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Study of SiO_2-filled polysiloxane system through dynamic rheological measurements

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Recently polysiloxane filled with well-dispersed silica (SiO_2) nanoparticles has been an increasing research focus for the purpose of a high level of reinforcement for silicone rubber [1]. It is generally accepted that the reinforcing effects not only result from the filler network [2] induced by aggregation of filler particles, but also depend on parameters such as particle size, structure, and the degree of surface interaction. Additionally, it is well-known that incorporation of fillers into polymers will cause a considerable change in rheological behavior and viscoelastic properties, both highlighting the secondary structure of the filler clusters. In this study, two types of SiO_2 nanoparticles with similar particle size and surface chemistry structure, i.e., SiO_2 aerogels and colloidal SiO_2 spheres were added into poly(methylvinyl)-siloxane (PMVS). Our ultimate objective is to understand the effect of microstructure of SiO_2 nanoparticles on the dynamic rheological properties of PMVS/SiO_2 system. To our knowledge, few reports concerning these aspects have been published.

The PMVS samples were commercially available products ($\bar{M}_w = 600\,000$, $\bar{M}_n = 355\,000$). SiO_2 aerogels were synthesized using a super critical drying technique, while colloidal SiO_2 spheres were prepared by a conventional sol-gel process [3] and the TEM observation for them were shown in Figs 1 and 2 respectively. The typical properties of the two types of SiO_2, together with other commercial SiO_2 powders, are given in Table I. A widely used bifunctional organosilane, i.e., bis(3-triethoxysilylpropyl) tetrasulfane (TESPT), was used to aid the dispersion and distribution of SiO_2. The formulation for the composites was PMVS, 100; Silica, 40; Diphenyl silandiol, 3; and TESPT, 6. The mixing process was conducted using a two-roll mill for 15 min at room temperature. The dynamic mechanical measurements were performed on an advanced rheometric expansion system (ARES) using parallel plate geometry model (radius = 25 mm and thickness = 2 mm) at 25 °C. The strain sweep test was conducted with a frequency of 0.1 $rad \cdot s^{-1}$ by varying the strain from 0.01 to 100%; the frequency sweep test was performed within the frequency range from 100 to 0.01 $rad \cdot s^{-1}$. All tests were done in the linear viscoelastic region.

The relationship between dynamic storage modulus G' and strain for SiO_2/PMVS systems was presented in Fig. 3. As can be seen, the apparent decrease of G' at critical strain amplitude (γ), i.e., the so called *Payne effect* [2], was prominently enhanced upon increasing the surface structure from non-porous SiO_2 spheres to porous SiO_2 aerogels. Meanwhile, in addition to an elevated level of G', the linear viscoelastic region was also remarkably shortened, in order of the strain, $\gamma_1 < \gamma_2 < \gamma_3$. The phenomenon mentioned can be interpreted on the basis of the formation and its destruction of filler aggregates network [4]. It seems that SiO_2 nanoparticles with higher surface structures are more prone to form a strong secondary filler structure, though with a weakened ability to resist deformation.

Fig. 4 presents the frequency dependency of G' at 25 °C and 0.1 $rad \cdot s^{-1}$ for PMVS filled with SiO_2 nanoparticles of different structure. It is apparent that the composites containing inner-porous SiO_2 aerogels display an extraordinary frequency-independent rheological behavior in the lower frequencies region. According to our previous work [5–7], the *Newtonian* viscoelastic plateau in the terminal region can be attributed to the existence of filler network. In contrast, the composites filled with colloidal SiO_2 spheres, which possess similar surface areas to that of SiO_2 aerogels, present a slight deviation from the linear rheological equation $\log G' \sim 2 \log \omega$ [5–7], indicating an agreement with the results as shown in Fig. 3.

TABLE I Typical properties of SiO_2 with different structure

Property	Colloidal silica spheres	Silica aerogels	Silica powders
N_2(BET) Surf. area (m^2/g)	280	416	26
Elementary particle diameter (nm)	20	20	200–450
DBP adsorption ($10^{-6}m^3/100$ g)	224	252	160
CTAB ads. Surf. area (m^2/g)	126	82	–
PH (4% Suspension in H_2O)	6.7	6.8	6.6

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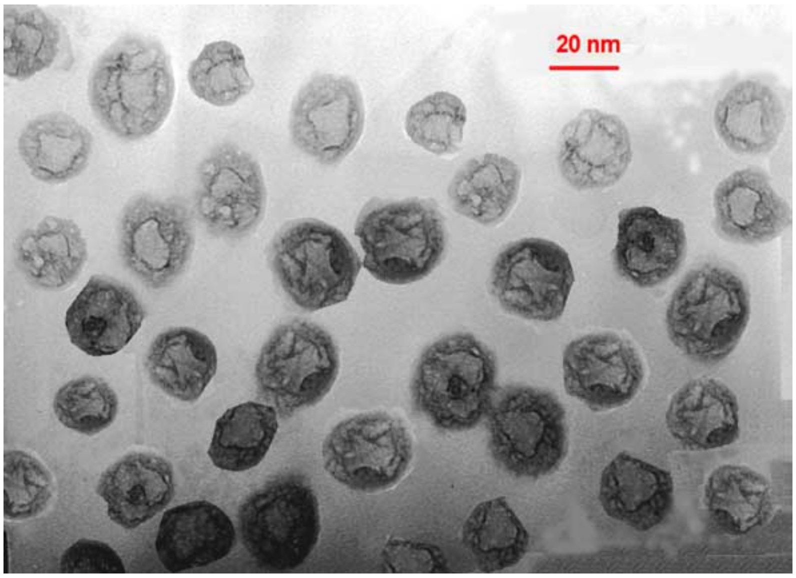

Figure 1 TEM of SiO_2 aerogels.

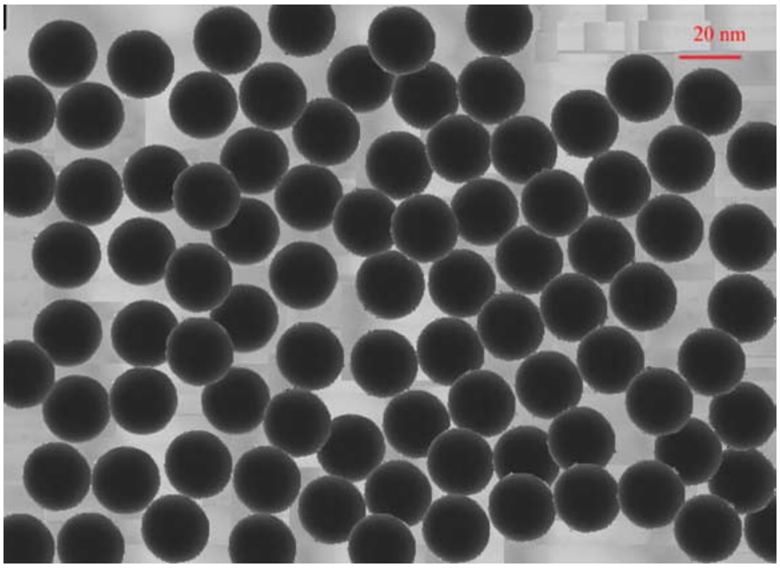

Figure 2 TEM of colloidal SiO_2 spheres.

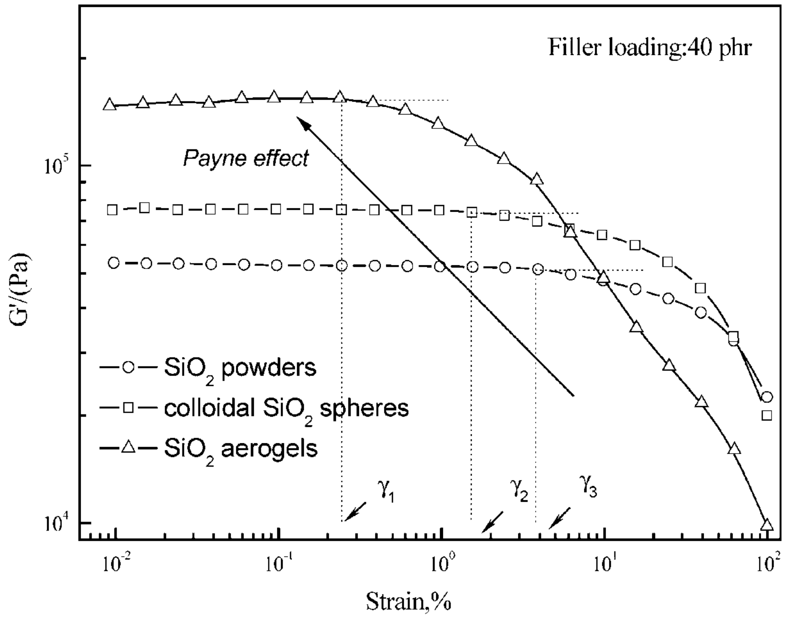

Figure 3 Strain dependence of Storage modulus (G') at 25 °C and 0.1 $\mathrm{rad \cdot s^{-1}}$ for PMVS filled with SiO_2 nanoparticles with different surface structure.

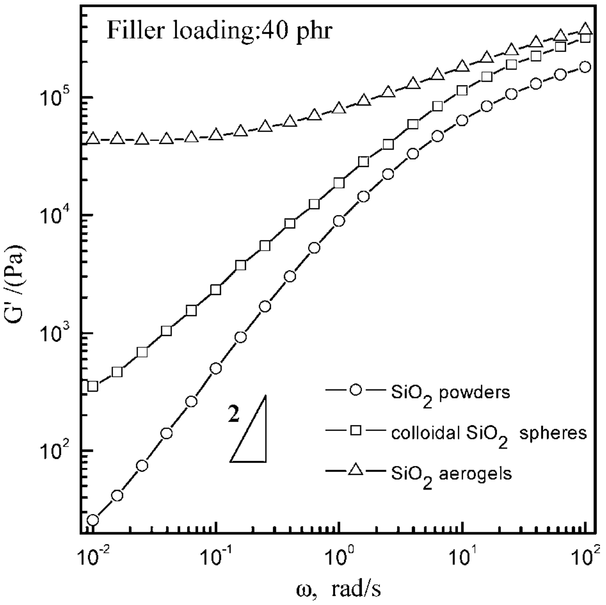

Figure 4 Frequency dependence of storage modulus (G') at 25 °C for PMVS filled with SiO_2 nanoparticles with different surface structure.

It is generally, believed that the filler aggregate network is formed directly through filler-filler interactions and indirectly through polymer chains, bridging two different particles or entanglements of different polymer chains adsorpted onto two adjacent particles [2, 8]. According to the discussion above, it is predicted that to someextent the promoted filler networks result from the adsorption of PMVS chains onto the surface of silica nanoparticles, since the filler-filler interactions are considerably reduced by treatment with TESPT. Furthermore, the destruction of filler network against deformation may involve in desorption of polymer chains from the SiO_2 particles.

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