

# Improvement of nano silica particle dispersability into polymer matrix

Chika Takai, Masayoshi Fuji, Minoru Takahashi

Ceramics Research Laboratory, Nagoya Institute of Technology

e-mail: [chy-koro88@crl.nitech.ac.jp](mailto:chy-koro88@crl.nitech.ac.jp)

URL: <http://www.crl.nitech.ac.jp/>

Keywords: Nano particle, Surface modification, particle dispersion, composite material

## INTRODUCTION

Composite materials composed of inorganic particles and polymers have been developed with the purpose of improving the physical properties, such as strength, heat resistance, and elastic modulus. There is no repulsive force between particle surfaces in an organic medium; hence, the interaction between particles works always as attractive. Because of this, it is difficult to obtain uniformity dispersion in polymer matrix.

It is well known that particle surface strongly depends on particle behavior. Surface modification is a common technique to change surface property of inorganic particle. In this study, surface treatment based on surface modification was proposed. There are two advantages. One is to decrease apparent interaction between nano particles using polymer coating. The other is to increase wettability between particle surface and matrix using similar chemical structure to polymer matrix. Then treated particles were dispersed into polymer precursor to prepare organic inorganic composite. Here, treated silica nano particles were used to disperse into polyimide matrix. First, silica surface was modified with APTS silane coupling reagent to introduce  $\text{NH}_2$  group on particle surface. Second, PMDA and DDE which are monomers of polyimide were used to coat modified silica surface. One side of anhydride group of PMDA was reacted with  $\text{NH}_2$  group of modified silica surface. The other side of anhydride group of PMDA was reacted with  $\text{NH}_2$  group of DDE at ambient temperature. These reactions were repeated 8 times. The treated particles were dispersed into polyimide precursor then prepared silica/polyimide nanocomposite. Particle dispersability was confirmed by TEM observation and particle surface characterization was performed by FT-IR and TG/DTA analysis.

## RESULTS AND DISCUSSION

Surface modification was completed well by the autoclave method. This is an anhydrate reaction between free silanol group on particle surface and hydroxyl group of APTS. FT-IR spectra of

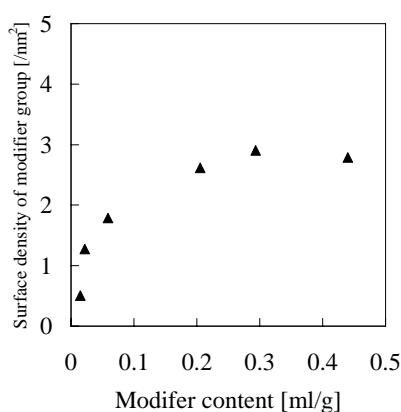


Figure 1. Determination of surface density of modifier groups on silica surface as a function of modification amount.

unmodified and modified silica with different amount of APTS silane coupling reagent showed followings. With increasing in amount of APTS, intensity of  $3747\text{ cm}^{-1}$  band caused by O-H stretching vibration of silanol decreased and three new band caused by C-H stretching vibration of APTS appeared and increased. It indicates attachment of APTS with silica surface. In order to characterize modified silica surface, surface density of modifier groups was determined by TG/DTA analysis. With increasing in modifier amount, surface density increased and showed about  $2.8\text{ /nm}^2$ . From these results, almost all surface free silanol groups would react with APTS. Surface free silanol groups was estimated about  $3\text{ OH/nm}^2$  from Grignard reagent method. At next step, modified surface was coated with PMDA and DDE as above mentioned. Figure 2 shows the IR spectra for unmodified silica, modified silica, and coated silica. For the unmodified silica, a band at  $3747\text{ cm}^{-1}$  due to the OH stretching vibration of the free silanol group was observed. In modified silica, this band disappeared and three new bands between  $2915$  and  $2985\text{ cm}^{-1}$  appeared. These bands are due to the C-H stretching vibration, indicating the attachment of APTS to the silica. The IR spectra of the resultant coated silica contain peaks at  $1456$ ,  $1740$ , and  $1777$ . These bands are caused by C-N stretching, asymmetric imide

C=O stretching, and symmetric C=O stretching, respectively. Hence, the NH<sub>2</sub> functional groups in modified silica are able to react with the anhydride end groups of PMDA and the other end groups of PMDA are able to react with the end groups of DDE. The nanocomposite consisting of polyimide and the coated particle was prepared. TEM observations of polyimide/silica nanocomposite are shown in Figure 3. The thickness of sample fragments was 300 nm. Coated particles were well-dispersed into polyimide matrix. Particles were separated each other and the distance between particles was about 12 nm. In the insert magnified figure, thinned film (thickness about 2 nm) was formed on the surface of the coated particle, which is assumed to be the results of polyimide coating.

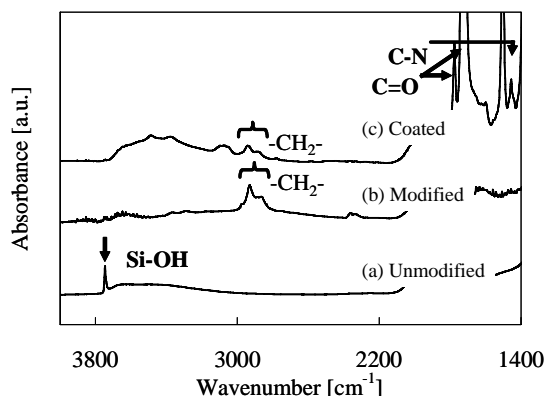


Figure 2. FT-IR spectra of unmodified, modified, and coated particle.

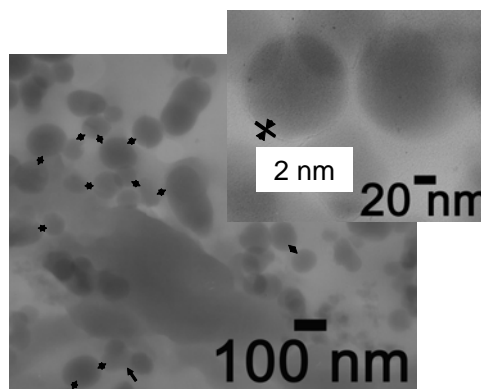


Figure 3. TEM observations of coated silica in polyimide matrix.

## CONCLUSION

We have successfully improved particle dispersability into polymer using proposed surface treatment technique. It has been confirmed by TEM studies as well as formation of polymer coating on the particle surface. It is thought that the polymer coating on the particle surface could prevent from particle aggregation and improve wettability between particle surface and polyimide. This technique is an effective way to obtain highly controlled polyimide/silica nanocomposite.

---

## SELF INTRODUCTION

**Name:** Chika TAKAI

**Affiliation:** Ceramics Research Laboratory, Nagoya Institute of Technology

My favorite things are....

- Driving my car HONDA civic (EG6 SiR).
- Drinking beer
- English conversation
- Watching movies, scuba diving, snorkeling, etc.



2002 BA degree at NIT

2004 MA degree at CRL in NIT

Now I'm a doctorate student under Prof. Takahashi and Dr. Fuji's lab. My research work focuses on development of particle dispersion in slurry and its characterization. I'm happy to join their group for 5 yrs.