

Synthesis and Application of a Silica Nanocomposite Filler Using Water Glass and a Resole-Type Phenol Resin

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ABSTRACT: Composite plastics in which silica was dispersed homogeneously were prepared from a resole-type phenol resin and a silica-sol using water glass. The silica (10–50 nm) was dispersed into resin particles of 2–20 μm in size. The powder that was obtained (nanocomposite filler) and a curing reagent were then mixed, and the resulting mixture was processed by using heat and pressure to yield plastics containing nanocomposite fillers. The coefficients of friction factor of the resulting plastics composites

decreased by half and the amount of wear that they suffered decreased to just one tenth of that of the unfilled material, while their wear-resistance was greatly improved. The new plastics displayed good sliding properties, while also maintaining good fluidity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3748–3753, 2009

Key words: water glass; nanocomposite filler; plastics; sliding property

INTRODUCTION

Organic polymer materials such as plastics can contain many defects on properties such as heat resistance, weather resistance, etc. Sol-gel methods have been developed to dissolve these defects or to disperse inorganic particles on a nanometer scale, and these techniques have now been expanded to a wide range of applications. Experiments to mix and disperse inorganic particles have been undertaken by many researchers, and it has been reported that improvements in various functions affecting the properties of plastics are now expected.^{1–17} However, despite of these advances, there are still some problems, such as decreasing fluidity and the onset of cracking, which must be solved. There are a few reports that cover these results.¹⁸ Reports on the utility of these developments are restricted to thick films or coating materials, therefore there are a few reports that cover these results.¹⁸ Although silica-hydrosol methods have been tried, which involves an inorganic–organic hybridization using water glass, there are only a few successful examples in which it has been possible to achieve the desired utility and to maintain functionality at the same time.^{19,20} Our new approach to plastics that offers both utility and functionality is based on the use of a conventional nanocomposite filler. It is possible to

prepare nanocomposite fillers from plastics (resole-type phenol resin) and a silica sol, which prepared from water glass. In this article, the preparation processes for the nanocomposite filler and the inorganic–organic hybridizing plastics were studied, and physical properties, such as bend-strength, fluidity, and sliding coefficients of the inorganic–organic hybridized plastics were investigated. The nanocomposite filler and the plastics were obtained and characterized by their viscosity and by Fourier transform infrared spectroscopy (FTIR) and transmission electron microscope (TEM). Also, mechanical properties were examined.

EXPERIMENTAL

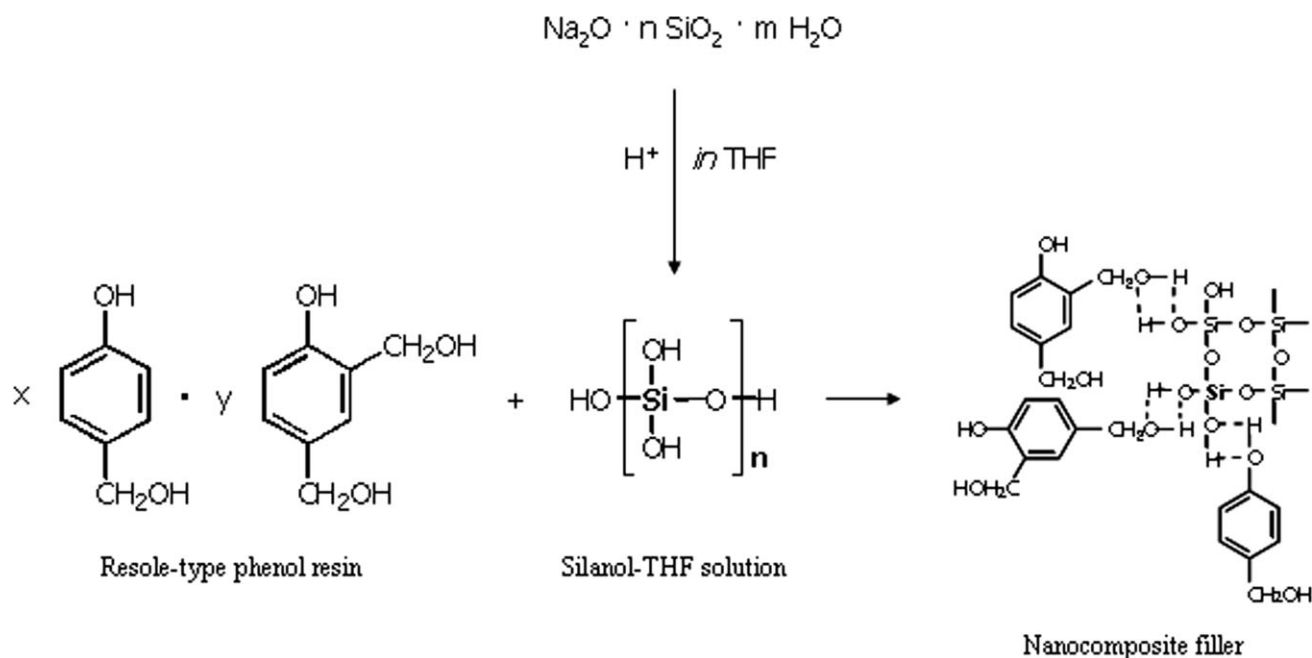
Materials

Aqueous sodium silicate [water glass ($\text{Na}_2\text{O}\cdot n\text{-SiO}_2\cdot m\text{H}_2\text{O}$): JIS third class, where $n = 3.23$, $\text{Na}_2\text{O} = 9.8\%$, $\text{SiO}_2 = 29.67\%$] was supplied by Fuji Chemical Industry. Resole- and novolak-types phenol resins (Sumitomo Bakelite Co., Ltd.) were used without further purification. Tetrahydrofuran (THF) (Nacalai Tesque) and hexamine (Nacalai Tesque) were supplied commercially and were used without purification.

Measurements

FTIR spectra were recorded on a Nicolet spectrophotometer (FT/IR4700) over the wave number range 4000–400 cm^{-1} , using the KBr method. A Labo Jet

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Scheme 1 Preparation procedure for nanocomposite filler, using water glass.

Mill (Nippon Pneumatic Mfg., Co., Ltd.) was used to break the composite into particles with dimensions of microns or several microns. A laser-scattering particle-size distribution analyzer LA-910 (Horiba, Ltd.) was used to measure the distribution of the particle sizes. The fracture surfaces of the nanocomposite filler were imaged by using a TEM (HF-2000, Hitachi), which was operated with a high-tension voltage of 10 kV. Atomic force microscopy (AFM) experiments were carried out on the plastics at room temperature in air using an Olympus NV 2000. Most of the images were obtained by tapping-mode (ACAFM) with a silicon nitride cantilever (OMCL-AC240TS-C2; Olympus Optical Co., Ltd.) with a constant of 15 N/m and a frequency of 20 KHz. Scanning rates varied from 1 to 2 Hz. All of the images presented in this work were obtained reproducibly over at least three points on the sample surfaces. Fluidity was measured by using fluid meter, which was operated for 10 min at 125°C on a 30° slope. Sliding properties were measured by the "Ring on-disk" method using a friction and wear tester (Frictorion, Model EFM-III-EN, Orientec), which was operated for 30 min at 2500 kgf/cm² m/min. Bend-strength was measured using an autograph (AG-5000B, Shimadzu), which was operated by a three-piece method (span: 50 mm, speed: 50 mm/min). Hardness was measured using a durometer (Rockwell, Model ORK-A, Mitutoyo), which was operated at 100 kgf (diameter of steel pill: 6.35 mm). Dynamic mechanical analysis was performed on a Rheovibron DDV-II-EP (Orientec) at a heating rate of 2°C/min and a frequency of 11 Hz.

Preparation of silanol-THF solution

A solution (3.2 mol/L : 150 mL) of water glass was added to 2N sulfuric acid (150 mL) in a 500 mL disposable PP cup, and the mixture was then stirred. The resulting solution was cooled in ice to 0°C. After it was confirmed that the pH of the solution was between pH 2 and 3, the solution was transferred to a 500 mL separable funnel. THF (200 mL) was added, and the mixture was then stirred vigorously for 3 min while sodium chloride (80 g) was added. The mixture was left to stand for 30 min at 4°C in refrigerator, during which time the THF layer separated.

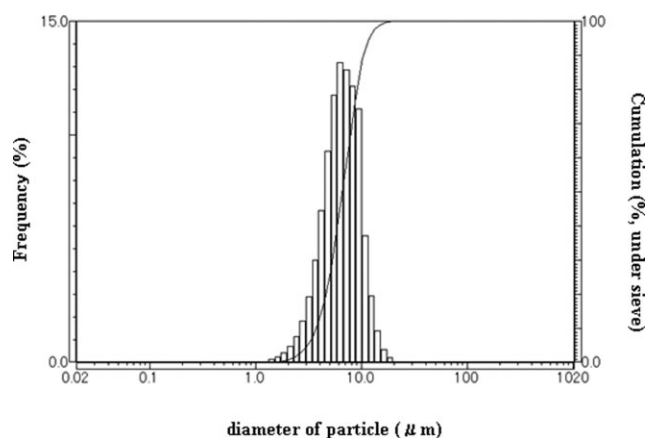


Figure 1 Particle size of the nanocomposite filler.

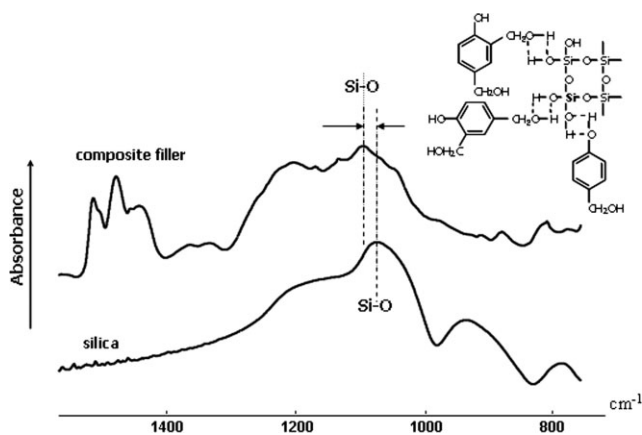


Figure 2 FTIR spectra of the nanocomposite filler (top) and silica (bottom).

Preparation of the nanocomposite filler

The preparative procedure is indicated in Scheme 1. A resole-type phenol resin (nonvolatile content = 40.0%) (2000 g) was placed in a reaction vessel, and then methanol (2000 g) was added with stirring. A silanol-THF solution (nonvolatile content = 13.5%) (1482 g) was added dropwise while vigorously stirring the obtained solution (concentration = 20.0%). The mixture was transferred into a resin tray and allowed to stand at room temperature for 24 h, during which time the mixture became a gel. After gelation, the solvent was removed for 8 h at room temperature under reduced pressure (−95 to −90 kPa). The composite was broken by milling and was ground minutely by a jet mill. The particle sizes of the resulting nanocomposite filler were between 2 and 20 μm (Fig. 1).

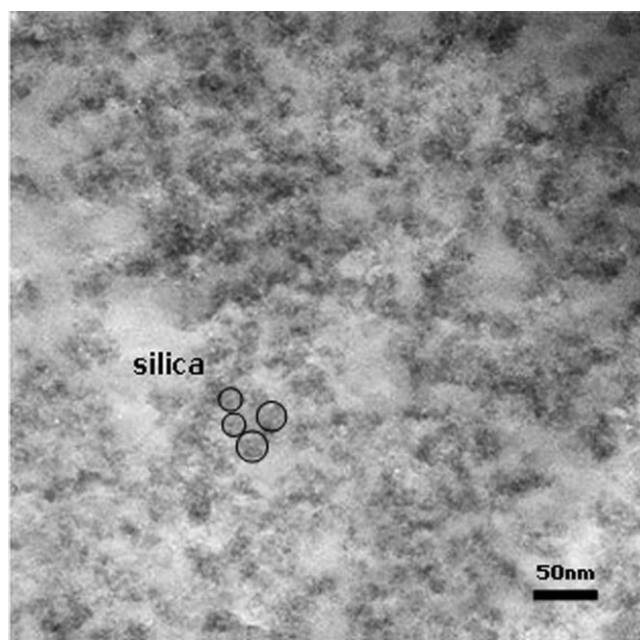


Figure 3 TEM observation of the nanocomposite filler.

Preparation of plastics containing the nanocomposite filler

Hexamine (8 g) was added to a phenol resin (novolak-type) powder (72 g) in a reaction vessel and an amount of the nanocomposite filler (20 g) was added, after which the mixture was mixed. The product was pressed for 15 min at 160°C under a pressure of 49 MPa. In this product, the content of silica was 8%. Various resins (4, 12, 16%, etc.) were prepared similarly.

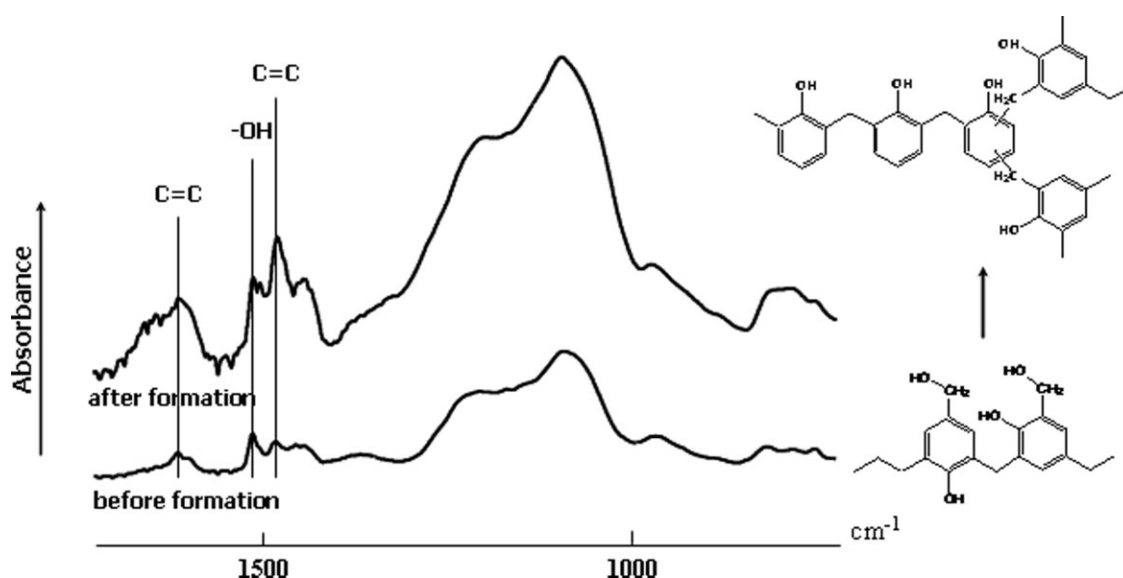


Figure 4 FTIR spectra of phenol resin containing nanocomposite filler. Top trace is after formation and bottom trace is before formation.

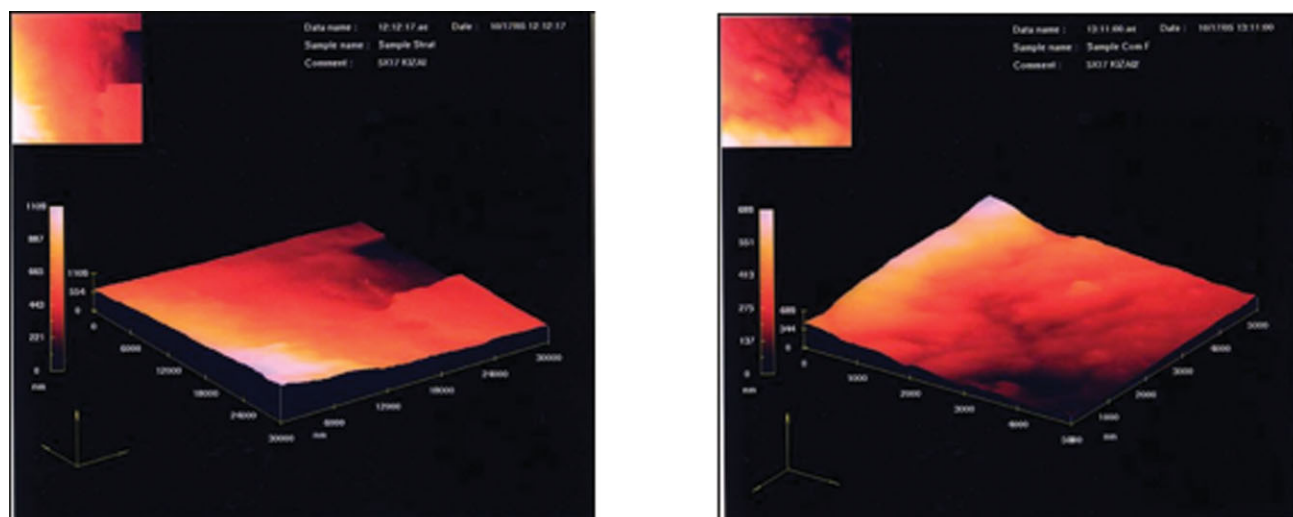


Figure 5 AFM topological images of phenol resin (left) and phenol resin containing nanocomposite filler (8%) (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Characterization of the nanocomposite filler

Figure 2 shows the FTIR spectra of both the silica and the nanocomposite filler that were prepared from the phenol resin (resol-type) and the water glass. Both the silica and the nanocomposite filler exhibit peaks that are characteristic of the siloxane bond at $1000\text{--}1100\text{ cm}^{-1}$. The peak for siloxane in the nanocomposite filler is shifted by 30 cm^{-1} toward higher wavenumber. Observation of the spectra shown in Figure 2 provides strong evidence for an interaction between the resole-type phenol resin and siloxane. Figure 3 displays a TEM micrograph of the nanocomposite filler. The TEM image of the nanocomposite in Figure 3 shows silica (gray part, about $10\text{--}50\text{ nm}$ diameter) in a resole-type phenol resin particle ($2\text{--}20\text{ }\mu\text{m}$) and silica dispersed equally.

Plastics containing nanocomposite filler

Figure 4 shows FTIR spectra obtained from plastics before and after their formation. Before formation, a hydroxyl group that is characteristic of methylol in

resol-type phenol resin and novolak-type phenol resin was found. However, after formation, this hydroxyl group had markedly decreased. Observation of the spectra shown in Figure 4 gives evidence, which the nanocomposite filler possessed reactivity.

The results of AFM measurements of the phenol resin and of phenol resin containing the nanocomposite filler (content of silica: 8%) are shown in Figure 5. The surface of the “pure” phenol resin is relatively smooth. On the other hand, the phenol resin containing the nanocomposite filler is much more uneven, with undulations ranging from tens to hundreds of nanometers.

Table I shows various properties (bend-strength, hardness, and fluidity) of the phenol resin containing the nanocomposite filler (content of silica: 4 and 8%). The values for bend-strength increase with increasing content of the additive (nanocomposite filler). The hardness values are almost the same for resins containing the additive, although those with the additive (content of silica: 4 and 8%) are slightly lower than the value for the additive-free resin. Although the fluidity values decrease slightly with increasing additive content, the fluidities of the plastics that are obtained are of the same order, and the fluidities of these plastics are higher than those obtained using the sol-gel method. In experiment, the fluidity of plastics formed using the sol-gel method is minimal.

The results of our determinations of the sliding properties of the additive-free phenol resin and the resin containing the nanocomposite filler (content of silica: 8%) are shown in Figure 6. Although the sliding face of the additive-free material is quite badly worn, the material containing the additive has not

TABLE I
Bend Strength, Hardness, and Fluidity of Phenol Resins Containing Nanocomposite Filler

Property Composite	Bend strength (MPa)	Hardness (HRM)	Fluidity (mm)
SiO ₂ 0%	112	125	17.5
SiO ₂ 4%	124	124	16.3
SiO ₂ 8%	135	123	14.8

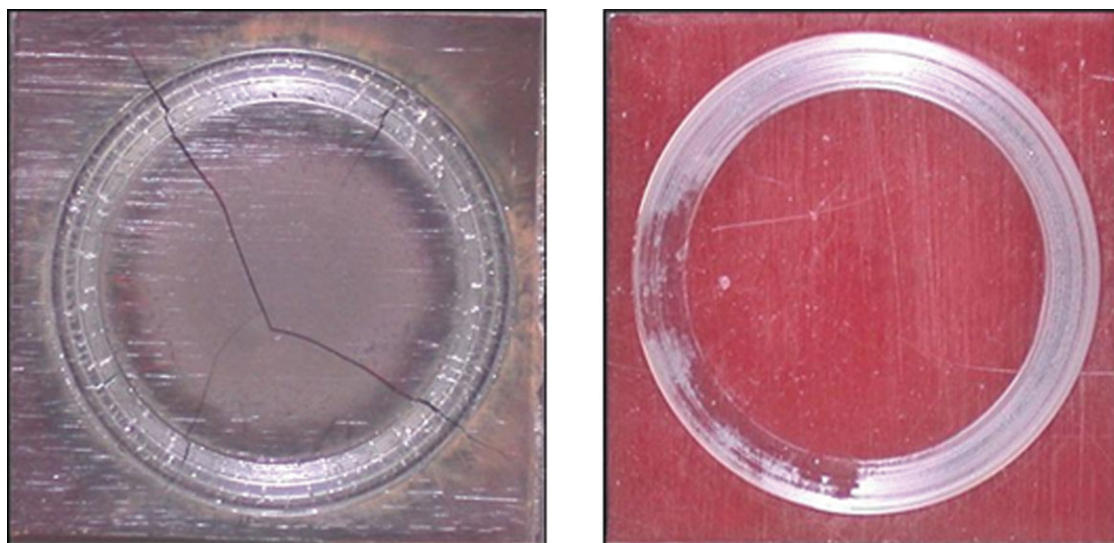


Figure 6 Observation of sliding in phenol resin (left) and in phenol resin containing nanocomposite filler (8%) (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

worn nearly as much. Even though there is scoring caused by rubbing of the sliding face, the amount of wear is only 1/10 (or less) of that of the additive-free material (Fig. 7). Also, the coefficient of friction of the material containing the additive changed to about half its value or below of the additive-free material. The PV limit of the material containing the additive was higher than it of the additive-free mate-

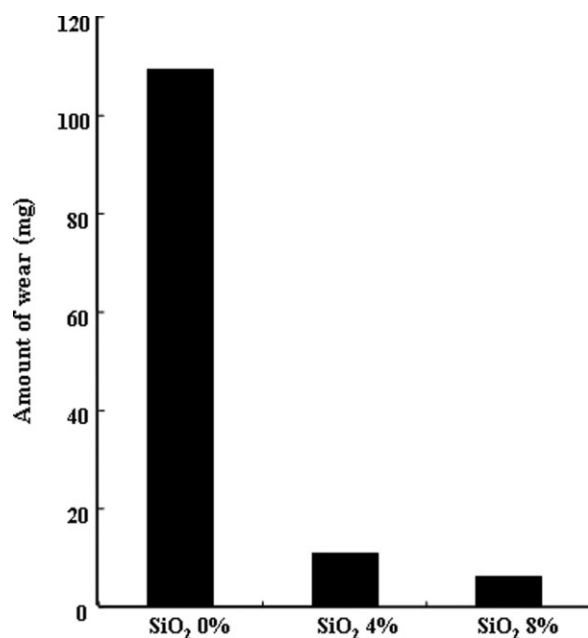


Figure 7 Amount of water for phenol resin with and without the nanocomposite filler.

rial, and the value of PV limit of the material containing the additive was more than two times.

CONCLUSIONS

A nanocomposite filler was prepared from a resole-type phenol resin and a silanol-THF solution (which was prepared using water glass), and different plastics (novolak-type phenol resin) were prepared using the filler. The optimum content of silica was synthetically found to be between 4 and 8%. The obtained resins maintained their conventional properties and also displayed new functionality, such as improved fluidity and sliding properties. For example, since the coefficient of friction is half of that displayed by the raw material, and the amount of wear that the material suffers is 1/10 or less, the resulting resins can be confirmed as displaying qualities that are derived from "nanohybridization." On the other hand, the fluidity of the filled resins is nearly the same as that of the "pure" material so it is still adequate in terms of processing. It was therefore demonstrated to obtain improved functionality while maintaining utility for a plastic material by using a nanocomposite filler method.

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