

EFFECT OF INCORPORATING STARCH/SILICA COMPOUND FILLERS INTO UNCURED SSBR ON ITS DYNAMIC RHEOLOGICAL PROPERTIES*

Hong Li^{a,c}, Yi-hu Song^{a,b} and Qiang Zheng^{a,b**}

^aDepartment of Polymer Science and Engineering, Zhejiang University; Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Hangzhou 310027, China

^bNational Engineering Research Center for Compounding and Modification of Polymeric Materials, Guiyang 550025, China

^cSchool of Material and Architectural Engineering, Guizhou Normal University, Guiyang 550014, China

Abstract The dynamic rheological properties of a composite composed of solution-polymerized styrene butadiene rubber (SSBR) filled with starch/silica (SiO₂) compound fillers were studied by means of temperature, frequency and strain sweeps, respectively, and the influence of the starch content in the compound fillers (SCCF) on the rheological behaviors was discussed. It is found from frequency sweeps that a maximum of loss tangent ($\tan\delta$) appears at 20 rad/s, which is independent of SCCF. G' of the composites decreases whereas $\tan\delta$ and critical strain (γ_c) of Payne effect increase with increasing SCCF. The reasons for these are believed to be that both SiO₂ and starch could form filler networks due to interaction of hydrogen bonding between them, and the interactions between SiO₂ and SSBR are stronger than those between starch and SSBR. Moreover, increasing SCCF in the compound fillers is in favor of improving the stability of the filler networks. Furthermore, $\tan\delta$ values at 0°C and 60°C representing the properties for the wet traction and the rolling resistance of SSBR composites respectively can be improved by partial replacing SiO₂ with starch. However, the reinforcement effect of starch to SSBR is weaker than that of SiO₂ due to starch agglomeration.

Keywords: Styrene butadiene rubber; Silica; Starch; Rheological behavior.

INTRODUCTION

Carbon black (CB) is a reinforcing filler commonly used for producing vulcanized rubber products with high performance. CB is wholly dependent on the nonrenewable sources of petroleum and natural gas. In the mean time the energy consumption and CO₂ emission from automobiles have become a serious threat to the environment, peoples have no option but to employ other fillers such as SiO₂^[1, 2], starch^[3] and clay^[4] to partially replace it. SiO₂ instead of CB has been preferentially selected for preparing vulcanizates with a unique combination of tear strength, abrasion resistance, age resistance and adhesion properties. A combination of SiO₂ and CB is highly efficient to lower the rolling loss and to improve the wet skid resistance so as to produce green tires with limit energy consumption and CO₂ emission from automobiles. Such tires can reduce fuel consumption by approximately 6% and provide reduced emissions of pollutants^[5, 6]. The main disadvantage of using SiO₂ lies in its high cost with respect to CB and its high surface polarity leading to the formation of filler agglomerates through hydrogen-bonding. Silane coupling agent such as bis(triethoxysilylpropyl)-tetrasulfide (TESPT) can be used to prevent it from agglomeration through modifying the dispersion of SiO₂ particles.

As a natural, cheap, biodegradable and environmentally friend biopolymer with abundant sources, starch has been received more and more attention in rubber industry^[7–9]. The surfaces of starch contain a large amount

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**Corresponding author: Qiang Zheng (郑强), E-mail: zhengqiang@zju.edu.cn

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of hydroxyl groups as the silica (Fig. 1). Modification of polymer matrix and starch^[10] and utilization of compatibilizers or coupling agents^[11] are effective to improve the properties. Incorporation of starch in green tires brings marked effects to reduce weight, rolling resistance, noise and emissions and to increase fuel efficiency^[12, 13]. Goodyear Tire Co. has used a starch-based material, BioTRED, to partially replace lampblack and SiO₂ contained normally in the tire mixture. It was reported that Goodyear GT3 was the first one on the market using BioTRED, and Ford of Europe expects to use it on fuel-economic version of the Ford Fiesta^[14].

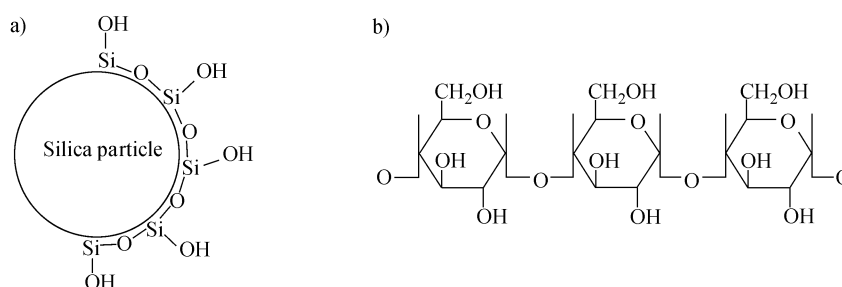


Fig. 1 Schematic representation of surface for the silica (a) and starch (b) with hydroxyl groups

It should be pointed out the addition of filler in a rubber matrix strongly affects the viscoelastic behavior that are directly related to rolling resistance of tires^[15]. The dynamic viscoelastic properties of CB or SiO₂ filled rubbers have thereby attracted much more attentions^[16, 17]. Moreover, filled rubbers can be characterized by specific nonlinear viscoelastic behaviors including high hysteresis, stress softening (Mullins effect) and strain dependent dynamic modulus (Payne effect). To our knowledge, although the preparation and the mechanical properties have been extensively studied, the dynamic viscoelastic behavior of starch filled rubbers has rarely been reported to date. The aim of this article is to probe the dynamic rheological behaviors of solution-polymerized styrene butadiene rubber (SSBR) filled with compound fillers composed of starch and/or SiO₂.

EXPERIMENTAL

Materials and Sample Preparation

Solution-polymerized styrene butadiene rubber (SSBR PR1205, 25% styrene) was provided by Qimei Co., China. Starch (average diameter 10 μm) was purchased from Shanghai Wangwei Food Co., China. Silica (SiO₂, Ultrasil VN3 GR, pH 5.4–7.0, surface area 175 m²/g, average diameter 20 nm) was product of DEGUSSA Co., German. Silane coupling agent bis-(triethoxysilylpropyl)-tetrasulfide (TESPT) was purchased from Nanjing Crompton Shuguang Organosilicon Specialties Co., China. Stearate, wax, zinc oxide, and antioxidant 6PPD were obtained from Shanghai Jinghui Chem. Techn. Co., China.

Rubber composites were formulated with 50 phr (parts per hundred rubber) fillers, 2.5 phr zinc oxide, 1 phr stearate, 2 phr antioxidant and 1 phr wax. The total loading of the starch/SiO₂ compound fillers was constant while the starch content in the compound fillers (SCCF) was varied from 0 to 100%. Starch and SiO₂ were mixed with TESPT first. The resultant mixture was then mixed with SSBR and other ingredients on a two-roll mill at 50°C, followed by a further mixing in a HAAKE Rheometer (Thermo Haake PolyLab System, German) at 150°C at 30 r/min for 10 min. The resultant composites were then compressed into discs of 2.5 mm in diameter and 1.5 mm in thickness at 100°C and 10 MPa.

Dynamic Rheological Measurements

Dynamic rheological measurements were performed on an Advanced Rheometric Expansion System (ARES, TA. Instrument, USA) with strain and frequency sweeps using parallel plate mode at 150°C. A sample was placed between the plates, and dynamic torsional shear was applied to it at 1 rad/s by varying strain from

1%–100% during the test. The frequency sweep was conducted at 1% strain within the frequency region from 100 to 0.01 rad/s.

The temperature sweep test was carried out at strain 1% and frequency 1 rad/s in the temperature range from -90°C to 100°C .

Morphological Observation

The filler dispersion was observed by transmission electron microscopy (TEM, JEM-1230, Electron Co. Japan). Ultra-thin sections of the unfilled SSBR and the filled compounds with a thickness of 200–300 nm were obtained by cryogenic ultramicrotoming.

RESULTS AND DISCUSSION

Figure 2 shows the dynamic storage modulus (G') and the loss tangent ($\tan\delta$) as a function of temperature for SSBR composites containing 50 phr compound fillers with different starch contents (SCCF). The G' curves are identical to each other for the composites with SCCF = 0% and SCCF = 20%. Nevertheless, $\tan\delta$ curve reveals that the composite with SCCF = 0% exhibits a very weak relaxation peak around 30°C . This peak might come from the molecular relaxation at the SSBR/ SiO_2 interface, and it is absent in the composites containing both starch and SiO_2 . Increasing SCCF up to 60%, however, causes a considerable decrease in G' at $T > -75^{\circ}\text{C}$. The $\tan\delta$ curves show the glass transition temperature (T_g) of SSBR at $T_g = -76^{\circ}\text{C}$ and a secondary weak relaxation peak at 74°C . The location of $\tan\delta$ maximum does not vary while the corresponding relaxation magnitude at T_g increases with increasing SCCF, which might be ascribed to the interactions between starch and SSBR weaker than those between SiO_2 and SSBR. The secondary relaxation is evident for the composite with SCCF = 0% while it is indistinct for the composite with SCCF = 60%. The reason for the result can also be ascribed to that interactions between starch and SSBR are weaker than those between SiO_2 and SSBR.

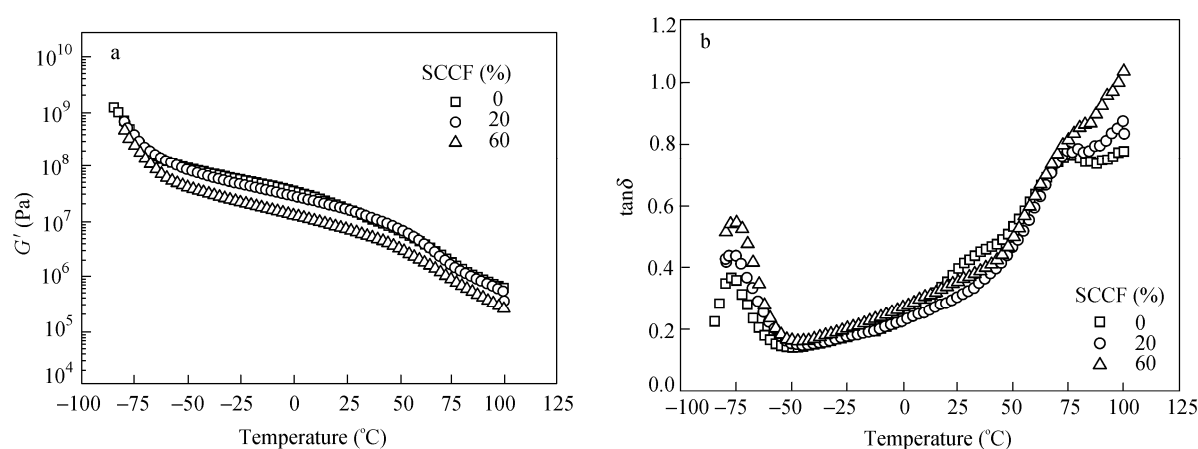


Fig. 2 Dynamic storage modulus (G') (a) and loss tangent ($\tan\delta$) (b) as a function of temperature at 1% strain and 1 rad/s for SSBR filled with 50phr compound fillers of different SCCF values

The $\tan\delta$ values at 0°C and 60°C reflect the wet traction and the rolling resistance, respectively^[18]. A high $\tan\delta$ value at 0°C gives rise to a good wet traction property, while a small $\tan\delta$ value at 60°C corresponds to a good rolling resistance property after vulcanization. The $\tan\delta$ values at 0°C are 0.235, 0.230, and 0.273 and the corresponding values at 60°C are 0.637, 0.601, and 0.634 for the compound fillers-filled composites SCCF = 0%, 20%, and 60%, respectively, which means that the properties for the wet traction and the rolling resistance of SSBR composites can be improved by partially replacing SiO_2 with starch.

Figure 3 shows G' and $\tan\delta$ as a function of frequency (ω) at 1% strain in the linear viscoelastic region for the SSBR composites at 150°C . G' decreases whereas $\tan\delta$ increases with increasing SCCF in the ω region

studied. It is a general characteristic for filled rubbers that G' increases with increasing ω at high ω region. The curves exhibit a viscoelastic plateau in the ω region below 0.1 rad/s, which can be attributed to the formation of the network structure due to filler agglomeration^[19]. $\tan\delta$ shows a maximum at $\omega = 12$ rad/s independent of SCCF, reflecting a characteristic relaxation of SSBR macromolecules. The peak value of $\tan\delta$ increases with increasing SCCF. In case SCCF is below 40%, $\tan\delta$ value is lower than 1.0 in the whole ω range investigated, indicating a high elastic nature of this uncured composites.

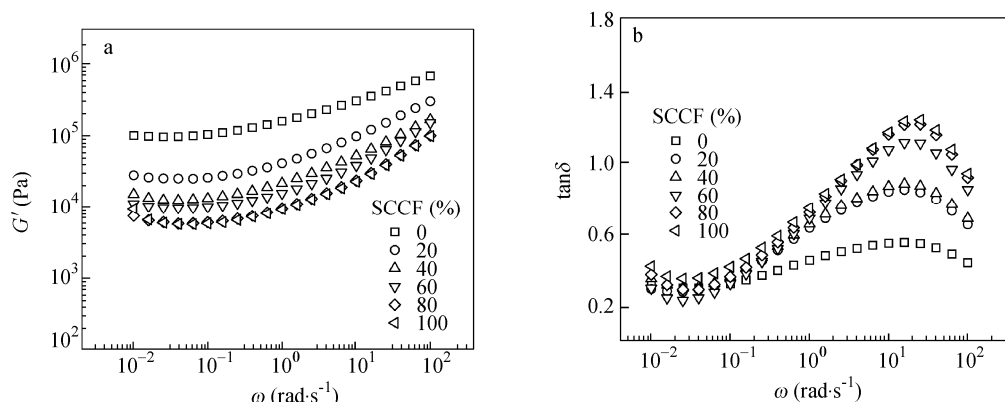


Fig. 3 Dynamic storage modulus (G') (a) and loss tangent ($\tan\delta$) (b) as a function of frequency (ω) at 1% strain and 150°C for SSBR filled with 50 phr compound fillers of different SCCF values

Strong interactions between SiO₂ particles and styrene butadiene rubber (SBR) result in the formation of bound rubber, which is involved in the high level of reinforcement^[20]. The content of bound rubber increases with increase of the storage time^[21] and approaches about 30.9% in 50 phr SiO₂ filled SBR composites after being stored for several months^[22]. Angellier *et al.*^[23] prepared nanocomposite materials using latex of nature rubber as matrix and waxy maize starch nanocrystals as reinforcing phase and found that in case of its loading above 10 wt%, starch nanocrystal could form a continuous network within the matrix due to hydrogen bonding between nanoparticles. The existence of starch network results in an excellent reinforcement without significantly decrease in elongation at break. The appearance of the plateau in the terminal region is related to the formation of filler networks of both SiO₂ and starch due to hydrogen bonding.

Figure 4 presents G' and $\tan\delta$ as a function of strain (γ) for the SSBR compounds at 150°C. SiO₂ shows a strong reinforcement as compared with starch. Both G' and $\tan\delta$ remain constant at initial storage modulus (G'_0)

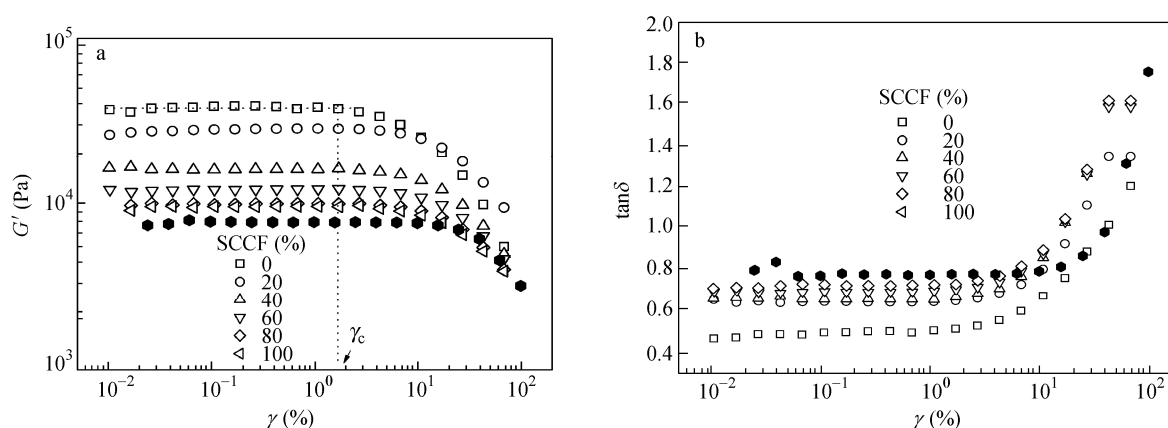


Fig. 4 Dynamic storage modulus (G') (a) and loss tangent ($\tan\delta$) (b) at 1 rad/s and 150°C as a function of strain γ for unfilled SSBR (solid symbol) and SSBR filled with 50 phr compound fillers of different SCCF values (hollow symbols)

and loss tangent ($\tan\delta$), respectively until γ reaches a critical strain (γ_c) and, hereafter, G' decreases and $\tan\delta$ increases rapidly at high γ amplitudes. The nonlinear γ dependences of G' and $\tan\delta$ for highly filled rubbers is referred to Payne effect^[24].

Figure 5 demonstrates G'_0 and γ_c as a function of SCCF. It is seen that G'_0 decreases from 38 kPa to 9.5 kPa for the compounds filled with 50 phr SiO_2 or starch, respectively. On the other hand, the γ_c value increases considerably with increasing SCCF from 0% to 40% while γ_c remains constant at high SCCF.

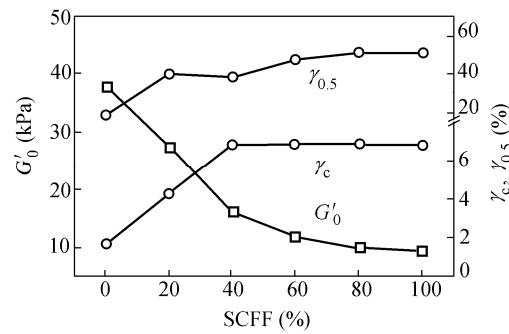


Fig. 5 Initial storage modulus (G'_0), critical strain (γ_c), strain value on condition of ($G' - G'_\infty$) being half of its value ($\gamma_{0.5}$) as a function of SCCF values

The most common interpretation to the Payne effect is involved in the dynamical processes of breakage and reformation of the filler network. According to a model proposed by Kraus^[25], G' is related to γ by

$$\frac{G'(\gamma) - G'_\infty}{G'_0 - G'_\infty} = \frac{1}{1 + (\gamma/\gamma_{0.5})^{2m}} \quad (1)$$

in which $\gamma_{0.5}$ is the shear strain value where $(G' - G'_\infty)$ reaches half of its value ($G'_0 - G'_\infty$) at $\gamma = 0$, and G'_∞ is referred to the modulus at the high strain amplitude limit. The parameter m gives the γ sensitivity of the filler-filler contact breakage. Though G'_∞ is not much smaller than G'_0 in crosslinked elastomers, G'_∞ can be ignored for studying the Payne effect of uncrosslinked polymer melts at strains far below the terminal amplitude. In this case, Eq. (1) could be reduced to

$$G'(\gamma) = \frac{G'_0}{1 + (\gamma/\gamma_{0.5})^{2m}} \quad (2)$$

This equation can be applied to fit the data in Fig. 4(a), and the resultant values of $\gamma_{0.5}$ and m are demonstrated in Figs. 5 and 6, respectively. It can be seen that both $\gamma_{0.5}$ and m increase with increasing SCCF. In general, the higher value of fitting parameter m is the more slow decrease of G' with increasing γ , suggesting a more slow or

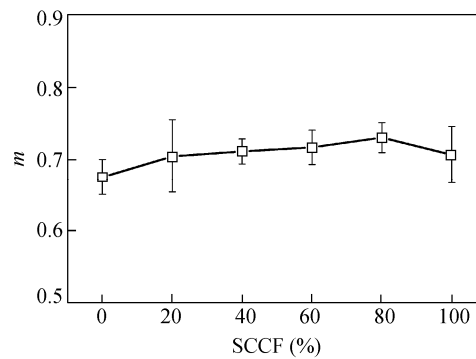


Fig. 6 The γ sensitivity of the filler-filler contact breakage (m) as a function of SCCF values

weak breaking down of filler network structure as γ increases. Even replacing of SiO_2 with starch results in a decrease in the reinforcement effect, the compound fillers system could improve the stability of the filler network with respect to straining.

Figure 7(a) shows the TEM micrograph of the unfilled SSBR. Pure SSBR exhibits a microphase-separated morphology, suggesting the existence of short polystyrene (PS) blocks. The weak relaxation peak at 74°C observed in the Fig. 2 may thus be assigned to the glass transition of the short PS blocks, which is lower than T_g of the bulk PS phase. Figures 7(b) and 7(c) show the typical micrographs for the compound with $\text{SCCF} = 5$. The starch particles with a size of 100–400 nm in diameter might be well dispersed in the matrix (Fig. 7b). However, starch aggregates are considerably abundant in the samples (Fig. 7c). These aggregated structures might be responsible for the weak reinforcement of starch to SSBR. According to the morphological observation, the dispersions of starch aggregates and SiO_2 particles in the SSBR matrix are schematically shown in Fig. 7(d).

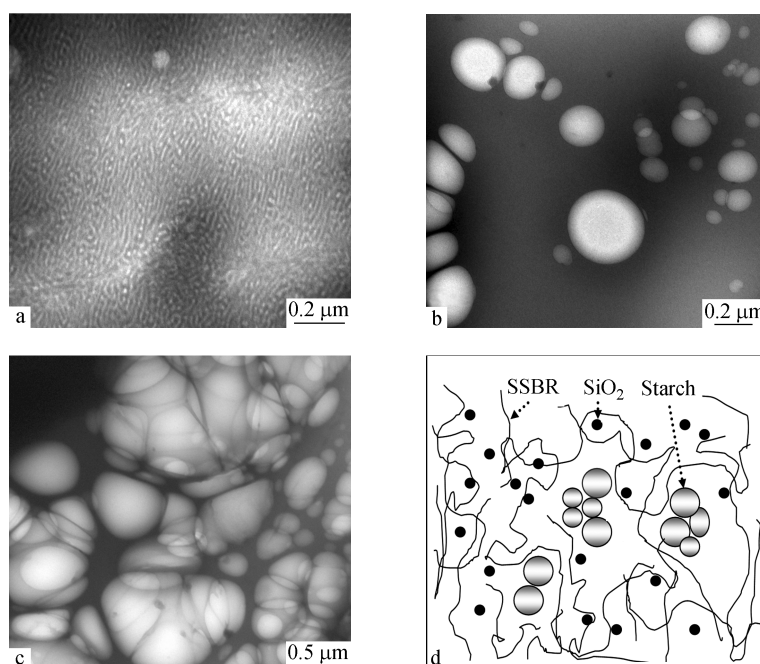


Fig. 7 TEM photographs for the unfilled SSBR (a) and SSBR filled with starch (b and c) and schematic drawing of the starch/ SiO_2 compound filler in the SSBR system (d)

CONCLUSIONS

The dynamic rheological properties of composites of SSBR filled with 50 phr starch/ SiO_2 compound fillers have been investigated using temperature, frequency and strain sweep modes, respectively. The results reveal that the location of $\tan\delta$ maximum is independent on the starch content in the compound fillers (SCCF), while G' decreases with increasing SCCF. Increasing SCCF causes a considerable decrease in G' at $T > -75^\circ\text{C}$ due to the weaker reinforcement effect of starch than SiO_2 . On the other hand, the critical strain (γ_c) for Payne effect increases with increasing SCCF, suggesting an improvement of the stability of the filler network under shear strain. Replacing SiO_2 with starch results in release of absorbed SSBR molecules, but in cases SCCF is below 40%, the $\tan\delta$ value is lower than 1.0 in the whole frequency region tested, implying the high elastic nature of the uncured SSBR system. Furthermore, partial replacement of SiO_2 with starch leads to a slight increase in $\tan\delta$ value at 0°C and a slight decrease in $\tan\delta$ value at 60°C .

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