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

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, but 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 law 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 [3–5]. Through general methods of polymer production, the layers can be not 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 (FAAM) 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 FAAM 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),...
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 for 1 minute and blended in the second and third minutes with the required amount of modified clay. The compounds were then 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 air atmosphere of nitrogen with 20 ml/min nitrogen flow rate.

2.4 Characterization

2.4.1 X-Ray diffraction (XRD) analysis

X-ray diffraction study was conducted using Shimadzu XRD 6000 diffractometer with CuK (λ= 0.15406 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 2.79 nm.

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>Exchange cation</th>
<th>2θ (degree)</th>
<th>d-Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MMT</td>
<td>Na⁺</td>
<td>6.88</td>
<td>1.28</td>
</tr>
<tr>
<td>FA<del>SF</del>–MMT</td>
<td>RCO-NH₃⁺</td>
<td>3.36</td>
<td>2.79</td>
</tr>
<tr>
<td>K-ILT</td>
<td>K⁺</td>
<td>7.80</td>
<td>1.18</td>
</tr>
<tr>
<td>FA<del>SF</del>–ILT</td>
<td>RCO-NH₃⁺</td>
<td>6.45</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 3 XRD analysis of composites of NR / unmodified MMT, ILT and NR / modified MMT nanocomposites obtained from the XRD study.

<table>
<thead>
<tr>
<th>Composite/ clay</th>
<th>1 phr</th>
<th>2 phr</th>
<th>3 phr</th>
<th>4 phr</th>
<th>5 phr</th>
<th>6 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/Na-MMT</td>
<td>1.35</td>
<td>1.37</td>
<td>1.34</td>
<td>1.32</td>
<td>1.30</td>
<td>1.29</td>
</tr>
<tr>
<td>NR/FA<del>SF</del>–MMT</td>
<td>3.05</td>
<td>3.19</td>
<td>3.34</td>
<td>3.21</td>
<td>2.98</td>
<td>2.85</td>
</tr>
<tr>
<td>NR/K-ILT</td>
<td>1.22</td>
<td>1.23</td>
<td>1.25</td>
<td>1.21</td>
<td>1.20</td>
<td>1.19</td>
</tr>
<tr>
<td>NR/FA<del>SF</del>–ILT</td>
<td>1.36</td>
<td>1.37</td>
<td>1.38</td>
<td>1.39</td>
<td>1.36</td>
<td>1.33</td>
</tr>
</tbody>
</table>

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

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 FS~SF~ MMT nano composite 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
The increase in FA$_{SP}$ decomposition temperatures in organoclay suggests a strong intermolecular interaction between the cations of alkylammonium and the clay. In other words, their decomposition temperature increases after the FA$_{SP}$ ion is intercalated and bound to the clay silicate layers. Thermo gravimetric analyses were also performed on the microcomposite NR / 3 phr K- ILT (Fig.1g), NR / 2 phr Na- MMT (Fig.1h), NR / 4 phr FA$_{SP}$ – ILT (Fig. 1i ) and NR / 3 phr FA$_{SP}$ – MMT (Fig. 1j) nanocomposite to assess the effect of unmodified nanocomposite, poorly changed clay (poor organoclay FA$_{SP}$-ILT) and altered clay material (organoclay FA$_{SP}$ MMT) in the thermal properties of 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$_{SP}$ – MMT (Fig. 1j) at 375 °C compared to pure NR (Fig. 1f), NR / 3 phr K- ILT (Fig. 1g), NR / 2 phr Na- MMT (Fig. 1h), NR / 4 phr FA$_{SP}$ – ILT (Fig. 1i) microcomposite, respectively at 265, 270, 285 and 290 °C.

3.3 Transmission electron microscopy (TEM)

Fig. 2 shows transmission electron microscopy micrographs of NR composites supported by 4 phr FA$_{SP}$ – ILT and 3 phr FA$_{SP}$ – MMT. The FA$_{SP}$ – 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$_{SP}$ – 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.

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.

References


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

Fig. 2 TEM micrographs of (a): NR/4 phr FA$_{SP}$ – ILT microcomposite and (b): NR/3 phr FA$_{SP}$ –MMT nanocomposite

2. ábra Transzmissziós elektronmikroszkóppal készített felvételek: (a): NR/4 phr FA$_{SP}$ –ILT mikrokompozit és (b): NR/3 phr FA$_{SP}$-MMT nanokompozit


