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# Preparation of $CaCO_3$-$SiO_2$ composite with core-shell structure and its application in silicone rubber

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A new $CaCO_3$-$SiO_2$ composite with core-shell structure was successfully prepared by mechano-chemistry method (MCM). SEM and FTIR indicated that $SiO_2$ particles were homogeneously immobilized on the surface of $CaCO_3$. The well dispersion of this $CaCO_3$-$SiO_2$ composite into silicone rubber can not only reduce the usage amount of $SiO_2$, but also improve the mechanical properties of silicone rubber. By the calculation, the theoretical numbers of the $SiO_2$ particles is about 10 times as large as that of $CaCO_3$ particles in the $CaCO_3$-$SiO_2$ composite. Mixing $CaCO_3$-$SiO_2$ composite in silicone rubber can enhance the breaking strength of the silicone rubber about 18% as high as that when mixing the pure $SiO_2$. And the elongation at break is about 14% less than that of adding the pure $SiO_2$ sample.

**Keywords:** calcium carbonate, silica, silicone rubber, mechnao-chemistry.

## INTRODUCTION

Hydrated Silica ($SiO_2 \cdot nH_2O$) is composed of amorphous silica which is nanometer (1–100 nm) or submicron (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 disperse[3–7].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 ($CaCO_3$) is produced by crushing and grinding the minerals containing $CaCO_3$, 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 $CaCO_3$–$SiO_2$ composite is synthesized by the MCM. $CaCO_3$ is used as the core material. The small $SiO_2$ particles can immobilize homogenously on the surface of $CaCO_3$, which can reduce the aggregation of $SiO_2$ particles. By means of mechanical functions, the MCM makes the $SiO_2$ and $CaCO_3$ particles react physically and chemically with each other[10]. Adding $CaCO_3$-$SiO_2$ composite into silicone rubber can not only reduce the usage amount of $SiO_2$, but also improve the mechanical properties of silicone rubber. It can hope that $CaCO_3$-$SiO_2$ composite can become the ideal material to substitute the pure $SiO_2$ 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 |
| $H_2O$ [ω%] | 0.3 |
| Tap density [g/mL] | 0.8 |

### Synthesis of $CaCO_3$-$SiO_2$ 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 mechao-chemistry process) can cause the surface activation of the silica and $CaCO_3$ particles. The two new activated particles can combine together by physical or chemical functions

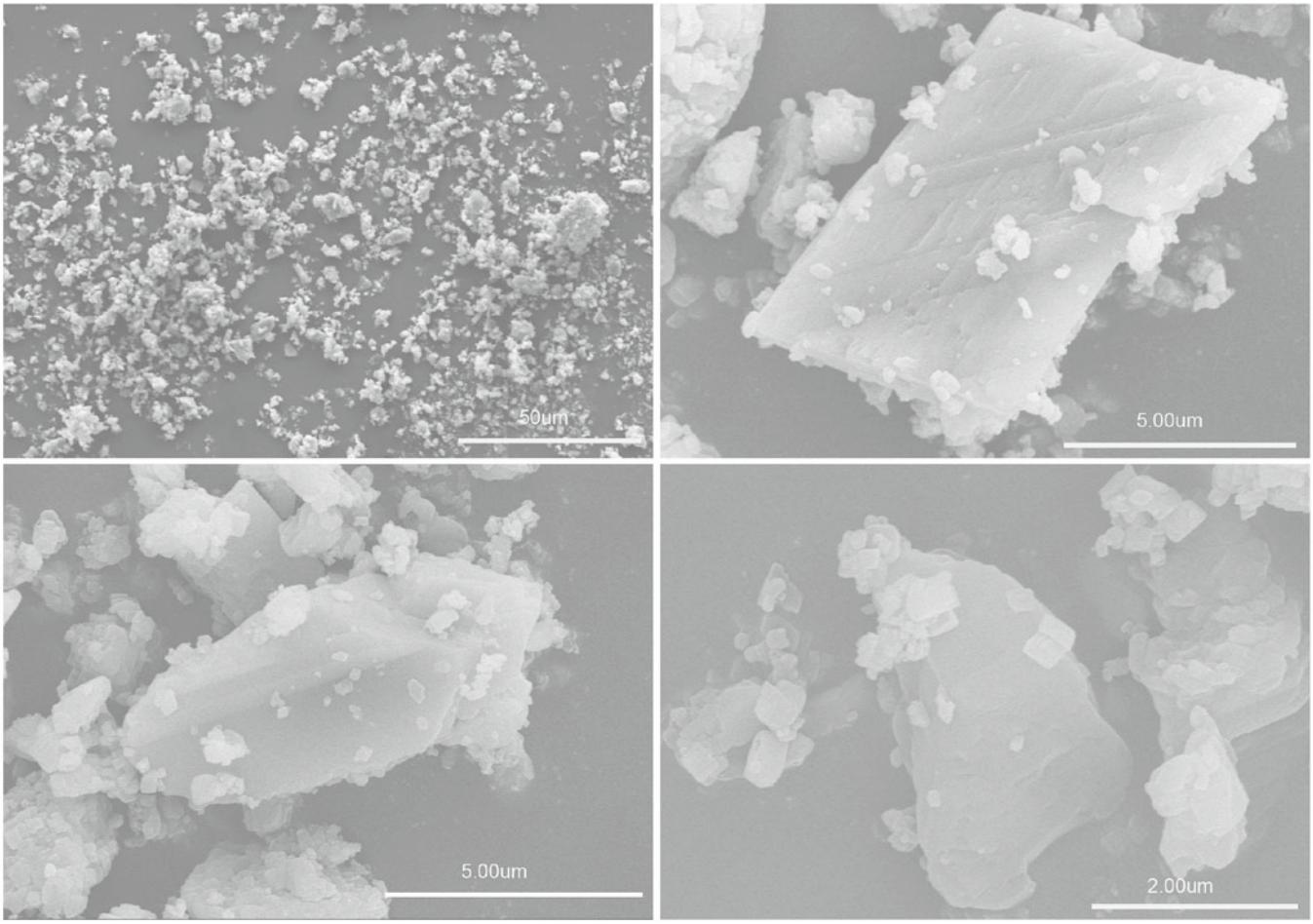


**Figure 1.** SEM images of ground calcium carbonate

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

### Characterization

The size distribution of the $CaCO_3$-$SiO_2$ 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 4000–450 $cm^{-1}$. Powder X-ray diffraction (XRD) was performed on an X/max-rA Advance diffractometer with Cu Kα radiation.

### Preparation of Rubber

The $CaCO_3$-$SiO_2$ 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 |
| $CaCO_3$-$SiO_2$ composite | 45 |
| Hydroxyl silicone oil | 3.5 |
| Zinc stearate | 2 |
| Vulcanizing agent | 1.2 |

### Mechanical Performance Measurement

According to the national standard GB/T 528-2009[13], 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 $CaCO_3$-$SiO_2$ Composite

The size distribution of $CaCO_3$, $SiO_2$, and $CaCO_3$-$SiO_2$ composite are showed in Figure 2. Compared with $CaCO_3$ and $SiO_2$, the $CaCO_3$-$SiO_2$ composite "grows" up obviously. It is the result of combination of $CaCO_3$ and $SiO_2$. The size of $CaCO_3$-$SiO_2$ composite is about 0.1–10 um. 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 $CaCO_3$-$SiO_2$ 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 $CaCO_3$-$SiO_2$ 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

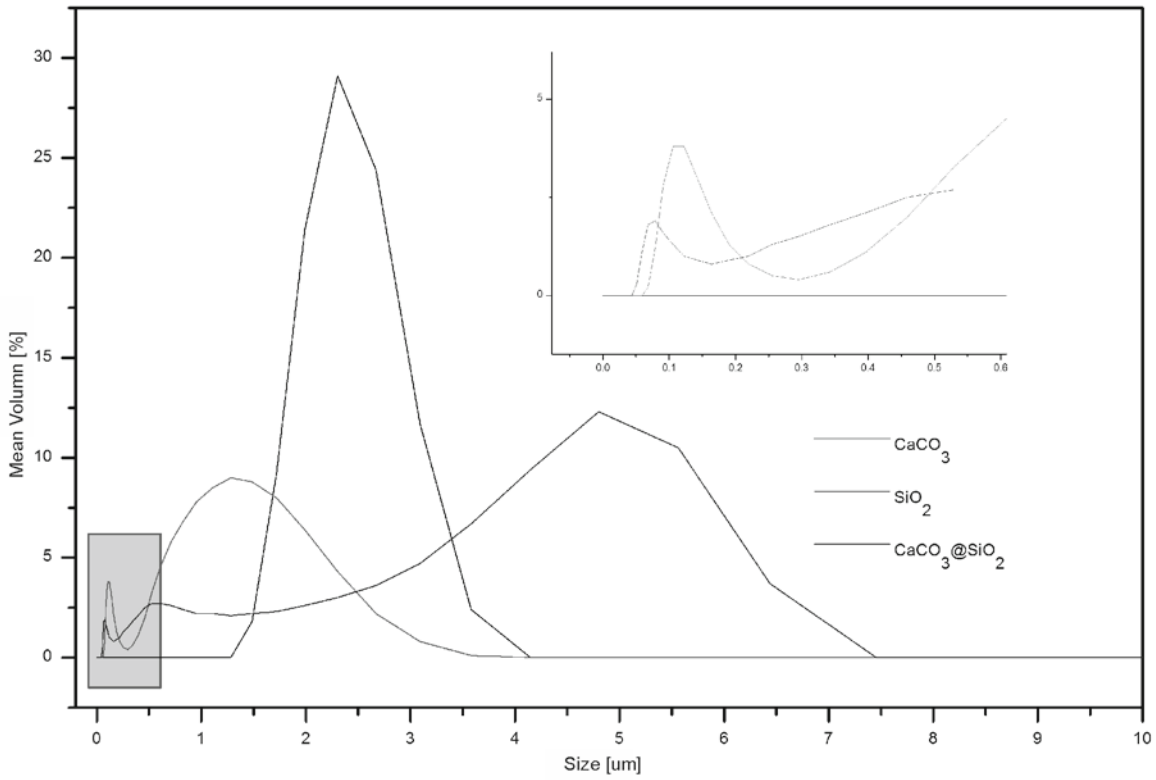


**Figure 2.** Size distributions of $CaCO_3$, $SiO_2$ and $CaCO_3$-$SiO_2$ composite

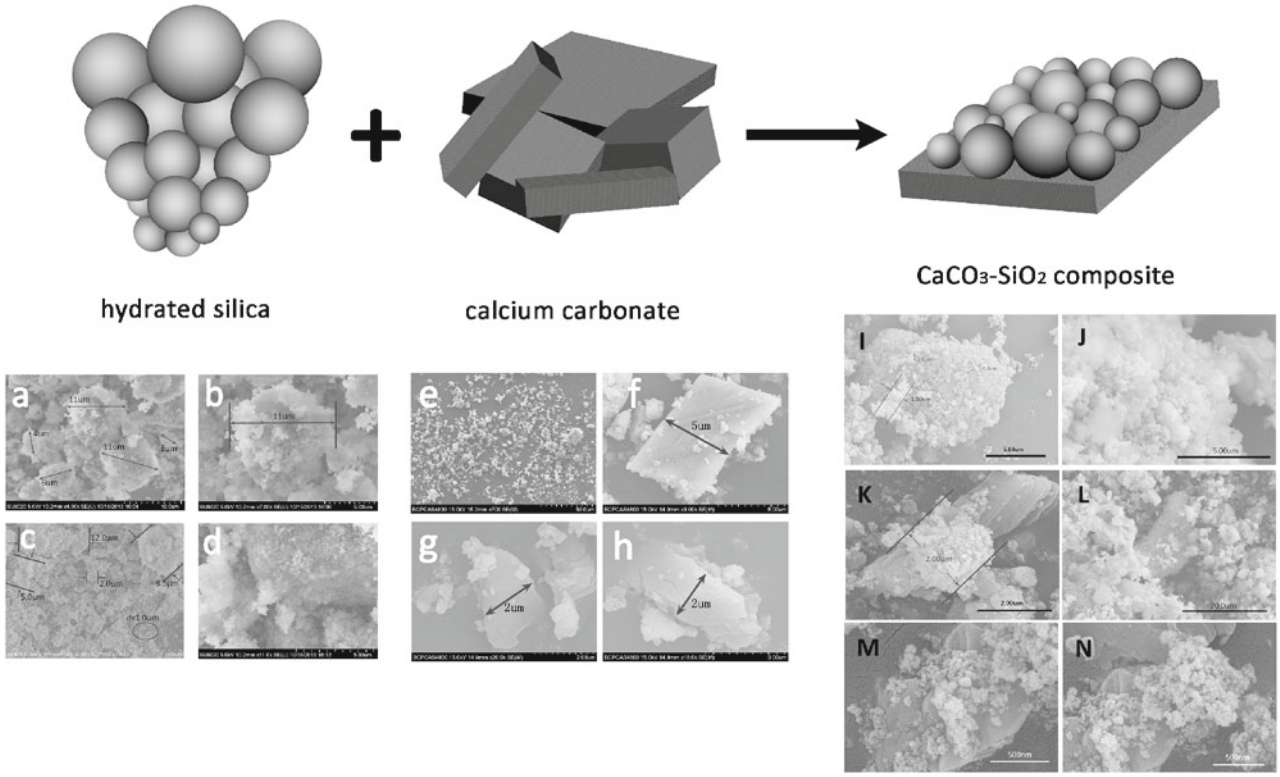


**Figure 3.** Schematic illustration and the corresponding SEM images of the synthesis of $CaCO_3$-$SiO_2$ composite.

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 $CaCO_3$-$SiO_2$ 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 $CaCO_3$-$SiO_2$ composite.

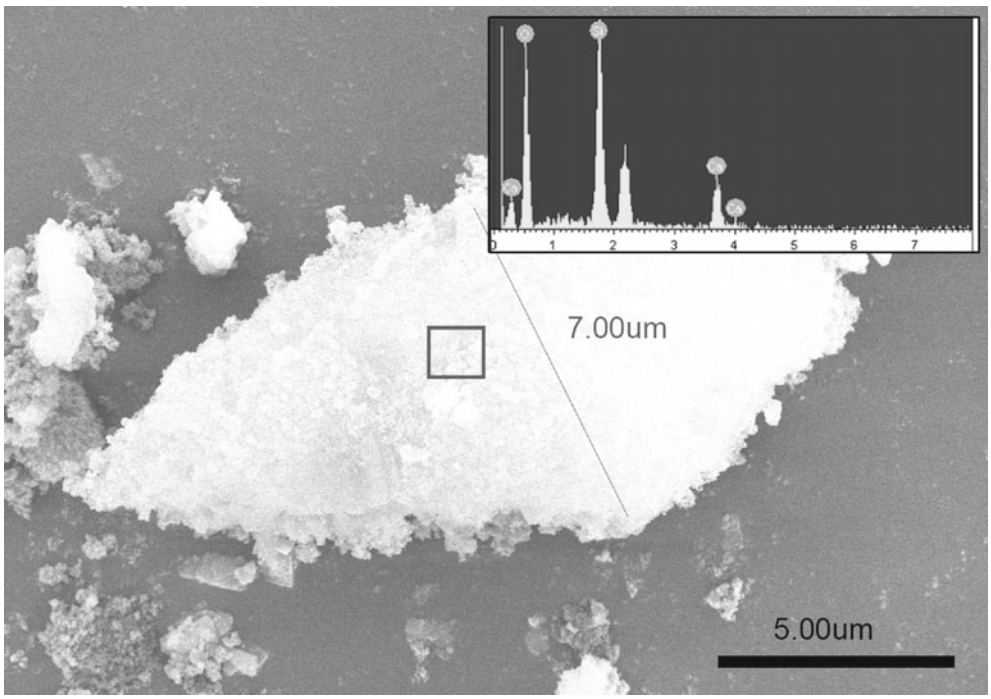


**Figure 4.** TSEM image of fully coated $CaCO_3$-$SiO_2$ composite particle and the EDS results

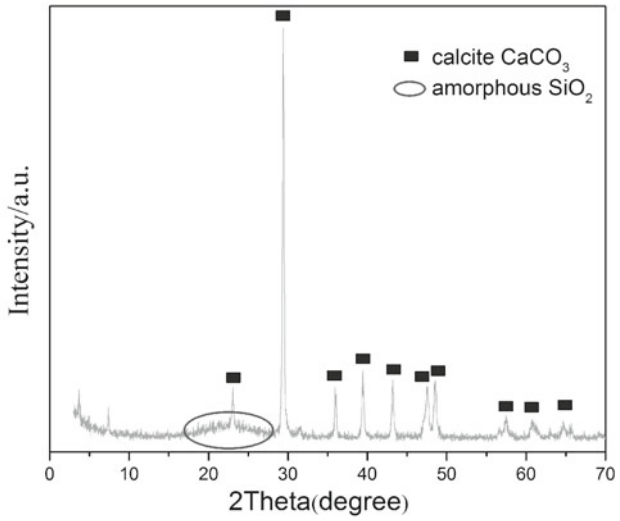


**Figure 5.** XRD pattern of the $CaCO_3$-$SiO_2$ composite

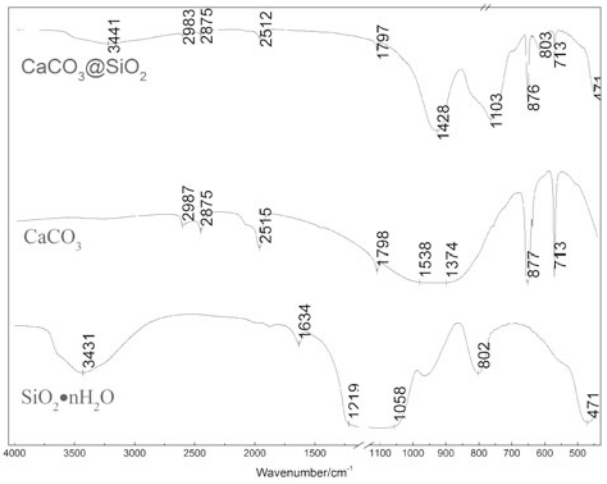


**Figure 6.** FT-IR spectrogram of $CaCO_3$-$SiO_2$ composite, $SiO_2$, and $CaCO_3$

**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 $CaCO_3$-$SiO_2$ Composite

The Fourier transform infrared spectroscopy of $CaCO_3$-$SiO_2$ 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 $CaCO_3$-$SiO_2$ 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 $CO^{3-}$ turns sharper, which changed from 1538~1374 $cm^{-1}$ 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 $SiO_2$ and $CaCO_3$ here have been through the process of MCM, and then dried in the oven.

1428 $cm^{-1}$. That means the chemical surroundings of $CO^{3-}$ 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 $CaCO_3$ contain mostly the $Ca^{2+}$. And the surface of silica contains mostly silicon hydroxyl (Si-OH)[14, 15].

Based on the analysis above, it is speculated that $SiO_2$ and $CaCO_3$ are combined by the reaction of their hydroxy functional group[16–18].

### The Reinforce of $CaCO_3$-$SiO_2$ Composite in Silicone Rubber

The breaking strength δ and elongation at break ε of the silicone rubber filled by $SiO_2$ and $CaCO_3$-$SiO_2$ composite are showed in Table 4.

The $CaCO_3$-$SiO_2$ composite can enhance the breaking strength δ about 18% more than $SiO_2$. And the elongation at break ε is about 14% less than $SiO_2$.

Compared with the simple blend of $SiO_2$ and $CaCO_3$, the $CaCO_3$-$SiO_2$ 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 $CaCO_3$-$SiO_2$ composite particles are well distributed between 1 um to 5 um 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.

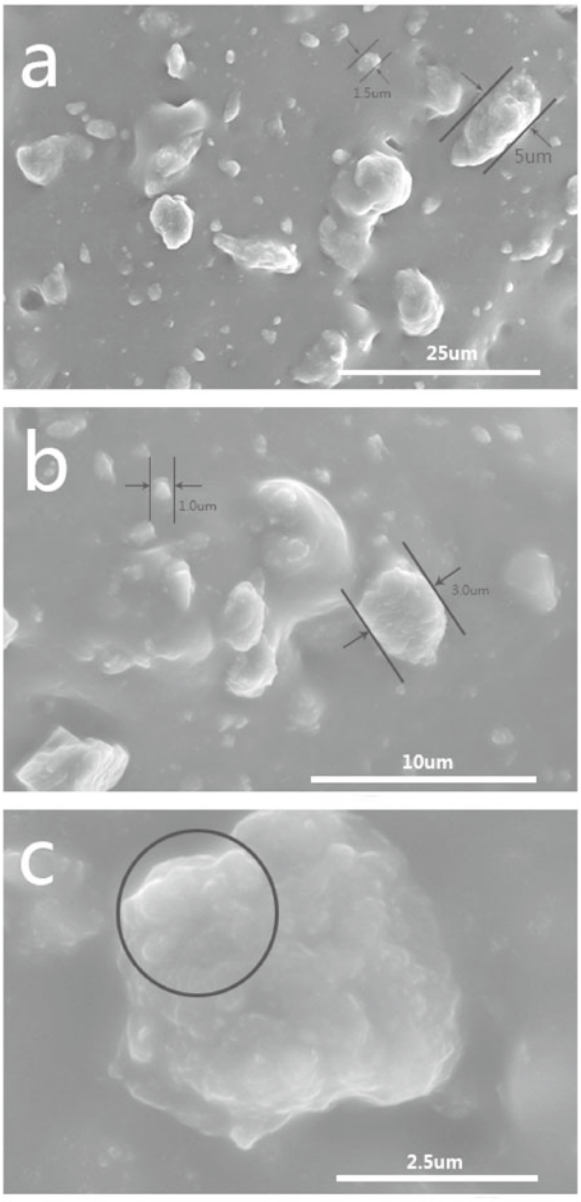


**Figure 7.** SEM images of the cross section of the silicone rubber filled by $CaCO_3$-$SiO_2$ composite

## CONCLUSION

The $CaCO_3$-$SiO_2$ composite is synthesized in MCM by taking ground calcium carbonate as core and hydrated silica as shell materials. The results show that the small $SiO_2$ particles are well dispersed on the surface of $CaCO_3$ particles. The $SiO_2$ particles are tightly connected with $CaCO_3$ through the Si-O-Ca bond. By the calculation, the theoretical number of the $SiO_2$ particles is about 10 times as large as that of $CaCO_3$ particles in the $CaCO_3$-$SiO_2$ composite. Mixing $CaCO_3$-$SiO_2$ composite in silicone rubber can enhance the breaking strength of the silicone rubber about 18% as high as that when mixing the pure $SiO_2$. And the elongation at break is about 14% less than that of adding the pure $SiO_2$ sample. Therefore, the $CaCO_3$-$SiO_2$ composite might be ideal additive to be in place of the pure $SiO_2$ in the application of silicone rubber.

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