Flame Retardant Medium-Density Fiberboard with Expanded Vermiculite

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This study investigated the effect of expanded vermiculite (EV) on the flammability properties of medium-density fiberboard (MDF), which was evaluated by limiting oxygen index (LOI) and simultaneous thermal analysis (TG-DSC). In addition, the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the samples were studied. The results indicated that the addition of EV increased the LOI of MDF, while it decreased the MOR and MOE of MDF quite rapidly. The TG data showed that the fiber-charring rate of the fire retardant MDF increased sharply, more than 10 times that of untreated MDF. Moreover, with increasing of the ratio of the EV and fiber (V/F), it increased the fiber-charring rate of the MDF sharply, decreased the temperature of the maximum mass loss, and decreased the maximum mass loss rate of MDF. The DSC test results indicated that the total temperature range of the exothermic stage had extended and that the first peak in the exothermic stage decreased rapidly with increasing of V/F ratio.

Keywords: Expanded vermiculite; Flame retardant; Flammability properties; Mechanical properties; Thermal analysis

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INTRODUCTION

Medium density fiberboard (MDF) is one of the most commonly used wood-based composites. It is manufactured by wood fibers bonded together with a synthetic resin under heat and pressure (Koch 1972; Maloney 1993). Medium density fiberboard has been widely applied in furniture, building materials, and laminate flooring because of its advantages such as its smoother surface, easier machinability, and good weathering properties (Ustaomer *et al.* 2008). However, its flammability properties have limited its applications. Therefore, improving the fire retardant properties of MDF is necessary.

Vermiculite, which is generally composed of trioctahedral and a lamellar hydrated aluminum iron magnesium silicate, tends to expand when it is heated to elevated temperatures, due to the inter-lamellar generation of water steam (Valšová and Martynková 2012; Nguyen *et al.* 2013). Expanded vermiculite (EV), which is prepared by calcining the vermiculite ore or its concentrate, shows many exceptional properties, such as a low bulk density of 80 kg/m^3 to 120 kg/m^3, a low thermal conductivity of 0.04 W/(m·K) to 0.12 W/(m·K), and a comparatively high melting point 1240 °C to 1430 °C). It is also chemically inert, durable, and environmentally safe. These properties make vermiculite a promising heat insulating material (Suvorov and Skurikhin 2003; Nguyen *et al.* 2013). Therefore, EV, as a flame retardant additive, has been widely used in various materials in recent years, such as plaster composites (Martiasa *et al.* 2013), board (González-Prieto *et* *al.* 2012), lightweight cement based refractory (Koksal *et al.* 2012), bitumen (Liang *et al.* 2013; Zhang *et al.* 2013), coating (Takahashi *et al.* 2006), poly-L-lactic acid (PLA) nanocomposites (Jesús Fernández *et al.* 2013), and polypropylene (Ren *et al.* 2011; Chen *et al.* 2013). However, there is limited work published on the application of EV in MDF. The aim of this study was to investigate the effects of EV on the mechanical and flammability properties of MDF, including the modulus of rupture (MOR), modulus of elasticity (MOE), limiting oxygen index (LOI), and simultaneous thermal analysis (TG-DSC).

EXPERIMENTAL

Materials

Eucalyptus fiber, with moisture content of 9.79%, was supplied by the Weihua Group Co., Ltd., (Guangzhou, China). The EV of 80 to 100 mesh size was supplied by the Chuanshi mineral processing plant (Shijiazhuang, China). Melamine modified urea formaldehyde resin powder (MUF) was used as an adhesive and was supplied by the Langfang Sengbang Chemical Co. Ltd. (Langfang, China).

Manufacture of MDF

Theoretical design of unit MDF

The theoretical design value of unit MDF is shown in Table 1.

Table 1. Theoretical Design Value of unit MDF

Type of board	V/F ratio	Volume (mm^3)	Density (g/cm^3)	Total quantity (g)	Proportion of unit MDF			
					Water	MUF	Fiber	EV
MDF 0	0	220 × 205 × 5	0.80	180	8%	16%	76.0%	0
MDF 2	2/5						54.3%	21.7%
MDF 3	3/5						47.5%	28.5%
MDF 4	4/5						42.2%	33.8%
MDF 5	5/5						38.0%	38.0%

*Note: Total quantity of MDF is the sum of the water, MUF, fiber and EV.

Manufacturing processes

The fiber and MUF were organic polymers, while EV was an inorganic small molecule mixture. Therefore, the MUF addition of flame retardant MDF was more than normal MDF to maintain its mechanical properties. EV, fiber, MUF, and water were weighed as shown in Table 1 and mixed for 3 min. The mixture was poured into a 220 mm × 205 mm wood frame mold and shaped to the desired dimension board after being prepressed for 2 h. It was hot-pressed using a small-scale laboratory press (model BY302X2/2 150T, Suzhou Machinery Manufacturing Cooperation, Suzhou, China). Different MDFs had different ratios of EV and fiber (V/F). The abbreviations MDF 0, MDF 2, MDF 3, MDF 4, and MDF 5 were used to express MDF with V/F ratios of 0, 2/5, 3/5, 4/5, and 5/5, respectively.

Performance Testing

Modulus of rupture (MOR) and modulus of elasticity (MOE)

The MOR and MOE of the specimens were tested according to the 3-point bending test (GB/T 17657 2013). The MOR and MOE values were obtained from the same sample. For every type of MDF, 15 samples of 150 mm × 50 mm × 5 mm were tested.

Limiting oxygen index (LOI)

The LOI value is the minimum amount of oxygen in an oxygen-nitrogen mixture that is required to support combustion over 3 min, or until the specimen is consumed more than 5 cm from the top. The flame retardance of a sample improves with an increasing LOI value. The LOI values were determined in accordance with GB/T 2406.2 (2009). For every type of MDF, 15 samples of 150 mm × 10 mm × 5 mm were tested.

Simultaneous thermal analysis (TG-DSC)

Simultaneous thermal analysis, including thermogravimetry (TG) and differential scanning calorimeter (DSC) analysis, was run in a static nitrogen or oxygen atmosphere using a heating rate of 10 K/min. MDF was ground into powder after drying for 24 h at 80 °C and then used as a test sample for TG-DSC. Samples of 5 mg were heated from an ambient temperature (28 °C) up to 800 °C, at a rate of 10 °C/min under air atmosphere.

RESULTS AND DISCUSSION

Modulus of Rupture (MOR) and Modulus of Elasticity (MOE)

The test results for the MOR and the MOE of MDF with different *V*/*F* ratios are presented in Table 2. With increasing of *V*/*F* ratio, the MOR and MOE of MDF decreased rapidly. According to GB/T 11718 (2009), the minimum MOR and MOE of MDF should be no less than 26 MPa and 2600 MPa, respectively. The MOR and MOE of MDF met the standard values when the *V*/*F* ratio was no more than 3/5. However, the addition of EV reduced the MOR and MOE greatly. The fiber and MUF were organic polymers, while the EV was an inorganic small molecule mixture, which resulted in their poor compatibility. The possibility of EV depositing on the fibers influenced the mechanical properties of MDF as the *V*/*F* ratio increased (Hashim *et al.* 2009). Thus, the intermolecular force and the sliding friction force between the components of the MDF decreased rapidly, resulting in a reduced MOR and MOE.

Table 2. MOR and MOE of MDF with Different *V*/*F* Ratios

Item	MDF 0	MDF 2	MDF 3	MDF 4	MDF 5
MOR (MPa)	40.8	27.9	26.5	19.8	10.8
MOE (MPa)	3530	3060	2710	2270	1050

Limiting Oxygen Index (LOI)

As shown in Fig. 1, the LOI values of MDF that was treated with EV were higher than the untreated MDF. With increasing of *V*/*F* ratio, the LOI values increased. After adding EV, a proximate linear proportional relationship was found between the LOI values and the *V*/*F* ratios. The LOI value of MDF 2, where the *V*/*F* ratio was 2/5, was 35.1, which increased 19.0% compared with that of MDF 0 and proved the effects of EV on MDF. In addition, the LOI value of MDF 5 is 40.7. The addition of EV could hinder the penetration of oxygen into MDF, and therefore reduce the possibility of further combustion, due to its relatively lower permeability coefficients for all gases and higher aspect ratio of silicate layers (Takahashi *et al.* 2006; Zhang *et al.* 2013).

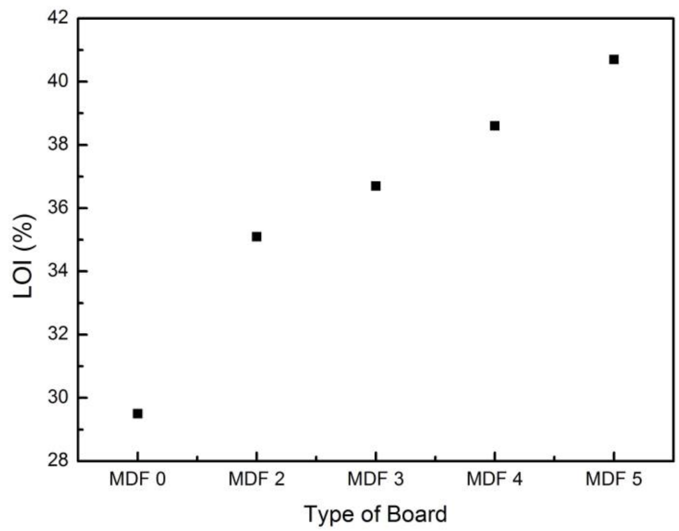

Fig. 1. LOI values of MDF with different *V*/*F* ratios

Simultaneous Thermal Analysis (TG-DSC)

Thermogravimetric analysis (TG)

The TG curves of MDF with different *V*/*F* ratios are shown in Fig. 2. With the increasing *V*/*F* ratio, the residues of MDF increased rapidly. The residues of MDF 0, MDF 2, MDF 3, and MDF 4 were 0.56%, 28.01%, 36.17%, and 39.82%, respectively. The EV was made of chemically inert materials, and its residues remained 96.5% at 800 °C (Liang *et al.* 2013). Therefore, the char residues of the MDF with different *V*/*F* ratios are shown in Table 3, which ignored the mass variation of EV. The fiber-charring rate of the fire retardant MDF increased sharply, more than 10 times that of the untreated MDF. These results indicated that the higher thermal stability of the MDF resulted in a milder degradation of the MDF (Becker *et al.* 2011). In addition, the existence of EV could improve the antioxidation property and the thermal stability of char, due to its higher aspect ratio of silicate layers (Xue *et al.* 2015).

Heat-resistance index of MDF with different *V*/*F* ratios was shown in Table 1 (Gu *et al*. 2016a,b). Heat-resistance index of MDF increased with the increasing of *V*/*F* ratio. The corresponding heat-resistance indexes of MDF 0, MDF 2, MDF 3, and MDF 4 were 98.2 °C, 105.3 °C, 111.4 °C, and 120.6 °C, respectively. This indicated that the thermal stabilities of MDF increased with increasing of *V*/*F* ratio.

As shown in Fig. 2, the variation trends of different MDF were similar. Therefore, the TG curves of MDF could be divided into three stages of weight loss: drying stage, charring stage, and calcining stage (Qu *et al.* 2011). In the drying stage, the mass loss of the MDF was due to water evaporation. The mass loss of the MDFs decreased with the increasing of *V*/*F* ratios; they were 8.14%, 7.41%, 5.72%, and 5.21%, respectively. In the charring stage, the mass loss of MDF was mainly due to hemicellulose and partial cellulose decomposition (Liodakis *et al.* 2009). Although the variation trends of MDFs were similar, the temperature of the maximum mass loss and the maximum mass loss rate of MDF were inversely related to the *V*/*F* ratio. This can be described as 311.7 °C, 6.210%/min, 286.8 °C, 4.101%/min, 285.5 °C, 3.931%/min, and 281.0 °C, 3.832%/min, respectively. In addition, the slopes of the TG curves of the MDFs varied greatly. These phenomena indicated that the EV could reduce the degradation of cellulose effectively. In the calcining stage, the mass loss of MDF was mainly due to the lignin and partial cellulose decomposition (Liodakis *et al.* 2009). The maximum mass loss rate of MDF 0 was approximately 2.0%/min, while that of MDF 4 was approximately 1.1%/min. In addition, the slopes of the TG curves gradually became smooth with the increasing *V*/*F* ratios. Therefore, the addition of EV effectively reduced fiber decomposition in the calcining stage and made the decomposition process smooth.

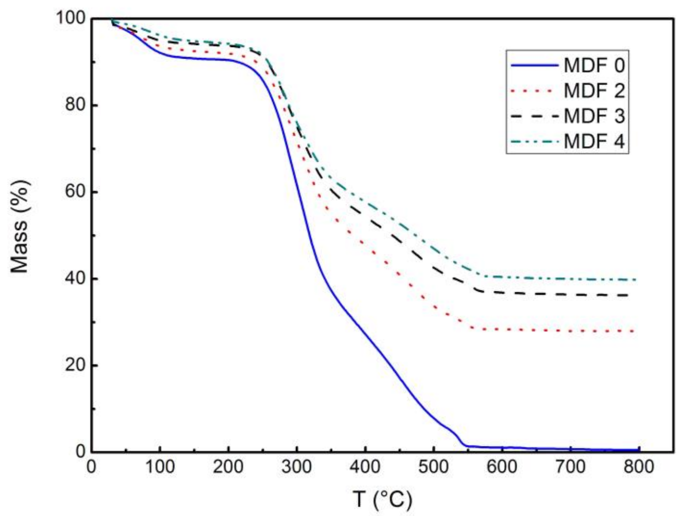

Fig. 2. The TG curves of MDF with different *V*/*F* ratios

Table 3. Char Residues and Heat Resistance Index of MDF with Different *V*/*F* Ratios

Type of board	Temperature (°C)		Heat-resistance index (°C)	Addition ratio of EV of unit MDF (%)	Fiber charring rate (%)
	T_5	T_{30}			
MDF 0	72	286	98.2	0	0.56
MDF 2	81	304	105.3	21.7	6.40
MDF 3	99	313	111.4	28.5	7.67
MDF 4	137	319	120.6	33.8	6.02

*Note: The fiber-charring rate is the difference between the char residues and the addition ratio of EV

Heat resistance index = $0.49[T_5 + 0.6(T_{30} - T_5)]$, T_5, T_{30} is the decomposing temperature at 5%, 30% weight loss, respectively (Gu *et al*. 2014, 2015).

Differential scanning calorimeter (DSC)

The DSC curves of MDF with different *V*/*F* ratios had four peaks and could be divided into three stages: drying stage, charring stage, and calcining stage (Fig. 3). In the drying stage, the area of the endothermic peak decreased as the *V*/*F* ratio increased, agreeing with the TG analysis. In the charring and the calcining stage, the initial temperature and the final temperature of the peaks increased with the increasing *V*/*F* ratio, and therefore the total temperature range of the three peaks in the exothermic stage increased to 297.0 °C, 301.8 °C, 307.6 °C, and 309.3 °C, respectively. In addition, the first peak in the exothermic stage reduced rapidly with the increasing of *V*/*F* ratio. Thus, the EV reduced the decomposition rate of fiber and extended the temperature range in the exothermic stage, which benefitted the charring of the fiber. The position of the first peak in the exothermic stage remained approximately constant with the *V*/*F* ratio increasing, showing that the EV did not affect hemicellulose decomposition. In the exothermic stage, the heat release amount of the second peak first increased then decreased with the increasing of *V*/*F* ratio to 421.1 °C, 509.5 °C, 479.7 °C, and 422.1 °C, respectively, while that of the other peaks decreased with the increasing *V*/*F* ratio. This result was attributed to the partial delay in cellulose decomposition and the inhibition of cellulose decomposition with increasing of *V*/*F* ratio.

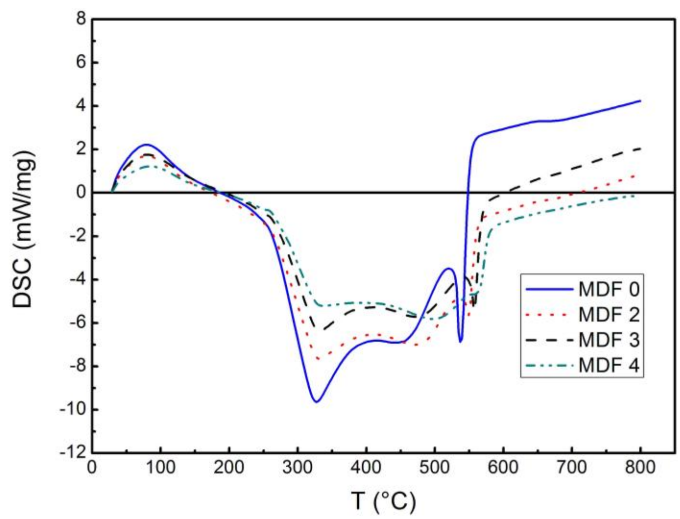

Fig. 3. The DSC curves of MDF with different *V*/*F* ratios

CONCLUSIONS

1. The MOR and the MOE of MDF decreased rapidly with increasing of *V*/*F* ratio. MDF met the standard values for MOR and MOE when the *V*/*F* ratio was no more than 3/5.
2. The LOI of MDF increased with increasing of *V*/*F* ratio. The LOI value of MDF 2 was 35.1, which increased 19.0% compared with that of MDF 0.
3. With increasing of *V*/*F* ratio, the residues of the MDF increased rapidly. More importantly, the fiber-charring rate of the fire retardant MDF increased sharply, more than 10 times that of the untreated MDF. In addition, the temperature of the maximum mass loss and the maximum mass loss rate of MDF decreased with increasing of *V*/*F* ratio.
4. The DSC results indicated that the total temperature range of the three peaks in the exothermic stage was extended, and the first peak in the exothermic stage reduced rapidly with increasing of *V*/*F* ratio.

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