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Structural Study of Polyethylene/Montmorillonite Systems

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The effect of modification of montmorillonite (with 3-aminopropyltrimethoxysilane or hexadecyltrimethylammonium chloride) on the mechanical properties of the composites based on HDPE Hostalen ACP 5831 with the modified montmorillonite as filler, was studied. The structures of the fillers and nanocomposites were characterised by the scanning electron microscopy and X-ray diffraction study. The effect of the filler modification on the mechanical parameters of the nanocomposites and their structure was assessed on the basis of determination of the mechanical resistance, elongation at maximum tearing stress, bending strength, deformation at the maximum force and elasticity modulus on bending (three-point bending strength).

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1. Introduction

In this study white mineral powder fillers have been used in order to improve the mechanical properties of plastomers and elastomers. For example, polymer nanocomposites from the group of silicates whose parameters are dramatically improved upon addition of a small amount of the filler (1–7%) are commercially available. The improvement is observed in the bending strength, deformation at the maximum force and elasticity modulus on bending and the maximum tearing stress. The fillers are solid mineral materials water insoluble, easily dispersed in the composite upon mixing. The much-refined organic or inorganic fillers make a dispersed and insoluble phase in polymers [1]. The final mechanical and physical properties of the products significantly depend on the physical and chemical character of the filler surface, its surface area and particle size.

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Introduction of a nanofiller into the polymer matrix has been found to result in an increased elasticity modulus, increased thermal stability, and increased resistance to organic solvents and improved optical quality. A very important factor is the filler dispersion in the polymer matrix. To achieve the strengthening effect of the polymer, the energy of adhesion of the filler to the polymer must be greater than that of the polymer cohesion. Clay minerals have been often used as fillers. The important features of clays include: plasticity, specific surface structure and the related ability of shape preservation on drying, ability to form at certain temperatures a material of great mechanical strength, high adsorption capacity, ability to swell and capacity to ion exchange [1–3].

Bentonite is a clay mineral formed as a result of *in situ* weathering of volcanic ashes. Its name comes from the first exploited bed in Fort Benton, Wyoming State, USA. Bentonite is composed of 48–56% SiO_2, 11–22% Al_2O_3, 5% (or more) Fe_2O_3, 4–9% MgO, 0.8–3.5% CaO, 12–24% H_2O, admixtures of Na_2O, K_2O and others. Its main component is montmorillonite (60–75%) of the 2:1 packet structure. A single packet is made by three layers: two external tetrahedral ones (silicon oxide Si_2O_5) and the internal octahedral one (aluminium oxide-hydroxyl $Al_2O_4(OH)_2$). Montmorillonite has high adsorption capacity and swelling ability, the high content of Na^+ ions leads to considerable swelling of the mineral, leading sometimes to total separation of the crystal [4–8].

Samples of montmorillonite were modified by selected silanol promoters of adhesion (coupling agents) and tertiary ammonium salts. The paper presents the information on the microstructure of the modified fillers and the final composites obtained with their use, studied by SEM images and XRD measurements of the modified and unmodified samples. The modified fillers were used for production of nanocomposites based on polyethylene. The nanocomposites were subjected to a number of strength tests to determine the maximum tearing stress, elongation at maximum tearing stress, bending strength, deformation at the maximum force, elasticity modulus on bending.

The study was undertaken to establish the effect of addition of modified and unmodified montmorillonite to a selected polyethylene on the properties of the so obtained composite. The aim of the study was to obtain and characterise new polymer fillers made of montmorillonite (lamellar silicate) unmodified and modified with 3-aminopropyltrimethoxysilane and hexadecyltrimethylammonium chloride.

2. Material and methods

The material studied was bentonite obtained from the Zakłady Górniczo-Metalowe "Zębiec" (Starachowice, Poland). At the first stage montmorillonite was separated from the bentonite, then the filler was modified with the coupling agents from the group of silanes and quaternary ammonium salts:

- 3-aminopropyltrimethoxysilane;

• hexadecyltrimethylammonium chloride.

At the next stage, the filler was grounded in a mortar and sieved through the mesh size 0.063 mm. The modification was performed with 1–3 volume fractions of the modifier per 100 weight fractions of the filler. The best results were obtained for the admixture with 3 volume fractions and only these results are given in the paper. The modification with lower volume fractions did not produce considerable changes in the properties of the composite. The modifying factor was dissolved in a 1:1 mixture of ethyl alcohol and water. The contents were mixed by a homogeniser type MPW-309 (Mechanika Precyzyjna, Poland) for 1 h and dried in air for 48 h. After drying the composites were prepared by a double screw extruding press (BTSK 20/40D made by Bühler) of 4% filling, with the matrix of HDPE Hostalen ACP 5831D (LyondellBasell Industries). To achieve homogeneous mixing of the components they were placed in a special container. At the next stage, the montmorillonite composites obtained were shaped by an injection moulding press Battenfeld Plus 35/37 UNILOG B2. The products were subjected to physical and mechanical tests at the Institute of Synthetic Material Processing "Metal-chem" in Toruń.

The diffraction measurements were performed in the range $3.0 < 2\theta \leq 60^\circ$ with the Cu K_α radiation ($\lambda = 1.5412$ Å). The morphology of cross-sections of the pure and modified samples of montmorillonite and the nanocomposites was analysed under an electron scanning microscope (Zeiss EVO 40) at the voltage of 19 kV and under different magnifications from the range $250-5000\times$. The powdered samples of the filler were placed on a table of 5 mm in diameter in the form of a drop of suspension in t-butanol. The solution was evaporated and the powder left was covered with a film of gold in a sputter coater. The samples of nanocomposites were directly covered with a gold film.

The mechanical tests were performed at the testing stand TIRA test 27025 (TIRA Maschinenbau, GmbH, Germany) on the oar-shaped samples [PN-EN ISO 527:1998]. Five tests were performed to determine the maximum tearing stress, elongation at the maximum tearing stress, bending strength, deformation at the maximum force, elasticity modulus on bending of the composite samples filled with the unmodified montmorillonite and montmorillonite modified with 3-aminopropyltrimethoxysilane and hexadecyltrimethylammonium chloride, and on samples of pure HDPE polymer.

3. Results and discussion

Table shows the mechanical parameters of the HDPE polymer composite samples containing pure montmorillonite clay mineral and that modified with 3-aminopropyltrimethoxysilane and hexadecyltrimethylammonium chloride compounds.

The maximum tearing stress and the elongation at maximum tearing stress obtained during experiments were compared for all samples. The process of modification results in changes in some mechanical properties of the filled composites.

TABLE

Mechanical properties of the composites upon static tensile stress (A — maximum tearing stress [MPa], B — elongation at maximum tearing stress [%]) and on three-point bending (C — bending strength [MPa], D — deformation at maximum force [%], E — elasticity modulus on bending [MPa]). HDPE/MMT-1 — HDPE/MMT modified with 3-aminopropyltrimethoxysilane; HDPE/MMT-2 — HDPE/MMT modified with hexadecyltrimethyl-ammonium chloride.

Composite	A	B	C	D	E
Pure HDPE	38	9.7	17.2	7.57	640
HDPE/MMT pure	40	8.1	19.4	7.52	700
HDPE/MMT-1	39	9	19.5	7.58	700
HDPE/MMT-2	41	8.5	18.8	7.52	751

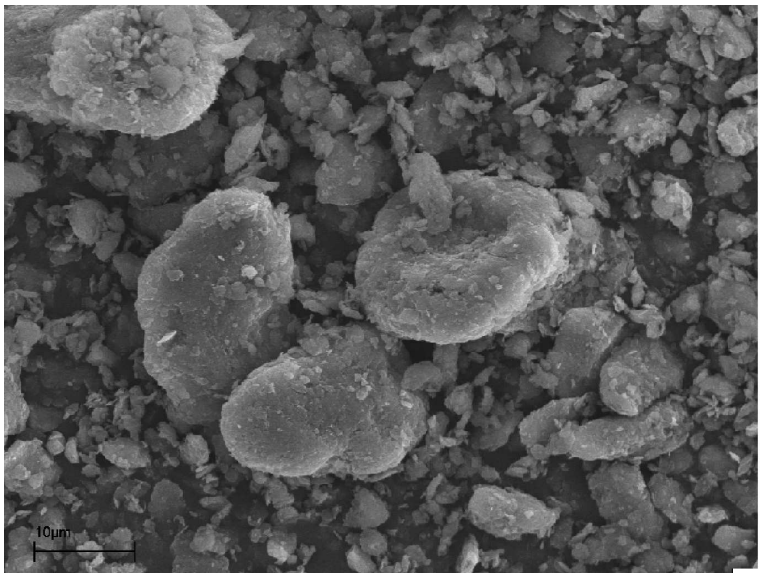

Fig. 1. Unmodified montmorillonite.

For pure HDPE the maximum tearing stress was lower than for the composites. The modification with hexadecyltrimethylammonium chloride seems more effective than that with 3-aminopropyltrimetoxysilane. The results of the three-point bending test have shown that the bending of the filled composites requires greater force than that of the pure polymer (Table). Moreover, the elasticity modulus on bending is also higher for the composites filled with the modified montmorillonite

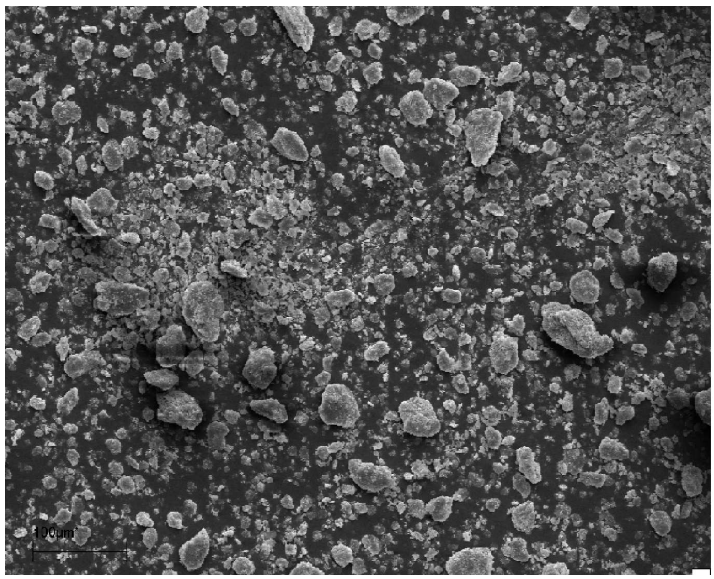

Fig. 2. Montmorillonite modified with hexadecyltrimethylammonium chloride.

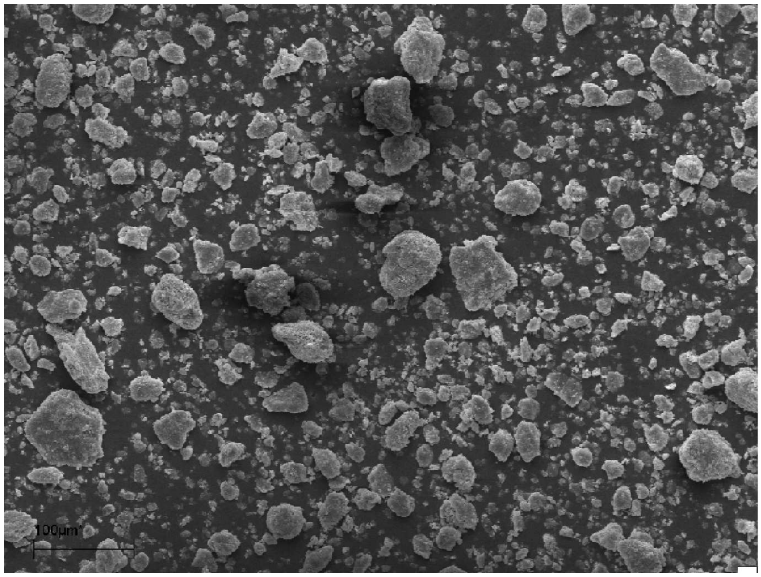

Fig. 3. Montmorillonite modified with 3-aminopropyltrimethoxysilane.

than for the pure polymer. It reaches the highest value for the montmorillonite modified with hexadecyltrimethylammonium chloride. As far as the value of the deformation at maximum force is concerned, the effect of filling is practically insignificant.

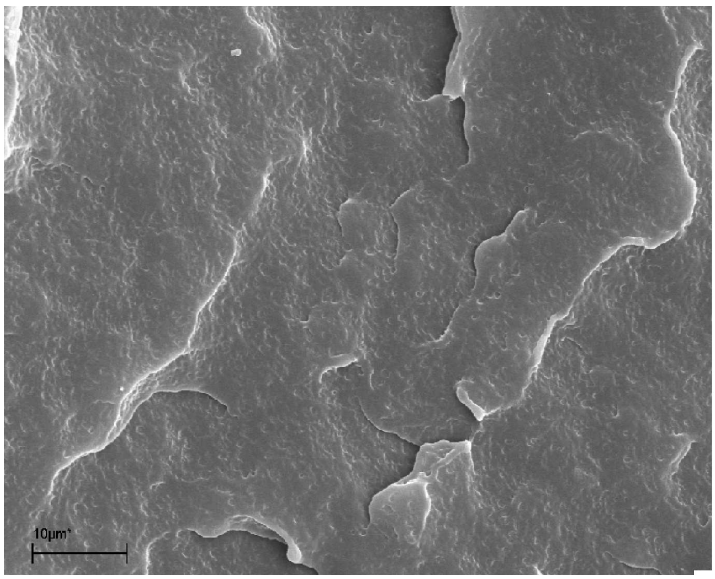

Fig. 4. HDPE Hostalen ACP 5831D.

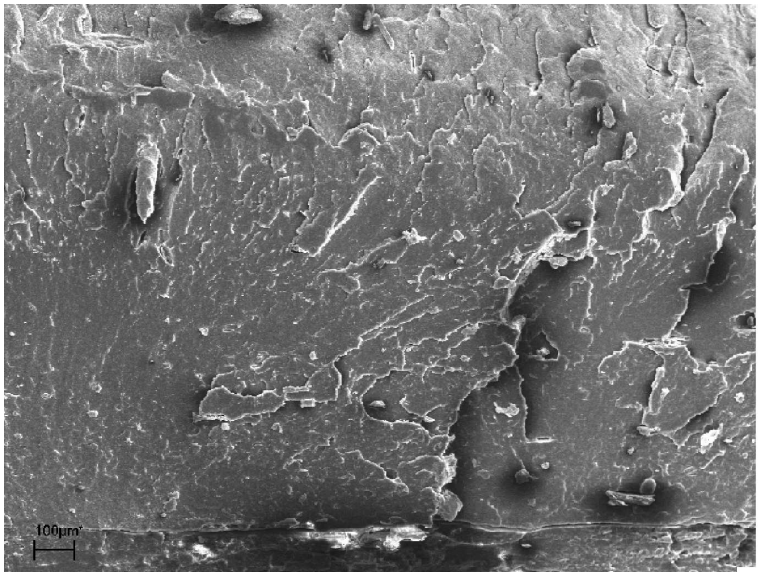

Fig. 5. HDPE/MMT.

The surface morphology observed by scanning electron microscopy (SEM) has shown more regular shapes of the particles of the modified montmorillonite (Figs. 1–3). This effect is also seen in the SEM images of the composites (Figs. 4–7). The SEM image of the unmodified montmorillonite reveals the residues

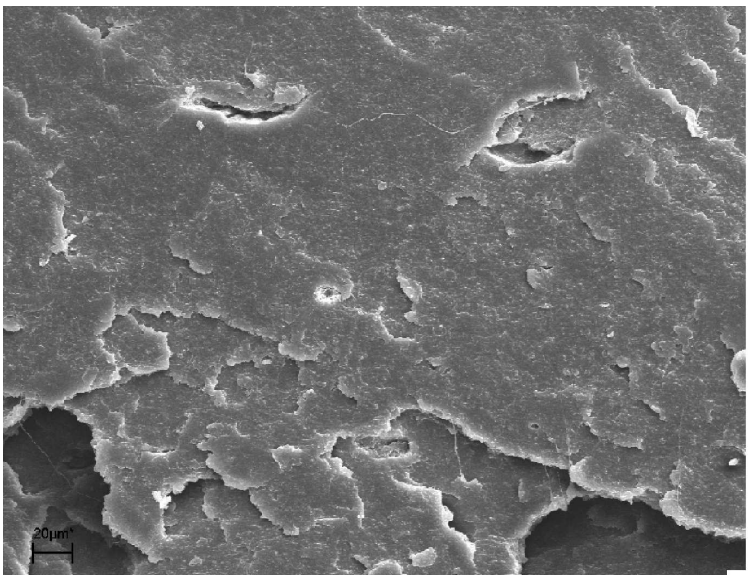

Fig. 6. HDPE/MMT modified with 3-aminopropyltrimethoxysilane.

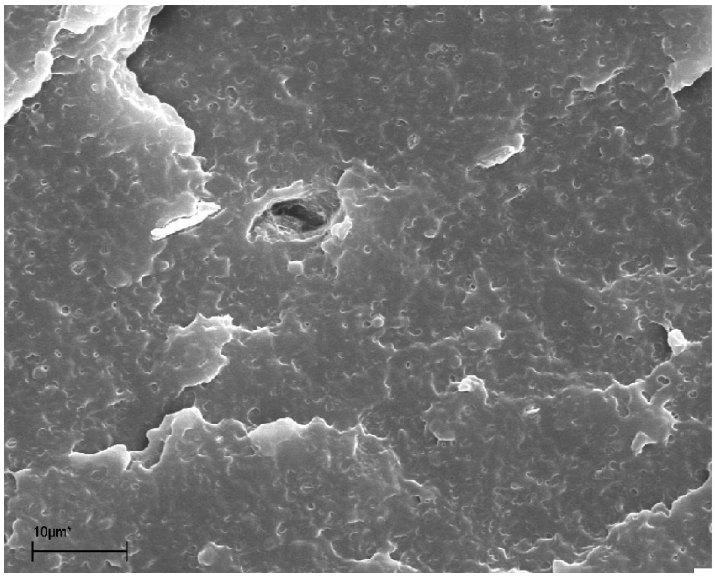

Fig. 7. HDPE/MMT modified with hexadecyltrimethylammonium chloride.

of the filler in the matrix, which is not detected for the composites with modified montmorillonite. The X-ray diffraction (XRD) spectrum of the unmodified montmorillonite (MMT) (Fig. 8) in the angle range from 4 to 20° of the 2θ angle shows a characteristic diffraction peak ($2\theta \approx 7°$) assigned to the (001) plane. On the basis

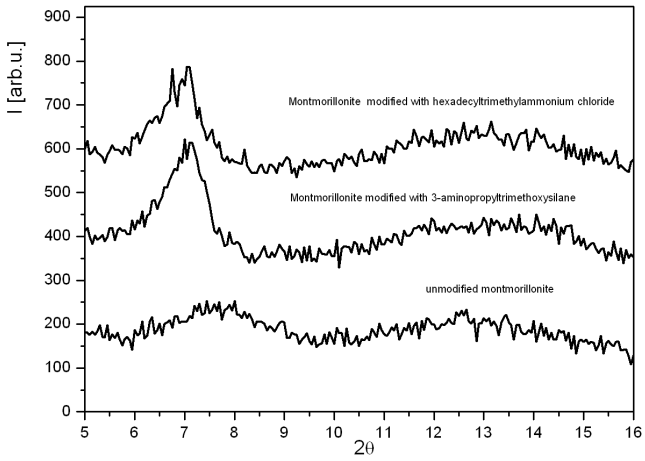

Fig. 8. Diffractograms of the unmodified montmorillonite (bottom plot), montmorillonite modified with 3-aminopropyltrimethoxysilane (middle plot), and montmorillonite modified with hexadecyltrimethylammonium chloride (top plot).

of the 2θ angle at the diffraction maximum, the parameter d_{001} describing the interplanar distance in montmorillonite was calculated to be $d_{001} = 1.15$ nm. Analysis of the position of the diffraction peak (001), occurring in the same range of the 2θ angle for the montmorillonite modified with 3-aminopropyltrimethoxysilane and hexadecyltrimethylammonium chloride has shown a shift of the diffraction maxima towards lower angles, which means an increase in the interplanar distance in montmorillonite. For the two samples with modified montmorillonite the parameter d_{001} was found to be of about 1.25 nm. The diffraction peaks used for determination of this parameter had greater intensity and smaller FWHM relative to those in the spectra of the unmodified montmorillonite. Therefore, the samples with the modified montmorillonite are characterised by greater ordering resulting from the presence of the modifiers in the inter-packet space.

4. Conclusions

The composites obtained with montmorillonite modified with 3 volume fractions of 3-aminopropyltrimethoxysilane or hexadecyltrimethylammonium chloride were characterised by high homogeneity of the filler particles. The positive effect of the filler modification was also noted in improvement of such parameters as the elasticity modulus, tensile stress and tearing stress. The effects of modification of the fillers were tested by the XRD measurements for the unmodified and modified montmorillonite and by microstructure SEM observations.

In general, the results have shown that the composites obtained HDPE/MMT, HDPE/MMT modified with 3-aminopropyltrimetoxysilane, and HDPE/MMT modified with hexadecyltrimethylammonium chloride are characterised by better mechanical properties than the initial pure polymer HDPE.

Acknowledgments

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