A comparative study of the modified phyllosilicate group of minerals isoprene for a new nanocomposite preparation

Izoprén ásványok módosított rétegszilikát csoportjának összehasonlító vizsgálata új nanokompozit fejlesztéséhez

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Abstract

In this study, new nanocomposites of biopolymers were prepared. Sunflower oil synthesized fatty amides (FA_{sf}), used as an organic compound to change the natural group of mineral clay phyllosilicate, sodium montmorillonite (Na- MMT) and potassium illite (K- ILT). The clay modification was accomplished by stirring the clay particles in an aqueous (FA_{sf}) solution which increases the clay layer distance from 1.28 to 2.79 nm of MMT and 1.18 to 1.33 nm of ILT because the action exchange capacity Na- MMT is much greater than the low cation exchange capacity K- ILT. The improved Na-MMT was then used as a natural rubber (NR) nanocomposite isoprene preparation. The modifier's interaction in the clay layer was defined by X- ray diffraction (XRD). The nanocomposite was synthesized through melt mixing of modified clay (MMT) and NR by a traditional method. Using XRD, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA), the nanocomposite was characterized. The results of XRD and TEM verified nanocomposite growth. Compared to pure NR, NR modified MMT nanocomposites show higher thermal stability. FA_{sf} as a vegetable oil derivative to modify clay will reduce dependence on surfactants based on petroleum. Such nanocomposite is considered environmentally friendly in addition to renewable resources.

Keywords: natural rubber, nanocomposite, fatty amides, phyllosilicate

Kulcsszavak: természetes gumi, nanokompozit, zsírsavamidok, rétegszilikát

1. Introduction

Thermoplastic elastomers are a class of rubber-like polymers, but can be treated as a thermoplastic polymer [1]. When combining rubbers and plastics, the most impressive results were obtained by the thermoplastic elastomers. The most suitable type of rubber for natural rubber producing countries are thermoplastic natural rubber among the different nonplastic rubbers. There have been several studies on processability and rheological properties in this field [2]. Clay (mineral phyllosilicate group) is one of the most commonly used non-black rubber fillers. It is a cheap natural mineral that was an important part of the rubber industry, it is used as an economical filler to adjust the processing and performance of natural and synthetic rubbers, but due to its large particle size and low surface operation, the strengthening ability of clay is small. The clay particles in the polymer matrix could only be spread on the microscale even though the clay consisted of layers of silicate with a planar structure of 1 nm thickness [3-4]. Through general methods of polymer production, the layers can not be isolated from each other. The most recent way to improve clay's enhancement potential is achieved by adjusting clays hydrophilic form to organophilic. This is

achieved by replacing clay interlayer cations with organic cations like alkylammonium. Some researchers have been able to intercalate different polymers in the clay interlayer using modified clay to prepare polymer/clay nanocomposites [5,6]. For modification of Na- MMT and K-ILT, mixed fatty amides (FA_{sf}) synthesized with vegetable (sunflower) oil were used. Modified Na- MMT was used to prepare new nanocomposite rubber/clay and modified K-ILT was used to prepare new traditional composite rubber/clay. In this study, two forms of rubber composite's properties have been explored using the above group of minerals of phyllosilicate. With FA_{sf} as a modifier for production of rubber/MMT nanocomposite and rubber/ILT traditional composite [7], rubber/modified Na-MMT is more thermal stability was observed compared to those used rubber/ modified K-ILT.

2. Materials and Methods

2.1 Materials

Sunflower was obtained from Ngo Chew Hong Oils and Fats(M) Sdn. Phyllosilicate was from Novo Nordisk, Denmark's. Urea, sodium hydroxide, and hexane were purchased from Merck, Germany. The Malaysian Rubber Board (MRB),

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Malaysia, kindly provided the natural rubber (NR) of SMR (CV60) grade. Both chemicals used were available in the highest purity.

2.2 Preparation of organoclay

Organoclay was made with a method of cationic exchange, where was Na^+ , triacylglyceride synthesized (FA_{SF}) alkylammonium ion was shared in the MMT. The procedure was prepared as mentioned by Al-Mulla et al. [7,8]. In a watery solution, in 600 ml of hot distilled water, sodium montmorillonite (Na-MMT) (4.00 g) was vigorously stirred for 1 hour to form a clay suspension [9,10]. FA_{SF} (4.50 g) was then dissolved in 400 ml of hot water and concentrated hydrochloric acid (16.00 ml). After being vigorously stirred at 80 °C for 1 hour, the organoclay suspension was filtered and washed with distilled water until a 1.0M silver nitrate solution. It was dried for 72 hours at 60 °C. The mixture was ground until the particle size was 100 ml before the nanocomposite was prepared [11-13].

2.3 Preparation of NR/ modified clay

An internal mixer (Haake Poldrive) prepared the planned quality of NR. For the first time, the NR was softened for 1 minute and blended in the second and third minutes with the required amount of modified clay. The compounds were then molded for 10 minutes with a pressure of 150 Kg/cm² in an electrically heated hydraulic press at 130 °C. The compounds were immediately cooled for 5 minutes at the end of the molding cycle [14]. Table 1 lists the quantity of NR and the modified clay used in this analysis.

Sample identity	Weight of NR (g)	Weight of modified clay (g)
NR modif.0	30.00	0.00
NR modif.1	29.70	0.30
NR modif.2	29.40	0.60
NR modif.3	29.10	0.90
NR modif.4	28.80	1.20
NR modif.5	28.50	1.50
NR modif.6	28.20	1.80

Modif.0, modif.1, modif.2, modif.3, modif.4, modif.5 and modif.6 = 0, 1, 2, 3, 4, 5 and 6 phr, respectively.

Table 1 Weight of modified NR and clay (modified Na-MMT and K-ILT)
1. táblázat Természetes gumi és agyag (módosított Na-MMT és K-ILT) aránya az egyes mintákban

2.4 Characterization

2.4.1 X-Ray diffraction (XRD) analysis

X-ray diffraction study was conducted using Shimadzu XRD 6000 diffractometer with CuK ($k = 0.15406 \text{ nm}$) radiation.

2.4.2 Thermogravimetric analysis (TGA)

A Perkin Elmer model TGA7 Thermogravimetry analyzer was used to test the thermal stability of the samples. The samples were heated from 35 to 800 °C with a 10 °C/min heating rate under the atmosphere of nitrogen with 20 ml/min nitrogen flow rate.

2.4.3 Transmission electron microscopy (TEM)

The dispersion of clay has been analyzed using electron microscopy (EFTEM) for energy filtering transmission. TEM images were taken in a 120 KeV acceleration voltage LEO 912 AB EFTEM. The specimens were made using a cryomicrotome Ultracut E (Reichert and Jung). With a diamond knife at 120 °C, thin pieces of about 100 nm were sliced [7].

3. Results and discussion

3.1 X-ray diffraction measurements

X-ray diffraction technique was used to measure the distance of the silicate layers from the clay and alkyl ammonium cations from the interlayer. This has also been used to calculate the distribution of modified clays in the NR matrix by the silicate layers. Table 2 indicates the alkylammonium (FA_{SF} -MMT and poorly modified FA_{SF} -ILT) interlayer gap of natural clay (Na-MMT) and modified clays [15]. The interlayer gap of Na-MMT for FA_{SF} -ILT and FA_{SF} -MMT has been extended from 1.18 nm to respectively 1.32 and 1.28 to 2.79 nm.

Type of clay	Exchange cation	2 θ (degree)	d-Spacing (nm)
Na-MMT	Na^+	6.88	1.28
FA_{SF} -MMT	RCO-NH_3^+	3.36	2.79
K-ILT	K^+	7.80	1.18
FA_{SF} -ILT	RCO-NH_3^+	6.45	1.32

Table 2 X-ray diffractometer of unmodified MMT, ILT and modified MMT, ILT
2. táblázat Röntgen diffraktométeres mérési eredmények módosított és módosítatlan MMT és ILT esetén

Table 3 summarizes the intercalated silicate layer in NR / unmodified MMT and NR / modified MMT nanocomposites obtained from the XRD study.

Composite/ clay	d-Spacing (nm)					
	1 phr	2 phr	3 phr	4 phr	5 phr	6phr
NR/Na-MMT	1.35	1.37	1.34	1.32	1.30	1.29
NR/ FA_{SF} -MMT	3.05	3.19	3.34	3.21	2.98	2.85
NR/K-ILT	1.22	1.23	1.25	1.21	1.20	1.19
NR/ FA_{SF} -ILT	1.36	1.37	1.38	1.39	1.36	1.33

Table 3 XRD analysis of composites of NR / unmodified MMT, ILT and NR / modified MMT, ILT

3. táblázat Röntgendiffrakciós analízis eredményei: természetes gumi és módosított MMT, ILT kompozitok valamint természetes gumi és módosított MMT, ILT kompozitok

3.2 Thermo gravimetric analysis (TGA)

Fig. 1 shows the weight loss curves for K-ILT, Na-MMT, FA_{SF} -ILT, FA_{SF} -MMT, NR. NR/ 3phr K-ILT, NR/2phr Na-MMT and NR/ 4phr FA_{SF} -ILT microcomposite, NR/ 3phr FA_{SF} -MMT nanocomposite containing water due to hydrated sodium cation (Na^+) intercalated inside the clay layers. The main difference between the unmodified clay thermogram and the organoclay thermogram is that the organic components in the organoclay decompose between 200 and 500 °C. As temperature rises 165 to 610 °C, the FA_{SF} decomposed. The cycle of decomposition at about 320 °C (Fig. 1c). It can be found that FA_{SF} -MMT decomposition temperatures (Fig. 1e) are higher than K-ILT (Fig. 1a), Na-MMT (Fig. 1b), pure FA_{SF} (Fig. 1c) and FA_{SF} -ILT

(Fig. 1d) temperatures. The increase in FA_{SF} decomposition temperatures in organoclays suggests a strong intermolecular interaction between the cations of alkylammonium and the clay. In other words, their decomposition temperature increases after the FA_{SF} ion is intercalated and bound to the clays silicate layers. Thermo gravimetric analyzes were also performed on the microcomposite NR / 3 phr K-ILT (Fig. 1g), NR / 2 phr Na- MMT (Fig. 1h), NR / 4 phr FA_{SF} - ILT (Fig. 1i) and NR / 3 phr FA_{SF} - MMT (Fig. 1j) nanocomposite to assess the effect of unmodified nanocomposite, poorly changed clay (poor organoclay FA_{SF} -ILT) and altered clay material (organoclay FA_{SF} MMT) in the thermal properties rubber matrix, the TGA results are shown in (Fig. 1f, g, h, i, j). The onset of nanocomposite degradation is higher for NR containing FA_{SF} - MMT (Fig. 1j) at 375 °C compared to pure NR (Fig. 1f), NR / 3phr K- ILT (Fig. 1g), NR /2 phr Na- MMT (Fig. 1h), NR / 4 phr FA_{SF} - ILT (Fig. 1i) microcomposite, respectively at 265, 270, 285 and 290 °C.

Fig. 1 TGA thermograms of (a): K-ILT, (b): Na-MMT, (c): FA_{SF} , (d): FA_{SF} -ILT, (e): FA_{SF} -MMT, (f):NR, (g): NR/3phr K-ILT, (h): NR/2 phr Na-MMT, (i): NR/4 phr FA_{SF} -ILT, (j):NR/3 phr FA_{SF} -MMT

1. ábra Termogravimetriai vizsgálatok eredményei (TGA): (a): K-ILT, (b): Na-MMT, (c): FA_{SF} , (d): FA_{SF} -ILT, (e): FA_{SF} -MMT, (f):NR, (g): NR/3phr K-ILT, (h): NR/2 phr Na-MMT, (i): NR/4 phr FA_{SF} -ILT, (j):NR/3 phr FA_{SF} -MMT

The results show that the thermal stability improves in (Fig. 1j) with the addition of the FA_{SF} -MMT, up to 3 phr loadings, and an increase above this percentage does not boost thermal stability. The presence of homogeneously dispersed silicate in the polymer surface obstructs the permeability of volatile degradation products from the substrate and helps to prolong nanocomposite degradation [16,17].

3.3 Transmission electron microscopy (TEM)

Fig. 2 shows transmission electron microscopy micrographs of NR composites supported by 4 phr FA_{SF} -ILT and 3 phr FA_{SF} -MMT. The FA_{SF} -ILT micrograph of NR/4 phr reveals that stack morphology is completely preserved in the NR matrix due to the incompatibility of both components (Fig. 2a). Dark bundles are the thickness of each layer of clay or agglomerates. Image, Fig. 2b shows TEM images of nanocomposites NR / 3 phr FA_{SF} -MMT showing good properties and composite effects. The dark bundles of the changed clay are scattered with an intercalated state in the NR matrix, which can be seen in the pictures [18]. Table 3 displays the silicate interlayer gap of the clay layer from the XRD study.

Fig. 2 TEM micrographs of (a): NR/4 phr FA_{SF} -ILT microcomposite and (b): NR/3 phr FA_{SF} -MMT nano-composite

2. ábra Transzmissziós elektronmikroszkóppal készített felvételek: (a): NR/4 phr FA_{SF} -ILT mikrokompozit és (b): NR/3 phr FA_{SF} -MMT nanokompozit

4. Conclusions

Sunflower oil synthesized fatty amides (FASF) have been used as an organic compound to modify the natural group of mineral clay phyllosilicates (Na-MMT & K-ILT). The presence of long chain fatty acids in FASF suggests that they should only be useful as surfactants to modify Na- MMT. Using modified MMT, new rubber / clay nanocomposites (nano- NR) were prepared. Rubber nanocomposites developed using FASF as a modifier display more thermal stability compared to microcomposites produced on the basis of poorly configured ILT with NR, these are considered environmentally friendly nanocomposites.

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