Properties of Organic–Inorganic Composite Materials Prepared from Acrylic Resin Emulsions and Colloidal Silicas

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ABSTRACT: To design an organic–inorganic composite material with colloidal silica as the inorganic component, an acrylic resin emulsion and an organic silane hybridized acrylic resin emulsion were prepared by emulsion polymerization. The organic–inorganic composite films were prepared by blending the emulsion and the colloidal silica. The contact angles for water, gloss at 60°, and the transparencies of those films were measured. The dispersion state of colloidal silica in films was observed with a scanning electron microscope (SEM) and a transmission electron microscope (TEM). From these results, the contact angle for water of the organic–inorganic composite film obtained from the silane hybridized acrylic resin emulsion was lower than that of the organic–inorganic composite film obtained from an acrylic resin emulsion. The contact angles for water in organic–inorganic composite films with colloidal silicas were lower than those of the films without the colloidal silicas. The films prepared from silane hybridized acrylic resin emulsion composites with colloidal silicas of less than 100 nm were more hydrophilic. SEM and TEM observations demonstrated that some aggregations of the small colloidal particle silica were densely dispersed on the film surface. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2051–2056, 2006

Key words: surfaces; emulsion polymerization; nanocomposite; silicas

INTRODUCTION

Recently, organic–inorganic hybrid composites consisting of an organic compound and an inorganic compound have been expected to provide new high functional materials. Since organic–inorganic hybrid composites have both the flexibility of an organic component and the hardness of an inorganic component, they have attracted much attention. Therefore, these organic–inorganic composite materials have been investigated in many fields such as medical, electronic, cosmetic, adhesive, surface coating materials,[1–3] and separation membranes.[4–8]

In coating materials for architecture, one of the methods to improve the coating surface relies on an organic–inorganic hybridization using a condensed alkyl silicate of tetra alkoxyl silane.[9] Tomita et al. reported the additional effect and the morphology of the condensed alkyl silicate of tetra alkoxyl silane in the coating layer.[10,11] This method is effective for the solvent-based coating of two liquid types, and gives a hydrophilic property to the material because of the hydrolysis of alkyl silicate during film formation. However, it has a limited application for the waterborne coating containing an organic liquid component because these coated materials are changed with time and the resulted materials are not chemically stable. Furthermore, it is essential to replace solvent-based coatings with waterborne-based coatings because organic solvent vapor concentrations have to be controlled for environmental, health, and security reasons. Although waterborne coatings have been reported to improve the binder so as to give the same performance as solvent-based coatings, such as high weather durability, water resistance, mechanical properties and so on, waterborne coatings do not provide satisfactory stain resistance.

In this study, to prepare the organic–inorganic composite films, colloidal silicas were selected as inorganic components, and acrylic resins were prepared by conventional emulsion polymerization of methylmethacrylate (MMA), 2-ethylhexylacrylate (2EHA), and methylacrylic acid (MA), and a silane-hybridized acrylic resin prepared by the core/shell emulsion polymerization of MMA, 2EHA, MA, and 3-methacryloxypropyl trimethoxysilane (3MOPTMOS) were employed as organic components. The distribution state of the colloidal silica in composite films was observed by various measurements, and the effect of the colloidal silica on the physical properties of the organic-inorganic composite films was investigated.

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TABLE I
Ingredients for the Acrylic Emulsion and the Silane Hybridized Acrylic Emulsion

Ingredients	Acrylic resin emulsion (g)	Silane-hybridized acrylic resin emulsion (g)
MMA	333	378
2EHA	242	242
MA	10	10
Ion exchange water	592	592
HITENOL 08E	5	5
KPS	2	2
3MOPTMOS	–	5
Aqueous ammonia solution	5	5

EXPERIMENTAL

Materials

Reagent grade methacrylic acid (MA), methylmethacrylate (MMA), 2-ethylhexylacrylate (2EHA) as monomers, potassium peroxodisulfate (KPS) as an initiator, and an aqueous solution of 28% ammonia were obtained from Wako Pure Chemical Industries, Japan. Emulsifiers (Polyoxyethylene alkyl ether sulfates: HITENOL 08E) were obtained from Dai-Ichi Kogyo Seiyaku Co., Japan. 3-Methacryloxypropyl trimethoxysilane (3MOPTMOS) was obtained from Shin-Etsu Chemical Co. Colloidal silicas were obtained from Catalysts and Chemicals Ind. Co., Japan and Nissan Chemical Industries, Japan. 2,2,4-Trimethyl-1,3-pentanediolmonoisobutyrate was obtained from Kyowa Hakko Kogyo Co. The above reagents were used without further purification.

Emulsion polymerization

Two types of emulsions were synthesized as organic components in this study. Acrylic resin emulsions consisted of a mixture of MMA, 2EHA, and MA and were prepared by emulsion polymerization. Silane hybridized acrylic resin emulsions were prepared by feed polymerization adding MMA and 3MOPTMOS to the above-mentioned acrylic resin emulsion. Ingredients for the preparation of emulsions are listed in Table I. The detailed procedure for the acrylic resin emulsion polymerization was as follows.

An aqueous solution dissolved 1 part HITENOL 08E in 267 parts ion exchange water, 333 parts MMA, 242 parts 2EHA, and 10 parts MA were emulsified at 1000 rpm using a mixer to prepare an emulsified mixture. The emulsified mixture of 5 wt % and 1 part KPS were added in a separable 1-L flask equipped with a thermometer and a dropping funnel and a condenser, containing 1 part HITENOL 08E dissolved in 275 parts ion exchange water at 75°C. This mixture was kept at 80°C for 10 min. Both the remaining emulsified mix-

ture of 95 wt % and 1 part KPS dissolved in 50 parts ion exchange water as initiator were continuously dropped with stirring at 80°C for 3 h. Then, the reaction mixture was kept at 80°C for 1 h. After cooling, 5 parts of an aqueous ammonia solution were added to the reaction mixture for neutralization.

The silane hybridized emulsion polymerization was carried out as follows. The first half of this emulsion polymerization process was the same as the abovementioned acrylic resin emulsion polymerization. After the continuous dropping of the remaining emulsified mixture of 95 wt % and 1 part KPS dissolved in 50 parts ion exchange water at 80°C for 3 h, the mixture of 45 parts MMA and 5 parts 3MOPTMOS was continuously dropped in the reaction mixture at 80°C for 3 h. After 1 part KPS was added to the reaction mixture, it was kept at 80°C for 1 h. After cooling, 5 parts of an aqueous ammonia solution were added to the mixture for neutralization.

Characterization of acrylic emulsions

Solid contents of acrylic resin emulsions and silane hybridized acrylic resin emulsions were determined gravimetrically after drying in an air oven at 105°C for 3 h. Viscosities of acrylic resin emulsions and silane hybridized acrylic resin emulsions were determined using a Brookfield Viscometer (model BM, Tokimec) at 25°C. Minimum film-forming temperatures (MFT) were determined using temperature gradient bars (Shimakawa) as specified by ISO 2115 standards. The particle sizes of acrylic resin emulsion and colloidal silica were measured by LB-550 (Horiba Co.).

Film preparation

The colloidal silica, the acrylic resin emulsion or the silane hybridized acrylic resin emulsion and 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate as a coalescent were mixed in appropriate ratios and stirred for 30 min. These mixtures were used as coating solutions for the preparation of their respective films. Films for observing morphologies, contact angles for water and gloss measurements were prepared by spreading casting solutions onto black acrylic resin plates and complete drying at room temperature for 2 weeks. The thickness of these dried films was 30~50 μm.

Measurements of surface of acrylic emulsion-colloidal silica composite films

The lyophilized films of the acrylic resin emulsion containing the colloidal silica and the silane hybridized acrylic resin emulsion containing the colloidal silica were coated with a layer of evaporated osmium and then were observed by a scanning electron micro-

TABLE II
Characteristics of the Acrylic Resin Emulsion and the Silane Hybridized Acrylic Resin Emulsion

	Acrylic resin emulsion	Silane hybridized acrylic resin emulsion
Solid (%)[a]	50.3	50.1
Viscosity (mPa s)[b]	120	1500
pH	8.4	8.7
Average particle diameter of acrylic emulsion (nm)	154	163
MFT (°C)	41	47
Contact angle for water on film surface (°)	84.2	57.3
Gloss at 60°	87.0	84.4
Transparency (lightness value)	0.53	0.93

a 105°C, 1 h.
b BM, 60 rpm, 23°C.

scope (SEM, Field Emission Scanning Electron Microscope JSM-6700F, Jeol) at an accelerating voltage of 15 kV. The acrylic resin emulsion-colloidal silica composite films were embedded in epoxy resin and sliced into this films (thickness = 50 nm) with a microtome (Leica; Reichert Ultracut E). The structure of films was observed by a transmission electron microscopy (TEM, JEM-100CX, Jeol) at an accelerating voltage of 80 kV. The silane hybridized acrylic resin films containing colloidal silica and the acrylic resin films containing colloidal silica were dried at room temperature for 2 weeks to completely remove a coalescent in the films. The contact angles for water of these films were measured by an automatically dynamic contact angle meter (CA-V, Kyowa Interface Science Co.) at 25°C. The surface gloss at 60° was measured with a micro-TRI gloss reflectometer (GM-268, Konica Minolta Holdings).

RESULTS AND DISCUSSION

### Characteristics of acrylic resin emulsion and silane hybridized acrylic resin emulsion

In this study, to investigate characteristics of organic–inorganic composite films containing colloidal silica, two types of emulsions such as acrylic resin emulsion and silane hybridized acrylic resin emulsion were prepared. In Table II, characteristics of the emulsions and the films prepared from the two emulsions are shown. The gloss at 60° and the transparency of the silane hybridized acrylic resin film were inferior to those of the acrylic resin film. However, the hydrophilicity of the silane hybridized acrylic resin film was superior to that of the acrylic resin film. These results suggest that sylanol groups, which are formed by the hydrolysis of 3MOPTMOS, appear on the surface of acrylic resin emulsion particles. As can be seen from Table II, the viscosity of silane hybridized acrylic resin emulsion was higher than that of acrylic resin emulsion. This increase in the viscosity is mainly caused by the fact

that water soluble origomers of MMA and 3MOPTMOS in the emulsion aggregate around sylanol groups of particle surface of silane hybridized acrylic resin emulsion. Consequently, the surface of the film prepared from the silane hybridized acrylic resin become more hydrophilic.

Figure 1 shows TEM images of the cross section of the films obtained from the acrylic resin emulsion and the silane hybridized acrylic resin emulsion, respectively. In these TEM observations, the Si phase is a dark image and the acrylic resin phase is a bright image. Although the dark image in the acrylic resin film was not observed, in the silane hybridized acrylic resin film, a profile of Si was observed around the polymer particle. Therefore, the silane hybridized acrylic resin film has the morphology of the core/shell structure but not the homogeneous structure.

Properties of films containing colloidal silicas

Colloidal silicas used in this study are listed in Table III. Acrylic resin films and silane-hybridized acrylic resin films with 5 and 10 wt % of colloidal silicas

500nm   500nm

(a)   (b)
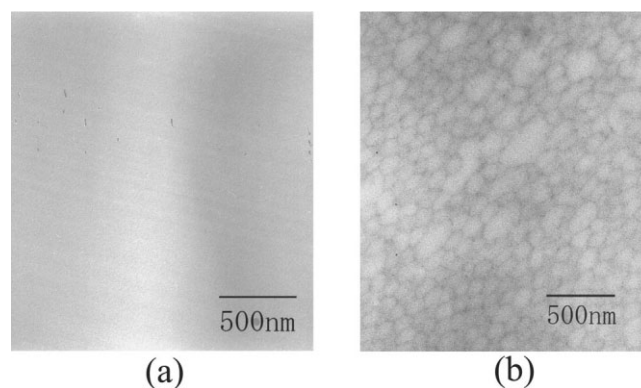
Figure 1 TEM images of (a) an acrylic resin film and (b) a silane hybridized acrylic resin film.

TABLE III
The Characterization of Colloidal Silica

Average particle diameter median diameter (nm)	SiO_2 content (%)	Na_2O content (%)	Viscosity (mPa s)	pH
7.5	20.5	0.75	3.0	10.0
25.0	48.3	0.62	4.1	10.0
62.0	40.5	0.14	3.3	9.6
104.3	40.8	0.36	3.0	10.0
112.6	40.3	0.05	2.6	9.3
223.5	40.7	0.03	2.2	9.3
330.3	40.6	0.01	2.1	8.7

having different particle diameters to the acrylic resin emulsion and the silane hybridized acrylic resin emulsion, respectively, were prepared. Figure 2 shows the results of the contact angle for water of films with 5 and 10 wt % content of various colloidal silicas for each emulsion. Contact angles for water of organic–inorganic composite films had a tendency to decrease with decreasing particle diameters of the colloidal silica. Contact angles for water tended to decrease and were significantly influenced by the additional amount of colloidal silica in the film. Especially, when a colloidal silica of less than 100 nm was used, the contact angle for water effectively decreased. Moreover, contact angles for water of films consisting of silane hybridized acrylic resin emulsions and colloidal silicas were smaller than those of films composed of acrylic resin emulsions and colloidal silicas.

In Figure 3, the effect of the particle diameter of colloidal silica on the gloss at 60° is shown. The gloss at 60° of the films consisting of acrylic resin emulsions and colloidal silicas were higher than those of the films composed of silane hybridized acrylic resin
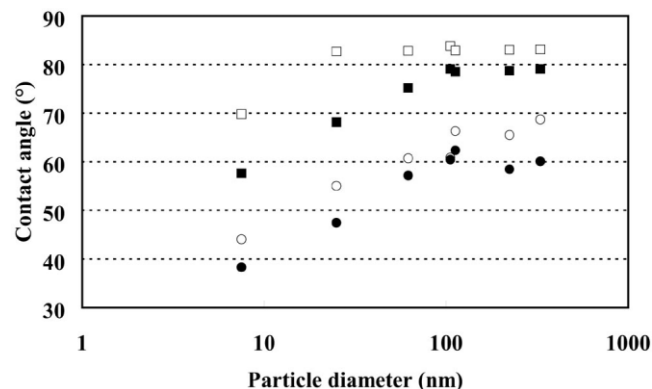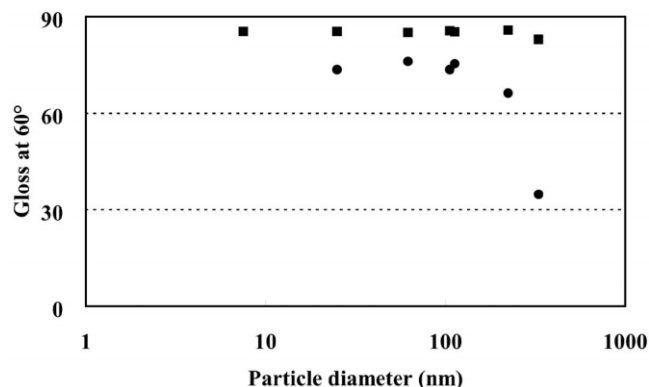

Figure 3 Relationship between colloidal silica particle diameters in films and gloss at 60°. (■): colloidal silica content to acrylic emulsion, 10%; (●): colloidal silica content to silane-hybridized acrylic emulsion, 10%.

emulsions and colloidal silicas, and were approximately constant for each particle diameter of the colloidal silica. In contrast with the gloss at 60°, organic–inorganic composite films obtained from the acrylic resin emulsion and organic-inorganic composite films obtained from the silane hybridized acrylic resin emulsion as colloidal silica of more than 100 nm were remarkably decreased.

Film transparency was evaluated by measuring the lightness value (L^*) for the organic–inorganic composite film on the black acrylic resin plate. In general, L^* of the transparent film is in the order of 0–5, and L^* of the turbid film is more than 5. Figure 4 shows the relationship between the particle diameter of colloidal silica and the L^*. The L^* of organic–inorganic composite films containing colloidal silica were higher when the particle diameter of colloidal silica was larger. The L^* of silane hybridized acrylic resin films containing larger particle diameters of colloidal silica was significantly higher than those of acrylic resin films. Figures
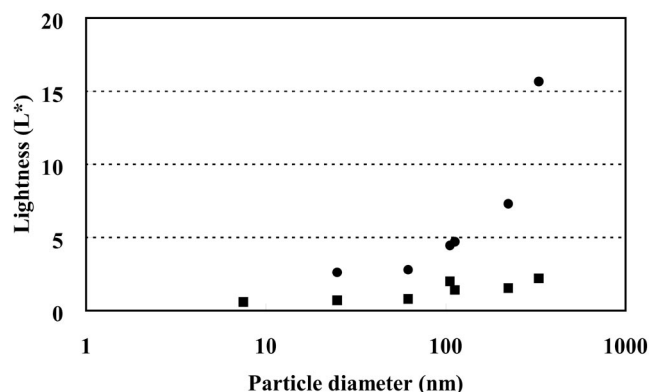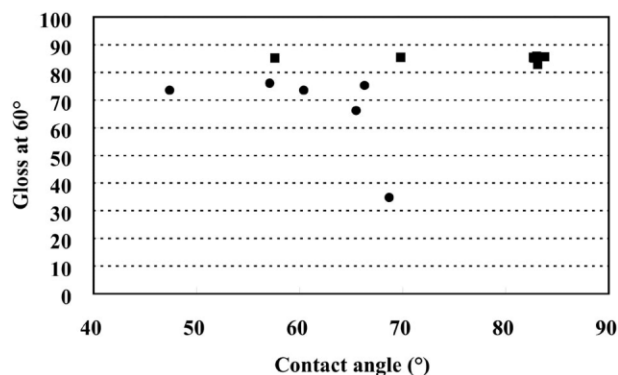

Figure 2 Relationship between colloidal silica particle diameters in films and contact angles for water. (□): colloidal silica content to acrylic emulsion, 5%; (■): colloidal silica content to acrylic emulsion, 10%, (○); colloidal silica content to silane hybridized acrylic emulsion, 5%; (●): colloidal silica content to silane hybridized acrylic emulsion, 10%.

Figure 4 Relationship between colloidal silica particle diameters in films and lightness (L*). (■): colloidal silica content to acrylic emulsion, 10%; (●): colloidal silica content to silane hybridized acrylic emulsion, 10%.
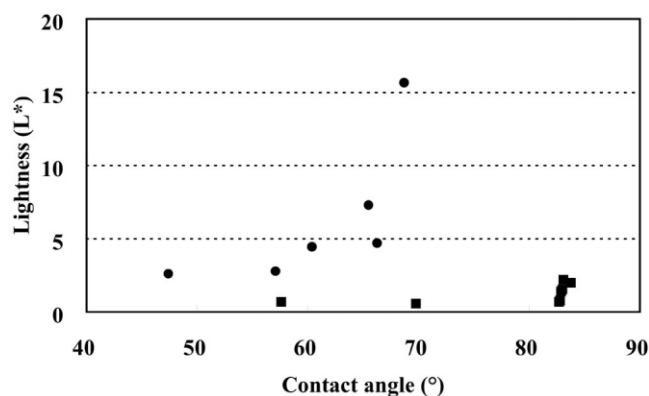
Figure 5 Relationship between gloss at 60° and contact angles for water on film surfaces. (■): the acrylic resin film containing the colloidal silica, (●): the silane hybridized acrylic resin film containing the colloidal silica.

5 and 6 show the relationship between the contact angle for water and the gloss at 60°, and between the contact angle for water and the L^*, respectively. The gloss at 60° and L^* of the acrylic resin film containing the colloidal silica were independent of the contact angle for water, but those of the silane hybridized acrylic resin film containing colloidal silica were dependent on the contact angle for water, in particular the higher contact angle, i.e., the film prepared from the colloidal silica with larger particle diameters.

These results suggest that interactions between colloidal silicas and polymer particles in silane hybridized acrylic emulsions are formed.

Morphology of film containing colloidal silica

In Figure 7, SEM images of acrylic resin composite film surfaces and the silane hybridized acrylic resin composite film surfaces are shown. In composite films containing smaller colloidal silicas, silica particles
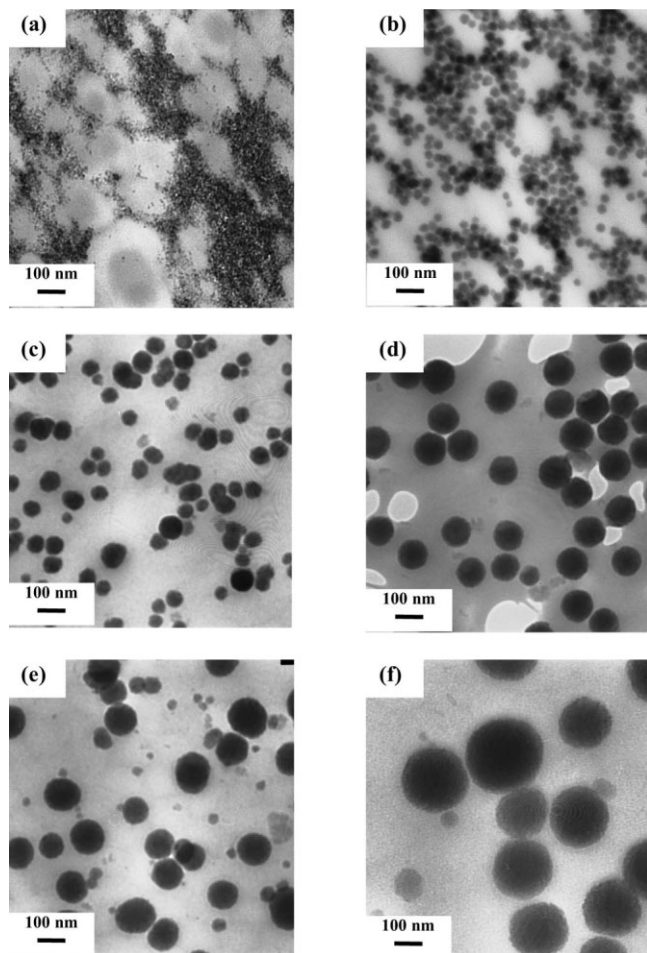

Figure 6 Relationship between lightness and contact angles for water of film surfaces. (■): the acrylic resin film containing the colloidal silica, (●): the silane hybridized acrylic resin film containing the colloidal silica.
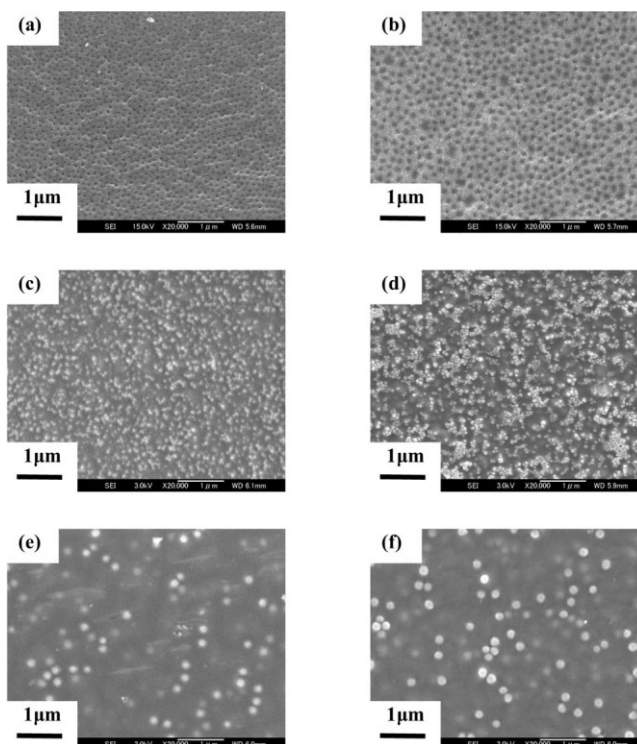
Figure 7 SEM images of acrylic resin films and silane hybridized acrylic films containing nano-silica particles: (a) acrylic resin film containing 7.5 nm colloidal silica particles, (b) silane hybridized acrylic resin film containing 7.5 nm colloidal silica particles, (c) acrylic resin film containing 62 nm colloidal silica particles, (d) silane hybridized acrylic resin film containing 62 nm colloidal silica particles, (e) acrylic resin film containing 223.5 nm colloidal silica particles, (f) silane hybridized acrylic resin film containing 223.5 nm colloidal silica particles.

were uniformly distributed on the surface of composite film. These observations support that the hydrophilicity of composite films is significantly dependent on the distribution of colloidal silicas in composite films and as shown by the results in Figure 2. Furthermore, in acrylic resin composite films, colloidal silicas existed more in composite films than on film surfaces. On the other hand, the colloidal silica in the silane hybridized acrylic resin composite film existed more on the film surface. These results support that the surface of the silane hybridized acrylic resin composite film containing smaller colloidal silica is more hydrophilic when compared with that of the acrylic resin composite film. The fact that the gloss at 60° of the silane hybridized acrylic resin composite film with larger colloidal silica was low when compared with that of the acrylic resin composite film can be attributed to the fact that the distribution of larger colloidal silica exist on the composite film surface. Furthermore, the fact that the composite film containing larger colloidal silica particles was turbid supports the above discussion. On the basis of the above results, the dif-

From these results, when colloidal silica particles of 7.5 nm are used, they tend to aggregate during the drying process during composite film formation. Even when silane-hybridized acrylic resin emulsions were used as organic components for the proportion of organic–inorganic composite films, if colloidal silica particles aggregate during film formation, some colloidal silica aggregation would disperse densely around the film's surface.

CONCLUSIONS

In this work, the preparation and characterization of organic–inorganic composite films containing colloidal silica were investigated. We demonstrated that the organic–inorganic composite film from a silane hybridized acrylic resin emulsion and colloidal silica was more hydrophilic than that of acrylic resin and colloidal silica. From the observations of SEM and TEM, it was found that some aggregations of colloidal silica particles were dispersed densely on the composite film surface. Moreover, when the smaller colloidal silica was used as an inorganic component for the preparation of organic–inorganic composite films containing colloidal silica, the surface of organic–inorganic composite films became more hydrophilic.

Figure 8 TEM photographs of thin cross sections of silane hybridized acrylic resin composite films containing various colloidal silica particles. Particle diameter: (a) 7.5 nm, (b) 25 nm, (c) 62 nm, (d) 104.3 nm, (e) 112.6 nm, (f) 223.5 nm.

ference of the dispersion state on the film surface of acrylic resin emulsions and silane hybridized acrylic resin emulsions can be explained as follows: in silane hybridized acrylic resin emulsions, surface layers of particles with the formation of Si shell layers on emulsion particles are tensed. When emulsion particles aggregate, smaller colloidal silica particles are flicked out, a number of cohesion bodies is formed, and consequently, cohesion bodies densely aggregate on surfaces surrounding films. On the other hand, in the acrylic resin emulsion, small colloidal silica particles are buried under the acrylic emulsion particles and, consequently, colloidal silica particles that are exposed on the film surface are very few.

In Figure 8, TEM images of thin cross sections of silane hybridized acrylic resin composite films containing various colloidal silica particles are shown.

References

1. Wei, Y. D.; Jin, G.; Wei, D.; Xu, Y. J. J Appl Polym Sci 1998, 70, 1689.
2. Chen, J.-I.; Chareonsak, R.; Puengpipat, V.; Marturunkakul, S. J Appl Polym Sci 1999, 74, 1341.
3. Ogomi, D.; Serizawa, T.; Akashi, M. J Biomed Mater Res A 2003, 67, 1360.
4. Uragami, T.; Okazaki, K.; Matsugi, H.; Miyata, T. Macromolecules 2002, 35, 9156.
5. Uragami, T.; Katayama, T.; Miyata,T.; Tamura, H.; Shiraiwa, T.; Higuchi, A. Biomacromolecules 2004, 5, 1567.
6. Uragami, T.; Katayama, T.; Miyata, T. Trans Mater Res Soc Jpn 2004, 29, 3295.
7. Ohshima, T.; Matsumoto, M.; Miyata, T.; Uragami, T. Macromol Chem Phys 2005, 206, 473.
8. Ohshima, T.; Matsumoto, M.; Miyata, T.; Uragami, T. Macromol Chem Phys 2005, 206, 1638.
9. Onishi, K.; Terashima, H.; Isozaki, O. Jpn. Pat. 2869443 (1999).
10. Tomita, R.; Urano, S. Kohiki, S. J Jpn Soc Colour Mater 2001, 74, 460.
11. Tomita, R.; Urano, S.; Kohiki, S. J Jpn Soc Colour Mater 2001, 74, 466.