# Synthesis and Characterization of Silica Nanocomposite *In Situ* Photopolymerization

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**ABSTRACT:** This study was carried out on nanocomposites consisting of nanometer silica fillers embedded in thermoset polymers that were prepared via the *in situ* polymerization of ultraviolet (UV) curable systems containing different contents of nanometer silicas by irradiation of UV light. Because of the introduction of nanosilicas, the curing rates of the UV curing of dispersing systems were played down; that is, the curing times were prolonged, but the mechanical properties of the nanocomposites, such as tensile strength and Young's modulus, increased, and the thermostability of the nanocomposites at temperatures lower than 400 K improved. The dispersing states of nanometer silicas within the polymer matrix were characterized by transmission electron microscopy, and the results show that the nanometer silicas had good homogeneously dispersing states within nanocomposites containing less than 3 wt % nanometer silicas. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 837–840, 2003

**Key words:** nanocomposites; silicas; photopolymerization

## INTRODUCTION

In recent years, nanocomposites have become a major part of new synthetic materials all over the world, for applications ranging from mechanics and tribology to optics, magnetism, and electronics.[1–4] Inorganic–organic nanocomposites are generally organic polymer composites with inorganic nanoparticles. In the polymer-based nanocomposite field, the unique properties of the nanoparticle surface atoms are used to modify synthetic polymers. This kind of nanocomposites has attracted more and more attention.[5,6] They combine the advantages of polymers, such as elasticity, transparency, and moldability, with those of inorganic nanoparticles, such as rigidity and catalysis. However, it is very difficult to manufacture nanocomposites with the nanoparticles dispersed uniformly because nanoparticles have very high surface energies and are prone to agglomerate into larger particles during the preparation of materials. Generally speaking, many approaches have been tried to solve the problems, for example, the vapor deposition, precursor, nanoreactor, intercalation polymerization, and supermolecular self-assembly techniques. Among these methods, dispersing *in situ* polymerization may be the most desirable method for preparing nanocomposites because the types of nanoparticles and the nature of polymer precursors can vary in a wide range to meet the requirements. As far as the *in situ* polymerization technique is concerned, there are many methods for manufacturing nanocomposites, such as thermal polymerization,[7] high-energy irradiation polymerization,[8] and chemical polymerization.[9] The ultraviolet (UV) curable technique as a new technology[10–12] has been widely used in chemical reactions to prepare organic materials such as film,[13] bulk,[14] and other irregular types of film materials.[15] There have been few reports on UV curable technique used to prepare nanocomposites, let alone a report on the technique of fabricating nanosilica composites based on an organic matrix such as epoxy acrylate as the continuous phase and inorganic nanoparticles such as silicas as the discontinuous phase. This kind of composite has been applied in coatings as a protective layer and in enhanced materials, such as rubber, plastic, and fiber. So, the synthesis of nanocomposites by means of the UV curable technique is thought to have significance in the new materials field.

Nanometer silicas are available as individual particulate beings approximately less than 20 nm. They have the potential to improve heat deflection temperatures and to increase the tensile strength and the modulus of composite materials; so, nanometer silicas are very

useful in the reinforcement of thermoplastic and thermosetting polymers if they are dispersed well into polymer matrices. Primarily because of the formation of aggregates originating from the incompatibility of the chemistry of the silica particle surface and many matrix polymers, the mechanism of how silicas get into polymers has caused considerable concern.[16,17] To overcome some limitations of dispersing of silicas into preformed polymers studies on the methods by which nanosilicas are dispersed into polymer precursors and, subsequently, *in situ* polymerization have been conducted.[18] In some studies of nanocomposites fabricated according to these methods,[19] not only did the nanoparticles give rise to higher rigidities, but they increased the yield stress of nanoparticle-reinforced polymers compared to that of the pure polymer. Therefore, the method of nanosilica dispersion by *in situ* polymerization is available to fabricate nanocomposites.

This study was focused on the synthesis and characterization of nanocomposites containing nanometer silicas. Nanosilicas were dispersed into a UV curable solution by a supersonic vibrator and mechanical stirrer, and meanwhile, an active comonomer as a codisperser was used to improve the quality of the dispersion of nanoparticles. Then, the mixture was photoinitiated to polymerize *in situ* to form nanocomposites under UV irradiation.

## EXPERIMENTAL

Difunctional monomers of diethylene glycol dimethacrylate and 1,6-hexanediol diacrylate and oligmers of biphenyl A epoxylacrylate (CN120) were gifts from UCB Co. (Brussels, Belgium) and Sartomer Co. (Exton, PA), respectively. Irgacre 907 [2-methyl-1-(4-methylthiophenyl)-2-morpholinopropanone-1] as a photoinitiator was a gift from Ciba-Geigy (Hong Kong). Silicas with grain sizes from 10 to 15 nm were received from Zhoushan Nanomaterials Co. (Zhoushan, China). Monofunctional monomers of butyl acrylate and 4-vinyl pyrrolidone were purchased at market. All of the chemicals were used as received. After the solid powder silicas were added in different ratios (all wt %) to liquid active components containing oligmers (about 20–50%), monomers (45–75%), and photoinitiator (3%), the mixtures were stirred by a mechanical stirrer and a supersonic vibrator at room temperature for nearly 1 h to get stable dispersing systems. The dispersing mixtures were coated on an even glass plane to obtain thin films or poured into sample cells to obtain $3 \times 10 \times 60$ mm$^3$ specimens for mechanical measurement. The photopolymerization was completed on a UV curer (UV125, Beijing Expoit Co.) by the irradiation of high-pressure mercury lamps with a UV intensity of 0.4 m W/cm$^2$ for less than 1 min to obtain solidified nanocomposite samples
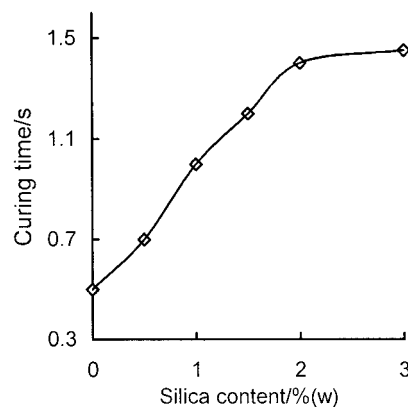


**Figure 1** Effect of nanosilicas on UV-curable time of the dispersion system.

for testing; photopolymerization time was recorded simultaneously. The mechanical properties of the photocured nanocomposites were determined with a WD-5 all-purpose electrical tester with a 500-N load cell (Changchun Testing Machine Factory No. 2) at ambient temperature with no strict humidity control. Thermogravimetric analysis was carried out with a TG–DTA (WCT-1, Beijing Optics Instrument Co.). The samples (ca. 20 mg) were heated under static air at a heating rate of 10°C min$^{-1}$. To study the dispersing states of nanosilicas in the nanocomposites, the samples, which were cut to pieces 90 nm thick at ambient temperature by a diamond knife, and collected on a copper grid, were observed by means of transmission electron microscopy (TEM) with a Jeol JEM100SX instrument. Before any measurement, the massive samples were subjected to a drying procedure; that is, they were stored under a primary vacuum at 80°C for at least 24 h.

## RESULTS AND DISCUSSION

In the presence of nanometer silicas, the rate of photopolymerization of the stable suspension was obviously affected during UV irradiation. Figure 1 shows that photocured time increased; that is, the photocured rate of the dispersing mixtures slowed down little by little with increasing nanosilica content. This may have resulted from the nanometer silicas' ability to absorb UV irradiation. Nanosilicas have an absorbtion ability with maximum 76% in the UV range. Some information is shown in Figure 2. The curve is the transmittance of the UV–visible light of the UV curable dispersing suspension containing nanometer silicas that contained no photoinitiator; the curve indicates that the dispersing suspension had the ability to absorb UV light. The intensity of UV irradiation that could be absorbed by a photosensitizer was reduced during photopolymerization. Therefore, the initiative effect of photoinitiators, which is thought to be an
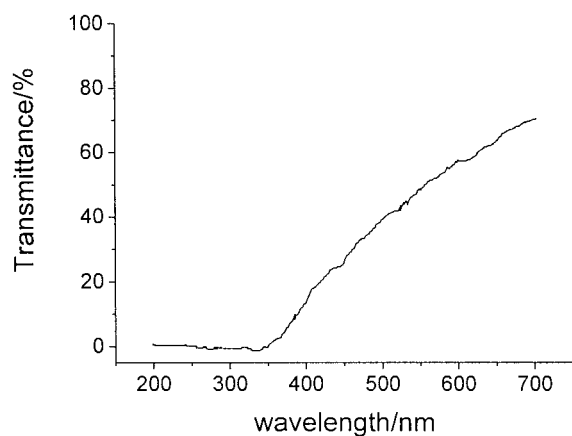
**Figure 2** UV–visible transmittance curve of the UV-curable dispersing suspension containing nanometer silicas.

ability of curable components to convert into solid materials by photosensitizers, decreased.

Figure 3 is the transmission electron micrograph of the nanocomposites. The image in Figure 3 illustrates that nanosilicas were in a homogeneous dispersion state with a narrow size distribution in photopolymerized nanocomposites. The dots in the image appear at about 10–15 nm, and they conformed with the nanosilicas that were embedded in the polymer matrix. The uniformed dispersing state of the nanometer silicas within the matrix showed well that the method dispersed the nanosilica powder into the curable solution with mechanical stirring and ultrasonic vibration is available. Certainly, the good dispersion of nanosilica powder in the organic component was more or less related to the surface treatment of the nanosilicas with chloric silicane. Meanwhile, the surface structure of the nanosilicas may have also played a role. The surface of nanometer silica particles are usually rich in OH groups because of the formation of silanol functionalities during manufacturing. The silanol groups residing on the particles form hydrogen bounds with
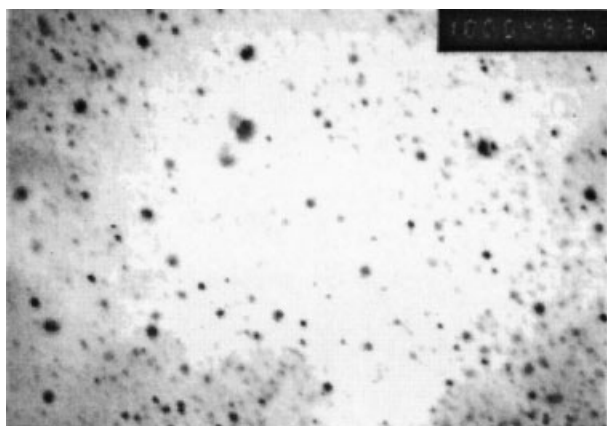


**Figure 3** Transmission electron micrograph of the nanocomposite with 3% nanosilicas.
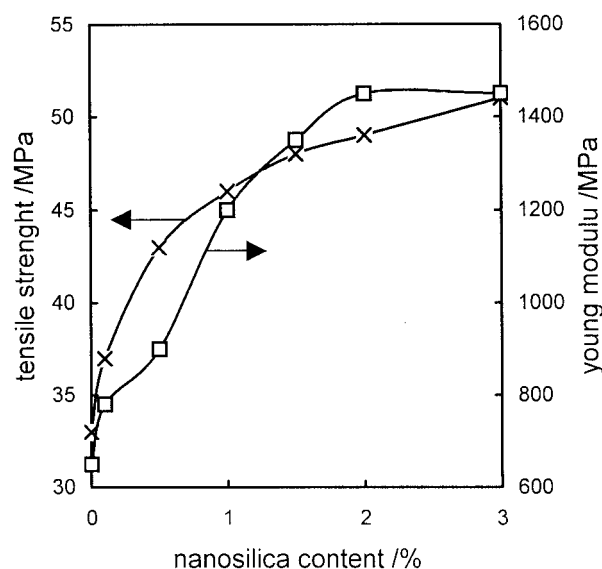


**Figure 4** Mechanical property curves of UV-cured composites with nanosilicas.

the OH groups of epoxylacrylate structure units, one of the components in the matrix, and lead to an increase in the compatibility of nanosilicas with matrix. When the sample of nanocomposites containing 5% nanometer silicas was observed with TEM, the image showed that the nanometer silicas were not in uniformed dispersing states, and there were some states of nanosilica aggregation in the matrix. This phenomenon may be related to the content of nanometer silica powder. The higher the content was, the more aggregations of nanometer silicas there were. These hydrogen bounds from the OH groups on the nanosilicas, even weak ones, hold individual silicas particles together, and the aggregates remain intact, even under the best mixing conditions, if stronger filler–polymer interactions are nonexistent.

The mechanical measurement results of the photopolymerized nanocomposite are shown in Figure 4. Evidently, the tensile strength and Young's modulus of the photocured nanocomposites increased with increasing nanometer silica by 100 and 150%, respectively, compared to the neat photocured copolymer matrix. This demonstrated that the nanosilicas played an important part in the reinforced photocured nanocomposites. However, the samples with more than 3% nanometer silicas within the nanocomposites were too brittle to measure; even the measurement data obtained possessed no regularity. So, in this article, we present nothing about samples with more than 3% nanometer silica within the nanocomposites. Curable components, namely, active comonomers and oligmers, possess a certain contractibility during the photocuring process. This phenomenon results in structural disfigurement in matrices cured by UV irradiation; therefore, the neat photocured matrix has only a
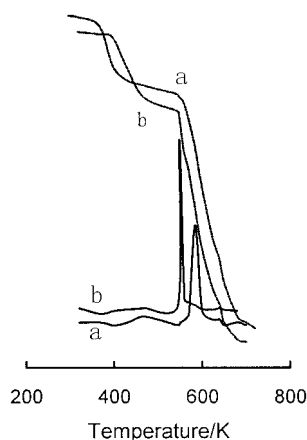
**Figure 5** Thermogravimetry and differential thermogravimetry curves of nanocomposites with silicas: (a) 0 and (b) 1 wt %.

low tensile strength. In the presence of nanometer silicas, however, the particles restrained the contractibility of copolymerizable components. Also, the particles filled in the structural disfigurement of volume constriction from copolymeric monomers and oligmers. So the nanoparticles served to boost up the mechanical properties of the matrix. To account for the observed reinforcement, we put forward some assumptions about the microconstruction of the nanocomposites: one of them is the existence of an interphase.[18] This particular interphase consisted of a matrix fraction, which exhibited vitreous properties because of its closeness to the inorganic particle surface. The elevated mechanical properties were related to the existence of the interphase. So, the nanocomposites possessed a high tensile strength with a maximum at about 50 MPa, and the tensile strength increased with increasing nanosilica content. When the contents of nanosilica in the composites reached a certain value, for example, more than 3% in the matrix, there were obvious aggregation states of the nanometer silicas within the nanocomposites. Consequently, stress localization developed due to the microstate difference of the nanofiller. This stress localization tended to break the network within the nanocomposites and resulted in decreasing mechanical properties.

The thermal stability of the silica nanocomposites is shown in Figure 5; the thermogravimetry rate denote that the rate of thermogravimetric loss of the silica nanocomposites was bigger than that of neat matrix, namely, 7.27 and 5.01 mg/min respectively. The quantity of thermogravimetric loss was 79% for neat composites and 83.4% for silica nanocomposites. The ther-

mogravimetry curves indicate that the thermal stability of the nanocomposites improved at low-temperature extent because of the swelling of nanometer silicas but decreased at elevated temperature extent—the critical temperature was about 400 K. This result suggests that the nanometer silicas possessed an effect of thermal catalysis decomposition. Naturally, the nanosilicas' effect of thermal catalysis decomposition was present not only in photocured acrylate materials but also in polyamide 6 prepared *in situ* from the condensation polymerization of caprolactam.[20]

## CONCLUSIONS

We developed a new way to deal with the challenges encountered in the preparation of inorganic–organic nanocomposites, in which the dispersion of nanometer silicas in the organic solution was realized by a combination of ultrasonic vibration and mechanical agitation and in which the synthesis of nanocomposites containing uniformly dispersed nanometer silicas was achieved by means of UV irradiation. The nanocomposites possessed higher mechanical properties at certain silica contents and good thermal properties below 400 K.

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