

PVC Inorganic Hybrids Based on Kaolinite/Urea Intercalates

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Abstract—Polymer/clay hybrids materials receive much attention due to their interesting mechanical and thermal properties. Composites of poly(vinyl chloride) have been prepared by melt intercalation method using commercial type of pure kaolinite (SAK47), urea intercalated kaolinite (SAK47/urea), and intercalated/exfoliated kaolinite after washing of urea from kaolinite-urea (del. SAK47). In the next step the untreated and treated kaolinite was modified by Bis(2-ethylhexyl)phthalate, DEHP, (SAK47/DEHP, SAK47/urea/DEHP and del. SAK47/DEHP). For the PVC/kaolinite composites the suspension type of PVC with K value 60 was used. Untreated and treated kaolinite samples as well as PVC composites were examined by X-ray diffraction (XRD) and microscopy (SEM). The interactions between kaolinite and modifier were discussed by FTIR-ATR. Tested mechanical properties were improved almost for all PVC mixtures. The highest values of tensile strength and E-modulus were observed for PVC+del.SAK47/DEHP.

Keywords- PVC; composite; kaolinite; urea; DEHP

I. INTRODUCTION

In worldwide commercial importance, polyvinyl chloride (PVC) is the third most widely produced plastic, after polyethylene and polypropylene [1]. It was first recognized and characterized in 1835 by Henri Victor Regnault and it became commercially significant in Germany prior to World War II [2]. PVC can be modified by large amounts of modifying agents like plasticizers, fillers (calcium carbonate, kaolinite, and calcined kaolinite), and so on. This material can offer many good properties, such as low flammability, high chemical resistance, barrier properties low cost, and formulating versatility. On the other hand, the properties such as its poor impact toughness and low heat-softening temperature limit its application [3]. Next PVC mixtures disadvantage is migration and toxicity of some additives used in PVC, which may have a negative impact on the environment and human health. For all that, PVC production is expected to exceed 40 million tons by 2016 [4].

Kaolinite is a common phyllosilicate mineral, with a general chemical formulation $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. This clay has 1:1 dioctahedral structure which is composed of tetrahedral sheets SiO_4 and octahedral sheets $(\text{Al}_2(\text{OH})_4)$. The layers linked together by hydrogen bonds between surface

hydroxyl groups on the octahedral side and the basal oxygen atoms on the tetrahedral side [5]. Because of hydrophobic properties of kaolinite and hydrophilic character of polymer the modification of kaolinite is necessary. The separation of kaolinite results in particle size reducing and an increase of the specific surface area. The good kaolinite modification result in better intercalation between filler and polymer matrix. In addition the properties of composite materials could be improved. Kaolinite has many industrial applications; it is used in paper, paint, rubber, plastics and ceramics industries. Its largest applicability as filler in PVC is on production electrical cables or film anti-blocking, tiles and so one [6-9].

This paper follows up our research of PVC inorganic hybrids based on kaolinite/urea. In this part it is compared the kaolinite/urea based PVC composition with kaolinite/urea/DEHP mixtures. All presented mixtures were prepared by melt intercalation. The morphology and mechanical properties composites based on pure kaolinite, urea intercalated kaolinite, intercalated/exfoliated kaolinite after washing of urea from kaolinite-urea, and kaolinite additionally modified with DEHP were examined and compared. Furthermore, infrared spectroscopy was used in order to get insight into interactions between minerals and modifier at a molecular level.

II. EXPERIMENTAL

A. Materials

Suspension type of polyvinyl chloride (Neralit 601) with K-value 60 (Spolana a. s., Czech Republic) was used as the polymer matrix.

Three types of filler were studied: commercial kaolinite, urea intercalated kaolinite, and intercalated/exfoliated kaolinite after washing of urea. Firstly, Kaolinite SAK47 (LB Minerals) was investigated without any additional treatment in received state. Beside kaolinite as a main component of SAK47, it contains quartz and mica as admixtures as was revealed using X-ray diffraction method. According to data available from producer of SAK47 82 % of particles are smaller than 10 μm [10].

Next urea was used for the intercalation of SAK47. The sample preparation was performed according to procedure described by Valaskova 'et. al.' [11] and Zykova 'et. al.'

[12]. 500 g of SAK47 (LB Minerals) was homogenized for 5 min with 330 g of urea (Lachner, p.a. grade) in vibrating mill. Intercalation of urea into kaolinite interlayer was achieved by 48 hours long heating of the homogenized mixture at 95 °C in laboratory oven [11,12].

Further delamination of kaolinite was achieved using 5 hour long low-temperature ultrasound washing of urea with distilled water. This process is explained in detail in publications [11,12]. For 100 g of intercalate 3 l of distilled water was used. After washing liquid portion was removed by sedimentation, obtained solid portion was dried at 60 °C. By this way was obtained del. SAK47 (intercalated/exfoliated kaolinite after washing of urea).

Finally all three types of filler (SAK47, SAK47/urea, and del. SAK47) were treated by Bis(2-ethylhexyl)phthalate (DEHP). DEHP is an organic compound with the formula $C_6H_4(C_8H_{17}COO)_2$ and it is the most important phthalate, Untreated and treated kaolinite was modified by DEHP (DEZA a.s., Czech Republic) in laboratory mixer at 80 °C for 1 hour and then dried on the oven at 100 °C for 24 hours. After treatment the powder was obtained.

B. PVC Composite Processing

PVC/kaolinite composite samples were prepared, in accordance with Zykova ‘et. al.’ [12], via the 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 I. PVC/KAOLINITE MIXTURES COMPOSITION

Polymer	Filler	wt. (%)	Sample name
sPVC			Unfilled PVC
sPVC	SAK47	5	PVC+SAK47
sPVC	SAK47+DEHP	5	PVC+SAK47/DEHP
sPVC	SAK47/Urea	5	PVC+SAK47/urea
sPVC	SAK47/Urea/DEHP	5	PVC+SAK47/urea/DEHP
sPVC	Del. SAK47	5	PVC+ del. SAK47
sPVC	Del. SAK47/DEHP	5	PVC+ del. SAK47/DEHP

C. Methods

X-ray diffraction was (XRD) obtained using PANalytical X’Pert PRO diffracto-meter equipped with CuK_{α} radiation ($\lambda = 0.154 \text{ nm}$) 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 composites by a VEGA\LMU. Before examination, samples were coated by thin layer of Ag/Pd.

Mechanical properties were measured by Alpha Technologies Tensometer 2000 and a speed of testing was 500 mm/min. The dogbone specimens (type V in accordance with standard CSN EN ISO 527-2) were used for the measurement.

III. RESULTS AND DISCUSSION

X-ray powder diffraction method was used to observe urea and urea/DEHP intercalation process. Significant segments of XRD patterns described process of intercalation as well as delamination are pictured in Figure 1. Decrease in intensity of d_{001} basal diffraction of kaolinite with maxima at $d=0.717 \text{ nm}$ is evident after the intercalation with urea. The new peak with maxima at $d=1.072 \text{ nm}$ is connected with formation of kaolinite-urea complex [11] and is connected with increase in interlayer distance due to the insertion of urea molecules. After the washing this diffraction disappears (see pattern del. SAK47) in Figure 1. After DEHP addition to SAK47 the maximum $d= 0,717 \text{ nm}$ intensity is decreased, but it is still very strong. In the case of SAK47/urea/DEHP the original maximum of kaolinite at $d=0.7171 \text{ nm}$ was almost disappeared and the maximum at $d=1.072 \text{ nm}$ is lower comparing SAK47/urea intercalate. This fact could be connected with lower organization of layers. For del. SAK47/DEHP is the basal diffraction d_{001} on the same position as for del. SAK47. The peak intensity reveals that the intercalation and delamination of kaolinite was not complete in this case.

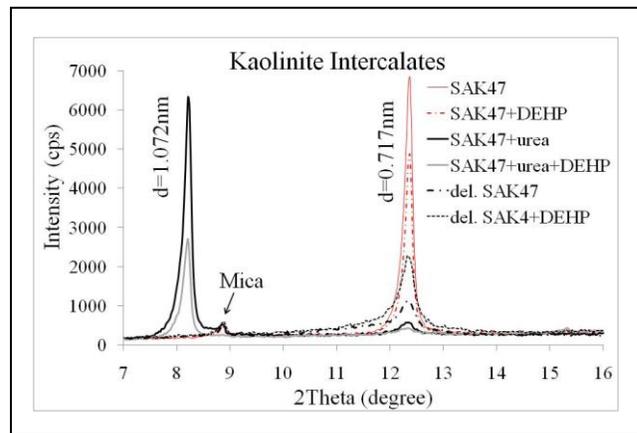


Figure 1. XRD of used fillers: unmodified SAK47, intercalated SAK47/urea, del. SAK47, SAK47/DEHP, SAK47/urea/DEHP and del. SAK47/DEHP.

Next Figures 2-4 demonstrate the XRD patterns of unfilled PVC and PVC/kaolinite samples. In Figure 2 is observed that in the PVC+SAK47 composite the

characteristic peak of kaolinite (d_{001}) is still visible. It indicated that filler still keeps its original crystal structure.

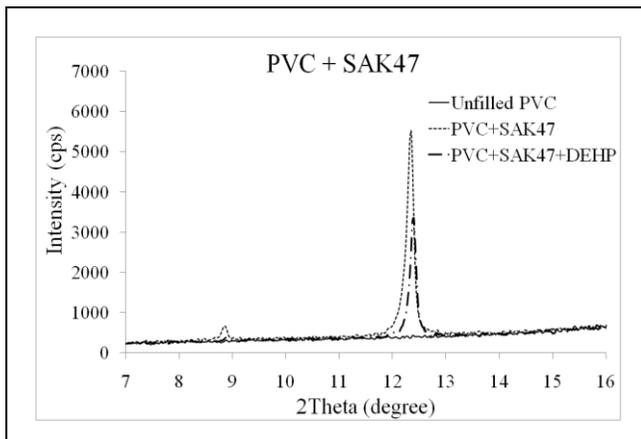


Figure 2. XRD patterns: Pure PVC, PVC/SAK47 and PVC/SAK47/DEHP.

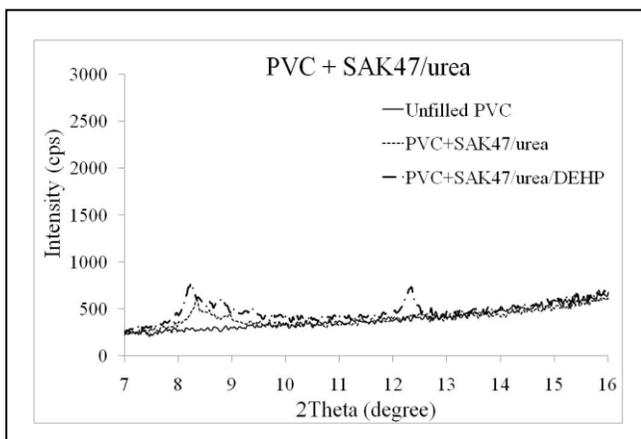


Figure 3. XRD patterns: Pure PVC, PVC/SAK47/urea and PVC/SAK47/urea/DEHP.

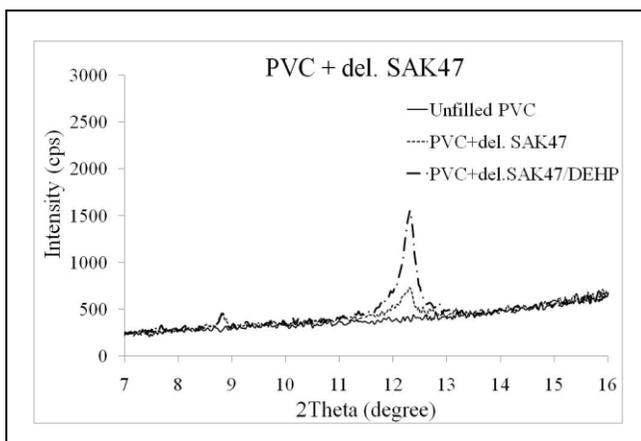


Figure 4. XRD patterns: Pure PVC, PVC/del.SAK47 and PVC/del.SAK47/DEHP.

For the PVC+SAK47/DEHP kaolinite maximum intensity was fall down around 40 %. This fact could indicate the

improved kaolinite dispersion in polymer matrix. The $d=0,717$ nm is almost disappeared in case of PVC+SAK47/urea and PVC+SAK47/urea/DEHP composite (Figure 3). It was observed broad low intensity peak at $d=1.072$ nm, which is connected with increase of interlayer distance. Next in the pattern of PVC+del.SAK47 (Figure 4) the kaolinite diffraction peak at $0,717$ nm also almost disappears. On the other hand when the DEHP was employed to the process of del.SAK47 modification the intensity of this maximum was increased. The intensity of (d_{001}) is around 70 % lower comparing PVC+SAK47 mixture. From XRD results that modified kaolinites are probably more dispersed into the polymer matrix than untreated SAK47.

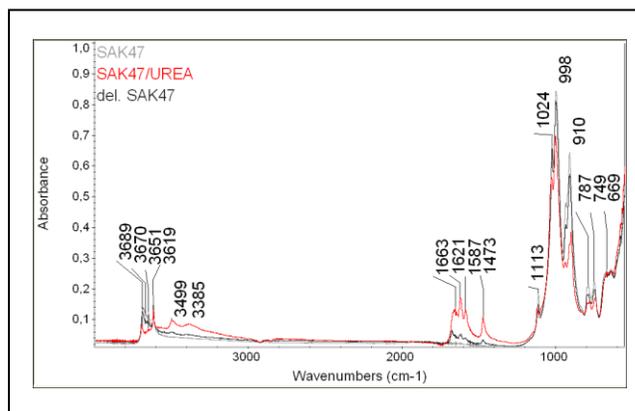


Figure 5. FTIR-ATR spectra of natural kaolinite SAK47 and modified kaolinite SAK47/urea, del. SAK47.

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 Figure 5 and 6. 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} in Figure 5 [3,13]. Next vibrations 1113 , 1026 and 910 cm^{-1} characterize the Si-O stretching vibrations. O-Al-OH stretching vibrations are connected with vibrations 787 , 749 and 669 cm^{-1} . The general features of kaolin intercalated with urea (SAK47/urea) are practically the same as for SAK47 (Figure 5). 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. 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 spectra SAK47/urea modification by DEHP are showed in the Figure 6. New vibration was observed in the region above 3000 cm⁻¹. Next new maximum is at 1781 and 1417 cm⁻¹. It is supposed that they could be connected with the DEHP and urea interactions.

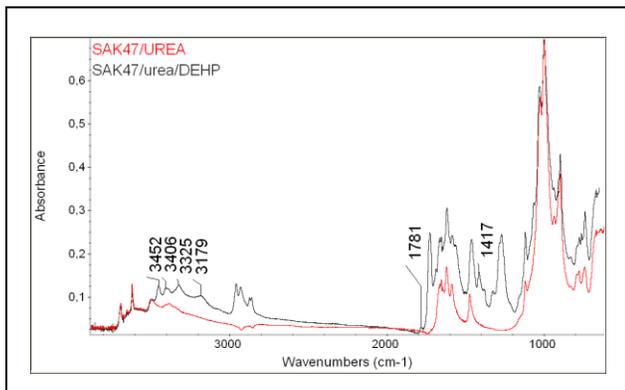


Figure 6. FTIR-ATR spectra of SAK47/urea and SAK47/urea/DEHP.

SEM was used for the morphological study of the unmodified and modified kaolinite within the PVC matrix. The structure PVC composites based on untreated and treated SAK47 modified by urea was previously described in paper [12]. It was observed that the PVC filled by 5 wt. % of untreated kaolinite (SAK47) shows inhomogeneity which suggests the poor interfacial adhesion between polymer and filler, see Figure 7. On the other hand, PVC filled by 5 wt. % of SAK47 modified by urea indicated better dispersion with low amount of aggregates. In composition PVC/del.SAK47 kaolinite layers seem to be delaminated into individual layers or stacks of several layers of kaolin in PVC. In the case of DOP the homogeneity was further improved. These results are in good agreement with XRD and mechanical properties.

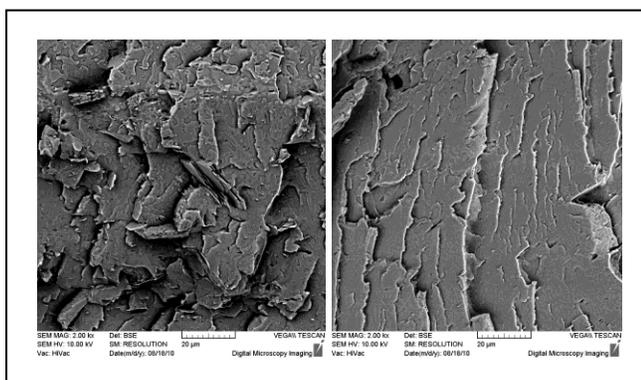


Figure 7. SEM: PVC/SAK47 and PVC/SAK47/urea.

Mechanical properties tested PVC composites are summarised in Table 2. It can be seen that the tensile strength all presented PVC composite samples is higher as compared to unfilled PVC. The lowest value of tensile strength from tested PVC composites has the mixture PVC+SAK47/urea. The highest value was observed for

PVC+del.SAK47/DEHP with change around 13 % comparing pure PVC. In addition, all composite samples also show E-modulus increase as compared to unfilled PVC. The Sample PVC+del.SAK47/DEHP offers the highest value with an improvement 28 %. The lowest E-modulus from tested composites was obtained for PVC+SAK47 (untreated kaolinite). Generally it could be said that highest values of E-modulus gives the compositions with additional treatment with DEHP. It could indicated that these mixtures offers better dispersion in polymer matrix.

TABLE II. MECHANICAL PROPERTIES OF PVC/KAOLINITE MIXTURES

Samples	Tensile Strength (MPa)	S ^a (Mpa)	E-modulus (MPa)	S ^a (MPa)
Unfilled PVC	46.0	2.9	1630	85
PVC+SAK47	49.5	1.82	1630	156
PVC+SAK47/DEHP	49,7	0,80	1756	77,0
PVC+SAK47/urea	48.6	1.51	1995	169
PVC+SAK47/urea /DEHP	50,4	1,83	2006	165
PVC+ del. SAK47	51.7	0.24	1689	161
PVC+ del. SAK47/DEHP	52,2	0,41	2082	145

^a standard deviation

IV. CONCLUSION

The effect of the untreated, treated kaolinite by urea and DEHP on the morphology and mechanical properties was investigated.

Firstly, XRD and FTIR study confirms that kaolinite modification results in intercalation of the SAK47. FTIR-ATR spectra indicated hydrogen bonding of urea to the kaolinite surface through its NH group. Furthermore 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. FTIR spectra kaolinite/urea modified by DEHP show new vibration in the region above 3000 cm⁻¹, 1781 and 1417 cm⁻¹. It is supposed that they could be connected with the DEHP and urea interactions.

The XRD patterns show that the urea and DEHP have the influence on the PVC composite morphology. The largest changes in XRD patterns were observed by compositions based on urea and urea/DEHP.

Tested mechanical properties, tensile strength and E-modulus, were improved almost for all PVC mixtures. The highest values of tensile strength and E-modulus were observed for PVC+del.SAK47/DEHP with change around 13 % and 28 % comparing pure PVC. This improvement could be connected with delamination of kaolinite layers, which results in the increase of the specific surface area.

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