are the topic of many researches and scientific works, in which their properties like flammability and barrier properties as well as

mechanical one are taken into account. Recently, nanocomposite materials based on polyethylene matrix filled with montmorillonite attracts the scientists attention [10-13].

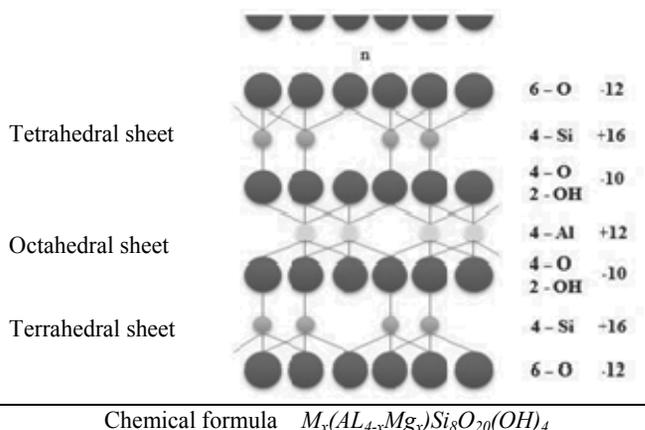


Fig. 2. Model of montmorillonite structure and approximate chemical formula where M - is cation positive one (e.g. Na^+ , H^+) and x is in the range of 0.5-1.3

The purpose of this paper is to characterised MMT particles as a reinforcement in polyethylene based composite material and determine its influence on the mechanical properties of obtained materials

2. Material and method

2.1. Materials

In the work, there have been used high density polyethylene (PE-HD) with medium molecular weight marked as SABIC B5429 produced by Saud Basic Industries Corporation. As a reinforcement montmorillonite with trade name Cloisite®15Å kindly provided by Southern Clay Products. It is natural montmorillonite modified with quaternary ammonium salt. Basic properties of materials, given by the producer, are placed in Tables 1 and 2

Table 1. Specification of polyethylene B5429

Mechanical Properties	
Elongation at Break [%]	>500
Tensile Strength at Break [MPa]	19.0
Tensile Strength, Yield [MPa]	28.0
Flexural Modulus [GPa]	1.0
Flexural Strength [MPa]	25
Izod Impact, Notched [J/cm]	1.8
Thermal Properties	
Vicat Softening Point [°C]	124
Brittleness Temperature [°C]	<= -75
Processing Properties	
Melt Temperature [°C]	190-220

Table 2.
Main characteristics of Cloisite®15Å

Typical Properties:	
Organic Modifier	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT}^{(1)} \quad \text{Cl}^- \\ \\ \text{HT} \end{array}$
Modifier Concentration	125 meq/100g clay
Moisture [%]	< 2
Weight Loss on Ignition [%]	43
Density [g/cm ³]	1.66
Typical Dry Particle Sizes	
d _{10%} [μm]	2
d _{50%} [μm]	6
d _{90%} [μm]	13
X Ray Results	d ₀₀₁ = 31.5Å

⁽¹⁾Where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14)

2.2. Processing method

Within the framework of experiment there has been produced composite materials based on polyethylene with

1 wt%, 3 wt% and 5 wt% content of montmorillonite and for comparison samples without reinforcement have been also produced. The proper amounts of components have been mixed in high-speed propeller mixer. The mixture of MMT and PE were put into special cartridge and proper specimen have been injection moulded (Roco Multipress pro) into previously prepared plaster moulds (Table 3). Obtained composite materials are abbreviated respectively as PE/MMT_1%, PE/MMT_3%, PE/MMT_5% and PE.

Table 3.
Constant injection processing set-up

Stage	
Mold temperature [°C]	220
Injection pressure [MPa]	0.7
Cooling time [min]	30

2.3. Characterization

The morphology of PE granules after milling with MMT were observed in the light microscope type Leica MEF4A. The investigation of morphology of Cloisite®15Å and the brittle fracture of composites (obtained after immersion in liquid nitrogen) were executed in an electron scanning microscope SUPRATM25 produced by ZEISS with accelerating voltage 20 kV, applying the magnification of up to 100000x. Energy Dispersive (EDS) method with were applied to confirm the presence of MMT particles.

Static tensile tests of PE/MMT composites were carried out on the universal strength machine Zwick Z100.

The measurements were carried out at room temperature with a crosshead speed 10 mm/min and pre-load 2 N/mm² (according to PN-EN ISO 527-1:1998). For each material a minimum of 5 samples were tested to determine average value.

Hardness measurements of investigated composites were made by the ball indentation method according to PN-EN ISO 2039-1:2004 standard with load equal to 132 N and investigation time 30 s.

3. Results and discussion

The microstructure of Cloisite®15Å can be observed in Fig. 3. On the micrographs layered character of montmorillonite and diversified particale size from several hundred nm to even a dozen or so μm what is in agreement with producer declare. The x-ray energy dispersive spectrum indicates the presence of sodium, calcium, magnesium and iron cations in investigated montmorillonite.

The results of materialographic investigations of PE/MMT composition after milling in high-speed propeller mixer are introduced on microphotographs (Fig. 4). It can be observed non-uniform fusion of montmorillonite particles on the surface of PE granules. This particles are strictly connected to the PE surface and are of diversify thickness.

Figures 5, 6 and 7 shows distribution of MMT particles in PE matrix. MMT particles are uniformly present in whole volume of composite materials, however the size of aggregates varies from the several hundred of nm up to nearly 20 μm. The most uniform distribution of nanofiller can be observed for PE/MMT_1% composite, but the smallest agglomerates of MMT particles are present in the case of PE/MMT_3% composites. PE/MMT_5% shows the worst distribution of nanofiller and the biggest agglomerates of it. From above SEM micrographs it can be concluded that presented method of composite preparation leads to microcomposite materials, it does not enable intercalation or exfoliation of silicate nanofiller.

The results of static tensile tests permitted to qualify the influence of MMT concentration on mechanical properties of PE/MMT composites. In Fig. 8, representative stress-strain curves of polyethylene and polyethylene/montmorillonite composites are shown. As it can be seen, a montmorillonite content of 3 wt% leads to a highest increase of the tensile strength and tensile modulus equal to 17.5% in comparison to pure polyethylene (Table 4). Probably, agglomerates formation of MMT particles results in a reduction of effective surface area, which can undergo matrix-filler interactions. In the case of material containing 3 wt% of montmorillonite the smallest agglomerates of the filler are observable, what results in higher effective structure area as in the 5 wt% composites.

The results of hardness measurements are also placed in Table 4. The average values are in the range of 32 up to 48 HB. The highest increase in hardness is observed for composite material with 5 wt% content of montmorillonite while the lowest value is in the case of pure polyethylene. The percentage change in hardness equals to 6.2 % for PE/MMT_1%, 31% for PE/MMT_3% and 48.5 % for PE/MMT_5% in comparison to material without silicate filler.

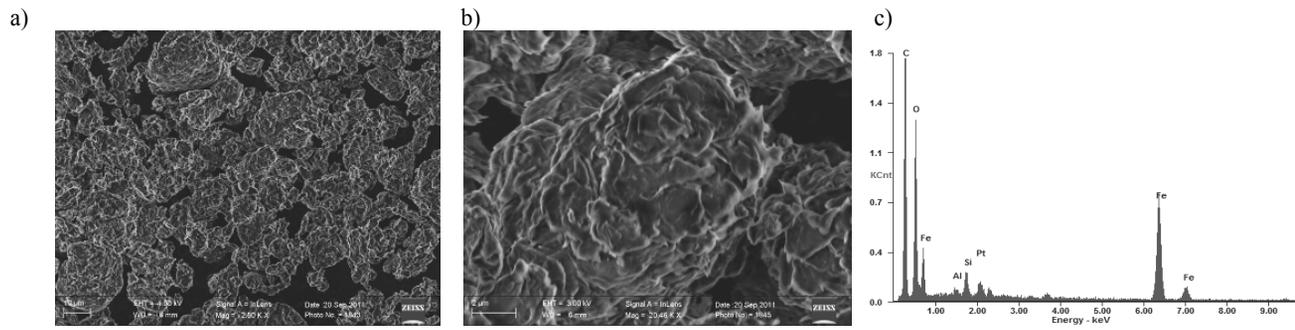


Fig. 3. SEM micrographs of Cloisite®15Å a) mag. 2500x, b) mag 20500x and c) X-ray energy spectrum of the sample

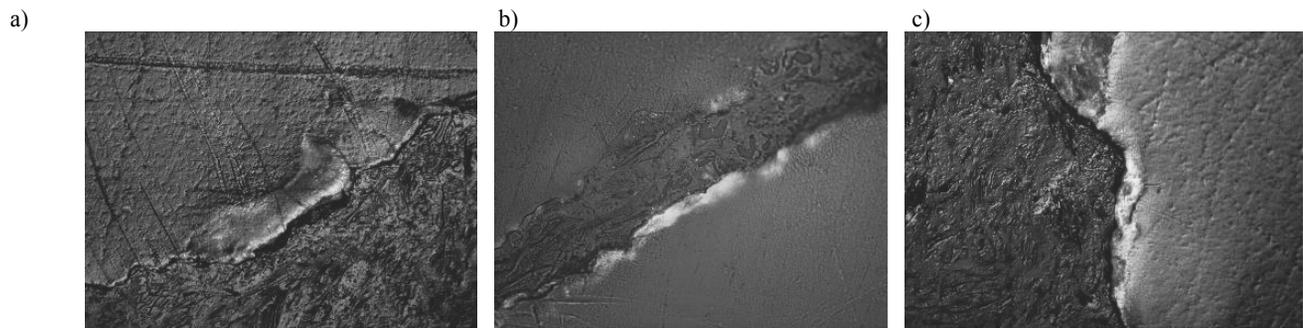


Fig. 4. Microstructure of composite materials: a) PE/MMT_1%, b) PE/MMT_3%, c) PE/MMT_5%; Mag 500x

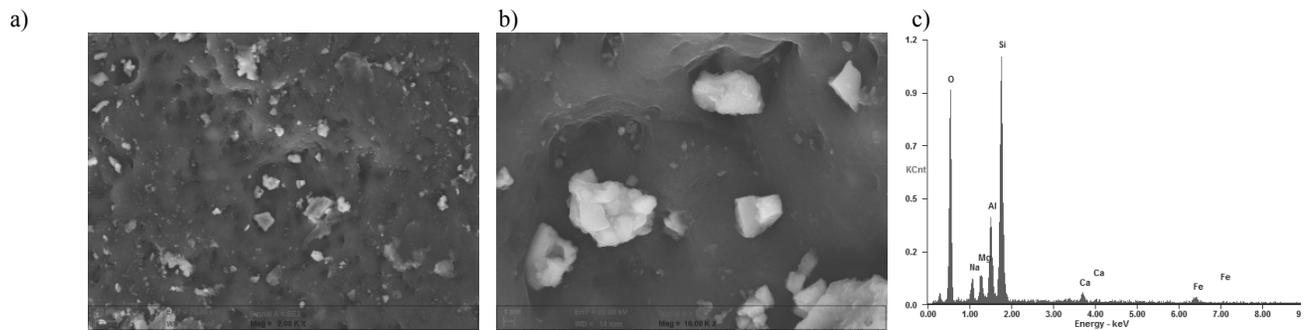


Fig. 5. SEM micrographs of PE/MMT_1% composite a) mag. 2000x, b) mag 10000x and c) X-ray energy spectrum from area of MMT particle

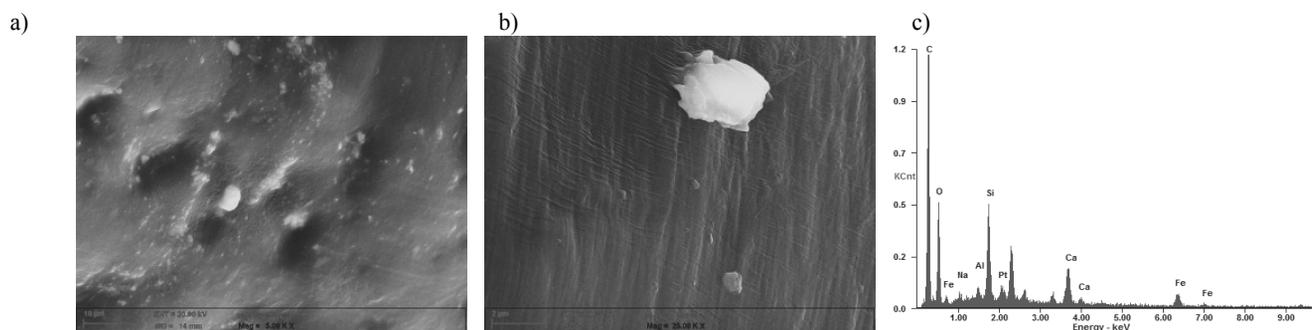


Fig. 6. SEM micrographs of PE/MMT_3% composite a) mag. 5000x, b) mag 25000x and c) X-ray energy spectrum from area of MMT particle

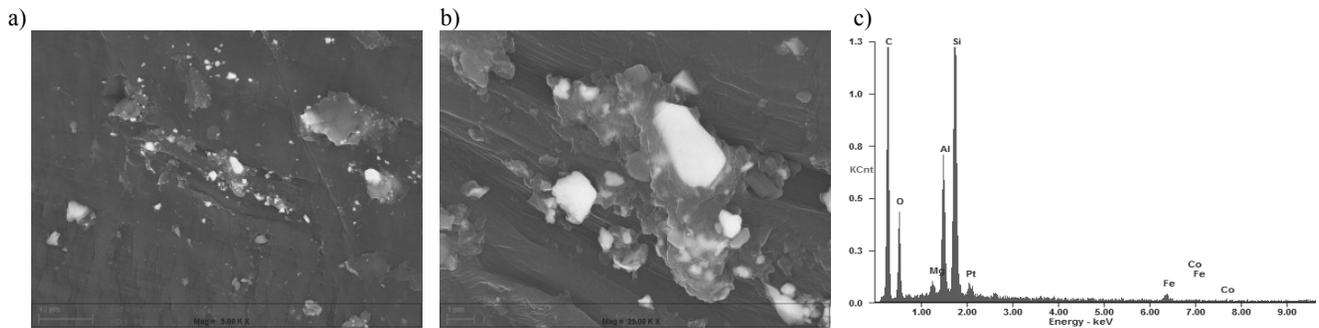


Fig. 7. SEM micrographs of PE/MMT_5% composite a) mag. 5000x, b) mag 25000x and c) X-ray energy spectrum from area of MMT particle

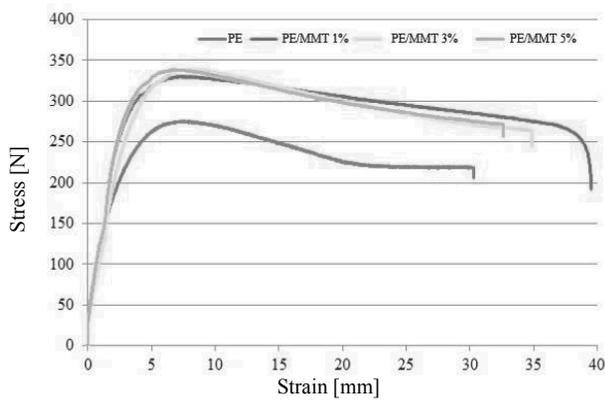


Fig. 8. Stress-strain curves of PE and PE/MMT composites

Table 4. Mechanical properties of PE/MMT composite materials and pure PE

Material	Tensile strength R_m [MPa]	Tensile modulus E [MPa]	Ball indentation hardness HB
PE	19	367	32
PE/MMT_1%	21	400	34
PE/MMT_3%	23	405	42
PE/MMT_5%	22	393	48

Comparing obtained results of PE/MMT composite materials investigations with scientific literature it can be observed similar relation between amount of introduced montmorillonite and strength properties of composites. It means that this properties are better up to some content, strictly defined and equal to 4-5 wt%, and then the get worse. [12]

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