

# **Effect of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the flammability and thermal degradation properties of epoxy composites**

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**Abstract:** As-received sepiolite/epoxy systems and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite/epoxy systems were prepared, and the contents of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were kept as 2 and 4 wt%, respectively. Compared with sepiolite, the effect of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the flame retardancy, combustion properties, thermal degradation, thermal degradation kinetics and thermomechanical properties of epoxy resin was investigated systematically by limiting oxygen index (LOI), cone calorimeter (Cone), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Some interesting results had been acquired. The addition of sepiolite decreased heat release rate (HRR), total smoke production (TSP) and smoke production rate (SPR), and obviously improved LOI values of epoxy composites. Compared with sepiolite, the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further reduced parameters mentioned above of epoxy composites, and further enhanced LOI values and char residues after cone test. There might be a synergistic effect between sepiolite and Fe<sub>3</sub>O<sub>4</sub> on flame retardant epoxy composite. TGA results indicated that the addition of sepiolite had slight effect on the thermal degradation of epoxy composites; however, the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite accelerated the thermal degradation of epoxy composites. DMA results showed that the addition of both sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite increased the glass transition temperature (T<sub>g</sub>) of epoxy composite. The results obtained in this paper supplied an effective solution for developing excellent flame retardant properties of polymeric materials.

**Keywords:** Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite; Flame retardancy; Epoxy composite; Thermal degradation properties; Thermomechanical properties

## 1. Introduction

Polymer-based materials have been almost used everywhere in the current society. However, due to the flammability of most polymeric materials, series flame retardant technologies have been developed to different polymers in recent years, such as polyolefin<sup>[1-4]</sup>, polyester<sup>[5, 6]</sup>, rubber<sup>[7]</sup>, etc. Amongst these polymeric materials, due to the outstanding properties of strong adhesion, good mechanical properties, low shrinkage, high thermal stability, an excellent solvent and chemical resistance, epoxy resin (EP) have widely applied in the fields of adhesives, coating, laminates and composites and electronic/electrical insulation <sup>[8-12]</sup>. As well as other common polymers, its high flammability of epoxy resin badly restricted its application in the fields which needed good flame retardancy of materials. Thus, increasing researchers are interested in improvement of the flame retardancy of epoxy resin <sup>[13-15]</sup>.

To enhance the flame retardancy of epoxy resin, a feasible solution was through incorporation of both non-reactive and reactive flame retardants <sup>[16]</sup>. Recently, kinds of boron- <sup>[17, 18]</sup>, phosphorus- <sup>[19, 20]</sup> and silicon-containing <sup>[21, 22]</sup> flame retardants have been introduced into epoxy resin to improve its flame retardancy. To acquire the favorable flame retardancy of epoxy resin, a higher loading of these flame retardants should be added. However, the higher loading of these flame retardants might damage the mechanical properties of epoxy resin. Over the past decades, nanocomposite technology has aroused a great deal of attention <sup>[23]</sup>. It has been found that clay, such as montmorillonite (MMT) <sup>[24, 25]</sup> and sepiolite <sup>[26-28]</sup>, is an effective candidate to improve the flame retardancy of polymeric materials. Sepiolite, a type of clay, is a kind of hydrated magnesium silicate with a needle-like structure. And it is very different from other phyllosilicates with a lamellar structure and its ideal chemical formula is  $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4 \cdot (\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  <sup>[26, 27]</sup>. Its structure is composed of two layers of silica tetrahedrons which are linked by magnesium ions in octahedral coordination. And silica tetrahedrons extend as a continuous layer; however, the octahedral sheets are not continuous, which is different from other phyllosilicates <sup>[26, 27]</sup>. Sepiolite is easily processable in polymeric materials because of its structural

characteristics. Especially, the addition of sepiolite improved the mechanical properties <sup>[29-31]</sup> and flame retardancy of polymeric materials <sup>[26, 27, 32, 33]</sup>. Borriello et al <sup>[26]</sup> has reported effects of sepiolite on thermal degradation and flame retardancy of epoxy resin. The results indicated that addition of pre-heated sepiolite slightly affected the thermal degradation properties and obviously improved the flame retardancy of epoxy resin in reducing the heat release rate. What is more, there are some papers which reported the synergistic effect on the flame retardancy between sepiolite and intumescent flame retardants <sup>[27, 32]</sup>. And the suitable additive amount of sepiolite further improved the flame retardancy of intumescent flame retardant polymeric materials. However, there is no paper reported the effect of Fe<sub>3</sub>O<sub>4</sub>-sepiolite on the flame retardancy and thermal degradation properties of epoxy composites.

In this work, as-received sepiolite/epoxy systems and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite/epoxy systems were prepared. Compared with sepiolite, the effect of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the flame retardancy, combustion properties, thermal degradation, thermal degradation kinetics and thermomechanical properties of epoxy resin was investigated systematically by limiting oxygen index (LOI), cone calorimeter (Cone), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Some interesting results had been acquired.

## **2. Experimental**

### **2.1 Materials**

Epoxy resin (L20) was provided by Faserverbundwerkstoffe<sup>®</sup> Composite Technology (Germany). Diamino Diphenyl sulfone (DDS) was purchased from TCI Chemicals Company. Sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were supplied by TOLSA Co. Ltd. (Madrid, Spain), and used as received. Sepiolite doped with a 35% of Fe<sub>3</sub>O<sub>4</sub> particles was synthesized according to the procedure described by A Esteban-Cubillo et al <sup>[34]</sup>.

### **2.2 Preparation of epoxy composites**

A fixed weight fraction (2, 4 wt%) of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was used for

the preparation of epoxy composites. In order to achieve a satisfactory dispersion, a three-roll mill from EXAKT® 80E (Advanced Technologies GmbH, Germany) was utilized to mix sepiolite and epoxy resin for 15 min. The whole suspension was milled two times to obtain a uniform dispersion. And firstly, the gap between the feed roll and the apron roll was set to be 90 and 20  $\mu\text{m}$ . Secondly, the gap between the feed roll and the apron roll was set to be 60 and 20  $\mu\text{m}$ . Then, the suspension was heated to 125 °C followed by adding DDS to the above suspension and stirring for 15 min until DDS totally dissolved. Subsequently, the suspension was put into a vacuum oven at 110 °C for 10 min in order to drive off all of bubbles. And then the suspension was immediately poured into the pre-heated silicon-rubber moulds. The curing procedure was set as follows: 160 °C for 2 h, 180 °C for 2 h and 200 °C for 1 h. Following the procedure, epoxy resin, epoxy composite with 2% sepiolite, epoxy composite with 4% sepiolite, epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were prepared.

## **2.3 Measurements**

### **2.3.1 Thermogravimetric analysis (TGA)**

A Q50 Instruments (TA Instruments Co., USA) thermogravimetric analyzer was utilized to investigate thermal stability properties of samples at heating rates of 5, 10, 20, 30 and 40 °C/min, respectively. About 10 mg of the sample was examined at a flowing rate of 90 mL/min from 30 to 700 °C in N<sub>2</sub> atmosphere. All samples were run in duplicate. The mass of the instrument was reproducible to within  $\pm 0.1\%$ , and the temperature was reproducible to within  $\pm 1$  °C.

### **2.3.2 Limiting oxygen index (LOI)**

An oxygen index model instrument (Fire Testing Technology, UK) was exploited to test LOI value of sample, and sheet dimensions of the sample were 130 mm  $\times$  6.5 mm  $\times$  3.2 mm according to ASTM D2863-97.

### **2.3.3 Cone Calorimeter (Cone)**

The flammability of epoxy composites was characterized by a cone calorimeter (Fire Testing Technology, UK), following the procedures in ISO 5660-1. Square specimens (100 mm × 100 mm × 3 mm) were mounted into aluminum foil and irradiated horizontally at a heat flux of 50 kW/m<sup>2</sup>. Each sample was run in three times.

#### **2.3.4 Dynamic Mechanical Analysis (DMA)**

A dynamic mechanical analyzer (DMA Q800, TA Instruments) was utilized to investigate thermomechanical properties of epoxy composites, and the dimensions of the sample were 35 mm × 10 mm × 2 mm. The operation procedure was set as follows: the heating rate was 3 °C/min, the loading frequency was 1 Hz, the oscillation amplitude was 15 μm, the temperature ranged from room temperature to 280 °C and the clamp was a single cantilever one.

### **3. Results and discussion**

#### **3.1 Flammability of sepiolite based epoxy composites via LOI test**

To investigate effect of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the flame retardancy of epoxy composite, limiting oxygen index (LOI) test was carried out. The effect of the content of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the flame retardancy of epoxy composite was shown in Figure 1. LOI value of epoxy composite with 2% sepiolite reached 29.8%, which was higher than that of epoxy resin, 23.8%. It indicated that the addition of 2% sepiolite badly improved flame retardancy of epoxy resin. And LOI value of epoxy composite with 4% sepiolite was 30.1%, which was similar to that of epoxy composite with 2% sepiolite. The addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further enhanced the LOI value of epoxy composite. The LOI value of epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was 33.8%, which was much higher than that of epoxy composite with 2% sepiolite; and LOI value of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was 36.7%, which was also much higher than that of epoxy composite with 4 % sepiolite. This indicated that there existed synergistic effect between sepiolite and Fe<sub>3</sub>O<sub>4</sub> on the flame retardancy of epoxy resin.

### 3.2 Combustion behaviors of sepiolite based epoxy composites via cone test

Cone calorimeter was utilized to investigate flammability and potential fire safety of polymeric materials under-ventilated conditions. And it was one of the most effective bench-scale tests and exploited to predict the combustion behaviors of polymeric materials in a real fire [21]. In order to investigate the effect of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the combustion properties of epoxy composites, cone calorimeter test was carried out. Some important data obtained from the cone calorimeter test, such as peak heat release rate (PHRR), time to PHRR (TPHRR), fire growth rate index (FIGRA), time to ignition (TTI), total smoke production (TSP), residue and total heat release (THR), were also summarized in Table 1.

**Heat release rate (HRR).** HRR curves of epoxy composites with different contents of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were presented in Figure 2. It was noted that the neat epoxy resin burned faster after ignition and a sharp PHRR appeared with a PHRR value of 1193 kW/m<sup>2</sup>. In the case of epoxy composite with 2% sepiolite, the PHRR value was 1288 kW/m<sup>2</sup>, which was 8.0% higher than that of neat epoxy resin, and this phenomenon was accordant with the results of Borriello et al [26]. However, the PHRR value of epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was 1093 kW/m<sup>2</sup>, which was 8.4% lower than that of neat epoxy resin. This indicated that the effect of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on flame retardancy of epoxy resin was better than that of sepiolite. In the case of epoxy composite with 4% sepiolite, the PHRR value was 963 kW/m<sup>2</sup>, which was 19.5% lower than that of neat epoxy resin. What is more, the PHRR value of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was 883 kW/m<sup>2</sup>, which was 26.0% lower than that of neat epoxy resin. This also indicated that the effect of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on flame retardancy of epoxy resin was better than that of sepiolite. And there might exist synergistic effect between sepiolite and Fe<sub>3</sub>O<sub>4</sub> on the flame retardancy of epoxy resin. Comparing HRR curves in Figure 2, it was noted that there was an obvious delay of PHRR for epoxy composite with 4% sepiolite and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. The system released heat when it began to burn. For epoxy composite with 4% sepiolite, the heat release rate increased quickly to a flat, and then arrived at a maximum PHRR, and gradually

was flattened down. For epoxy composites with 4%  $\text{Fe}_3\text{O}_4$ -sepiolite, the heat release rate reached a PHRR quickly after combustion, then decreased slowly, and then increased to a maximum PHRR, and gradually was flattened down. This phenomenon may be caused by the formation of char layer. The formed char layer protected the epoxy composites from both mass/heat transfer, reducing the heat release. However, the char layer might not stand the higher temperature for a long time, because the char layer was fragile and cracked.

Figure 3 presented the digital photographs of the residual char after cone test. It was observed that the char layer of epoxy resin was the most fragile and cracked. There were many pores on the surface of the char layer, therefore, the char layer did not effectively prevent both mass and heat transfer. Compared with epoxy composites with 2% sepiolite, the char layer of epoxy composites with 4% sepiolite was more compact and strong, and it was the reason for better flame retardancy of epoxy composites with 4% sepiolite than that of epoxy composites with 2% sepiolite. While in case of epoxy composites with  $\text{Fe}_3\text{O}_4$ -sepiolite, the color of char layer was orange, which was caused by the color of  $\text{Fe}_2\text{O}_3$ . This indicated that  $\text{Fe}_3\text{O}_4$  was oxidized to form  $\text{Fe}_2\text{O}_3$  in combustion process of epoxy composites with  $\text{Fe}_3\text{O}_4$ -sepiolite. Compared with epoxy composites with 2%  $\text{Fe}_3\text{O}_4$ -doped sepiolite, the char layer of epoxy composites with 4%  $\text{Fe}_3\text{O}_4$ -doped sepiolite was more compact and strong. And this was also the reason for better flame retardancy of epoxy composites with 4%  $\text{Fe}_3\text{O}_4$ -doped sepiolite. Compared with epoxy composites with sepiolite, the char layer of epoxy composites with  $\text{Fe}_3\text{O}_4$ -doped sepiolite was more compact and thick. It protected epoxy composites to transfer heat and mass, improving the flame retardancy of epoxy composites.

From Figure 2 and Table 1, it can be observed that the TTI values of epoxy composite with sepiolite, 49 and 61 s, respectively, were higher than that of neat epoxy resin, 45 s. There was an initial delay period before epoxy composite started to release heat, and the reason for this phenomenon was that the temperature of epoxy composite was below the thermal degradation temperature of epoxy matrix. And this indicated that the addition of sepiolite improved the thermal degradation temperature



of epoxy matrix. However, the TTI value of epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite, 42 s, was lower than that of neat epoxy resin; and that of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was the same as that of neat epoxy resin. The reduction of TTI might be due to the fact that doped Fe<sub>3</sub>O<sub>4</sub> accelerated thermal degradation of epoxy matrix, and that the system began to release heat when the volatiles produced during the thermal degradation started to burn.

**Mass Loss (ML).** Figure 4 presented mass loss (ML) curves of sepiolite based epoxy composites. At the end of burning, there were 7.6, 12.9, 17.0, 24.3 and 27.9 % of residue char left, respectively, for pure epoxy resin, epoxy composite with 2% sepiolite, epoxy composite with 4% sepiolite, epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. From Figure 4 and Table 1, it was noted that the addition of sepiolite increased the amount of residual char for epoxy resin, and that the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further increased the amount of residual char for epoxy resin. This indicated that the addition of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite might catalyze epoxy matrix to form more residual char to prevent epoxy matrix from mass/heat transfer.

**Smoke release.** Total smoke production (TSP) and Smoke production rate (SPR) were the key cause of death during fire [27]. Thus, the investigation of TSP and SPR for polymeric composites would be useful in showing the potential hazard under well-ventilated conditions indicated by these materials [35]. TSP and SPR curves of sepiolite based epoxy composites were presented in Figure 5 (a) and (b), respectively. At the end of combustion, compared with pure epoxy resin, TSP of sepiolite based epoxy composite was more than that of pure epoxy resin, and TSP increased with the increase of the additive amount of sepiolite. This indicated that the addition of sepiolite resulted in the incomplete combustion of epoxy composite, releasing more amount of smoke. However, the addition of doped Fe<sub>3</sub>O<sub>4</sub> reduced the release of smoke, showing in the decrease of TSP of epoxy composites; while the TSP values of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite based epoxy composite were still higher than that of pure epoxy resin. From Figure 5 (b) and Table 1, it was observed that the SPR values of sepiolite based epoxy composite were higher than that of pure epoxy resin during the

combustion process, and peaks of SPR values were much higher than that of pure epoxy resin, which were accordant with TSP results. However, the addition of doped Fe<sub>3</sub>O<sub>4</sub> decreased SPR of epoxy composites, especially epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite.

Combined the analysis of LOI and cone tests, it was made a conclusion that the addition of sepiolite improved flame retardancy of epoxy composite, and the addition of doped Fe<sub>3</sub>O<sub>4</sub> sepiolite further improved flame retardancy of epoxy composite. There might be a synergistic effect between sepiolite and Fe<sub>3</sub>O<sub>4</sub> to flame retard epoxy resin. The addition of doped Fe<sub>3</sub>O<sub>4</sub> catalyzed epoxy resin to form more amount of char residue. And this prevented epoxy matrix from mass/heat transfer, resulting in the improvement of flame retardancy of epoxy composites.

### **3.3 Thermal degradation properties of sepiolite based epoxy composites**

#### **3.3.1 Thermal degradation properties of sepiolite based epoxy composites**

The effect of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite on the thermal stability of epoxy composites was revealed through TGA test. TGA and DTG curves of sepiolite based epoxy composites were depicted in Figure 6, respectively; and the related data were displayed in Table 2. From Figure 6, it was observed that all of the TGA curves of sample studied were unimodal and displayed only one degradation step in the experimental temperature range. And this suggested that the incorporation of sepiolite, Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite into epoxy exhibited no significantly effect on the thermal degradation mechanism of epoxy matrix. It was clear from Figure 6 and Table 2 that the addition of sepiolite had no obvious effect on the thermal stability of epoxy composites. The onset degradation temperatures of epoxy composites with sepiolite, T<sub>onset</sub>, defined as the temperature at which 5% mass loss occurred, were very close to that of pure epoxy resin and almost no change in peak temperature was observed with the addition of sepiolite. However, the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite decreased the T<sub>onset</sub>s of epoxy composites. The T<sub>onset</sub>s of epoxy composites with 2% and 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were decreased by about 25 °C and the peak temperatures were also reduced by 45 and 42 °C, respectively. The results mentioned above indicated

that the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite accelerated the thermal degradation of epoxy composites. More amount of char residue in epoxy composites were found, while the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further improved the amount of char residue. This indicated that the addition of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite promoted the formation of char residue. And this result also suggested that sepiolite catalyzed epoxy resin to form more char residue, and the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further catalyzed epoxy resin to form more char residue.

From Figure 6 and Table 2, it was noted that the addition of sepiolite reduced the degradation rate at peak temperature of epoxy composite, and the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further obviously decreased the degradation rate at peak temperature of epoxy composite. This indicated that the residue formed effectively protected epoxy matrix from heat/mass transfer. And this improved the flame retardancy of epoxy composites.

### 3.3.2 Kinetics of thermal degradation for sepiolite based epoxy composites

There were many multiple heating rate methods to investigate the thermal degradation kinetics of polymeric materials, such as Flynn-Wall-Ozawa method, Friedman method and Kissinger method [36]. Flynn-Wall-Ozawa method (Ozawa method) did not need understanding the thermal degradation mechanism of polymeric materials, and was utilized to calculate the activation energy for different conversion values by fitting the plots of  $\log \beta$  versus  $1/T$  shown in formula (1).

$$\log F(\alpha) = \log \frac{AE}{R} - \log \beta - 2.315 - 0.4567 \frac{E}{RT} \quad (1)$$

Where  $\beta$ ,  $A$ ,  $E$  had the known meanings,  $F(\alpha)$  was the integral function of conversion [37]. Ozawa's calculations were applicable to all points on the TG curves [38, 39]. Therefore, it was capable to provide reasonably reliable data. In order to obtain the activation energy, Ozawa method was widely used in polymeric materials, especially in flame retardant polymeric materials.

The thermal degradation kinetic analysis of epoxy resin, epoxy composite with 4% sepiolite and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was investigated with a steady flow of N<sub>2</sub> at different heating rates of 5, 10, 20, 30 and 40 °C/min. The

Ozawa plots of epoxy resin, epoxy composite with 4% sepiolite and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were depicted in Figure 7, and the calculated activation energy and correlation coefficient were displayed in Tables 3 and 4, respectively. From Figure 7, it was noted that the fitting straight lines were nearly parallel, indicating the application of Ozawa method to the systems in the conversion range studied was applicable. However, the favorable fitting line was failed when the conversion was over 50% for epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. This might result from some complicated reaction mechanism because of the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. It was observed that the activation energies of epoxy composite with 4% sepiolite were higher than those of pure epoxy resin at the same conversion. This revealed that the addition of sepiolite improved the thermal stability of epoxy resin. The activation energies of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were higher than those of epoxy composite with 4% sepiolite at lower conversions ( $\alpha < 20\%$ ); however, those of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were lower than those of epoxy composite with 4% sepiolite at higher conversions ( $\alpha > 25\%$ ). This indicated that the addition of doped Fe<sub>3</sub>O<sub>4</sub> might catalyze some chemical reactions in the thermal degradation process of epoxy resin and accelerated the thermal degradation of epoxy resin at higher conversions ( $\alpha > 25\%$ ).

### **3.4 Dynamic Mechanical Analysis (DMA) of sepiolite based epoxy composites**

Dynamic mechanical test over a wide temperature was very sensitive to physical and chemical structure of polymeric materials. And it was used to investigate secondary transitions, glass transitions and yield information about the morphology of polymeric materials [23]. Figure 8 displayed the dynamic mechanical analysis (DMA) curves for storage modulus  $E'$  and loss factor  $\tan\delta$  of sepiolite based epoxy composites. And the storage modulus at 30 °C and glass transition temperature ( $T_g$ , obtained from  $\tan\delta$  peak) were shown in Table 5. The DMA plots of storage modulus versus temperature were as a function of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite loading. The storage modulus of epoxy composite with 2% sepiolite was a little lower than that of pure epoxy resin; however, the addition of 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite obviously reduced

the storage modulus of epoxy composite at lower temperature, compared with pure epoxy resin. This behavior was explained in terms of interfacial interactions between sepiolite and epoxy resin. The reduced interfacial interactions between Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite and epoxy resin improved the mobility of epoxy matrix around Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. And the storage modulus values of epoxy composite with 4% sepiolite were higher than those of pure epoxy resin at lower temperature; however, those of epoxy composite with 4 % Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite were very close to pure epoxy resin. This indicated that the addition of doped Fe<sub>3</sub>O<sub>4</sub> reduced the storage modulus values of epoxy composite. The reason for this phenomenon might be that the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite reduced the interfacial interactions between sepiolite and epoxy, improving the mobility of epoxy matrix around Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite. From Figure 8, it was noted that the storage modulus values of sepiolite based epoxy composite were higher than the corresponding value of pure epoxy at higher temperature. Similar results had been reported for epoxy/20% EMS/C30B nanocomposite by Mohanty et al [40]. This behavior might be due to higher crosslink density and increase in the stiffness of polymeric materials caused by well dispersed clay platelets [41].

The  $\tan\delta$  curves of sepiolite based epoxy composites were depicted in Figure 8, and glass transition temperature ( $T_g$ ) was determined from the peak of  $\tan\delta$  curves. It was interesting to note that the  $T_g$ s of sepiolite based epoxy composites were increased by about 5 °C compared with pure epoxy resin. And this resulted from the restriction of mobility of polymer chains and/or the increase in cross-linking density by the addition of sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite at higher temperature.

#### **4 Conclusions**

As-received sepiolite/epoxy systems and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite/epoxy systems had been prepared. The results indicated that LOI value of epoxy composite with 4% sepiolite was improved to 30.1% from 23.8% for pure epoxy resin. And LOI value of epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite was further enhanced to 36.7%. The cone results revealed that the addition of sepiolite decreased heat release rate (HRR), total smoke production (TSP) and smoke production rate (SPR) of epoxy composites.

Compared with sepiolite, the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite further reduced parameters mentioned above of epoxy composites, and further enhanced char residues after cone test. There might be a synergistic effect between sepiolite and Fe<sub>3</sub>O<sub>4</sub> on flame retardant epoxy composite. TGA results indicated that the addition of sepiolite had slight effect on the thermal degradation of epoxy composites; however, the addition of Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite accelerated the thermal degradation of epoxy composites. DMA results showed that the addition of both sepiolite and Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite increased the glass transition temperature (T<sub>g</sub>) of epoxy composite. An increased cross-linking density would be responsible for the increase of T<sub>g</sub>. The results obtained in this paper supplied an effective solution for developing excellent flame retardant properties of polymeric materials.

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### **Figure and table captions**

Figure 1 LOI values of sepiolite based epoxy composites

Figure 2 HRR curves of sepiolite based epoxy composites

Figure 3 Digital photographs of residue char for epoxy matrix (a), epoxy composite with 2% sepiolite (b), epoxy composite with 4% sepiolite (c), epoxy composite with 2% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite (d) and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite (e) after cone test

Figure 4 ML curves of sepiolite based epoxy composites

Figure 5 TSP (a) and SPR (b) curves of sepiolite based epoxy composites

Figure 6 TG and DTG curves of sepiolite based epoxy composites in N<sub>2</sub> atmosphere

Figure 7 Ozawa plots of epoxy resin (a), epoxy composite with 4% sepiolite (b) and epoxy composite with 4% Fe<sub>3</sub>O<sub>4</sub>-doped sepiolite (c) at following fractional weight losses

Figure 8 Storage modulus (a) and Tan $\delta$  (b) curves of sepiolite based epoxy composites

Table 1 Data obtained from cone test

Table 2 Data obtained from TG and DTG curves

Table 3 Activation energy of sepiolite based epoxy composite according to Ozawa's method

Table 4 Correlation coefficient of the Ozawa plots of sepiolite based epoxy composites

Table 5 Data obtained from DMA test

Table 1 Data obtained from cone test

Sample	PHRR(kW/m <sup>2</sup> ) [% reduction]	TPHRR <sup>a</sup> (s)	FIGRA (kW/m <sup>2</sup> /s)	TTI (s)	TSP (m <sup>2</sup> )	PSPR <sup>b</sup> (m <sup>2</sup> /s)	THR ( MJ/m <sup>2</sup> )	Residue (%)
Epoxy	1193 [-]	90	13.3	45	23	0.30	76	7.6
2% -Sepiolite-Epoxy	1288 [-8.0]	95	13.6	49	29	0.42	78	12.9
4% -Sepiolite-Epoxy	963 [19.5]	135	7.1	61	37	0.35	101	17.0
2%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	1093[8.4]	100	10.9	42	25	0.29	83	24.3
4%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	883[26.0]	125	7.1	45	26	0.26	89	27.9

Note: a, TPHRR stands for time to PHRR; b, PSPR stands for peak smoke production rate.

Table 2 Data obtained from TG and DTG curves

Sample	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	R <sub>max</sub> (%/°C)	Residue (%)		
				500°C	600°C	680°C
Epoxy	354	419	1.3	19.2	16.9	16.2
2% -Sepiolite-Epoxy	352	417	1.2	23.8	21.8	20.7
4% -Sepiolite-Epoxy	350	413	1.0	29.5	27.2	24.7
2%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	329	374	0.7	40.2	35.3	29.7
4%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	328	377	0.7	39.2	35.4	33.4

Table 3 Activation energy of sepiolite based epoxy composite according to Ozawa's method

Conversion $\alpha$ (%)	Activation energy $E$ (kJ/mol)		
	epoxy	4% -Sepiolite-Epoxy	4%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy
5	193	193	209
10	187	213	221
15	181	217	234
20	187	223	243
25	200	223	212
30	209	241	226
40	221	257	230
50	234	269	237
60	243	274	--
Mean	190	234	226

Table 4 Correlation coefficient of the Ozawa plots of sepiolite based epoxy  
composites

Conversion $\alpha$ (%)	Correlation coefficient r		
	Epoxy	4% -Sepiolite-Epoxy	4%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy
5	0.9999	0.9931	0.9929
10	0.9963	0.9957	0.9882
15	0.9938	0.9943	0.9877
20	0.9904	0.9929	0.9898
25	0.9903	0.9930	0.9941
30	0.9921	0.9934	0.9936
40	0.9947	0.9953	0.9952
50	0.9978	0.9940	0.9926
60	0.9991	0.9916	--

Table 5 Data obtained from DMA test

Sample	Storage Modulus (30 °C) /MPa	T <sub>g</sub> /°C
Epoxy	2367	171
2% -Sepiolite-Epoxy	2311	177
4% -Sepiolite-Epoxy	2449	176
2%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	1987	176
4%-Fe <sub>3</sub> O <sub>4</sub> -Sepiolite-Epoxy	2359	174