Influence of Incorporating CaCO₃ into Room Temperature Vulcanized Silicone Sealant on Its Mechanical and Dynamic Rheological Properties

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ABSTRACT: Silicone sealants with low modulus and high elongation were prepared by using ketoxime silane as chain extender agent, and a novel silane coupling agent acting as adhesion promoting agent was synthesized. Mechanical properties of vulcanized polydimethylsiloxane (PDMS) filled with large amounts of carbonate calcium (CaCO₃) and dynamic viscoelastic properties of unvulcanized samples were investigated through electronic multifunctional tensile tests, dynamic mechanical analyzers, and dynamic rheological measurements. The results of mechanical tests indicate that diminishing the particle diameter size, narrowing the particle diameter distribution, and increasing the filler amount lead to a relative high tensile strength and modulus at 100% elongation, but a relative low elongation at break. The reasons for these are believed to be the evolution of molecular interactions and the formation of additional physical crosslinking induced by the filler network. Compared to virgin PDMS, there is a significant elevation of glass transition temperature with filler addition. On the other hand, the results of dynamic rheological measurements reveal that as filler amount increases, the span of the linear viscoelastic region in which dynamic storage modulus (G') is constant in low strain amplitude narrows. However, a characteristic plateau phenomenon appears in low frequency regions together with increasing the width and height of the modulus plateau. This phenomenon is also ascribed to the formation of a filler network due to filler–polymer and filler–filler interaction. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2027–2035, 2007

Key words: mechanical properties; dynamic rheological behavior; filler network; particle diameter; polydimethylsiloxane

INTRODUCTION

Silicone sealants with low modulus and high elongation have good thermal characteristics, chemical resistance, and environmental stability over a vast temperature range, and offer excellent hydrophobicity and gap-filling capabilities between surfaces.[1,2] The sealants belong to room temperature vulcanized silicone, which is stable in the absence of moisture and can cure to an elastomer upon moisture. Having series of excellent properties, especially low modulus (< 0.4 MPa), high elongation (> 800%) characteristics, and good adhesion capacities, silicone sealants are used in highway, airport, bridge, and tunnel joints on which extreme movement occurs.[3,4] However, a major drawback of silicone sealants lie in that their poor mechanical properties induced by weak intermolecular forces between polymer chains. The strength of vulcanized sealants without reinforcement is weak (< 0.2 MPa), so that they are almost useless. Hence, reinforcing fillers are used to improve their mechanical properties. CaCO₃ filler has been extensively applied in room temperature vulcanized silicone sealant due to its advantages such as steady properties, low cost, good dispersion in silicone sealants, and so on.[5,6]

Properties of silicone sealants are governed by the composition, filler size and distribution, and strength of the interfacial bonding between the polymers and the fillers. An important feature in filled polymeric systems is the formation of a secondary particulate network structure when the particle loading is above gelation (percolation) threshold.[7] Depending on whether interparticle attractions and the interactions between the particles and polymer chains are stronger or not, there is either a particle–particle or particle–matrix "network" formation.[8] In addition, the dynamic viscoelastic measurements for filled polymers

have been a well-established approach to study the interaction of filler and polymeric matrix.[9,10] On the other hand, the degree of sag and extrudability of silicone sealants are two important factors for their industrial application, and lower amount of filler will not satisfy the requirement for degree of sag while the higher leads to a poor extrudability. Hence, it is vital to determine proper filler amount to ensure the optimum properties of silicone sealants.

Although many literatures are related to the preparation of silicone sealant with low modulus and high elongation, few reports were dealt with ketoxime silane, which was used as chain extender agent. They mainly used acetamido, alkoxy, and aminoxy silane as chain extender systems, while each of them has its own disadvantage.[11–14] It is a fact extensively accepted that dynamic viscoelastic properties are very important in academic research and commercial application for polysiloxane materials.[15] Many papers have been related to the rheology of particle filled polydimethylsiloxane (PDMS) such as fumed silica, glass bead, and barium titanate.[16–22] To our knowledge, few studies concerning silicone sealants composed of PDMS filled with high amounts $CaCO_3$ have been reported up to date.[23–25] The aim of present work is to synthesize a novel silane coupling agent, which is available for adhesion promoting agent and apply ketoxime silane as chain extender agent, to prepare silicone sealants, and moreover, to investigate the effect of $CaCO_3$ filler on the mechanical properties of silicone sealants and the interactions between the filler and polymeric matrix through dynamic viscoelastic measurements.

EXPERIMENTAL

Materials and samples preparation

The hydroxyl-terminated polydimethylsiloxane (PDMS, $\eta = 50{,}000$ cp, 25°C) was a commercially available product from GE Toshiba Silicones, Japan. $CaCO_3$ was supplied by Hunan Jinxin Chemical Co., China. The crosslinking agent (methyl tributanoxime silane), chain extender agent (dimethyl dibutanoxime silane), and catalyst (dibulytin didodecylate) were purchased from Hangzhou Guibao Chemical Co., Taixing Pigment Additive Fac,. and Shanghai Reagent Co., respectively. The adhesion promoting agent was prepared in our own laboratory.

The adhesion promoting agent was synthesized through the addition reaction by using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (KH-792) and acrylonitrile. Equivalent acrylonitrile was put into the round-bottomed flask loaded with KH-792. The reaction proceeded under reflux conditions for 2–4 h at temperature range from 50 to 70°C. Then, the

TABLE I
Formulations for Silicone Sealant

Materials	Content (phr)
PDMS	100
CaCO3	Variable[a]
Crosslinking agent	5
Chain extender agent	6
Adhesion promoting agent	1
Catalyst	0.1

[a] The filler content was set as following: 70, 80, 90, 100, and 110 phr, respectively.

product was purified and fractions between 200 and 220°C were collected under 730 mmHg.

The preparation of the silicone sealants with low modulus and high elongation was carried out in a planet mixer (XSJ-2, Chengdu Keqiang Polymer Engineering Co., China) in vacuum at room temperature, following a prescription as given in Table I. The mixing procedure is as follows: PDMS and $CaCO_3$ were put into the planet mixer and were mixed for 2 h with a rotor speed of 50 rpm. Crosslinking agent and chain extender agent were added and were mixed for 10 min, and then catalyst and adhesion promoting agent were added and mixed of another 10 min. Finally, the product was extruded in a 310-mL plastic cylinder for storage and measurements.

Properties measurements

FTIR spectrum was obtained through Bruker Vector 22 spectrometer (Bruker Co., Germany). The sample film was prepared on a KBr tablet. ^{1}H-NMR analysis was conducted on a Bruker Advance DMX 500 spectrometer (Bruker Co., Germany) using $CDCl_3$ as solvent. Elemental analysis was performed on Thermo Finnigan Flash EA1112 analyzer (Finnigan Co., USA).

The particle size was measured on a LS particle size analyzer (LS230, Shanghai Qianxin Co., China). Before test, the sample was agitated under ultrasonic condition for 5 min in ethanol.

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 mold under 25°C and 55 RH% for 7 days, and then were stamped out into dumbbell type.

Dynamic mechanical analyses were performed on a dynamic mechanical analyzers (DMA Q800, TA Instrument, USA) in the model of dynamic tempera-

ture ramp sweep, using rectangular specimens with a thickness of 1.5 mm and a width of 12.5 mm. For the temperature sweep, the test was conducted with a frequency of 10 rad/s and strain amplitude of 30 μm by varying the temperature from −130°C to 25°C, and the ramp rate was set at 5°C/min.

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 within the frequency region from 100 to 0.01 rad/s under a constant strain of 1%.
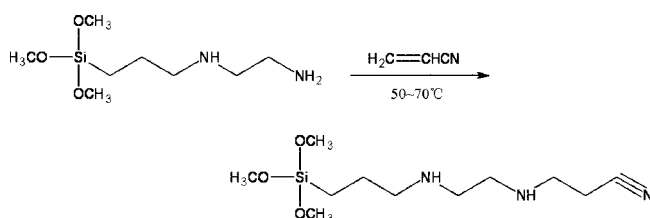
Morphological observation

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

RESULTS AND DISCUSSION

Synthesis and characterization for adhesion promoting agent

Scheme 1 gives the reactive equation of adhesion promoting agent. The IR spectra for the product are shown in Figure 1. It can be found that in IR spectra there exists an absorption peak at 2247 cm^{-1}, which is ascribed to the vibration of $-C\equiv N$. This indicates that the $-C\equiv N$ functional group in acrylonitrile has been added to the molecular structure of product. The single absorption peak appearing at 3298 cm^{-1} is ascribed to the stretching vibration of N—H. A double peak in the vicinity of 3298 cm^{-1} will appear if a $-NH_2$ group exists. Hence, we can conclude that it is the hydrogen atom of $-NH_2$ group that adds to the double bond of acrylonitrile. The peaks appearing at 2900 and 1100 cm^{-1} are ascribed to the vibration of C—H and Si—O, respectively. The result is confirmed further by ^{1}H-NMR spectra as shown in Figure 2. The single absorption peak appearing at δ = 3.55 is ascribed to the proton of

Si—OCH$_3$. Because of the influence of $-C\equiv N$, there exist many peaks for proton of $-CH_2-$ between δ = 0.5 − 3.0. Table II gives the results of elemental analysis for adhesion promoting agent, indicating that the purity of product is high.

Influence of particle diameter size and distribution on mechanical properties

Table III shows the influence of four types of CaCO$_3$ particles with different diameter and distribution on mechanical properties for vulcanized silicone sealants. From the size distribution diagram as shown in Figure 3, it can be seen that the filler AC and ZL have a single peak distribution of size with an average diameter of 1.41 and 4.00 μm respectively. The filler AR has a polydispersity in size with an average diameter of 3.71. The mechanical properties of the vulcanized sealants containing these three types of fillers are almost the same within experimental error.
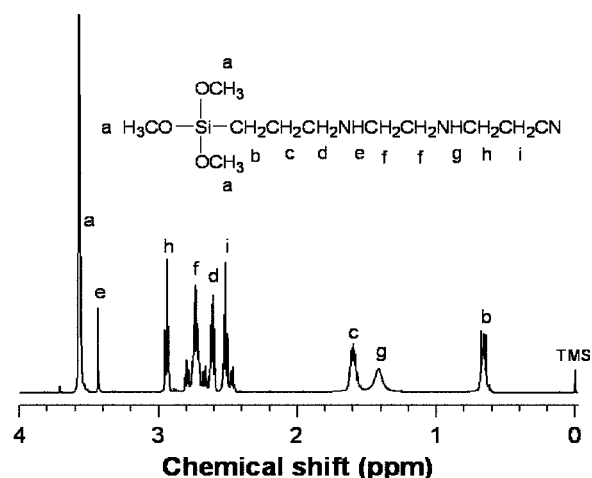

Figure 1 IR spectra of adhesion promoting agent.

Figure 2 ^{1}H-NMR spectra of adhesion promoting agent.

Scheme 1 Reactive equation of adhesion promoting agent.

Element	Experimental (%)	Calculated (%)
Carbon	47.44	48.00
Nitrogen	15.36	15.27
Hydrogen	9.16	9.09

As compared with AR, the size distribution of ZL is much great and the average diameter is very large. The sample containing ZL shows a high elongation at break, a low modulus at 100% elongation, and a low tensile strength as compared with those of the sample containing filler AR. Hence, it is believed that filler with a large size and a wide size distribution is preferable to increase the elongation at break and to decrease the tensile strength and modulus at 100% elongation.

The reinforced mechanism caused by filled particles is due to the linking of aggregates by polymer. It is believed that a single polymer chain is adsorbed on two separate aggregates, resulting in the formation of physical crosslinkage. Fillers with large size or wide size distribution lead to less contact sites and a decrease in the physical crosslink density, resulting in a high elongation at break. As a result, these vulcanized silicone sealants were endowed with a low tensile strength and modulus because of the reduced molecular interactions.

Influence of filler amount on mechanical properties

The filler JL as representative is used to investigate the influence of filler amount on mechanical and dynamic viscoelastic properties. Figure 4 gives the plot of mechanical properties of silicone sealant versus filler content. It is noted that, with increasing the filler amount, there appear an increasing tendency in tensile strength and modulus at 100% elongation while a decreasing tendency in the elongation at break. As mentioned earlier, increase of the filler amount results in more contact sites, leading to a high physical crosslink density. On the other hand,

it is believed that a stronger molecular interaction is dealt with the increase of the probability for polymer chain entanglements. Also, the formed network will become more rigid, increasing the tensile strength and modulus. It is noted that these networks tend to breakdown at lower strains, which causes a decrease in the length of the LVE (linear viscoelastic range) region during the strain sweeps. This will be further discussed in the following section. In brief, the evolution of mechanical properties can be attributed to the more filler–filler, filler–polymer, and polymer–polymer interactions and the additional physical crosslinkage induced by the filler network.

Moreover, there exists a transition in the mechanical properties when filler content is 90 phr. We have suggested that this transition is due to the agglomeration conditions of fillers. In fact, this could be regarded as a critical value, above which the agglomerative particles intercontact with each other and form a continuous network. This leads to an abrupt change in the macroscopic properties.

Influence of filler amount on dynamic mechanical properties

Figure 5(A) shows the DMA curves of dynamic storage modulus (G') versus temperature for samples with different filler contents. Obviously, the G' value increases with the filler contents, which is ascribed to the more filler–filler and filler–polymer interactions. There appear two transition regions for all samples. The former is the glass transition of sealant samples, while the latter is attributed to melting behavior of PDMS[26]. Figure 5(B) presents plots of loss tangent (tan δ) versus temperature for samples with different filler contents. We can obtain exact transition temperature through the peak value of tan δ. Compared to the virgin PDMS with glass transition temperature (T_g) of $-127°C$, addition of filler elevates the T_g of vulcanized sealant samples to $-110°C$. We ascribe this to the restricted segmental mobility imposed by the crosslinking sites (highly constrained amorphous phase). However, there is no distinct evolution among samples from 70 to 100 phr. This might be related to the unchanged network formation by

TABLE III
Influence of Filler Particle Diameter and Distribution on Mechanical Properties
of Silicone Sealant with CaCO₃ Content of 100 phr

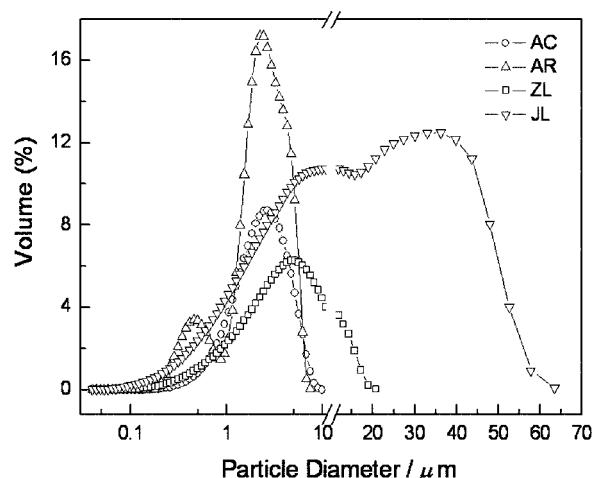| Filler type	Particle average size (μm)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)
AC	1.41	2.54 ± 0.02	731 ± 7	0.17 ± 0.01
AR	3.71	2.50 ± 0.03	742 ± 10	0.16 ± 0.00
ZL	4.00	2.48 ± 0.01	758 ± 4	0.16 ± 0.01
JL	14.40	2.23 ± 0.02	835 ± 5	0.12 ± 0.00

Figure 3 Particle diameter distribution of different $CaCO_3$ type.

chemical crosslinking, which is dominated in the total crosslinking. In view of PDMS having crystalline capacity with decreases of temperature,[26] there is a melting transition zone being approximately −36°C.

Influence of filler amount on dynamic viscoelastic properties

Figure 6(A) presents plots of G' versus strain amplitude measured at 25°C and 10 rad/s. It is obvious that in all cases, a linear viscoelastic behavior corresponding to strain-independent G' can be observed at small strain. However, G' drops sharply with increasing strain up to a critical value. A remarkable decrease in G' above the critical strain is attributed to the existence of filler network in elastomer matrix

and is referred to as Payne effect.[27,28] It is believed that the filler network is formed directly through filler–filler interactions and indirectly through polymer chains bridging different particles or entanglements of different polymer chains adsorption onto adjacent particles. Hence, the G' value at critical strain amplitude reflects the strength and stability of filler network. It is worth noting that increasing the $CaCO_3$ amount from 70 to 110 phr leads to an increase in the G' value at small strain amplitude, while the span of the LVE region in which G' remains constant decreases significantly. To give an obvious observation for the effect of filler amount on G' value, we draw a curve of G' versus filler content as given in Figure 7. It is seen that there is a slight increase in G' with increasing $CaCO_3$ from 70 to 90 phr, while G' increases much rapidly in case $CaCO_3$ content is above 100 phr.
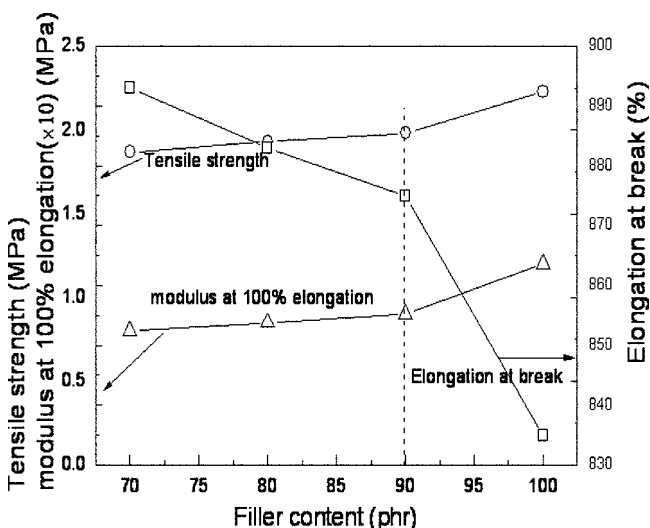

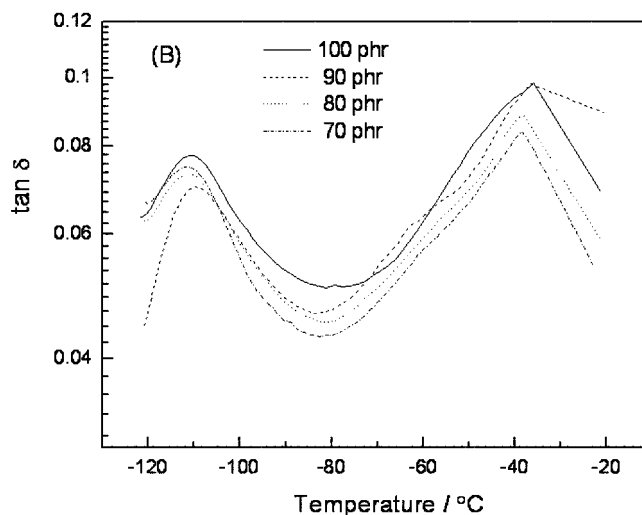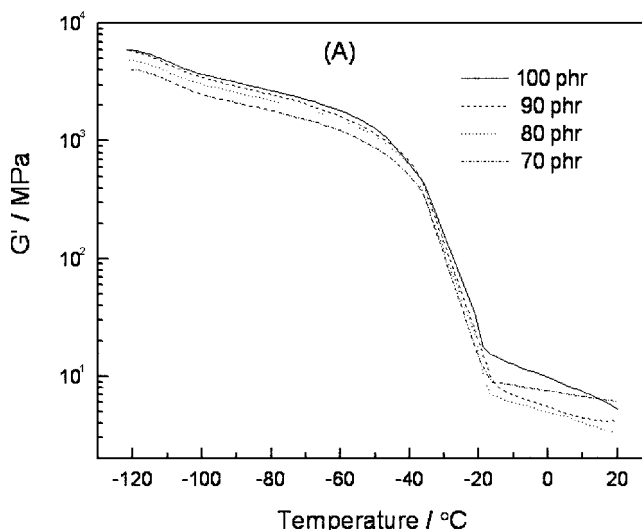**Figure 4** Mechanical properties of silicone sealant with different filler contents.

Figure 5 Temperature dependence of (A) dynamic storage modulus (G') and (B) dynamic loss tangent (tan δ) for vulcanized sealant samples with different filler contents.
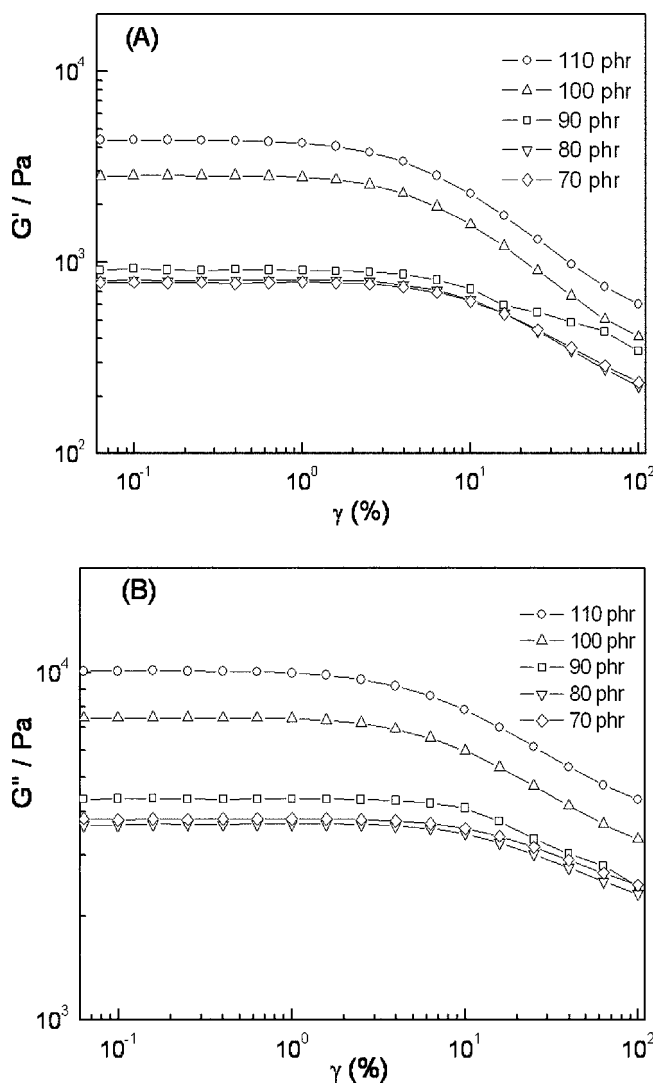
Figure 6 Strain (γ) dependence of (A) dynamic storage modulus (G') and (B) dynamic loss modulus (G'') at 25°C and 10 rad/s for PDMS filled with different CaCO$_3$ contents.

Figure 6(B) gives dynamic loss modulus (G'') as a function of strain amplitude within the region from 0.01% to 100%. Similar to the trend in G', the extent of the linear viscoelasticity region in the low strain amplitude in G'' also decreases with increasing filler amount and above this region G'' value decreases suddenly with increasing strain amplitude. If G' is mainly related to filler network, which is broken down during dynamic strain, G'' is regarded to be substantially controlled by the breakdown and reformation of the filler network.[27] In addition, there is no indication of strain-induced agglomeration over the strain amplitude covered as observed for carbon black filled rubber.[29] If strain-induced agglomeration occurred, a maximum of G'' would appear in the low strain amplitude. In the case of fumed silica, maximum G'' has been observed at the end of the linear

viscoelasticity region due to the disruption of filler agglomerates.[18] On the basis of the dynamic data, one could conclude that the interaction between CaCO$_3$ particles is not as strong as that in fumed silica. Similar to Figure 6(A), there is a big jump in G'' value when CaCO$_3$ content increases from 90 to 100 phr.

Figure 8(A) shows a plot of G' versus frequency (ω) of the compounds at different filler weight fraction measured at 25°C and strain 1%. It can be found that the G' increases with increasing CaCO$_3$ amount, which has been attributed to the solidification of polymer chains on particle surfaces, resulting in a high modulus layer of polymer matrix surrounding filler particles.[30,31] Additionally, G' decreases linearly with decreasing ω for all the samples in the high ω region, but the linear viscoelastic behavior disappears in the low ω region. This phenomenon declares that the PDMS/CaCO$_3$ compounds display an extraordinary ω-independent rheological behavior, which is generally referred to a secondary plateau or terminal shoulder-like trend. According to our previous work,[32] the secondary plateau can be attributed to the existence of filler network, and G' value in the plateau reflects the level of filler network formation. Hence, the width and height of the modulus plateau in relation to the filler network progressively increase as the filler content increases from 70 to 110 phr, especially between 90 and 100 phr, which is in agreement with the observations in Figure 4. Figure 8(B) presents G'' as a function of ω of the compounds at different filler weight fraction. All the samples show varying tendencies upon decreasing ω, similar to those as given in Figure 8(A).

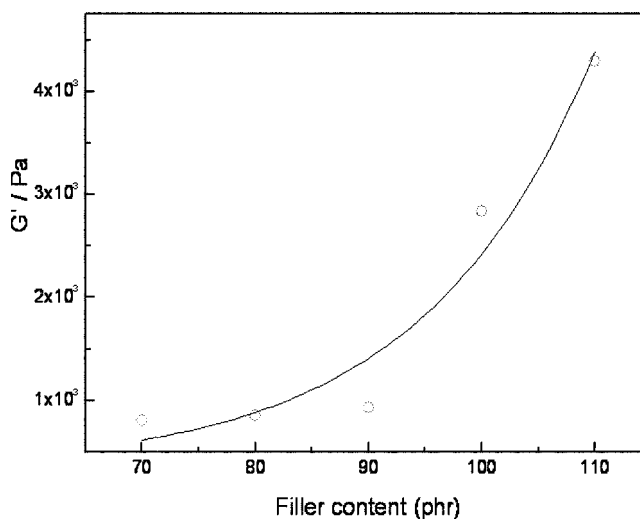Figure 8(C) gives the plot of tan δ versus ω for the compounds at different filler content at 25°C. With

Figure 7 Filler contents dependence of dynamic storage modulus (G') for the compounds.
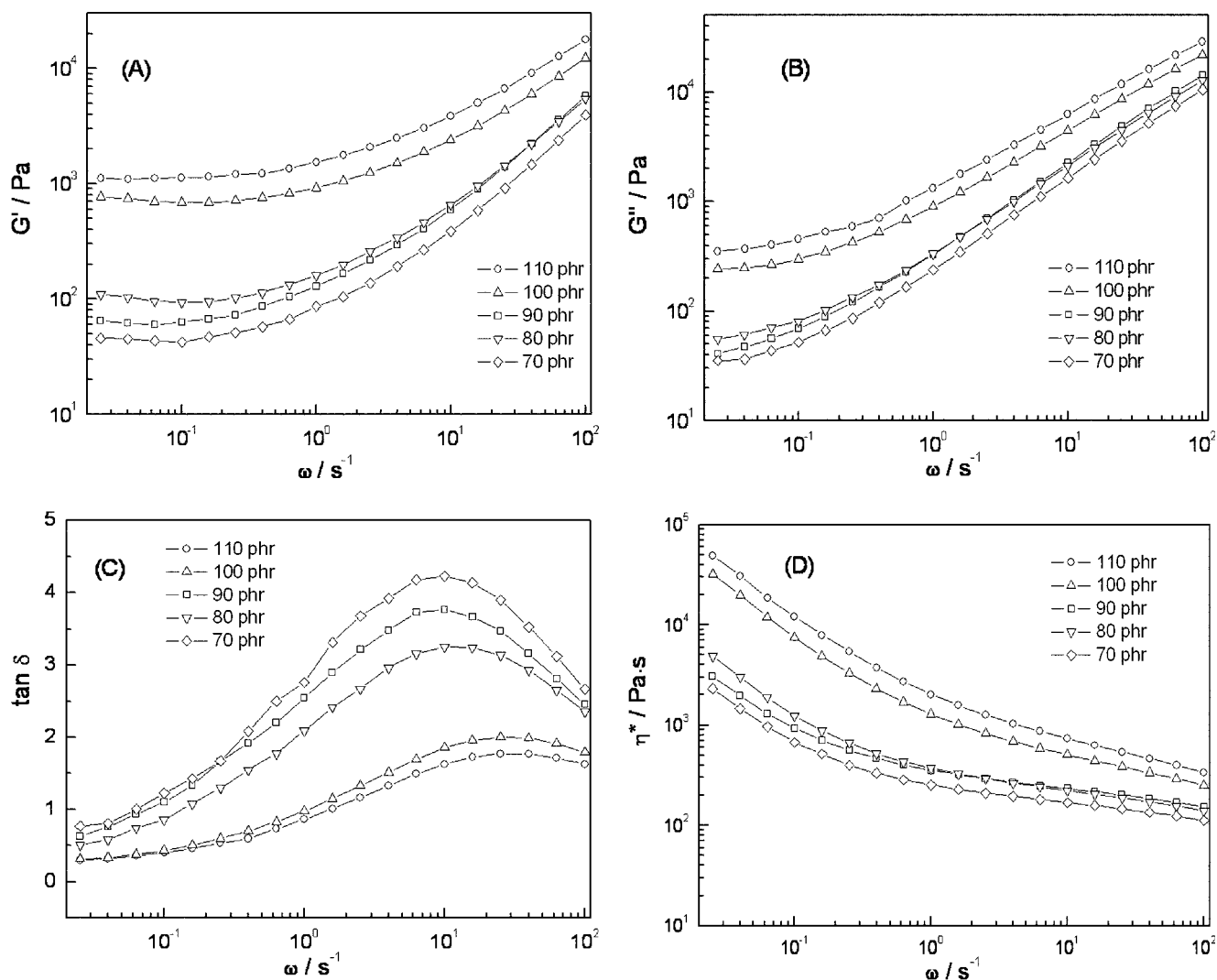
Figure 8 Frequency (ω) dependence of (A) dynamic storage modulus (G'), (B) dynamic loss modulus (G''), (C) dynamic loss tangent (tan δ), and (D) complex viscosity (η^*) at 25°C and strain (γ) 1% for PDMS filled with different CaCO$_3$ contents.

decreasing ω, there appears a peak in the plot at around 10 rad/s for the samples containing CaCO$_3$ of 70–90 phr and at 30 rad/s for the samples containing CaCO$_3$ of 100 and 110 phr, respectively. With increasing the filler content, there appears a decrease in tan δ value. As far as dynamic relaxation is concerned, a high tan δ value is apparently related to a loosely formed filler network. On the other hand, increasing the filler content results in a decrease in the polymer volume fraction, leading to a low tan δ value.

Figure 8(D) shows a plot of complex viscosity (η^*) versus ω of the compounds measured at 25°C and strain 1%. The Newtonian region in viscosity can hardly be observed for all samples, while viscosities increase as ω decreases, indicating an apparent yielding phenomenon. The yield stress could be viewed

as the minimum stress being exerted on the sample to observe a deformation, which is well-observed in fumed silica/PDMS systems due to strong interaction between polymer and filler.[33] Hence, one can conclude that CaCO$_3$ imparts similar reinforcement to PDMS as fumed silica although it is relative weaker.

Figure 9 gives four TEM photographs of vulcanized silicone sealant samples with different filler content, in which the bright region represents PDMS phase while the dark region represents filler particles. Obviously, in the samples containing 70–90 phr CaCO$_3$, the filler particles form aggregates with varying size, while in the sample containing 100 phr CaCO$_3$, the particles intercontact with each other and form a continuous network, indicating further an agreement with statements above.
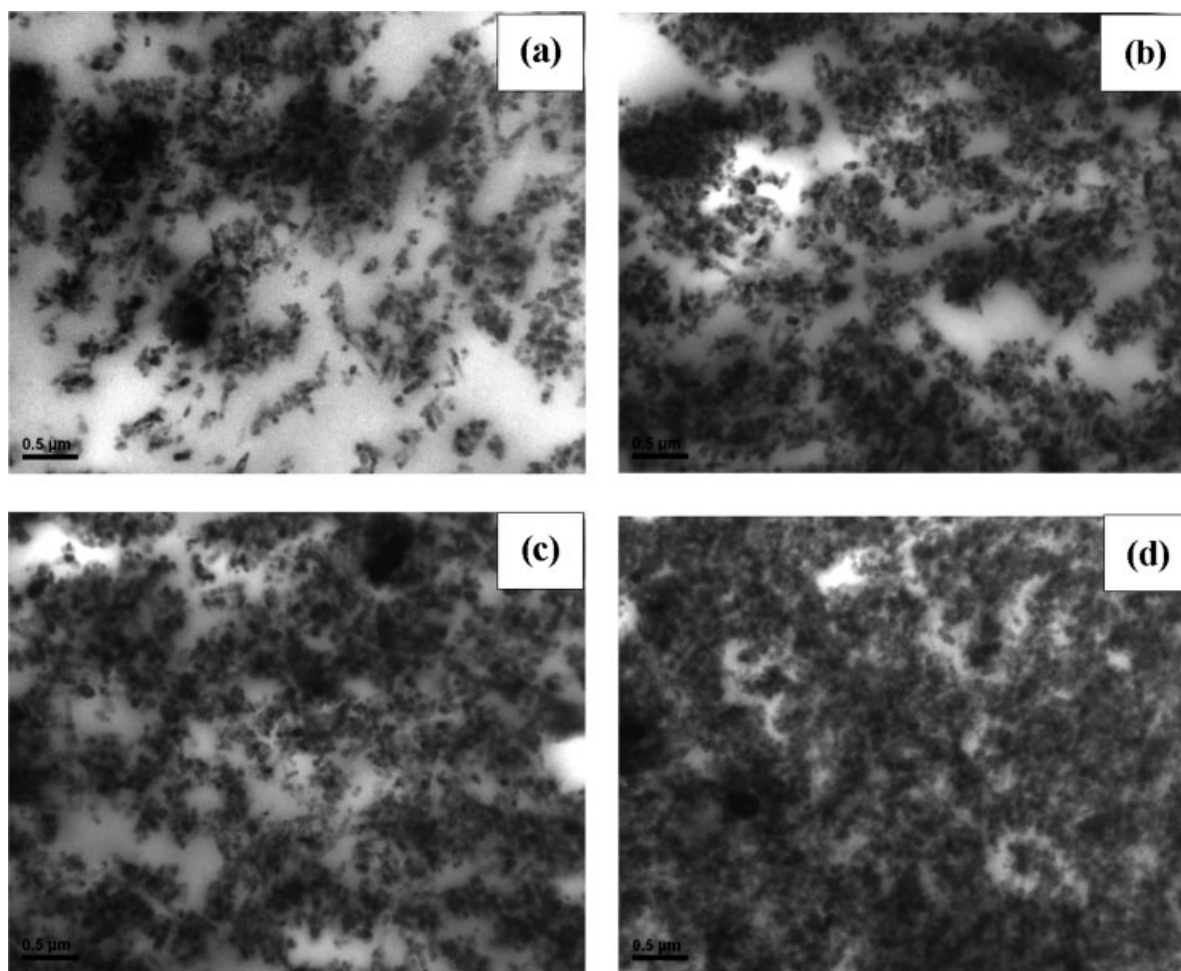
Figure 9 TEM photographs for silicone sealants with different CaCO$_3$ contents: (a) 70 phr; (b) 80 phr; (c) 90 phr; (d) 100 phr.

CONCLUSIONS

Silicone sealants having low modulus and high elongation have been prepared by using ketoxime silane as chain extender agent, and a novel silane coupling agent acting as adhesion promoting agent was also synthesized. The chemical structures of the product were confirmed by IR, ^{1}H-NMR, and element analysis. Decreasing average diameter and narrowing particle diameter distribution of particle lead to a relative high tensile strength and modulus at 100% elongation, but a relative low elongation at break, which can be related to additional physical crosslinking induced by the filler network. Moreover, increasing the filler amount leads to a same result, which is attributed to the promoted filler–filler, filler–polymer, and polymer–polymer interactions. As compared with virgin PDMS, there is a significant elevation of glass transition temperature due to the restricted segmental mobility imposed by the crosslinking points. With the increase of filler amount, the span of the linear viscoelastic region narrows, and a characteristic plateau phenomenon appears in low frequency regions, and the width and height of the modulus plateau increase. We ascribe this phenomenon to the formation of a filler network through filler–polymer and filler–filler interaction. There is a big jump between 90 and 100 phr filler, indicating a reinforced interaction and formation of a continuous network. TEM photographs confirm to this conclusion. All the samples show an apparent yielding phenomenon due to strong interaction between polymer and filler.

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