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Material and rheological properties of (glycidoxypropyl) trimethoxysilane modified colloidal silica coatings

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Abstract

Colloidal coating solution was prepared to enhance the hydrophilic property of the film surface. Water and ethanol were used as the dispersion media and (glycidoxypropyl) trimethoxysilane (GPS) as a binder in the colloidal silica coatings. Ethylene diamine was added to the colloidal silica solution as the curing agent. The colloidal silica solution was regarded as a hard-sphere suspension model with low volume fraction of the silica particles. Rheological properties of the silica suspensions modified with GPS have been investigated as a function of pH and concentration. The acidic solution showed high viscosity change by fast hydrolysis reaction and adsorption of the organic binders on the surface of silica particles. However, the hydrolysis was slow at the basic condition and the binders combined with themselves by condensation. The viscosity change was smallest at pH 7. The viscosity increased with the curing time after adding ethylenediamine, and the increase of viscosity at low pH was higher than that at high pH. The hydrophilic properties of the coating film were investigated by the contact angle of water and film surface. The smallest contact angle was shown under the strong acidic condition of pH 2.

Keywords **:** modified silica coating, sol-gel method, hydrophilic property

1. Introduction

In recent years, a number of methods for the surface treatments have been investigated in attempts to obtain desirable surface properties. In particular, the hydrophilic property of the coating surface is one of the most important characteristic properties for inkjet print film coatings, photographic films, medical delivery system, and so on (Van Ooij *et al.*, 1993; Blizzard and Cottington, 1995; Martinson *et al.*, 1995). The useful method to enhance the hydrophilic property of the film surface is a colloidal coating using the organic binders.

General ceramic coatings are treated at high temperature to get their adhesive strength. However, these heat treatments can destroy some substrate of polymer films. Since the colloidal coatings are prepared at low temperature, the film substrates are not destroyed. The organic binders are used as the coupling agents to improve the adhesive bond between the organic polymer and the inorganic mineral. The organic binders become integral parts of the coating substrate in the colloidal coating process (Chu *et al.*, 1997; Daniels and Francis, 1998). Organosilanes were also used as a binder in polymer composite materials (Ikuta *et al.*, 1990; Plueddemann, 1982).

Sol-gel methods are composed of three reactions such as hydrolysis, adsorption, and condensation. Typical organic binders are trifunctional organosilanes. They have the formula of R-Si-$(OR)_3$, where R is a hydrocarbon chain with epoxy group and R is an alkyl group (Plueddemann, 1982). The coupling mechanism depends on a link between the organofunctional groups and the hydrolysable groups. Alkoxy groups of the organic binder are hydrolyzed in water to build the silanol groups. Acid and base catalyze the hydrolysis reaction. The hydrolysis is fast at acids of low pH, but is slow at pH 7 (Pohl and Osterholtz, 1985). The hydrolysis reaction is controlled irreversibly by a large excess of water and followed by condensation and adsorption. Since silanols have three functional groups, large crosslinked network polymers are possible. At the strong acidic conditions, the organic binders are adsorbed on the surface of silica particles through the silanol reactions, while another alkoxy group remains available for the reaction with the matrix resin.

In recent years, the rheological properties for hard sphere suspensions of high concentration were investigated using steady shear test, creep test, and so on (Jones *et al.*, 1991). Batchelor showed that the silica suspensions were Newtonian at low concentration (Batchelor, 1977). Another rheological study for the suspension of the non-colloidal

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spherical particles in the polymer solutions was also carried out (Kim, 2001). Effect of the organic binder on viscosity of the polymer resin system is influenced by coupling reactions. However, there are few rheological studies for the suspension system with organic binder.

In this study, the hydrophilic property of the film surface was pursued by the colloidal silica solution, and ethylenediamine as a curing agent. Objectives of this study are to describe the relation between the material properties of coatings and the rheological properties of solution. In addition, effects of initial solution pH and composition of solution are discussed briefly.

2. Experiments

2.1. Materials

A commercial silica suspension (Ludox-LS, Aldrich chemicals) was used to prepare the coating media. Ludox-LS consisted of 30 wt% silica colloid particles (12 nm average diameter) and 70 wt% water. pH of Ludox-LS suspension was measured at 9.6, because base was added to stabilize the suspension. 3-(Glycidoxypropyl) trimethoxysilane (GPS, Aldrich Chemicals) was used as an organic binder, where GPS monomer has three methoxy groups for hydrolysis and one epoxy group for curing. The methoxy groups are hydrolyzed by water, form the silanol group and combine with the hydroxyl group of silica particle in solution. The organic chains react with the curing agents of ethylenediamine and form the crosslinked structures on the film surface. Ethanol was added to solution to increase the solubility of the organic binder for water. These reaction mechanisms were shown simply in Fig. 1.

To prepare a suspension for coating, water was added to the as-received suspension to make the Ludox-LS of the water mass ratio of 1 : 1. This suspension was diluted with ethanol. After stirring the suspension for 20 minutes, GPS was added, and GPS concentrations varied from zero to a half of silica particle weight. Acid or base was added as a catalyst followed by GPS. pH was adjusted with nitric acid and ammonia water. The reaction was terminated after 24 hours and then ethylenediamine was added as a curing agent. Coatings were made from the suspension of approximately 20 cP viscosity by the dip coating method. The speed of the dip coating was fixed at 7.8 mm/sec. Polyethylene terephthalate (PET) film was used as a substrate and the coated PET film was dried in an air convection oven for 1 hour at 80°C. Flow chart for preparation of coating film was shown in Fig. 2.

2.2. Characterizations

The solution viscosity was measured by the viscometer (Brookfield DV II + LV with adapter) and the rheometer

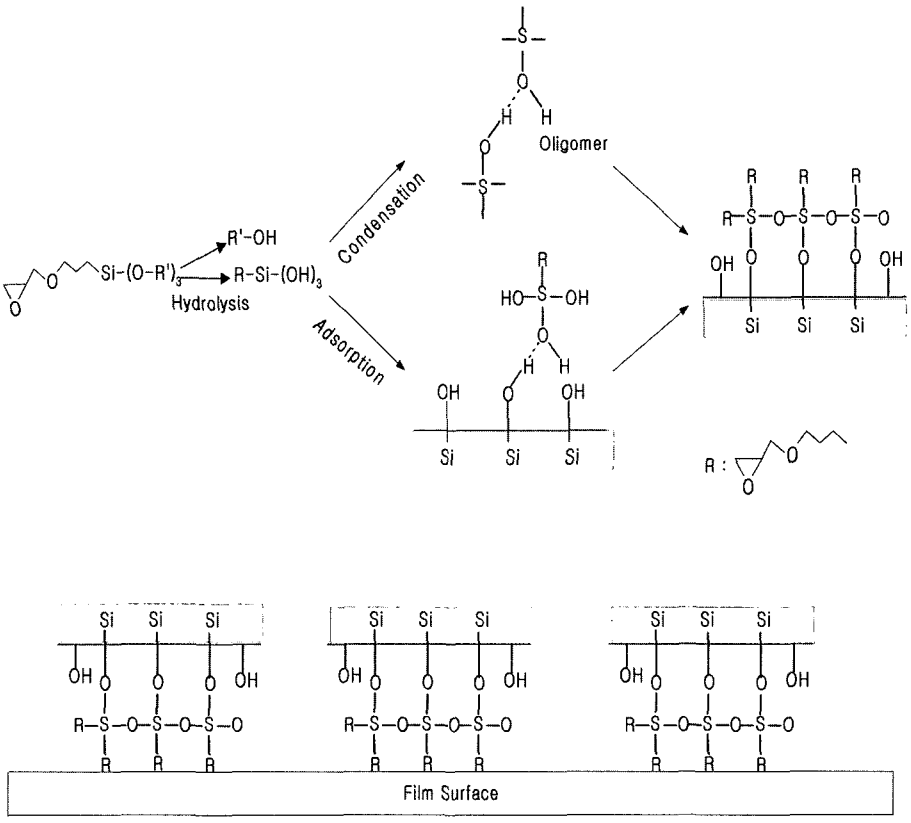


Fig. 1. Reaction mechanism of sol-gel method.

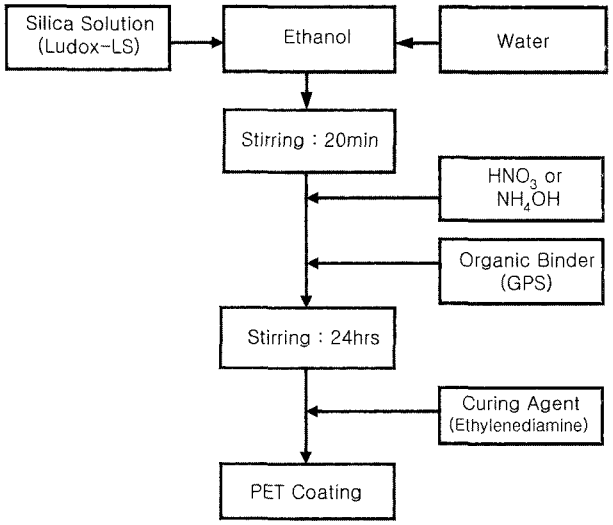


Fig. 2. Experimental procedure.

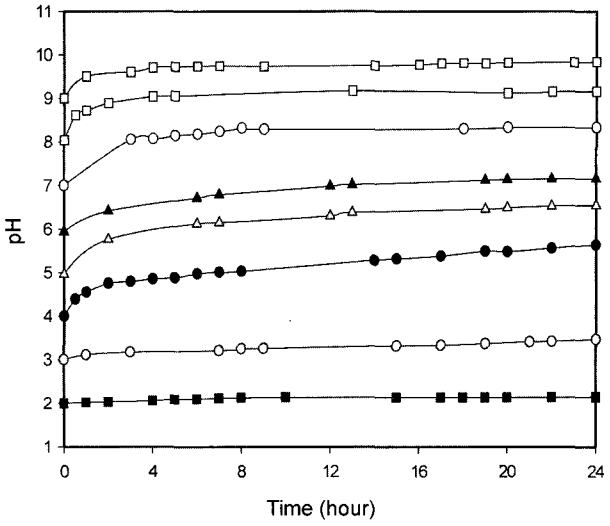


Fig. 3. pH change for reaction time (WR = 0.33).

(TA Instruments AR2000) at 30°C. Prior to the rheological characterization, the suspensions were stirred for 20 minutes, because nanoparticles had a higher tendency to agglomerate due to the interparticle interactions of nanoparticles. This stirring process ensured that the suspension was adequately homogenized. After stirring for 20 minutes, the flow behaviors of the suspension were characterized under the steady shear flow. The viscoelastic properties of the suspensions were determined by the oscillatory shear tests with rheometer. Contact angle goniometer (ERMA G-1 and Kyowa Interface Science CA-DT) was used to monitor the hydrophilic property of films. The deionized water was used to measure the contact angle on the film surface. The surface microstructures of film and powder were observed by the field emission scanning electron microscope (Hitachi FE-SEM 4300). Before SEM examination, the films were dried in an air convection oven for 1 hour at 80°C.

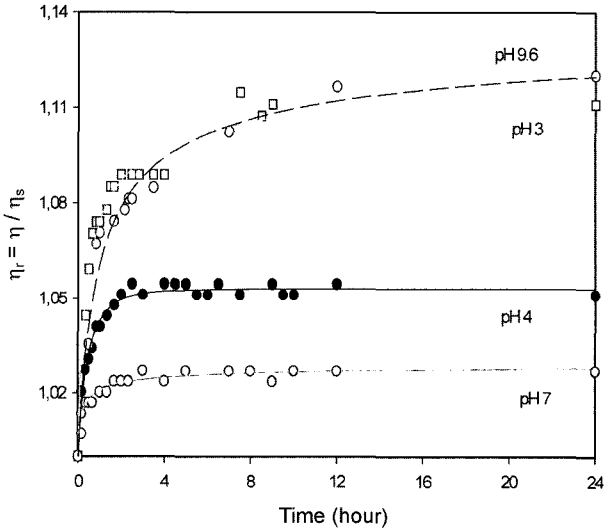


Fig. 4. Viscosity change for reaction time (WR = 0.33).

3. Results and discussion

3.1. Properties of suspensions

The material properties of suspension and films depended on the initial pH of suspension. As mentioned above, GPS monomer has three methoxy groups and one epoxy group. When GPS is added to water, three methoxy groups are hydrolyzed. After hydrolysis, the condensation reaction occurred at GPS monomers to form the oilgomers. The hydrolysis rate was high in strong acid and base with a minimum value at pH 7. Adsorption was faster at acid while condensation was faster at higher pH 8.

pH and viscosity changes of solution are shown in Figs. 3 and 4 where WR is the weight ratio of GPS to silica particles. pH change of solution at strong acid of pH 2 was very small, but increased slowly at higher pH of 4, 5, and 6. Under acidic condition, an initial hydrolysis of GPS was relatively rapid and finished after about 1 hour. Then they condensed to higher oligomers for about 4 hours. pH change shown in Fig. 3 is caused by these reaction mechanisms. The viscosity changes in Fig. 4 show that the reaction rate is increasing at strong acid and at base more dramatically where η_s is the solution viscosity without GPS. The relative viscosity (η/η_s) change of 3% at pH 7 means that the hydrolysis is very slow at pH 7 and the rate determining reaction. However, the viscosity change at pH 3 or pH 9.6 was about 12% while reaction is fast at strong acid of pH 3 and base of pH 9.6 due to the catalysts of acid and base. These conditions were related to the material properties of the coated film.

The viscosity as a function of the shear rate is shown in Fig. 5 for the colloidal suspension. The colloidal suspen-

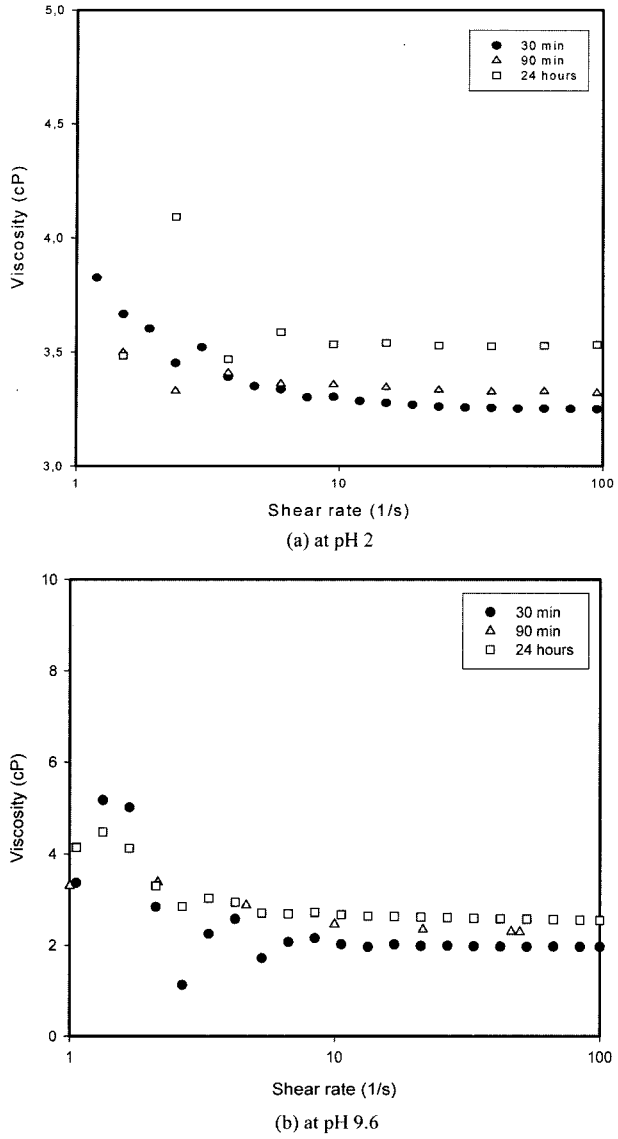


Fig. 5. Viscosity as a function of shear rate for different time (WR = 0.33).

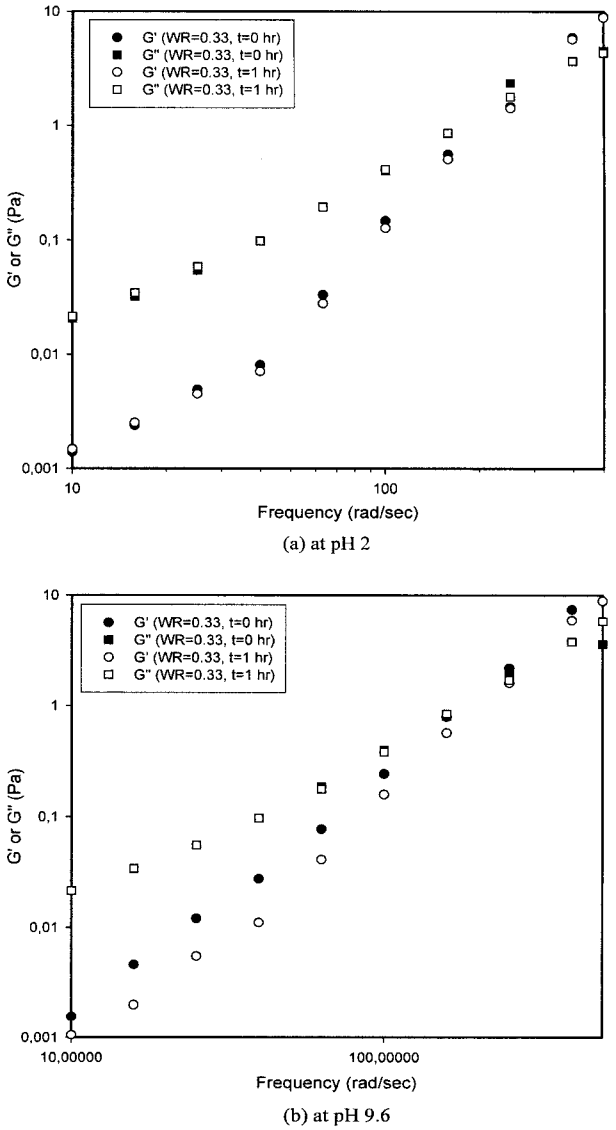


Fig. 6. Storage and loss modulus as functions of angular frequency for the suspensions.

sions showed the shear thinning behavior, but they exhibited more and more unstable properties at low shear rates. At small shear rates, the inter-particulate forces dominate over the hydrodynamic forces relatively, so that the rheological response is dependent on the resulting structural interaction. As the shear rate was increased, the hydrodynamic forces also were increased due to the flow induced structuring of the nanoparticles and the viscosity was decreased at high shear rates. Since the silica particles and the organic binders (GPS) combined each other with time, the colloidal particle size was increased, and the colloidal suspensions exhibited more and more high viscosity with the increase of the reaction time and showed Newtonian behavior.

The storage and loss modulus of colloidal suspensions are shown in Fig. 6 for different pH. The viscous properties are dominant at low frequency. Two functions intersected at a characteristic frequency, and the elastic properties were dominant above this frequency. The loss modulus G" was independent of the reaction time for different pH. However, the storage modulus change was dependent on the pH of suspensions. The difference of storage modulus between time $t = 0$ and $t = 1$ hour was very small at pH 2, but it was large at pH 9.6. The elastic properties of the colloidal suspension were effected not the silica particles but the GPS, because the amounts of silica particles were not changed during the reaction. As mentioned in the previous section, after GPS hydrolyzed with water, it was absorbed on the silica particle quickly at low pH. So there were very small free GPS to com-

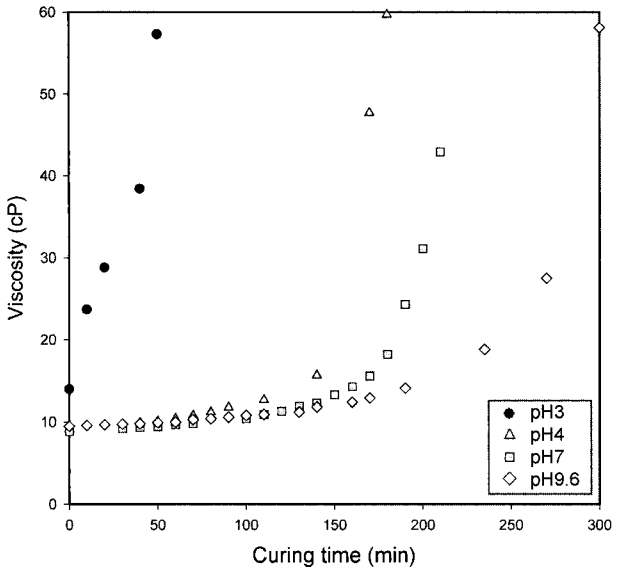


Fig. 7. Viscosity for curing time at different pH.

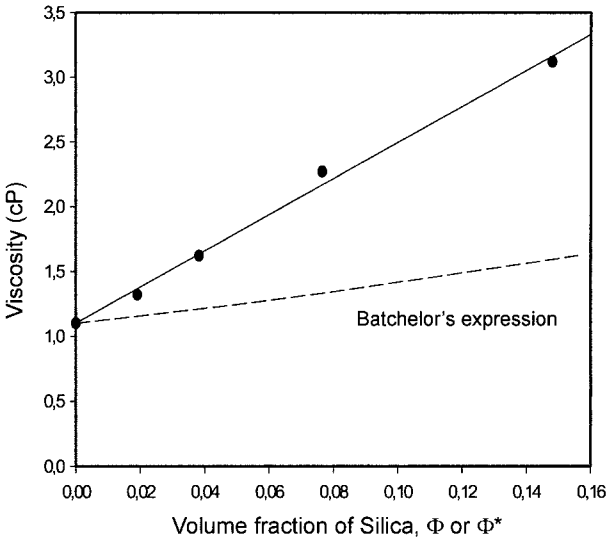


Fig. 8. Viscosity as a function of volume fraction of silica particles at pH 2.

bine each other. The elastic properties of the suspensions were not changed with reaction time by these results. On the other hand, GPS was combined each other and formed oligomers at high pH, and the stored deformation energy (elastic property) of the suspensions was changed with reaction time.

Fig. 7 shows the viscosity change after the addition of ethylenediamine. The viscosity of suspension was increased abruptly under the acidic condition and the elastic response to stress appeared during gelation. The viscosity was increased fast under the acidic condition, because the adsorption reaction of GPS on the surface of the silica particle was fast at acid and then the silica particles were combined with each others strongly by lots of GPS molecules on surface. Since the condensation reaction among GPS molecules was faster under the basic conditions, there were small GPS molecules on the surface by adsorption. So the bonds with other silica particles were weak at base.

The viscosity as a function of the particle concentrations was shown in Fig. 8. The best-fit line for experimental data of Fig. 8 was given by

$$\eta_r = 1 + 12.7\ \Phi^* \tag{1}$$

where Φ^* was the particle volume fraction without consideration of the hydrodynamic volume. The dash straight line was given by Batchelor's expression, i.e.,

$$\eta_r = 1 + 2.5\ \Phi + 6.2\ \Phi^2 \tag{2}$$

where Φ was the hydrodynamic volume fraction of particles in the suspension. Then the hydrodynamic volume fraction is calculated as follows

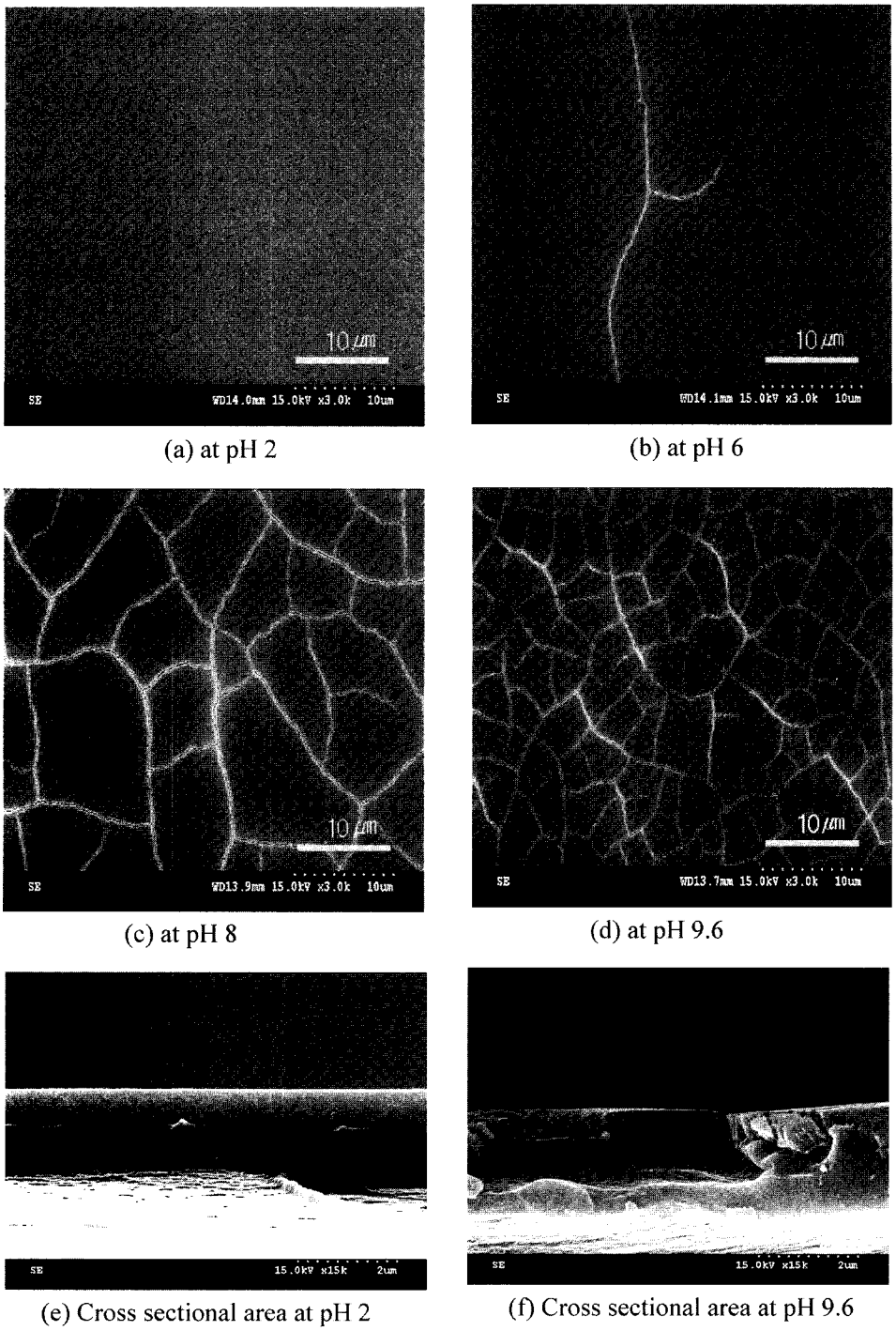
$$\Phi = \text{weight concentration} \times \text{specific volume} \tag{3}$$

The specific volume of 5.0 ml/g was estimated from the slope of Fig. 8. This specific volume is higher than that of previous report (de Kruif, *et al.*, 1985), but the trend was similar to other studies. The difference between the best fit-line and previous report was caused by the particle size difference. A hydrodynamic volume can be influenced by the micropores and liquid layering on the particles surface. However, there were few pores in our experiments, because the pores were closed off by siloxane bridges (Jones, Leary, and Boger, 1991).

Properties of coating film

pH conditions and suspension compositions determine the surface modification. The coating microstructures consisted of silica colloids and GPS. At low R values, most of GPS are adsorbed on the surface of silica particles in the suspension. However, as the amount of GPS increases, the unadsorbed GPS keeps further condensation reaction. The microstructures which show the cracking behavior of colloidal coatings are influenced by modifications of GPS, the addition of GPS and curing agents.

Fig. 9 shows SEM images of the coating surfaces prepared from the silica solution with GPS (R = 0.2) added at different pH. The SEM results indicated that even though the organic binder (GPS) was added to the colloidal suspension, the surface morphology of coating films depended on the pH used for the modification of the silica particles with GPS. The coating prepared from the acidic suspension (pH 2) showed the smooth surface without cracking. Under the basic conditions, GPS was condensed quickly and did not adsorb on the surface of the silica particle. Finally, they adhered poorly on the surface of PET film and there were lots of cracks after drying. These results indicated that addition of the GPS did not affect on the strength between



(a) at pH 2 (b) at pH 6

(c) at pH 8 (d) at pH 9.6

(e) Cross sectional area at pH 2 (f) Cross sectional area at pH 9.6

Fig. 9. SEM photographs of the coating surfaces prepared at different pH (WR = 0.2).

silica particles. The coatings prepared under the acidic conditions and the ethylenediamine addition gave good results, because these conditions led to adsorption of GPS on the surface of silica particles and allowed the strong formation of amine-epoxy bonds.

The hydrophilic property of the coating films was confirmed by the contact angle measurement. Figs. 10 and 11 show the contact angle of the films with GPS added at different pH. The contact angles of the coating films were dependent on the pH of suspension. Especially, in the case of the coating films prepared under highly acidic condition (pH 1 and 2) the contact angles were very small. It seems that the hydrophilic property of the coating film may be physically related to the surface morphology of the coating

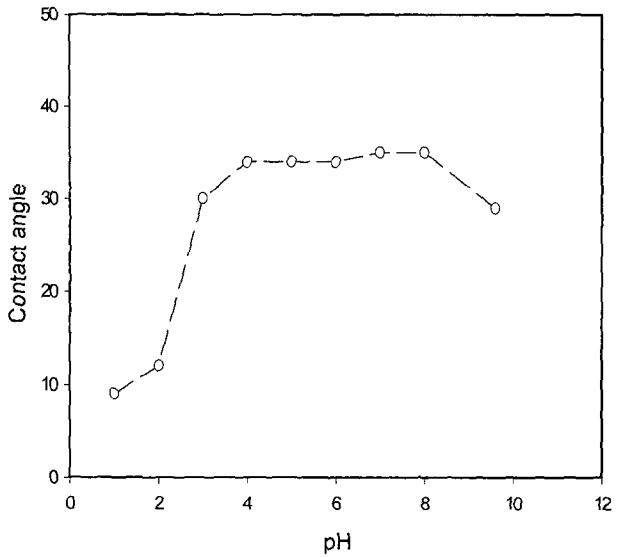


Fig. 10. Contact angles of surface as a function of solution pH

film. A contact angle of water on the film surface depended on the crack and roughness of the film surface. The smooth surfaces were observed in the coating films prepared under the acidic condition, while the rough surfaces were obtained under the basic condition. Since the adsorption on the surface of silica particle was faster than condensation reaction at acid, GPS was adsorbed on the surface initially and then combined with GPS each other. The epoxy groups on the surface of the silica particle were large and the adhesive properties of the silica particles were better at strong acid, because the amount of GPS on the surface at strong acid was larger than the amount at weak acid or base.

4. Conclusions

A suspension was prepared to coat the organic film for the hydrophilic properties. Interactions between GPS and silica particles in the suspension have been affected three reaction mechanisms of hydrolysis, adsorption and condensation. Viscometer was used to verify the reaction mechanism and to observe the material properties of the suspension. The loss modulus changes were small under both conditions, but the storage modulus change under basic condition was larger than that under acidic condition. Since the elastic properties of the colloidal suspension were effected not the silica particles but the GPS, the reaction mechanisms could be proved from those rheological results.

The suspension pH and amounts of GPS were both critical processing parameters for controlling the material

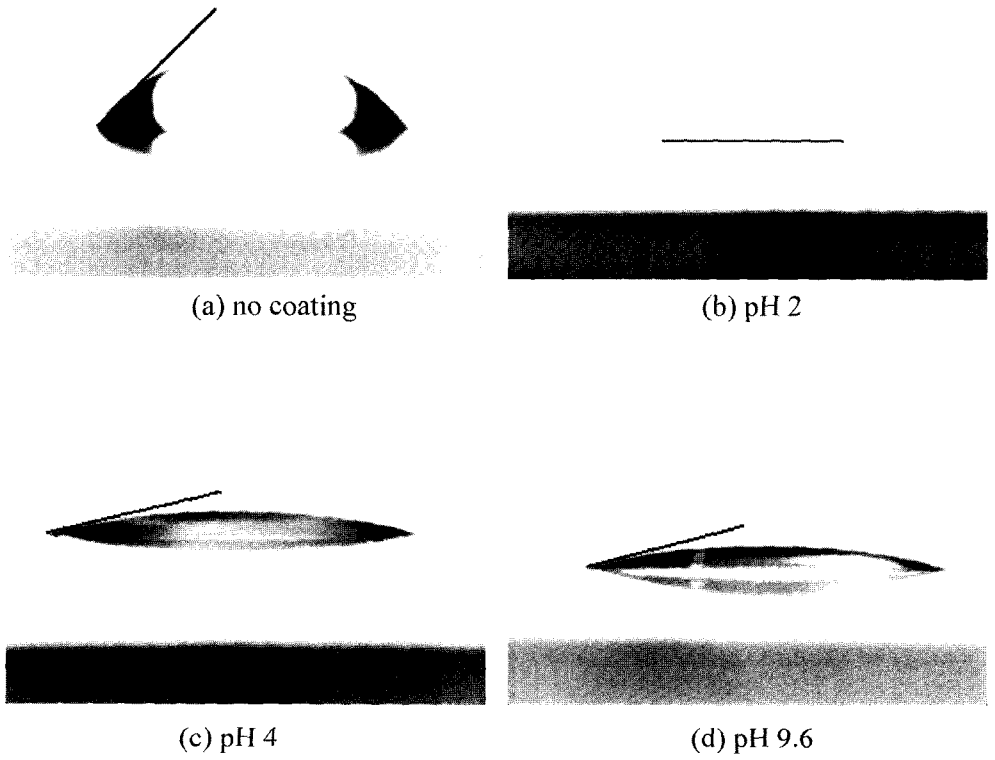


Fig. 11. Contact angle images of surface as a function of solution pH.

properties. Addition of GPS as the organic binder in the silica solution caused the decreasing of cracks on the film surface at strong acid. Amounts of GPS were not important effects at pH 4 or higher pH. Coatings showed less cracks with decrease of pH and the contact angle was decreasing at strong acid. Both the adsorption and the condensation increased the viscosity of solution at strong acid and base.

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