PVC KAOLINITE/UREA HYBRIDS

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Abstract

Poly(vinyl chloride) hybrids have been prepared by melt intercalation method using both natural and modified kaolinite. Kaolinite is the most common two-sheet type clay mineral. It is mined and processed in a number of countries and it serves as an important industrial mineral used in the manufacture of ceramics, medicine, coated paper, food additives and cosmetics. Kaolinite (SAK47) was modified with urea, (SAK47/urea), to expand the interlayer basal spacing. Next the intercalated/exfoliated kaolinite (del. SAK47) after washing of urea from kaolinite-urea intercalate was prepared. The interactions between kaolinite and urea were discussed by FTIR-ATR.

Keywords: PVC, kaolinite, urea, intercalate, composite, nanocomposite

1. INTRODUCTION

Clay minerals form a major part of inorganic matter of soils. Among rich group of clay minerals, kaolinite has an important role because of its high abundance in nature, relatively pure chemical composition, and well characterized crystal structure [1, 2, 3]. It is mined and processed in a number of countries and it serves as an important industrial mineral used in the manufacture of ceramics, medicine, coated paper, food and cosmetics additives, polymer fillers. Kaolinite is the most common layered aluminosilicate type 1:1 with a general chemical formulation Al₂Si₂O₅(OH)₄. Kaolinite dioctahedral structure is composed of tetrahedral sheets and octahedral sheets. For that reason, each layer has two different surfaces parallel to the (001) plane. First one, tetrahedral, is formed from basal oxygen atoms of the tetrahedral (SiO₄) sheet, while second one, octahedral, is formed from surface hydroxyl groups of the octahedral (AlO₆) sheet, Fig. 1 [4]. The resulting layers are held together by hydrogen bonds forming a distinct space between the layers and this causes the cleavage and softness of the mineral, too [1]. Natural clays predominantly exist in a form of small particles (few μm in diameter or less) what predetermines their high specific surface area and high chemical surface activity. These characteristics can be directly related to physico-chemical properties of clays such as swelling, wetting, adsorption, ion-exchange, reactivity, catalytic activity, etc. [4]. A specific feature is the capability of a number of clays to accommodate various molecular species in their interlayer spaces. Following property is often used to modify the clay to enhance the properties of other material.

In worldwide commercial importance, polyvinyl chloride (PVC) is the third most widely produced plastic, after polyethylene and polypropylene [5]. It was first recognized and characterized in 1835 by Henri Victor Regnault and it became commercially significant in Germany prior to World War II. [6]. PVC can be modified by large amounts of modifying agents like plasticizers, fillers (calcium carbonate, kaolinite, and calcined kaolinite), and so on.

In this research, the PVC/kaolinite composite preparation by the melt intercalation method is reported. In addition the influence untreated, urea intercalated kaolinite and intercalated/exfoliated kaolinite with urea
washing by low-temperature on the morphology is investigated. Additionally, infrared spectroscopy was used in order to get insight into interactions between minerals and urea modifier at a molecular level.

2. EXPERIMENTAL

2.1 Materials

Suspension type of polyvinyl chloride (Neralit 601) with K-value 60 obtained from Spolana a. s., Czech Republic was used as the polymer matrix. Four types of filler were studied. Firstly, Kaolinite SAK47 without any additional treatment in as received state. Beside kaolinite as a main component of kaolinite SAK47 it contains quartz and mica as admixtures as was revealed using X-ray diffraction method. According to data available from producer of SAK47 [7] 82 % of particles are smaller than 10 micrometers. For the intercalation of this kaolinite urea was used. For washing of urea from this kaolinite/urea intercalate distilled water was used.

2.2 Kaolinite intercalation with urea

500 g of SAK47 (LB Minerals) was homogenized for 5 min with 330 g of urea (Lachner, p.a. grade) in vibrating mill (VM4). Intercalation of urea into kaolinite interlayer was achieved by 48 h long heating of the homogenized mixture at 95 °C in laboratory oven (Memmert UNB200). Delamination of kaolinite was achieved using 5 h long low-temperature ultrasound washing (SONOREX RK100) of urea with distilled water (for 100 g of intercalate 3 l of distilled water). After washing liquid portion was removed by sedimentation, obtained solid portion was dried at 60 °C (Memmert UNB200).

2.3 PVC hybrids processing

PVC/kaolinite composite samples were prepared via melt intercalation method on the two-roll mill Collin W100T for 20 minutes, using speed 10 rpm and the temperature of the front and behind rolls was 181 and 177 °C. The exact composition of the polymer/clay composites can be seen in Table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>wt. %</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPVC</td>
<td>-</td>
<td>-</td>
<td>Unfilled PVC</td>
</tr>
<tr>
<td>sPVC</td>
<td>SAK47</td>
<td>5</td>
<td>PVC+SAK47-5wt.%</td>
</tr>
<tr>
<td>sPVC</td>
<td>SAK47/Urea</td>
<td>5</td>
<td>PVC+SAK47/urea -5wt.%</td>
</tr>
<tr>
<td>sPVC</td>
<td>Del. SAK47</td>
<td>5</td>
<td>PVC+ del. SAK47-5wt.%</td>
</tr>
</tbody>
</table>

2.4 Methods

X-ray diffraction (XRD) patterns was obtained using PANalytical X’Pert PRO diffracto-meter equipped with CuKα radiation (λ = 0.154 nm) at room temperature. The scans were taken in a 2θ range from 4 to 30 °, with 0.02 ° step size and the counting time of one scan 5 s.

Fourier transform infrared spectrometer (FTIR) Avatar 320 (Nicolet CZ, s.r.o) was employed to get insight into interactions between mineral and urea modifier at a molecular level. ATR method was used with number of scan 64.

The scanning electron microscopy (SEM) photographs of the samples were taken to assess the morphology kaolin/PVC hybrids by a VEGA\LMU. Before examination, samples were coated by thin layer of Ag/Pd.
3. RESULTS AND DISCUSSION

Process of urea intercalation is clearly observable using X-ray powder diffraction method. Significant segments of XRD patterns described process of intercalation as well as delamination are pictured in Fig. 1. Decrease in intensity of d001 basal diffraction of kaolinite with maxima at d= 0.7171 nm is evident after the intercalation with urea. The origination of peak with maxima at d = 1.072 nm is connected with formation of kaolinite-urea complex [8] and is connected with increase in interlayer distance due to the insertion of urea molecules and after the washing this diffraction disappears (see pattern del.SAK47) in Fig. 1. The incompleteness of intercalation as well as delamination of kaolinite structure reveals presence of kaolinite 001 basal diffraction peak (assigned as d001) on the diffraction patterns of samples after intercalation and washing procedure.

![Fig 1 XRD patterns of pure kaolinite and kaolinite/urea intercalate](image1)

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Fig. 2 displays the XRD patterns of unfilled PVC and PVC/kaolinite hybrids samples. In Fig. 2 is observed that in the PVC composite samples containing 5 wt.% of filler, the kaolinite characterization diffraction peak fully disappear but diffraction peak at d = 1.072 nm is still visible. In addition, the kaolinite characterization diffraction peak in PVC/kaolinite, 5 wt. %, after washing procedure also almost disappears. This indicates that urea modified kaolin and intercalated/exfoliated kaolinite is probably more dispersed into the polymer matrix than unmodified kaolinite.

![Fig 2 XRD patterns of PVC and PVC/kaolinite hybrids](image2)

Fig 2 XRD patterns of PVC and PVC/kaolinite hybrids

The FTIR-ATR method was used to study the changes in the kaolinite structure after intercalation. The spectra of unmodified and modified kaolinite are presented in Fig. 3. There are three kinds of hydroxyl groups in unmodified kaolinite SAK47: inner-surface hydroxyl group at 3689 and 3670 cm\(^{-1}\), inner hydroxyl 3619cm\(^{-1}\), and absorbed water hydroxyl with vibration 3651 cm\(^{-1}\) [8, 9]. The vibration 1113, 1026 and 910
cm\(^{-1}\) characterized the Si-O stretching vibrations. O-Al-OH stretching vibrations are connected with vibrations 787, 749 and 665 cm\(^{-1}\). The general features of kaolin intercalated with urea (SAK47/Urea) are practically the same as for SAK47. Nonetheless, there are some differences in the NH stretching region of SAK47/Urea spectrum. Two new bands appear at 3499 and 3385 cm\(^{-1}\). These bands could refer to a small amount of hydrogen bonding of urea to the kaolinite surface through its NH group. Further, in the region 1400–1700 cm\(^{-1}\) the changes in spectra of SAK47/Urea was noticed. The new vibrations at 1663, 1621, 1587 and 1473 cm\(^{-1}\) were observed comparing unmodified SAK47. This may suggest that modification by urea results in some intercalation of the SAK47. After washing with distilled water the intensity of observed vibration connected with urea are dropped, but they are still visible. This fact could indicate that the bonded part of intercalation agent stay in the clay structure after washing.

![FTIR-ATR spectra of natural SAK47 and modified kaolinite/urea intercalates](image)

**Fig 3** FTIR-ATR spectra of natural SAK47 and modified kaolinite/urea intercalates

![SEM images](image)

**Fig 4** SEM images: (a) PVC, (b) PVC/5wt.% SAK47, (c) PVC/5wt.% SAK47/urea, (d) PVC/5wt.% del.SAK47
SEM was used for the dispersion evaluation of the unmodified and modified kaolinite platelets within the PVC matrix. Fig. 4 displays SEM images of (a) unfilled PVC, (b) PVC/SAK47 (c) PVC/SAK47/urea, (d) PVC/del.SAK47 with 5 wt.% of filler.

It can be seen that the PVC filled by 5 wt. % of unmodified kaolinite (SAK47) (fig. 5b) showing inhomogeneity which suggests the poor interfacial adhesion between polymer and filler. On the other hand, PVC filled by 5 wt. % of SAK47 modified by urea has no aggregates hence has the best dispersion of kaolinite to polymer matrix and we can say that the interfacial adhesion between two phases is improved. From the last picture fig. 5d we can see that clay layers are almost delaminated into individual layer structure of kaolin in PVC hence the filler has probably bigger specific surface area and also strong interaction between polymer and filler. It can be concluded that the results are also in accordance whit XRD analysis.

4. CONCLUSION
The effect of the untreated, treated kaolinite by urea and intercalated/exfoliated kaolinite on the morphology was investigated.

Firstly, XRD and FTIR study confirms that modification by urea results in intercalation of the SAK47. FTIR-ATR spectra indicated hydrogen bonding of urea to the kaolinite surface through its NH group. Futhermore the rest of urea was observed in spectra after distilled water washing. This fact could indicate that the bonded part of intercalation agent stay in the clay structure after washing.

From the comparison of results obtained from XRD analysis and SEM it was found that the urea have the significant influence on the PVC composite morphology. In the other words, the filler with urea have the best dispersion within the polymer matrix. In addition, the intercalated/exfoliated kaolinite had also good level of dispersion in polymer as compared to PVC with untreated kaolinite.

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LITERATURE