

MONTMORILLONITE AND VERMICULITE MODIFIED BY N-VINYLCAPROLACTAM AND POLY(N-VINYLCAPROLACTAM) PREPARATION AND CHARACTERIZATION

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Abstract

The N-vinylcaprolactam, NVCL, is a monomer with amphiphilic character. Poly(N-vinylcaprolactam), PNVCL, is a non-ionic, water soluble polymer from the poly N-vinylamide group, which has potential use in biological applications. Vermiculite and montmorillonite are naturally occurring clay minerals widely used as nanofillers for polymers. In this study, vermiculite and montmorillonite were modified by NVCL and PNVCL for subsequent use as nanofiller into the poly(N-vinylcaprolactam). Amount of monomer or polymer added to the clay mineral was based on cation exchange capacity (CEC) of the each clay. The process of modification was held in ethanol. From the Fourier transform infrared spectroscopy (FTIR) spectra can be assumed that clay minerals are successfully modified by NVCL and PNVCL. X-ray powder diffraction (XRD) patterns show successful intercalation of clay, because the basal diffraction of each clay mineral showed the shift from 1.256 nm to 1.502 nm in case of montmorillonite with NVCL and from 1.225 nm to 1.492 nm in vermiculite sample intercalated by the same compound. The samples were characterized by FTIR, XRD and scanning electron microscopy (SEM).

Keywords: Clay minerals, N-vinylcaprolactam, Poly(N-vinylcaprolactam), Intercalation

1. INTRODUCTION

N-vinylcaprolactam, NVCL, is a monomer with amphiphilic character. This monomer possesses hydrophilic carboxylic group and made lactam ring where the amide group is connected to the hydrophobic vinyl group. Poly (N-vinylcaprolactam), PNVCL, is a polymer with hydrophilic carboxylic and cyclic amide groups and hydrophobic carbon-carbon chain. PNVCL is non toxic polymer which makes it ideal for use in medicine and environmental applications [1]. Utilization of clays is very in demand, mainly in nanocomposites. Natural clay particles have hydrophilic property [2], high adsorption capacity, specific surface area, swelling capacity, solubility and nontoxicity for human [3]. Polymer nanocomposites containing clay minerals are very used. For good dispersion of clay mineral into the polymer matrix is useful to change the hydrophilic character to organophilic, which improve dispersion of clay mineral in polymer matrix. The clay minerals are successfully intercalated by organic compounds (e.g.: octadecylamine [4], n-butylammonium chloride [5], dodecyltrimethylammonium bromide [5], dioctadecyldimethylammonium bromide [5]). These organo-modified clays are used as filler for different polymers where improve mechanical and thermal properties [6,7]. Intercalation of clay minerals by the polymer or monomer which is used as precursor for polymerization decrease the number of compound in final polymer which is demand for application e.g: medicine, environment. The aim of this study was preparation of clay minerals intercalated by organic compounds for further usage as filler for polymer composites.

2. MATERIALS AND METHODS

2.1 Materials

Montmorillonite (Mmt) from Ivančice deposit (Czech Republic) and Vermiculite (Ver) from Santa Luzia deposit (Brasil) were obtained from Grena a.s., Czech Republic. Both of the samples were milled in vibrating mill and sieved to obtain the fraction smaller than 40 μm for the experiment. The cation exchange capacity (CEC) was 105 meq/100g for montmorillonite and 113 meq/100g for vermiculite. Then was prepared monoionic form by cation exchange reaction with 1 mol.dm⁻³ sodium chloride aqueous solution (samples were marked as Na_Mmt and Na_Ver). N-vinylcaprolactam was obtained from Sigma Aldrich and was used also as precursor for preparation of poly(N-vinylcaprolactam) by US patent no.2.335.454 [8].

2.2 Sample preparation

Clay mineral was first mixed with ethanol for 2 h at 50°C. After that was cooled to room temperature without mixing. N-vinylcaprolactam at the amount corresponding to approximately 3 X CEC of each clay was added and poly(N-vinylcaprolactam), where was added the same amount as in the case of NVCL, were dissolved in ethanol before addition to the solution containing clay minerals. The solution with organics was poured into constant stirring mixture of clay mineral. This solution was mixed overnight at laboratory temperature. Finally, the mixture was centrifuged and the product was dried at 30 °C. The samples were marked as Mmt_1, Ver_1 for samples of clay minerals with N-vinylcaprolactam and Mmt_2, Ver_2 for samples with poly(N-vinylcaprolactam).

2.3 Methods

The X-ray powder diffraction (XRD) patterns were measured on X-ray diffractometer Rigaku Ultima IV (reflection mode, Bragg-Brentano arrangement, CuK α radiation) in ambient atmosphere under constant conditions (40 kV, 40 mA). The micrographs of samples were performed by Scanning electron microscopy (SEM) on PHILIPS XL-30 equipped with energy dispersive spectrometer EDAX. The samples for SEM were coated by gold, because the clay minerals are not conductive. The infrared spectra (FTIR) were measured by single reflection ATR technique with a diamond crystal on infrared spectrometer with Fourier transformation Nicolet 6700 FT-IR (Thermo Nicolet, USA). Mid-FTIR spectra were recorded in the range from 400-4000 cm⁻¹, with resolution of 4 cm⁻¹ and 32 scans.

3. RESULTS AND DISCUSSION

3.1 XRD characterization of modified clays

The XRD pattern of Na_Mmt (Fig. 1a) show basal 001 reflection with value of interlayer distance $d = 1.256$ nm which is characteristic for Na-form of Mmt. The interlayer distance increased to $d = 1.502$ nm in Mmt_1 (Fig. 1b) and to $d = 1.485$ nm in Mmt_2 (Fig. 1c). This expansion of interlayer distance signifies intercalation of NVCL and PNVCL in Mmt.

The XRD pattern of Na_Ver (Fig. 2a) shows basal 002 reflections with values of interlayer distance $d = 1.225$ and $d = 1.131$ nm which was ascribed to the hydrate stage with one water layer [9]. The interlayer distance increased to $d = 1.492$ nm and $d = 1.291$ nm in Ver_1 (Fig. 2b) and $d = 1.480$ nm, $d = 1.264$ nm and $d = 1.143$ nm in Ver_2 (Fig. 2c). This expansion of interlayer distance as well as for Mmt signifies intercalation of NVCL and PNVCL in Ver. The XRD pattern of Ver_2 shows that intercalation was not fully and the original structure of Na_Ver was partially preserved.

Reflections of pure NVCL and PNVCL were not present on XRD patterns of samples Mmt and Ver (patterns are not shown) means that NVCL or PNVCL are not present on the surface of Mmt or Ver. Nevertheless, intensity of pure PNVCL is very low so its reflections may be overlapped by reflections of Mmt or Ver.

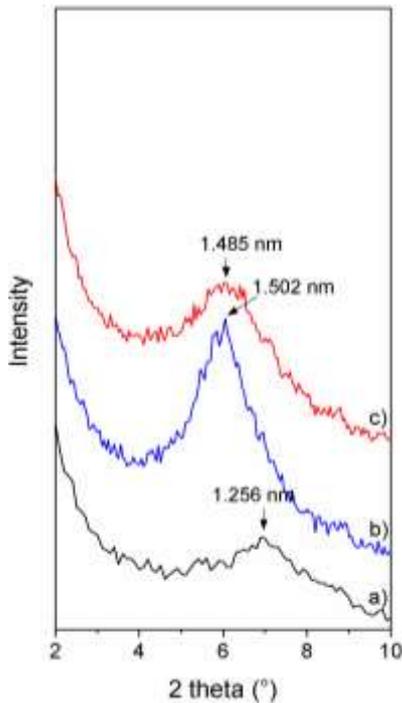


Fig. 1.: XRD pattern of sample Na_Mmt (a), Mmt_1 (b) and Mmt_2 (c)

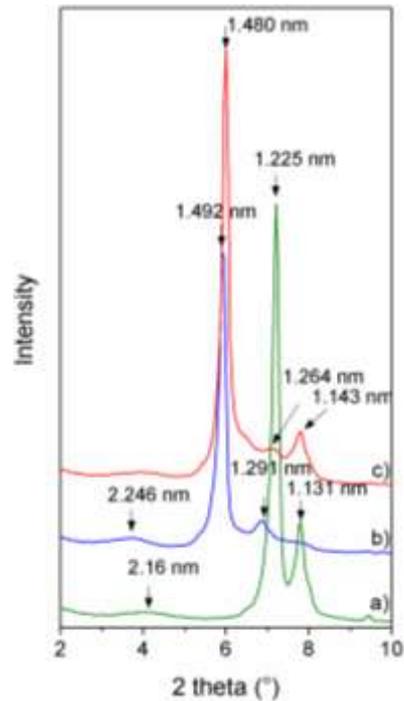


Fig. 2.: XRD pattern of sample Na_Ver (a), Ver_1 (b) and Ver_2 (c)

3.2 FTIR analysis of modified clay minerals

Fig. 3. shows the FTIR spectra of montmorillonite with NVCL and PNVC, respectively. The spectra of pure Na-Mmt (Fig.3c) exhibits bands at 3692 cm⁻¹ which is due to presence of kaolinite; 3621 cm⁻¹ and 3412 cm⁻¹ peaks are attributed to the structural OH groups and H-O-H stretching vibration of water molecule, respectively [10,11]. Moreover, the band at 1639 cm⁻¹ corresponds to OH deformation vibration of water. The band at 1427 cm⁻¹ is due to presence of calcite [12]. The most intense band at 998 cm⁻¹ is related to the Si-O stretching vibrations. The position at 913 cm⁻¹ corresponds to Al-OH deformation vibration [13]. The band at 797 cm⁻¹ is attributed with AlMgOH bending vibration [10]. The Si-O-Al and Si-O-Si deformation vibrations in Na-Mt spectrum were observed at 518 cm⁻¹ and 461 cm⁻¹, respectively [10,11].

Spectra of Mmt modified by NVCL (Fig.3b) shows the bands of Mmt as well as new bands. More precisely, band at 3621 cm⁻¹ corresponds to Al-O-H vibration in Mmt, the band at 2932 cm⁻¹ is attributed to aliphatic C-H stretching vibration [1]. The band at 1626 cm⁻¹ can be attributed to either the H-O-H vibration in Mmt or C=O stretching of NVCL [1]. The broad band at 1441 cm⁻¹ is characteristic for -CH₂- [1], but this band can also arise by overlap of characteristic peak of calcite present in Mmt at 1427 cm⁻¹. The bands at 995 cm⁻¹, 915 cm⁻¹, 795 cm⁻¹ and 513 cm⁻¹ belong to Mmt and are described above. These peaks also do not show significant shifts. On the other hand, band at 453 cm⁻¹, which is also characteristic for Mmt is shifted compared with pure Mmt (461 cm⁻¹).

In the case of Mmt with PNVC (Fig. 3d), the spectra contain characteristic peaks of Mmt and also PNVC. More precisely, band at 3623 cm⁻¹ is characteristic for Mmt, the bands of pure PNVC at 2920 cm⁻¹ and 2853 cm⁻¹ which correspond to aliphatic C-H stretching vibration are shifted to 2928 cm⁻¹ and 2859 cm⁻¹ in the composite with Mmt, respectively [1]. Next band at 1620 cm⁻¹ is due to C=O stretching vibration [1], this band should overlap the characteristic band of Mmt at 1636 cm⁻¹. Very similar case occurs with band at 1445 cm⁻¹ which is attributed to -CH₂- [1] and also can overlap the band of Mmt at 1427 cm⁻¹. The most intensive band of Mmt is shifted to higher wavenumbers to 1004 cm⁻¹. The FTIR spectra also present other characteristic bands of Mmt, but their shifts are not significant: 915 cm⁻¹, 797 cm⁻¹, and 516 cm⁻¹ which were described above. Band at 457 cm⁻¹ of Mmt₂ is shifted from 461 cm⁻¹ in Na_Mmt, this band corresponds to Mmt.

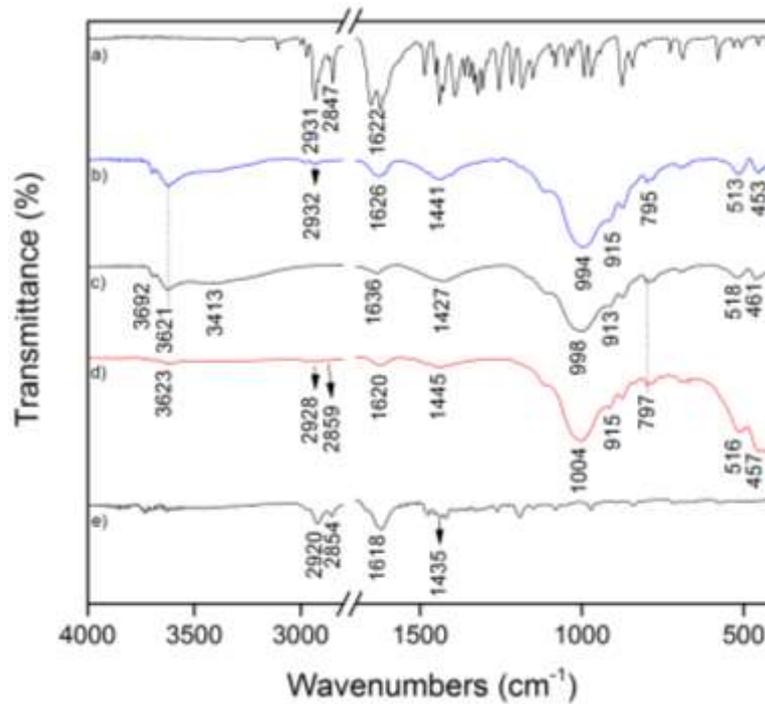


Fig. 3 FTIR spectra of a) NVCL, b) Mmt_1, c) Na_Mmt, d) Mmt_2, e) PNVCL

On the Fig. 4. are illustrated FTIR spectra of Na_Ver, Ver_1, Ver_2, NVCL and PNVCL. The spectra of pure Na_Ver (Fig. 4c) exhibits band at 3670 cm^{-1} which is valence vibration of octahedral hydroxyls of Mg_2AlOH [10]. The broad band at 3396 cm^{-1} belongs to the OH-stretching of water. The position at 1638 cm^{-1} is due to H-O-H bending vibrations of water. The band at 1071 cm^{-1} , which is shoulder of the most intensive band at 957 cm^{-1} , is assigned to stretching vibration of Si-O bonds of amorphous silica [14]. The most intensive band at 957 cm^{-1} is related to the Si-O stretching. The band position at 815 cm^{-1} corresponds to tetrahedral Al-O bending. The weak bands at 746 cm^{-1} and 661 cm^{-1} are related to in plane deformation vibration of Al-O-Si bonds of vermiculite. The band at 450 cm^{-1} involves bending vibration Si-O-Si [10].

The sample Ver_1 (Fig. 4b) exhibits characteristic bands of Ver and also of NVCL. The first band at 3670 cm^{-1} is attributed to Mmt and is describe above. The new band position at 2933 cm^{-1} corresponds to aliphatic C-H stretching vibration and position at 2858 cm^{-1} is also characterized by aliphatic C-H stretching but this band is shifted against pure PNVCL (2847 cm^{-1}). Bands at 1648 cm^{-1} and 1624 cm^{-1} correspond to the C=C double bond and characteristic stretching vibration of carbonyl group, respectively [1]. The most intensive band of Ver is shifted from 957 cm^{-1} to 953 cm^{-1} and also its shoulder at 1071 cm^{-1} is shifted to 1075 cm^{-1} . The bands at 751 cm^{-1} and 658 cm^{-1} are attributed to Na_Mmt which is described above.

In the case of Ver_2 (Fig. 4d) it can be observed the new bands which are attributed with PNVCL and also characteristic bands of Na_Ver. The bands at 3674 cm^{-1} and 3388 cm^{-1} are characteristic for Ver and are shifted from the position of original Na_Ver (3670 cm^{-1} and 3396 cm^{-1} , respectively). The new bands at 2933 cm^{-1} and 2854 cm^{-1} belong to the aliphatic C-H stretching are shifted to 2933 cm^{-1} and 2858 cm^{-1} in Ver_2 sample, respectively [1]. Characteristic carbonyl peak at 1618 cm^{-1} [1] is overlapped by the intensive band of Ver at 1636 cm^{-1} . The most intensive band of Ver is shifted from 957 cm^{-1} to 943 cm^{-1} , but the shoulder of this band at 1070 cm^{-1} is not shifted. The shift is also observed in band at 815 cm^{-1} which is shifted to 820 cm^{-1} in Ver_2. The other bands at 745 cm^{-1} and 662 cm^{-1} , which are characteristic for Ver, do not show significant shifts.

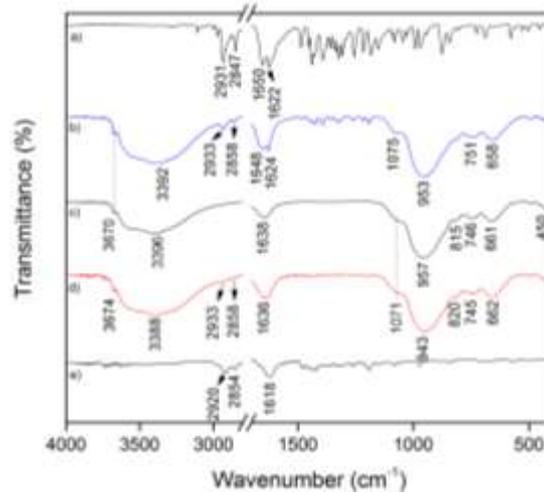


Fig. 4.: FTIR spectra of a) NVCL, b) Ver_1, c) Na_Ver, d) Ver_2, e) PNVCL

3.3 Scanning electron microscopy

Fig. 5. shows the micrographs from SEM analysis of Mmt samples. As can be seen, the surface of Mmt modified by NVCL or PNVCL is smooth compared with pure Na_Mmt, which shows roughened surface. The modified clays show compact, undisturbed surface, which should support the theory that the modifiers are not on the surface of clay but in interlayer space.

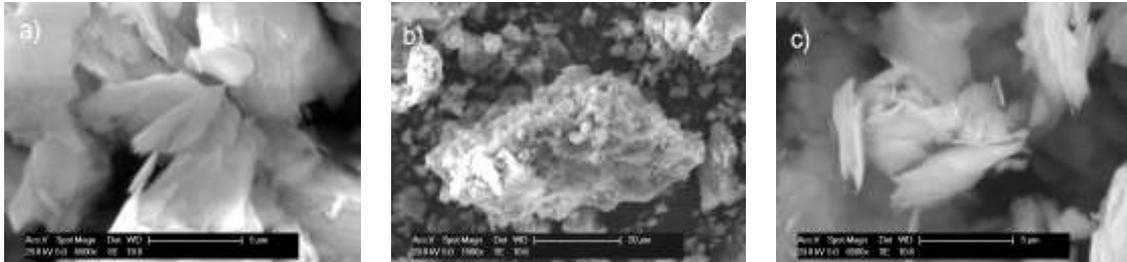


Fig. 5.: SEM micrographs of a) Mmt_1, b) Na_Mmt, c) Mmt_2

More complicated situation occurs in case of Ver (Fig. 6.). Pure vermiculite shows typical layered structure with regular arrangement. But in both cases of organoclays should be observed the roughened surface and cannot be seen the structure and arrangement of Ver. In this case may cause the covering of the Ver by modifiers.

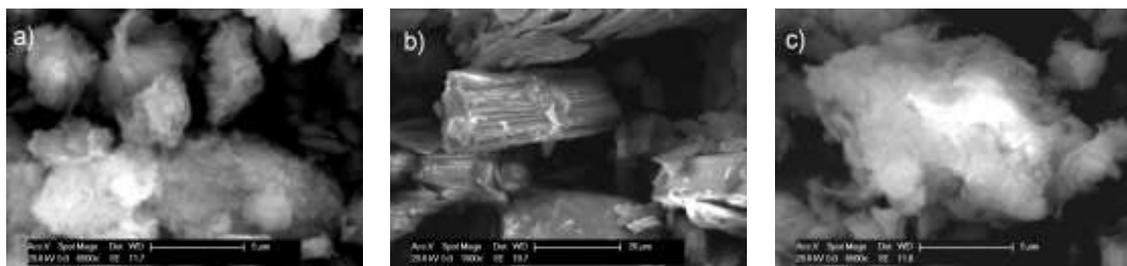


Fig. 6.: SEM micrographs of a) Ver_1, b) Na_Ver, c) Ver_2

CONCLUSION

The intercalated montmorillonite and vermiculite were successfully prepared by direct interaction with two modifiers, N-vinylcaprolactam and poly(N-vinylcaprolactam). The intercalation was mainly confirmed by XRD patterns where were observed shift of basal reflections to the higher degrees 2 theta. The FTIR spectra show the characteristic bands for both clay minerals and modifiers, and also the shifts of several bands which show possibly interaction between modifier and clay mineral. SEM analysis proved that surface of modified vermiculite is more roughened opposite pure vermiculite. On the other hand, montmorillonite shows different behaviour. The modified montmorillonites are smooth and pure clay is roughened.

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