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The Study of the Interaction between Silica Filler and Silicone Rubber

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Abstract. The interaction between silica filler and silicone rubber was studied by swelling ratio, Kraus curve and crosslinking density test. The results showed that lower values of Vro/Vrf and swelling ratio in modified filler system suggests good filler-matrix interactions. The composites with silane coupling agents show higher crosslink-density compared that of untreated ones. In the light of the above statement, it can be concluded that modification of filler is the crucial factor in creating a good interaction between the filler and silicone rubber.

1. Introduction

The incorporation of small particle size fillers to crosslinked elastomer matrix results in substantially improved mechanical properties [1-3]. Nowadays, the use of silica particles, instead of carbon black, has proved to be of interest in the reinforcement of rubbers [4]. Since silica is an essential ingredient of most rubber formulations and has a considerable influence on the performance of the final product, it is important to know how rubbers are affected by the nature of silica filler [5]. The main focus of this work lies on the influence of the nature of silica (loading, surface area, structure and surface activity) on the properties of silicone rubber.

2. Experimental

2.1. Materials

Polydimethylsiloxanes (PDMS) with a viscosity of 50000 Pa.s, purchased from Dow Corning Company, was employed. Methyltris (methylethylketoxime) silane (MOS), supplied by Hubei Huanyu Chemical Co,. Ltd, was used as the cross linker because of its multiple functionalities. Fumed silica with the particle size less than 40 μm, obtained from Galaxy Chemical Co. Ltd in Wuhan of China, was treated with promoting agent and added as reinforcing filler. No further purification of the chemicals was required.

2.2. Preparation

It refers to a two-component silicone rubber (SR). The representative chemical constituents of the SR used in this study consist of cross-linker (component A) and hardener (component B) in a mixing ratio of A: B=1: 0.03. Modified silica added as filler was already in component A. After the mixing of component A and component B, silicone rubber formed.

2.3. Characterization

2.3.1. Kraus equation. In this example we can see that there are footnotes after each author name and only 5 addresses; the 6th footnote might say, for example, 'Author to whom any correspondence should be addressed.' In addition, acknowledgment of grants or funding, temporary addresses etc might also be indicated by footnotes.

$$V_{ro}/V_{rf} = 1 - m\left[\frac{f}{1-f}\right] \quad (1)$$

2.3.2. Swelling ratio. The vulcanizate having a thickness of 1.2 mm was cut into rectangular shape with weight about 0.7g. The samples were first extracted for 12h using acetone as a solvent. Then, the sample was dried in a vacuum oven at room temperature. The swelling ratio (Q) was determined using Eq. (2). The value of swelling ratio of each vulcanizate was the average of the three specimens:

$$Q = (Ws - Wu)/Wu \quad (2)$$

Where Ws is the weight of swollen sample and Wu is the weight of extracted and dried sample before swelling.

2.3.3. Crosslink density. Samples were swollen in toluene under room temperature for 72 h to achieve the equilibrium swelling. Then the samples were dried in a vacuum oven for 36 h at 80 ℃ to remove residual solvent. The volume fraction of the rubber in the swollen gel, which was used to represent the crosslink density of composite, could be given as followed [6]:

$$\nu = 1/2M_c \quad (3)$$

Where Mc is the molecular weight between crosslinks.

$$M_c = \frac{-\rho_p \nu_n \phi^{1/3}}{[(1-\phi)+\phi+\chi\phi^2]} \quad (4)$$

Where v is the molar volume of the solvent; ρp, the density of the polymer; χ, the interaction parameter; and ϕ, the volume fraction of the swollen sample. χ is given by the equation.

$$\chi = \beta + \frac{V_s}{RT}(\delta_S - \delta_P)^2 \quad (5)$$

Where β is the lattice constant; Vs is the molar volume of the solvent; δs and δp are the solubility parameters of the solvent and polymer, respectively; R, the gas constant; and T, the absolute temperature. The swelling of silicone rubber were carried out in toluene and the crosslink density was determined.

3. Results and Discussion

3.1. Kraus Equation

Kraus theory was employed to interpret equilibrium swelling measurements to estimate the degree of adhesion between elastomer and filler particles. Fig 1 shows the results of Kraus curve between the modified and unmodified filler system. According to the theory given by Kraus, the lower value of Vro/Vrf suggests good filler-matrix interactions, while a higher ratio is significant of bad interactions. As seen in Fig 1, it can be concluded that the better interaction between the modified filler and the silicone rubber can be obtained than that of the unmodified ones.

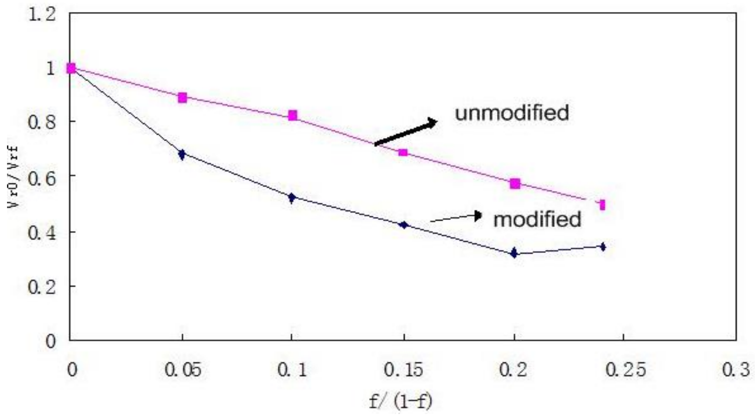

Figure 1. Kraus curve of modified and unmodified filler

3.2. Swelling Ratio

The swelling ratio versus the filler (modified) content for the composites is shown in Fig 2. It is observed that the swelling ratio decreased with the increasing modified filler content. The swelling curves of modified silica/rubber composites are similar to those of virginal silica/rubber composites and the unmodified filler system shows a higher swelling ration compared to that of modified filler composites. It can be explained that the filler-rubber interaction plays an important role in the swelling ratio of the filler/rubber composites and the decrease in filler-rubber interaction is thought to be a cause for the reduction in swelling resistance, which is inversely proportional to swelling ratio. After the filler was modified, the contact area between the filler and the SR matrix increases [7-9], and the increase of the interaction between the filler and the SR matrix, which results in the lower swelling ratio compared to that of the original filler/rubber composites. As silica loading increases, the overproportion increase of filler loading makes the contact surface increase, and higher aggregation of silica particles occurred. Thus, the inner-aggregate distances become smaller and the probability for the formation of a filler network increases at high concentrations, which results in the decrease of the interaction between filler and rubber matrix and the swelling ration increase.

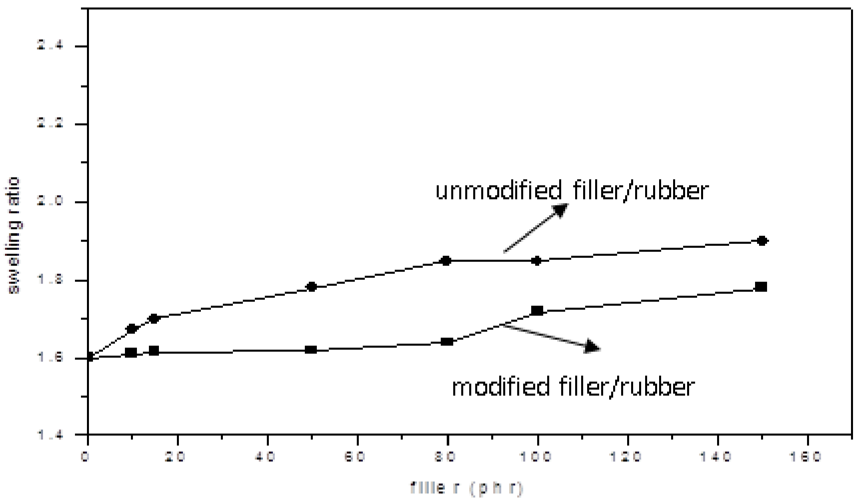

Figure 2. Effect of filler content on the swelling ratio of composites

3.3. Crosslinking Density

The results of crosslinking density of the silica/rubber composites are listed in Table 1. As seen, the crosslink density of the composites after silane surface treatments is increased compared to that of untreated silica/rubber composites. In general, when silane coupling agents are introduced onto silica surfaces in the composites, two interfaces exist between the silicas and the rubber: the interfaces between silicas and silane coupling agents and between silane coupling agents and rubber. Therefore, the composites with silane coupling agents show higher crosslink-density compared that of untreated ones [10].

Table 1 Results of crosslinking density

Samples	unmodified	Modified
M_c(g/mol^{-1})	6500	8670

4. Conclusions

The study on the modified silica and the interaction between modified filler and PDMS were performed. The results showed that lower values of Vro/Vrf and swelling ratio in modified filler system suggests good filler-matrix interactions. The composites with silane coupling agents show higher crosslink-density compared that of untreated ones.

5. Acknowledgments

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