# Influence of kaolinite modification on the PVC composites properties

JITKA ZYKOVA<sup>1</sup>, ALENA KALENDOVA<sup>1</sup>, VLASTIMIL MATEJKA<sup>2</sup>, PETR ZADRAPA<sup>1</sup>, JIRI MALAC<sup>1</sup> <sup>1</sup> Department of polymer engineering, Faculty of technology Tomas Bata University in Zlín TGM 275, 762 72 Zlín CZECH REPUBLIC <u>zykova@ft.utb.cz</u>

> <sup>2</sup> Department of Nanotechnology Centre VŠB-Technical University of Ostrava
> 17. listopadu 15/2172, 70833 Ostrava-Poruba CZECH REPUBLIC

*Abstract:* - Funcionalization of the filler surface is very important factor for achieving good interaction between filler and polymer matrix. In addition the mechanical as well as chemical properties, thermal stability, gas permeability, and flammability can be substantially improved. Hence, the intercalation of kaolinite by urea was performed. Untreated and treated kaolinite samples were examined by X-ray diffraction (XRD) spectra were measured and interpreted. Samples intercalated with urea and subsequently exfoliated during washing exhibit a variable intensity of the 001 diffractions of kaolinite (K) and the presence of interstratified intermediate kaolinite phase was also approved. For the PVC/kaolinite composites the suspension type of PVC with K value 60 was used. Commercial type of pure kaolinite, urea intercalated kaolinite, and intercalated/exfoliated kaolinite after washing of urea from kaolinite-urea intercalate were used as the filler. PVC/kaolinite compounds were prepared by the melt intercalation method. Morphology of prepared samples and their mechanical stability was tested.

Key-Words: PVC, composite, kaolinite/urea intercalate, delamination, melt intercalation

### 1 Introduction

Polymer composites have a long history. Despite these materials are still one of the most dynamically development materials in the 21st century because of the ability propose to not only reduce cost, but to improve properties, such as mechanical, thermal and barrier properties of the final polymer product.

Polyvinyl chloride (PVC) is one of the most extensive thermoplastic materials in the world due to its valuable properties, wide applications, high chemical resistance, barrier properties and low cost [1,2]. On the other hand, thermal stability and processibility of PVC is inferior compared with common polymers, for example polyethylene (PE), polypropylene (PP), polyamide (PA). These properties could be reinforced compounding PVC with inorganic or organic fillers. The most useful fillers in PVC are calcium carbonate, kaolinite, and calcined kaolinite [3,4].

Kaolinite is a common phyllosilicate mineral, with a general chemical formulation  $Al_2Si_2O_5(OH)_4$ . This clay has 1:1 dioctahedral structure which is composed of tetrahedral sheets  $SiO_4$  and octatedral sheets  $(Al_2(OH)_4)$ . Individual layered consists of both sheets which are closely connected by hydrogen bond between

surface hydroxyl groups on the octahedral side and the basal oxygen atoms on the tetrahedral side. Because of hydrophobic properties of kaolinite and hydrophilic character of polymer the modification of kaolinite is necessary. Therefore, kaolinite layers are often separated by intercalation agents such as dimethyl sulfoxide or urea. 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 Kaolinite be improved. 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 antiblocking, tiles and so one [5-8].

In this research, the PVC/kaolinite composite preparation by the melt intercalation method is reported. In addition the influence of treated, untreated and intercalated/exfoliated kaolinite on the morphology and mechanical properties is investigated.

# 2 Experimental

#### 2.1 Materials

In this work, 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 [9] 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 Modification of kaolinite with urea

The sample preparation was performed according to procedure described by Valaskova et. all [10]. 500 g of SAK47 (LB Minerals) was homogenized for 5min 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 5h long low-temperature ultrasound washing (SONOREX RK100) of urea with distilled water (for 100 g of intercalate 3l of distilled water). After washing liquid portion was dried at 60 °C (Memmert UNB200).

#### 2.3 PVC composite processing

PVC/kaolinite composite samples were prepared 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.

#### 2.4 Methods

*The scanning electron microscopy* (SEM) photographs of the samples were taken to assess the morphology kaolin/PVC composites by a VEGA $\$  Before examination, samples were coated by thin layer of Ag/Pd.

*X-ray diffraction* was (XRD) obtained using PANalytical X'Pert PRO diffracto-meter equipped with

 $CuK_{\alpha}$  radiation ( $\lambda = 0.154$  nm) at room temperature. The scans were taken in a  $2\Box$  range from 4 to 30°, with  $0.02^{\circ}$  step size and the counting time of one scan 5s.

Mechanical properties were measured by Alpha Technologies Tensometer 2000 and a speed of testing was 500 mm/min. For the measurement the dogbone specimens (type V) were used.

Table 1. The composition of PVC/kaolinite samples

	Filler				
Polyme	r Filler	Modifier	wt. %	Sample name	
sPVC		-		Unfilled PVC	
sPVC	SAK47	-	3	PVC+SAK47-3wt.%	
sPVC	SAK47	-	5	PVC+SAK47-5wt.%	
sPVC	SAK47	-	7	PVC+SAK47-7wt.%	
sPVC	SAK47	Urea	3	PVC+SAK47/urea -3wt.%	
sPVC	SAK47	Urea	5	PVC+SAK47/urea -5wt.%	
sPVC	SAK47	Urea	7	PVC+SAK47/urea -7wt.%	
sPVC	Del. SAK47	-	3	PVC+ del. SAK47-3wt.%	
sPVC	Del. SAK47	-	5	PVC+ del. SAK47-5wt.%	
sPVC	Del. SAK47	-	7	PVC+ del. SAK47-7wt.%	

#### 2.5 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 d<sub>001</sub> 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 [10] 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.S4K47) in Fig. 1. The incompleteness of intercalation as well as delamination of kaolinite structure reveals presence of kaolinite 001 basal diffraction peak (assigned as  $d_{001}$ ) on the diffraction patterns of samples after intercalation and washing procedure. Fig. 2, 3 and 4 display the XRD patterns of unfilled PVC and PVC/kaolinite composite samples. In Fig. 2 is observed that in the PVC composite samples containing 3 wt. % of kaolinite the kaolinite characteristic peaks  $(d_{001})$  are still visible. It means that kaolin still keeps its original crystal structure. However, the d<sub>001</sub> is almost disappeared in PVC/kaolinite-urea

composite samples as well as the diffraction peak at d= 1.072 nm. It is interesting that in the case of PVC/kaolinite-urea composite, 5 wt. %, 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. While, PVC filled by 5 wt. % of kaolinite have the highest intensity of this peaks. When PVC is filled by 7 wt. % of kaolinite the intensity of peaks is similar as in Fig. 1.

Mechanical properties results of unfilled and filled PVC are summarised in table 2. It can be seen that the tensile strength of almost all PVC composite samples is slightly higher as compared to unfilled PVC. It is also observed that with the increasing filler loading the tensile strength is decreased. When the modification of filler by urea is compared with the other fillers it is seems that this sample have the lowest values of the tensile strength at the 7 wt. %, especially. The highest tensile strength is PVC filled by observed for 5 wt. % of intercalated/exfoliated kaolinite (del. SAK47). In addition, almost all composite samples also show Emodulus increase as compared to unfilled PVC. The highest E-modulus has PVC filled by 7 wt. % of delaminated kaolinite (del. SAK47) which is about 27 % higher. The second highest value of E-modulus gives sample with SAK47/urea-5 wt. % the improvement is about 22 %. It means that these PVC sample has better filler dispersion to polymer matrix. On the other hand, the worst sample is PVC filled by the 3 wt. % intercalated/exfoliated kaolinite (del. SAK47). In the case of unmodified kaolinite the values are relatively stable with improvement to 10%.

Table 2. Results of mechanical properties	Table 2.	Results	of mec	hanical	properties
---	----------	---------	--------	---------	------------

Samples	Tensile Strength (MPa)	S <sup>a</sup>	E-modulus (MPa)	S <sup>a</sup>
nfilled PVC	46,0	2,90	1630	85,0
VC+SAK47-3wt.%	51,6	0,79	1741	128
VC+SAK47-5wt.%	49,5	1,82	1630	156
VC+SAK47-7wt.%	49,2	1,20	1732	106
VC+SAK47/urea-3wt.%	48,4	0,97	1691	144
VC+SAK47/urea -5wt.%	48,6	1,51	1995	169
VC+SAK47/urea -7wt.%	43,6	1,25	1574	140
VC+ del. SAK47-3wt.%	50,5	0,77	1455	140
VC+ del. SAK47-5wt.%	51,7	0,24	1689	161
VC+ del. SAK47-7wt.%	47,5	1,33	2079	111

<sup>a</sup> standard deviation



Fig. 1 The XRD patterns of unmodified and modified kaolinite



Fig. 2 The XRD patterns of PVC, and PVC/kaolinite composites



Fig. 3 The XRD patterns of PVC, and PVC/kaolinite composites



Fig. 4 The XRD patterns of PVC, and PVC/kaolinite composites

SEM was used for the dispersion evaluation of the unmodified and modified kaolinite platelets within the PVC matrix. Fig. 5 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. As a result, this sample had also the best mechanical properties. It can be concluded that the results are also in accordance whit XRD analysis.



Fig. 5 SEM images of (a) unfilled PVC, (b) PVC/5 wt. % SAK47, (c) PVC/5 wt.% SAK47+urea and (d) PVC/5 wt. % del. SAK47

## **3** Conclusion

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

Firstly, 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 better dispersion in polymer as compared to PVC with untreated kaolinite. The addition only small amount of unmodified kaolinite (until 5 wt. %) into polymer matrix mechanical properties are improved. The tensile strength was improved more than 5 % and E-modulus about 20 %. In case of treated kaolinite by urea (5 wt. %) it was approximately observed the same E-modulus improvement as for 3 wt. % of intercalated/exfoliated kaolinite. This enhancement is probably connected with delamination of kaolinite layers, which results in a particle size reducing and the increasing of the specific surface area. Thus, the interaction between polymer and filler is stronger.

#### 4 ACKNOWLEDGMENTS

This work was supported by the internal grant of TBU in Zlín No. IGA/16/FT/10/D funded from the resources of specific university research.

#### References:

- [1]S. Zhu, Y. Zhang, Y. Zhang, C. Zhang, Effect of CaCO<sub>3</sub>/LiCO<sub>3</sub> on the HCl generation of PVC during combustion, Polymer Testing, Vol. 2, 2003, 539 – 543.
- [2]F. Gong, M. Feng, Ch. Zhao, S. Zhang, M. Yang, *Thermal properties of poly(vinyl*

*chloride)/montmorillonite nanocomposites.* Polym Degrad and Stab, Vol. 84, 2004, 289-294.

- [3]M. Pan, X. Shi, X. Li, H. Hu, L. Zhang, *Morphology* and Properties of PVC/clay Nanocomposites via in Situ Emulsion Polymerization. Journal of Applied Polymer Science, Vol. 94, 2004, 277-286.
- [4]AB. Shehata, MA. Hassan, NA. Darwish, *Kaolin Modified with Resin-Iron Chelate as Flame Retardant System for polypropylene,* Journal of Applied Polymer Science, Vol. 92, 2004, 3119–3125.
- [5]T.A. Elbokl, C. H. Detellier, *Intercalation of cyclic imides in kaolinite*, Jurnal of Colloid and Interface Science, Vol. 323, 2008, 338-348.
- [6]Y. Turhan, M. Dogan, M. Alkan, Poly(vinyl chloride)/Kaolininte Nanocomposites: Characterization and Thermal and Optical Properties. Ind. Eng. Chem. Res. Vol. 49, 2010. 1503-1513.
- [7]L. Domka, A. Malicka, N. Stachowiak, Production and Structural Investigation of Polyethylene Composites with Modified Kaolin, Acta Physica Polonoca A, Vol. 114, No. 2, 2008.
- [8]S. J. Der Gaast, M. Zbik, J. T. Kloprogge, G. N. Paroz, Birdwood kaolinite: a highly ordered kaolinite that is difficult to intercalate/an XRD, SEM and Raman spectroscopic study, Applied Clay Science, Vol. 20, 2002, 177-187.
- [9]LB MINERALS, s.r.o. <http://www.lbminerals.cz/en/products/2-kaolinites/13-blendedkaolinites/76-sak-47>
- [10]M. Valášková, M. Rieder, V. Matějka, P. Čapková, A. Slíva, *Exfoliation/delamination of kaolinite by low-temperature washing of kaolinite–urea intercalates*", Applied Clay Science, Vol. 35, 2007, 108–118.