# Organic–Inorganic Microhybrid Materials via a Novel Emulsion Mixing Method

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ABSTRACT: Water-dispersible urethane acrylate anionomers (UAAs) were prepared using anionic dimethylol propionic acid and silica emulsion was prepared by a sol-gel process using poly(vinyl pyrrolidone) and tetraethoxysilane. The above two emulsions were mixed, and UAA/silica composite gels were prepared. FTIR, X-ray diffraction, SEM, and AFM were used to verify the structure and the inclusion of silica in the composite gels. To investigate the influence of silica in UAA gels on the physical properties, the tensile strength and elongation at break were measured, and the annealing effect was evaluated by the physical properties. As the silica content increased, the tensile strength of the composite gels increased; however, up to a certain amount of silica, phase separation was induced and physical properties were reduced. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1597–1605, 1999

Key words: urethane acrylate anionomer; hydrogel; sol-gel process; hybrid; polar cluster

### INTRODUCTION

Recently, the modification of water-soluble or water-dispersible polymers with hydrophobic moieties was widely reported. These polymers play an important role in biomedical, pharmaceutical, and membrane applications. Hydrophobically modified hydrogels show a heterophasic structure in aqueous media. This structure has received the main focus because of its potentially important and fundamentally interesting properties.<sup>1-3</sup> Generally, polyurethane hydrogels are prepared using an interpenetrating network of polyurethane which has hydrophilic moieties and diacrylates.<sup>4–7</sup> In our previous studies,<sup>8</sup> an urethane acrylate anionomer (UAA) was synthesized and applied to hydrogels. A UAA oligomer has both hydrophilic and hydrophobic segments at the same molecule, so this resin could be emulsified without any external surfactant. In the process of emulsification, hydrophilic and hydrophobic moieties are aggregated with each other, and in the gelation process, the separated structure is maintained, that is, ionic domains (polar clusters) are formed in the UAA hydrogel matrix. Polar clusters in the UAA hydrogel are worked as a reservoir of hydrophilic solvents and it is possible to modify the hydrogel using various methods.

In this study, UAA emulsion and colloidal silica emulsion were used to prepare the polyUAA/ silica hybrid composite hydrogels using the phase-inversion emulsion polymerization method.<sup>9,10</sup> In the case of UAA emulsion, hydrophilic micropores are formed during gelation, so the silica component can be incorporated with interaction between the polar clusters and the silica components. To investigate the inclusion of silica in composite gels and the effect of the silica component on the physical properties, various measurements were executed.

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UAA	TDI	PTMG	DMPA	HEMA	TEA
Type	(mol)	(mol)	(mol)	(mol)	(mol)
UAA55 UAA46 UAA37	$0.15 \\ 0.15 \\ 0.15$	$0.05 \\ 0.04 \\ 0.03$	$0.05 \\ 0.06 \\ 0.07$	$0.15 \\ 0.15 \\ 0.15$	$0.1 \\ 0.12 \\ 0.14$

Table I Recipe of UAAs

### **EXPERIMENTAL**

# **Materials**

In the synthesis of UAA, poly(tetramethylene glycol) (PTMG,  $M_w = 1000$ , Hyosung BASF, Korea) was dried and degassed at 60°C under a vacuum. 2,4-Toluene diisocyanate (TDI, Junsei Chemical Co., Japan) was purified by filtration. 2-Hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co., USA) and dimethylol propionic acid (DMPA, Aldrich) were used without further purification. Triethylamine (TEA, Junsei) was used for the neutralization of UAA, and *n*-methyl-2-pyrrolidone (NMP, Lancaster Synthesis, England) was used as a solvent. Potassium persulfate (KPS, Shinyo Pure Chemicals, Japan) was used as an initiator for gelation. In the preparation of the silica emulsion, tetraethoxysilane (TEOS, 95%, Aldrich) and ammonia water (NH<sub>4</sub>OH, 28%, Junsei), ethanol (Lancaster Synthesis, England), and



Scheme 1 The schematic representation of urethane acrylate (UAA) synthesis.

Sample	UAA (10 g)	Silica Emulsion	Water	KPS
USG-1	UAA55	0 g	15 g	0.1 g
USG-2	UAA55	1 g	14 g	0.1 g
USG-3	UAA55	3 g	12 g	0.1 g
USG-4	UAA55	5 g	10 g	0.1 g
USG-5	UAA46	0 g	15 g	0.1 g
USG-6	UAA46	1 g	14 g	0.1 g
USG-7	UAA46	3 g	12 g	0.1 g
USG-8	UAA46	5 g	10 g	0.1 g
USG-9	UAA37	0 g	15 g	0.1 g
USG-10	UAA37	1 g	14 g	0.1 g
USG-11	UAA37	3 g	12 g	0.1 g
USG-12	UAA37	5 g	10 g	0.1 g

 Table II
 Recipe of UAA/Silica Composite Gels

poly(vinyl pyrrolidone) (PVP,  $M_w = 40,000$ , Sigma, USA) were used without further purification.

# Synthesis of UAA<sup>8</sup>

UAAs were synthesized through four-step processes. PTMG and DMPA as a hydroxyl group and NMP as a solvent were charged into a 500-mL four-necked kettle with a reflux condenser, a thermometer, a mechanical stirrer, and an inlet system for N<sub>2</sub> gas. NMP was used as the solvent of DMPA and the agent for reducing the viscosity of the final produced resin. A large amount of NMP is favorable in respect to the dissolution aspect. However, NMP is worked as impurities to the final product, so the amount of NMP used was determined as 18% of the total weight of the final produced resins. This mixture was heated to 50°C slowly with  $N_2$  purging and stirring until DMPA was dissolved completely. Then, TDI was dropped into the reactor so that the isocyanate group of TDI reacts with the hydroxy group of PTMG and DMPA. Then, the mixture was stirred and reacted at 70°C for 5 h. The reaction was allowed to proceed until the theoretical isocyanate content reached one-half of the original isocyanate content as determined by the di-*n*-butylamine back titration<sup>11</sup> method. In this method, a NCO-terminated prepolymer could be prepared. Then, HEMA was dropped into the reactor for the introduction of the vinyl group. The mixture was then heated to 70°C slowly with stirring and reacted for 4 h. The end point of the reaction was confirmed by the disappearance of the IR absorption peak at  $2270 \text{ cm}^{-1}$ , corresponding to the stretching vibration of the NCO group. For neutralizing the resin, TEA was added at room temperature while stirring for 30 min. Because excess moles of TEA were needed to neutralize the DMPA completely, twice as much TEA was used to moles of DMPA. The molar ratio of the reagents in the synthesis of UAAs is illustrated in Table I and the schematic representation is shown in Scheme 1.

# Preparation of UAA/Silica Hybrid Composite Hydrogels

Silica emulsion was prepared by a sol-gel process<sup>12</sup> of TEOS. An aqueous solution was prepared by mixing water, 1 wt % of ammonia water, and 5 wt % of PVP. PVP was used as a stabilizer for the silica particles. After the solution was clearly mixed, 10 wt % of TEOS was poured into the mixture and reacted for 2 h at room temperature under a nitrogen environment. After TEOS was poured, the solution became turbid. However, as the reaction proceeded, the solution became clear and relatively transparent 2 h later. In this process, a silica emulsion could be obtained.

For the preparation of UAA/silica composite gels, firstly, UAA/silica emulsions were prepared by a phase-inversion emulsification method of a UAA/silica emulsion mixture. Ten grams of UAA and x g of the silica emulsion were mixed homogeneously and then (15 - x) g of water was dropped slowly into the mixture with vigorous stirring. Then, KPS was added and dissolved completely for the gelation process. The emulsion was poured into the flame  $(12 \text{ cm} \times 8 \text{ cm} \times 2 \text{ mm})$  and reacted at 60°C for 2 h. In this method, waterswollen composite hydrogels were obtained and then washed with water and acetone several times and dried at 35°C for 2 days. Washing with acetone required removing the stabilizer in the composite gels and drying at a low temperature to minimize the shrinkage of the resulting gels. The recipe for the composite gels is shown in Table II.

The amount of the silica emulsion was limited to 5 g because of the high viscosity of the emulsion. As the amount of the silica emulsion increased, the viscosity of the emulsion also increased, and up to 5 g of silica emulsion, it was impossible to prepare the homogeneous samples for test because of the high viscosity. Generally, in the case of hybridization by the sol-gel process, the acidic condition is more favorable than is the basic condition because of the shapes of the silica



Scheme 2 The schematic representation for the formation of the composite gels.

compounds formed through the sol-gel process. However, in this study, the emulsion could not be obtained at the acid state, so only ammonia water was used to adjust the pH.

#### Measurements

To verify the precipitation of silica in the UAA hydrogels, attenuated total reflectance (ATR, Nicolet Model 5-DX) in IR radiation was measured. Wide-angle X-ray diffraction (WAXD) patterns were measured with a Rigaku Denky Model RAD-C diffractometer using CuK $\alpha$  radiation and at 3°/min. Thermogravimetric analyses (TGA, Perkin–Elmer TGA-7) were used to measure the amount of silica in the composite gels as an indi-

rect method with a 10°C/min heating rate. The physical properties of the composite gels were measured with a HOUNDSFIELD Model Instron at room temperature using a crosshead speed of 5 mm/ min and a load cell capacity of 500 kgf. The morphology was investigated by scanning electron microscopy (SEM, Hitachi Model) and atomic force microscopy (AFM, Autoprobe Electronics module Model No. APEM-1000). We used commercially available tips of silicon nitride and the cantilevers of silicon nitride covered with gold on the back for the laser-beam reflection. The surface topography was scanned by monitoring the cantilever deflection which is obtained from the angle deflection of a laser beam falling on the top of the cantilever.

Silica particle



**Figure 1** Comparison of UAA and UAA/silica gels using ATR: (a) USG-1; (b) USG-4.



Figure 2 WAXD patterns with the amount of silica emulsion: (a) USG-9; (b) USG-11; (c) USG-12.



**Figure 3** TGA thermograms of UAA and UAA/silica composite gels: (—) USG-9; (····) USG-11; (-···) USG-12.

# **RESULTS AND DISCUSSION**

In our previous studies,8 UAA was synthesized and applied to hydrogels. UAA can be emulsifiable without adding surfactants, so it is applied in the field of coatings, paints, and hydrogels, etc. In the case of the soap-free emulsion of UAA that is polymerized with KPS, as the temperature of the medium increases, the emulsion formed by the microphase separation between hydrophobic and hydrophilic segments was aggregated and broken at the same time, that is, initiator radicals penetrate into the emulsion droplets and gelation proceeds as soon as the droplets are aggregated with each other. Thus, UAA gel that maintains the microphase separation between the hydrophilic and hydrophobic segments can be formed. On the other hand, silica particles made by the sol-gel process have surface hydrophilic hydroxyl groups.

Table III Amount of Silica in Composites Using TGA

	Calculated (%)	Measured (%)	
USG-11	2.49	2.49	
USG-13	4.01	3.95	

Char yield of USG-9 that is UAA was 9.07% at 500°C.



**Figure 4** Physical properties of the composite gels: (a) tensile strength; (b) elongation at break; (■) UAA55 series; (●) UAA46 series; (▲) UAA37 series.

So, it is expected that silica components can be precipitated in the hydrophilic microdomain of UAA gels, because microdomains in UAA gels have clusters of carboxyl groups. Surface hydroxyl groups of silica are interacted by the hydrogen bond and/or ester linkage; therefore, properties of the composite gels are enhanced. The schematic representation for the above gelation procedure is shown in Scheme 2.

ATR of IR radiation was measured to verify the inclusion of silica in the composite gels. Figure 1

shows IR subtraction spectra for the UAA gel and the composite gel. Two peaks are shown for distinguishing UAA from the composite gel. The absorbance of the Si—O—Si asymmetric stretching vibration peaks appeared around  $1100 \text{ cm}^{-1}$ . This band originally appears as a doublet; however, peaks of UAA appear as a similar wavenumber, so the doublet peak is not discernible. Around 500 cm<sup>-1</sup>, a Si—O—Si bending peak is also shown.<sup>1</sup> The inclusion of silica is confirmed by two characteristic peaks.

The crystallinity of UAA and the UAA/silica hybrid composite gels was investigated by a WAXD pattern, and the results are illustrated in Figure 2. The characteristic peaks of UAA gel are shown at  $2\theta = 23^{\circ}$  and  $28^{\circ}$ . In the hybrid composite, as the amount of silica content increased, the intensity of the peaks decreased. These reults explain that the hybridization of UAA affects the crystallization of UAA in the course of gelation. The surface hydroxyl groups of polar clusters in the UAA gels. So, the crystallization of polar clusters is inhibited by the hydrogen bond between the carboxyl groups and the hydroxy groups.<sup>13</sup>

By the above two measurements, it was verified that silica was precipitated in the composite gels. TGA was used to measure the quantitative



**Figure 5** Tensile strength of composite gels after annealing: ( $\blacksquare$ ) UAA55 series; ( $\bullet$ ) UAA46 series; ( $\blacktriangle$ ) UAA37 series.



**Figure 6** Morphologies of UAA and UAA/silica composite gels by SEM: (a) USG-9; (b) USG-11; (c) USG-12.

analysis of the amount of silica in the UAA composite gels. Because UAA gels are completely decomposed around 450°C whereas silica is not decomposed at all, the composite gels are heated to above 500°C. The amount of silica in the UAA composite gels could be decided relatively. The TGA thermograms for three unfilled and microcomposite hydrogels are displayed in Figure 3.

It is clear that incorporation of silica does not profoundly affect the onset of the thermal decomposition of UAA gels. However, as the amount of silica increased, the char yield of the composites also increased. The results are shown in Table III.

TGA thermograms show a transition temperature around 300°C. This transition point is due to the remaining water, ethanol, and TEOS, which are formed by a residual reaction at high temperature and are unreacted. The physical properties of the composite gels were executed, and the results are illustrated in Figure 4.

As the amount of silica increased, the tensile strength increased, whereas elongation at break decreased. These results show that the hydroxy groups of silica are interacted with the carboxyl groups by the hydrogen bond and/or ester bond. Physical or chemical interaction makes composite gels denser, so physical properties are elevated. To investigate the effect of physical properties due to annealing,<sup>14</sup> the composite gels were annealed for 4 weeks at 80°C, and the tensile strength was measured (Fig. 5).

After annealing, unreacted TEOS in the composite gels is reacted further and the surface hydroxyl groups condense more, so the physical properties were enhanced more or less. However, in the case of USG-4, USG-8, and USG-12, the tensile strength decreased because of phase separation between silica and the UAA gels. These results could be verified by the morphology of the composite gels.

The morphology of composite gels was investigated by SEM and AFM. SEM images are shown in Figure 6. USG-9, an unfilled UAA gel, is shown with a rough fracture surface because of the rubbery character of the UAA gels. However, USG-11 and USG-12 are dense relative to USG-9. The morphology of USG-11 is relatively homogeneous and dense. However, in the case of USG-12, silica domains are formed and phase separation occurred. Phase separation is due to decreasing of the physical properties of the composite gels.

The surface morphology of the gels was also investigated by AFM and the resulting images are shown in Figure 7. Three-dimensional images of the surface in AFM can be produced with a subnanometer resolution. In particular, quantitative determinations of surface-roughness parameters and of their distribution are obtained. In our studies, AFM was measured with the tip in contact with the sample surface (contact mode), and short-range repulsive forces were probed. In the case of USG-9, the surface is smooth. In the case of USG-10, however, silica domains roughen the surface.



**Figure 7** Surface morphology of UAA/silica composite gels by AFM (contact mode): (a) USG-9; (b) USG-10.

# **CONCLUSIONS**

UAA/silica composite gels were prepared by using an emulsion-mixing method. Structural analysis was executed through ATR measurement and verified the inclusion of silica in the composite gels. WAXD was measured to investigate the site where silica is precipitated. In these results, silica is precipitated in polar clusters of the UAA gels. As the silica content increases, the tensile strength of the composite gels also increases. However, up to a certain amount of silica, phase separation was induced and physical properties are reduced. Annealing of the composite gels caused the further reaction and this is a factor to increase the physical properties. These phenomena were verified by the morphology using SEM and AFM measurements.

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