Investigation of structural, morphological and dynamic mechanical properties of unvulcanized PDMS/silica compound

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Abstract

In this study, the interaction between the silica filler and polydimethylsiloxanes (PDMS) was investigated from the aspects of the bound rubber and morphological characterization. With special attention to the dynamic properties, the dynamic test was conducted by dynamic shear rheometer. The results show that the modified fillers disperse uniformly within PDMS matrix without aggregation and connect closely with the matrix than that of the unmodified fillers. Surface modification of filler increases the bound rubber content. The increase in silica loading leads to an increase in the silica-silica interaction and a decrease in filler-rubber interaction, which results in the aggregation of fillers and the increase of the bound rubber content. It was apparent that storage modulus, loss modulus and tanδ of unvulcanized PDMS/filler compounds filled with treated silica filler were lower than that of the untreated silica system. Moreover, the tanδ decreases with increasing silica loading.

Keywords: PDMS; silica; modification; bound rubber; dynamic properties.

Introduction

Due to the fact that typical pure SR usually has poor properties, such as tensile modulus, the introduction of fillers is an effective method to enhance the mechanical properties of SR. It is important to understand the interaction between the SR and the modified fillers. Extensive works in the silica/rubber system have been focused on the reinforcement effect, and the primary discussion on the development in silica/rubber system has also been focused on the interactions between silica particles and rubber molecules [1]. Besides, the numerous experimental investigations and the various processes that have been invoked to explain filler reinforcement of elastomers have been reviewed [2]. Most of these processes depend upon "Payne effect" of reinforcement, cross-linking density and mechanical properties improved by the filler reinforcement. However, complete study of the interaction between the silicone rubber and fillers is still a challenging issue because it could not be satisfactorily attained.

As it is evident, silicone rubbers are made by a vulcanization (cure) process converting low molecular weight linear polydimethylsiloxanes (precursor fluid) to a polymer network. Polydimethylsiloxane (PDMS) which is recognized as an important

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organosilicon material can make more silicic products [3]. The study of interaction between PDMS and silica filler would further reveals the reinforcement of the filler-SR. However, limited attention has been drawn on the interaction between PDMS and silica filler.

In this paper, the unvulcanized PDMS/silica compound was prepared and the interaction between silica filler and PDMS was investigated from the aspects of the bound rubber, morphology. With special attention to the dynamic properties, the dynamic shear rheometer (DSR) was employed. As a result, the relationship between the modification of the silica filler and silica content, dynamic properties, morphology and the bound rubber of the unvulcanized PDMS/silica compound was found.

Experimental

Materials
Polydimethylsiloxanes (PDMS) with a viscosity of 50000 Pa.s was purchased from Dow Corning Company. Silica filler, DBP absorption $200 cm^3/100g$, with the average size of particle 20 μm, was purchased from Zhejiang Wynca Chemical Industry Group Company in China. Silane coupling agent, KH550 $[NH_2CH_2CH_2Si(OC_2H_5)_3]$, supplied by Diamond Advanced Material of Chemical Company in Hubei province of China, was used to modify the silica filler.

Surface treatment of SiO₂
The silica filler particles were dried in vacuum oven at 80 ℃ for 2 days. A certain amount of KH550, silane-coupling agent was dissolved in absolute alcohol and then SiO_2 was added to form a suspension. The mixture was stirred at room temperature for 6 h and stayed still for 24 h. Then the mixture was centrifuged and the silica filler was washed with absolute alcohol to remove the residual silane coupling agent. Finally, the SiO_2 particles were dried in vacuum oven at 80 ℃ for 2 days. After treated, the reactions between active silane coupling agent and SiO_2 which would lead to the hydrolysis of three Si-O-C_2H_3 groups in the silane molecule produces Si-OH groups. These OH groups then reacted with the OH groups on the surface of SiO_2 filler to form Si-O-Si groups, and release H_2O as the condensation product. These silane molecules, attached to the silica surface, might further link together to form a cross-linking structure surrounding the silica filler particles.

Preparation
A certain amount, 15phr, 50 phr and 80 phr 100 phr and 150 phr of modified filler (the phr unit represents the parts per hundred parts of rubber by weight) were mixed with PDMS using a two-roll mill at 30 ℃ and rolled for 3 times. Then, the PDMS/silica compound formed in unvulcanized state and the product was sealed in a can.

Measurements

Morphological characterization
In order to investigate the dispersion state of the modified silica particles in PDMS matrix, Scanning Electron Microscopy (SEM) was employed. The sample morphology was further investigated using an optical microscope made by Nikon Co., Japan. Squashed slides of PDMS/filler compound were prepared and viewed under the microscope at a magnification of 400.

Equilibrium swelling measurement - Bound rubber

Bound rubber measurement was conducted by solvent extraction in toluene at room temperature. For the determination, approximately 1 g of compound was placed into a stainless-steel wire-mesh cage of a known weight. The cage was then immersed in solvent in a jar for 4 days, and the toluene was replaced every day with fresh solvent. After extraction, the rubber and the cage were dried in an oven at 125 ℃ for 5 hours. The amount of bound rubber was calculated according to the following equation [4]:

$$R_b(\%) = 100[W_{fg} - W_t[m_f/(m_f + m_r)]]/W_t[m_r/(m_f + m_r)]$$

Where R_b is the bound rubber content, W_{fg} is the weight of filler and gel, W_t, the weight of the sample, m_f the fraction of the filler in the compound, and m_r the fraction of the rubber in the compound.

DSR tests

A Dynamic Shear Rheometer (DSR, Physica MCR 101, made by Anton Paar Co.Ltd. of Austria), was used to show the dynamic mechanical properties.

Under the strain-controlled mode, storage modulus, loss modulus and phase angle (tanδ) of PDMS/silica compound were determined with the frequency of 10 rad/s and DSR shear tests were conducted at room temperature (23±2℃).

Results and discussion

Morphology of silica/rubber composites

Figure 1 (a) and (b) are the images of the compounds added with 15 phr modified filler and 15 phr unmodified filler. It can be seen from Figure 1 (b) that partial coalescence was unavoidable and the filler particles aggregate in the samples with unmodified filler. Moreover, the modified filler particles shown in Figure 1 (a) are rather homogeneously dispersed. The above phenomenon attributes to the surface energy of the fillers. Because of the disparities between the surface energy of the filler and that of the polymer matrix, silica fillers are difficult to disperse well in PDMS and they are easily to form agglomerate [5]. After the filler had been modified, the surface energy of the fillers decreases and the filler particles disperse in PDMS more evenly and easily. Thus, the contact area increases and results in the increase of the interaction between the filler and PDMS, as shown in Figure 1 (a).

The filler distributions for the weight fractions of 15 phr modified and 15 phr unmodified filler are further investigated by optical microscopy, as shown in Figure 2 (a) and (b). In the latter case, large agglomerates were observed whereas in the former, there were no agglomerates and the fillers were perfectly dispersed in PDMS matrix. This phenomenon further supports the results as shown in SEM images of Figure 1 (a) and (b).
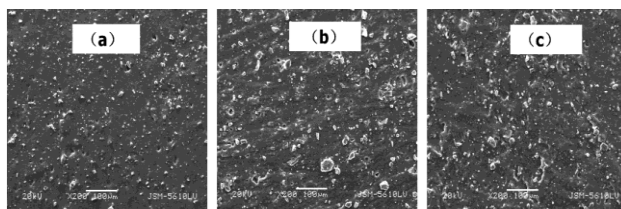
Figure 1. SEM images of filler/SR composites:
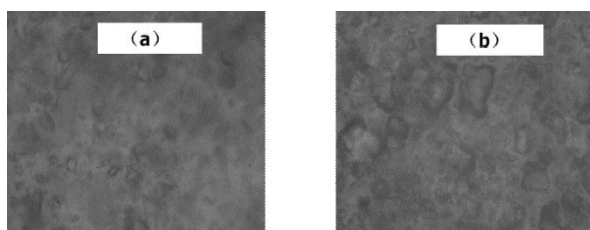(a) 15 phr modified filler, (b) 15 phr unmodified filler; (c) 150 phr modified

Figure 2. Optical microscope images of filler/SR composite

Figure 1 (c) is the image of the compound added with 150 phr modified filler. Comparing with the image of the filler/PDMS compound added with 15 phr modified filler as shown in Figure 1 (a), the particles aggregate seriously and the interaction between fillers and PDMS is weak. This can be ascribed to the fact that the over-proportional increase of filler loading makes the contact surface of fillers increase. Thus, the further increase in silica loading should lead to an increase in the silica-silica interaction and hence, a decrease in filler-PDMS interaction results in the aggregation of fillers [6].

Bound rubber
Swelling measurements are very useful to characterize the network degradation, and provide information on the polymer network chain density and percentage of soluble fraction [7]. The insoluble polymer in swelling measurement is often referred to the bound rubber, and bound rubber is the rubber portion that can no longer be separated from the filler when the rubber matrix is extracted in a good rubber solvent (toluene) over a specified period of time, usually at room temperature.

It was discovered that bound rubber content in unvulcanized PDMS/filler compounds is important because of the fact that it affects physical properties of the rubber vulcanizing [8]. In this study, bound rubber measurement was conducted by solvent extraction in toluene at room temperature for three days. In order to approach the influence of the surface modification of the filler on the bound rubber, the samples were prepared using different silica fillers, including the modified filler and unmodified filler. Effect of the silica filler content on bound rubber was also investigated, and the corresponding bound rubber contents were measured. The results are shown in Tables 1 and 2.

Table 1. Results of bound rubber

Filler	Unmodified	Modified
Bound rubber	8.9 %	25.9%

Table 1 shows the influence of filler surface modification on the bound rubber content. It is apparent that surface modification of filler increases the bound rubber content. This increase of bound rubber content as the increase of filler loading is in good agreement with several authors [9]. For composites filled with inorganic particles, the polymer can be divided into two parts. One is the free part, where the state of molecular chain is the same as that in the pure PDMS matrix. The other is defined as the bound part which is formed by the physical or chemical adsorption of the polymer chains and the fillers relating to the chemical properties of the filler surface and the interfacial area between the polymer and the fillers. After the fillers were modified by silane modifier, the chemical bonding between the filler and PDMS occurs which results in the increase of the bound part of PDMS.

The influence of the modified filler loading on the bound rubber is reported in Table 2. It is apparent that the bound rubber content increases dramatically as the modified filler content increases from 50 phr to 150 phr. The notable increase of the bound rubber content is due to the fact the interfacial area and the interaction between PDMS matrix and filler increase as the modified filler loading increases. As a result, the volume of the bound part and the bound rubber content increased.

Table 2. Effect of the modified filler content on the bound rubber

Modified filler /phr	Bound rubber/%
50	8.9
80	18.7
100	25.9
150	32.7

Dynamic properties analysis by DSR

Dynamic rheology property is sensitive to filler dispersion in polymers. However, a straightforward description of dynamic shear rheology of unvulcanized filler/PDMS compound is still missing so far.

In this study, we systematically study the rheology properties for unvulcanized PDMS/ filler compound by analyzing storage modulus, loss modulus and tanδ of the compound using DSR test. Dynamic properties tested by DSR allows a very detailed investigation of the dynamic behavior on a much easier and faster way than that of the common dynamic analysis of the composites by dynamic mechanical analysis (DMA).

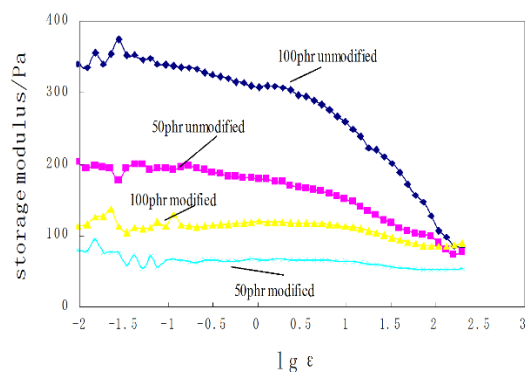**Modification of filler on the dynamic properties of compounds**

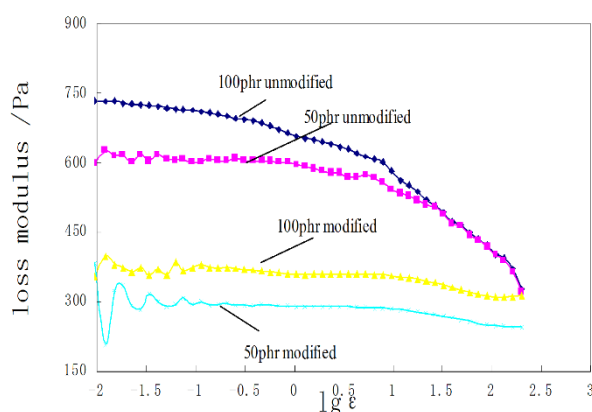**Figure 3.** Effect of filler modification on storage modulus of compound

Figure 4. Effect of filler modification on loss modulus of compound

Strain sweep experiments at fixed frequency and temperature were performed on series of samples with different modified and unmodified silica filler. The dynamic properties of samples filled with treated SiO_2 and untreated SiO_2 are shown in Figure 3. It was apparent that storage modulus of unvulcanized PDMS filled with treated SiO_2 was lower than that of PDMS/untreated SiO_2 compounds. This can be explained that the rheological response of polymer-based materials is influenced substantially by the extent of polymer/filler interactions, which in turn depend upon the surface treatment of the particles and the nature of the polymeric matrix. Surface treatment of the filler can improve the degree of wetting of the fillers and the dispersion of SiO_2 (as shown in Figure 1). Hence, the interfacial area is greatly increased and the interaction between PDMS matrix and filler strengthened after the treatment. Therefore, the storage modulus of the treated filler compound is lower than that of the untreated ones.

Moreover, the plateau that corresponds to a linear viscoelastic behavior is readily seen in Figure 3. It can be observed that in the unvulcanized filler/PDMS compound, the low strain modulus G_0 raises more than the high strain modulus G_∞, resulting in a non-linear viscoelastic behavior. The non-linearity amplitude

in the case of the modified filler compound is smaller than the one observed for the untreated silica filler compounds.

Figure 4 shows the loss modulus curve of compound filled with treated and unmodified SiO_2 filler. It was apparent that loss modulus of the compounds with unmodified filler were higher than those of modified filler composites. The above phenomenon is attributed to the surface modification of the mineral filler. After the filler had been modified, the surface energy of the filler decreases and the contact area between the filler and the PDMS matrix increase. Hence, the slippage of the chain of PDMS was restricted and the internal friction of PDMS- filler and filler-filler was reduced, which results in the lower loss modulus values.

The ratio of the loss and storage module, known as loss factor (tanδ), corresponds to the ratio of energy dissipated to energy stored in a deformation cycle. Figure 5 shows the plot of tanδ of the modified and unmodified filler versus displacement of silica/PDMS compound. It can be seen that a lower tanδ obtains as the silica filler is modified. One knows that the energy losses under deformation condition of the filled system resulted from internal friction and breaking/reforming of filler-polymer at contact points is the main cause of the rise of tanδ with increase in strain. When the fillers were modified, there is a greater extent of filler-PDMS interaction because the fraction of filler-immobilized polymer has increased. The energy losses of internal friction among fillers decrease and a lower tanδ obtained.
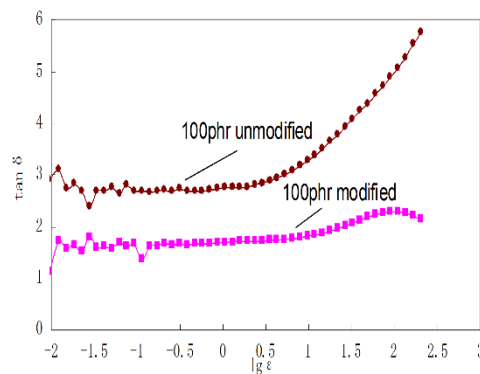

Figure 5. Effect of filler modification on tanδ

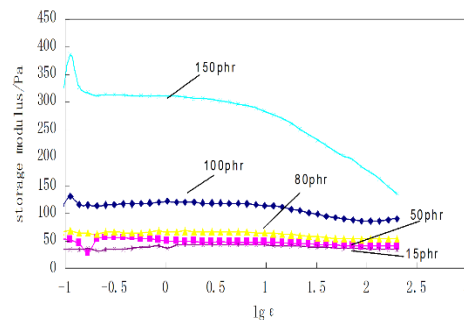**Effect of filler content on the dynamic properties of compounds**

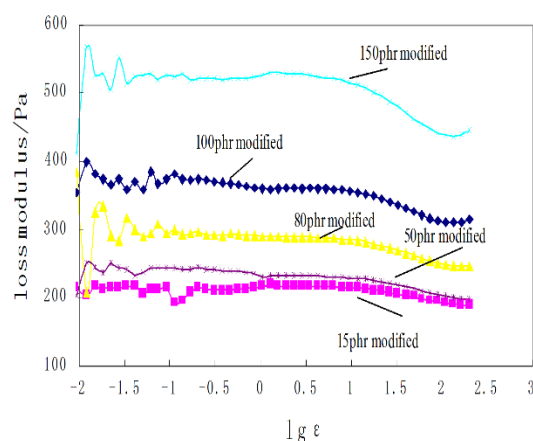**Figure 6.** Effect of filler modification on storage modulus

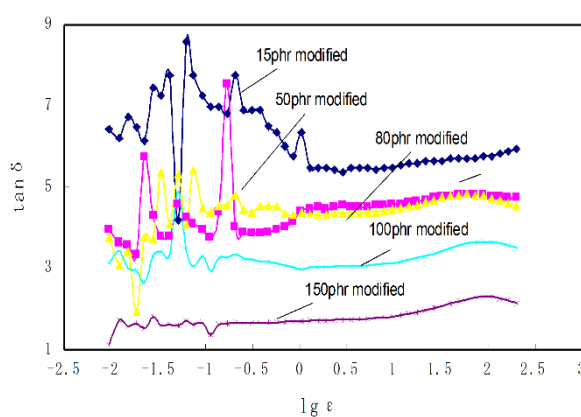**Figure 7.** Effect of filler loading on loss modulus of compound

Figure 8. Effect of filler loading on tanδ of compound

Figures 6-8 show the dynamic properties of samples with different modified filler content. Results are presented in terms of elastic storage modulus G' versus strain in Figure 6. The plateau that corresponds to a linear viscoelastic behavior is readily seen. Above a certain filler loading level, the lineal behavior is lost and compounds exhibit a modulus drop trend, known as "Payne effect", and the magnitude of the "Payne effect" increases with increasing filler content. From Figure 6, it can be seen that the increase of the filler content makes the storage modulus of compound increase. It can be ascribed to the reason that the compounds having higher content of filler exhibit strong dependence of

storage modulus on shear strain, indicating the greater disruption of filler-filler interaction.

Figure 7 shows the loss modulus-strain spectrum of PDMS/filler compounds filled with different modified SiO_2 filler content. It was apparent that loss modulus of the compounds with higher filler content increases the loss modulus as the strain increases. This is due to the fact that the inter-aggregate distances become smaller with rising filler content and therefore the probability for the formation of a filler network increases. Therefore, when the compounds were subjected to external stress, the external energy was dissipated by the friction between particle-particle and particle-

matrix interaction, and the loss modulus of compounds increases.

Figure 8 gives the corresponding tanδ curves for PDMS matrix-filler compounds. As seen, there is a significant decrease in tanδ with increase in filler content. The decrease in tanδ values with increase of filler content is the result of the reduction of the soft elastomeric phases imparted by rigid silica particles. The result also suggests that the filler network was completely broken down at higher strains.

Conclusion

Concerning the above discussion, the following concluding remarks seem pertinent:

(1) The modified filler disperse uniformly within silicone rubber matrix without aggregation and connect closely with the matrix than that of the unmodified fillers. Increase of the modified fille content results in the aggregation of fillers and bad dispersion in compound.

(2) Surface modification of filler increases the bound rubber content, and the increasing amount of silica results in the increase of the bound rubber content.

(3) (4) It was apparent that storage modulus, loss modulus and tanδ of compounds filled with treated SiO_2 were lower than that of PDMS/untreated SiO_2 system. The increase in the storage modulus and loss modulus with increasing silica content is mainly caused by the increase in strong filler-filler interaction. There is a significant decrease in tanδ with increase in filler content.

Acknowledgments

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