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Influence of modified inorganic fillers on thermal and spectral properties of n-component system of polymer blends

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Abstract

The inorganic (mineral) fillers based on kaolinite and montmorillonite are important ingredients which affect the characteristics of polymer mixtures and their products. Apart from rubber, chemistry of sulfur vulcanization affects the vulcanization system, which consists of vulcanizing agent, activators and accelerators. To proceed the sulfur vulcanization, is an important step the interaction between the curing ingredients and the creation of active sulfurating agent, which is involved in the networking of rubber macromolecules. This article is concerned with examining the interactions between the components of the vulcanization system and modified mineral fillers on the basis of clay minerals, namely phyllosilicates structure type 1:1 (kaolinite) and structure type 2:1 (montmorillonite), without the use of a polymeric matrix. Prepared n-component systems of the type of component / components – clay (in 1:1 ratio by mass) were studied by IR spectroscopy, X-ray diffraction analysis and thermal methods that allow detection of changes in the course of reactions rubber components, without the presence of the rubber matrix.

Keywords: kaolinite; montmorillonite; rubberizing component; cure temperature; thermal analysis; IR spectroscopy

1. Introduction

In the past, mineral fillers were mainly used because of reduced price as well as achievement of the white color of rubber products. The current trend is to use the clay minerals (montmorillonite, kaolinite) as nanofillers in the polymer blends because their small amount can affect the desired properties [1]. Kaolinite represents (phyllosilicate structure type 1:1) one of the most important mineral fillers which are used into the rubber mixtures. Kaolinite is the

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majority mineral of kaolin but it can also contain other related minerals – phyllosilicates which represent a group of smectites (montmorillonite), talc (illite), mica or feldspar. In recent years kaolinite could be used as a substitute for activated carbon as an adsorbent due to its availability and low price, and its good sorption properties [2]. The layered structure of kaolinite consists of one silica tetrahedral (SiO₄) unit stacked together with one gibbsite octahedral (AlO₆) units. Hydrogen bonding between the adjacent layers prevents expansion (swelling) of kaolin beyond its basal spacing of 0.72 nm. The unit cell of kaolinite has a neutral charge [3–5].

Montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. Isomorphous substitutions of Si⁴⁺ cation by Al³⁺ cation in the tetrahedral layer and those of Al³⁺ cations by Mg²⁺, Fe²⁺ etc. cations in the octahedral layer of the aluminosilicate structured clay minerals result in a negative charge which is balanced by the cations such as Na⁺, K⁺, Ca²⁺ etc. [6, 7]. Outstanding feature of this clay structure is that water and other organic/inorganic molecules can enter between the layers to expand basal spacing (“c” crystallographic direction). Thus, basal spacing in montmorillonite varies from a minimum value of 9.6 Å when there are non-polar molecules between the unit layers and above [8]. Chemistry of sulfur vulcanization affects the vulcanization system which consists of vulcanizing agent, activators and accelerators. To achieve the sulfur vulcanization, an important step is the interaction between the curing ingredients and the creation of active sulfurlating agent which causes the networking of rubber macromolecules [9, 10].

In the introduced study natural kaolinite from deposit Kaznĕjov with treatment of copper acetate has been modified and natural montmorillonite from Slovak deposit Jelšový Potok by the treatment of copper chloride has been modified. The main aim of the work was the investigation of 2- and 3-component systems which had been prepared on the basis of various alternations in relation to modified kaolin (CuKA) and montmorillonite (CuMMt) in function of filler, zinc oxide (ZnO) and stearic acid (SA) which were used as activators while benz-1,3-thiazol (Bt) was selected to be in a function of accelerator.

The effects of the treatments were examined by techniques of thermogravimetry/differential thermal analysis (DTA/TG), infrared spectroscopy (FTIR) and by XRD analysis.

2. Experimental

Kaolinite sample used in relation to this investigation was from a natural deposit Kaznĕjov. The chemical composition of the given sample was 44.9 % SiO₂, 47.49 % Al₂O₃, 3.34 % K₂O, 1.45 % Fe₂O₃, 1.61 % TiO₂ and LOI (lost of ignition) 9.24 %. Montmorillonite sample used in relation to this investigation was from a natural deposit Jelšový potok. The chemical composition of the given sample was 61.65 % SiO₂, 20.16 % Al₂O₃, 3.18 % MgO, 2.77 % Na₂O, 2.43 % Fe₂O₃. Chemicals for chemical treatment such as copper acetate (Cu(CH₃COO)·H₂O), copper chloride CuCl₂, sodium hydroxide (NaOH), zinc oxide (ZnO) and stearic acid (SA) were purchased from local supplier (Centralchem, Ltd) and benzothiazole Bt was purchased from Merck, Ltd. and used without further purification.

Compounds were mixed in porcelain mortar in the ratio of 1:1 by mass. We prepared systems of 2- and 3-components with modified clay minerals and heating samples at cure temperature 140 °C. The thermogravimetry TG and DTA was carried out on Derivatograph MOM Hungary from room temperature up to 800 °C in an air atmosphere at a heating rate of 10 °C.min⁻¹. Infrared absorption spectra were recorded using the FTIR Spectrometer Tensor 27 where the wavelength range was 4000 – 400 cm⁻¹ and the resolution was 4 cm⁻¹. X-ray powder diffraction (XRD) patterns were recorded on the high-temperature diffractometer (Panalytical Empyrean, software: High score, Cu Kα radiation in the region between 3° and 20° of (2Ө) at a speed of 2°/min⁻¹.

3. Results and discussion

3.1. Thermal analysis

For study of thermal behavior of the components with modified CuKA and CuMMt and their changes the thermal methods DTA/TG were used. On the DTA curve of CuKA+SA in Fig. 1, there is the occurrence of the two small endothermic effects at ~ 78 and ~ 109 °C. The first endothermic effect corresponds to the melting point of stearic acid and the second one indicates that after heating CuKA with stearic acid, copper stearate was formed. According
to literature data, melting point of copper stearate is about ~ 106 – 120 °C [11]. On the basis of decrease of dehydroxylation temperature to 553 °C, we assumed an interaction and a change in the structure of kaolin. After interaction of CuKA+SA+ZnO, the DTA curve exhibited an endotherm peak at ~ 128 °C corresponding to the melting point of zinc stearate [12]. In relation to the DTA curve of CuKA+Bt (Fig. 1), a broad exothermic peak with a maximum at 335 °C was observed and it is the most intense change. We assume that given exotherm is related to the thermal decomposition of benzothiazole which was physically bound to the surface of the modified kaolin [13].

Curves of CuMMt with cure compounds are compiled in the Fig. 2. Heating system CuMMt with SA was stearic acid intercalated into the interlayer space of modified form of montmorillonite and it could cause the further interaction between SA and present metal ion. On the basis of the DTA curves of CuMMt+SA (Fig. 2), there is the occurrence of the endothermic effects at ~ 90 and ~ 86 °C which can be attributed to the melting point of stearic acid or melting point of copper stearate [14].

The endotherm peaks at ~ 131 and 136 °C on curve CuMMt+SA+ZnO corresponding to the melting point of zinc stearate [12]. Using the DTA curves combinations (Fig. 3a), CuMMt+Bt several exothermic effects is observed at higher temperatures. Transition metal cations (Cu^{2+}) are characterized by relatively strong coordination properties and they allowed creating complex with Bt compound. Due to interaction between benzothiazole and Cu^{2+}, the thermal degradation is shifted to the higher temperatures (~ 700 °C) in comparison to the thermal decomposition of pure benzothiazole (267 °C) which can be seen in Fig. 3b. Thus we can assume that there was the occurrence of benzothiazole intercalation into the interlayer of modified CuMMt [15–17].
3.2. IR spectroscopy

Table 1 lists the selected absorption bands of the samples CuKA+SA+ZnO and CuKA+Bt. Vibration bands at \( \sim 1705 \sim 1707 \text{ cm}^{-1} \) and \( \sim 1472 \sim 1413 \text{ cm}^{-1} \) are attributed to the stretching vibration of the carboxylate group \( \nu_{\text{asym}}(\text{COO}) \) and \( \nu_{\text{sym}}(\text{COO}) \) in free stearic acid. At \( \sim 1586 \text{ cm}^{-1} \) and \( 1470 \sim 1444 \text{ cm}^{-1} \) are observed new absorption bands corresponding to the stretching vibration \( \nu_{\text{asym}}(\text{COO}^-) \) and \( \nu_{\text{sym}}(\text{COO}^-) \) of copper stearate carboxylate group [17]. Heat treatment of CuKA, stearic acid and zinc oxide was connected with stretching vibrations of carboxylate group \( \nu_{\text{asym}}(\text{COO}^-) \sim 1590 \sim 1538 \text{ cm}^{-1} \) and \( \nu_{\text{sym}}(\text{COO}^-) \sim 1468 \sim 1398 \text{ cm}^{-1} \), corresponding to the formation of zinc stearate. In relation to IR spectrum of CuKA+Bt, new band at \( \sim 3060 \text{ cm}^{-1} \) corresponding to the stretching vibration of CH aromatic ring of benzothiazole were observed. Skeletal vibration corresponding to the stretching vibration of the benzene ring \( \text{C} \equiv \text{C} \) occurs at \( \sim 1553 \sim 1581 \text{ cm}^{-1} \). The IR spectra are also recognized for the bands of stretching vibrations of \( \text{C} \equiv \text{N} \) and \( \text{N} = \text{C} \sim \text{S} \) groups at \( \sim 1454 \sim 1452 \text{ cm}^{-1} \) and at \( \sim 1420 \sim 1426 \text{ cm}^{-1} \), respectively [17]. These new bands confirmed that when modified form of CuKA with benzothiazole was heated, the complex compound was created there [18].

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>CuKA+Bt (cm(^{-1}))</th>
<th>CuKA+SA+ZnO (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(\text{C-H})_{\text{as}} )</td>
<td>3060</td>
<td>-</td>
</tr>
<tr>
<td>( \nu(\text{C-C}) )</td>
<td>1581 – 1520</td>
<td>-</td>
</tr>
<tr>
<td>( \nu(\text{C-N}) )</td>
<td>1454</td>
<td>-</td>
</tr>
<tr>
<td>( \nu(\text{N=C-S}) )</td>
<td>1424</td>
<td>-</td>
</tr>
<tr>
<td>( \nu_{\text{sym}}(\text{C-H}) )</td>
<td>-</td>
<td>2955 – 2916</td>
</tr>
<tr>
<td>( \nu_{\text{sym}}(\text{C-H}) )</td>
<td>-</td>
<td>2848</td>
</tr>
<tr>
<td>( \nu_{\text{sym}}(\text{COO}^-) )</td>
<td>-</td>
<td>1589 – 1540</td>
</tr>
<tr>
<td>( \nu_{\text{sym}}(\text{COO}^-) )</td>
<td>-</td>
<td>1468 – 1399</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>CuMMt (cm(^{-1}))</th>
<th>CuMMt+Bt (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(\text{OH}) )</td>
<td>3626</td>
<td>3624</td>
</tr>
<tr>
<td>( \nu(\text{H-O-H}) )</td>
<td>3441</td>
<td>3441</td>
</tr>
<tr>
<td>( \delta(\text{H-O-H}) )</td>
<td>1641</td>
<td>1658 – 1632</td>
</tr>
<tr>
<td>( \nu(\text{C-H})_{\text{as}} )</td>
<td>-</td>
<td>3098</td>
</tr>
<tr>
<td>( \nu(\text{C=C}) )</td>
<td>-</td>
<td>1585 – 1513</td>
</tr>
<tr>
<td>( \nu(\text{C=N}) )</td>
<td>-</td>
<td>1458, 1383</td>
</tr>
<tr>
<td>( \nu(\text{N=C-S}) )</td>
<td>-</td>
<td>1420</td>
</tr>
</tbody>
</table>

In the Table 2, there are selected bands of the IR spectra of CuMMt and CuMMt+Bt which were recorded at wavelength range \( 4000 \sim 400 \text{ cm}^{-1} \). In relation to IR spectrum of CuMMt+Bt, new bands at \( \sim 3098 \text{ cm}^{-1} \) corresponding to the stretching vibration of CH aromatic ring of benzothiazole were observed. Skeletal vibration corresponding to the stretching vibration of the benzene ring \( \text{C} \equiv \text{C} \) occurs at \( \sim 1558 \sim 1513 \text{ cm}^{-1} \). The IR spectra are also recognized for the bands of stretching vibrations of \( \text{C} \equiv \text{N} \) and \( \text{N} = \text{C} \sim \text{S} \) groups at \( \sim 1458, 1383 \text{ cm}^{-1} \) and at \( \sim 1420 \text{ cm}^{-1} \), respectively [16, 19, 20]. Benzothiazole with different transition metal ions forms complex compounds, and it is the most frequently coordinated through the atom of nitrogen or sulfur, respectively. Hydrophobisation of organo-modified clay surface was connected with the disappearance or reduced-intensity
bands of stretching vibrations of H\textsubscript{2}O at \(\sim 3439 - 3441\) cm\textsuperscript{-1}. Residual molecules of water form hydrogen bonding with benzothiazole molecules, thus affecting the arrangement of the organic molecules of Bt in the interlayer space of montmorillonite to bimolecular layers parallel to the basal surface [21, 22]. Vibration bands in IR spectrum of samples CuMMt+SA and CuMMt+SA+ZnO also confirmed formation of copper stearate and zinc stearate which were created at cure temperature.

### 3.3. XRD analysis

Diffraction patterns of the samples were obtained at a room temperature as well as at the high-temperature diffraction experiments in the temperature range \(25 - 250^\circ\)C. From the diffraction pattern CuKA+Bt (Fig. 4a), the reflection at \(\sim 5.6^\circ\) (d = 1.58 nm) corresponding to formation of the complex on the basis of connection benzothiazole together with copper ions which is in the structure of kaolinite. The intensity of the reflection with high temperature increased but it disappeared at \(\sim 200^\circ\)C. Heating process of the sample CuKA+SA (to 120 \(^\circ\)C) is connected with a small reflex at 6.10° 2\(\theta\) corresponding to the observation of copper stearate [23]. This reflection was not observed at high temperatures and it was probably because of copper stearate melting at \(\sim 106 - 120^\circ\)C. Transition from liquid-crystalline phase to an isotropic liquid occurs around 250 \(^\circ\)C but it cannot be estimated precisely because the thermal decomposition of copper stearate occurs simultaneously. From the diffraction pattern of CuKA+SA, the reflection at \(\sim 8.82^\circ\) (d = 1 nm), the intensity of which increased with temperature, was observed. Sidheswaran et al. [24] considered reflection at \(\sim 8.2^\circ\) (2\(\theta\)), d = 1.1 nm as evidence of successful intercalation.

**Fig. 4.** a) X-ray powder diffraction patterns of the CuKA+Bt at different temperatures and after heating at 25 \(^\circ\)C, b) X-ray powder diffraction patterns of the CuMMt+SA at different temperatures and after heating at 25 \(^\circ\)C.

Diffraction spectra of the CuMMt+SA are shown in Fig. 4b. Increasing the temperature to 150 \(^\circ\)C, the value of the interlayer space \(d(001)\) of the sample CuMMt was increased from 1.25 to 1.45 nm. On this basis, we assume that stearic acid was intercalated into the interlayer space of montmorillonite [25]. At temperatures above the melting point (\(\sim 70^\circ\)C), stearic acid created a single-layer complex in the interlayer space of smectites with a thickness of one molecule (monomolecular arrangement). This complex decomposed at \(\sim 250^\circ\)C and there is occurrence of the decrease of \(d(001)\) to 1.29 nm in samples [24, 26]. On the basis of the diffraction patterns of CuMMt+Bt, there is the shift of the first basal reflection of montmorillonite to the lower values and the interlayer space was increased to \(d(001) = 1.64\) nm. According to the mentioned facts, the benzothiazole was intercalated into modified CuMMt. In accordance with a literature, molecules of Bt were arranged to bimolecular layers parallel to the basal surface of montmorillonite [22].
4. Conclusion

The introduced paper was focused on examining of the interactions between the components of the vulcanization system and modified inorganic filler on the basis of modified clay minerals Cu²⁺-kaolinite and Cu²⁺-montmorillonite and it was without use of a polymeric matrix. Thermal analysis and IR spectroscopy revealed that in the presence of ZnO and SA at a cure temperature zinc stearate both in modified kaolinite and montmorillonite was formed. Heating process of Cu²⁺-kaolinite and Cu²⁺-montmorillonite with stearic acid led also to the formation of copper stearate. From results of X-ray analysis, we can assume that stearic acid was intercalated both into CuKA and CuMMt. Present copper ion has an impact on the mutual interaction between the modified CuKA and benzothiazole which was physically bound to the surface of the modified kaolinite. Benzothiazole with different transition metal ions forms complex compounds, and it is the most frequently coordinated through the atom of nitrogen or sulfur, respectively. Heating at a cure temperature the benzothiazole was intercalated into modified CuMMt. Molecules of Bt were arranged to bimolecular layers parallel to the basal surface of montmorillonite. Modification of fillers by Cu²⁺ cations promotes mutual interaction of clay minerals with accelerator on the basis of thiazole and with activator represented by stearic acid. The presented results provide new information about the use of modified clay products in the function of fillers and it can be verified by preparation of model rubber mixtures.

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