



THERMAL, FLAMMABILITY, AND MORPHOLOGICAL PROPERTIES OF SEPIOLITE-FILLED ETHYLENE PROPYLENE DIENE MONOMER COMPOSITES

(Sifat Terma, Kemudahbakaran dan Morfologi bagi Komposit Etilena Propilena Monomer Diena Terisi Sepiolit)

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Abstract

The effects of different sepiolite contents on the thermal stability, flammability, and morphological properties of sepiolite-filled ethylene-propylene-diene monomer composites were studied. These sepiolite-filled composites, containing 0-70 parts per hundred rubber (phr) of sepiolite fillers, were prepared through the conventional processing method of using a two-roll mill. The results demonstrated a significant increase in the thermal stability of the composites when sepiolite loading was increased compared to unfilled composites. The results also showed a decrease in the linear rate of burning of the composites with increasing sepiolite loading. The morphological study confirmed the presence of unburned sepiolite, which increased the flammability resistance of the composites.

Keywords: sepiolite, flammability, rubber, thermal stability, morphology

Abstrak

Kesan kandungan sepiolit yang berbeza terhadap kestabilan terma, kemudahbakaran, dan ciri-ciri morfologi bagi komposit etilena-propilena-monomer diena terisi sepiolit telah dikaji. Komposit terisi sepiolit yang mengandungi 0 hingga 70 bahagian per seratus getah (bsg) telah disediakan melalui kaedah lazim menggunakan mesin pengisar bergulung dua. Keputusan menunjukkan peningkatan ketara pada kestabilan terma komposit apabila kandungan sepiolit ditambah berbanding dengan komposit tidak terisi. Hasil kajian turut menunjukkan penurunan kadar pembakaran selari komposit ini dengan penambahan kandungan sepiolit. Kajian morfologi mengesahkan kehadiran sepiolit yang tidak terbakar yang telah meningkatkan ketahanan kemudahbakaran komposit ini.

Kata kunci: sepiolit, kemudahbakaran, getah, kestabilan terma, morfologi

Introduction

The demand for clay minerals expands through various applications and their role has undoubtedly become more profound since the discovery of clay varieties at the end of the last century. Clay minerals are produced through the weathering process, in which the clay species experience changes through sedimentation and burial courses [1]. Clay minerals have long been incorporated in plastics or elastomer matrix as fillers. Clay-based materials have been most widely investigated among other potential nanocomposite alternatives, possibly due to the abundant sources of clay materials and because the study of their intercalation chemistry is already established [2]. Currently, the most

intensive researches have been focused on layered silicates based on the smectite class of aluminum silicate clays, especially on montmorillonites (MMT) as the reinforcing phase [3]. However, these nanofillers are not the only type of nanoclays that can be incorporated into polymer matrices. Recently, several studies have focused on the use of sepiolite, a nanofiller with a needle-like morphology, to reinforce nanocomposites [4].

Sepiolite can be expressed as $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{OH}_2)_4(\text{H}_2\text{O})_8$ [5, 6], and it is also chemically known as the hydrated magnesium silicate [7]. This compound belongs to the 2:1 phyllosilicate structure; one octahedral sheet is sandwiched between two tetrahedral sheets. It is microfibrillar, with 2-10 nm particles and exhibits nanosized tunnel structures [8, 9]. The fibrous-like structure of sepiolite is believed to be more easily dispersed in the polymer matrix compared to platelet-like minerals, such as MMT [10]. Moreover, sepiolite can prevent flocculation when it is distributed within the network of a polymer and reduce filler agglomeration [5]. The presence of clay particles within a polymer matrix could enhance fire retardant properties. These particles can contribute to the formation of a char layer at the silicate surface, behaving as a barrier that reduces the oxygen transmission rate, retards the spread of flames, and help to keep the structural integrity of the burned sample [11]. As a potential filler, sepiolite offers promising advantages that could improve the mechanical, thermal, and flammability properties of the composites as well as reduce cost.

Polymer matrices, such as natural rubber [12, 13], nitrile rubber [14], styrene butadiene rubber [15, 16], silicone rubber [17], acrylonitrile butadiene styrene [18], polyether imide [19], and polyamide 6 [20] have been filled with sepiolite to improve their properties. However, little attention has been paid to the properties of sepiolite in ethylene-propylene-diene monomer (EPDM). Wang et al. [21] conducted several preliminary investigations based on the surface free energy of EPDM/Sepiolite nanocomposites. However, they had only reported a limited number of properties of the EPDM/Sepiolite composites. Therefore, further studies are necessary to generate positive results from the various properties of the sepiolite-filled EPDM composites.

Based on a literature survey, none of the previous reports have dealt with the effects of sepiolite on the thermal stability, flammability, and morphology of the char residue of EPDM/Sepiolite composites. Thus, this study has focused on investigating the potential effects of using sepiolite as fillers on the thermal stability, flammability, and morphological properties of EPDM/Sepiolite composites at various loadings.

Materials and Methods

Materials

The EPDM used in this study was Vistalon 2504N that contained 54% ethylene, with 3.6% of ethylidene norbornene (ENB) and Mooney viscosity [ML (1+4) at 125 °C] of 26.8 (Mooney Unit), which was purchased from ExxonMobil. The density of the EPDM was 0.818 g/cm³ as measured using an analytical balance (Precisa, model XB 220A). The sepiolite clay was purchased from Hebei DFL Minmet Refractories Corp., China. Meanwhile, other compounding ingredients were purchased from Bayer (M) Ltd., namely, zinc oxide, stearic acid, tetramethyl thiuram disulphide (TMTD), mercaptobenzothiazole (MBT), and sulphur.

Sample preparation

The sepiolite was dried in an oven for 24 hours at 80 °C before mixing to remove any existing moisture. Table 1 lists the compounding formulations for EPDM/Sepiolite composites, in which each compound was prepared using a laboratory scale (160 × 320 mm²) and a two-roll mill (model XK-160). All composites were mixed for 21 minutes according to the ASTM D3568. The optimum cure time (t_{90}) and scorch time (t_{s2}) were obtained by utilising the Monsanto Moving Die Rheometer (model MDR2000) at 160 °C. Based on their respective t_{90} values, the compounds were compression moulded into 3 mm rectangular sheets, with a dimension of 125 mm × 13 mm × 3 mm using the KAO-Tieh GO Tech Compression Moulding Machine, at 160 °C with a force of 10 MPa.

Table 1. Compounding formulations for EPDM/Sepiolite Composites (phr)

Materials	Content (phr)
EPDM	100
Zinc Oxide	5
Stearic Acid	1.5
TMTD ^a	1.5
MBT ^b	0.8
Sulphur	1.5
Sepiolite	0,10,20,30,70

^a Tetramethyl thiuram disulphide,

^b Mercaptobenzothiazole

Thermal analysis

Thermogravimetric analysis (TGA) was performed on 10 mg samples that were heated from 30 to 600 °C at a ramp rate of 20 °C/min, under nitrogen flow (50 mL/min) using a Perkin Elmer Pyris 6 thermogravimetric analyser. The analysis involved measuring weight loss as a function of temperature where the TGA curve was recorded.

Flammability test

The samples' flammability was tested using the horizontal burning test in accordance with ASTM D635. Initially, samples with a dimension of 125 mm × 13 mm × 3 mm were prepared. The flame was ignited on one end of the sample using natural gas. The burnt length and the time for the flame front to reach the 25 mm reference mark, and travel to the 100 mm reference mark were recorded. Equation (1) was used to calculate the linear rate of the burning samples.

$$V = 60L/t \quad (1)$$

where V is the linear burning rate, L is the burnt length, and t is the time in minutes [22].

Morphological study

The morphology of the charred surfaces of the EPDM/Sepiolite composites was examined under the Zeiss Supra 35-VP field emission scanning electron microscope (FESEM) at 1,000x magnification. The test specimens were first coated with a thin layer of gold-palladium. The coating was necessary to eliminate any electrostatic charges during the examination.

Results and Discussion

Thermal stability analysis

Figure 1 and Table 2 present the thermal degradation properties of EPDM/Sepiolite composites in comparison with unfilled EPDM compound. In general, weight loss is used to determine the thermal stability of the polymer composites. The heating process will prompt the production of volatile products, hence reducing the weight of the compound [23].

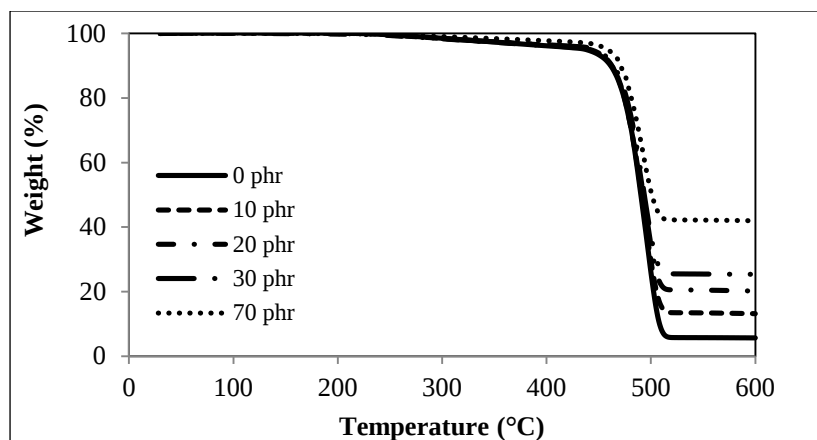


Figure 1. TGA curves for unfilled EPDM and sepiolite-filled EPDM composites

Table 2. Thermal properties of unfilled EPDM and sepiolite-filled EPDM composites

Sepiolite Content (phr)	Temp at 5% wt. Loss (°C)	Temp at 50% wt. Loss (°C)	Max wt. Loss (%)	Char Residue at 600 °C (%)
0	432	489	56.4	5.7
10	438	491	52.3	13.2
20	440	492	44.1	20.2
30	446	494	42.3	25.4
70	458	500	34.5	41.9

Overall, all sepiolite-filled EPDM composites exhibited improved thermal stability. The data showed that the incorporation of sepiolite into the EPDM matrix had increased the overall thermal stability of the composites because sepiolite acted as a thermal insulator [24]. For instance, the temperature at 5% of weight loss of unfilled EPDM compound was at 432 °C, while 70 phr of sepiolite in the EPDM had increased the temperature up to 458 °C. The char residue at 600 °C was increased from 5 to 41%, with sepiolite clay loadings that ranged between 0 to 70 phr. This result indicated that sepiolite was the mass transport barrier [17]. Reduction in the thermal energy transfer had halted the thermal degradation process, while the decomposition process was hindered by the fibrous structure of the sepiolite. These deterrents had resulted in the reduced rate of volatility loss, and higher amount of residues. Additionally, the well-dispersed sepiolite may have restricted the mobility of the polymer chains, which led to the delayed heating.

Flammability analysis

Figure 2 displays the effect of different sepiolite loadings on the flammability of EPDM/Sepiolite composites, as determined by the linear rate of burning. The linear rate of burning was reduced when sepiolite concentration was increased. The EPDM composite with 70 phr sepiolite exhibited the longest burnout time compared to the unfilled composites and subsequently, exhibited the lowest linear rate of burning. The linear rate of burning agreed with the thermal properties of the composites, as previously discussed. The fibrous structure of the sepiolite and the formation of carbonaceous char layers during the burning process had contributed to the fire resistance nature of these composites [25]. During the burning process, sepiolite had formed a protective layer of char on the matrix surface, by acting as an insulating barrier against oxygen, and preventing heat from reaching the underlying matrix. Therefore, the amount of decomposed volatiles that escaped from the interior polymer matrix was reduced, which resulted in a longer time to burn, and subsequently, reduced the linear rate of burning. This process was further inhibited by the formation of char at higher filler loadings, which shielded

the underlying EPDM matrix from heat.

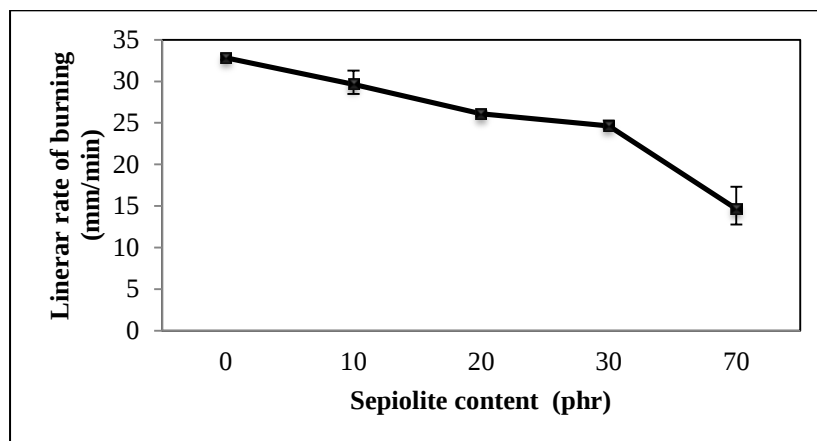


Figure 2. The effect of different sepiolite loadings on the flammability of EPDM/Sepiolite composites

Morphologies of charred surfaces

Figures 3(a) and (b) show the charred surfaces of EPDM/Sepiolite composites at 30 and 70 phr of sepiolite loadings, respectively. The 30 phr sepiolite, as observed in Figure 3(a), had delayed the burning time of the composite due to the presence of unburned sepiolite. The unburned sepiolite had impeded the transport of flammable vapour, thus reducing the flammability rate of the EPDM/Sepiolite composite. This observation confirmed the reduction of the linear rate of burning and the increment of char residues of the EPDM/Sepiolite composites, as shown by the TGA results when the sepiolite loadings were increased.

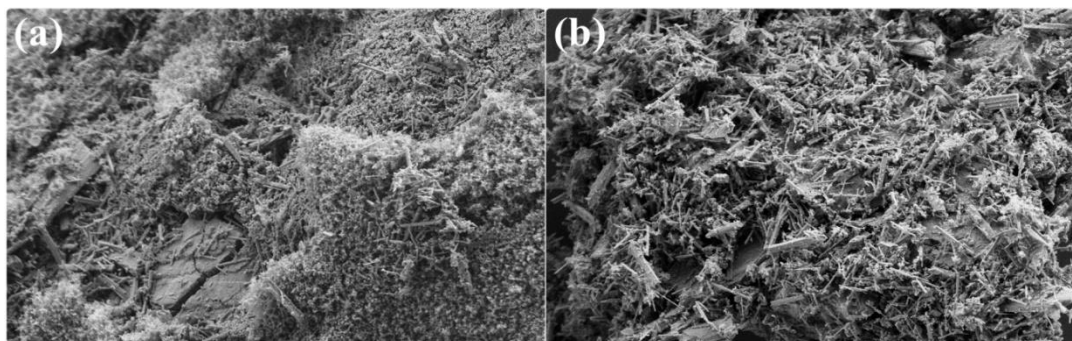


Figure 3. Char residues collected following the flammability test of EPDM/Sepiolite composites, with sepiolite loadings of: (a) 30 phr; and (b) 70 phr at 1,000 $\times$ magnification

Conclusion

The thermal stability of the EPDM/Sepiolite composites was remarkably improved with increased clay loadings compared to the thermal stability of the unfilled compound. Sepiolite had acted as a thermal insulator by reducing the transfer of thermal energy through the composites. The presence of unburned sepiolite had reduced the linear rate of burning of the EPDM/Sepiolite composites. FESEM micrographs confirmed that the unburned sepiolite particles had created a protective barrier, which reduced the linear rate of burning.

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