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The effect of kaolin modification of silane coupling agents on the properties of the polyethylene composites

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This paper shows the results of using the modified kaolin by silane coupling agents in HDPE composite and the effect of surface modifications of fillers on the properties of polyethylene composites. In the first stage pure and modified kaolin was subjected to a number of tests in order to determine the backfill density, water and paraffin oil absorbability, the surface area and pore volume, the morphology of their grains, thermal analysis and the FT-IR spectroscopy.

In the second stage the composites, which were moulded into the samples that could be subjected to further tests, were produced. The samples were characterised by the determination of the hardness according to Shore, the elasticity modulus, the tensile strength and tearing strength.

The modification of the kaolin surface has resulted in a substantial improvement of the strength parameters of the obtained polyethylene composites.

Keywords: kaolin/HDPE composites, modified fillers, silane coupling agents.

INTRODUCTION

Kaolin is a mineral filler of natural origin most often used in the production of plastic and elastomer materials. The composites obtained after their introduction into the polymer matrix are characterised by the improved strengthening physical properties[1]. One of the main components of kaolin is the mineral kaolinite, being hydrated aluminium silicate of the formula: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Kaolinite is 1:1 dioctahedral clay mineral composed of structurally asymmetric layers. One side of the layer is gibbsite-like with aluminium atoms coordinated octahedrially with applied oxygen atoms and hydroxyls. The other side of the layer is constituted by the silicate layer structure, where the silicon atoms are coordinated thetrahedrially to oxygen[2]. At the interface of each group of the layers there are hydroxyl groups. Three fourth of the OH^- groups being the external hydroxide groups are at the surface of a kaolinite packet and their protons take part in hydrogen bonds of the lengths of 3.13, 3.00 and 2.29Å. The other OH^- groups are inside the packet; they are called the internal hydroxyl groups, and are involved in the shortest hydrogen bonds of 2.96 Å. Hydrogen bond formation changes the polarization of the OH bonds so that the positive charge is shifted towards the protons[3]. The lamellar structure of the kaolinite is responsible for their excellent cleavage and easy separability into thin sheets. The lamellar packets are electrically neutral. The packets are linked through the hydrogen bonds made with the involvement of the hydroxyl groups coordinated about a single packet and about the silica atoms in the neighbouring packet[4]. The paper reports on the production of kaolin filled polymers, their characterisation and the effects of the kaolin modifications with silane coupling agents significantly improving the strength of the composites.

EXPERIMENTAL

Substrates

The KOG kaolin from the Surmin-Kaolin mine in Nowogrodziec near Bolesławiec was used. The kaolin surface was modified with the following silane -coupling agents made by Unisil, Tarnów:

– 3-isocyanatepropyltrimethoxysilane **3iso**
– 3-aminopropyltrietoxysilane **3A**
– N-2-aminoethyl 3-aminopropyltrimethoxysilane **N2**
– Vinyltriethoxysilane **V**
– 3-methacryloxypropyltrimetoxysilane **M**
– 3-chloropropyltrimethoxysilane **Ch**

Modification of fillers

The surface modification was performed at room temperature in a 1:1 water-ethanol solution with a 1 – 3% vol addition of the silane coupling agent, in the MPW-309 mixer until the plastification of the plastic solid. The air-dried sample was ground in the mortar and sieved through a mesh size 0.063mm.

Filler testing

Pure and modified kaolin was subjected to a number of tests in order to determine their bulk density PN-80/C-04404/03, water[5] and paraffin oil absorbability PN-87/C-04404/1. The surface area and pore volume distribution were determined on the ASAP 2010 Sorptometer and the SEM photographs of the samples were taken to assess the morphology of their grains by the PHILIPS SEM 515. The gravimetric measurements (TG, DTG, DTA methods) were determined on a thermogravimeter Setaram TGA[6]. The IR spectra were taken on the Bruker FT-IR IFS 66/s spectrometer.

Composite preparation

Polyethylene Hostallen ACP 5831 D made by Basell Orlen Polyolefins was selected because of a wide range of applications for the production of objects that have to

Table 1. The absorbing capacities and the bulk density of kaolins

Type of the filler	Water absorbing capacity [cm^3/100g]	Paraffin oil absorbing capacity [cm^3/ 100g]	Bulk density [g/cm^3]
Pure kaolin	150±50	50±50	1.56± 0.01
Kaolin modified with 3-isocyanatepropyltrimethoxysilane	160±50	200±50	1.68± 0.01
Kaolin modified with 3-aminopropyltrietoxysilane	200±50	220±50	1.70± 0.01
Kaolin modified with N-2-aminoethyl 3-aminopropyltrimethoxysilane	250±50	250±50	1.73± 0.01
Kaolin modified with vinyltriethoxysilane	300±50	90±50	1.78± 0.01
Kaolin modified with 3-methacryloxypropyltrimetoxysilane	400±50	100±50	1.84± 0.01
Kaolin modified with 3-chloropropyltrimethoxysilane	390±50	70±50	1.89± 0.01

show high mechanical strength. The composites with the modified fillers were produced at the Institute of Plastics Processing „Metalchem" in Toruń, using a screw extruder BTSK 20/40D made by Bűhler . There were 4% of fillers in the composites. The composites were moulded into the samples that could be subjected to further tests.

Composite testing

The samples were characterised by the hardness according to the Shore scale PN-80C/04238, the PN-EN ISO 527/1998 elasticity modulus, the tensile strength and tearing strength at the TIRA test 27025 stand PN-EN ISO 527/1998.

RESULTS AND DISCUSSION

Table 2. The surface area of kaolins

Type of the filler	Surface area BET [m^2 /g]
Pure kaolin	10.85 ± 0.06
Kaolin modified with 3-chloropropyltrimethoxysilane	11.67 ± 0.06
Kaolin modified with 3-isocyanatepropyltrimethoxysilane	12.32 ± 0.08
Kaolin modified with 3-aminopropyltrietoxysilane	12.43 ± 0.06
Kaolin modified with N-2-aminoethyl 3-aminopropyltrimethoxysilane	12.67 ± 0.08
Kaolin modified with vinyltriethoksysilane	15.49 ± 0.09
Kaolin modified with 3-methacryloxy propyltrimetoxysilane	16.60 ± 0.09

Table 3. The pore size of kaolins

Type of the filler	Pore size [nm]
Pure kaolin	11.204 ± 0.001
Kaolin modified with 3-chloropropyltrimethoxysilane	9.854 ± 0.001
Kaolin modified with N-2 aminoethyl-3-aminopropyltrimethoxysilane	9.755 ± 0.001
Kaolin modified with 3-aminopropyltriethoxysilane	9.569 ± 0.001
Kaolin modified with 3-isocyanatepropyltrimethoxysilane	9.506 ± 0.001
Kaolin modified with vinyltriethoxysilane	7.647 ± 0.001
Kaolin modified with 3-methacryloxypropyltrimethoxysilane	6.980 ± 0.001

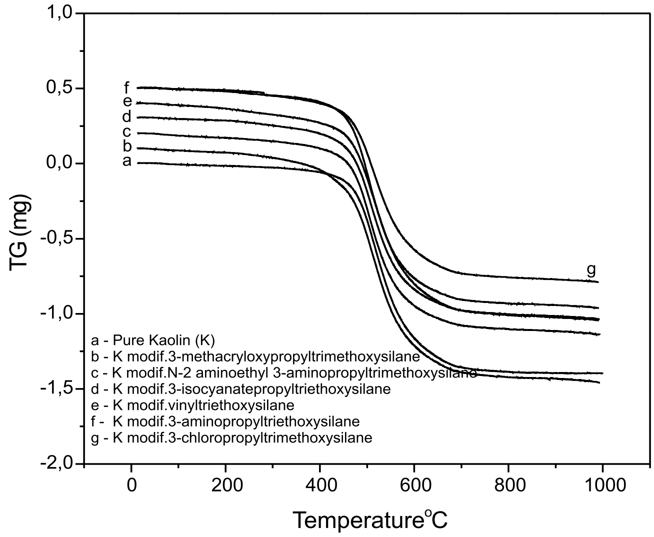

Figure 1. The TG-Thermogravimetric curves of the kaolin samples

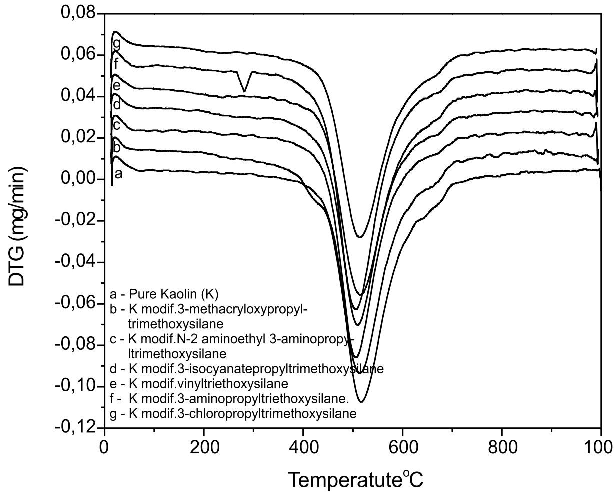

Figure 2. The DTG-Thermogravimetric curves of the kaolin samples

The modification of kaolin with silane coupling agents significantly improves the physicochemical parameters of the mineral fillers (Tables 1 – 3).

The surface area increased, the pore sizes are reduced, the bulk density increases and the

hydrophilous-hydrophobic properties were improved. The obtained fillers are characterised by significant thermal stability (Figs. 1 – 4).

On heating the samples release the water that can originate from the following:

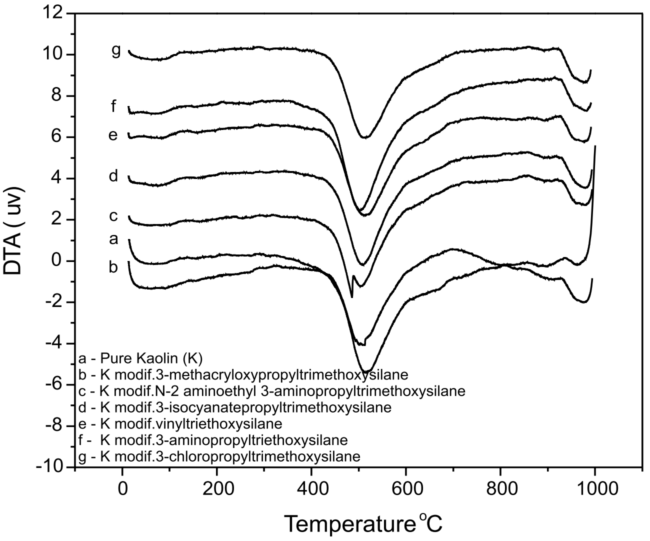

Figure 3. The DTA curves of the kaolin samples

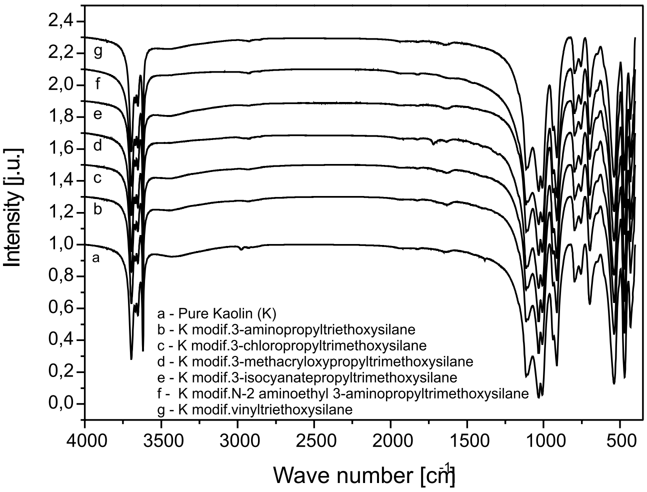

Figure 4. The FT-IR spectrum of kaolins in the range of 4000 – $400cm^{-1}$

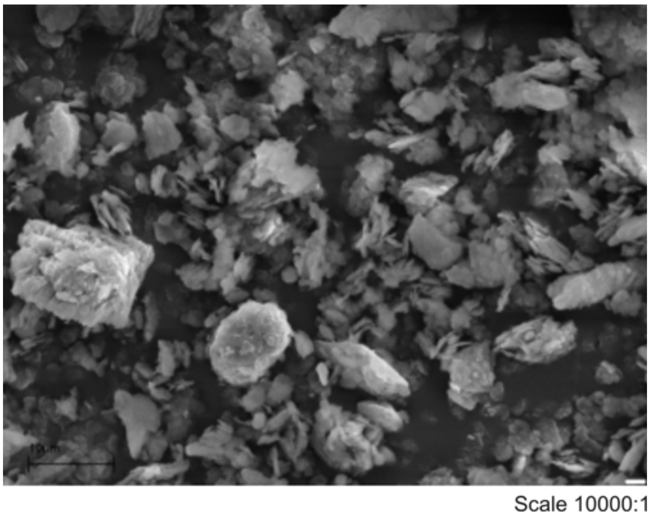

Photo 1. Pure kaolin mined in KOG „Surmin-Kaolin" in Nowogrodziec

– the multilayer adsorbed water that can be released at 125°C

– the monolayer adsorbed water released completely above 250°C

– the water liberated in the process of the decomposition of the organic compounds of lignin and tannin, making about 0.05 – 1.8% of the water contained in kaolin

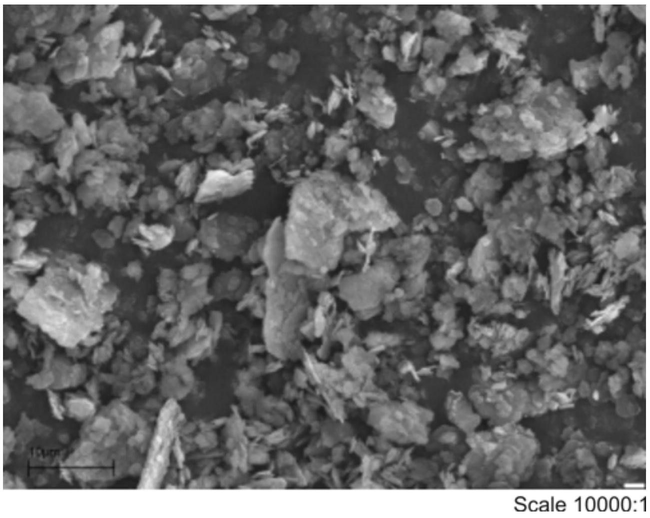

Photo 2. Kaolin modified of 3-chloropropyltrimethoxysilane

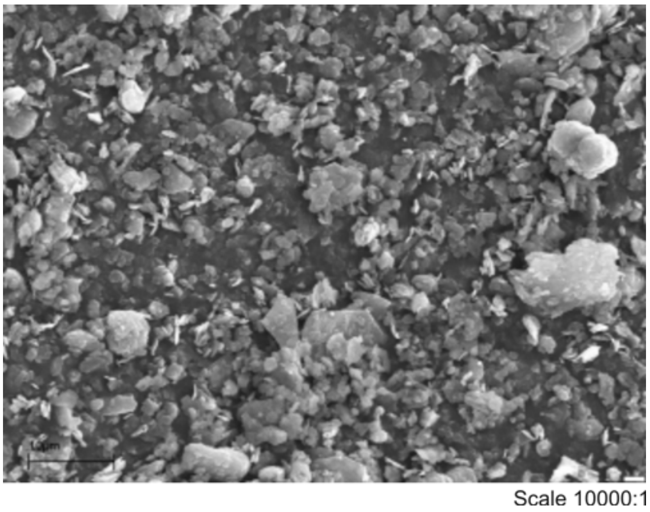

Photo 3. Kaolin modified of 3-isocyanatepropyltrimethoxysilane

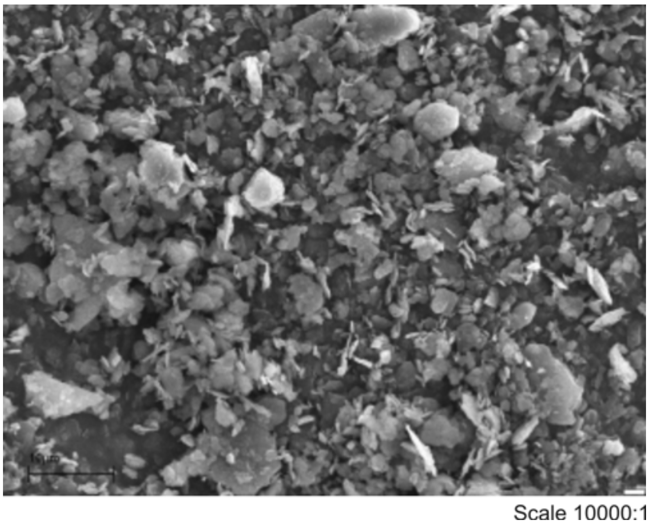

Photo 4. Kaolin modified of 3-aminopropyltriethoxysilane

– the dehydroxylation water liberated as a result of the transition of the octahedral aluminol group to the tetrahedral aluminooxane group at temperatures ranging from 350 do 700°C, corresponding to the temperatures of kaolin calcination,

– the chemically bound water; at about 900°C the remaining OH groups are lost leading to the formation of the aluminium-silica spinel $Al_2O_3 \cdot SiO_2$ and silica,

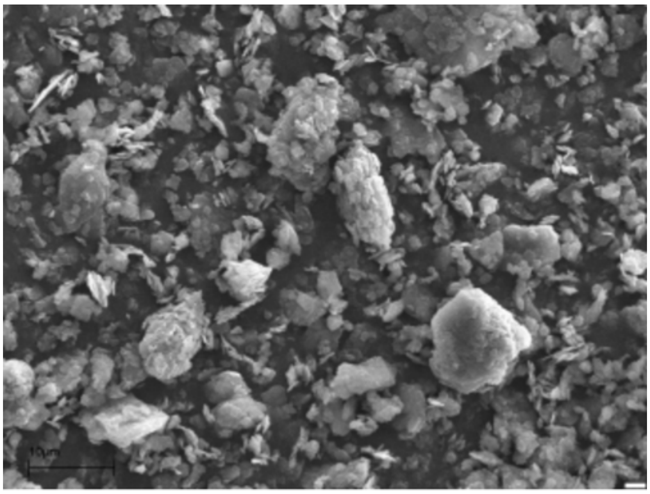

Photo 5. Kaolin modified of N-2-aminoethyl 3-aminopropyltrimethoxysilane

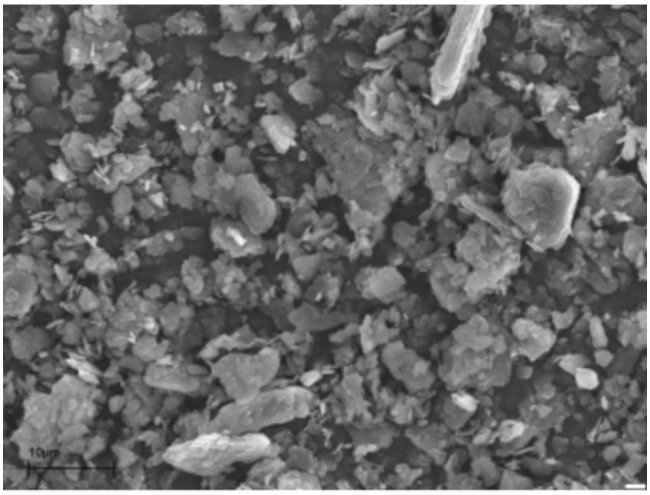

Photo 6. Kaolin modified of 3-methacryloxypropyltrimethoxysilane

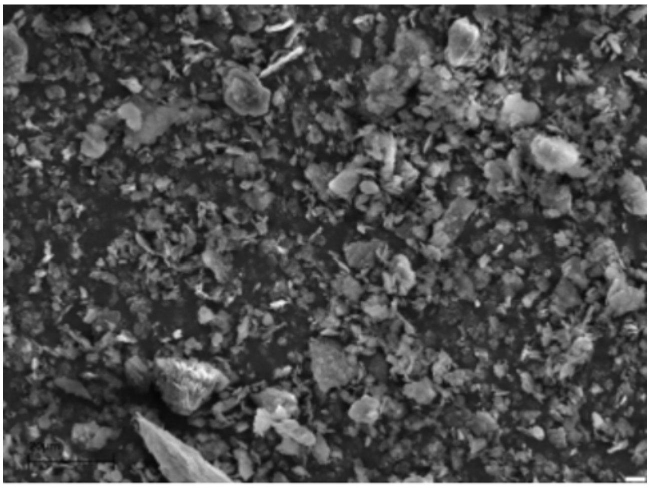

Photo 7. Kaolin modified of vinyltriethtoxysilane

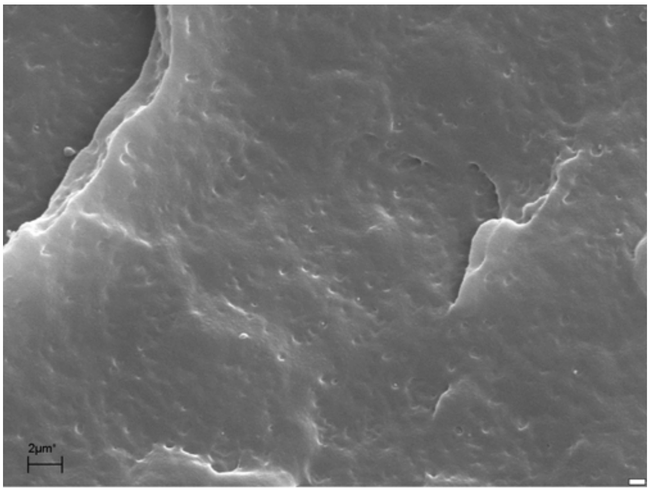

Photo 8. HDPE Hostalen

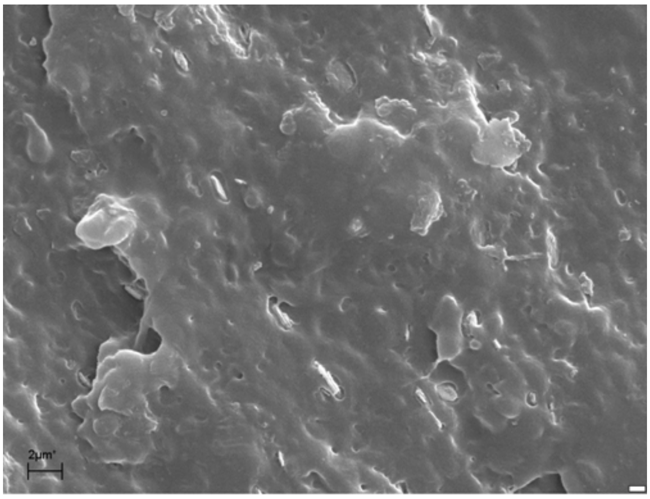

Photo 9. HDPE / pure kaolin

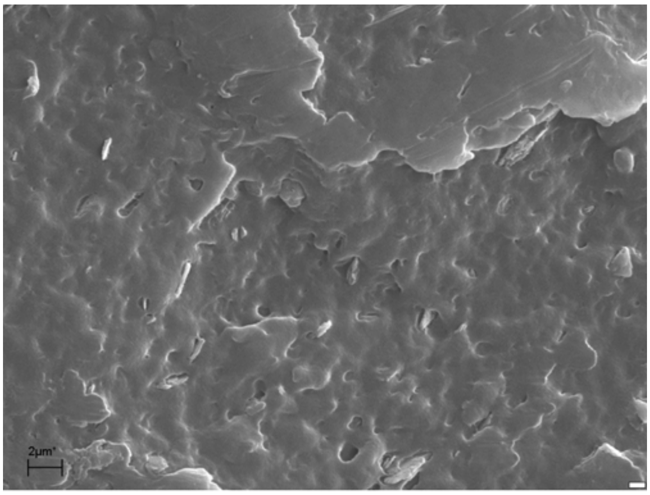

Photo 10. Composite HDPE/ kaolin modified of 3-isocyanatepropyltrimethoxysilane

In the range of 1150 – 1225°C the spinel phase is transformed into mullite and the silica becomes cristobalite[6].

The results of the FT-IR study confirm the presence of kaolinite by revealing four characteristic absorption bands, at about 3600 cm^{-1} assigned to the OH groups vibrations. The absorption bands permit the identification of the types of lamellar silicates as the spectrum of halloysite showed two bands, while those of nakrite and dyckit show three bands[7]. The bands, characteristic of kaolin are at 3700 and 3620 cm^{-1}, whose presence also indicates a high degree of the system ordering[8]. At about 1680 and 1230 cm^{-1} there are the bands assigned to the deformation vibrations of the OH groups, testifying to the presence of the water bound in the aluminium silicate gallery. In the range of 900 – 1100 cm^{-1} there are the bands typical of the Si-O

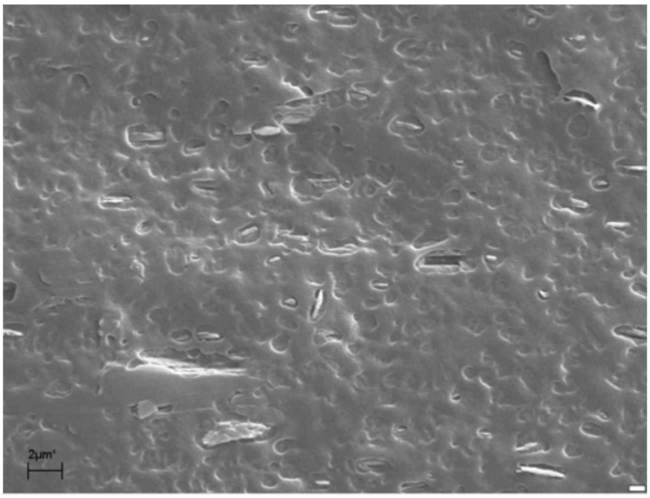

Photo 11. Composite HDPE/ kaolin modified of 3-aminopropyltriethoxysilane

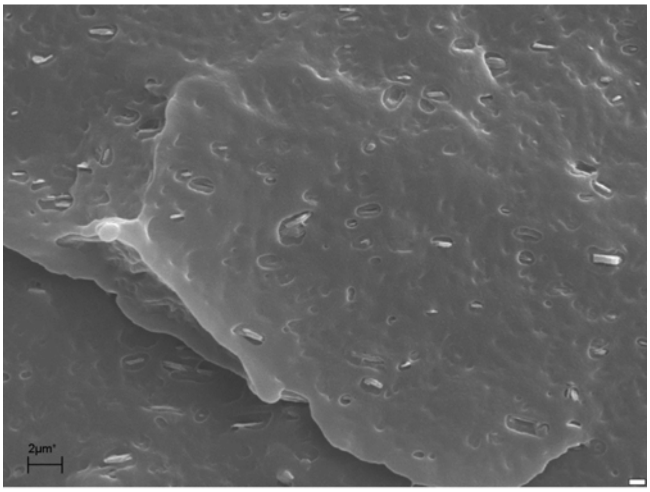

Photo 12. Composite HDPE / kaolin modified of 3-chloropropyltrimethoxysilane

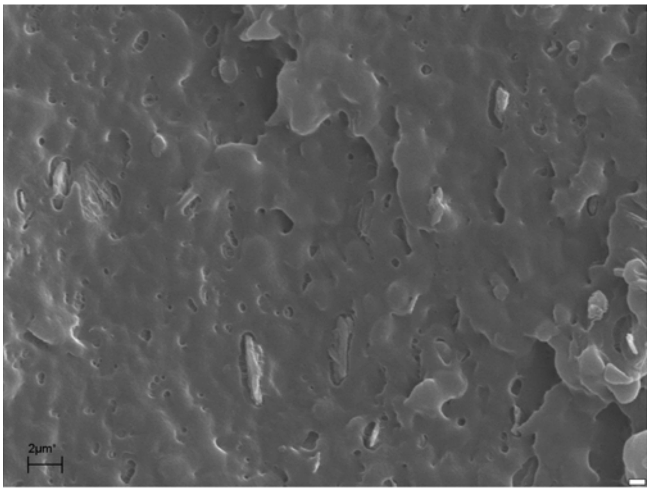

Photo 13. Composite HDPE/ kaolin modified of N-2 aminoethyl 3-aminopropyltrimethoxysilane

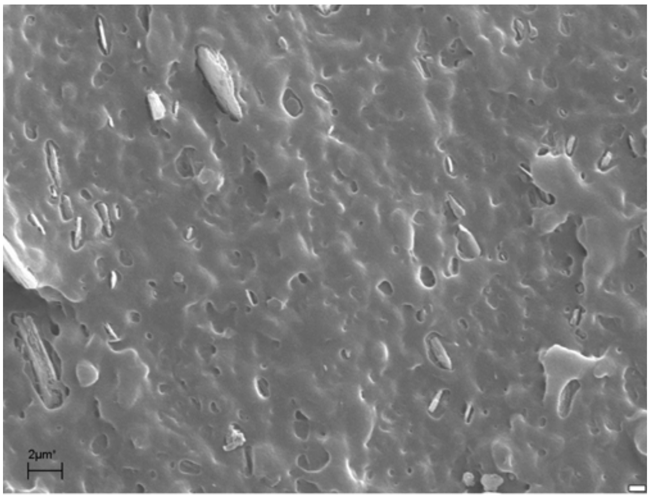

Photo 14. Composite HDPE / kaolin modified of vinyltriethoxysilane

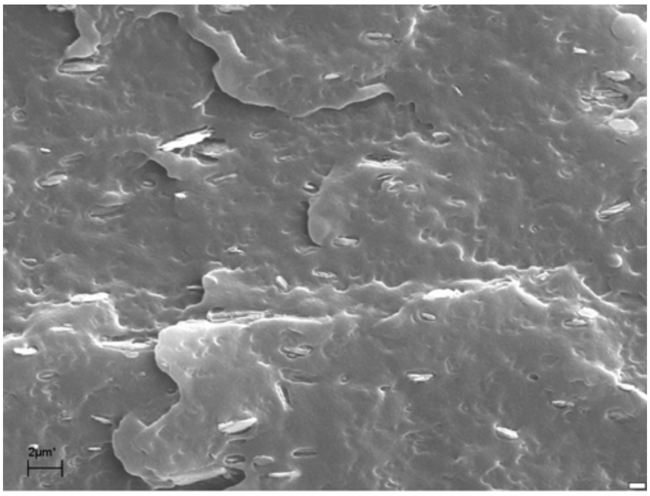

Photo 15. Composite HDPE/ kaolin modified of 3-methacryloxypropyltrimethoxysilane

bending vibrations and the poorly separated band assigned to the Si-O stretching vibrations. A gradual decrease in the band intensity is observed above 950 cm^{-1}, as a result of silane species adsorption on the kaolin surface[9]. The spectrum of kaolin modified with 3-chloropropyltrimethoxysilane shows an additional band at about 800 cm^{-1}, typical of the C-Cl bonds. The SEM photograph (Phot.1 – 7), of this filler shows the uniform size of the grains and a considerable increase in the surface area as a result of the formation of agglutinations and additional layers on the surface of the pseudo-hexagonal sheets. On the basis of the results obtained the most effective one is the modification with 3-methacryloxypropyltrimethoxysilane and vinyltriethoxysilane as the use of such modified fillers has significantly improved the properties of polyethylene composites (greater hardness and elasticity modulus) with respect to those of the unfilled polymer and the polymer filled with the unmodified filler. The kaolin modification with the above two compounds also brings a correction in the physico- or mechanical parameters: the tearing strength and mean tensile stress increase, while the unit elongation on stretching and on tearing decreases. The SEM photographs of the composite (Phot. 8 – 15), reveal a homogeneous distribution of the modified filler in the polymer matrix, achieved thanks to the modification improved character of the filler-polymer and filler-filler interactions. The composites filled with the modified kaolin are more stable than the unfilled polymer or the polymer filled with the unmodified kaolin.

Table 4. The elasticity modulus and the hardness of the polyethylene composites

Nanocomposite	Elasticity modulus [MPa]	Hardness [° Sh D]
Pure HDPE	1103	63
HDPE/pure kaolin	1224	64
HDPE / kaolin Ch	1175	65
HDPE/kaolin N2	1192	64
HDPE/ kaolin 3A	1215	64
HDPE/ kaolin3iso	1220	64
HDPE/ kaolin V	1203	66
HDPE/ kaolin M	1237	66

Table 5. The mechanical parameters of the polyethylene composites

Nanocomposite	Mean tearing stress [MPa]	Elongation on the mean tearing stress [%]
HDPE	3.61 ± 0.81	17.70 ±2.30
HDPE/pure kaolin	3.06 ± 0.75	13.47 ± 1.91
HDPE / kaolin Ch	24.79 ± 20.24	11.55 ± 2.20
HDPE/kaolin N2	40.63 ± 1.42	9.97 ± 0.45
HDPE/ kaolin 3A	40.76 ± 0.59	9.59 ± 0.47
HDPE/ Kaolin 3iso	32.95 ± 17.24	10.22 ± 2.04
HDPE/ kaolin V	17.83 ± 20.27	11.96 ± 2.94
HDPE/ kaolin M	41.27 ± 1.78	9.61 ± 0.59

Table 6. The mechanical parameters of the polyethylene composites

Nanocomposite	Mean tensile stress [MPa]	Elongation on the maean tensile stress [%]
HDPE	38.08 ± 1.05	9.74 ± 0.84
HDPE /pure kaolin	39.36 ± 0.61	8.37 ± 0.35
HDPE / kaolin Ch	39.38 ± 1.18	9.59 ± 0.30
HDPE/kaolin N2	40.84 ± 1.28	9.62 ± 0.40
HDPE/ kaolin 3A	41.21 ± 0.53	9.30 ± 0.45
HDPE/kaolin 3iso	40.57 ± 1.64	9.11 ± 0.33
HDPE/ kaolin V	40.00 ± 1.10	8.77 ± 0.61
HDPE/ kaolin M	41.54 ± 1.67	9.24 ± 0.53

CONCLUSIONS

The modification of kaolin fillers with silane coupling agents significantly improves their physicochemical properties and hence the properties of the obtained composites. As follows from our results, the modification of the fillers with silane coupling agents substantially improves their dispersion in the polymer matrix and hence reduces the tendency towards the agglomeration of particles, leading to a decreased strength of the filler-filler interactions and the increased strength of the filler-polymer interactions. The modified fillers are stronger bonded to the polymer which improves the physico- or mechanical parameters of the composite and permits the extension of the range of their applications.

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