



Significantly improved rubber-silica interface via subtly controlling surface chemistry of silica

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ABSTRACT

It has been commonly acknowledged that particle dispersion and interfacial interactions are vital in determining the ultimate performance of polymer composites. However, the interplay between dispersibility and interfacial interaction in polymer composites has not been explicitly unraveled. In this contribution, a series of silica with controlled surface chemistry are prepared to reveal the effects of subtle change in surface property of filler on the structures and mechanical performance of the rubber composites. On the basis of thermodynamic theory, the dispersibility of modified silica in rubber is quantitatively evaluated by using surface energy. The modified silica was introduced into styrene-butadiene rubber (SBR) to investigate the effects of surface modification on the dispersion of silica and interfacial interaction of the rubber composites. It has been demonstrated that subtle change in surface chemistry of silica drastically improves its dispersibility in rubber matrix, leading to much improved accessible surfaces and hence much complete interfacial reaction. At very low grafting content (0.2 molecule/nm²), improved modulus (44%) and wet-traction (54%), together with reduced rolling-resistance (11%), are concurrently observed.

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1. Introduction

Due to weak mechanical performance of neat rubbers, the reinforcement of rubber by filling with various fillers such as carbon black and silica is essential for most of practical applications. It is well known that the dispersion of fillers and the interfacial interactions are two vital factors in determining the final performance of rubber composites [1–3]. A variety of methods have been employed to improve the dispersion state and the interfacial interaction. Strategies such as intensive shearing [4], surface pre-treatment of filler [5,6], and incorporation of dispersants [7,8] have been demonstrated to be effective in improving the dispersion of fillers. Enhancement of interfacial interactions is generally achieved by interfacial modification [9,10]. Pre-treatment by interface modifier on filler is effective to improve the interfacial interactions [11]. Besides, *in situ* interfacial modification of rubber composites is promising and industrially-favored. For instance, sulfide-containing silanes, such as, bis-(γ -triethoxysilylpropyl)-tetrasulfide (TESPT), have been widely used in rubber industry [12,13].

On the one hand, stronger interfacial interactions may lead to improved dispersion of fillers via lowering reaggregation energy among the particles [14]. It is argued that the polymer-filler interactions only have a secondary effect on composites by affecting the filler dispersion state or the load transfer between the filler and polymer [15]. On the other hand, the formation of interphase may be influenced by the accessibility of filler surfaces, which is determined by the dispersion state of the filler. In other words, the overall fraction of the interphase may rely on the dispersion state of fillers. The larger the accessible surface, the higher interphase fraction is expected. Consequently, the dispersion state and the interfacial reactivity interplay to determine the ultimate performance of rubber composites.

During rubber compounding with specific processing conditions, the actual dispersion state of fillers is actually determined by the surface property, i.e. the thermodynamics, of fillers. As mentioned above, the dispersion interplays with interfacial reactions. And thus, the surface property of filler may exert significant effect on the interfacial interaction, and hence ultimate performance of rubber composites.

It is worthy to note that the interactions among filler particles are generally much stronger than interfacial interaction [16,17].

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Actually, the dispersion of fillers in rubber matrix during processing is a kinetically controlled process [4]. Under normal processing conditions, it is believed that dispersion kinetics can not guarantee the ideal dispersion of particles. Therefore, the interfacial properties and the ultimate performance of rubber composites are actually limited by the insufficient dispersion. Although vast literatures deal with interfacial modification of rubber composites, one important question remains to be answered. That is, how significantly will the surface property of filler affect the interfacial property, and thus ultimate performance of a rubber composites, under specific processing conditions? To date, the quantitative influence of surface property on rubber performance has not been unraveled.

In this study, a series of modified silica with controlled surface property were prepared, and the effects of the subtle change of surface property on the dispersivity, the interfacial interactions and the ultimate performance of rubber composites were fully investigated. Accordingly, the interplay between surface property (dispersion) and interfacial interactions has been established, which provides deeper insights for the rational design of polymer composites.

2. Experimental

2.1. Raw materials

Styrene-butadiene rubber (SBR), trademarked SBR1502 (with 23.5 wt% content of styrene), was manufactured by Lanzhou Petrochemical Co. Ltd., Lanzhou, China. Precipitated silica WL180 (specific surface area of 200 m²/g) was provided by NanPing Jialian Chemicals, China. Methyl trimethoxy silane (MTMS, purity ≥97%) and bis-(γ -triethoxysilylpropyl)-tetrasulfide (TESPT) were purchased from Alfa Aesar. Other rubber additives, including zinc oxide (ZnO), stearic acid (Sta), N-cyclohexyl-2-benzothiazole sulfonamide (CZ), 2, 2'-dibenzothiazole disulfide (DM), sulfur (S) were industrial grade and used as received.

2.2. Preparation of MTMS-modified SiO₂

Silica was covalently grafted with MTMS, and the surface chemistry of silica was adjusted by varying the MTMS dosage and reaction time. Detailed reaction condition is supplied in [supporting information](#). The sample code MS_x represents the modified silica with grafting density of x MTMS molecule/nm², which is calculated with the weight of grafted MTMS (evaluated by thermal gravimetric analysis) and the specific surface area of silica.

2.3. Preparation of SBR composites

For preparation of SBR composites, SBR was first mixed with silica on a two-roll mixer for 5 min, and then other additives were added successively. The basic formulation of the composites is as follows: SBR, 100 g; silica, 40 g; TESPT 1 g; ZnO, 5 g; Sta, 1 g; CZ, 1.5 g; DM, 0.5 g; S, 1.5 g. After that, the mixture was compounded for another 5 min. The resulted compounds were then compression molded into 1 mm thick sheets at 160 °C for optimized curing time, which is determined by a vulcameter. In this work, the nomenclature SR- x /T represents the TESPT-modified SBR composites filled with silica with grafting density of x MTMS molecule/nm². When x is equal to 0, it refers to pristine silica-filled SBR composites. For comparison, SBR composites without *in situ* modification by TESPT were prepared following similar protocols without adding TESPT, which was coded as SR- x .

2.4. Characterizations

Fourier transform infrared (FTIR) measurements were carried out on a Bruker Vector 70 FTIR spectrometer with a resolution of 4 cm⁻¹ and a range from 3800 to 400 cm⁻¹. Solid-state cross polarization-magic angle spinning (CP/MAS) ¹³C nuclear magnetic resonance (NMR) measurements were performed on a Bruker AVANCE DRX 400 spectrometer. Thermogravimetric analysis (TGA) was conducted on a TA Q50 thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere. Contact angle measurements were conducted on the automatic contact angle meter OCA 40 Micro (DataPhysics Instruments, Germany). The contact angle was recorded within 2 s after liquid deposition. Water and glycerol were used as the test liquids. To prepare the samples for the contact angle measurements, silica powders were pressed into thin disks using a powder tablet press, and SBR was dissolved in toluene, coated onto a glass slide, and then dried to form a film. Rubber Processing Analysis (RPA) was performed on a RPA 2000 analyzer (Alpha Technologies, USA) with frequency of 1 Hz at 60 °C. Dynamic mechanical analysis (DMA) was carried out on a TA DMA Q800 in tensile mode. Temperature sweep measurements were performed at a frequency of 1 Hz and a heating rate of 3 °C/min from -80 to 80 °C and with a dynamic load at 0.5% strain. The dynamic mechanical parameters, loss factor tan delta at 0 and 60 °C, were measured at a frequency of 10 Hz and with a dynamic load at 0.1% and 5% strain, respectively. Frequency sweeping master curves were established by using the time temperature superposition principle (TTS), after measuring a combined temperature frequency sweep at temperatures from -50 °C to 80 °C and frequencies from 0.1 Hz to 100 Hz. Transmission electron microscopy (TEM) for the ultramicrotomed samples was performed on a JEOL2100 instrument. Scanning electron microscopy (SEM) was observed using a ZEISS Merlin instrument. Curing characteristics were determined at 150 °C by a U-CAN UR-2030 vulcameter. Tensile test was conducted on a U-CAN UT-2060 instrument following ISO standard 37–2005.

3. Result and discussion

3.1. Preparation of silica with controlled surface chemistry

By controlling the preparation condition, a series of MTMS-modified silica with different grafting density were prepared. TGA was conducted on pristine and modified silica to evaluate the grafting content. The mass loss of pristine silica exhibits two major weight loss stages at 30–200 and 200–600 °C, which are due to the release of physically adsorbed water, and the dehydration of silanol groups, respectively (Fig. 1(a)) [18]. In comparison with pristine silica, the weight loss behavior of the modified silica is distinctly different. At the temperature lower than 200 °C, the weight loss originated from the release of water is reduced. This is reasonable as the grafted MTMS increases the hydrophobicity of silica and hence hinders the absorption of water. The weight loss of the modified silica in the second stage is obviously larger than that of pristine silica, which is attributed to the decomposition of the grafted MTMS. From the weight loss between 200 and 600 °C, together with the specific surface area, the grafting density of the modified silica is calculated in the range of 0.14–0.43 MTMS molecule/nm². Detailed calculation is described in [supporting information](#).

The evolution of FTIR spectrum of the modified silica along the increase in grafted density is depicted in Fig. 1(b). The absorption bands around 798 and 1100 cm⁻¹ are assigned to asymmetric and symmetric stretching vibration of Si–O–Si, respectively. Compared with pristine silica, the new peaks around 2976 and 2884 cm⁻¹,

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