

INFLUENCE OF SURFACE-MODIFICATION FOR CALCIUM CARBONATE ON THE INTERACTION BETWEEN THE FILLERS AND POLYDIMETHYLSILOXANE*

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Abstract The surface of calcium carbonate (CaCO_3) particles was modified with stearic acid (SA) and the chemical structures of the product were characterized by FT-IR analysis. The interaction between polydimethylsiloxane (PDMS) and CaCO_3 fillers with different surface character was investigated by means of dynamic rheological and bound rubber tests for uncured compounds and mechanical properties measurements for the corresponding vulcanites. The results of dynamic tests indicate that with the increase of SA mass fraction, the span of the linear viscoelastic region broadens and the height of the modulus plateau decreases. The reasons for these are ascribed to that the SA decreases the surface energy of filler particles and weakens their tendency to agglomerate. Moreover, the results of mechanical measurements reveal that the vulcanized compound filled with modified filler has a relative high tensile strength induced by a reinforced interaction between filler and polymer matrix, which is confirmed by the bound rubber tests and transmission electron microscopy (TEM) observations.

Keywords: Polydimethylsiloxane; Stearic acid; Surface modification; Filler network; Viscoelastic behavior.

INTRODUCTION

Nowadays, composite materials which are composed of a polymer matrix and filler particles play an increasing role because of their lighter weight and better corrosion resistance^[1]. Recent years, for the special engineering requirement of high building and concrete establishment joints, room temperature vulcanized (RTV) silicone sealants mainly consisting of polydimethylsiloxane (PDMS) filled with filler particles have become to the research hotspots^[2, 3]. In this respect, nano-calcium carbonate (CaCO_3) has been extensively applied in RTV sealant industries due to its several remarkable benefits such as abundant raw material resource, stable properties and low price as compared with fumed SiO_2 ^[4, 5]. Incorporating CaCO_3 particles into PDMS based materials can not only reduce the manufacturing cost but also impart enhanced performances such as tensile strength, modulus, elongation, thixotropy and storage stability. Although many papers have been dealt with the particle filled PDMS system^[6–10] and CaCO_3 filled polymer system^[11–14], few studies concerning on PDMS filled with CaCO_3 have been reported up to date.

It is known that the hydrophilic and lipophobic character of CaCO_3 make it difficult to disperse uniformly in polymeric matrix. Particulate CaCO_3 usually agglomerates, leading to the weakness of its interfacial interaction with polymer chain^[15]. In general, those zones of weaker cohesion are where flaws and other defects will be initiated upon stressing and cause failure of the composite materials. Hence, it is necessary to modify the surface of CaCO_3 in order to enhance the filler and polymer interaction.

It should be emphasized that understanding the rheology of composites is not only essential for optimizing

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their compounding and processing but also for achieving the targeted end properties. It is accepted that measurements of dynamic viscoelastic behavior for filled polymer systems has been a well-established approach to probe the interaction between filler and polymer matrix and the filler dispersion condition^[16]. Although some literatures have involved in the surface modification of CaCO_3 ^[11, 17–19], to our knowledge, few reports concerning the effect of modified agent content on the dynamic viscoelastic behavior of PDMS/ CaCO_3 compounds have been reported^[20]. The aim of present paper is to modify the surface of CaCO_3 fillers with stearic acid and to examine the interaction between PDMS and CaCO_3 based on dynamic rheological and bound rubber tests for uncured compounds, and mechanical properties measurements for the corresponding vulcanites.

EXPERIMENTAL

Materials and Sample Preparation

The hydroxyl-terminated polydimethylsiloxane (PDMS, $\eta = 50$ Pa·s at 25°C) was a commercially available product from GE Toshiba Silicones Co., Japan. CaCO_3 (average particle diameter = 40–80 nm) was supplied by Hunan Jinxin Chemical Industry Co., Ltd, China. The stearic acid and crosslinking agent (methyl tributanoxime silane) were purchased from Hangzhou Oil and Fat Chemical Industry Co., Ltd, and Hangzhou Guibao Chemical Industry Co., Ltd, China, respectively.

The surface-modification for CaCO_3 fillers was performed on a high speed mixer followed by a procedure: (1) CaCO_3 was put into the high speed mixer and was heated, and consequently mixed until the temperature reached 105°C. At this temperature the stearic acid was added. The temperature of mixer and ramp rate were set at 125°C and 2 K/min, respectively. (2) The mixers were mixed for another 5 min after the temperature approached 125°C. Finally, the product was cooled to room temperature for preparation of PDMS/ CaCO_3 compounds.

The preparation of PDMS/ CaCO_3 compounds was carried out in a planetary mixer (XSJ-2, Chengdu Keqiang Polymer Engineering Co. China) with a rotor speed of 50 r/min under vacuum at room temperature. 100 phr PDMS and 80 phr CaCO_3 were put into the planetary mixer and were mixed for 90 min, and then 5 phr crosslinking agent was added and mixed for another 10 min. Finally, the product was extruded in a plastic cylinder (310 mL) for storage and measurements.

Characterization and Measurements

FT-IR and particle size analysis

Fourier transform infrared (FT-IR) analysis was conducted through Bruker Vector 22 spectrometer (Bruker Co. Germany). The flake sample was prepared on a press machine. The particle size analysis was performed on a LS particle size analyzer (LS230, Shanghai Qianxin Co. China). Before test the sample was agitated in ethanol for 5 min under ultrasonic condition.

Rheological tests

The dynamic rheological properties were measured on an advanced rheometric expansion system (ARES, TA Instrument. USA) in the model of dynamic strain sweep and dynamic frequency sweep, using disc specimens with a thickness of 2.0 mm and a diameter of 25 mm. For the strain sweep, the test was conducted with a frequency of 10 rad/s by varying the strain from 0.01% to 100%. For the frequency sweep, the test was performed at the frequencies from 100 rad/s to 0.01 rad/s at strain within the linear viscoelastic region determined by strain sweep of 1%.

Mechanical properties measurements

The tensile strength, elongation at break and tensile modulus at 100% elongation were measured on an electronic multifunctional tensile test machine (SANS-CMT4204, Shenzhen Sans Testing Machine Co. China) under tensile rate of 500 mm/min at room temperature. The specimens for measurements were vulcanized in a mould under 25°C and 55% relative humidity for 7 days and were then stamped out into dumbbell type. The value of each mechanical property parameter was determined by the average of four specimens.

Bound rubber tests

The procedure for the test of bound rubber content used here was based on the method proposed by Wolff^[21]. The small pieces of about 2 g of filled compounds were immersed in 25 mL toluene for 7 days at room temperature. After extraction, the rubber-like gel was dried in an oven at 70°C until the sample weight approached constant. The percentage of the bound rubber content was calculated according to the equation as given by

$$R_B = \frac{W_{fg} - W \left[\frac{m_f}{m_f + m_p} \right]}{W \left[\frac{m_f}{m_f + m_p} \right]} \times 100$$

in which W_{fg} is the weight of rubber-like gel, m_f is the weight of filler in the compound, m_p is the weight of polymer in the compounds, and W is the weight of the specimen tested.

Morphological observation

Transmission electron microscopy (TEM, JEM 1200EX, Electron Co. Japan) was used for observing the filler dispersion. Vulcanized samples were microtomed and sections of 100 nm were obtained for observation.

RESULTS AND DISCUSSION

Characterization for Surface-Modified CaCO_3

Figure 1 presents the IR spectra of CaCO_3 filler without and with 2 wt% stearic acid (SA) modification, respectively. There exists a single absorption peak at 1455.7 cm^{-1} for unmodified CaCO_3 , which is ascribed to the stretching vibration of $\text{C}=\text{O}$. For modified one, however, the intensity of such peak becomes much stronger and the wavenumber shifts 6.6 cm^{-1} towards high wavenumber direction. This phenomenon is caused by the interaction of SA with CaCO_3 and the peak can be attributed to the vibration of RCOOCa . Moreover, the absorption peaks appearing at 2853, 2920 and 3438 cm^{-1} are assigned to the stretching vibration of $-\text{CH}_2$, $-\text{CH}_3$ and $-\text{OH}$, respectively. Hence, we can conclude that the SA has adsorbed onto the surface of CaCO_3 firmly through the ion bond.

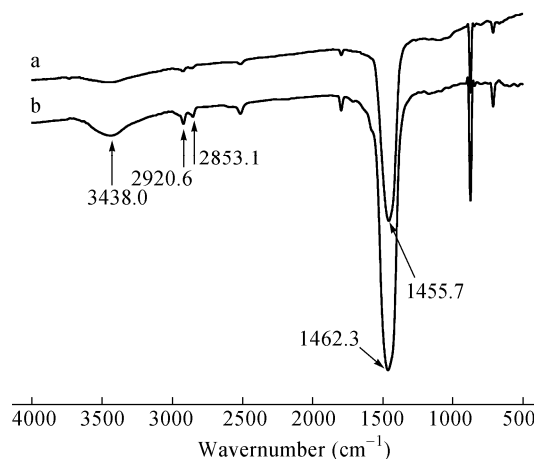


Fig. 1 IR spectra of unmodified CaCO_3 (a) and modified CaCO_3 (b) with 2 wt% stearic acid

Figure 2 gives the particle size distribution diagram of CaCO_3 filler without and with 2 wt% SA modification, respectively. It is seen that the modified CaCO_3 has a much great particle size distribution and becomes polydisperse, *i.e.* the number of peaks increases from 2 to 4. In addition, the surface-modification of filler particles also augments the average particle diameter. The reasons for these are believed to be that the SA

covered on the particulate surface changes the inorganic rigid particle from monodisperse to chain shape and turn “rigid” to “flexible”, leading to a greater distribution and a larger particle size. Figure 3 gives the TEM images of CaCO_3 filler before and after surface modification, which could support the argument further.

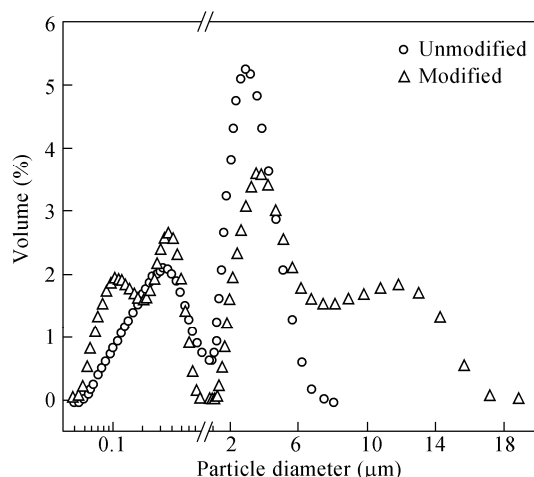


Fig. 2 Particle diameter distribution of CaCO_3 with different surface character

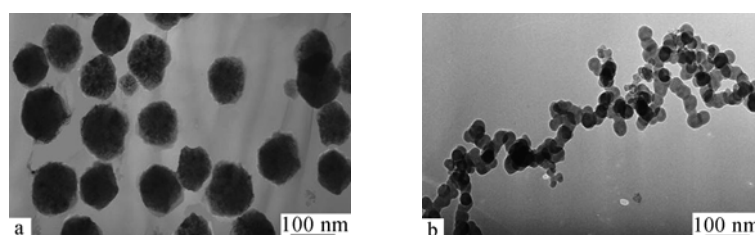


Fig. 3 TEM images of CaCO_3 filler with different surface character obtained in anhydrous ethanol: (a) unmodified and (b) modified

Effect of Stearic Acid Mass Fraction on Dynamic Viscoelastic Behavior

Figure 4 shows the plots of dynamic storage modulus (G') versus strain amplitude (γ) measured at 25°C and 10 rad/s for the PDMS/ CaCO_3 compounds with a constant filler content (80 phr) but different level of filler surface-modifications by SA. It can be found that in all cases, a linear viscoelastic behavior corresponding to strain-independent G' can be observed at small strain amplitude ($\gamma < 1\%$). However, G' drops sharply with increasing strain up to a critical value (γ_c). A remarkable decrease in G' above γ_c is attributed to the existence of filler network in elastomer matrix and is referred to as “Payne effect”^[20, 22]. The nonlinear viscoelastic behavior can be related to the deagglomeration of filler particles and molecular disentanglement between PDMS and CaCO_3 at high γ . Moreover, there exists a minimum G' value but not a G' plateau when γ reaches 100%^[10], which could be ascribed to that the PDMS/ CaCO_3 compounds are unvulcanized. It is believed that the filler networks form directly due to filler-filler interactions and indirectly due to polymer chains bridging different particles or entanglements of different polymer chains adsorption onto adjacent particles. Hence, the G' value at γ_c reflects the strength and stability of filler network. It is worth emphasizing that increasing the SA mass fraction from 0 to 6% leads to a decrease in G' at small γ , whereas the span of the linear viscoelastic region in which G' remains constant increases. This phenomenon can be explained in view of that the organic monolayer covered on the filler surface decreases the surface energy and makes the filler become more hydrophobic. As a result, the probability of particle agglomeration decreases and the filler network structure formed weakens^[23]. Moreover, filler surface-modification also improves the compatibility of filler and polymer matrix, leading to a stronger interaction between them. However, there exists a critical filler loading (20 phr) for the PDMS/ CaCO_3

compounds, beyond which particle-particle interaction is predominant over particle-polymer interaction^[24]. In addition, it is well known that the γ_c will decrease with increasing filler content for particle filled polymer systems^[25, 26]. Hence, filler surface modification can not only reinforce the interaction between polymeric matrix and filler but also increase the filler contents in case of the same “Payne effect” appearing for particle filled systems. This would be of great value in engineering application for particle filled PDMS materials.

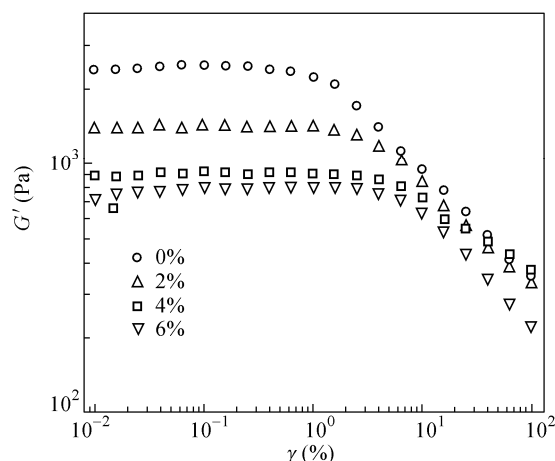


Fig. 4 Strain (γ) dependence of dynamic storage modulus (G') measured at 10 rad/s and 25°C for PDMS filled with unmodified and modified CaCO_3

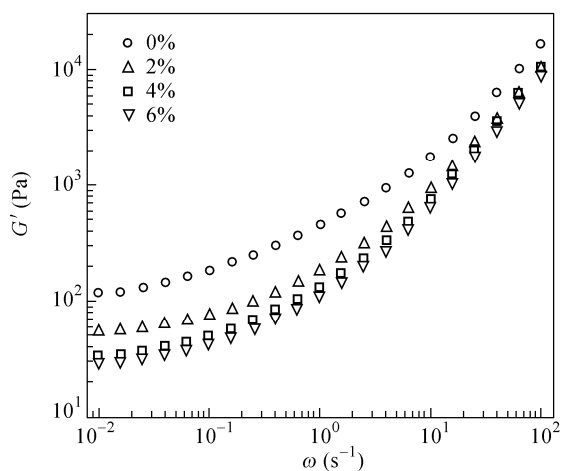


Fig. 5 Frequency (ω) dependence of dynamic storage modulus (G') measured at strain 1% and 25°C for PDMS filled with unmodified and modified CaCO_3

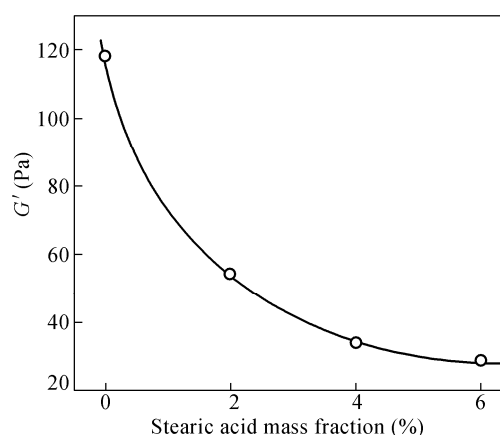


Fig. 6 Frequency (ω)-independent dynamic storage modulus (G') as a function of mass fraction of stearic acid for the PDMS/ CaCO_3 compounds

Figure 5 presents the curves of G' versus frequency (ω) measured at 25°C and strain 1% for the PDMS/ CaCO_3 compounds with a constant filler content (80 phr) but different level of filler surface-modifications by SA. It can be seen that G' decreases linearly with decreasing ω for all samples in the high ω regions, but the linear viscoelastic behavior disappears in the low ω regions. This phenomenon declares that all compounds display an extraordinary ω -independent rheological behavior in the low ω regions, which is generally referred to a “secondary plateau” or “terminal shoulder-like trend”. It is believed that the solid-like behavior is a special viscoelastic behavior of multiphase polymer systems and the reasons for long time relaxation are involved in the formation of three-dimensional ordered structure such as framework, filler

network, agglomerates and so on^[20, 27]. Hence, the width and height of the modulus plateau in relation to filler network decrease with increasing SA mass fraction from 0 to 6%. Figure 6 presents the plot of ω -independent G' as a function of SA mass fraction for the PDMS/CaCO₃ compounds. It is obvious that with increasing SA mass fraction G' decreases but levels off when SA mass fraction approaches 4%, which can be related to a maximum level of surface-modification. The same evolution trend corresponding to strain-independent G' also can be found in Fig. 4.

Effect of Stearic Acid Mass Fraction on the Formation of Bound Rubber

Figure 7 gives the dependence of bound rubber formation on SA mass fraction for PDMS/CaCO₃ compounds with a constant filler content (80 phr). In general, bound rubber means the rubber portion that can no longer be separated from filler when the rubber batch is extracted in a good solvent (such as toluene) for rubber over a specified period of time at room temperature. The formation of bound rubber involves physical adsorption, chemical adsorption and mechanical interaction and is unanimously believed to be the macroscopic result of rubber-filler interactions^[28]. It can be seen from Fig. 7 that with the increase of SA mass fraction, the bound rubber content (ϕ_R) of the compounds increases, implying a reinforced interaction between filler and polymer matrix. Moreover, it is noted that the curve levels off in the high mass fraction regions which shows agreement with the varying tendencies as presented in Fig. 6.

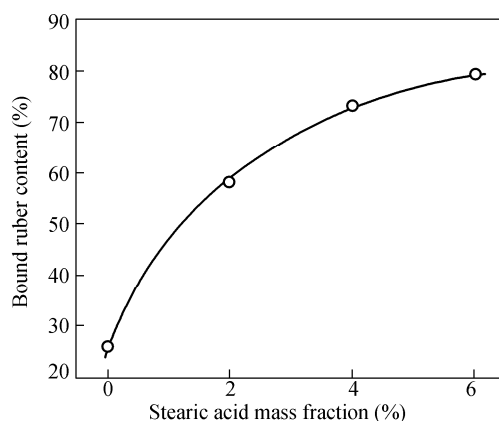


Fig. 7 Bound rubber content as a function of mass fraction of stearic acid for the PDMS/CaCO₃ compounds

Effect of Different CaCO₃ Filler on Mechanical Properties

Figure 8 presents the column diagram of the mechanical properties for vulcanized samples without filler, with unmodified filler (80 phr) and with 2 wt% SA modified filler (80 phr). It can be seen that the sample without filler has a low tensile strength and a low elongation at break which make it has almost no application value. Moreover, incorporating CaCO₃ filler into PDMS could improve its mechanical properties dramatically. As compared with the sample containing unmodified filler, the sample containing modified one has a relative high tensile strength, a high elongation at break and a relative low modulus at 100% elongation. We attribute those phenomena to a much stronger interaction between filler and polymeric matrix, because the SA adsorbed onto filler surface decreases the probability of particle aggregates and improves the compatibility between filler and polymeric matrix. On the other hand, the adsorption of SA also increases the particle size and size distribution as shown in Fig. 3, which are preferable to increase the elongation at break^[23]. As a result, the vulcanized sample containing modified filler was endowed with a high tensile strength and a high elongation at break.

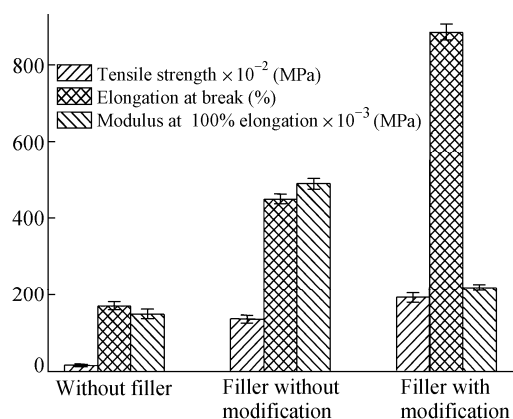


Fig. 8 The effects of different fillers on mechanical properties of vulcanized PDMS/CaCO₃ compounds

However, the sample containing modified filler has a relative low modulus. It is known that the tensile strength is the predominant factor of the sample at break, and the modulus is the predominant factor when the length of the vulcanized sample is stretched by 100%. The former implies total interaction while the latter implicates partial interaction between the filler and polymeric matrix. It seems that the particle aggregates play a predominant role when the length of sample is stretched lower to 100%. Hence, the sample containing modified filler was endowed with a low modulus because of the low probability of particle aggregates.

Effect of Different CaCO₃ on Morphological Behavior

Figure 9 gives the TEM images of vulcanized PDMS/CaCO₃ samples with different filler surface character, in which bright region represents PDMS phase while dark region represents filler particles. It can be found that large agglomerates of 1–2 μm are visible which means the unmodified fillers are not well dispersed in the polymer matrix; whereas in the sample containing modified one, the filler particles are dispersed uniformly. The results of TEM observation are consistent with the conclusions based on the viscoelastic behavior, bound rubber and mechanical properties measurements mentioned above.

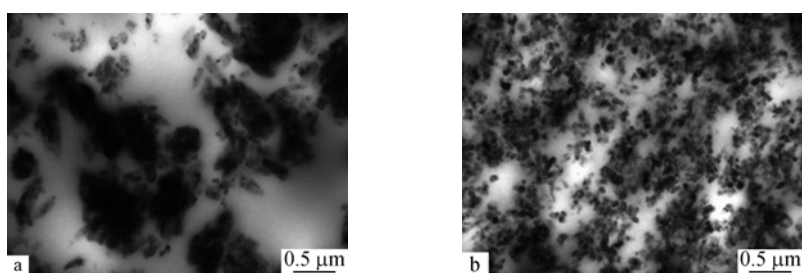


Fig. 9 TEM images of vulcanized PDMS/CaCO₃ compounds with different surface character: (a) unmodified and (b) modified

CONCLUSIONS

The surface of CaCO₃ filler was modified with stearic acid (SA) through varying mass fraction from 0 to 6% and the chemical structures of the product were characterized by FT-IR analysis. As SA mass fraction increases, the dynamic storage modulus (G') in small strain range decreases and the span of the linear viscoelastic region broadens. The reasons for these are ascribed to the decreased particle-particle interaction and weak filler network structure, because the surface-modification of CaCO₃ fillers could decrease their surface energy and their tendency to agglomerate with each other. The results of bound rubber tests reveal a reinforced interaction between polymer and filler with increasing SA mass fraction. Moreover, the modified filler endows vulcanized

samples with higher tensile strength and longer elongation at break, but relative low modulus at 100% elongation. The resultant stronger interactions and higher tensile strength are resulted from the improvement of compatibility between filler and polymer due to the absorption of SA onto the filler surface. Furthermore, the organic monolayer on the filler surface broadens the particle size and the size distribution, resulting in a high elongation at break. It is suggested that a relative low modulus for sample containing modified filler is resulted from less filler agglomeration. TEM observations confirm the conclusions further.

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