Effect of Particle Size on the Properties of Mg(OH)$_2$-Filled Rubber Composites

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ABSTRACT: A novel nanomagnesium hydroxide powder and three kinds of micro-Mg(OH)$_2$, with different particle sizes, were chosen as fillers and mixed with ethylene–propylene–diene monomer rubber (EPDM) to form a series of composites by a traditional rubber-processing technique. The results showed that the mechanical properties of composites improved with decreasing particle size. The nanocomposites were far stronger than the microcomposites, which also supported the view that rubber reinforcement requires nanoreinforcement. The effect of particle size on the fire resistance of composites was investigated by cone calorimetry and limiting oxygen index analysis, which showed that the particle size of powder had an impact on the fire resistance of composites. For the composites filled with untreated powder, the peak value of heat release rate decreased and T_{ign} increased with decreasing particle size. In conclusion, the fire resistance of nanocomposites was better than that of microcomposites. Surface modification of particles sometimes substantially improved the mechanical properties of nanocomposites, but had no effect on either the mechanical properties of microcomposites or the fire resistance of nanocomposites and flame retardance. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2341–2346, 2004

Key words: nanocomposites; particle size distribution; flame retardance; microstructure; fillers

INTRODUCTION

The use of polymeric materials has increased sharply over the past few decades. A great concern regarding their flammability was noted and methods were investigated to reduce their potential hazard. Flame-retardant additives are most widely used in practice. However, to avoid the corrosive, toxic, and smoky halogen compounds, much more concern is directed to the harmless fillers such as magnesium and aluminum hydroxide. Magnesium hydroxide, an effective flame-retardant filler, because of its high decomposition temperature, can be used in a wider range of thermoplastics than can aluminum hydroxide.[1,2] There have been many investigations on the properties of polymer composites filled with Mg(OH)$_2$.[3–5]

It is difficult to compromise between the mechanical properties of composites and the modified combustion characteristics when preparing halogen-free fire-resistant composites. The particle size of fire-retardant additives is one of the main concerns, although other concerns are: (1) How does the particle size of additive influence the properties of composites, especially fire resistance? (2) Is fire resistance of composites improved with decreasing particle size? Some researchers have discussed these interesting questions, although their conclusions are different.[6,7]

With the development of nanotechnology, greater numbers of kinds of nanoparticles are available. Nanomagnesium hydroxide is now commercially available. In theory, the reinforcement of nanofiller in rubber is better than that of microfiller. Four kinds of Mg(OH)$_2$, with different particle sizes, were chosen to investigate the influence of particle size on the mechanical properties and fire resistance of composites.

EXPERIMENTAL

Materials

Ethylene–propylene–diene monomer rubber (EPDM; Sumitomo Chemical Co., Ltd., Chiba, Japan) was used as the matrix material. Micro-Mg(OH)$_2$ and nano-Mg(OH)$_2$ (Beijing Fine Chemical Plant, China) were

a) 800 mesh   b) 1250 mesh   c) 2500 mesh
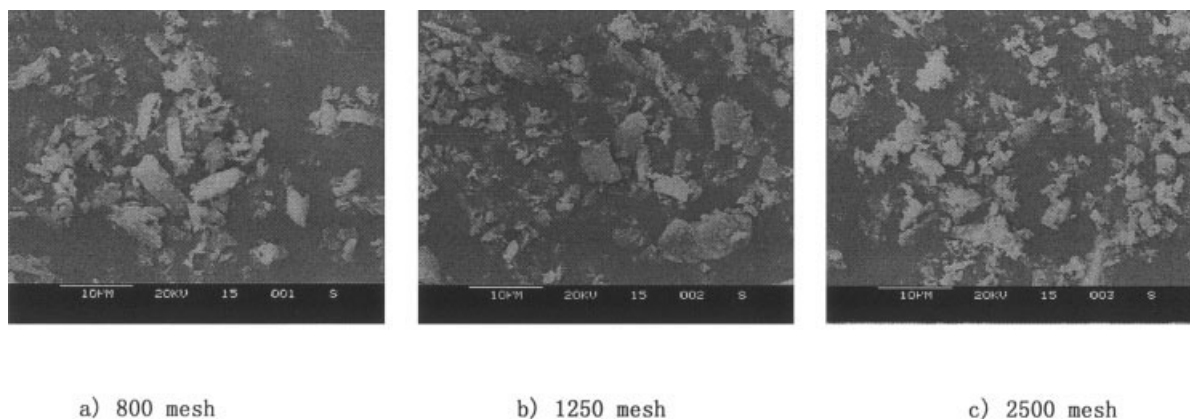
Figure 1 SEM micrographs of micro-Mg(OH)$_2$ with different particle sizes.

dispersed in EPDM. The coupling agent used was silicone (Shuguang Chemical General Co., Zhejiang, China). Other materials are commercial products.

Basic formula (phr): EPDM-505A, 100; zinc oxide, 5; stearic acid, 1; Captax (mercaptobenzothiazole; Parasson Corp., Fullerton, CA), 0.5; accelerator TT (tetramethylthiuram disulfide), 1; sulfur, 1.5.

Sample preparation

In this work, the contents of Mg(OH)$_2$ incorporated into rubbers varied at 20, 40, 60, 80, and 100 phr (parts per hundred rubber). In each case, the sample was mixed on a two-roll mixer by standard procedure, then was vulcanized in a compression molder.

Characterization

Mechanical testing

Specimens were die-cut from the vulcanized sheet and used after at least 16-h storage at room temperature. The mechanical properties of the composites were tested at constant temperature and humidity, as described by an ASTM test method.

Scanning electron microscopy

For SEM characterization, the micro-Mg(OH)$_2$ particles were prepared on each specimen at room temperature, and micrographs were obtained using S-250-III SEM (Cambridge, UK).

Transmission electron microscopy

TEM experiments were performed using an H-800-1 transmission electron microscope (Hitachi, Japan) to acquire a direct visualization of nano-Mg(OH)$_2$ particles. The nanoparticles were dispersed in ethanol, then

vibrated ultrasonically to prevent agglomerating before the observation.

Payne effect

The Payne effect of gross rubber was measured at 60°C and 1 Hz as a function of strain amplitude at 0.28, 0.7, 1.4, 2.8, 7, 14, 28, 70, 140, 280, 350, and 420% using a Monsanto RPA-2000 apparatus (Monsanto, St. Louis, MO).

Other analyses

Dynamic thermal analysis (DTA) of Mg(OH)$_2$ was performed by a PCT-1A differential thermal balance (Beijing Optical Instrument Factory, Beijing, China), with the temperature increasing from room temperature to 600°C, at a speed of 10°C/min. The limiting oxygen index (LOI) of composites was measured according to ASTM specifications. A cone calorimeter was used to assess the thermal characteristics of composites. This study presents data for 50 and 35 kW/m^2 of heat-flux exposure. The particle size of particles was measured by a Mastersize 2000 particle-sizing instrument (Malvern Instruments, Worcestershire, UK).

RESULTS AND DISCUSSION

Morphology of Mg(OH)$_2$

Figure 1 shows the SEM microphotographs of micro-Mg(OH)$_2$ with different particle sizes. We can con-

TABLE I
Particle Size of Micro-Mg(OH)$_2$

	800 mesh	1250 mesh	2500 mesh
Particle diameter (μm)	2.03	2.47	2.93

Figure 2 TEM image of nano-Mg(OH)$_2$.

TABLE II
LOI (%) of Composites Filled with Mg (OH)$_2$

	60 phr	80 phr	100 phr
800 mesh	24.2	25.3	26.8
1250 mesh	24.0	25.5	26.6
2500 mesh	24.2	26.2	27.0
Nano	24.5	26.0	27.0

clude that the Mg(OH)$_2$ samples constitute sheetlike particles. Because of the wide diameter distribution and self-aggregation of Mg(OH)$_2$ particles, the accurate particle diameters cannot be attained from SEM micrographs. We measured the particle diameters by use of a Mastersize 2000 particle-sizing instrument and the results are shown in Table I.

Figure 2 is a TEM image of nano-Mg(OH)$_2$, which is a hexagonal sheetlike particle. The diameter of nano-Mg(OH)$_2$ particles is about 100 nm, and the thickness is <50 nm.

Magnesium hydroxide is an inorganic flame retardant. When magnesium hydroxide is heated, it decomposes to magnesium oxide with the release of water, and at the same time the process will adsorb a great deal of heat to lessen the temperature on the surface of materials, retard the decomposition of polymer, and reduce the formation of combustible compounds. The released water vapor can dilute the oxygen on the surface of materials to reduce the burning rate. In addition, magnesium hydroxide can delay the time before ignition and suppress the release of smoke. Magnesium oxide with high activity can also adsorb many substances, including free radicals and carbon.[1,8]
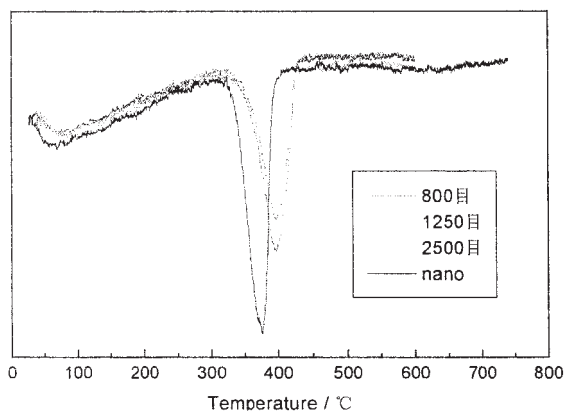
To study the flame-resistance mechanism of magnesium hydroxide, we investigated the thermal characteristic of Mg(OH)$_2$ with different particle sizes. The DTA curves used to compare the decomposition temperature of particles with different sizes, shown in Figure 3, show that the decomposition temperature of nanoparticles (380°C) is lower than that of microparticles (400°C), and the endothermic peak of nanoparticles is also relatively higher. We conclude that nanoparticles decompose earlier than micro-Mg(OH)$_2$ and the endotherm of the nanoparticles is greater than that of micro-Mg(OH)$_2$. Nanoparticles can more effectively lower the flame temperature at the surface of materials and reduce the formation of combustible compounds.

LOI values of composites filled with Mg(OH)$_2$, with different particle sizes, are shown in Table II. With increasing filler content, the LOI of composites show a certain improvement, but the particle size has no obvious effect on the LOI of composites. The released water of Mg(OH)$_2$ samples with different particle sizes is almost identical, which can explain why the LOI of composites change only slightly under the same loading. Thus, the LOI cannot be used as the only parameter to depict the fire resistance of composites. Experimentally, we also found that the composites filled with micro-Mg(OH)$_2$ have melt droppings from the surface, but nanocomposites do not show this phenomenon in the process of burning and its residue retains its fine shape: the network structure of nanoparticles in composites can hold the shape, which
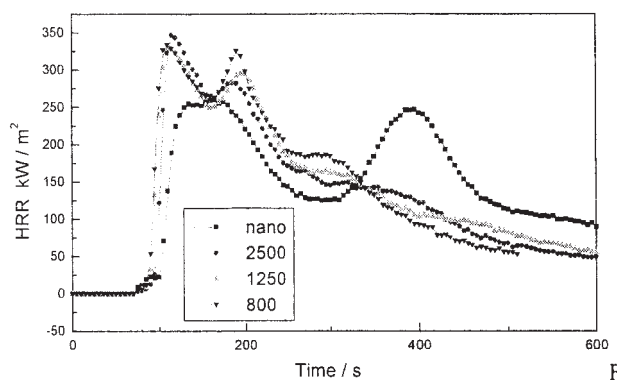

Figure 3 DTA curves of Mg(OH)$_2$ with different particle sizes.

Figure 4 Heat release rate curves of Mg(OH)$_2$/EDPM = 100/100 composites.

TABLE III
Peak Value of HRR and T_{ign} of Composites

	800	1250	2500	Nano
		Untreated		
Peak value, kW/m²	334.16	329.14	346.92	259.43
T_{ing}/s	81	82	89	95
		Treated		
Peak value, kW/m²	301.76	336.84	360.34	248.94
T_{ing}/s	141	84	83	79

provides further evidence that the fire resistance of nano-Mg(OH)$_2$ is better than that of micro-Mg(OH)$_2$.

A cone calorimeter is a new apparatus to measure the combustibility of materials, according to ISO5660-93 specifications. The test results evaluate the combustibility of materials. The heat release is a key parameter in ISO5660, which is closely related to fire scale, fire-spread speed, and potential effective inhibition solutions. Thus the four kinds of composites filled with 100 phr Mg(OH)$_2$ with different particle size were tested by use of a cone calorimeter to investigate the effect of particle size on the combustibility of composites. With respect to the most important parameter, the heat-release rate (HRR) peak value of nanocomposites is obviously less than that of microcomposites, and the ignition time of nanocomposites is the longest, as shown in Figure 4 and Table III. These results strongly confirm the flame resistance advantage of nano-Mg(OH)$_2$.

Payne effect of composites

Figure 5, which shows the Payne effect of gross rubber with Mg(OH)$_2$ contents, indicates that there is a plateau region in the curve at a certain content, which means that the dynamic modulus of composites does not change with increasing strain and suggests that the network structure is not destroyed. When the strain reaches the critical value, however, the G' of the
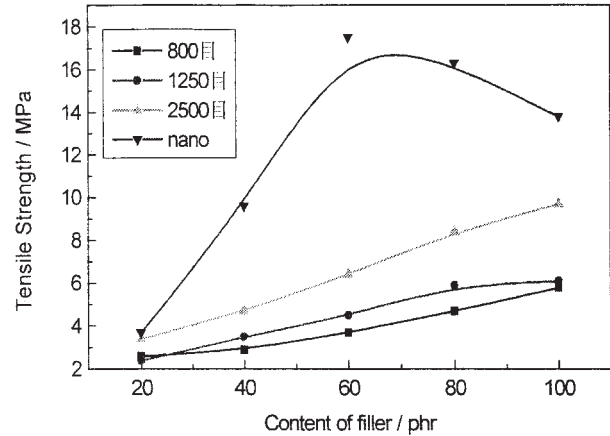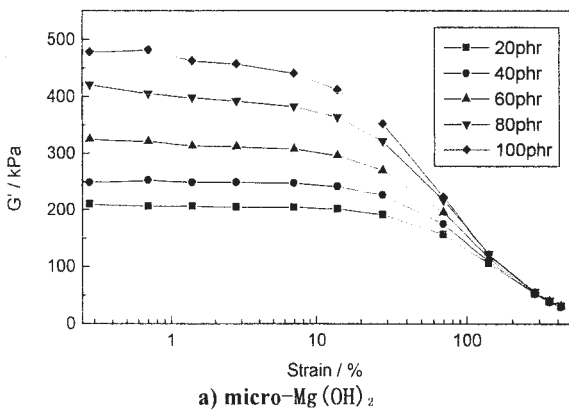

Figure 6 Effect of Mg(OH)$_2$ with different particle sizes on the tensile strength of composites.

composite quickly decreases to another plateau, an indication that the nanopowder's network structure is destroyed. The rapid decrease of modulus is related to the breakage of the particles' network. The higher the filler content, the stronger the network structure and the higher the modulus. There are networks in both nano- and micrometer systems, but their structures are different. Figure 5 shows that the initial moduli of nanocomposites are higher than those of microcomposites at any loading, given that the surface activity and quantity between nanoparticles and microparticles are distinct. Because of the high activity, self-aggregation, and strong macromolecular chain absorption of nanoparticles, it is easy for them to form a network with high density, thus effectively limiting the movement of rubber molecules. We also studied the compound rubber of four kinds of composites [EPDM/Mg(OH)$_2$ = 100/100]. The compound rubber of the nanocomposite is 8.7 g/100 g Mg(OH)$_2$, but the tests for the microcomposites failed because the particles passed through the stainless mesh, which indicates the surface activity of nanoparticles is much greater than that of microparticles.
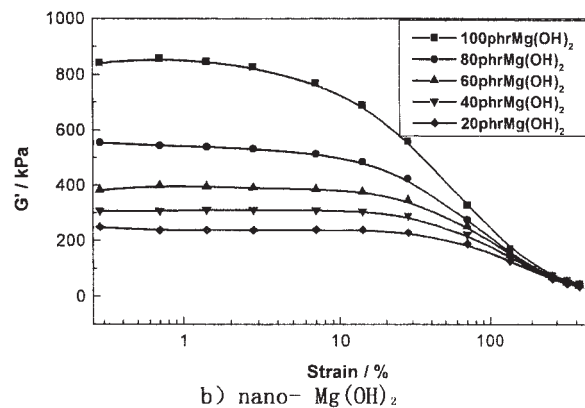

a) micro-Mg(OH)$_2$

b) nano-Mg(OH)$_2$

Figure 5 Plots of Payne effect of composites filled with different contents of Mg(OH)$_2$.
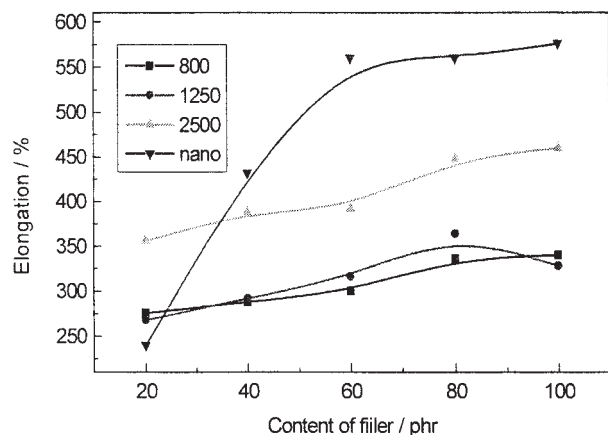
Figure 7 Effect of Mg(OH)$_2$ with different particle sizes on the elongation at break of composites.
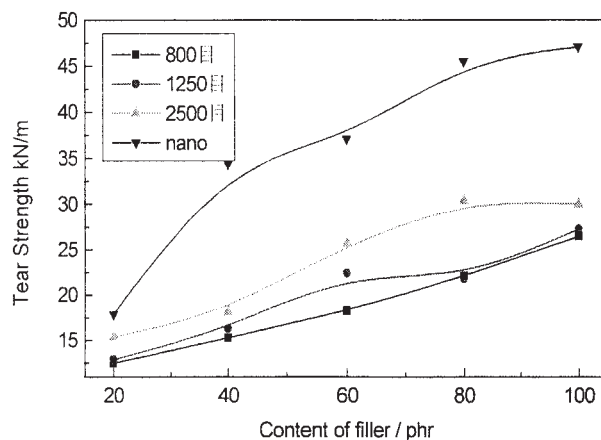

Figure 8 Effect of Mg(OH)$_2$ with different particle sizes on the tear strength of composites.

Mechanical properties of composites

As shown in Figure 6, within a certain content, the tensile strength of the four composites is enhanced with increasing filler content. The difference is that there is a maximum of tensile strength to the composite filled with nano-Mg(OH)$_2$. At the same content, the smaller the size of particles, the larger the composite strength. The tensile strength of the nanocomposite can be as much as 10 times higher than that of the matrices at the filler content of 60 phr. This proves that the reinforcing effect of nano-Mg(OH)$_2$ is very significant. Based on experiments and previous research, Hamed et al.[9,10] concluded that efficient reinforcement must be "nanoreinforcement," which was reconfirmed by our experiments.

With increased loading, the elongation at break of four composites filled with different particle size Mg(OH)$_2$ is improved for all. Improvement of the nanocomposite's elongation is evident, but not so for the composites filled with microparticles, especially at contents < 60 phr. In addition, the rising trend of elongation of microcomposite with 2500 mesh is the same as that of other microcomposites, although the elongation is relatively higher as shown in Figure 7.

At a low content (20 phr), elongation of the nanocomposite is 240%, lower than that of micro-Mg(OH)$_2$. The reason is that, when these nanoparticles disperse in rubber, well-dispersed particles play the role of crosslinker to retard movement of the chain. Oppositely, at the same content, the quantity of microparticles is small and the activity is low, so the action of microparticles is weak. With increasing content, the particles form agglomerates. The extension deformation of these agglomerates under the stress and the slide of interfacial molecules will improve the elongation. Figure 8 shows the tear strength of composites. The tear strength of composites filled with different particle sizes of Mg(OH)$_2$ is enhanced with increasing

content, and the advantage of nanocomposites is verified again by the nanocomposites showing the highest tear strength.

Effect of surface modification on composites' properties

The disadvantage of Mg(OH)$_2$ is that it requires large amounts to achieve the desired degree of flame retardance, which would aggravate the agglomeration of particles and make the mechanical properties worse. That is probably why the nanocomposites show a peak in the mechanical-property curves with increasing filler content. The surface treatment on inorganic powder can efficiently improve the interfacial action between powder and polymer, dispersibility, and reinforcement ability of powder. To acquire excellent fire resistance and mechanical properties at the same time, it would be necessary to treat the surface of Mg(OH)$_2$.

It can be concluded that the mechanical properties of nanocomposites are substantially improved at loadings of 40 and 100 phr, whereas those of microcomposites remain almost unchanged after Mg(OH)$_2$ is encapsulated with silicone (as shown in Table IV and Table V). Surface treatment ameliorates the dispersion

TABLE IV
Properties of Composites Filled with Untreated and Treated Micro-Mg(OH)$_2$ by Treatment

Property	Content of filler/phr			
	40	40[a]	100	100[a]
Modulus at 100%, MPa	1.6	1.5	3.7	3.3
Tensile strength, MPa	4.7	5.1	9.7	9.6
Elongation at break, %	388	356	460	300
Permanent set, %	12	8	34	8
Tear strength, kN/M	18.2	17.3	30	28.2
LOI, %	21.6	23.3	25.2	26.2

[a] Filled with treated Mg(OH)$_2$.

TABLE V
Properties of Composites Filled with Untreated and Treated Micro-Mg(OH)$_2$

Property	Content of filler/phr			
	40	40[a]	100	100[a]
Modulus at 100%, MPa	1.9	1.8	4.2	6.1
Tensile strength, MPa	9.6	14.1	13.8	17.7
Elongation at break, %	432	404	576	296
Permanent set, %	12	8	56	12
Tear strength, kN/M	34.4	25.1	47.1	36.5
LOI, %	20.5	22	27	28.2

[a] Filled with treated Mg(OH)$_2$.

Figure 10 Contrast of HRR curves of composites filled with untreated and treated nano-Mg(OH)$_2$.

of nano-Mg(OH)$_2$ and strengthens the interfacial action between filler and polymer matrix. However, the number of active hydroxyls on the surface of micro-Mg(OH)$_2$ is few and the interaction with silicone is weak, so the effect of silicone is unsatisfactory, which is in agreement with the test results of compound rubber that, when the particle size of fillers is reduced to the nanolevel, the surface activity of particles is greatly improved. In addition, according to the LOI, the improvement of dispersion is beneficial to the fire resistance of composites. The effect of surface treatment on the HRR of composites was also investigated. As shown in Figure 9, the HRR peak of the composite filled with treated nano-Mg(OH)$_2$ is still the smallest. Moreover, the ignition time of composites is obviously shortened, except for 800 mesh (the heat flux exposure to the composites with treated particles is 35 kW/m^2). The second HRR peaks of all four composites diminishes, which is the reason that the combustible organic surface treatment agent between the rubber and Mg(OH)$_2$ makes heat transmission easier during the burning of materials, which should be further investigated. In contrast to untreated filler–filled composites, the HRR peak of treated composites decreases, and the second HRR peak rises and the ignition time
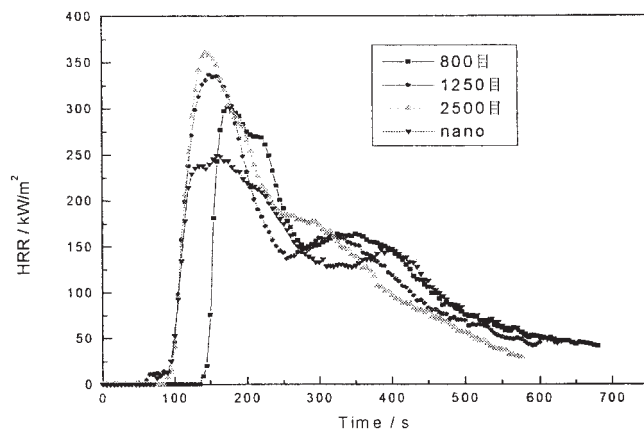
shortens, attributed to uniform burning inside composites as a result of the well-dispersed particles as shown in Figure 10.

CONCLUSIONS

1. The fire resistance of nano-Mg(OH)$_2$ was better than that of micro-Mg(OH)$_2$ in rubber.
2. The effect of nano-Mg(OH)$_2$ particle size is substantial in rubber reinforcement.
3. Surface modification of nano-Mg(OH)$_2$ particles substantially improves the properties of nanocomposites, but had little effect on fire resistance. Moreover, the effect of silicone is negligible on micro-Mg(OH)$_2$ particles.
4. Nano-Mg(OH)$_2$ performs well both in mechanical properties and fire resistance, which makes it a promising flame retardant.

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Figure 9 Heat-release rate (HRR) curves of treated Mg(OH)$_2$/EDPM = 100/100 composites.