

Mechanical and Surface Hardness Properties of Ultraviolet-Cured Polyurethane Acrylate Anionomer/Silica Composite Film

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ABSTRACT: An organic-inorganic composite was prepared by mixing silica emulsion with urethane acrylate anionomer (UAA) emulsion. The silica emulsion was prepared by sol-gel process, and stabilized by a steric stabilizer, polyvinyl pyrrolidone. UAA/silica composite film was made by an ultraviolet curing method. The mechanical and rheological properties of the UAA/silica composite were greatly improved. This composite also showed thermal stability during increase of temperature. Surface hardness was improved with increasing silica content up to proper amount of silica. However, in abrasive test, because UAA/silica composite film has a more abrasive contact area than UAA film, the former was abraded much more than the latter. In comparison to UAA film, the UAA/silica composite showed much smoother abrasive surface and less roughness. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 968–975, 2000

Key words: urethane acrylate anionomer; emulsion; UV-curing; sol-gel process; hydrophilic domain; surface hardness

INTRODUCTION

The diverse sorts of film, prepared by the ultraviolet (UV) curing method, are applied to many industrial fields because of the short preparation period and the simple manufacture technologies. Also, waterborne coating recently has been used to decrease air pollution and to improve aspects of occupational health and safety.^{1–6} Because these coating products require strong mechanical and thermal properties, many researchers have studied some methods to improve these properties. Inorganic material, for example, has been incorporated into organic continuous phase.^{7,8} Thus, interactions between inorganic filler and polymer network improve many conditions such as mechanical properties, thermal properties, and sur-

face hardness, etc. Many methods to prepare inorganic/organic composites have been investigated variously, e.g., melt blend, colloidal dispersion, and sol-gel process.^{9–11} The sol-gel process, which is composed of hydrolysis and condensation reaction, has some advantages such as high purity of products and low preparing temperature.^{12–14} Ikeda and Kohjiya¹⁵ and Chiang et al.¹⁶ reported that the sol-gel process enables ductile organic material to have high mechanical properties by incorporating silica particles into butadiene rubber networks.

In a previous study,¹⁷ we prepared a polyurethane acrylate anionomer (UAA)/silica hybrid composite hydrogel using the emulsion-mixing method. By strengthening the interaction between the UAA network and silica droplets, the emulsion-mixing method showed improvement of many properties. The UAA/silica composite hydrogel had a tendency to increase in mechanical property with the amount of silica emulsion.

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Table I The Recipe of Urethane Acrylate Anionomer (Unit : Mol)

Sample	TDI	PTMG	DMPA	HEMA	TEA
US 5	0.15	0.05	0.05	0.15	0.1
US 6	0.15	0.04	0.06	0.15	0.12
US 7	0.15	0.03	0.07	0.15	0.14

In this study, film properties of UAA/silica composite prepared by the emulsion-mixing method were investigated. Surface hardness improved with the amount of silica content, and was confirmed by atomic force microscopy (AFM) and abrasive test.^{18,19} The mechanical property was surveyed through tensile strength and elongation at break, as well as storage modulus (G') and loss modulus (G'') with frequency change. Also, thermal property was investigated by using a rheometer at the temperature range between 30 and 100°C.

EXPERIMENTAL

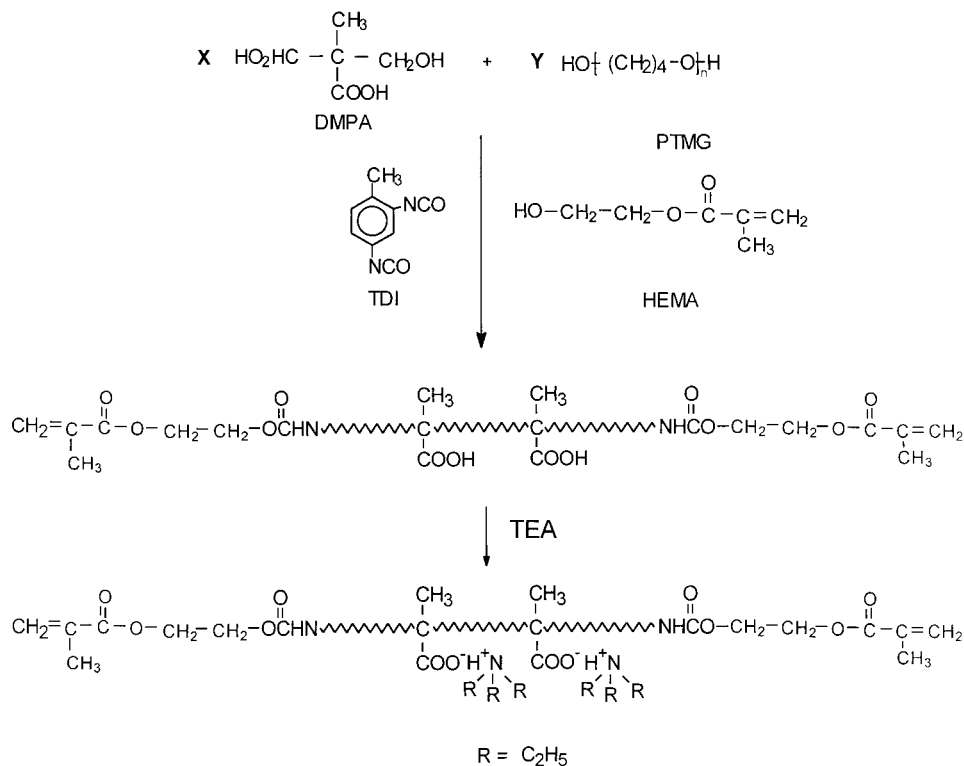
Materials

In the synthesis of UAA, polytetramethylene glycol (PTMG) ($M_w = 1000$, Hyosung BASF) was dried and degassed at 60°C under vacuum. 2,4-

Toluene diisocyanate (TDI) (Junsei Chemical Co.) was purified by filtration. 2-Hydroxyethyl methacrylate (Aldrich Chemical Co.) and dimethylol propionic acid (DMPA) (Aldrich Chemical Co.) were used without further purification. Triethylamine (TEA) (Junsei Chemical Co.) was used for neutralization of UAA. *n*-Methyl-2-pyrrolidone (NMP) (Lancaster Synthesis) was used as a solvent. In the preparation of silica emulsion, tetraethoxysilane (TEOS) (95%, Aldrich Chemical Co.), ammonia water (NH_4OH) (28%, Junsei Chemical Co.), and polyvinyl pyrrolidone (PVP) ($M_w = 40,000$; Sigma) were used without further purification. Benzophenone (Janssen Chemical Co.) was used as a photo-initiator for UV curing.

Synthesis of UAA

UAA was synthesized by four step processes. PTMG and DMPA as a hydroxyl group and NMP



Scheme 1 Schematic representation of urethane acrylate (UAA) synthesis.

Table II The Recipe of UAA/Silica Composite

Sample	UAA	Silica Emulsion	Water	Benzophenone
US 5-0	US5(20g)	0g	6g	0.3g
US 5-1	US5(20g)	1g	6g	0.3g
US 5-2	US5(20g)	2g	6g	0.3g
US 5-3	US5(20g)	3g	6g	0.3g
US 5-4	US5(20g)	4g	6g	0.3g
US 6-0	US6(20g)	0g	6g	0.3g
US 6-1	US6(20g)	1g	6g	0.3g
US 6-2	US6(20g)	2g	6g	0.3g
US 6-3	US6(20g)	3g	6g	0.3g
US 6-4	US6(20g)	4g	6g	0.1g
US 7-0	US7(20g)	0g	6g	0.3g
US 7-1	US7(20g)	1g	6g	0.3g
US 7-2	US7(20g)	2g	6g	0.3g
US 7-3	US7(20g)	3g	6g	0.3g
US 7-4	US7(20g)	4g	6g	0.3g

as a solvent were charged into the 500-mL four-necked kettle with a reflux condenser, a thermometer, a mechanical stirrer, and an inlet system for N_2 gas. NMP was used as the dissolution agent of DMPA and the agent of reducing the viscosity of final produced resin. A large amount of NMP is favorable in respect to the dissolution aspect; however, NMP is impurity, so the amount of NMP used was determined to 18% of total weight of final produced resins. This mixture was heated slowly to 50°C with N_2 purging and stirring until DMPA was dissolved completely. Then, TDI was dropped into a four-necked glass reactor so that the isocyanate group of TDI would react with the hydroxy group of PTMG and DMPA. Then, this mixture was stirred and reacted at 70°C for 5 h. The reaction was allowed to proceed until the theoretical isocyanate content reached half of the original isocyanate content as determined by the di-*n*-butylamine back titration method.²⁰ Then HEMA was dropped into the reactor for the introduction of the vinyl group. This mixture was then heated slowly to 70°C with stirring and reacted for 4 h. The reaction end point was confirmed by the disappearance of the IR absorption at 2270 cm^{-1} corresponding to stretching vibration of the NCO group. For neutralizing this resin, TEA was added at room temperature while stirring for 30 min. Excess mol of TEA was needed as neutralizing agent of DMPA, so twice the amount of TEA was used in comparison to DMPA. The molar ratio of reagents in the synthesis of UAA is illustrated in Table I and the schematic representation is shown in Scheme 1.

Preparation of UAA/Silica Composite

Silica emulsion was prepared by sol-gel process of TEOS. Aqueous solution was prepared by mixing water, 1 wt % of ammonia water and 5 wt % of PVP. PVP was used as a stabilizer for 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, silica emulsion could be obtained.

For preparation of UAA/silica composite film, first, UAA was mixed with benzophenone with a mechanical stirrer. Then, emulsion was prepared by phase-inversion emulsification method of UAA. The x g of silica emulsion was poured into these UAA emulsions and the mixture was stirred vigorously to mix homogeneously. The UAA/silica mixing emulsion was poured into the flame ($12 \times 8 \times 0.2\text{ cm}$), and then the water was evaporated completely under 50°C overnight under vacuum. The dried UAA/silica mixing material was cured with an air irradiating static UV lamp (450 watt, UV lamp from Ace Glass Co.) for 5 min and post-cured at 80°C for 5 h. The film obtained was cut to measure mechanical property and thermal property. The recipe of the composite gels is shown in Table II.

As the amount of silica emulsion increased, the viscosity of the emulsion also increased, and for up to 4 g of silica emulsion, it was possible to

prepare the proper samples for various measurements. In hybridization by the sol-gel process, the acidic condition is generally more favorable than the basic condition because of the shape of silica compound formed through the sol-gel process. However, in this study, emulsion was not formed at the acid state, only ammonia water was used to adjust the pH.

Measurements

The morphology in the cross section was investigated through scanning electron microscopy (SEM) (Hitachi model). The surface hardness was measured by abrasive test (Yasudaseiki Seisakusho, Ltd., Y.S.S. tester). The test was executed with 1 kg of taber type cell for rotation of 500 times. The topography and hardness of the abrasive surface were verified by AFM (PSI, Autoprobe CP). With the tip (diameter, 10 nm) in contact with the sample surface, short repulsive force was probed. In addition, the cantilever had 0.40 N/m of spring constant and oscillated at its proper frequency (45 kHz). The mechanical properties such as tensile strength and elongation at break were investigated by a HOUNSFIELD model INSTRON. At this time, the samples were cut into dumbbell shapes. The rheological property of the UAA/silica composite was examined by rheometer (ARES, Rheometric Scientific). This installation also was used to examine the thermal property.

RESULTS AND DISCUSSION

Preparation of UAA/Silica Composites

In a previous study,⁶ UAA was prepared by incorporating DMPA into urethane acrylate. Because the amount of DMPA is proportional to the hydrophilic property, UAA, which has a large amount of DMPA moiety, was readily converted to O/W emulsion through the phase inversion emulsification method.^{21,22} In this study, the UAA/silica composite was prepared by mixing both silica emulsion and UAA emulsion. First, silica emulsion could be prepared by the sol-gel process. The sol-gel process is composed of hydrolysis and condensation reaction, and needs materials such as metal alkoxide, water, and catalyst. Also, because these water and metal alkoxides are immiscible, a mutual solvent such as alcohol is usually used as a homogenizing agent. When these solvents were

added into the UAA emulsion, the solvents had a tendency to inhibit the phase separation of the UAA microemulsion. Because UAA/silica composite film was prepared through phase separation, the UAA emulsion should have stable phase separation structure between hydrophilic and hydrophobic domains. Therefore, PVP was used to sta-

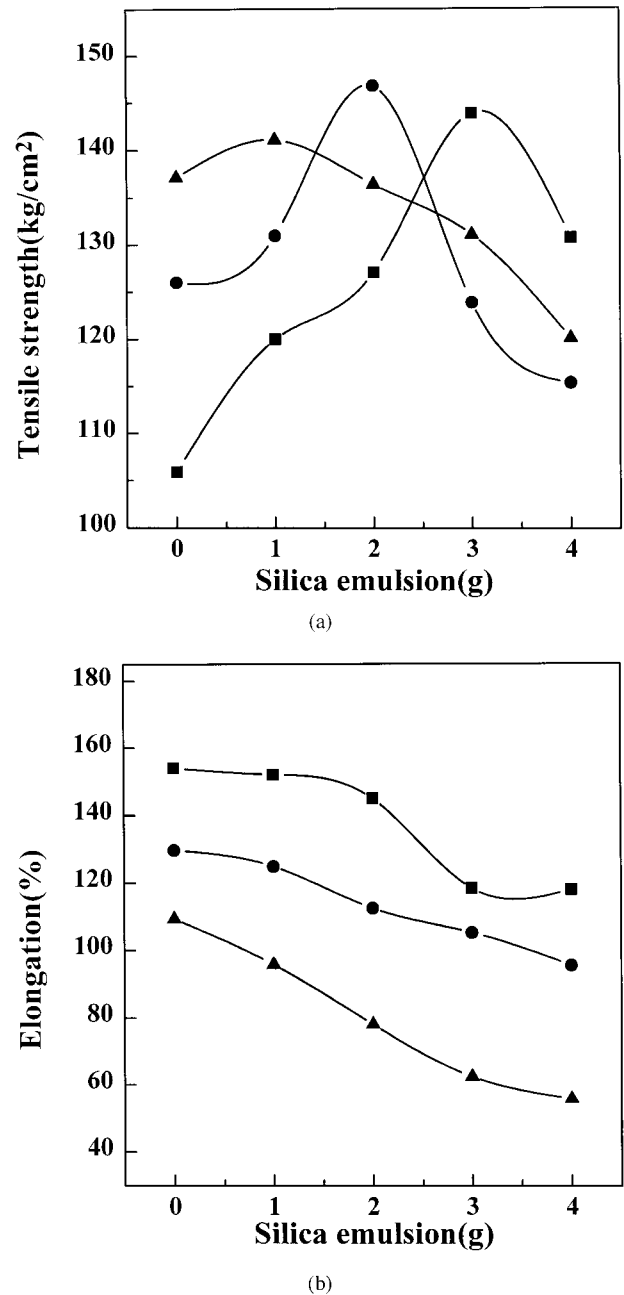
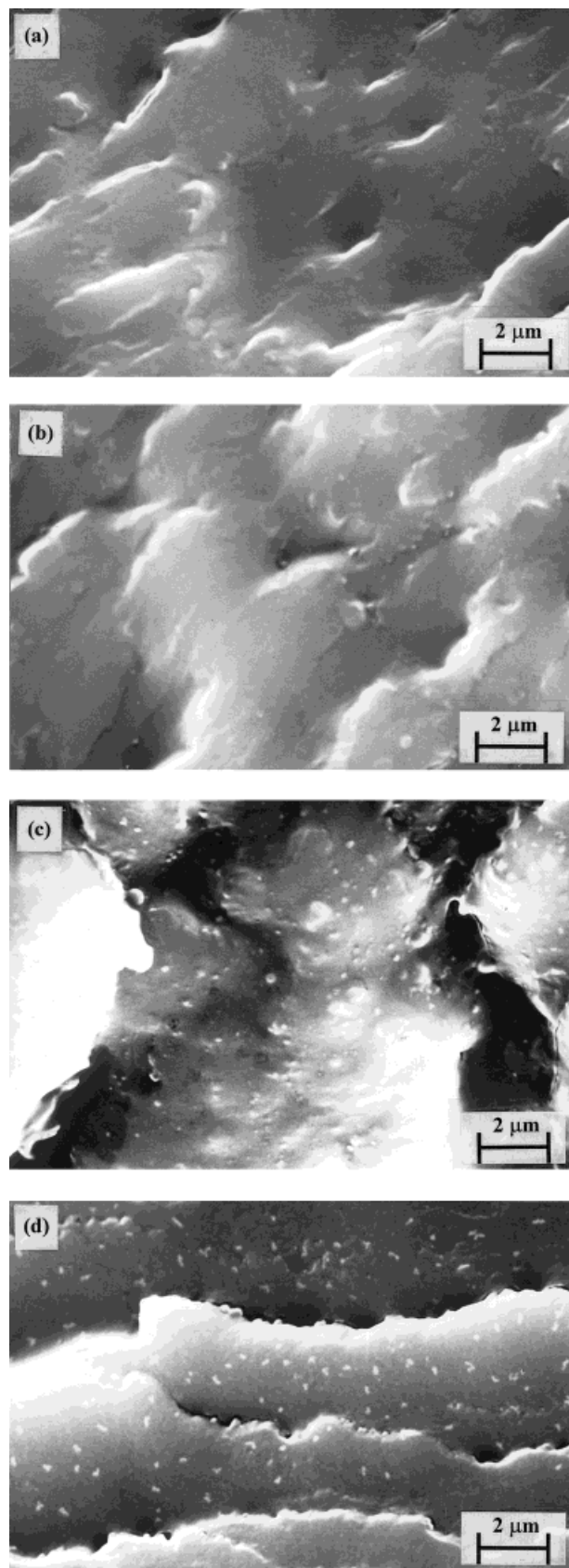


Figure 1 Tensile strength (a) and elongation at break (b) of UAA/silica composite films with the content of silica emulsions. (■) US 5 series; (●) US 6 series; (▲) US 7 series.



bilize the mixing emulsion of UAA and silica. UAA emulsion was formed by the micro-phase separated structure between hydrophobic and hydrophilic segments. Silica particles that were made by the sol-gel process had hydrophilic hydroxyl groups on the surface. Therefore, it was expected that silica particles would be precipitated in the hydrophilic micro-domain of UAA film.

Mechanical Property

When the proper amount of silica emulsion was added to the UAA emulsion, the UAA/silica composite could be prepared without destroying the hydrophilic and hydrophobic domain of mixing emulsion. UAA/silica composite showed improvements in tensile strength, whereas elongation at break decreased. These results showed that the hydroxyl groups on silica particles were interacted with carboxyl groups by hydrogen and/or ester bonds. These physical or chemical interactions make composite films much denser. For example, as showed in Figure 1(a), the tensile strength of sample US 5 series increased until reaching 3 g of silica emulsion. The mechanical properties of the US 6 and 7 series also increased until the proper emulsions were added. As the molar ratio of DMPA to PTMG increased, decreased behavior in tensile strength appeared earlier. This decrease occurred by macro-phase separation of the silica particle with the UAA network. As the molar ratio of DMPA to PTMG increases, the size of hydrophilic domain of composite decreases. In other words, because ionic interaction of the hydrophilic domain increased with increasing ionic groups of DMPA, this strong ionic interaction force shrank each hydrophilic domain. Thus, the hydrophilic domain of US 7 was smaller than that of US 5. As showed in Figure 1(a), decreased behavior in tensile strength was inversely proportional to the molar ratio of DMPA to PTMG.

Morphology and Surface Property

The morphology of composite films was investigated by SEM. US 7-0, in which no silica content was filled in UAA film, showed rough fracture

Figure 2 Morphologies of UAA and UAA/silica composite films by scanning electron microscopy. (a) US 7-0; (b) US 7-1; (c) US 7-2; (d) US 7-4.

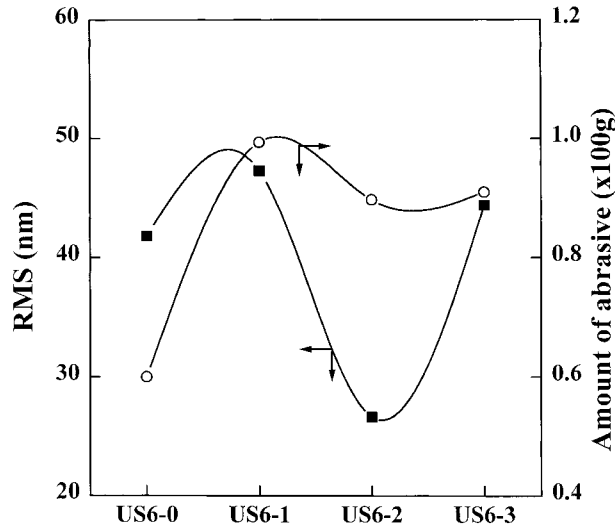


Figure 3 Abrasive amount by abrasive test and root mean square (RMS) roughness of US 6 series.

because of the rubbery character of UAA. US 7-1, in which 1 g of silica emulsion was added, showed similar morphology in comparison with the US 7-0. On the other hand, because US 7-4 has a small domain by strong quenching force of carboxylic groups, it showed that the excess silica particles were separated from the micro-domain. SEM images are shown in Figure 2.

As proved by many researchers, the interaction between silica droplets and UAA network had an influence on surface hardness. Surface hardness of composite increased with the amount of silica content before phase separation. These properties were proved by abrasive test and AFM measurement. First, as seen in Figure 3, the abrasive property had a similar tendency to that of tensile strength. Because of the absence of phase separation between silica droplets and the UAA network, a strong interaction of US 6-2 resulted in good abrasive resistance. However, US 6-3 showed a lower surface hardness property than US 6-2. It was assumed that the phase separation between silica particle and UAA of US 6-3 decreased the interaction between those.

Despite that US 6-0 has no silica content, it showed the lowest abrasive amount. Because UAA film itself has lower abrasive contact area than the UAA/silica composite, the former had less abrasive amount than the latter. Therefore, though UAA film had lower tensile strength than the composite, it had higher abrasive resistance than that of the composite. Vemura and Ikeda²³ and Seefield et al.²⁴ had explained this abrasive

property of rubber by using the relationship between abrasive contact area and dynamic modulus. Second, AFM showed characteristics of the silica composite by investigating the roughness and topology of the abrasive surface. Like the abrasive test, RMS (root mean square) roughness appeared the lowest in the US 6-2 because of good interaction between the filler and polymer. However, in contrast to the abrasive test, noncomposite US 6-0 showed more roughness than US 6-2 did. This could be demonstrated by the ductile property of the rubber material. AFM topographies of the UAA/silica composite compensated for roughness property. As seen in Figure 4, US 6-2a, where "a" means sample after abrasive test, has smoother topography than that of US 6-0a.

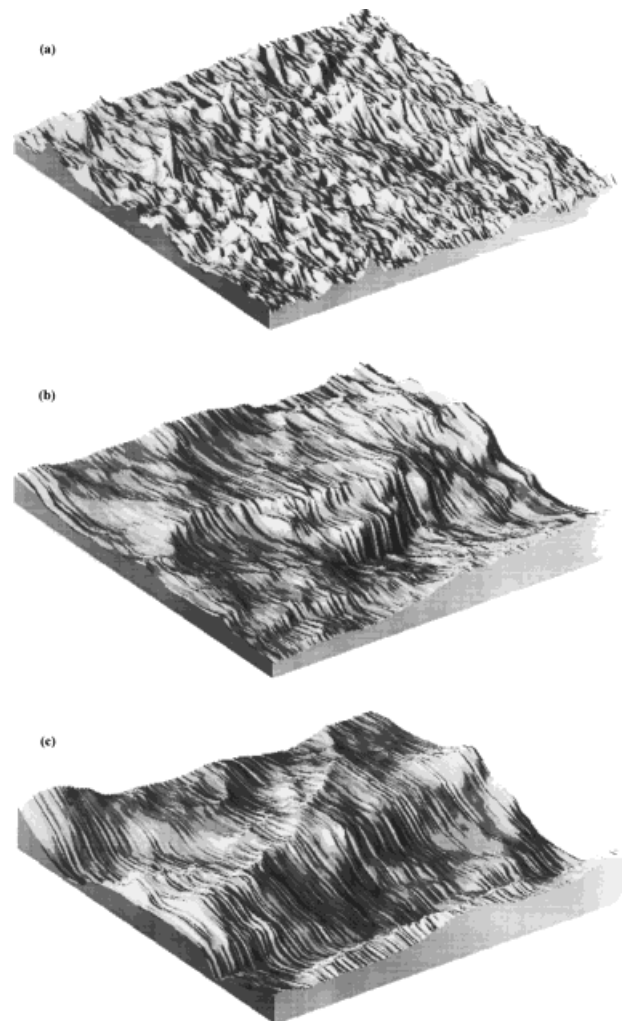


Figure 4 Topographies of UAA and UAA/silica composite films by atomic force microscopy. (a) US 6-0; (b) US 6-0a; (c) US 6-2a.

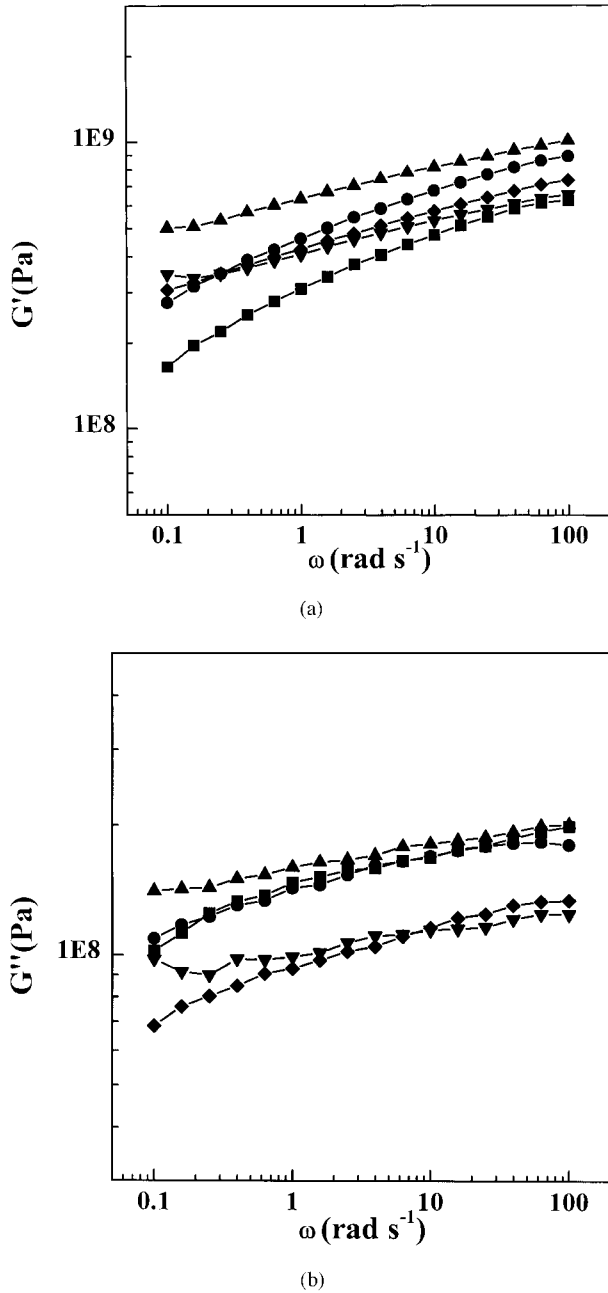


Figure 5 Storage modulus (a) and loss modulus (b) of UAA/silica with frequency. (■) US 6-0; (●) US 6-1; (▲) US 6-2; (▼) US 6-3; (◆) US 6-4.

Thermal Property

To investigate the rheological property of UAA/silica composite film, storage modulus (G') and loss modulus (G'') with frequency were measured. Because interaction between UAA and silica droplets increases with increasing silica content, G' of US 6-1 and 2 was shown to be higher than

US 6-0, whereas US 6-3 and 4 had lower G' than US 6-1 and 2 because of micro-phase separation of the composite. Because silica droplet interrupts movement of the UAA network, US 6-4 showed the G' slope at low frequency plateau. Because no phase separation occurred between UAA and silica particles, G'' increases in sample US 6-1 and

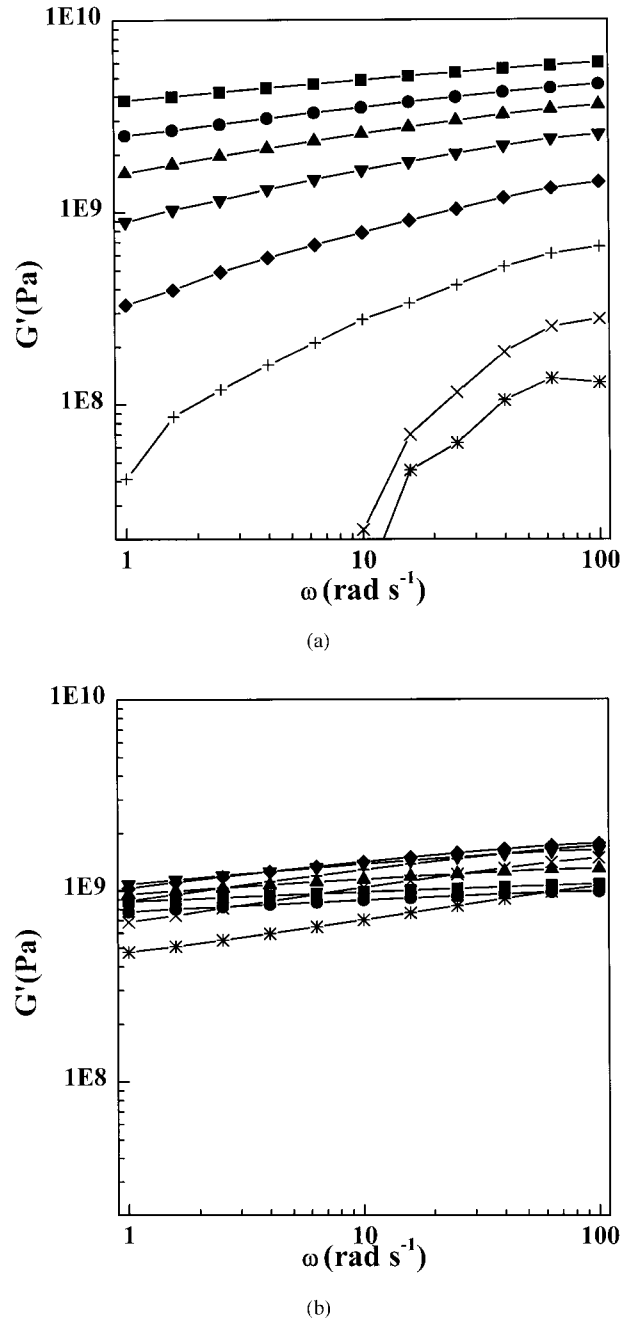


Figure 6 Thermal properties of US 7-0 (a) and US 7-4 (b) between 30–100°C. (■) 30°C; (●) 40°C; (▼) 50°C; (▼) 60°C; (◆) 70°C; (+) 80°C; (×) 90°C; (*) 100°C.

US 6-2. Because US 6-3 and 4 have phase separation between both components, the G' slope of these composites decreased in comparison with US 6-1 and 2. These mechanical properties of UAA/silica composite films are described in Figure 5(a,b).

Mechanical property of UAA was improved in comparison with urethane acrylate film, for the ionic hard segment domains play a role in reinforcing filler in the urethane acrylate network. Because coating film requires other properties such as thermal stability and resistance, many fillers have been incorporated into polymer film. Because the silica provides excellent thermal property, silica particle was incorporated in the UAA network. Thermal properties of the UAA/silica composite films are shown in Figure 6(a,b). Storage modulus with frequency was measured from 30 to 100°C (by 10°C gap). UAA film, unfilled with silica, was stable at 30°C. But storage modulus of UAA films decreased with increasing temperature. The storage modulus decreased significantly especially at 90 and 100°C. The UAA/silica composite showed strong thermal stability from 30 to 100°C, because silica particles interacted highly with UAA moiety and interfered with its mobility. Therefore, UAA/silica composites had a slight limitation in improving mechanical property above a certain amount; all composite films showed similar high thermal stability overall from 30 to 100°C.

CONCLUSIONS

UAA/silica composite film was prepared by using the emulsion-mixing method. UAA and silica emulsions were made by the phase inversion method and sol-gel process, respectively. Surface hardness was improved with increasing silica content up to a certain amount of silica emulsion. After abrasive test, topology of UAA/silica composite appeared smoother than the UAA film. On the contrary, due to ductile property of rubber, UAA/silica composite showed less abrasive resistance property than the UAA film. Tensile strength and modulus of the UAA/silica composite were improved with increasing silica content. The thermal property of the UAA/silica composite

films also was highly improved due to incorporation of silica.

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