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Mechanical properties, fire performance and thermal stability of magnesium hydroxide sulfate hydrate whiskers flame retardant silicone rubber

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Abstract Halogen-free flame retardant silicone rubber (SR) composites, using magnesium hydroxide sulfate hydrate (MHSH) whiskers as flame retardant have been prepared by a two-roll mill. Moreover, microencapsulated red phosphorus (MRP) was used as a synergist. Mechanical tests were performed to determine the tensile strength, elongation at break, and shore hardness of the composites. The morphology of fracture surface was observed by environmental scanning electron microscopy (ESEM). The results showed MHSH slightly reduced the tensile strength of the composites, but had obvious influence on the elongation at break. Meanwhile, Shore A hardness presented uptrend with increasing MHSH content. The addition of vinyl silicone fluid (VSF) could improve the compatibility of the MHSH whiskers in SR matrix, and therefore improved the mechanical properties of composites. The flammability properties of composites were investigated by limited oxygen index (LOI), UL-94 tests, and cone calorimetry experiments. It is found that MHSH whiskers can effectively improve the flame retardancy of SR composites due to the endothermic degradation of MHSH whiskers accompanied with the release of water vapor, and the formation of fibrous magnesia acting as a barrier layer. The incorporation of MRP in SR/MHSH whiskers system had a synergic fire retardant effect in the condensed and gas phase. In addition, thermogravimetric analysis (TGA) indicated the presence of MRP enhanced thermal stability of the SR/MHSH composites at higher temperature range, and remarkably promoted char residue yield.

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Introduction

Silicone rubber (SR) is one of the most important high-temperature-resistant synthetic rubbers with excellent thermal stability, low-temperature toughness, and electrical-insulating properties. It has been widely used in a number of industries, especially in electronic and electric products aspects [1–4]. In these fields, the flame retardancy requirement of materials is very high. However, once being ignited, SR can constantly burn though it has the properties of high-temperature-resistant and excellent thermal stability. So it is indispensable to develop the flame retardant SR.

In flame retardant systems of polymers, halogen-free flame retardant (HFFR) additives, typically magnesium hydroxide (MH) and aluminum trihydrate (ATH) have been widely used [5–9]. However, the high loading (>50 wt.%) required for adequate flame retardancy could be detrimental to the mechanical properties of the materials, especially SR itself having the poor mechanical properties. Recently, inorganic whiskers as flame retardant additives are attracting more and more interests of researcher because they not only improve the flame retardancy of the filled polymers, but also improve their mechanical properties [10–12]. This is because the whiskers are short, fiber-shaped single crystals with high tensile strength owing to their nearly perfect microstructure [13, 14].

In our previous study [15], it has been found that magnesium hydroxide sulfate hydrate (MHSH) whiskers significantly improve the flame retardancy of the filled polyethylene (PE), and organo-modified montmorillonite is an effective synergist in improving the flame retardancy of the PE/MHSH composites. Liu b et al. [16] researched the effects of the MHSH whiskers on the flame retardant ABS composites, and concluded that the MHSH whiskers content has great influence on the flame retardancy and rheological behavior of composites.

In this article, we investigated the effect of MHSH whiskers on the flame retardant SR composites, and microencapsulated red phosphorus (MRP) was expected as a synergist. The flammability properties were investigated using the cone calorimeter, LOI, and UL-94 tests. At the same time, the mechanical properties and thermal stability of composites were also studied.

Experimental

Materials

SR (Mw: 620,000) with a vinyl content of 0.17% and fumed silica (SiO_2, A-200) as reinforcement filler used in this work were produced by Dongjue Fine Chemicals Co., Ltd. (Nanjing, China). MHSH whiskers ($5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$) with a size of diameter <1μm and length > 10μm, and MRP were provided by Keyan Chemistry Company, China. VSF (10% vinyl content, kinematic viscosity: 1,000 cSt) was supplied by ShiSheng Organic Silicon Co., Ltd. (Guangzhou, China). Vulcanizing agent, bis (2, 4-dichlorobenzoyl) peroxide (DCBP), was provided by QiangSheng Chemical Engineering Company (JiangSu, China). All these commercial chemicals were directly used without further purification.

Preparation of samples

All the samples (Table 1) were prepared using a two-roll mill (XK-160, made in Jiangsu, China) at room temperature with the SR first softened, and fillers then added until a homogeneous batch was obtained. The VSF and vulcanizing agent were then added and processed until a visually good dispersion was achieved. The resulting mixtures were then compression molded into sheets (3 mm and 1 mm thickness). At the same time, the sample was vulcanized at 100°C for 10 min.

Characterization

The tensile tests were performed on a Universal Testing Machine DCS-5000 (Shimadzu, Japan) at room temperature and with a constant speed of 200 mm/min. All measurements were repeated five times and the values averaged. Shore A hardness was measured according to ASTM D618 using 6 mm thick samples on BAREISS Shore durometer (Germany).

LOI determination was performed according to ASTM D2863. Test specimens of dimensions (100 × 6.5 × 3) mm^3 were cut from pressed plates. The LOI test is widely used for comparing the flammability of polymeric materials, and is generally acknowledged to be useful for quality control purposes, although it does not purport to predict performance of a material in real fire conditions.

UL-94 vertical burning tests were carried out on sheets (3 mm thickness) according to the ASTM D-635-77. The test methods were generally reproducible to an accuracy of ±0.5%, giving useful comparison of the relative flammability of different materials.

The cone calorimetry experiments were carried out using a Stanton Redcroft cone calorimeter according to ISO 5660 under a heat flux of 35 kW/m^2. Exhaust flow rate was 24 L/s, and the spark was continued until the sample ignited. All samples (100 × 100 × 3) mm^3 were repeated thrice, and the results were reproducible within ±10%.

The morphology of fracture surface and char residue of the composites were observed and studied using an ESEM (Philips XL 30 ESEM-TMP) device. All samples were coated with gold-palladium film under vacuum before test.

TGA experiments were performed using a Netzsch STA 409C thermoanalyzer instrument under airflows of 50 mm/min. The specimens (about 10 mg) were heated from room temperature to 700°C at a linear heating rate of 10 °C/min.

Results and discussion

Mechanical properties

The mechanical properties of all samples filled and unfilled with the flame retardant additives are given in Table 2. As seen in Table 2, with the amount of MHSH whiskers increased, the tensile strength of the composites decreases gradually, and elongation at break is remarkably deteriorated. But Shore A hardness presents uptrend, and shows the highest value 76 at the loading of 60 phr (parts per hundred parts of rubber, by weight) MHSH whiskers. It is concluded that the addition of MHSH whiskers increases the viscosity of SR, and the elasticity is reduced, and therefore materials exhibit solid-like behavior.

In our experiments, the mechanical properties of the SR2 with VSF and SR2* without VSF were compared. It is found that the VSF decreases the viscosity of the composites and improves the mechanical properties of the

Table 1 Samples identification and compositions (phr)

Samples	SR	MHSH	MRP	VSF	DCBP
SR0	100	0	0	3	1.3
SR1	100	20	0	3	1.3
SR2	100	40	0	3	1.3
SR2*	100	40	0	0	1.3
SR3	100	60	0	3	1.3
SR4	100	37	3	3	1.3
SR5	100	33	7	3	1.3
SR6	100	30	10	3	1.3

Table 2 Mechanical properties of SR composites

Samples	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
SR0	7.17	516	58
SR1	6.88	373	70
SR2	6.15	355	74
SR2*	5.23	325	76
SR3	5.08	320	76
SR4	5.86	369	74
SR5	6.45	415	71
SR6	5.95	389	70

composites. According to Fig. 1(a), we can find that the interaction between MHSH whiskers and SR matrix is very weak, and the MHSH whisker is easier to be pulled out. However, after the 3 phr VSF addition, from Fig. 1(b), the MHSH whiskers are difficult to be pulled out during the tensile process, and display good orientation distribution. This indicates good interfacial adhesion between MHSH whiskers and SR matrix is obtained. A partial substitution of MHSH whiskers by MRP leads to the change of the mechanical properties of composites. Noticeably, sample SR5 containing 7 phr MRP has the higher tensile strength and elongation at break. Fig. 1(c, d) also represent that the addition of MRP could improve the dispersion of the MHSH whiskers in SR matrix. The MHSH whiskers are difficult to aggregate due to the partitioning effect of MRP particles (MRP particles around the MHSH whiskers inhibit the coalescence of the MHSH whiskers) around MHSH whiskers. However, less or more amount of MRP seems to not have good effect on the mechanical properties of composites.

Flammability properties

Cone calorimeter investigations can be used as a universal approach to compare and evaluate the fire behavior of polymer materials. All materials burned homogeneously under forced flaming conditions in the cone calorimeter with a stable flame zone above the surface. The heat release rate, especially peak HRR, has been found to be the most important parameter to evaluate fire safety [17]. Figures 2 and 3 respectively show the changes in the HRR for the SR composites with different MHSH whisker contents and the changes in the HRR for SR/MHSH whisker composites, combined with different amounts of MRP at the same levels of 40 phr FR additives. The corresponding cone data

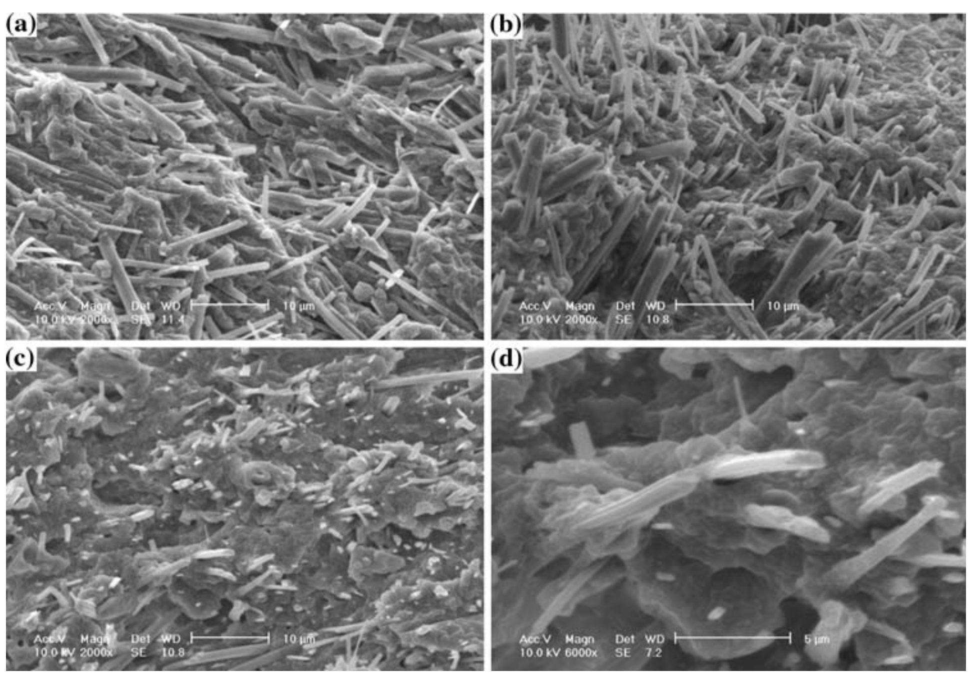

Fig. 1 ESEM micrographs of the fracture surface of (**a**) SR2*, (**b**) SR2, and (**c**, **d**) SR5

are presented in Table 3. In addition, the LOI tests and UL-94 tests are widely used to evaluate flame retardant properties of polymer materials. The LOI values and UL-94 results of SR composites are also listed in Table 3.

From Fig. 2, it is found that the peak HRR of SR composites reduce with increasing MHSH whiskers content. Compared to SR0, there is 63% reduction in the peak HRR for the composite containing 60 phr MHSH whiskers, whereas the reduction is 29% and 41% for the composites containing 20 and 40 phr MHSH whiskers. As seen in Table 3, the LOI values, the time to ignition (TTI), and the time to peak heat release (TTP) all increase with increasing MHSH whiskers content, and UL-94 V-0 is achieved at 60 phr loading. Meanwhile, the effective heat of combustion (EHC) (the ratio of the total heat release over the total mass lost) decreases significantly with the addition of MHSH whiskers. These results suggest that the improved flame retardancy of SR/MHSH composites is greatly dependent on the MHSH whiskers content. The flame retardant mechanism is mainly ascribed to the endothermic degradation of MHSH whiskers withdrawing heat from the substrate, and water vapor diluting the fuel supply present in the flame [18]. In addition, from Fig. 4 we can observe that the degradation products (mainly MgO) of MHSH whiskers have a high performance, because they still possess fibrous structure. Therefore, when accumulated on the underlying substrates, MgO whiskers and the emigrated silica from SR combustion improve the barrier effect which limits the transfer of both the volatile products and oxygen.

The comparison of the HRR behavior of MHSH whiskers partially replaced by MRP at the same 40 phr FR loading levels is shown in Fig. 3. When MRP is present, combustion of the composites shows different HRR features with that of SR2 containing no MRP, and different MRP contents can result in different flame retardant effect

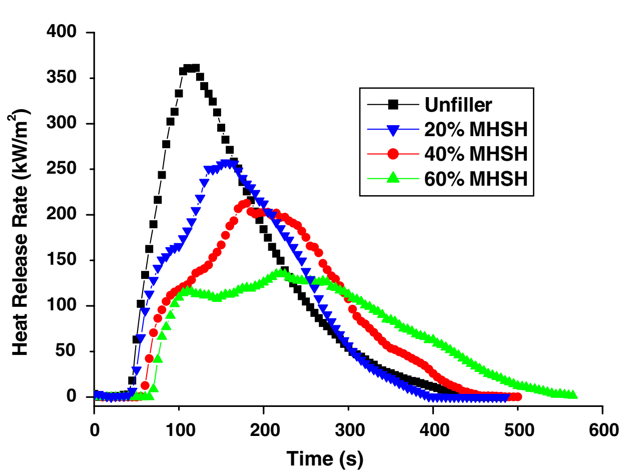

Fig. 2 HRR curves for SR and its composites with 20, 40, and 60 phr MHSH whiskers

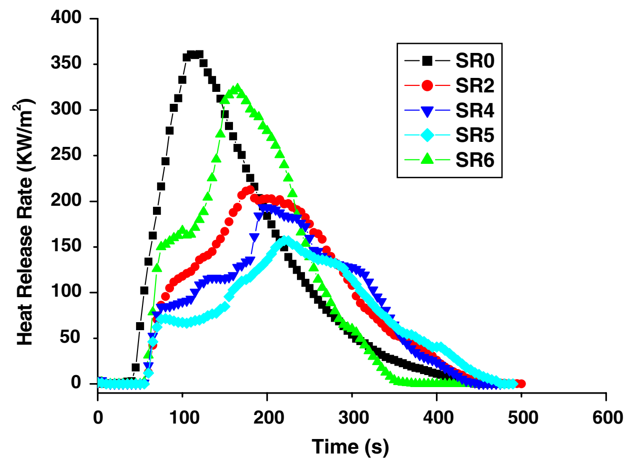

Fig. 3 HRR curves for SR/MHSH whisker composites, combined with different amounts of MRP at the same levels of 40 phr FR additives

on materials. The HRR of SR4 and SR5 sample is reduced by comparing SR2 sample especially at the onset stage of burning. Moreover, it is found that the TTP is increased greatly, whereas the TTI has no remarkable change. According to Table 3, we can see that the incorporation of MRP into the SR/MHSH whiskers composites increases the LOI values, and the SR5 sample has the highest LOI value 38.5 and achieves V-0 in UL-94 tests. These results demonstrate that a synergistic effect occurs when MHSH whiskers and MRP, both are present, which leads to the improvement of the fire performance of flame retardant SR. The mechanism of the flame retardant synergy may be that the water vapor released from MHSH whiskers is favorable to promote the formation of phosphoric acids from phosphorus oxide, and form a glassy layer acting as a protective shield on the burning substrate [19]. The ESEM micrographs (Fig. 4) also show that the SR5 composite form more compact network structure based on MgO whiskers backbone after combustion, which can insulate the heat transfer and prevent the diffusion of the oxygen and the volatile products efficiently, leading to the reduction in HRR. In addition, the reduction of the EHC indicates the existence of a gas phase flame retardant mechanism [20, 21]. Too much MRP, however, has no benefit in improving the flammability properties due to its own inherent combustibility.

The fire performance index (FPI) and fire growth index (FGI) are parameters calculated from the directly measured data of cone calorimeter experiments, and can be used to give an overall assessment of the fire safety of a material in the cone calorimeter test [22, 23]. FPI (m^2 s/kW) and FGI (kW/m^2 s) are respectively defined as the ratio of the TTI to the peak HRR and the ratio of the peak HRR to the TTP. The higher the value of the FPI or the lower the value of the FGI, the higher is the product's safety rank. From

Table 3 LOI, UL-94 tests results and part data recorded in cone calorimeter experiments

Samples	LOI (%)	UL-94	TTI (s)	TTP (s)	Peak HRR (kW/m^2)	Mean EHC (MJ/kg)
SR0	24.0	BF	43	120	361.24	32.61
SR1	32.0	BF	45	155	257.36	27.54
SR2	35.2	BF	57	180	212.59	25.73
SR3	39.5	V0	66	220	135.29	21.73
SR4	37.5	BF	57	195	193.39	24.12
SR5	38.5	V0	59	220	156.96	22.56
SR6	37.0	BF	54	165	323.29	25.96

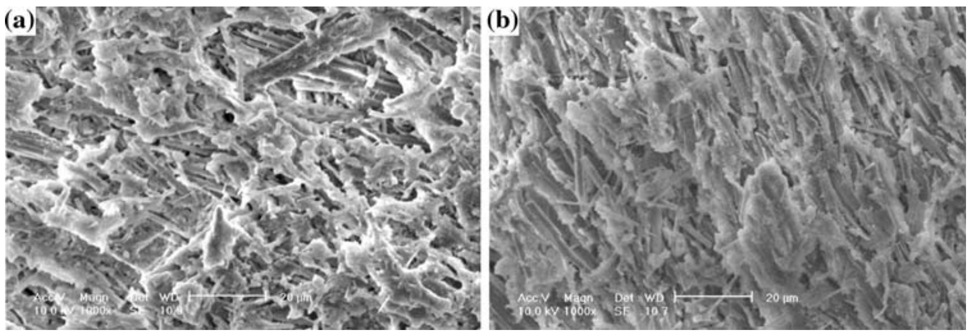

Fig. 4 ESEM micrographs of the char residue of (**a**) SR2, (**b**) SR5

Figs. 5 and 6, it's found that the FPI increased and the FGI decreased with increasing MHSH whiskers content, which indicates the higher MHSH whiskers loading has better flame retardancy on SR composites. For the SR/MHSH whiskers system containing MRP at the same levels of 40 phr FR additives, we see that the SR5 sample has the highest FPI and lowest FGI, whereas the SR6 sample containing too much MRP shows opposite results. Therefore, it may be concluded that the SR5 containing 7 phr MRP effectively improves the fire safety of SR.

Thermogravimetric analysis

Figure 7 shows TGA curves of SR and SR/MHSH whisker composites, combined with different amounts of MRP at the same levels of 40 phr FR additives. It can be seen that the TGA curves of the composites containing FR additives display several apparent degradation stages from room temperature to 700 °C, which is due to the degradation processes of MHSH whiskers and the reactive behavior between MHSH whiskers and MRP under the elevated temperature. The earlier initial degradation temperature of the sample containing FR additives is attributed to the dehydration of crystal waters from MHSH whiskers at the temperature range from 260 to 360 °C. Compared to the SR2 sample containing no MRP, the addition of MRP improves significantly the thermal stability of SR composites at the higher temperature range (>410 °C). The slope between 450 and 510 °C has a shift toward flat trend

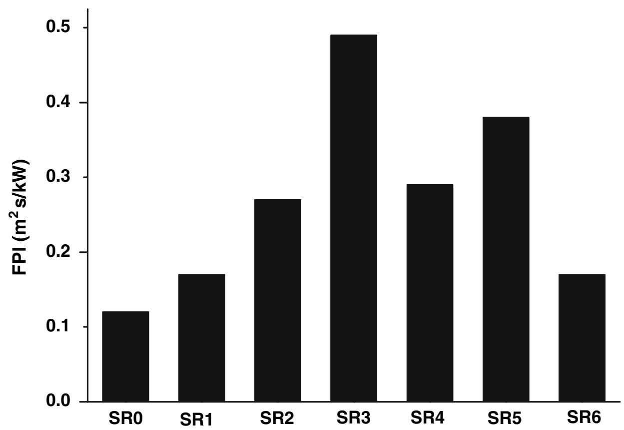

Fig. 5 Cone calorimeter fire performance index for SR composites

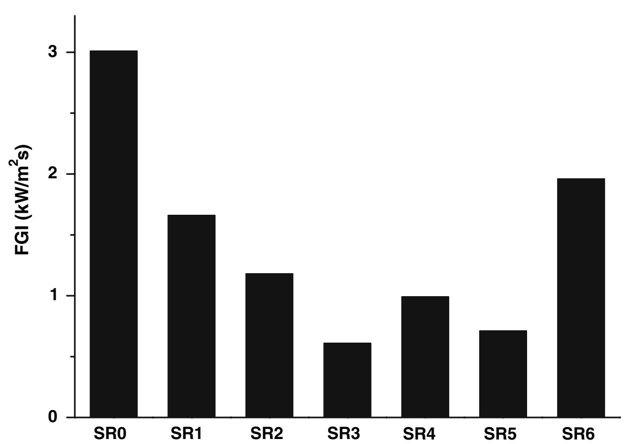

Fig. 6 Cone calorimeter fire growth index for SR composites

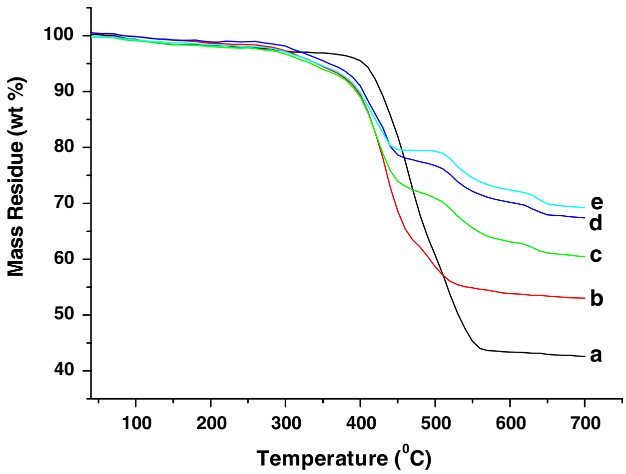

Fig. 7 The TGA curves of (a) SR0, (b) SR2, (c) SR4, (d) SR5, and (e) SR6

with increasing MRP content, which is due to the oxidation of phosphorus in the condensed phase, resulting in a subsequent mass gain. The final high-temperature residue of 53 wt.% is observed for SR2, whereas SR4-6 respectively show 60 wt.%, 67 wt.%, and 69 wt.% residue yield. It is generally considered that part of the phosphorus reacted to form oxygen-rich magnesium phosphates, which increased the inorganic residue [19]. In addition, it is found that too much MRP (10 phr) do not significantly improve the thermal stability of materials like SR4 and SR5. These results indicate that the MHSH whiskers and MRP can affect the thermal stability of the composites and with increasing MRP content, the thermal stability of SR/MHSH whiskers composites at the higher temperature range was improved.

Conclusion

The mechanical properties, fire performance, and thermal stability of MHSH whiskers and MRP flame retardant SR have been investigated. It has been found that MHSH whiskers significantly improve the flammability properties of the filled SR, and MRP is an effective synergist in improving flammability properties of the SR/MHSH composites. Compared to the SR2 sample containing no MRP, the SR5 sample with 7 phr MRP has higher LOI value 38.5, and achieves V-0 rate in UL-94 tests. Moreover, the higher FPI and the lower FGI also display the higher safety rank of SR5. Tensile tests show that MHSH whiskers slightly reduce the tensile strength of the composites, but have obvious influence on the elongation at break. Meanwhile, Shore A hardness presents uptrend with increasing MHSH whiskers content, and the materials exhibit solid-like behavior. The addition of VSF can improve the compatibility of the MHSH whiskers in SR matrix, and appropriate amount of MRP can improve the dispersion of the MHSH whiskers in SR matrix due to the partitioning effect of MRP particles, consequently the mechanical properties of composites are improved. Based on the thermal analysis, it is concluded that the earlier mass loss of the sample containing FR additives is attributed to the dehydration of crystal waters from MHSH whiskers at the temperature range from 260 to 360 °C. When MRP is combined with MHSH whiskers in SR, part of the phosphorus reacts to form magnesium phosphates, which increases the inorganic residue.

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