



## Structure and antibacterial properties of polyethylene/organo-vermiculite composites



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### ABSTRACT

Vermiculite (VER) was modified by cation exchange with hexadecyltrimethylammonium (HDTMA<sup>+</sup>) bromide in three concentrations and used as organo-VER clay mineral nanofillers (denoted as HDTMA<sup>+</sup>1-VER, HDTMA<sup>+</sup>2-VER, and HDTMA<sup>+</sup>3-VER) in polyethylene (PE). PE/organo-VER composites were prepared via a melt compounding technique and pressed into thin plates. The organo-VER nanofillers and composite plates were characterized by X-ray diffraction analysis which in combination with molecular modeling confirmed the intercalation of HDTMA<sup>+</sup> molecules. It was found that alkyl tails of HDTMA<sup>+</sup> molecules create a non-polar, water-free area which may help the PE chains to enter the VER interlayer space. The nanocomposite structure was confirmed for PE/HDTMA<sup>+</sup>3-VER. PE/organo-VER composites were also studied by scanning electron microscopy and light microscopy and by creep testing. Antibacterial activity of powder organo-VER nanofillers was tested on Gram-positive (G<sup>+</sup>) (*Staphylococcus aureus*, *Enterococcus faecalis*) and Gram-negative (G<sup>-</sup>) (*Escherichia coli*) bacterial strains. The most sensitive G<sup>+</sup> bacteria responded by stopping their bacterial growth after 24 h with a minimum inhibitory concentration (MIC) 0.014% (w/v) at all samples. Growth of G<sup>-</sup> bacteria was inhibited after 24 h with higher MIC value 0.041–10% (w/v) in relation to the content of HDTMA<sup>+</sup> in samples. The surfaces of PE/organo-VER composites are very active against G<sup>+</sup> bacterial strain *E. faecalis*. The number of bacterial colonies forming units (cfu) on surfaces of samples was reduced by approximately several orders. The number of bacterial colonies after 48 h was 0 cfu on the surface of PE/HDTMA<sup>+</sup>3-VER nanocomposite.

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### 1. Introduction

Clay mineral/polymer nanocomposites (CPN) are highly studied materials in recent decades. Studies presented by many authors confirmed that clay minerals as fillers in polymer matrix can improve mechanical properties and thermal stability [1–11], gas permeability resistance [11–13] and suppression of flammability [4,14]. Clay minerals modified with organic or inorganic compounds can also supply antibacterial properties to the prepared CPN [15–19].

Formation of the CPN is influenced by the nature of the clay mineral, polymer used as a matrix and method of preparation. CPN could be prepared by solution blending, melt intercalation and in situ polymerization procedures. Three types of composite structures can arise during interaction of clay mineral nanofillers and polymer: (1) Microcomposite (phases remained separated), (2) Nanocomposite intercalated (nanofiller is intercalated with polymer) and (3) Nanocomposite exfoliated (nanofiller is exfoliated in polymer) [20].

The clay mineral structure is hydrophilic and has to be modified to be compatible with a polymer matrix. The change into hydrophobic form is made by an exchange of cations by organic compounds, often quaternary ammonium salts or alkyl-amines [3,4,7,9–11,13–15,21–24]. The organic species as a host also expand the interlayer space and facilitate intercalation of polymeric

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chains, and then exfoliation of clay in a polymer matrix [21].

Quaternary ammonium compounds bearing long alkyl chains, such as hexadecyltrimethylammonium halides, have been frequently used for modification of layered silicates, especially montmorillonite [3,4,15,24–26] and less often vermiculite [7,9–11] for their further use as an additive to polymer.

Vermiculites are 2:1 layered silicates, with layers built up of one octahedral sheet sandwiched between two tetrahedral sheets. The central cations of octahedra (ideally  $\text{Al}^{3+}$ ) and tetrahedra (ideally  $\text{Si}^{4+}$ ) can be substituted by cations with lower valency. These substitutions resulted in a negative layer charge on silicate layers. Space between layers (interlayer space) is occupied by exchangeable hydrated cations, such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  etc., compensating the negative layer charge [27].

The magnitude of layer charge on vermiculite layers is important for the amount of intercalated organic molecules and for their arrangement in the interlayer space [28–30]. Types of cationic surfactant, length of alkyl chain and surfactant concentration are also important factors influencing the adsorbed amount and arrangement of alkyl chains in the interlayer space [30–41].

In the present work, vermiculite was modified with a long alkyl chain of surfactant and used as organo-vermiculite nanofiller to polyethylene. The nanofillers and composite materials were characterized by the X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), light microscopy (LM) and molecular simulations. Creep tests of composites were also performed to analyse the reinforcing effect of the fillers. The antibacterial activity of powder nanofillers was tested on Gram-positive ( $G^+$ ) (*Staphylococcus aureus*, *Enterococcus faecalis*) and Gram-negative ( $G^-$ ) (*Escherichia coli*) bacterial strains. Survival of the  $G^+$  bacteria *E. faecalis* was tested on the surface of plates pressed from polyethylene containing the organo-vermiculite nanofiller.

## 2. Materials and methods

### 2.1. Materials

Vermiculite (VER) from Santa Luzia, Brazil (Grena, a.s., Czech Republic) was milled in a planetary ball mill (Retsch PM4) for 20 min, and a sieved fraction  $<40 \mu\text{m}$  was utilized for the experiment. The cation exchange capacity (CEC) of VER was  $122 \text{ cmol}(+)/\text{kg}$  determined by cation exchange with  $\text{Cd}^{2+}$  and analysis of exchange cations using an atomic absorption spectrometry.

Hexadecyltrimethylammonium bromide,  $\text{C}_{19}\text{H}_{42}\text{NBr}$  (HDTMA<sup>+</sup>-Br) (Sigma Aldrich, Co.) was used for organophilization of VER.

Polyethylene (PE) was prepared as a mixture of three low-density polyethylenes (LDPE): 33 wt.% of Bralen VA 20–60 powder, 42 wt.% of Bralen VA 20–60 granulated, and 25 wt.% of Bralen FB2-17 powder (Slovnaft, Co., Slovak Republic).

### 2.2. Preparation of organo-vermiculite

Three concentrations of HDTMA<sup>+</sup>-Br were calculated on the basis of CEC values of VER as the multiples:  $0.375 \times \text{CEC}$ ,  $0.75 \times \text{CEC}$ ,  $1.5 \times \text{CEC}$ . Dispersions of VER with HDTMA<sup>+</sup>-Br (40 g of VER and 400 ml of HDTMA<sup>+</sup>-Br solution) were mixed for 6 h at  $70^\circ\text{C}$ , then centrifuged, washed with demineralized water until bromide ions were not present in the liquid residue ( $\text{AgNO}_3$  test was used) and dried at  $70^\circ\text{C}$  [42]. Dried samples were crushed in the mortar and sieved to the fraction under  $40 \mu\text{m}$ . According to used concentrations  $0.375 \times \text{CEC}$ ,  $0.75 \times \text{CEC}$ , and  $1.5 \times \text{CEC}$  the samples were denoted as HDTMA<sup>+</sup>1-VER, HDTMA<sup>+</sup>2-VER and HDTMA<sup>+</sup>3-VER, respectively.

### 2.3. Preparation of PE/organo-vermiculite

PE was mixed with organo-VER fillers (HDTMA<sup>+</sup>1-VER, HDTMA<sup>+</sup>2-VER, HDTMA<sup>+</sup>3-VER). The mixture was slowly poured into the Brabender kneading chamber (Brabender GmbH & Co. KG, type 815607) and heated to  $160^\circ\text{C}$ . Kneading of the mixture was carried out for a total of 10 min in two velocity intervals, first for 2 min at 10 rpm and the next for 8 min at 50 rpm. The mass was removed from the kneading chamber and composite plates of size  $125 \times 125 \text{ mm}$  and a thickness of 1 mm were pressed at  $160^\circ\text{C}$  from the stiff matter [43,44]. Resulting samples of PE/organo-VER composites (denoted as PE/HDTMA<sup>+</sup>1-VER, PE/HDTMA<sup>+</sup>2-VER, PE/HDTMA<sup>+</sup>3-VER) contained ~7 wt.% of the filler. PE matrix filled with pristine VER (denoted as PE/VER) was also prepared for comparison with PE/organo-VER samples.

### 2.4. Analytical methods and equipment

Atomic absorption spectrometer UNICAM 969 with flame atomization was used to determine the cation exchanged  $\text{Cd}^{2+}$  ions.

Structure characteristics of powder samples and composite thin plates were studied by the X-ray diffraction (XRD) patterns measured on the X-ray diffractometer RIGAKU Ultima IV (reflection mode, Bragg–Brentano arrangement,  $\text{CuK}\alpha$  radiation) under ambient temperature, and operating conditions 40 kV, 40 mA. Samples were scanned in the range of angle  $1.5^\circ$ – $50^\circ 2\theta$  with a step size of  $0.05^\circ$ .

Distribution of VER fillers in PE was evaluated using light microscopy. Images were obtained by an Olympus BX51 with camera UC30 at transition mode and a bright field of polarized light.

Structure of the samples was assessed by scanning electron microscope TESCAN VEGA/LMU. The smooth fracture of plates in liquid nitrogen was created before observation. The microscope was operated in high vacuum mode at acceleration voltage 10 kV and all samples were coated with an Au/Pt layer.

### 2.5. Molecular modeling

Space arrangement of the VER interlayer content was studied using an Accelrys Materials Studio modeling environment. A Forcite module was used for the geometry optimization of the prepared models. A Reflex module allowing the simulation of X-ray powder diffraction under the same conditions as in the experimental part of this work was used to determine the interlayer distances in all models.

### 2.6. Creep testing

The reinforcing effect of organo-VER nanofillers dispersed in a PE matrix was determined by a creep test performed on a home-made laboratory device producing pure tension. It represents measurement under applied constant tensile stress when the resulting strain detected in a length of the test specimen is measured as a function of elapsed creep time. For this purpose the composite materials were formed into the shape of plates by the compression moulding method at  $175^\circ\text{C}$ . Final test specimens were then punched out having dimension according to standard EN ISO 3167. The cross-section of specimens was approximately  $7 \text{ mm}^2$ , width was 10 mm and working length was 100 mm. Tests were conducted at a constant temperature of  $25^\circ\text{C}$  and at constant applied tensile stress of approx. 2.3 MPa (precise value given by the actual cross-section of the specimen).

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