

Preparation of CaCO₃-SiO₂ composite with core-shell structure and its application in silicone rubber

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A new CaCO₃-SiO₂ composite with core-shell structure was successfully prepared by mechano-chemistry method (MCM). SEM and FTIR indicated that SiO₂ particles were homogeneously immobilized on the surface of CaCO₃. The well dispersion of this CaCO₃-SiO₂ composite into silicone rubber can not only reduce the usage amount of SiO₂, but also improve the mechanical properties of silicone rubber. By the calculation, the theoretical numbers of the SiO₂ particles is about 10 times as large as that of CaCO₃ particles in the CaCO₃-SiO₂ composite. Mixing CaCO₃-SiO₂ composite in silicone rubber can enhance the breaking strength of the silicone rubber about 18% as high as that when mixing the pure SiO₂. And the elongation at break is about 14% less than that of adding the pure SiO₂ sample.

Keywords: calcium carbonate, silica, silicone rubber, mechano-chemistry.

INTRODUCTION

Hydrated Silica (SiO₂ · nH₂O) is composed of amorphous silica which is nanometer (1–100 nm) or sub-micron (0.1–1 μm) in scale. It has the characters of white, porosity, wear-resisting, anti-UV and intense interface activity, which makes it an important inorganic agent of chemical industry^{1,2}, especially in the rubber industry.

However, there are two obvious disadvantages for the hydrated silica in rubber application. Firstly, the hydrated silica has high mobility and is apt to splash in air. This fact makes it hard to blend with resin or other ingredients, leading to decreasing the mechanical performance of the silicone rubber. Secondly, the particle size of the hydrated silica is too small to disperse³⁻⁷. Thus, a lot of the hydrated silica will be aggregated together when it is mixed in the rubber. The really contact surface area of the hydrated silica with the rubber is the surface of the silica particles aggregation. This will discount the application performance and result in the waste of the hydrated silica. Obviously, if the inside silica particles are replaced with another dense material and fabricate a novel core-shell structure composite, the mobility and the splashing tendency can be decreased. At the same time, the rubber processing can be easier. In addition, the dispersion and the functional areas of hydrated silica can be improved to some extent. Moreover, if a cheaper core material is applied, the cost can be reduced at the same time.

Ground calcium carbonate (CaCO₃) is produced by crushing and grinding the minerals containing CaCO₃, such as calcite, marble, dolomite, limestone, etc. The micron-scale ground calcium carbonate (particle size: 1–100 μm) has the characteristics of dense, white (fluorescent whiteness: >90), low cost, and inactivity, which makes it an appropriate inorganic filler. The ground calcium carbonate is widely applied in the industry of plastics, rubber, coatings, and paper-making^{8,9}.

In our work, the CaCO₃-SiO₂ composite is synthesized by the MCM. CaCO₃ is used as the core material. The small SiO₂ particles can immobilize homogeneously on the surface of CaCO₃, which can reduce the aggregation of SiO₂ particles. By means of mechanical functions, the MCM makes the SiO₂ and CaCO₃ particles react

physically and chemically with each other¹⁰. Adding CaCO₃-SiO₂ composite into silicone rubber can not only reduce the usage amount of SiO₂, but also improve the mechanical properties of silicone rubber. It can hope that CaCO₃-SiO₂ composite can become the ideal material to substitute the pure SiO₂ in silicone rubber.

MATERIAL AND METHODS

Material

The hydrated silica and ground calcium carbonate is provided by Shijiazhuang Gaozong Silicon Product Co., Ltd, and Hubei Xinshanzhuoyue New Materials Technology Co., Ltd, separately. The sodium polyacrylate solution (PAAS) was 30% wt. The ammonia was analytic grade reagent without further purification. The other reagents including methyl vinyl silicone rubber, hydroxyl silicone oil, zinc stearate, and vulcanizing agent, were all analytically pure and used without further purification.

Table 1. Specifications of ground calcium carbonate

Items	Results
Fluorescent whiteness [%]	96.3
CaCO ₃ [ω%]	99.03
MgO [ω%]	0.08
Oil absorption [mL/100g]	42.31
H ₂ O [ω%]	0.3
Tap density [g/mL]	0.8

Synthesis of CaCO₃-SiO₂ Composite

100 g of hydrated silica, 6 g PAAS and 500 g grinding media are mixed into water. The silica is grinded for 90 minutes in a GSDM-S3 grinding machine and is disaggregated and refined to smaller particles. Then 100 g of ground calcium carbonate, 500 g grinding media and 6 g PAAS are added into the mixture. The pH was controlled at 10 with ammonia (30% wt)¹¹. The grinding time is set at 40 minutes, and the stirring rate is at 1600 rpm. The grinding process (also called the mechano-chemistry process) can cause the surface activation of the silica and CaCO₃ particles. The two new activated particles can combine together by physical or chemical functions

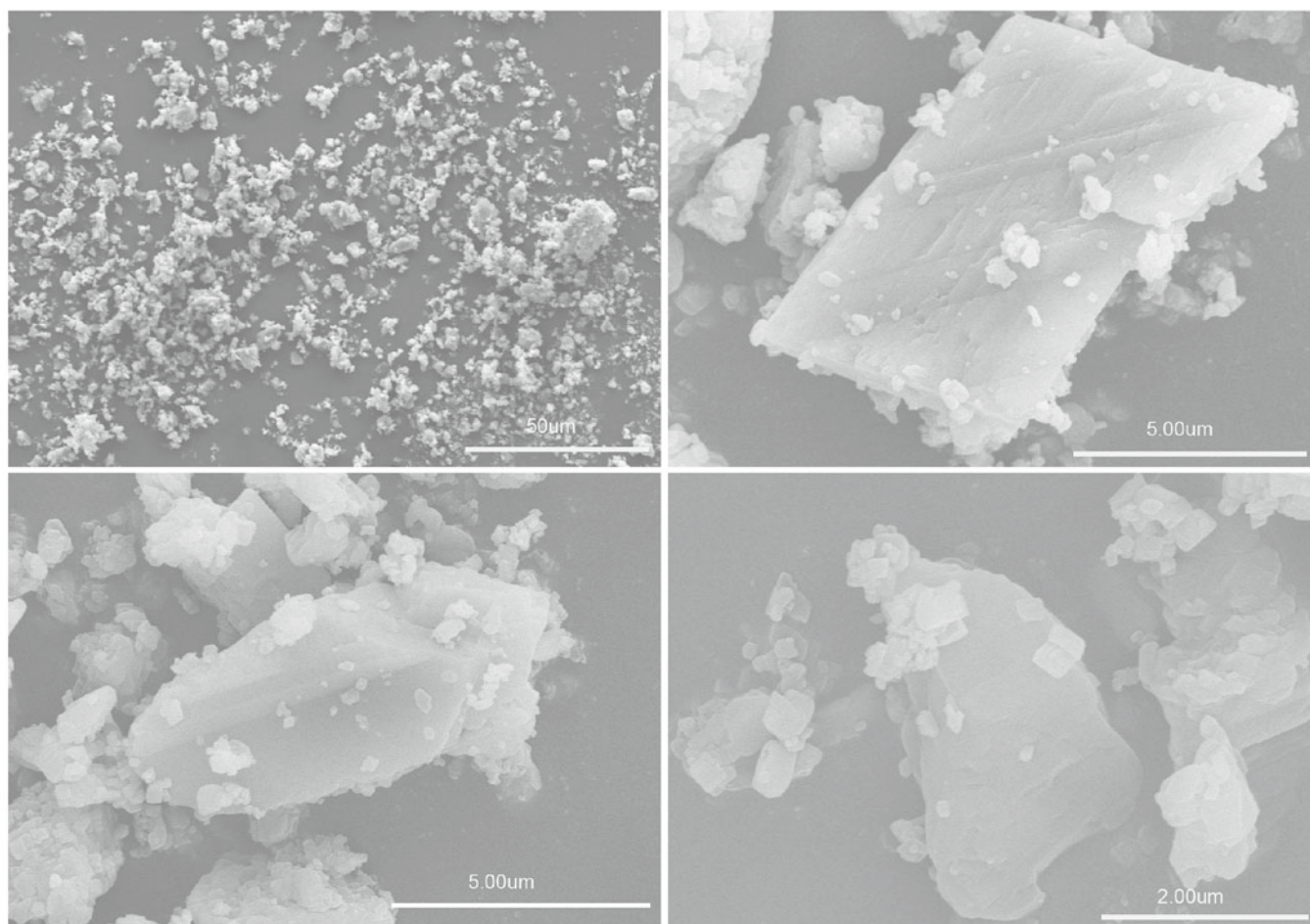


Figure 1. SEM images of ground calcium carbonate

After the mechano-chemistry process, the sample was disposed with centrifugation, desiccation, and grinding.

Characterization

The size distribution of the $\text{CaCO}_3\text{-SiO}_2$ composite was analyzed with the Malvern Zetasizer. SEM was carried out using a S4800 field emission scanning electron microscope. The fluorescent whiteness of the samples is tested by the Whiteness Meter (WSB-3, Shanghai Xinrui Instrument and Meter Co., Ltd.). Fourier transform infrared (FTIR) spectra were carried out using a Bruker spectrometer in the frequency range of $4000\text{--}450\text{ cm}^{-1}$. Powder X-ray diffraction (XRD) was performed on an X/max-rA Advance diffractometer with $\text{Cu K}\alpha$ radiation.

Preparation of Rubber

The $\text{CaCO}_3\text{-SiO}_2$ composite sample was added into the methyl vinyl silicone rubber according to the proportion listed in the Table 2, then via open mill, vulcanization, cooling, demould, and re-vulcanization at 200°C^{12} , silicone rubber with certain mechanical strength and toughness are prepared.

Table 2. The proportion of silicone rubber

Component	Weight [g]
Methyl vinyl silicone rubber	100
$\text{CaCO}_3\text{-SiO}_2$ composite	45
Hydroxyl silicone oil	3.5
Zinc stearate	2
Vulcanizing agent	1.2

Mechanical Performance Measurement

According to the national standard GB/T 528-2009¹³, the dumbbell-shaped rubber sample is made to test the breaking strength δ and elongation at break ϵ .

RESULTS AND DISCUSSION

The Results of Preparing $\text{CaCO}_3\text{-SiO}_2$ Composite

The size distribution of CaCO_3 , SiO_2 , and $\text{CaCO}_3\text{-SiO}_2$ composite are showed in Figure 2. Compared with CaCO_3 and SiO_2 , the $\text{CaCO}_3\text{-SiO}_2$ composite “grows” up obviously. It is the result of combination of CaCO_3 and SiO_2 . The size of $\text{CaCO}_3\text{-SiO}_2$ composite is about $0.1\text{--}10\text{ }\mu\text{m}$. In addition, the inner side of the figure shows the existence of the particles smaller than the hydrated silica, which shows that the grinding causes not only the growth, but also the diminution of the particles at the same time.

As shown in the inner side of the figure, the existence of the much smaller particles in the composite shows that the grinding causes not only the growth, but also the diminution of the particles at the same time.

To understand the preparation process better, the basic process of the composition is illustrated in Figure 3.

The $\text{CaCO}_3\text{-SiO}_2$ composite particles consist of fully coated CaCO_3 (I) and partially coated CaCO_3 by SiO_2 (J~f).

Figure 3 shows the MCM process of synthesizing $\text{CaCO}_3\text{-SiO}_2$ composite. The SEM images of the hydrated silica (a~d) and ground calcium carbonate (e~h) are shown in Figure 3 respectively. Figure 3(e~h) indicates

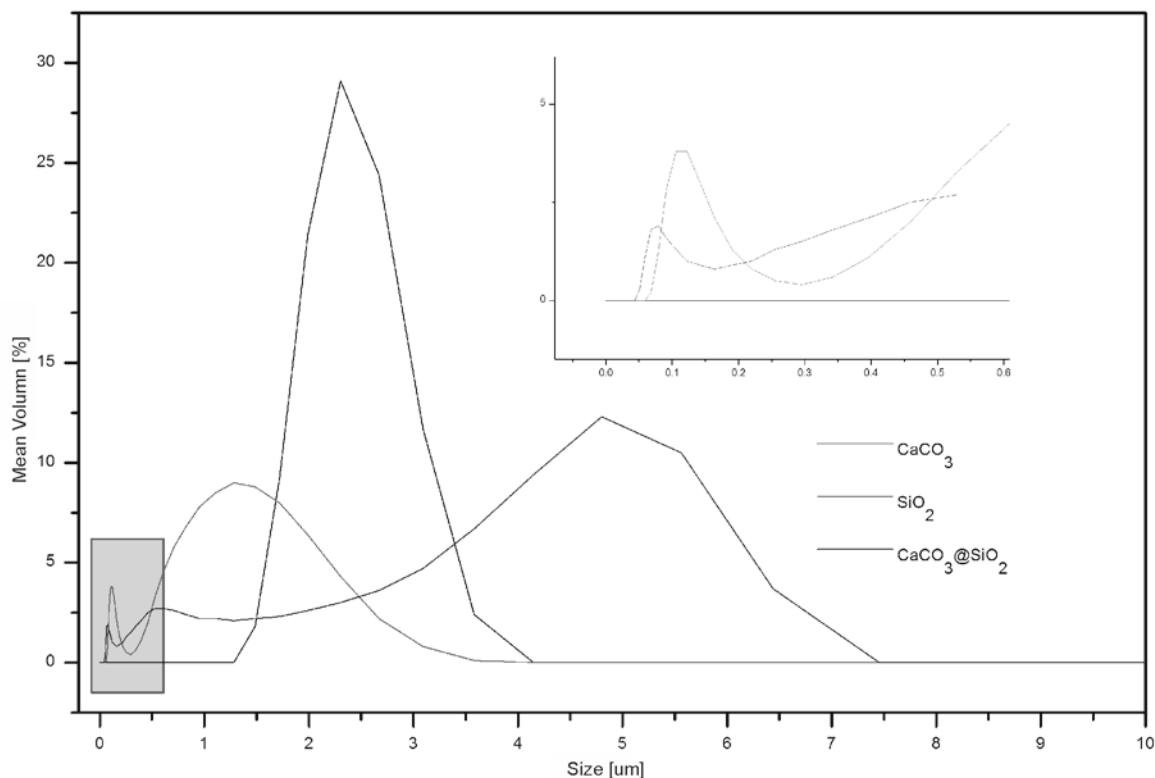


Figure 2. Size distributions of CaCO_3 , SiO_2 and $\text{CaCO}_3\text{-SiO}_2$ composite

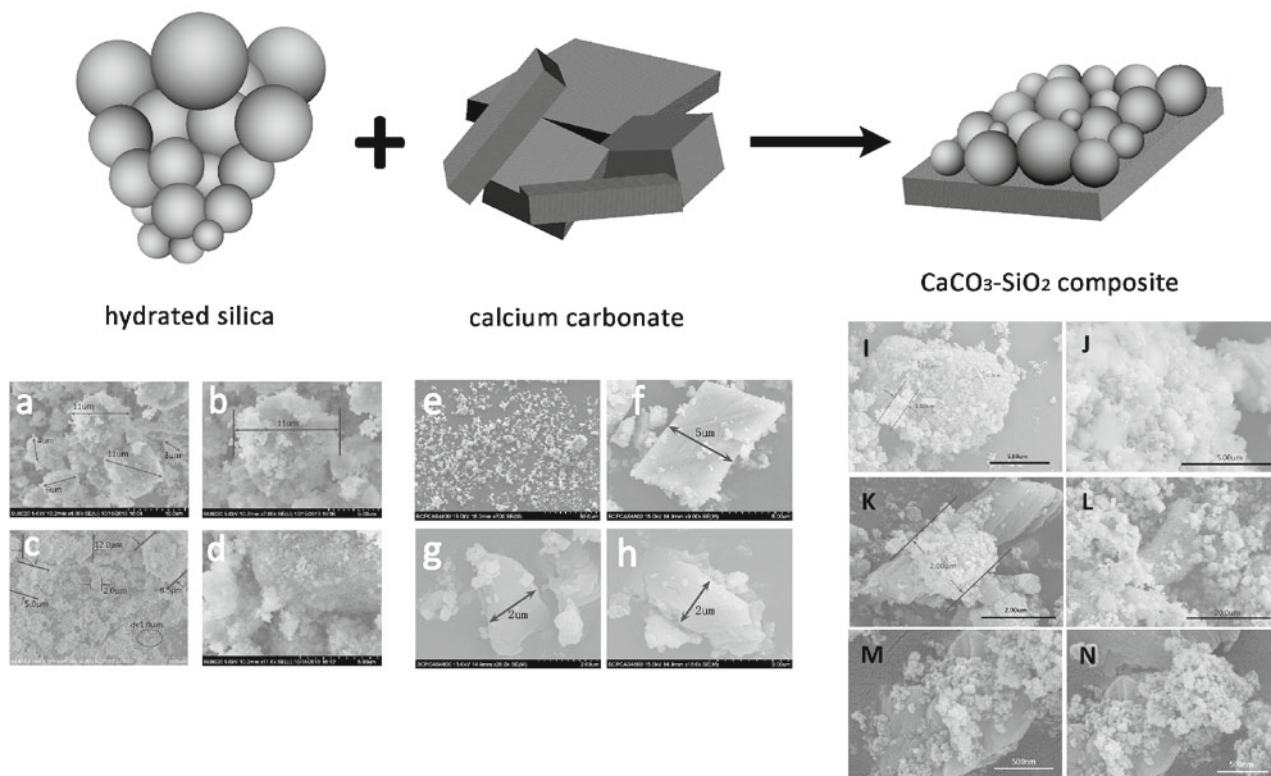


Figure 3. Schematic illustration and the corresponding SEM images of the synthesis of $\text{CaCO}_3\text{-SiO}_2$ composite.

the slice, prismatic, and other shapes of ground calcium carbonate, which are “distinctly angular” and easier to be distinguished from the tiny and sphere hydrated silica particles shown in Figure 3(a~d). After the MCM process, the fine SiO_2 particles and the “distinctly angular” CaCO_3 particles are synthesized in the form of core-shell structure. The aggregated silica coated calcium carbonate, entirely and partially. Figures 3(I~N) show the different coating structures. The entire coating is

illustrated in Figure 4, which can be demonstrated by the corresponding EDS results, listed at Table 3.

The XRD pattern of the $\text{CaCO}_3\text{-SiO}_2$ composite is shown in Figure 5. The characteristic peaks of calcite and the characteristic bulged peaks explain the existence of CaCO_3 and amorphous SiO_2 in the $\text{CaCO}_3\text{-SiO}_2$ composite.

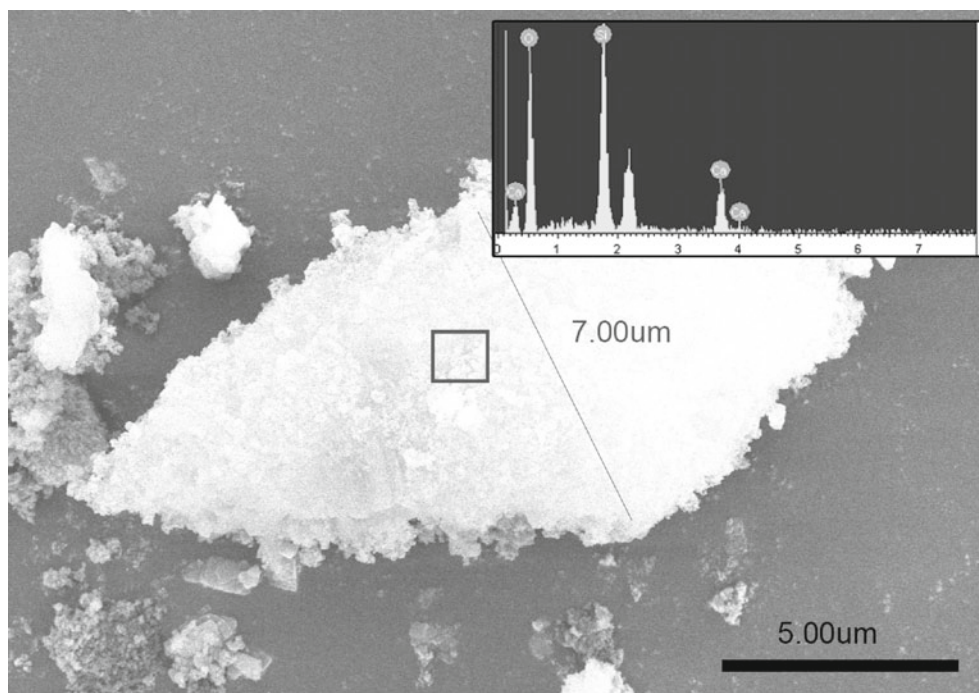


Figure 4. TSEM image of fully coated $\text{CaCO}_3\text{-SiO}_2$ composite particle and the EDS results

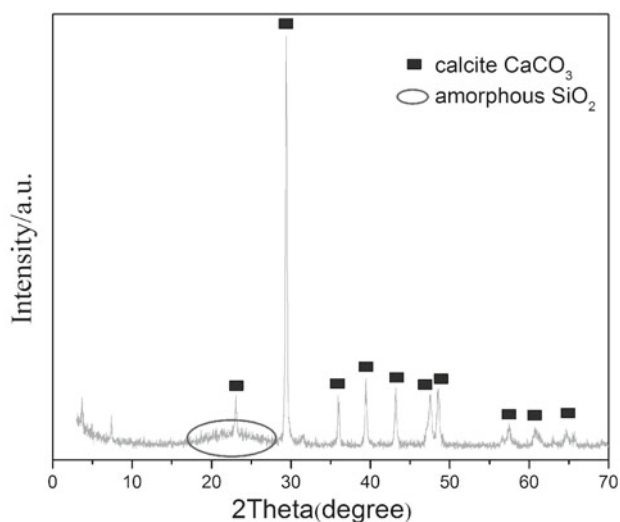


Figure 5. XRD pattern of the $\text{CaCO}_3\text{-SiO}_2$ composite

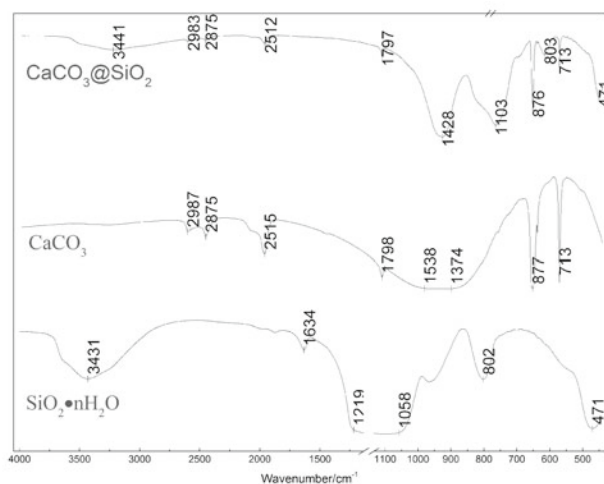


Figure 6. FT-IR spectrogram of $\text{CaCO}_3\text{-SiO}_2$ composite, SiO_2 , and CaCO_3

Table 4. The mechanical performance of silicone rubber filled by different materials

Elements	wt%	Atom [%]
O K	62.74	76.41
Si K	26.36	18.29
Ca K	10.89	5.30
Total	100.00	

The Synthesis Mechanism of $\text{CaCO}_3\text{-SiO}_2$ Composite

The Fourier transform infrared spectroscopy of $\text{CaCO}_3\text{-SiO}_2$ composite, SiO_2 and CaCO_3 are shown in Figure 6. In the spectrogram of SiO_2 , the valley in 3431 cm^{-1} and 1634 cm^{-1} represents respectively the stretching vibration and bending vibration of the hydroxy of the silica. The wide valley between 1219 cm^{-1} and 1058 cm^{-1} , the valley in 802 cm^{-1} and 471 cm^{-1} are the characteristic absorption valley of silica, which reflect the stretching vibration and bending vibration of Si-O bond.

In the spectrogram of CaCO_3 , the wide valley between 1538 cm^{-1} and 1374 cm^{-1} , the valley in 877 cm^{-1} and 713 cm^{-1} are the characteristic absorption valley of CO_3^{2-} in carbonate minerals. The wide valley between 1538 cm^{-1} and 1374 cm^{-1} is the characteristic absorption of calcite type, which represents the asymmetric stretching vibration of CO_3^{2-} . The valley in 877 cm^{-1} and 713 cm^{-1} relates to the bending vibration of C-O bond.

In the spectrogram of $\text{CaCO}_3\text{-SiO}_2$ composite, there are 3 features worthy of attention. 1). The absorption valley in 3431 cm^{-1} is wakened and broaden, which indicates the aggregation and hydroxy reduction of silica particles in the composite. Considered the SEM images of the composite, the aggregation and hydroxy reduction are caused by the combination of SiO_2 and CaCO_3 . The combination causes the hydroxy reduction, which means that the hydroxy functional group is involved in the reaction between the SiO_2 and CaCO_3 ; 2). The asymmetric stretching vibration absorption valley of CO_3^{2-} turns sharper, which changed from $1538\text{-}1374\text{ cm}^{-1}$ to

Table 3. EDS result of selected area

Reinforced material	Breaking strength δ /MPa	Elongation at break ϵ /%
SiO ₂ ^(a)	0.84	182.12
CaCO ₃ ^(a)	0.38	98.62
Simple blend of SiO ₂ and CaCO ₃	0.70	138.70
CaCO ₃ -SiO ₂ composite	0.99	156.95

^(a)For the sake of consistency and comparativeness, before adding into the methyl vinyl silicone rubber, the SiO₂ and CaCO₃ here have been through the process of MCM, and then dried in the oven.

1428 cm⁻¹. That means the chemical surroundings of CO³⁻ has changed during synthesis; 3). The stretching vibration absorption valley of Si-O bond sharpens and changes from 1219–1058 cm⁻¹ to 1103 cm⁻¹. That means the chemical surroundings of Si-O bond has changed during synthesis.

Because of the alkalinity of the synthesis system (pH = 10), the surface of CaCO₃ contain mostly the Ca²⁺. And the surface of silica contains mostly silicon hydroxyl (Si-OH)^{14, 15}.

Based on the analysis above, it is speculated that SiO₂ and CaCO₃ are combined by the reaction of their hydroxy functional group¹⁶⁻¹⁸.

The Reinforce of CaCO₃-SiO₂ Composite in Silicone Rubber

The breaking strength δ and elongation at break ϵ of the silicone rubber filled by SiO₂ and CaCO₃-SiO₂ composite are showed in Table 4.

The CaCO₃-SiO₂ composite can enhance the breaking strength δ about 18% more than SiO₂. And the elongation at break ϵ is about 14% less than SiO₂.

Compared with the simple blend of SiO₂ and CaCO₃, the CaCO₃-SiO₂ composite can enhance the mechanical performance of silicone rubber much better, which demonstrates the function of the MCM.

The SEM images of the rubber's cross section are shown in Figures 7. Most of the CaCO₃-SiO₂ composite particles are well distributed between 1 μ m to 5 μ m in size. The narrow size-distribution indicates the well particle-dispersion, which is a positive factor to enhance the mechanical performance of the rubber. The core-shell structure determines the well compatibility between rubber and the composite. The composite featured in the shell of silica are incorporated by silicone rubber, as shown in Figure 7.

CONCLUSION

The CaCO₃-SiO₂ composite is synthesized in MCM by taking ground calcium carbonate as core and hydrated silica as shell materials. The results show that the small SiO₂ particles are well dispersed on the surface of CaCO₃ particles. The SiO₂ particles are tightly connected with CaCO₃ through the Si-O-Ca bond. By the calculation, the theoretical number of the SiO₂ particles is about 10 times as large as that of CaCO₃ particles in the CaCO₃-SiO₂ composite. Mixing CaCO₃-SiO₂ composite in silicone rubber can enhance the breaking strength

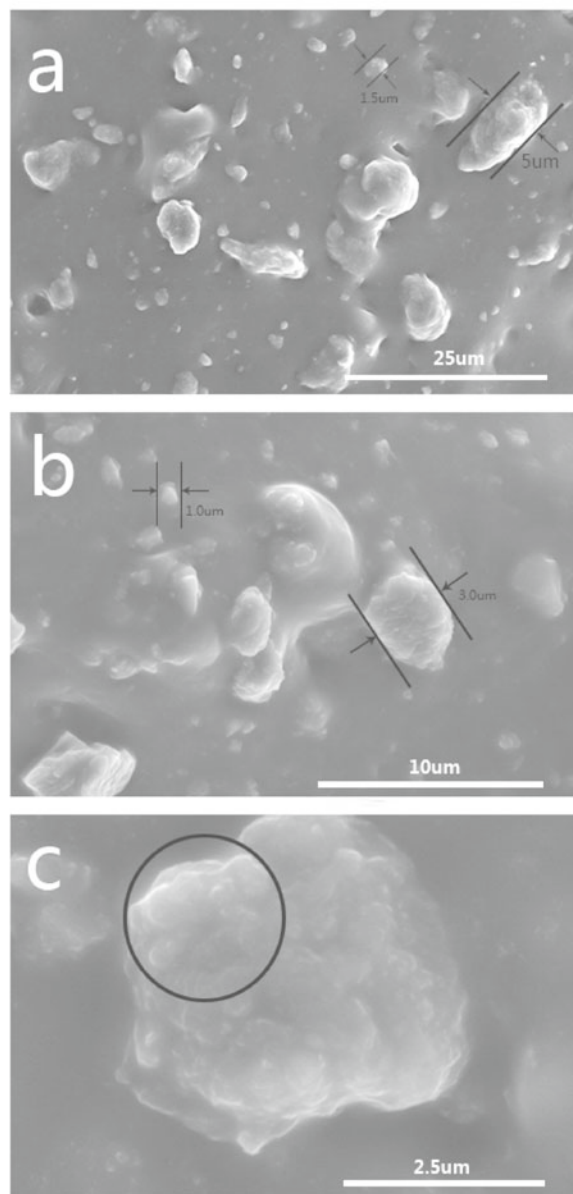


Figure 7. SEM images of the cross section of the silicone rubber filled by CaCO₃-SiO₂ composite

of the silicone rubber about 18% as high as that when mixing the pure SiO₂. And the elongation at break is about 14% less than that of adding the pure SiO₂ sample. Therefore, the CaCO₃-SiO₂ composite might be ideal additive to be in place of the pure SiO₂ in the application of silicone rubber.

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