

In Situ Polyurethane/Silica Composite Formation Via a Sol-Gel Process

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ABSTRACT: Polyurethane acrylate anionomer (PUAA)/silica composite gels were prepared by the sol-gel reaction of tetraethoxysilane (TEOS) and methacryloxypropyl trimethoxysilane (MPTS) incorporated to PUAA gels by using a swelling method. The formation and structure of composites were confirmed by FTIR, X-ray diffraction, and SEM. As a result, we found that silica components in composites are located within the ionic domains of their gels and interacted with PUAA via hydrogen bonding. This drastically enhanced the mechanical properties of the composites. Mechanical properties are also improved by MPTS, because MPTS improves the dispersibility and adhesion of silica components in PUAA/silica composite gels. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2327–2334, 2002

Key words: polyurethane acrylate anionomer (PUAA); sol-gel process; swelling; ionic cluster; silica

INTRODUCTION

In recent years, there have been intensive studies on the production of composite materials having microstructure in the fields of metals, ceramics, and polymers. Organic polymer-inorganic silica (or titanium oxide) composites especially have been widely investigated for improving physical properties and application.^{1–5} Inorganic silica is brittle but shows a number of beneficial properties such as surface hardness, transparency, high physical properties, and heat resistance. In contrast, organic polymers show good flexibility and low density but are thermally unstable. Therefore, considering the synergistic effect of two different materials, microhybrid techniques via sol-gel process have been proposed. The methods are

summarized as follows: (1) organic liquids, precursors of polymer precipitated in the porous metal oxide matrix are cured with heat or light, etc.⁶; (2) sol-gel liquids mixed with organic monomers are polymerized, and then solvent evaporation is executed successively^{7,8}; (3) the mixture of polymer and silicon alkoxide is hydrolyzed, and cocondensation is carried out.^{9–11} For example, Mauritz et al.^{1,12,13} reported that perfluorosulfonic acid ionomer/silica composites were prepared by an *in situ* sol-gel reaction by using a diffusion-controlled swelling approach.

In our previous studies,^{14,15} we found that hydrogels prepared by the phase-inversion polymerization of urethane acrylate anionomer (UAA) emulsions showed a microphase-separated structure. In the course of phase-inversion polymerization, the microphase separation between hydrophilic and hydrophobic segments occurs. This happens because the UAA emulsion droplets were aggregated and polymerized at the same time. As a result, the ionic domains could be maximized in polyurethane acrylate anionomer (PUAA) gels.

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In this study, water-dispersible UAAs were synthesized and polymerized to obtain microphase-separated hydrogels. By using this hydrogel, the composite gel was prepared by swelling and *in situ* sol-gel processes. Silica components incorporated in PUAA/silica composites were confirmed by FTIR, X-ray diffraction (XRD), viscosity measurements, and SEM. Finally, the influence of silica and coupling agent, methacryloxypropyl trimethoxysilane (MPTS), on physical properties was also investigated.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol) (PTMG, $M_w = 1000$, Hyosung BASF, Korea) was dried and degassed at 60°C under vacuum. 2,4-Toluene diisocyanate (TDI, Junsei Chemical, Japan), 2-hydroxyethyl-methacrylate (HEMA, Aldrich Chemicals), dimethylol propionic acid (DMPA, Aldrich Chemicals), triethylamine (TEA, Junsei Chemical), and *n*-methyl-2-pyrrolidone (NMP, Lancaster Synthesis, U.K.) were used without further purification. Potassium persulfate (KPS, Shinyo Chemicals, Japan) and azobisisobutyronitrile (AIBN, Junsei Chemical) were used after recrystallization. For the sol-gel process, tetraethoxysilane (TEOS, 98%, Aldrich Chemicals), MPTS (Aldrich Chemicals), hydrochloric acid (HCl, Junsei Chemical), and ethanol (99%, Lancaster Synthesis) were used.

Synthesis of UAA

UAA^{16,17} was synthesized by a four-step process. PTMG, DMPA, and NMP were charged into the reactor equipped with a reflux condenser, a thermometer, a mechanical stirrer, and an N₂ inlet system and dissolved homogeneously at the appropriate temperature. The mixture was reacted with TDI at 70°C for 5 h to synthesize the NCO-terminated prepolymer. The reaction condition was determined by the di-n-butylamine back-titration method.¹⁸ Then, HEMA was added and reacted at 70°C for about 4 h. The reaction was continued until disappearance of the IR absorption at 2270 cm⁻¹, corresponding to the stretching vibration of the NCO group. For neutralizing UAA, TEA was added at ambient temperature while stirring for 30 min. The recipes for synthesis and structure for UAA are illustrated in Table I and Scheme 1, respectively.

Table I The Recipe for Urethane Acrylate Anionomers (UAAs) Synthesis

	TDI (mol)	PTMG (mol)	DMPA (mol)	HEMA (mol)	TEA (mol)
UAA55 ^a	0.15	0.05	0.05	0.15	0.1
UAA46	0.15	0.04	0.06	0.15	0.12
UAA37	0.15	0.03	0.07	0.15	0.14

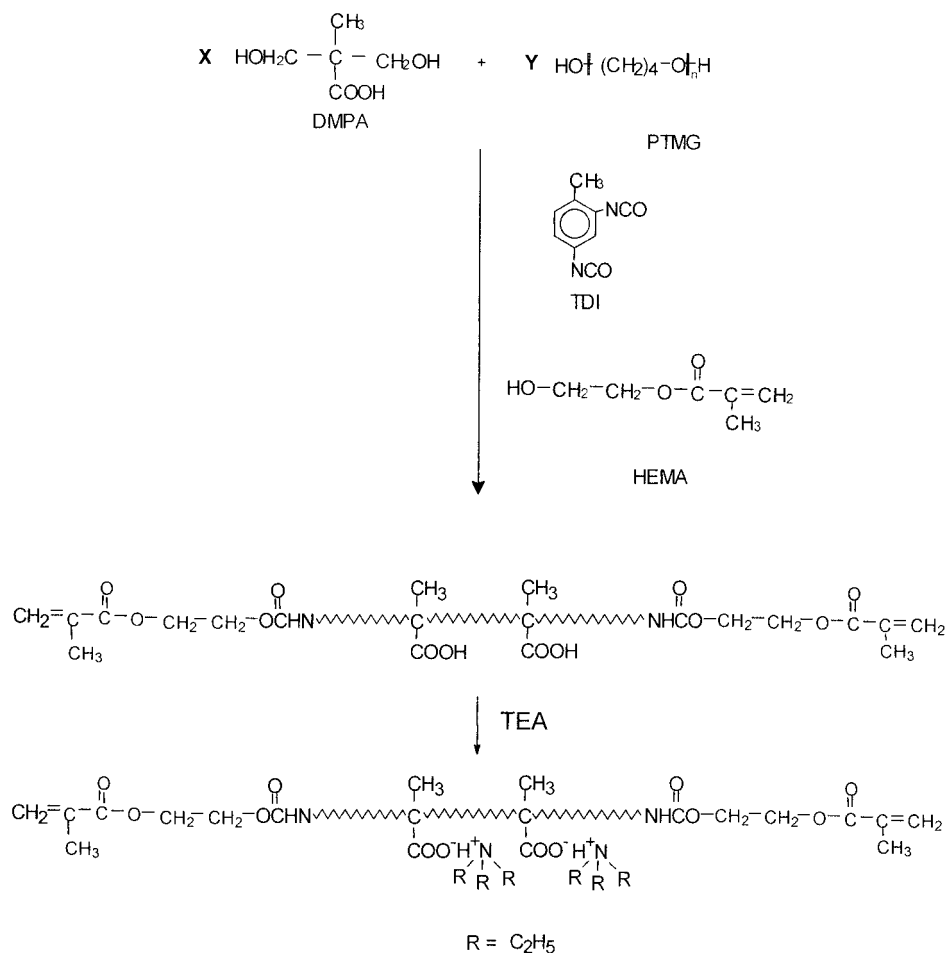
^a UAA_{*x*y}:*x* and *y* mean the molar ratio of PTMG to DMPA.

Preparation of PUAA/Silica Composite Gels

To produce the PUAA gel, a soap-free UAA emulsion containing water-soluble initiator was polymerized by the phase-inversion method.^{16,17} The solid content of UAA emulsion was fixed at 40 wt %. The emulsion was poured into the frame (12 cm × 8 cm × 2 mm) and sealed to prevent the evaporation of water. Polymerization was carried out at 60°C for 2 h. PUAA gel was recovered by washing with water and acetone repeatedly and finally drying at room temperature for 2 days. To prepare the PUAA/silica composite gel, PUAA gel, hydrated with ethanol, water, and small amount of HCl solution mixture, was placed into TEOS, MPTS, ethanol, and AIBN solution mixture, and then an *in situ* sol-gel process was carried out at 30°C for 2 h.¹⁹ Polymerization was executed at 80°C for 1 day to react the residual double bonds of MPTS completely. PUAA/silica composite gels were obtained after washing with acetone several times and drying. A standard recipe is summarized in Table II.

Measurements

To confirm that the silica component was incorporated into the PUAA composites qualitatively, attenuated total reflectance (ATR, Nicolet model 5-DX) and wide-angle x-ray diffraction (WAXD, Rigaku Denky model RAD-C) were measured. Thermogravimetric analysis (TGA, Perkin-Elmer TGA-7) was measured at 10°C/min heating rate for quantitative analysis. The interaction between polar clusters in UAA and silica components was confirmed by observation of the viscosity change with time by using a rheometer (ARES, Rheometrics). Mechanical properties of composite gels were measured with a Hounsfield model Instron at room temperature by using a crosshead speed of 5 mm/min and load cell capacity of 500 kgf. The morphology of the composites



Scheme 1 Schematic representation of UAA synthesis.

was observed with a scanning electron microscopy (SEM, Hitachi).

Table II The Recipe for PUAA/Silica Composite Gel Preparation

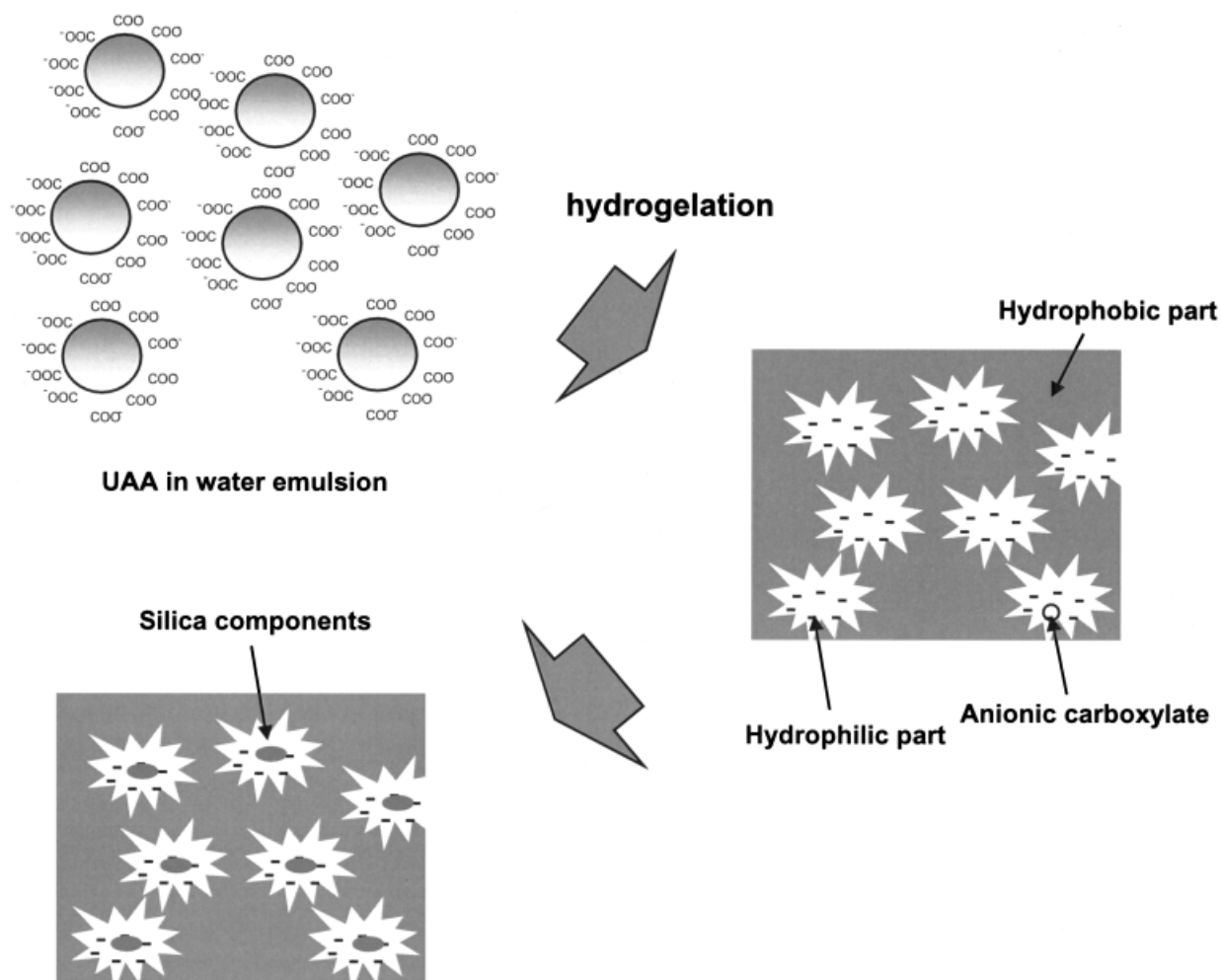
Sample	PUAA (10 g)	TEOS (g)	MPTS (g)	KPS (g)
USI-1	PUAA55 ^a	10	0	0.1
USI-2	PUAA55	9	1	0.1
USI-3	PUAA55	7	3	0.1
USI-4	PUAA55	5	5	0.1
USI-5	PUAA46	10	0	0.1
USI-6	PUAA46	9	1	0.1
USI-7	PUAA46	7	3	0.1
USI-8	PUAA46	5	5	0.1
USI-9	PUAA37	10	0	0.1
USI-10	PUAA37	9	1	0.1
USI-11	PUAA37	7	3	0.1
USI-12	PUAA37	5	5	0.1

^a PUAA_xy is hydrogel made using UAA_xy.

RESULTS AND DISCUSSION

When the UAA emulsion is polymerized¹⁴⁻¹⁶ by using the water-soluble initiator, KPS, the emulsions were aggregated by the penetration of initiator radicals into the emulsion droplets and polymerized at the same time.^{14,15} As a result, microphase-separated PUAA gels were formed. In this procedure, silica components having hydrophilic hydroxyl groups on its surface are expected to be precipitated into hydrophilic microdomains²⁰⁻²² of PUAA gels. The schematic representation of PUAA/silica composite formation is illustrated in Scheme 2.

Figure 1 shows the swelling behaviors of PUAA gels in water, ethanol, and HCl solution mixture.



Scheme 2 The schematic representation of composite gel formation.

All PUAAs gels reached an equilibrium state within 2 h and when the swelling ratio was below 30%. Generally, the anionic gels showed a low swelling ratio at the acidic conditions, whereas a high swelling ratio occurred under the basic condition.^{23,24} After equilibrium hydration, the swollen gels were placed into the sol-gel precursor solution and an *in situ* sol-gel process was carried out. Swollen TEOS and MPTS in hydrophilic domain were hydrolyzed by preswollen water. Consequently, the incorporated amount of silica is expected to be low in our system because of the low swelling ratio (Fig. 1). Generally, in the case of acidic condition used in the sol-gel process, highly branched or less crosslinked silica components could be obtained. This extends the contact area between silica and PUAAs. It is predicted that a large contact area grants more interaction force between PUAAs and silica components. By

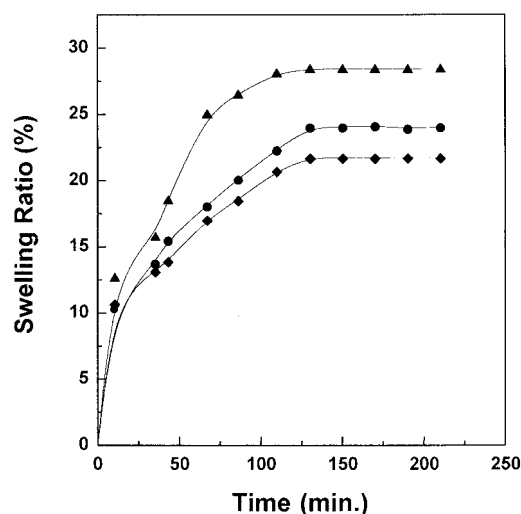


Figure 1 Swelling ratio of PUAAs gels in water, ethanol, and HCl mixture: (—♦—) UAA55; (—●—) UAA46; (—▲—) UAA37.

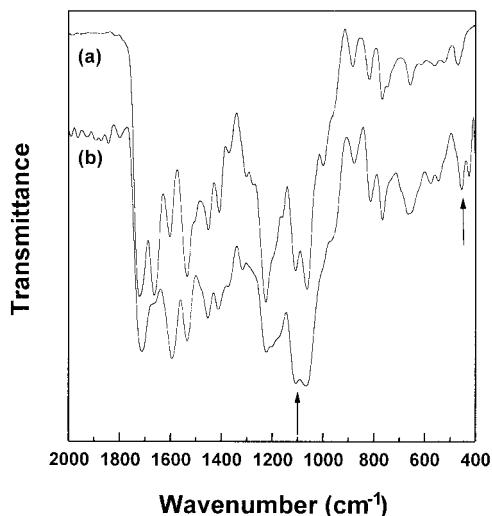


Figure 2 Comparison of PUA and PUA/silica composite gels using ATR: (a) PUA; (b) USI-9.

polymerizing the residual double bonds and silicon alkoxides, the silica containing semi-interpenetrating polymer network (IPN) composites were obtained. MPTS acted as a compatibilizer to enhance the interaction between PUA and silica components.

Silica components in PUA gels were confirmed by ATR of IR radiation spectra. The spectra of PUA gel and the composite are illustrated in Figure 2.

PUA/silica composites have two different characteristic peaks in comparison with the pure PUA gel.¹ These are the Si—O—Si peaks that arise from the asymmetric stretching vibration around 1100 cm^{-1} and bending vibration around 500 cm^{-1} . Through ATR measurements, the existence of silica components in PUA was confirmed indirectly.

To investigate the existent state of silica in PUA gels, the crystallinity of PUA and PUA/silica gels was measured by WAXD, and the results are illustrated in Figure 3.

Generally, it is known that the ionomers have some crystallinity due to the microdomains of aggregated ionic moieties. PUA having microdomains of carboxyl groups shows some characteristic peaks of crystallinity at $2\theta = 13^\circ$ and 28° in WAXD. In Figure 3, the peak intensity decreases with the increase of silica incorporated. Amorphous silica incorporated decreases the crystallinity of composites in comparison with that of PUA gel. This indicates that silica components exist in polar clusters of PUA composite gels. When PUA is hydrated with water, HCl, and

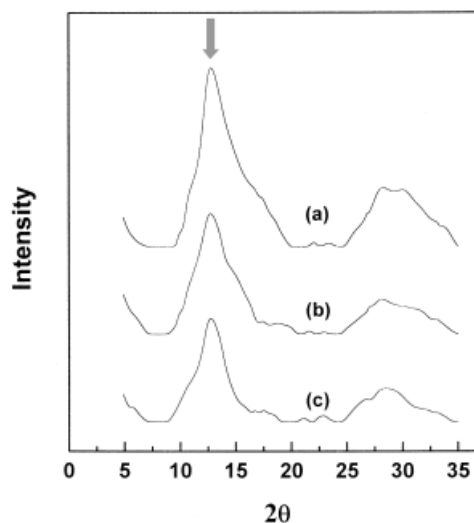


Figure 3 WAXD patterns with the amount of silica emulsion (CuK α radiation and $3^\circ/\text{min}$): (a) PUA; (b) USI-10; (c) USI-12.

ethanol mixture, the hydrophilic mixture is swollen in hydrophilic domains in PUA. Therefore, during sol-gel process, hydrolysis of TEOS and MPTS is processed in the polar cluster. This inhibits the crystallization of composites.²⁵

TGA was measured to investigate the quantitative analysis of silica incorporated in PUA gels. Organic components of PUA gels are decomposed completely above 450°C , whereas silica is not decomposed at all. PUA and composites were heated above 500°C and the amount of silica

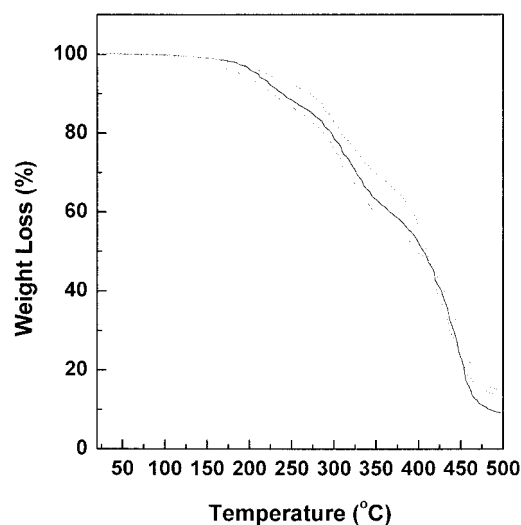


Figure 4 Thermogravimetric analysis thermograms of PUA and PUA/silica gels: (—) PUA; (····) USI-3; (-·-·-) USI-7 (----) USI-11;

Table III The Amount of Silica in Composites Using Thermogravimetric Analysis^a

Sample	Measured Silica Content (%)
USI-3	4.085
USI-7	4.605
USI-11	5.792

^a Char yield of PUAAs is 9.07% at 500°C.

in composites was calculated through total residues minus char yield (the amount of ash) of PUAAs. The TGA thermograms for PUAAs and PUAAs/silica gels are displayed in Figure 4.

Figure 4 shows that the incorporation of silica does not profoundly affect the onset of the thermal decomposition of PUAAs gels. The transition temperature appeared around 300°C because of the residual reaction of remaining water, ethanol, and TEOS occurring during the measurement. As the amount of silica increases, the char yield of the composites also increases. The results are summarized in Table III.

From WAXD measurement, it is thought that silica may be incorporated in polar clusters. Therefore, it is expected that a large amount of silica exists in ionic domains of PUAAs37 gel having a high degree of hydration (Fig. 1). From this

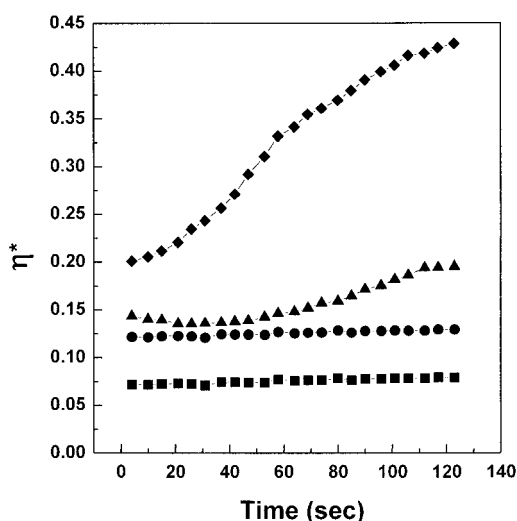


Figure 5 Viscosity change with the amount of silica components and time (All measurements were performed at 30°C, 6.28 rad/s with 40 wt% of solid content): (●) silica emulsion only; (■) UAA emulsion only; (▲) UAA-silica (10%) emulsion; (◆) UAA-silica (25%) emulsion.

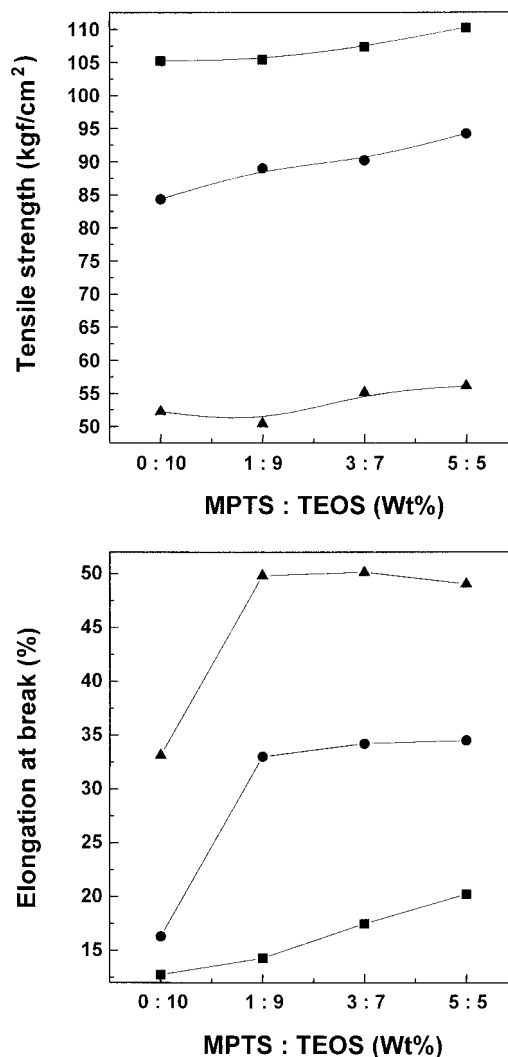


Figure 6 Mechanical properties of composites: (a) tensile strength; (b) elongation at break; (■) UAA37 series; (●) UAA46 series; (▲) UAA55 series.

point of view, the amount of silica incorporated in composites increases with the increase of carboxyl groups in PUAAs (PUAAs55 < PUAAs46 < PUAAs37). It means that hydroxyl groups of silica components existing in PUAAs/silica composites interact with ionic clusters of PUAAs via hydrogen bonding.

To verify the interactions between silica component and PUAAs, the viscosity change with the amount of silica was measured by dynamic time-sweep method and is shown in Figure 5.

The silica emulsion (10 wt %) prepared by the sol-gel process and UAA emulsion (25 wt %) showed a relatively low complex viscosity behavior. However, the complex viscosity of silica and

UAA emulsion mixture increases with the increase of silica emulsion ratio. This means that the interaction such as hydrogen bonding exists between ionic cluster in UAA and hydroxyl groups of silica components.

The mechanical properties of composite were also modified by the silica component incorporated into the PUAA. Figure 6 shows the tensile strength and elongation at break of the PUAA composites as a function of TEOS content.

The anionic content in PUAA gels has a dramatic influence on the mechanical properties. Tensile strength was improved and elongation at break decreased with the increase of ionic sites because of the microphase separation and the interaction between ionic sites. The tensile properties of the PUAA37 composite series having the most ionic domains were the most enhanced. As the amount of MPTS increased, tensile strengths and elongation at break also increased because of the penetration of acrylic polymers into the hydrophobic domains of PUAA. It is well known that composites having the fine and well-dispersed silica domain show high mechanical strength. The

morphology of composite gels was observed with SEM. SEM images are shown in Figure 7.

PUAA gel shows a rough fracture surface due to its rubbery character. However, the surface of USI-9, USI-10, and USI-12 are denser than that of pure PUAA gel. Silica is dispersed in PUAA similar to the particle shape in USI-9. Silica domains of USI-10 are more diffuse than that of USI-9, indicating that MPTS acts as a compatibilizer for silica and PUAA gel. As the amount of MPTS increases, the fracture surface morphology of composite gels becomes smooth. In contrast, the composite gels have no MPTS showing rough morphology. In summary, as the amount of coupling agent increases, mechanical strength improves because of the improvement of compatibility between silica components and PUAA.

CONCLUSION

PUAA/silica composite gels were prepared by swelling and sol-gel methods. Structural analysis was carried out through ATR, XRD, SEM, and WAXD measurements. Silica incorporated into the composites interacts with polar clusters in PUAA gels via hydrogen bonding. This enhances the mechanical properties of composites drastically. As the amount of MPTS increases, mechanical properties of composite gels also increase, because of the enhancement of compatibility between silica and UAA gels.

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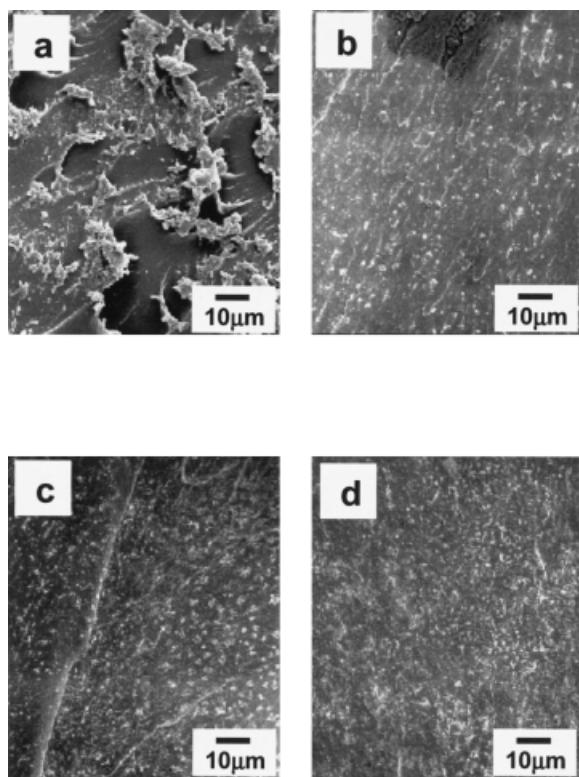


Figure 7 Morphologies of PUAA and PUAA/silica composite gels by SEM: (a) UAA; (b) USI-9; (c) USI-10; (d) USI-12.

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