



Research Paper

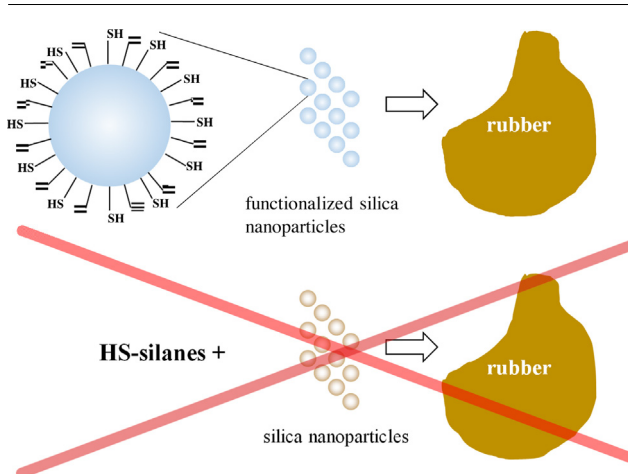
Double functionalization with mercaptopropyl and vinyl groups of the surface of silica nanoparticles and its application to tire rubber

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HIGHLIGHTS

- Mercaptopropyl and vinyl silanes are used for the one-pot functionalization of monodisperse silica.
- Re-dispersibility of nanoparticles is much improved by double functionalization with mercaptopropyl and vinyl groups.
- This mercaptopropyl-vinyl doubly-functionalized silica nanoparticles are used for the filler of tire rubber.
- The stress-strain curve is much improved.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of functionalized silica nanoparticles for polymer filler likely reduces the processes in the production of rubbers. We prepare in this study mercaptopropyltriethoxysilane- (MPTES) and vinyltriethoxysilane- (VTES-) functionalized silica nanoparticles to investigate re-dispersion of the particles and mechanical properties of the rubber for which these nanoparticles are used as filler. The direct synthesis provided nanoparticles with wide distributions of particle sizes except the case of use of equimolar VTES and MPTES. The uniformity in particle size was improved by consecutive hydrolysis/condensation of silanes, where the organosilanes were added in the solution of tetraethyl orthosilicate (TEOS) and ammonium. The re-dispersion of dried powder into the solvent was high (95%) for VTES-silica and low (1%) for MPTES-silica. The re-dispersion of VTES-MPTES doubly-functionalized silica (75%) was considerably improved from that of MPTES-silica. When this VTES-MPTES doubly-functionalized silica was used as the filler of tire rubber, the stress-strain curve was much improved from that with MPTES-silica.

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1. Introduction

Monodisperse silica nanoparticles have been widely used as filler of polymer materials [1,2]. Proper addition of such particles,

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together with curing agent such as sulfur, results in amelioration of mechanical properties, such as tensile, bending and impact strengths as well as elasticity, tensile creep, tribological properties and wearability. Heat distortion properties are known to be also improved [3–7]. Rubbers are too soft for most purposes of the end users and usually used after the incorporation of rigid fillers [8–10]. A gradual replacement of carbon black has stimulated the research on silica monodisperse nanoparticles [10].

In the present process of tire production, commercial silica nanoparticles are mixed by tempering rubber in the presence of sulfur-containing silane. This is simply because such coupling agents are bound both with silica surface and the polymer chain through chemical reactions with different parts of the molecule [11–13]. This process consists in the mixing of rubber with a blend of silica particles and the silane followed by raising the temperature [5,14–18]. This is complicated and the chemical reactions can be incomplete; unreacted silane molecules, both for mercapto and alkoxy groups, likely remain in the final rubber products.

In order to reduce the number of steps in rubber production and make this process more uniform and controllable, we develop in this study a novel method by using silica nanoparticles pre-functionalized with mercaptoalkyl group for the filler. The surface of silica nanoparticles is easily covered with organic functional groups uniformly and the use of functionalized particles possibly results in more uniform reactions between filler particles and rubber polymer than in the present process. Considering that agglomeration of nanoparticles easily occurs, one of the most important criteria is the dispersibility without reducing the reactivity of thiol functional group with rubber. Since the reactions between sulfur-containing silane, functional groups in the polymer and silica surface have not been well analysed in the molecular level, dispersibility and reactivity of newly-prepared functionalized monodisperse silica particles is explored in this study by comparing mechanical properties with a rubber prepared by standard procedure.

2. Experimental

Tetraethyl orthosilicate (TEOS, 96.0%), ethanol (99.5%) and aqueous solution of ammonium (25 wt%) were purchased from Wako Pure Chemical Industries, Ltd. (3-mercaptopropyl)triethoxysilane (MPTES, 98.0%) and triethoxyvinylsilane (97.0%) were obtained from Tokyo Chemical Industry, Co., Ltd. These commercial reagents were used without further purification.

Since the nanoparticles are easily aggregated and the mesopores are formed, silylation does not occur uniformly when using once-dried silica particles [19–21]. Thus we carried out silylation of silica nanoparticles dispersed in solvent. All silica nanoparticles were prepared by modified Stöber synthesis. The mixture of TEOS and organosilanes (VTES: MPTES = 3: 1, 2: 1, 1: 1, 1: 2 and 1: 3) was added to the water-ethanol mixed solvent. TEOS/organosilane molar ratio was varied to be 12/1, 24/1, 48/1 and 96/1. The water/ethanol weight ratio was 2/18. The total weight of solvent was 20 g and the total molar amount of TEOS and organosilane was 0.0144. Then 0.2 ~ 0.4 g of 25 wt% aqueous ammonium was added to the mixture, followed by continuous stirring for 3 h. Dilute sulfuric acid was added to precipitate the particles. The solution was removed by filtration, the powder was collected and dried at 373 K for 2 h. This method is hereafter called method A and abbreviated sim.

The alternative method was consecutive additions of silanes. The TEOS and VTES were mixed with water-ethanol solvent, then aqueous ammonium was added under vigorously stirring. The liquid was continuously stirred for additional 3 h. Then MPTES was added and the mixture was further stirred for 3 h. Finally, the powder

was precipitated after the addition of sulfuric acid, collected by filtration and dried at 373 K for 2 h. The amount of chemical substances are the same as in the first method except aqueous ammonia, which was fixed at 0.4 g. This method is hereafter called method B and abbreviated suite.

The uniformity in the size and shape of thus prepared nanoparticles was observed by a JEOL JSM-7001F scanning electron microscope (SEM). Fourier transform infrared spectra of silica nanoparticles were recorded using a JASCO FT/IR-4200 operated in 2 cm^{-1} of resolution and 20 times of scanning.

These nanoparticles were re-dispersed in water-ethanol solution by ultrasonic irradiation at 100 W for 15 min. The solvent was the same as used in the preparation. The particle size distributions in the re-dispersed powder was recorded by a Horiba LA950 Laser Particle Size Analyzer.

As for the preparation of rubber compounds, we used styrene butadiene rubber (SBR) with styrene content of 30%, silica, silane, stearic acid, zinc oxide, sulfur, and vulcanization accelerator, which were commonly used in the rubber industries. The ratio in mass of SBR, silica, silane, stearic acid, zinc oxide, sulfur and vulcanization accelerator were 100, 50, 4, 2, 2, 1.5, and 2.7, respectively. Silane is bis(triethoxysilylpropyl)disulfane (TESPD) and only used in the case of unfunctionalized silica. For the mixing procedure, SBR, silica, silane, stearic acid and zinc oxide were mixed in a Banbury mixer for 5 min, then the compounds were further mixed in a two roll mill for 10 min with sulfur and vulcanization accelerator. The obtained rubber compounds were pressed at 443 K for 15 min to get vulcanized rubber sheets with 2 mm thickness. The tensile properties of the vulcanized rubber sheets were obtained according to the JIS-6251.

3. Results and discussion

Fig. 1 depicts SEM photographs of VTES-MPTES doubly-functionalized silica nanoparticles prepared by method A. The mixing ratio of VTES and MPTES was changed from 3:1 to 1:3, as shown figures from (a) to (e), with various amount of ammonia used in the synthesis. In the use of 0.2 g of ammonium, the particle sizes are found to be narrowly distributed at around 10 ~ 20 nm and the precipitated particles are aggregated. This finding is not dependent on the VTES: MPTES ratio. Another common feature found in Fig. 1 is that the increase of ammonia content results in the increase in the average and distribution of particle sizes. Using 0.3 g of ammonia, the particle sizes becomes 20 ~ 40 nm for all VTES: MPTES ratios and the samples often contain a few larger particles than 80 nm. With 0.4 g of ammonium, the particle size becomes ca. 50 nm for VTES: MPTES = 1: 1 and more monodisperse than the other mixing ratio, which show wide distributions from 30 nm to 200 nm. In addition, the particles are not agglomerated as much as those from the other VTES: MPTES ratios. The optimum amount of ammonium for narrowing the distributions is probably influenced by the kinetics of the condensation, while that for the silane ratio is likely related with the fusion of the particles.

Fig. 2 depicts SEM photographs of VTES-MPTES doubly-functionalized silica nanoparticles with varying TEOS: organosilane ratio in method B. By this method, the samples prepared are more monodisperse and the particles are less aggregated than those in Fig. 1. Furthermore, the particle size remains almost the same even when the mixing ratio of TEOS and organosilane is changed. In this method, the silica particle formation occurs uniformly according to the processes in the Stöber synthesis, which the particles size is defined. After the addition of organosilane, the fixation of these silane through the reaction with the silanol on the surface of silica particles can compete with the particle size growth by the further dehydration-condensation of TEOS. However, when the mixture

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