

THE STUDY OF PROPERTIES OF NANOFILLERS ON THE BASIS OF NATURAL CLAY MINERALS AND THEIR APPLICATION IN POLYMER MATERIALS

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ABSTRACT: This work deals with the application of inorganic substances, specifically natural clay minerals, which are an important group of nanomaterials in organic polymers [1]. Their use improves physical-mechanical properties and quality of final vulcanizates. Main advantage of nanocomposites is improvement of properties of final products, which are especially increased by structural fortresses and modules near lower content of inorganic ingredients [2,3]. Nanocomposite materials were prepared on the basis of natural clay minerals and they were characterized by thermal and spectral methods. Then we compared found physical-mechanical properties and vulcanization characteristics of nanocomposites to commercially used polymer materials of original composition.

KEY WORDS: clay minerals, nanofillers, nanocomposites, polymer materials, physical-mechanical properties

1. INTRODUCTION

Natural inorganic fillers like talc, mica, chalk and bentonite are added to thermoplastics and thermosetting polymers in a number of situations. The main objectives of producing these polymer composites are the reduction of industrial costs and also the modification of certain characteristics such as stiffness, electrical insulation, thermal stability and optical properties [4]. However, in the majority of cases the increasing interest devoted to polymer-clay composites arises from the fact that delamination of relatively low amount of clay gives us the possibility to modify drastically not only mechanical properties of the polymer but also some of its physical properties [3]. Bentonite is a clay rock with dominant content of minerals from a group of smectites, most frequently montmorillonite, less beidellite, hectorite and saponite. The structure of montmorillonite with large substitution of Si^{4+} in the tetrahedral sheets, but especially of Al^{3+} in the octahedral sheet with poor bonding powers between basic structural elements leads to specific properties of bentonite [5].

2. EXPERIMENT

2.1 Characterization of the additive

The natural bentonite used in this study, denoted as P031 was obtained from deposit in the area of Lieskovec, Slovak republic, with montmorillonite purity of 50 - 70 %. The chemical composition of natural bentonite (in wt. %) is following: SiO_2 : 65.0, Fe_2O_3 : 7.0, CaO : 1.5, MgO : 2.0. A loss on ignition was 7.0 %. The grain curve of bentonite is presented in Fig. 1. This commercial product from firm Envigo inc. was submitted to measurements of thermal (DTA, TG) and spectral (FTIR, XRD) analysis.

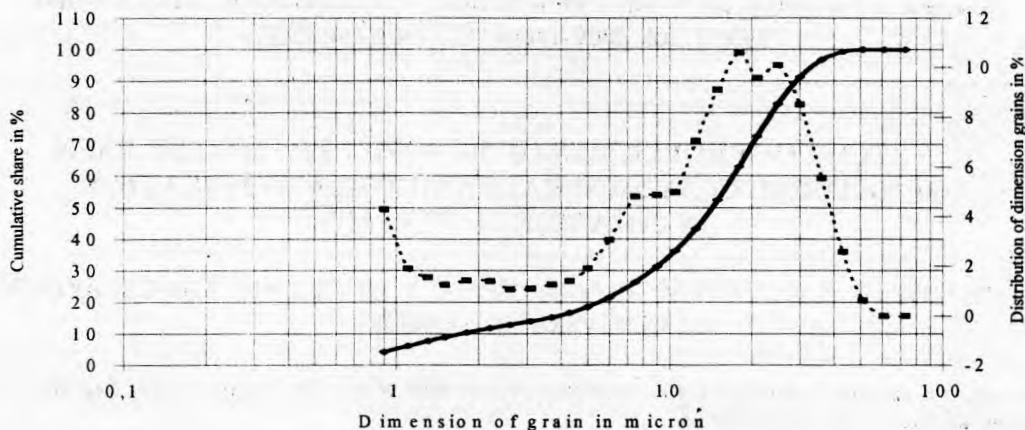


Fig. 1: The grain curve of natural bentonite

The exact mineralogical composition of natural bentonite was evaluated by spectral method of X-ray diffraction (XRD) analysis on a Philips PW 1730/1050 diffractometer. Diffraction pattern was recorded by using the plate-oriented technique with CoK α radiation (35 mA, 40 kV) and a position-sensitive detector using a step size of 0,020 and a step time of 2.4 s.

The FTIR spectra for the sample of natural bentonite were recorded by using KBr pellets on a MB AUXILIARY SAMPLE COMPT. FTIR spectrometer in the middle region (4000 - 400 cm⁻¹).

Thermal behaviour at the natural bentonite was investigated by differential thermal analyses (DTA), thermogravimetry (TG) simultaneously with Derivatograph (MOM, Hungary). Measurements were carried out under the following conditions: sample weights: 150 mg; average heating rate: 10 °C/min; reference material: annealed aluminium oxide; sample holders: alumina crucibles, temperature range: 25 - 900 °C.

2.2 Preparation of nanocomposite system polymer/clay

The reference and two model rubber mixtures (P031-5, P031-10) were prepared by two-stage mixing of natural rubber SMR-20 with additives, which were different in added amount of the natural bentonite P031 in function of filler. The correspondent compositions and the conditions of preparation of individual rubber mixtures are mentioned in Tab. 1.

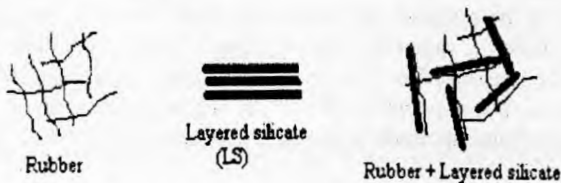


Fig. 2: Rubber and layered silicate

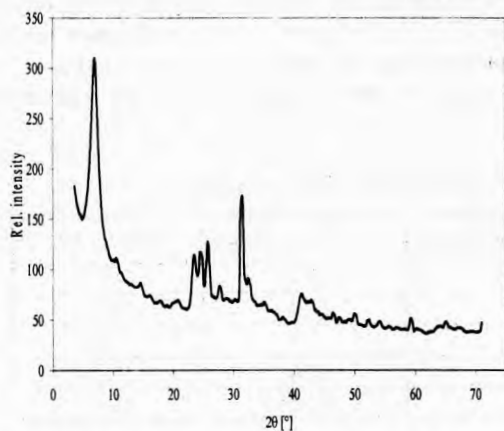
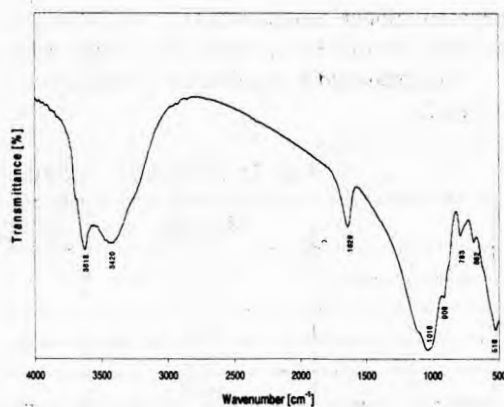
Tab. 1: The compositions and the conditions of prepared rubber mixtures

I. step of mixing			
Temperature	140 °C		
Rate of mixing	50 rpm/min		
Time of mixing	8 minutes		
Rubber mixtures	Reference mixture [dsk]	P031 - 5 [dsk]	P031 - 10 [dsk]
Natural rubber SMR-20	100	100	100
ZnO	4.6	4.6	4.6
Sulfenax CBS	1.5	1.5	1.5
Carbon black N 660	10	5	
P031	-	5	10
Time of stay	24 hours		
II. step of mixing			
Temperature	110 °C		
Rate of mixing	50 rpm/min		
Time of mixing	6 minutes		
Sulphur N	1.8		
Time of stay	24 hours		

3. RESULTS AND DISCUSSION

The analysis of the natural sample P031 by XRD confirmed the major presence of montmorillonite with structural formula $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})$. The content of quartz (SiO_2) presented 24.4 wt. %. The XRD pattern of the natural bentonite sample is given in Fig. 3.

The FTIR spectrum of natural bentonite is depicted in Fig. 4. The wavenumber and vibration types of natural bentonite are described as follows.

**Fig. 3:** The XRD pattern of the natural clay, bentonite**Fig. 4:** The FTIR spectra of natural bentonite

In the recorded spectra of natural bentonite a sharp peak at 3618 cm^{-1} was due to Al-OH stretching vibration. Peaks at 3420 and 1629 cm^{-1} were the H-O-H stretching and bending vibrations of the adsorbed water, respectively. Peak at 1018 cm^{-1} was attributed to Si-O stretching frequency. Tetrahedral bending modes were observed for Si-O-Al at 516 cm^{-1} . OH bending vibrations in

dioctahedral 2:1 layer silicates were assigned for Al-Al-OH at 908 cm^{-1} and for Mg-Fe-OH at 783 cm^{-1} . Peak at 682 cm^{-1} was due to the bending vibration of Si-O-Si.

DTA and TG curve of natural bentonite is mentioned in Fig. 4. DTA curve can be divided on two areas – the area of dehydration in the thermal interval of 20 - 300 °C and the area of dehydroxylation in the thermal interval of 500 - 1000 °C. At the area of dehydroxylation a destruction of the structure occurred and at that point new high-temperature phases started. Physically bounded molecular water got away by heating at temperatures up to 100 - 120 °C and the water in interlayer's space from 120 °C. The OH groups began to release at the temperature of around 500 °C and the dehydroxylation finished up to 800 °C.

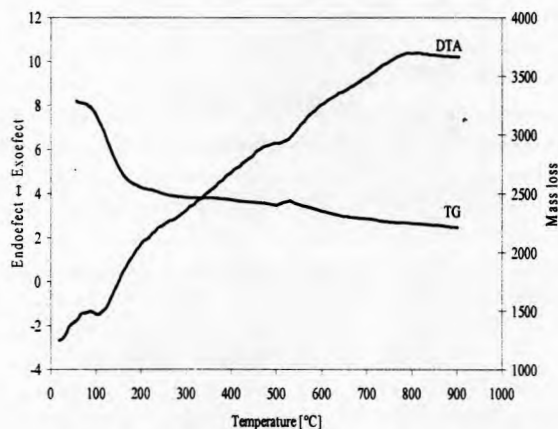


Fig. 4: DTA and TG of natural bentonite

At all rubber mixtures studied by method DSC, we recorded an exothermic reaction in the thermal interval of 180 - 200 °C, which characterizes vulcanization process. The behaviour of the prepared rubber mixture P031-5 was almost comparable to the behaviour of the reference rubber mixture. The rubber mixture P031-10 showed bigger anomaly than the reference rubber mixture.

The measured vulcanization characteristics of prepared modified rubber mixtures are mentioned in Tab. 2.

Tab. 2: Vulcanization characteristics of prepared rubber mixtures

	Measure	Reference mixture	P031 - 5	P031 - 10
M_L	N.m	5.0	2.7	1.8
M_H	N.m	45.0	43.8	38.5
t_s	min	1.5	1.5	4
t_{90}	min	3.5	4.6	8.2
R_v	min^{-1}	50.00	32.26	23.81

From Tab. 2 follows, that the values of M_L , M_H , t_s , t_{90} and R_v of studied rubber mixtures were different than the reference rubber mixture, what indicated a lower stiffness and a lower activity of the prepared modified rubber mixtures.

The physical and mechanical properties of the prepared rubber mixtures are mentioned in Tab. 3.

Tab. 3: Physical-mechanical properties of prepared rubber mixtures

Type of test	Measure	Reference mixture	P031 - 5	P031 - 10
Tensile strength	MPa	13.17	14.90	20.10
Modulus 300	MPa	5.77	8.29	7.58
Tensibility	%	685	539	796
Hardness	IRHD	47.6	46.2	43.3

The values of tensile strength and tensibility at the tested modified rubber mixture P031-5 were almost comparable to the reference rubber mixture. Both modified rubber mixtures displayed bigger anomalies at the modulus 300 in comparison to the reference rubber mixture. The growth of the tensile strength was higher for about 40 % at the rubber mixture P031-10. The measured lower values of hardness deposed about good mix of filler in the rubber mixtures and about its good compatibility with rubber matrix at both modified rubber mixtures. Similarly, values of tensibility showed a growth at the modified rubber mixture P031-10, what can be considered as an advantage, especially at the elastic application (sidewall of the tires, drift mixtures et al.).

4. CONCLUSION

From this study of physical-mechanical properties of the prepared modified rubber mixtures follows, that filler on the base of natural clay, bentonite which we used is suitable for application as nanofiller in rubber mixtures, because it improves the strength, elasticity et al. of final vulcanizates.

Acknowledgements: The authors sincerely thank the Slovak Grants VEGA 1/3161/06 and AV 4/2014/08 for their financial support, and also to all participants of Faculty of Industrial Technologies in Púchov and Ing. Vladimír Jorík, CSc. for very useful feedback on the work presented in this paper.

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