

# Preparation of (ethylene-methacrylic acid) copolymer/vermiculite composites

P. ZADRAPA, J. ZYKOVA, E. TRIPSKA, J. MALAC, L. KOVAROVA,  
 Department of Polymer Engineering, Faculty of Technology  
 Tomas Bata University in Zlín  
 Nám. T.G. Masaryka 275, 762 72 Zlín  
 CZECH REPUBLIC  
 zadrapa@ft.utb.cz

*Abstract:* - In this research, the effect of modified filler on mechanical properties of polymer/clay composite was studied. Firstly, the filler – vermiculite was modified by two methods. Former one was done by hexadecyltrimethylammonium bromide, the latter by maleic anhydride. The level of clay modification was determined by X-ray diffraction and Fourier transform infrared spectroscopy. Further, the fillers were compounded with the polymer matrix Surlyn 8920. The level of filler dispersion in polymer was studied by X-ray diffraction and their influence on physical properties was found by mechanical test. Their results showed that tensile modulus increased, while the tensile stress decreased for treated filler compounds.

*Key-Words:* - Clay, Vermiculite, Surlyn, Intercalation, Maleic anhydride, Hexadecyltrimethylammonium bromide

## 1 Introduction

During last two decades, scientists not only in polymer area were and still are focused on the study of nanocomposite materials. There are many works interested on carbon fibers or natural inorganic materials [1-4]. Especially these inorganic materials are attractive because they can be found in the nature with high availability. Many of them could be used as filler or even nanofiller. Most of these fillers belong to the silicate groups [5]. Minerals are hydrophilic; however majority of commercially important polymers are hydrophobic. It causes several problems with compatibility and miscibility between these two components. This situation could be solved by modification of filler to improve mentioned properties [5, 6]. Moreover, in the case of layered silicates, their structure could be changed. It is created by tetrahedral and octahedral layers in dependence on mineral type. Smectites, one part of silicates, with their 2:1 layered structure are the group of minerals, where modification could lead to intercalation or even to exfoliation of filler in polymer matrix [5, 6]. The most known representative is montmorillonite. There are several papers dealing with its modification and also with preparation of composite or nanocomposite with pure and modified montmorillonite [7, 8]. The improvement of the distance between layers could be done because of presence of exchangeable ions (e.g.  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ) contained inside the mineral interlayer. These ions are replaced by bigger organic one and in addition they causes rising of compatibility between polymer and filler [6]. Vermiculite, like montmorillonite has 2:1 layered

structure. It is more abundant, has a larger cation exchange capacity and until now is not as well studied as montmorillonite [9-11]. This could be caused by higher level of impurities and inhomogeneous inside its structure.

The present work deals with the modification of vermiculite and consequently its effect on the resulting properties of polymer/vermiculite composites.

## 2 Experimental part

### 2.1 Materials

The polymeric material used for this study was copolymer of ethylene and methacrylic acid, which methacrylic acid groups are partially neutralized by  $\text{Na}^+$  ions, commercially called Surlyn 8920, obtained from DuPont. As filler was used Vermiculite K-0 (particle size approximately 0.5 mm) purchased from MINKO-Václav Zedník. As a modification agent was used hexadecyltrimethylammonium bromide (HDTMA) purchased from Sigma Aldrich and maleic anhydride.

### 2.2 Preparation of modified vermiculite

At the beginning, natural vermiculite was pulverized on the powder (325 mesh). After that two methods for its modification were tested. The first was as follows: 35 g of the vermiculite powder was stirred in 350 ml of 4 M NaCl at room temperature for 48 hours. The slurry was washed by distilled water until the absence of Cl ions was confirmed ( $\text{AgNO}_3$  test). This procedure was done twice to remove more  $\text{Mg}^{2+}$  ions contained between vermiculite layers. The resulting slurry was dried in

microwave oven at 70 °C for 24 hours and subsequently pulverized. The gained Na<sup>+</sup> vermiculite (30 g) was introduced into 240 ml of 0.25 M aqueous solution of HDTMA. The slurry was stirred and heated to 70 °C for 6 hours. After that time, it was filtered until no Br<sup>-</sup> ions were confirmed by AgNO<sub>3</sub> test. Intercalated vermiculite was dried in vacuum oven at 65 °C for 24 hours. The filler is called OVMT or HDTMA vermiculite in the text.

For the second method, 25 g of nature vermiculite was stirred in 300 ml of 1 M HCl for 6 hours. The slurry was washed until pH of filtrate was not 7. HCl modified vermiculite were dried at 80 °C for 12 hours. Consequently, 16 g of this powder was mixed together with maleic anhydride in proportion to 1 : 1. Moreover, 36 ml of acetic acid was added into the mixture and stirred at room temperature for 12 hours. Then, the suspension was centrifuged and filtrated. Maleic anhydride modified vermiculite (MaVMT) was dried at 70 °C for 24 hours. Both modified vermiculite were consequently pulverized on particles with maximum size 40 µm.

### 2.3 Preparation of polymer/filler composite

The modified vermiculite (see 2.2) and natural vermiculite were mixed with the polymer. Polymer/filler composite was prepared by melt compounding on Brabender PlastiCorder PL2000, mixing chamber. The speed of compounding was 30 rpm and the duration was 10 minutes. The temperature of the chamber was 200 °C. Amount of filler in matrix was calculated to be a 5 wt%.

### 2.4 Measurements

X-Ray diffraction (XRD) analysis was carried out with a PANalytical XPert PRO Diffractometer with Cu K $\alpha$  radiation (wavelength  $\lambda = 0.154$  nm) in reflection mode to investigate the interlayer distance of clay in both powder and composites form. The analysis was performed from 2 to 10 2 $\theta$ . The interlayer distance was calculated using Bragg's laws.

Infrared spectra were collected using Fourier transform infrared (FTIR) spectrometer AVATAR 320, Nicolet. Data were collected using 64 scans per. The range of measurement was from 4000 cm<sup>-1</sup> to 550 cm<sup>-1</sup>.

Tensile test were performed on Instron 8871 according to standard ČSN EN ISO 527-2. Six specimens of the type 5A were cut from the moulded sheets in thickness of 2 mm. The crosshead speed was 1 mm/min to find modulus and after that it grew up to 50 mm/min.

Hardness was tested according to standard ČSN EN ISO 868. Three specimens 2 mm in thickness were cut from moulded sheets to achieve total thickness 6 mm.

## 3 Results and discussion

### 3.1 Filler characterization

X-ray diffraction and FTIR analysis were done to evaluate the changes in the vermiculite structure after the modification.

#### 3.1.1 X-ray diffraction

On the Figure 1, it can be seen X-ray spectrum for natural vermiculite and its modified forms. The bottom curve (Fig. 1a) shows spectrum for unmodified vermiculite. There are visible three peaks with interlayer distance 1.4, 1.2 and 0.98 nm. This variability is caused by various ions inside filler layers and moreover higher content of impurities in natural vermiculite powder. After ion exchange process (Fig. 1b), when the Mg<sup>2+</sup> ions were replaced by Na<sup>+</sup> ions, the first peak around 6.0° disappeared. The peak at 1.22 nm is typical for layers containing Na ions. The second peak at 1.14 nm is supposed to be for Mg<sup>2+</sup> ions inside the layers and the last one is for the impurities. These ions were consequently exchanged by HDTMA (Fig. 1d). As can be seen in this curve, there are two peaks. The former one is for clay with partially exchanged ion inside layers, the later again shows the impurities or the inhomogeneity in vermiculite structure. Nevertheless the interlayer distance was not improved.

Modification of the vermiculite by HCl (see Fig. 1c) caused delamination of the layers; however, there are still some impurities. Following intercalation by maleic anhydride improves interlayer distance to 1.42 nm (Fig. 1e).

#### 3.1.2 FTIR spectroscopy

FTIR spectroscopy shows changes in the structure after modification. The curve b) on the figure 2 is for natural vermiculite. The peak from 600 to 800 cm<sup>-1</sup> is for quartz, the next one around 1000 cm<sup>-1</sup> is for SiO bonds. After modification, can be seen, that absorbance of the SiO peak is changed. After modification of HCl, the SiO bonds are disordered and the peak absorbance drops (Fig. 2c). After the treating by maleic anhydride, there is peak around 1500 cm<sup>-1</sup>. On the other hand, intercalation by HDTMA causes increasing of absorbance of SiO bonds (Fig. 2a). Two peaks from 2700 to 3000 cm<sup>-1</sup> are significant for the modifying agent which is inserted to filler structure.

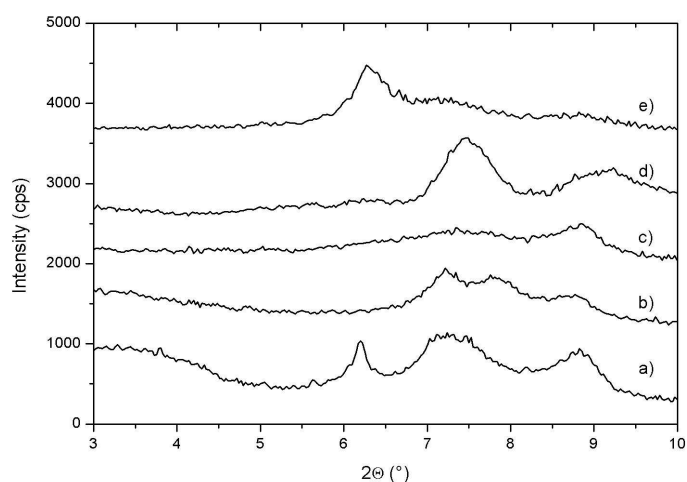


Fig. 1: XRD spectra of vermiculite a) pristine, b) Na ions modified, c) HCl modified, d) HDTMA intercalated and e) maleic anhydride treated.

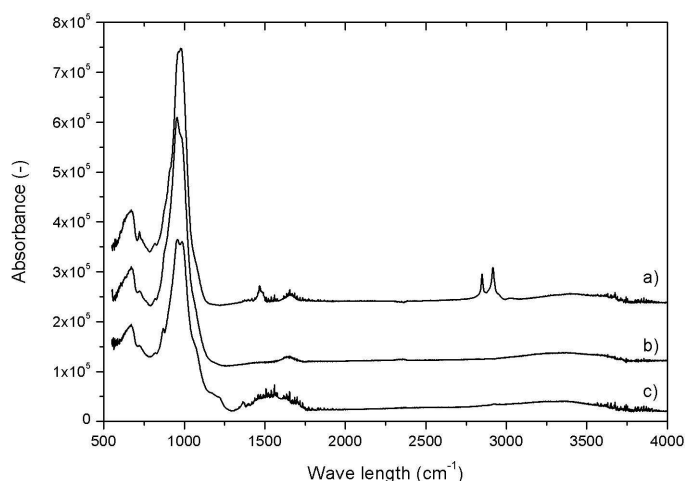


Fig. 2: FTIR spectra of vermiculite a) intercalated by HDTMA, b) natural and c) modified by maleic anhydride.

## 3.2 Composite characterization

### 3.2.1 X-ray diffraction

Figure 3 shows XRD spectra for polymer-clay composites. All curves has peak around  $8.7^\circ$  which is significant for impurities or irregularities. Both compounds with modified fillers have another two peaks around  $6.0^\circ$  and  $7.25^\circ$  (Fig. 3b and 3c). It means that interlayer distance of filler is 1.5 and 1.2 nm respectively. After compounding polymer with HDTMA modified vermiculite, interlayer partly increases from 1.2 nm to 1.5 nm of filler in compound. Contrary to maleic anhydride intercalated vermiculite, where the interlayer mostly decreased from 1.4 nm to 1.2 nm.

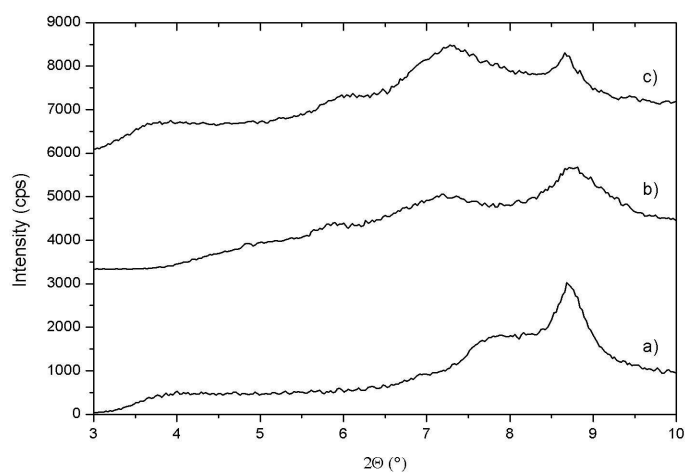


Fig. 3: XRD spectra of composite created from polymer Surlyn 8920 and a) pristine vermiculite, b) vermiculite modified by HDTMA and c) vermiculite intercalated by maleic anhydride.

### 3.2.2 Mechanical properties

Mechanical properties were done to discover the influence of filler and its modification on the properties of polymer – clay composite. Table 1 shows tensile properties and hardness of prepared compounds. As can be seen unfilled Surlyn 8920 has tensile stress at break 27.1 MPa. Natural vermiculite filled compound has similar stress at break as pure matrix. However, after the addition of modified filler, stress at break decreases. Both HDTMA and maleic acid modified vermiculite causes drop of composite stress nearly 12 % in comparison with pure polymer. On the other hand, the modulus rises over 55 % for both intercalated clays, in comparison with unfilled matrix. Addition of natural filler improves the modulus over 35 %. These results confirm the results from X-ray diffraction. The XRD curves for both modified fillers look very similar as well as their tensile properties.

In the table 1 is also shown hardness for all compounds. Pure matrix has hardness 58.5. For all filled matrixes, with natural and modified vermiculite, hardness grows over 13 % in comparison to unfilled polymer.

Tab. 1. Mechanical properties

| Comp. Surlyn/<br>Filler | Tensile stress<br>[MPa] | Tensile modulus<br>[MPa] | Hardness<br>[Shore D] |
|-------------------------|-------------------------|--------------------------|-----------------------|
| Pure                    | $27.1 \pm 0.2$          | $144 \pm 4.2$            | $58.5 \pm 0.4$        |
| VMT                     | $26.9 \pm 0.4$          | $195 \pm 5.1$            | $62.2 \pm 0.1$        |
| MA-VMT                  | $23.8 \pm 0.3$          | $227 \pm 4.8$            | $63.1 \pm 0.2$        |
| HDTMA-VMT               | $24.0 \pm 0.6$          | $222 \pm 7.1$            | $62.2 \pm 0.4$        |

## 4 Conclusion

This work was focused on the modification of vermiculite by two methods and on the effect this way prepared fillers on mechanical properties of polymer composite. X-ray diffraction analysis shows, that original vermiculite structure was not fully changed on the intercalation one. The reason could be higher content of impurities or structure irregularities contained in this type of vermiculite. The interlayer distance increased to 1.42 nm for maleic anhydride treated filler from basic 1.2 nm.

Natural vermiculite, as well as modified ones were compounded with polymer matrix. The level of filler dispersion in polymer was investigated with XRD. The interlayer distance was found to be 1.5, 1.2 and 1 nm for modified fillers, where the last value is for the impurities. For all compounds were measured mechanical properties. Tensile modulus was improved over 50 % in comparison to pure matrix, however tensile stress drop about 13 % for both compounds with modified fillers.

*Acknowledgement:*- This research has been supported by Ministry of Education, Youth and Sport of the Czech Republic (project MSM7088352101).

### References:

- [1] D. G. Lopez, M. M. Jubinski, M. J. Keith, M. Jason, A. J. King, I. Miskioglu, Effects of carbon fillers on tensile and flexural properties in polypropylene-based resins. *Journal of Applied Polymer Science*, Vol. 118, 2010, pp. 1620-1633.
- [2] R. Haggemueller, H. H. Gommans, A. G. Rinzler, J. E. Fischer, K. I. Winey, Aligned single-wall carbon nanotubes in composites by melt processing methods. *Chemical Physics Letters*, Vol. 330, 2000, pp. 219-225.
- [3] M. W. Kim, S. H. Lee, J. R. Youn, Effects of filler size and content on shrinkage and gloss of injection moulded PBT/PET/talc composites. *Polymer Composites*, Vol. 31, 2010, pp. 1020-1027.
- [4] E. Fekete, B. Pukanszky, Surface coverage and its determination: role of acid-base interactions in the surface treatment of mineral fillers. *Journal of Colloid and Interface Science*. Vol. 194, 1997, pp. 269-275.
- [5] G. Wypych, *Handbook of Fillers – A Definitive User's Guide and Databook*, ChemTec Publishing, 2000.
- [6] L. Ultracki, *Clay-Containing Polymeric Nanocomposites*, Rapra Technology Limited, 2004.
- [7] Y. Zhang, Q. Cai, Z. Jiang, K. Gong, Preparation and properties of unsaturated polyester-montmorillonite intercalated hybrid. *Journal of Applied Polymer Science*, Vol. 92, 2004, pp. 2038-2044.
- [8] Q. Ding, B. Liu, Q. Zhang, Q. He, B. Hu, J. Shen, Synthesis and characterization of polyurethane/montmorillonite nanocomposites by in situ polymerization. *Polymer International*, Vol. 55, 2006, pp. 500-504.
- [9] M. A. Osman, Organo-vermiculites: synthesis, structure and properties. Platelike nanoparticles with high aspect ratio. *Journal of Material Chemistry*, Vol. 16, 2006, pp. 3007-3013.
- [10] S. C. Tjong, Y. Z. Meng, A. S Hay, Novel preparation and properties of polypropylene-vermiculite nanocomposites. *Chemistry of Materials*, Vol. 14, 2002, pp. 44-51.
- [11] D. Plachá, G. S. Martynková, M. H. Rummeli, Preparation of organovermiculites using HDTMA: Structure and sorptive properties using naphthalene. *Journal of Colloid and Interface Science*, Vol. 327, 2008, pp. 341-347.