

# Preparation and Physical Properties of Transparent Organic–Inorganic Nanohybrid Materials Based on Urethane Dimethacrylate

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**ABSTRACT:** The aim of this study was to prepare transparent organic–inorganic nanohybrid materials with improved physical properties in comparison with the matrix polymer. Polymerizable silica nanoparticles were synthesized via the reaction of silanol groups on the surface of silica nanoparticles (particle diameter  $\approx$  12 nm) with isocyanate groups of 2-(methacryloyloxy)ethyl isocyanate (MOI) in ethyl acetate. In addition, the matrix monomer, urethane dimethacrylate, was prepared by the reaction of an MOI isocyanate group with the hydroxyl group of 2-hydroxyethyl methacrylate, and novel organic–inorganic nanohybrid materials were obtained at various silica con-

tents with bulk polymerization. The surface treatment of the silica nanoparticles and preparation of the matrix monomer were carried out in a one-pot reaction. The prepared hybrid materials retained high transparency, and the elastic modulus and surface hardness improved with increasing silica content. Moreover, the strength of the material containing 20 wt % silica was up to 30 MPa higher than that of the matrix polymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1611–1617, 2008

**Key words:** modification; nanotechnology; radical polymerization; silicas; transparency

## INTRODUCTION

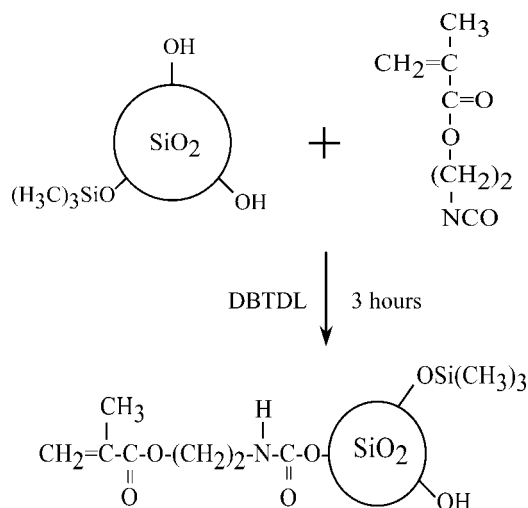
Generally, organic materials exhibit excellent flexibility, toughness, formability, and adhesiveness, but their heat-resistance properties are inferior to those of inorganic materials. In contrast, inorganic materials show a high elastic modulus, heat resistance, corrosion resistance, solvent resistance, and mechanical strength, but they are brittle, and their formability is very poor. Recently, the preparation of organic–inorganic nanohybrid materials by the combination of organic and inorganic materials at the nanoscale has been the subject of industrial and academic investigations, with the aim of creating materials with improved matrix properties.<sup>1–6</sup> The homogeneous dispersion of inorganic compounds in an organic matrix is important in the preparation of high-performance nanohybrid materials. In addition, the physical properties of hybrid materials are improved by bonding between the polymer matrix and the inorganic compounds at the interface. If we can prepare hybrid materials that satisfy these two requirements, an effect beyond the compound rule can be expected. Moreover, high-performance organic–inorganic hybrid materials possessing extra functions and properties, that is, properties not shown by the component

materials when used singly, can be developed. Some examples that have already been investigated are high-hardness materials containing silica particles,<sup>7–9</sup> high-refractive-index materials with titania,<sup>10–13</sup> clay-containing materials that show gas-barrier and fire-resistance properties,<sup>14–18</sup> and conducting materials containing carbon nanotubes.<sup>19–21</sup>

Hybrid materials prepared with silica nanoparticles have been the subject of extensive investigation. For example, the surfaces of inorganic nanofillers have been treated organically via sol–gel methods, with alkoxysilanes such as  $\gamma$ -methacryloxypropyl trimethoxysilane, to cause the dispersion of inorganic fine particles into the polymer matrix to improve adhesiveness at the organic–inorganic interface and properties such as elastic modulus and surface hardness.<sup>22–25</sup> However, the remaining silanol groups were found to exert a deleterious influence on the optical and thermal properties of the resulting organic–inorganic hybrid materials.

We developed novel transparent organic–inorganic hybrid materials with nanosized silica particles and acrylic resin.<sup>26</sup> These materials showed excellent transparency because of the homogeneous dispersion of inorganic compounds in the polymer matrix and adhesion between inorganic compounds and the polymer matrix at the interface, and the elastic modulus and surface hardness improved with increased silica content. However, the bending strength decreased as the silica content increased. The aim of this study was to prepare organic–inorganic hybrid

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**Scheme 1** Preparation scheme for the polymerizable silica nanoparticles.

materials that retained a high transparency and improved elastic modulus, surface hardness, and bending strength. The polymerizable silica nanoparticles were dispersed in a urethane dimethacrylate (MOI-HEMA) monomer, and the nanohybrid materials were prepared by copolymerization. For comparison, hybrid materials were also prepared with colloidal silica without surface treatment. The physical properties of the prepared hybrid materials were evaluated by UV-visible spectrometry, a three-point bending test, thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and volume contraction.

## EXPERIMENTAL

### Materials

Colloidal silica (particle diameter  $\approx 12$  nm, density =  $1.85$  g/cm<sup>3</sup>) dispersed in ethyl acetate (EAc-ST, silica content = 30.5 wt %) was provided by Nissan Chemical Co. (Japan) 2-(Methacryloyloxy)ethyl isocyanate (MOI) was supplied by Showa Denko K. K. (Japan). All other solvents and reagents were purchased from

Nacalai Tesuque, Inc. (Japan), and were used without further purification.

### Sample preparation

#### Preparation of the poly(urethane dimethacrylate)-polymerizable silica nanoparticles

The preparation scheme of the polymerizable silica nanoparticles is shown in Scheme 1. The composition of each sample is shown in Table I. The polymerizable silica nanoparticles were prepared by the reaction of the silanol groups of colloidal silica and the isocyanate group of MOI with di-*n*-butyltin dilaurate (DBTDL) as a catalyst. To introduce polymerizable groups to the colloidal silica surface, a given amount of MOI and DBTDL (DBTDL/MOI = 250–500 ppm) were added to EAc-ST. The reaction was carried out at room temperature for 3 h with stirring. The confirmation of the reaction was carried out by appearance of the peak of the NH group ( $1540$  cm<sup>-1</sup>) in Fourier transform infrared (FTIR) measurement. MOI-HEMA dispersed polymerizable silica nanoparticles were prepared by the addition of 2-hydroxyethyl methacrylate (HEMA) in ethyl acetate. The reaction was carried out at room temperature for 3 h with stirring. The reaction was confirmed by the peak disappearance of the —NCO group ( $2270$  cm<sup>-1</sup>) in FTIR measurement. MOI-HEMA dispersed polymerizable silica nanoparticles [MOI-HEMA/silica (treated)] were prepared by the evaporation of ethyl acetate. Copolymerization was carried out with benzoyl peroxide as the initiator at  $80^\circ\text{C}$  for 12 h, and then, the hybrid materials consisting of poly(MOI-HEMA) (PMOI-HEMA) and polymerizable silica nanoparticles were obtained. The hybrid materials were denoted as PMOI-HEMA/silica (treated).

#### Preparation of poly(urethane dimethacrylate)-colloidal silica

A given amount of EAc-ST was added to presynthesized MOI-HEMA. Colloidal silica dispersed MOI-

**TABLE I**  
Compositions of PMOI-HEMA/Silica (Treated) and PMOI-HEMA/Silica (Untreated) with Various Silica Contents

Sample code	Silica content (wt %) <sup>a</sup>	EAc-ST (g)	Silica content (g)	MOI (g)	HEMA (g)	Silica content (wt %) <sup>b</sup>
PMOI-HEMA	0	0	0	5.44	4.56	0.8
Treat-10	10	3.3	1	4.98	4.02	14.5
Treat-20	20	6.6	2	4.53	3.47	24.1
Treat-30	30	9.8	3	4.08	2.92	34.0
Sample code	Silica content (wt %) <sup>a</sup>	EAc-ST (g)	Silica content (g)	MOI-HEMA (g)		Silica content (wt %) <sup>b</sup>
Untreat-10	10	3.3	1	9.00		14.0
Untreat-20	20	6.6	2	8.00		23.5
Untreat-30	30	9.8	3	7.00		32.0

<sup>a</sup> Feed content.

<sup>b</sup> Measured content by TGA.

HEMA [MOI–HEMA/silica (untreated)] was prepared by the evaporation of ethyl acetate. MOI–HEMA/silica (untreated) was copolymerized with benzoyl peroxide as the initiator at 80°C for 12 h, and PMOI–HEMA/silica (untreated) was obtained. The composition of PMOI–HEMA/silica (untreated) is summarized in Table I.

### Analysis

The confirmation of the reactions was performed by FTIR (Nicolet model Avatar 320 spectrophotometer) (Japan) and  $^1\text{H-NMR}$  (Bruker model AVANCE 200FT NMR spectrometer) (Japan). FTIR spectra were measured in the region 4000–400  $\text{cm}^{-1}$  by the liquid film method with a Zn–Se Crystal cell and the attenuated total reflectance (ATR) method. Chemical shifts in the  $^1\text{H-NMR}$  spectra were reported as  $\delta$  values (ppm) relative to tetramethylsilane as an internal standard with acetone- $d_6$ .

Titration of the isocyanate groups was carried out to determine the amount of MOI that reacted with the silanol groups on the colloidal silica surface. An excess of MOI was used for the reaction, and di-*n*-butylamine was then added to terminate the residual NCO groups. After the reaction, unreacted di-*n*-butylamine was titrated with 0.1N aqueous HCl. Bromocresol green was used as an indicator, and the point at which the solution color changed from blue to yellow was regarded as the end point of the titration.

TGA (Seiko Instruments, Inc., model TG 30) (Japan) was carried out over the range 30–600°C with an aluminum pan under a nitrogen atmosphere at a heating rate of 10°C/min. Alumina powder was used as a reference material. Transmission electron microscopy (TEM) observation was carried out at 100 kV with a Hitachi model H-800 instrument (Japan). The investigated samples were cut down by a microtome to an 80-nm thickness. The transparency of the prepared materials was measured in the region 400–700 nm with a spectrophotometer (Jasco model V-520) (Japan). DMA of the hybrid material was carried out with a viscoelastometer (Seiko Instruments, Inc., model DMS6100) from 30 to 200°C at 1 Hz and at a heating rate of 2°C/min. The physical properties of the prepared materials were evaluated by a three-point bending test with a Tensilon mechanical tester (Orientec Co., Ltd., model RTC-1250A) (Japan). The monomer density ( $\rho_m$ ) was obtained with a pycnometer, and the polymer density ( $\rho_p$ ) was measured by the Archimedes method with a Mettler Toledo (Japan) solid density measuring instrument. The volume contraction was calculated with the following formula:

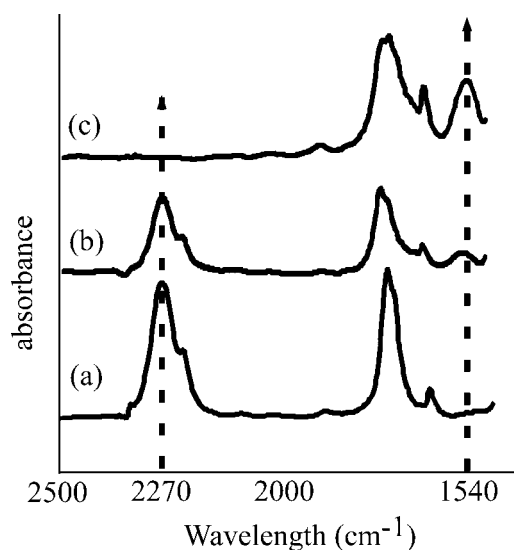
$$\text{Volume contraction (\%)} = 100 \times (1 - \rho_m/\rho_p)$$

## RESULTS AND DISCUSSION

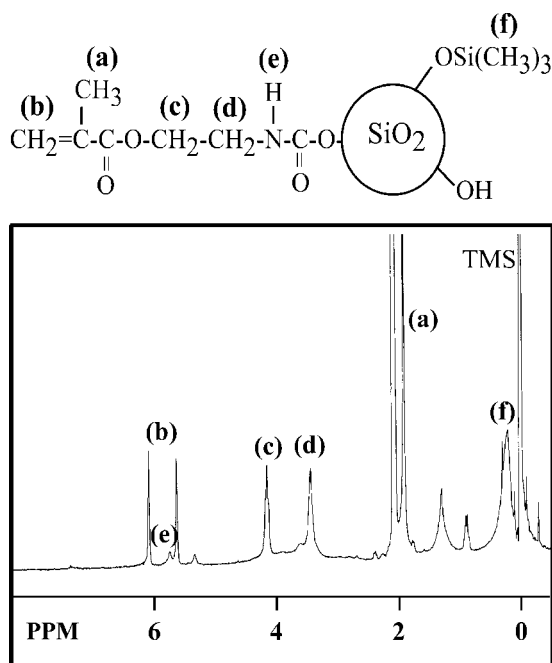
### Characterization of the polymerizable silica nanoparticles

IR spectra taken at each stage of preparation of MOI–HEMA/silica (treated) are shown in Figure 1. A comparison of Figures 1(a) and 1(b) reveals a reduction in the intensity of the  $-\text{NCO}$  peak of MOI (2270  $\text{cm}^{-1}$ ) and the appearance of an  $-\text{NH}$  peak (1540  $\text{cm}^{-1}$ ) representing the urethane bond, which confirms that a reaction occurred between MOI and colloidal silica. Furthermore, as shown in Figure 1(c), when HEMA monomers were added after the reaction between colloidal silica and MOI, the  $-\text{NCO}$  peak (2270  $\text{cm}^{-1}$ ) of the MOI unit disappeared. On the basis of these findings, the prepared material was identified as MOI–HEMA/silica (treated). The  $^1\text{H-NMR}$  spectrum of the polymerizable silica nanoparticles is shown in Figure 2. The trimethoxysilane peak of the colloidal silica surface, as well as all of the peaks of the MOI unit, were present in this spectrum, and thus, all peaks in this spectrum could be assigned to known entities. These FTIR and  $^1\text{H-NMR}$  results confirmed that polymerizable silica nanoparticles were prepared by the reaction of colloidal silica with MOI.

The titration experiments showed that the amount of MOI introduced onto the colloidal silica surface was 1.28 mmol/g of colloidal silica. With the assumption that the colloidal silica was in the form of spherical particles, the specific surface area of the particles was calculated with eq. (1) as 270  $\text{m}^2/\text{g}$ . In addition, the amount of coupled MOI units on 1  $\text{nm}^2$



**Figure 1** IR spectra at each stage of preparation of MOI–HEMA/silica (treated) in ethyl acetate: (a) before the reaction of MOI and colloidal silica, (b) after the reaction of MOI and colloidal silica, and (c) after the addition of HEMA to (b).

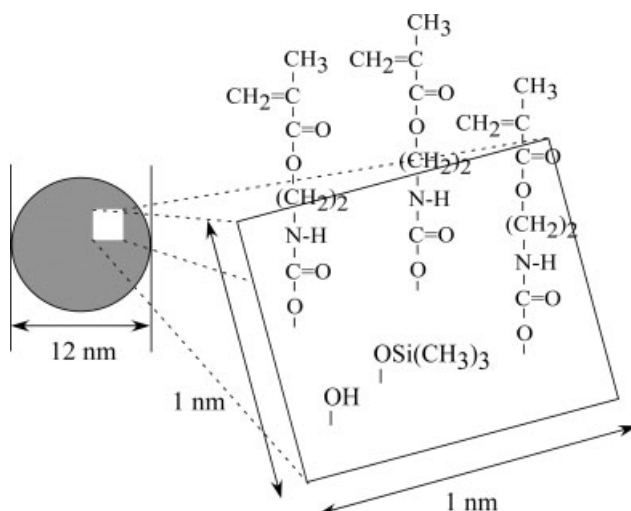


**Figure 2**  $^1\text{H-NMR}$  spectrum of polymerizable silica nanoparticles.

of particle surface calculated with eq. (2) was about 3 units/ $\text{nm}^2$ . An illustration of the polymerizable silica nanoparticles is shown in Figure 3. Moreover, when this result was converted to the number of MOI units per colloidal silica particle, it was shown that about 1400 units of MOI reacted with 1 colloidal silica particle:

$$S = 6/(D \times \rho) \quad (1)$$

$$N = (1.28 \times 10^{-3} \times R)/S \quad (2)$$



**Figure 3** Illustration of a polymerizable silica nanoparticle.

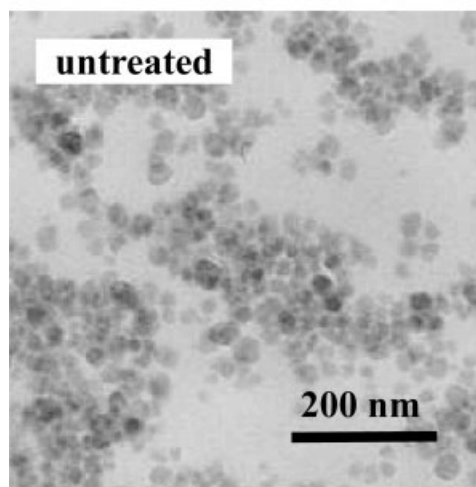
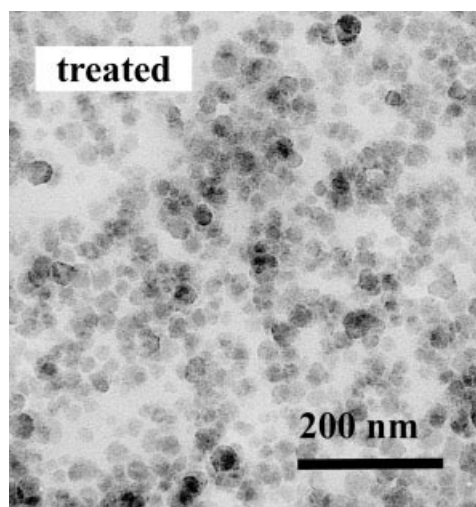
**TABLE II**  
Transmittance Values of PMOI-HEMA, PMOI-HEMA/Silica (Treated), and PMOI-HEMA/Silica (Untreated) with Various Silica Contents

Sample code	Transmittance (%)	Sample code	Transmittance (%)
PMOI-HEMA	88.9	Untreat-10	85.2
Treat-10	89.1	Untreat-20	74.3
Treat-20	89.7	Untreat-30	52.6
Treat-30	85.9		

where  $S$  is the specific surface area ( $\text{m}^2/\text{g}$ ),  $D$  is the diameter ( $\text{nm}$ ),  $\rho$  is the density ( $\text{g}/\text{cm}^3$ ),  $R$  is Avogadro's constant, and  $N$  is the number of MOI (unit/ $\text{nm}^2$ ).

#### Silica content of the prepared hybrid materials

The results of the TGA measurements of PMOI-HEMA/silica (treated) and PMOI-HEMA/silica



**Figure 4** TEM photographs of the hybrid materials containing 30 wt % silica: (top) PMOI-HEMA/silica (treated) and (bottom) PMOI-HEMA/silica (untreated).

**TABLE III**  
 $\rho_m$ 's,  $\rho_p$ 's, and Volume Contraction Rates of  
 PMOI–HEMA, PMOI–HEMA/Silica (Treated), and  
 PMOI–HEMA/Silica (Untreated)

Sample code	$\rho_m$ (g/cm <sup>3</sup> )	$\rho_p$ (g/cm <sup>3</sup> )	Volume contraction (%)
PMOI–HEMA	1.13	1.28	12.0
Treat-10	1.19	1.33	10.4
Treat-20	1.24	1.37	9.3
Treat-30	1.29	1.42	8.9
Untreat-10	1.19	1.33	10.5
Untreat-20	1.24	1.38	10.1
Untreat-30	1.29	1.42	9.0

(untreated) with various silica contents are shown in Table I. The introduction of polymerizable silica nanoparticles or colloidal silica in the PMOI–HEMA matrix in equal proportions to the previously determined compositions was confirmed from the residue weight at 600°C by TGA measurement.

### Physical properties of the prepared hybrid materials

#### Transparency

The transmittance values of the prepared hybrid materials are shown in Table II. Pure PMOI–HEMA showed a high transparency, and all types of PMOI–HEMA/silica (treated) retained a high transparency equivalent to that of pure PMOI–HEMA. However, all types of PMOI–HEMA/silica (untreated) were clouded, and the transmittance decreased with increasing silica content. From these results, we deduced that the compatibility between the PMOI–HEMA matrix and colloidal silica was low but could be improved by the introduction of MOI onto the surface of the colloidal silica.

TEM photographs of PMOI–HEMA/silica (treated) and PMOI–HEMA/silica (untreated) containing 30 wt % silica are shown in Figure 4. It was confirmed that the polymerizable silica nanoparticles were uniformly dispersed in PMOI–HEMA/silica (treated). However, there was high aggregation of colloidal silica in PMOI–HEMA/silica (untreated). From these results, we concluded that the level of dispersion of the nanosized silica particles had a significant effect on the transparency of the resulting hybrid materials

and that treatment of the silica surface with MOI is an effective method for preparing transparent hybrid materials.

#### Density and volume contraction

The  $\rho_m$ 's,  $\rho_p$ 's, and volume contraction of the prepared hybrid materials are summarized in Table III. The  $\rho_m$ 's and  $\rho_p$ 's of both PMOI–HEMA/silica (treated) and PMOI–HEMA/silica (untreated) were increased by the addition of nanosized silica particles with densities greater than that of the matrix polymer. In addition, the volume contraction values of PMOI–HEMA/silica (treated) and PMOI–HEMA/silica (untreated) were found to decrease with increasing silica content. The volume contraction of PMOI–HEMA/silica (treated) was smaller than that of PMOI–HEMA/silica (untreated) because the MOI units introduced to the silica nanoparticle surface acted as crosslinking agents. Overall, the prepared PMOI–HEMA/silica (treated) showed excellent dimensional stability.

#### Thermal properties

The storage modulus ( $E'$ ) values of PMOI–HEMA/silica (treated) and PMOI–HEMA/silica (untreated) at 35°C are summarized in Table IV. These values were found to increase with increasing silica content; thus, it was confirmed that the molecular mobility of PMOI–HEMA was suppressed by the addition of silica nanoparticles. To investigate these facts in detail, the interparticle distance of the silica nanoparticles was calculated from the volume percentage with eq. (3),<sup>27</sup> and the results are shown in Table V:

$$d = [(4\pi \times 2^{1/2}) / (3 \times V^{1/3})] - 2 \times r \quad (3)$$

where  $d$  is the interparticle distance (nm),  $V$  is the volume fraction of the silica particles, and  $r$  is the radius (nm).

The interparticle distance was found to decrease with increasing silica content, and the mobility of the PMOI–HEMA matrix seemed to be suppressed. This result was in agreement with those obtained by DMA measurement. Moreover, when PMOI–HEMA/silica (treated) was compared with PMOI–HEMA/

**TABLE IV**  
 $E'$  Values at 35°C and 5 wt % Loss Temperatures of the Prepared Hybrid Materials

Sample code	$E'$ (GPa)	Temperature (°C)	Sample code	$E'$ (GPa)	Temperature (°C)
PMOI–HEMA	2.08	281			
Treat-10	2.69	283	Untreat-10	2.49	277
Treat-20	3.65	283	Untreat-20	2.90	277
Treat-30	7.31	265	Untreat-30	4.93	264

silica (untreated) containing equal quantities of silica, the  $E'$  values for PMOI-HEMA/silica (treated) were higher than those of PMOI-HEMA/silica (untreated). In addition, a distinct  $\tan \delta$  peak was not observed from 30 to 200°C in any of the prepared samples. We concluded that PMOI-HEMA and the silica nanoparticles bonded covalently via the MOI units, and the molecular mobility seemed to be suppressed to a greater extent than when the untreated silica nanoparticles were used.

The 5% weight loss temperatures of the prepared hybrid materials, evaluated by TGA measurement, are shown in Table IV. The 5% weight loss temperatures of PMOI-HEMA/silica (treated) and PMOI-HEMA/silica (untreated) were roughly equivalent to that of PMOI-HEMA up to 20 wt % silica. However, the 5% weight loss temperatures of both the treated and untreated materials fell by about 20°C at a silica content of 30 wt %. This was probably due to the formation of low-molecular-weight fragments in the PMOI-HEMA matrix during bulk polymerization in the presence of excess silica nanoparticles.

### Mechanical properties

The elastic modulus, strength, and deflection of the prepared hybrid materials obtained from the three-point bending test are summarized in Table VI. The elastic moduli of both PMOI-HEMA/silica (treated) and PMOI-HEMA/silica (untreated) were found to increase with increasing silica content, probably because of the inhibition of molecular mobility in the polymer matrix. Moreover, as the MOI units introduced onto the silica surface acted as a crosslinking agent, PMOI-HEMA/silica (treated) was harder than PMOI-HEMA/silica (untreated). The strength of PMOI-HEMA/silica (treated) improved with increasing silica content up to 20 wt % silica but decreased at 30 wt %, whereas the strength of PMOI-HEMA/silica (untreated) decreased with increasing silica content. The decrease in the strength of PMOI-HEMA/silica (untreated) was probably caused by aggregation of the silica nanoparticles, whereas the reasons for the improvement in strength of PMOI-HEMA/silica (treated) up to 20 wt % silica were the homogeneous dispersion of the silica nanoparticles in the matrix and the interaction between colloidal silica and urethane bonds in the matrix polymer. The decrease in strength of PMOI-HEMA/

**TABLE V**  
Interparticle Distance of the Dispersed Silica

Sample code	Particle distance (nm)
Treat-10	23.4
Treat-20	14.1
Treat-30	9.5

**TABLE VI**  
Mechanical Properties of PMOI-HEMA, PMOI-HEMA/Silica (Treated), and PMOI-HEMA/Silica (Untreated) with Various Silica Contents

Sample code	Deflection (mm)	Strength (MPa)	Elastic modulus (GPa)
PMOI-HEMA	3.3	149	4.0
Treat-10	3.9	166	4.2
Treat-20	3.3	167	4.8
Treat-30	2.3	121	5.9
Untreat-10	2.6	138	4.2
Untreat-20	2.2	124	4.7
Untreat-30	1.0	84	5.6

silica (treated) at 30 wt % silica was probably caused by embrittlement.

### CONCLUSIONS

Transparent nanohybrid materials, PMOI-HEMA/silica (treated), were prepared colloidal silica treated with MOI units, whereas PMOI-HEMA/silica (untreated) was an opaque material. The dispersion of colloidal silica was improved by the treatment of the colloidal silica, and the colloidal silica was a homogeneous dispersion in the PMOI-HEMA matrix. Comparisons of dimensional stability, heat resistance, and mechanical properties of PMOI-HEMA/silica (treated) and PMOI-HEMA/silica (untreated) revealed that all of the physical properties of PMOI-HEMA/silica (treated) were superior to those of PMOI-HEMA/silica (untreated). These results seemed to be the effect that controlled the interface between colloidal silica and the matrix polymer. In particular, the strength of PMOI-HEMA/silica (treated) materials containing up to 20 wt % silica were improved. Because the interaction between colloidal silica and the matrix polymer was generated by the introduction of urethane bonds into the matrix polymer, the strength of PMOI-HEMA/silica (treated) was improved by the addition of silica particles. We concluded that surface treatment of colloidal silica with MOI units is a very useful method for the preparation of superior organic-inorganic hybrid materials.

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