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Thermal and spectral properties of natural bentonites and their applications as reinforced nanofillers in polymeric materials

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Abstract This study deals with possibility of the applications of inorganic substances specifically natural bentonite in function of reinforced nanofillers in polymeric materials. X-ray diffraction, FTIR spectroscopy and thermal analysis (TG, DSC and DTA) were used to characterize natural bentonite in more detail. At the prepared model, rubber compounds with various amounts of added filler were determinated vulcanization characteristics and physical–mechanical properties. The measured values were compared with the values of commercially used polymeric materials with the original composition.

Keywords Bentonite · IR spectroscopy · TG · DSC · DTA · Nanocomposites · Physical–mechanical properties

Introduction

Rubber is one of the versatile materials widely used in many applications. However, raw rubber has poor physical–mechanical properties, which we can improve using of various ingredients, such as accelerators, activators, crosslinking agents and fillers [1].

By adding fillers, such as clay or clay minerals, we can generate an infinite variety of materials with unique properties and competitive production costs [2]. These improvements at the polymer nanocomposites are connected with not only size, shape, dispersion and orientation of added filler but also with its surface area [3]. The contents of fillers on the basis of layered silicates are relatively low in the range 2–6 wt%, what is a big positive in compare with a high degree of filling, which is typical for conventional used fillers [4].

Besides increased modulus and strength, other factors such as tear properties, fracture toughness and abrasion resistance, thermal stability and flame retardancy can be expected as a result of clay addition to rubber [5–7].

X-ray, thermal analysis and spectral studies are very useful techniques for materials characterization. Therefore, it is not surprising that many authors have used these techniques for various materials investigation [8–27]. This article describes in detail thermal analyses (TG, DSC and DTA), X-ray diffraction and FTIR spectral data of used natural bentonite in function of filler and of the prepared model rubber compounds.

Experimental

Materials and methods

A bentonite product, which was used at the preparation of model rubber compounds, was obtained from deposit in the area of Lieskovec, Slovakia, with montmorillonite purity 50–70%. The chemical composition (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 natural bentonite is illustrated in Fig. 1.

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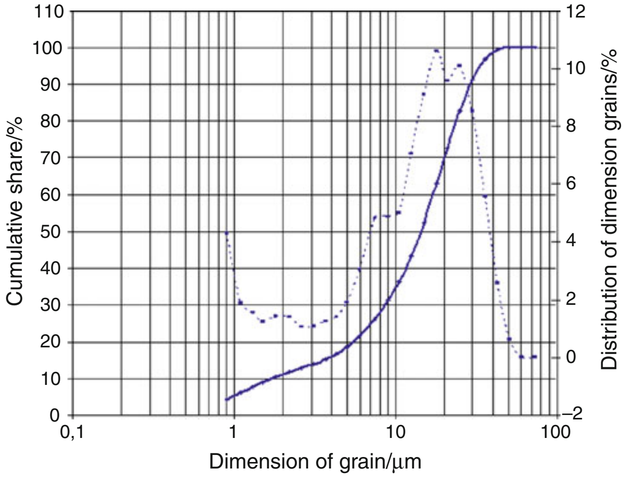

Fig. 1 The grain curve of natural bentonite

The detailed characterization of used filler, natural bentonite was obtained by measurements of thermal (TG and DTA), XRD and FTIR spectral analysis. The prepared model rubber compounds were investigated by DSC.

Thermal measurements

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were simultaneously carried out on a Derivatograph-MOM, Hungary (sample mass ~150 mg, temperature range 25–900 °C, heating rate 10 °C/min; reference material annealed aluminium oxide; sample holders alumina crucibles).

Differential scanning calorimetry (DSC) analysis was carried out on a PYRIS Diamond DSC Perkin Elmer calorimeter. Measurements were provided in the temperature range of 30–250 °C using foloowing experimental conditions: scanning rate of 10 °C/min, calibration of temperature and enthalpy was performed with the use of pure In.

Spectral measurements

X-ray powder diffraction (XRD) profile of pressed powder sample was recorded on a Philips PW 1730/1050 diffractometer (Co Kα radiation, 40 kV/35 mA, step size 0.020, time for step 2.4 s).

Fourier Transform Infrared (FTIR) spectra were obtained using KBr pellets on a MB AUXILIARY SAMPLE COMPT in the middle region (4000–400 cm^{-1}).

Preparation of rubber/clay nanocomposites

Natural rubber SMR-20 was used as the elastomeric matrix. Carbon black N660 was used as the conventional filler due to their size of particles was approximately identical with a size or a grain fineness of used natural bentonite. The composition of the model rubber compounds is given in Table 1 [28].

Table 1 The compositions of prepared rubber compounds

Compounds	Reference compound/phr	Model compound 1/phr	Model compound 2/phr
SMR-20	100		
ZnO	4.6	4.6	4.6
Sulfenax CBS*	1.5	1.5	1.5
Carbon black N660	10	5	–
Bentonite	–	5	10
Sulphur N		1.8	

* *N*-cyclohexyl-2-benzothiazolsulfenamid

The model rubber compounds were prepared by two-step mixing of the natural rubber SMR-20 with the filler and all the vulcanization ingredients except the sulphur N in mixing chamber of laboratory mixer Plastograf-Brabender at 140 °C for 8 min at mixing speed 50 rpm. The second step was made at 110 °C for 6 min at the same mixing speed after the sulphur had been added [29].

The slabs were obtained by a compression moulding of the prepared model rubber compounds using a laboratory press Buzuluk at 150 °C for optimum vulcanization time determined as t_{90} using rheometry. The specimens with a shape of double-ended spatulas were mechanically cut out from the vulcanized slabs [29].

Vulcanization performance

Determination of vulcanization performance (M_L, M_H, t_s, t_{90}, R_v) was made by vulcameter Monsanto 100 at 150 °C during 60 min [30].

Physical–mechanical properties

Physical–mechanical properties (tensile strength, modulus at 300 elongations M_{300} and tensibility) were measured at room temperature using an Instron at deformation rate 50 mm/min [31]. Hardness was measured at the same temperature using a hardness tester IRHD [32].

Results and discussion

Thermal analysis (DTA, TG, DSC)

Differential thermal analysis (DTA) and TG curves of natural bentonite is given in Fig. 2. The TG curve shows two mass loss steps at 20–500 °C and 500–1,000 °C. They

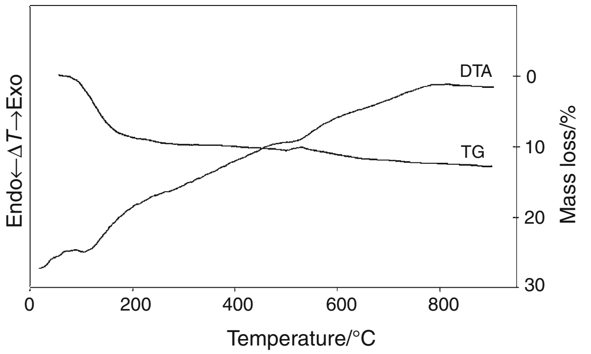

Fig. 2 DTA and TG of natural bentonite

correspond to the dehydration at 20–300 °C and dehydroxylation at 500–900 °C.

The DTA curve is possible to divide on two areas, the area of dehydration at 20–300 °C and the area of dehydroxylation at 500–900 °C (Fig. 2). At the area of dehydroxylation occured a decompostion of the structure and started the new high-temperature phases. The physically bounded molecular water was eliminated at 100–120 °C and the water in interlayer space at 120 °C higher temperature. The OH groups began to release at 500 °C and the dehydroxylation compleated at 800 °C.

In the DSC curves (Fig. 3) of all model rubber compounds was observed an exothermic reaction in the thermal interval 180–200 °C, which characterized the vulcanization process. The thermal behaviour at the model rubber compound 1 was almost comparable with the behaviour at the reference rubber compound. The rubber compound 2 showed that a bigger anomaly than the reference rubber compound.

XRD analysis

X-ray powder diffraction (XRD) analysis showed that the sample of natural bentonite contained mainly of montmorillonite with structural formula $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)$. The content of quartz (SiO_2) presented 24.4 wt%. The XRD pattern of the natural bentonite is given in Fig. 4.

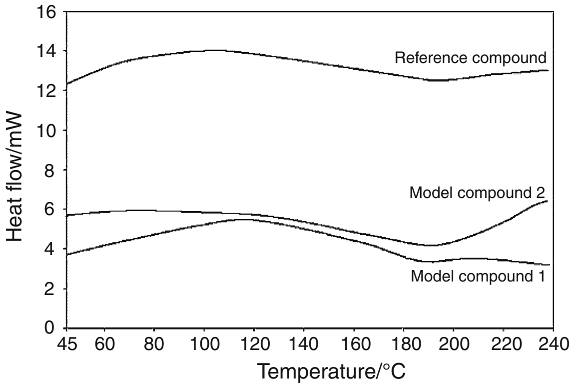

Fig. 3 DSC of model rubber compounds

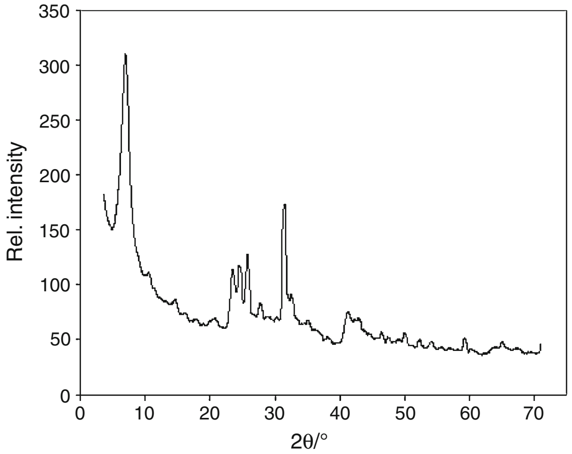

Fig. 4 The XRD pattern of the natural bentonite

FTIR spectroscopy

Fourier transform infrared (FTIR) spectra provided information on the minerals present in the sample and on the chemical composition of the dominant minerals (Fig. 5). The wavenumber and associated vibration types of natural bentonite are given in Table 2.

In the recorded spectra of natural bentonite, a sharp peak at 3,618 cm^{-1} was due to Al–OH stretching vibration. The peaks at 3,420 and 1,629 cm^{-1} were the H–O–H stretching and bending vibrations of the adsorbed water, respectively. The peak at 1,018 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}. A peak at 682 cm^{-1} was due to the bending vibration of Si–O–Si [33].

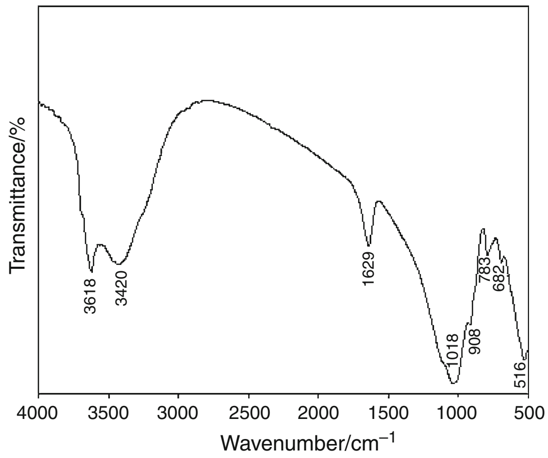

Fig. 5 The FTIR spectra of natural bentonite

Table 2 Wavenumber of absorption bands in FTIR spectra of bentonite

Type of vibration	v/cm^{-1}
v (AlOH)	3,618
v (H_2O)	3,420
δ (H_2O)	1,629
v (SiO)	1,018
δ (AlAlOH)	908
δ (MgFeOH)	783
v (SiOSi)	682
δ (SiOAl)	516

Vulcanization performance

The results of measured vulcanization performance of prepared model rubber compounds are present in Table 3.

It can be concluded from the obtained values in Table 3 that the used type of filler (natural bentonite) acts as an inactive filler in model rubber compounds in compare with the conventional filler (carbon black N660). We can see that with an increasing amount of natural bentonite in compound a viscosity decrease (lower values of M_L and M_H) and the optimal time of vulcanization (t_{90}) extend. At the model rubber compound 2, where is a total substitution of carbon black is more than 100% and the start of vulcanization (t_s) is expressively higher too. The values of rate coefficients of vulcanization (R_v), which characterize activity of ingredients in rubber compounds are markedly lower too. These measured values confirm our assumes, which result from chemical composition of natural bentonite, which contains 65% SiO_2 and the compound of other oxides. These substances are commonly used as inactive fillers in rubber technology [34, 35].

Physical–mechanical properties

The results of measured physical and mechanical properties of prepared model rubber compounds are present in Table 4.

The measured and evaluated values of physical–mechanical parameters show that tensile strength increases with an increasing content of natural bentonite in tested model rubber compounds. At 100% substitution of carbon black N660 is the tensile strength higher about more than 50%. On the other hand, the tensibility decreases with an increasing amount of natural bentonite in model rubber compound which is logical and confirms the elastomeric behaviour of model rubber compound [36, 37]. The values of hardness decrease with an increasing content of natural bentonite what relate with a less activity of natural bentonite in compare with the carbon black N660 and, therefore with a less interaction of polymer-filler [36, 37]. However, this decrease of hardness values is not very dramatic.

Table 3 Vulcanization performance of prepared model rubber compounds

	Measure	Reference compound	Model compound 1	Model compound 2
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

Table 4 Physical–mechanical properties of prepared model rubber compounds

Type of test	Measured	Reference compound	Model compound 1	Model compound 2
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

Conclusions

The FTIR, XRD, DTA and TG results of the investigated filler on the base of inorganic substances confirmed the values, which are typical for natural bentonite with a high content of clay mineral, montmorillonite.

It can be concluded from present study of properties of the prepared model rubber compounds that the addition of filler on the base of natural clay, bentonite has a positive effect on physical–mechanical properties of final vulcanizates. The presence of bentonite filler in the matrix results in an increased strength and elasticity.

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