Research Article

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Study on preparation and properties of bentonite-modified epoxy sheet molding compound

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Abstract: In this study, bentonite/epoxy sheet molding compound composites (BS/ESMC) were prepared with different bentonite contents (0.5, 1, 1.5, 2, 2.5, 5, and 10 wt%) by hot compression molding. The effects of BS content on the mechanical properties, thermal stability, and fire-retardant properties of samples were investigated. When the BS addition amount is 1.5%, the tensile strength, flexural strength, and impact strength reach the maximum, increasing by 24.15%, 26.56%, and 51.33%, respectively. The measurement of mechanical properties showed that the fracture toughness of BS/ESMC composite has been greatly improved from 71.41 to 108.07 MPa. As the content of the bentonite increases, the heat resistance of the sample increases, and the residual carbon content of the system increases by 61.54% when the amount of the bentonite added is 10%. In addition, the value of LOI increased from 25.6 to 27.9 with the addition of the bentonite.

Keywords: ESMC, bentonite, mechanical property, thermal stability, SMC

1 Introduction

Sheet molding compound (SMC) is a sheet molding material, which is mainly composed of resin, fiber-reinforced materials, fillers, and various additives. The demand for SMC is gradually increasing due to its excellent

dimensional stability, corrosion resistance, short molding cycle, and low price (1–6). Types of resins include unsaturated polyester, epoxy resin, and phenolic resin (7,8). Epoxy resin used in this study has excellent electrical, mechanical, and adhesive properties, which makes it the most widely used matrix resin for resin-based composites (9,10).

Generally, fillers can be divided into organic fillers and inorganic fillers based on their chemical composition. Inorganic fillers are mainly granular fillers made from natural minerals through mining and processing. Naturally occurring calcium carbonate is of low cost and easily available, with large size distribution and high stiffness, and so it is the most widely used filler in composite materials. However, the high surface energy of CaCO_3 will cause the mechanical properties of the composite to decrease (11).

Therefore, it is urgent to find new alternative fillers. Kadir and Mahmut (12) studied the reinforcement effect of different particle fillers in SMC composites formed by compression molding. Studies have shown that compared with SMC composites reinforced by CaCO_3 particles, basalt particles can effectively bond glass fibers and resin matrix together, thereby the tensile strength increased by approximately 15%, whereas the flexural strength was enhanced by 8% in SMC composites prepared by basalt particles. Noh et al. (13) optimized the content of glass fibers and hollow glass beads mixed in SMC to reduce the density of SMC products while maintaining their mechanical properties, which is of great significance to the realization of lightweight automobiles. In addition, some people added magnesium oxychloride crystal double salt to SMC to obtain composite materials with excellent flame retardant properties (14).

Goswami et al. (15) studied fiber composite sheets reinforced with natural shellac. The results showed that with the introduction of 10% shellac, the tensile strength and the flexural strength of the sheet were improved by 13.94% and 30.00%, whereas the impact strength was reduced by 3.11%. The continued addition of shellac

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would hinder the rigid three-dimensional structure, resulting in deterioration of mechanical properties. Asadi *et al.* (16) introduced 0.9 wt% cellulose nanocrystals into sheet molding compound composite and found that the resin matrix became hard, the interphase area changed, and the apparent modulus of the interface increased, which resulted in increases in the tensile strength by 30% and in the flexural strength by 33%.

Although there are many fillers currently in use, the addition of bentonite as a filler for ESMC has not been studied. Bentonite (BS) is a nanolevel (10^{-9} to 10^{-7} m) aluminosilicate clay mineral. Its main component is montmorillonite that consists of two layers of silicon–oxygen tetrahedron and one layer of aluminum–oxygen octahedron to form a unit crystal layer. Atoms are connected, and the crystal layers are connected by the oxygen layer, stacked along the C-axis, so that it has rigidity and does not slip between layers (17,18). The prepared material can improve the strength, heat, electricity, and other properties of the matrix due to the special structure of the silicate material. Brown *et al.* (19) used modified montmorillonite dispersed in thermosetting resin to prepare nanocomposites to obtain exfoliated and partially exfoliated epoxy/diamine nanocomposites with high heat distortion temperature and excellent flame-retardant properties. Takashi *et al.* (20) studied biodegradable resin/clay composite-modified materials, tested the mechanical properties of the materials, and found that the elastic properties and three-point bending properties have been significantly improved.

In this study, BS was introduced in ESMC as a filler, and the effect of BS concentration on the mechanical properties and thermal stability of BS/ESMC composites was determined. The property enhancement of ESMC composites as a result of BS additions are discussed in the context of two mechanisms:

- (i) matrix stiffening due to the presence of the BS, and
- (ii) a three-dimensional woven network structure enhances the interface bonding between EP and GF, which helps to improve the mechanical properties of composite materials (21).

2 Materials and methods

2.1 Materials

All the materials used in this study are commercially available. Epoxy resin (LY1564) was purchased from

Huntsman Company (USA) and was selected as a matrix material. Glass fiber with a diameter of 25–30 mm was purchased from Hubei Senxin Auto Parts Co., Ltd (China). CaCO_3 (400 mesh) was purchased from Sichuan Baoxing. Bentonite (DK-NF) with a diameter of 5–20 μm was obtained from Zhejiang Fenghong New Materials Co., Ltd. (China). Polyethylene polyamine (Chemically pure) provided by Wuhan Hongda Chemical Reagent Factory (China) was used as a curing agent.

2.2 Sample preparation

There are two steps in the production of ESMC composites. The first step is to prepare a prepreg formulation according to the given formula (Table 1) and incubated for a maturation period, which plays an important role in the adhesion between matrix and fiber. In addition, ultrasonic for 20 min during the process facilitates the dispersion of bentonite in the matrix. In the second step, under the effect of a constant pressure of 10 MPa, the ESMC plates were placed in a $200 \times 200 \times 4$ mm sheet mold for about 30 min at a temperature of 80–90°C.

The equipment used in the experimental process included electronic balance, flat vulcanizing machine, and oven.

2.3 Characterization

The morphological features of the broken composite surfaces are characterized by SEM (JSM-5610LV, Japan) with the accelerating voltage of 20 kV. The infrared image of ESMC composite was measured by the Intelligent Fourier transform infrared spectrometer (Nexus, USA)

According to the ASTM D7264M-15 (22) and ASTM D3039M-17 (23), a three-point bending test and a tensile

Table 1: The formulation of ESMC prepreg

Compound	Weight ratio
Glass fiber	24
Epoxy resin	100
Curing agent	10
Thickening agent	8
CaCO_3	120
bentonite	0–10
Other additives	4

test were conducted on the composite specimens by a hydraulic testing machine (CTM001, England). The impact strength was measured according to the ASTM standards (24). The duration of the impact test process is very short, but it is a complex failure process, and generally, there are three main energy absorption stages: (1) initial stage, including material compression, bending, internal friction, and the initiation of crack crazing; (2) crack growth stage, which may be accompanied by behaviors such as neck formation, interface debonding, torsion, and drafting; and (3) end stage, including splitting, separation, and fragmentation (25). The plates were cut into rectangular splines according to the standard. All the mechanical properties measurements were carried out at room temperature (23°C), and the average values obtained from at least five specimens were reported.

The German NETZSCH STA449C/3/G synchronous thermal analyzer was used to observe the thermal stability of ESMC composites. The heating process is carried out in N₂ atmosphere, and the temperature is increased from room temperature to 1,000°C at a rate of 10°C min⁻¹. The limiting oxygen index (LOI) was tested by the JF-3

oxygen index tester (Nanjing Jiangning Analytical Instrument Factory) according to ASTM D2863-2017 (26).

3 Results and discussion

3.1 Microstructure

The morphologies of the samples were characterized using SEM, and the results are shown in Figure 1. For samples without added bentonite, a smooth impact failure surface can be observed (Figure 1a). The glass fiber is easily separated from the matrix when subjected to external force due to the insufficient strength of the interface between the fiber and the matrix. Therefore, interface peeling leads to a decrease in mechanical properties. As shown in Figure 1b and c, the fracture surface of the bentonite/ESMC composites with 1.5 wt% added was uneven and very rough, and obvious laminar microcracks appeared after failure. With the increase of the bentonite content, there is a resin matrix covering the fiber surface in the impact section of the

Figure 1: SEM images of the fractured surfaces of the impact samples. (a) 0 wt% BS, (b) 1.5 wt% BS, (c) the enlarged observation SEM image when 1.5 wt% BS is added, (d) 2 wt% BS.

Figure 2: SEM images of the representative BS/ESMC composites samples. (a) 1.5 wt% BS, (b) 10 wt% BS.

sample (Figure 1d), indicating that the glass fiber and the matrix are well bonded. When the composite material is subjected to external force, due to the strong interfacial adhesion, the effect of the external force is transferred to the fiber. Hence, the mechanical properties of the ESMC plates are remarkably improved. When the content of bentonite reaches 10%, bentonite has a large amount of agglomeration (Figure 2b) due to its high surface energy (27,28). The resin cannot completely infiltrate all the bentonite, which reduces the interface strength between the fiber and the matrix. Therefore, the sample showed a decrease in mechanical properties.

3.2 Mechanical properties

Figures 3 and 4 show the change curve of the mechanical properties of the BS/ESMC composite material when the added amount of bentonite is changed from 0 to 10 wt%. The image shows that the mechanical properties of the sample increase with the amount of BS introduced, and the tensile strength, flexural strength, and impact strength reach the maximum when the BS addition amount is 1.5%, increasing by 24.15%, 26.56%, and 51.33%, respectively. However, all the strengths showed a clear downward trend as the content of bentonite continued to increase, which is consistent with the conclusion obtained by SEM.

The reason for the aforementioned results may be that bentonite is an inorganic clay mineral, which has greater rigidity and strength, playing a reinforcing role. In addition, the bentonite has a layered silicate structure, and the epoxy resin can easily enter the lamellar structure during the curing process to realize the intercalation of the bentonite, which is beneficial to the formation of a three-dimensional woven network structure. Therefore, it helps to improve the mechanical properties of composite

Figure 3: Effect of the content of the bentonite on the sample's tensile strength and flexural strength.

Figure 4: Effect of the content of the bentonite on the sample's impact strength.

materials. When the epoxy resin system is affected by an external force, the external force must overcome the strength of the matrix and the adhesion between the GF and the EP and break the bond between the BS and the matrix. In addition, the bentonite layer can not only cause silver streaks but also shift, turn, or terminate the silver streaks or cracks as a stress concentrator, which dissipates most of the energy to achieve toughening effects.

However, when the content of bentonite is too high, the epoxy resin cannot completely penetrate all the bentonite. Bentonite particles tend to agglomerate and form larger agglomerates due to their high surface energy. The agglomerates introduce defects in the resin matrix, which greatly reduces the mechanical properties of the composite material. In general, adding BS appropriately can improve the mechanical properties of ESMC composites.

3.3 FTIR of BS/ESMC composites

The infrared spectrum of the BS/ESMC composite is shown in Figure 5. The characteristic absorption peaks of epoxy groups in the “fingerprint area” are 830, 913, and $1,250\text{ cm}^{-1}$ (29). As the curing reaction of the epoxy resin progresses, the epoxy group gradually opens up, and the intensity of the band at 913 cm^{-1} gradually weakens. Moreover, the energy band is almost undisturbed during the curing process, so the content of epoxy groups can be sensitively reflected. In the infrared spectrum of the sample with

bentonite, the vibration peaks of Si–O bond, Mg–Al–OH bond, and Si–O–Mg bond can be observed at 1,040, 797, and 522 cm^{-1} , respectively. It shows that the skeleton structure of layered silicate is not destroyed during the curing process of epoxy resin.

3.4 Thermal stability

The effect of bentonite on the heat resistance of samples can be compared and analyzed by thermal weight loss experiments on BS/ESMC composites with different mass fractions of BS. From the curve shown in Figure 6 and the data presented in Table 2, it can be seen that as the content of bentonite increases, the heat resistance of the sample material is improved, which can be concluded by the obvious increase of the initial thermal decomposition temperature and the residual amount of the system at $1,000^\circ\text{C}$. The improvement in heat resistance may be explained as follows: first, there is a strong interaction between the epoxy resin macromolecular chain and the bentonite layer. The strong interface bonding limits the thermal movement of the molecular chain and increases its thermal decomposition temperature. Second, as an inorganic material, the elements such as Si and Al contained in the bentonite composition have excellent thermal conductivity, which can radiate heat in time and protect the internal structure of the material from damage. Finally, the bentonite layer has a barrier effect. It can not only block the conduction of external heat to the inside of the material but also prevent the degradation of epoxy

Figure 5: FTIR spectrum of the representative BS/ESMC composites samples.

Figure 6: The TG curves of the representative BS/ESMC composites samples.

Table 2: The TG data of the representative BS/ESMC composites samples

Content of BS	θ_i (°C)	$\theta_{\max}$ (°C)		θ_f (°C)	$\omega(C\cdot R)$ (%)
		Peak 1	Peak 2		
0	344	378	745	795	39
1.5	345	370	743	789	47
2.5	346	371	746	785	49
5	349	375	745	782	52
10	355	370	744	782	63

θ_i – initial decomposition temperature (system weight loss 5%);
 $\theta_{\max}$ – temperature of maximum weight loss rate; θ_f – termination temperature; $\omega(C\cdot R)$ – residual carbon at 1,000°C.

resin from spreading out, which can also lead to an increase in its thermal decomposition temperature. All in all, bentonite can improve the heat resistance of composite materials.

3.5 Fire-retardant properties

As shown in Figure 7, the LOI value of the sample measured in the experiment was 25.6 when the bentonite sample was not added. Under the same test conditions, the greater the oxygen index, the greater the amount of oxygen required for the sample to burn. Moreover, under the same oxygen concentration, the worse the burning degree, the better the flame-retardant performance of the sample. With the increase of the content of bentonite, the LOI showed an upward trend, indicating that BS has a flame-retardant effect on ESMC composites. However,

Figure 7: Effect of the content of the bentonite on oxygen index of samples.

when the added content of BS reached 2.5 wt%, the increase in LOI of the system gradually became flat, indicating that the flame-retardant effect of BS on the system is limited.

4 Conclusion

The BS/ESMC composites were successfully prepared. Compared with ESMC composites reinforced by CaCO_3 particles, mechanical properties, thermal stability, and fire-retardant properties of BS-reinforced composites have been significantly improved. In this article, the optimal bentonite content determined is 1.5%. The following are the major observations of this study:

- The increase in the bentonite content improves the tensile strength, flexural strength, and impact strength of the composite, but the excessive BS content leads to a decrease. When the BS content is 1.5%, the BS/ESMC composite reaches the highest tensile strength, flexural strength, and impact strength of 77.68, 230.75, and 108.07 MPa, respectively. Compared with 0% bentonite/ESMC composite, the tensile strength, flexural strength, and impact strength were increased by 24.15%, 26.56%, and 51.33%, respectively.
- Through the thermal weight loss experiment, it can be seen that with the increase of the bentonite content, the heat resistance of the sample material has been improved. As the amount of bentonite added is 10%, the residual carbon content of the system increases by 61.54%. This is because elements (Si, Al) contained in the bentonite component can dissipate heat in time. In addition, bentonite restricts the movement of resin molecular chains, which also leads to an increase in the thermal decomposition temperature.
- BS has a flame-retardant effect on ESMC composite materials. As the content of bentonite in the system increases, the LOI increased from 25.6 to 27.9. However, excessive BS has limited flame-retardant effect on the system.

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