Preliminary Study on the Dynamic Properties of PMVS Filled with Surface-treated Silica

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Abstract: Dynamic properties of polymethylvinylsiloxane (PMVS) filled with surface-treated silica (SiO_2) were studied using an advanced rheometric expansion system (ARES). The results revealed that the coupling agent, bis (3-triethoxysilylpropyl) tetrasulfane (TESPT) exerted a pronounced effect on the storage modulus (G'), and the effect of TESPT involved a frequency-dependent relation.

Keywords: Polymethylvinylsiloxane, silica, bis(3-triethoxysilylpropyl)tetrasulfane, rheological properties, surface treatment.

It is well known that silica (SiO_2) is one of the most important available fillers in application to reinforcement of elastomer, especially to the non-black case, such as reinforcement of silicone rubber. On the other hand, the rheological behavior of materials containing high concentration of fillers is important to the rubber industry because the addition of fillers dramatically change the viscoelastic properties of these materials. Although silicone rubbers filled with SiO_2 have been widely used for many years, their rheological properties have not been profoundly understood, and just few papers about this aspect have been published [1, 2]. The aim of this article is to study the dynamic behavior of polymethylvinylsiloxane(PMVS) filled with surface-modified SiO_2.

The PMVS samples were commercially available products ($\overline{M}_w$ = 300,000, $\overline{M}_n$ = 155,000). Fumed SiO_2 (hereafter named f SiO_2) was supplied by Hangzhou Yadong Silicone Rubber Co., Ltd (BET surface areas = $160 \pm 15 m^2 g^{-1}$, and the average primary particle size = 150 Å). Because these elementary spheres were covalently associated into clusters as soon as they are synthesized, the average equivalent size is 700 Å. A bifunctional organosilane, *i.e.* bis(3-triethoxysilylpropyl) tetrasulfane (TESPT), was used for the surface treatment of SiO_2, which was proved to be strongly effective in improving the ultimate properties of silicone rubber[3]. The incorporation of surface-modified SiO_2 into PMVS in the proportion of 1 to 5 was made through blending using a roll-mill for 30 min at room temperature. The dynamic mechanical measurements were performed with an advanced rheometric expansion system (ARES) using parallel plate geometry model (radius = 25 mm and thickness = 2 mm) at 25°C. All tests were done in the linear

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viscoelastic region (strain = 0.02% and frequency = 100 ~ 0.01 rad/s).

The relationship between dynamic storage modulus G' and strain for f SiO$_2$/PMVS (20/100) samples treated and untreated with TESPT are presented in **Figure 1**.   It can be seen that after the treatment, G' values of the blends were elevated from initially around 1×10^4 up to 1×10^5 Pa.   The main reason for this is thought to be that the ethoxy (—OC$_2$H$_5$) groups of TESPT react with silanol (Si—OH) groups on the silica surface, resulting in the formation of covalent bonds.   The enhanced interaction between the fillers and the rubber matrix leads to a considerable improvement in the modulus value. Additionally, there exist a plateau responsible for the linear viscoelastic behavior when strain is below the critical value, S$_c$ or S'$_c$ for the samples treated and untreated. Beyond the critical values, the blends display a decrease in G', which is so-called *"Payne effect"* [4].   Furthermore, the S$_c$ of the treated is lower than S'$_c$ of the untreated, which is attributed to the pronounced decrease of the formation tendency of filler network induced by the silanization of silica with TESPT[1, 2, 4].

Figure 1   Plot of dynamic storage modulus G' versus strain at 25 °C, 10 rad s^{-1} for PMVS filled with fSiO$_2$ treated and untreated with TESPT
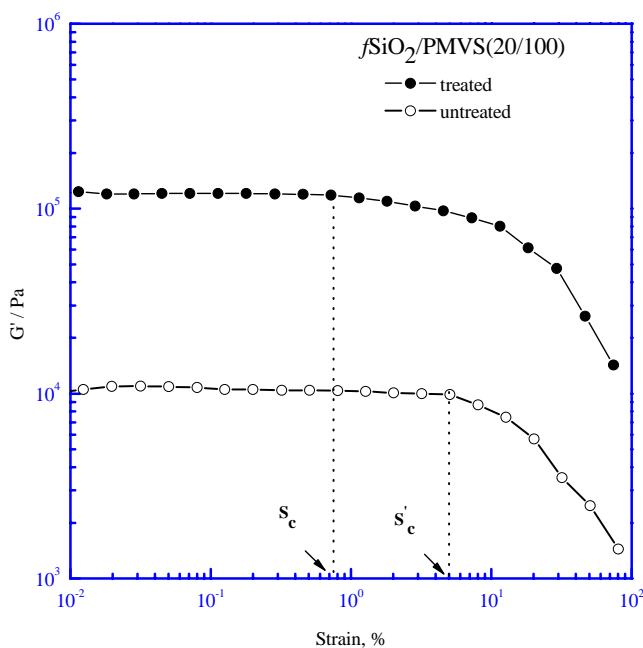
The dependences of G' on frequency ω for treated and untreated f SiO$_2$ samples are shown in **Figure 2**.   Similarly, G' values of the treated are higher than those of the untreated within the whole frequencies investigated.   So, combining the results shown in **Figure 1**, we conclude that PMVS filled with treated f SiO$_2$ possesses remarkably improved modulus.   It is interesting that both treated and untreated samples show a *"plateau-like"* phenomenon at low frequency range, which is related to the network formation of the fillers in the polymers matrix[1, 5].   On the other hand, according to the criterion that whether heterogeneous structure exists, *i.e.* whether the slope of plotting

lgG' against *lgω* at low frequencies is close to 2, as defined by linear viscoelastic theory[6]: *lg G' ∝ 2 lgω*, we suggest that there exist improved dispersion of fillers in the treated samples on the basis that the slope value of the treated samples is higher than the untreated. This phenomenon also accords well with some previous reports which claimed that surface-modification with TESPT facilitated the dispersion of fillers in the polymers[4]. Thus we owe the results aforementioned to the reason for the remarkable increase of G' for the treated samples as shown in **Figure 1**.

Figure 2   Plot of dynamic storage modulus G' versus frequency ω at 25°C for PMVS filled with *f* SiO$_2$ treated and untreated with TESPT
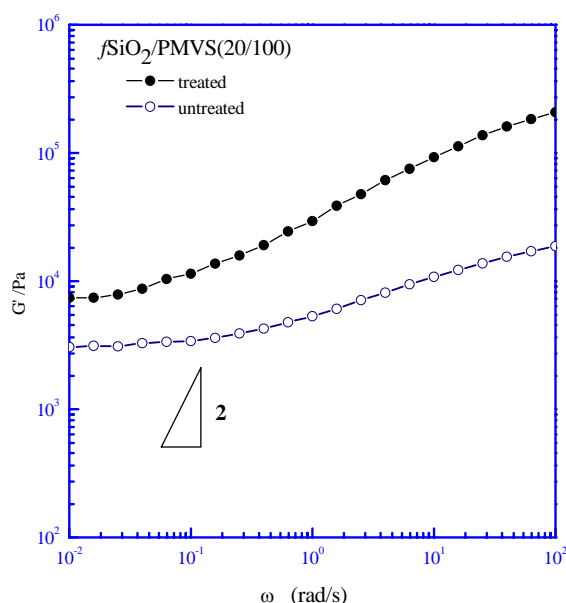
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