Unique Structure and Properties of Inorganic-Organic Hybrid Films Prepared from Acryl/ Silica Nano-Composite Emulsions

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ABSTRACT: Transparent films were prepared from nano-composite emulsions, which contained nano-size core-shell-type particles (ca. 60 nm in diameter) consisting of **colloidal silica** (inorganic core, ca. 30 nm in diameter) and poly(methyl methacrylate-*co*-*n*-butyl acrylate) (organic shell). The silica content in the film could be increased up to 150 wt/wt% by keeping its homogeneity. **It was revealed that the formation of such a core-shell structure is guided by the surface sedimentation of a nonionic surfactant above its clouding point to form an organic thin layer that can provide the sites for monomer absorption and polymerization.** The thermal and mechanical properties of **the resultant nano-composite** films were evaluated by various methods and compared with those of simple blend films of the corresponding acrylic emulsion and colloidal silica. It was clarified that the high-temperature resistance of the nano-composite films can be improved by the reinforcement effect of silica particles.

Key words: nano-composites; silica; core-shell structure; mechanical properties; thermal properties; reinforcement; acrylic film

INTRODUCTION

In the past decades, many research papers have been published on a variety of nano-composite systems consisting of polymeric materials and inorganic nano-particles. These composite systems are characterized by the unique properties originating from the nano-dispersion state of the inorganic components in the polymer matrix in which the polymer matrix provides excellent processability and flexibility while the inorganic nano-particles provide high mechanical properties and thermal stability.¹⁻¹⁹ These nanocomposite materials usually exhibit much better properties than the conventional organic/inorganic composites having micro- and macro-size structures and can be used for various purposes including plastics, rubbers, fibers, adhesives, and coatings.²⁰⁻²⁶

The ordinary nano-particle composites can be obtained by simply mixing inorganic particles in polymeric matrices. However, the nano-particles dispersed likely agglomerate to form an inhomogeneous mixing state with which the nano-size effect of the particles is minimized. In order to achieve the well dispersed state of nano-particles, core/shell-type structure where the inorganic particles are embedded into polymer particles ought to be effective. With this structure, the inorganic particles are separated from each other even when the core/shell-type particles are allowed to aggregate, and the interfacial adhesion between the polymer matrix and the inorganic particles can be retained in maximum. It has been uneasy, however, to **encapsulate** such nano-particles with polymeric materials. Various physicochemical and chemical processes have ever been tried for such purposes thus far. For instance, polymers are physicochemically precipitated or adsorbed onto the surface of inorganic particles by solvent evaporation or by means of electrostatic force or chemical or biochemical techniques.³⁻⁸ More often, polymerization is performed in the presence of inorganic particles for their coating or inclusion.⁸⁻¹⁷ In this case the surface of the inorganic nano-sized particles ought to be modified in order to make it compatibilize with the organic

interface and to prevent the particles from agglomerating during the polymerization. In many cases, the modifiers are covalently bonded onto the surface of inorganic particles prior to the polymerization. For example, the silica particles are pre-treated with an acrylic siloxane coupling agent for producing nano-composite emulsion consisting of nano-scale silica (up to 33 wt%) and poly(ethyl acrylate) (PEA)⁸⁻¹⁰. Alternatively, some surfactants and amphiphilic block copolymers such as urethane-acrylate nonionomers were used for surface modification of the particles.¹³⁻¹⁶ They are usually adsorbed on the surface of the particles to afford a monomer-absorbing layer on surface.

In our previous study, we succeeded in preparing a core/shell-type nano-composite emulsion (NC emulsions) by using a simple emulsion polymerization technique. In the resultant NC emulsion, each of the nano-scaled particles consisted of a silica nano-particle core of 20~30 nm in diameter and a polyacrylate coating layer having a thickness of ca. 15~20 nm.²⁷ This nano-scaled encapsulation of silica nano-particles was possible in the presence of nonionic surfactants of low cloud point as the modifiers. Mixing of such a nonionic surfactant in an aqueous dispersion of silica particles allowed the surfactant to precipitate on the surface of the particles above its cloud point to form an organic thin layer that can provide the sites for monomer absorption and polymerization by which the stable NC emulsions having a silica-to-polyacrylate ratio up to 150/100 in wt/wt% could readily be prepared. The NC emulsion thus obtained could form stable coating films on various substrates to show various interesting properties.

It has been well known that when inorganic particles are uniformly dispersed in a polymer matrix various improved properties involving mechanical and thermal properties can be attained.⁷ With our NC emulsion silica particles may be dispersed more uniformly in the polymer matrix than with the ordinary blends of colloidal silica and polymer emulsion, and various interesting properties specific to the nano-dispersed structure are expected to be

realized. The primary distinction of the NC emulsion was in the appearance of the hybrid film because its transparency can be retained at high silica contents. This feature is very important not only for their application to optical materials,²⁵ but also to paint and ink for which color matching is necessary. In this study, therefore, we evaluate various properties of the inorganic-organic hybrid films prepared from acryl/ silica NC emulsions in relation to the nano-dispersed structure.

EXPERIMENTAL SECTION

Materials

The colloidal silica used in the present study was ADEKA Corporation ADELITE AT-50 (abbreviated as AT-50) for which the average diameter of the silica particles was reportedly 20-30 nm and the silica content was 50 wt%. A nonionic surfactant, ADEKA REASOAP NE-10 (abbreviated as NE-10), was used as the reactive nonionic surfactant, which was also the product of ADEKA Co., Japan. Sodium dodecylbenzenesulfonate (SDS), butyl acrylate (n-BA), methyl methacrylate (MMA), methacrylic acid (MAA), and other chemicals were industrial grade reagents and were used as received.

NE-10: n=10

Polymerization procedure

The procedure used for preparing NC1-4 (vide infra) is shown as an example. Prior to the polymerization, a monomer mixture consisting of 69 g of MMA, 130 g of n-BA, and 1.0 g of MAA (or 99.5 g of MMA, 99.5 g of BA, and 1.0 g of MAA for NC2) was prepared.

Into a 1 L flask equipped with a condenser, a dropping funnel, and a mechanical stirrer was charged 340 g of AT-50 under nitrogen. A solution of 0.5 g of ammonium peroxydisulfate and 5.0 g of NE-10 in 140 g of water was added dropwise to AT-50 with vigorous stirring at 60 °C. After the addition, the temperature of the mixture was raised to 70 °C. To this mixture was added dropwise 5 g of the monomer mixture, and the contents were kept at 70 °C for 1 h. Then, a mixture of 0.6 g of APS and 24 g of SDS in 50 g of water and the rest of the monomer mixture were added dropwise sequentially. The reaction mixture was kept at 70°C for an additional hour to complete the polymerization. After the mixture was cooled to room temperature, 3.6 g of an aqueous ammonia solution (25 wt %) was added to control the emulsion's pH to pH=9-10.

Silica-free emulsions having monomer compositions corresponding to those of NC1-4 were also prepared by the conventional emulsion polymerization. Each of the resultant emulsions was blended with a predetermined amount of colloidal silica AT-50 to prepare the silica-polymer emulsion blends.

Temperature dependence of a colloidal silica containing NE-10

In an ordinary test tube (A), At-10 was diluted with distilled water to obtain a colloidal silica of 33.4 wt-% in solid content. In another test tube (B), an aqueous solution of NE-10 was prepared in a concentration of 5.0 wt-%. In the other test tube (C), a mixed solution of colloidal silica (33.4 wt-%) and NE-10 (12 wt-%) was prepared. The three tubes were kept at 60 °C for 16 h, cooled down to room temperature overnight, and warmed up again to 60 °C. The precipitation and gelation feature of each solutions were observed time to time.

Preparation of nano-composite films

A certain amount of each of the emulsions was cast on a polyethylene sheet or a glass plate (100×150 mm²) with an applicator to prepare a coating film of ca. 100 µm in thickness. The coating film was dried at 50 °C for 16 h to obtain a solid film having a thickness of ca. 40 µm.

Measurements

Tensile properties of the films were measured on an Orientec (Tokyo) STA1150 tensiometer. The sample films were cut into a size of 15×50 mm², and each specimen was stretched at a crosshead speed of 30 mm/min at 25 °C. The tensile properties were automatically calculated by the computer connected to the machine, and the average of at least six measurements was taken for each measurement. Dynamic mechanical analysis (DMA) was performed on a Rheogel-E4000 in tension mode at 32 Hz in a temperature range of -30~250 °C at a heating rate of 3 °C/min under nitrogen. DSC analysis was conducted at a heating rate of 10 °C/min on a Shimadzu DSC-50 thermal analyzer under nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments Hi-Res Modulated TGA 2950 analyzer under nitrogen or in air at a heating rate of 15 °C/min.

RESULTS AND DISCUSSION

Preparation of nano-composite (NC) emulsions

Several series of NC emulsions consisting of acrylic resin and silica particles were prepared according to the previously reported method²⁷, which is briefly described in the Experimental section. We chose three monomer compositions for the acrylic resins for preparing the NC emulsions; MMA: *n*-BA= 35:65, 50:50, and 65:35 (wt/wt%). The

resultant emulsions consisted of hybrid particles of 50~60 nm in diameter, and in each of which a silica particle of 20~30 nm in diameter was surrounded by an acrylic layer cage. We also prepared silica-free acrylic emulsions having identical monomer compositions as control samples. Hereafter, these silica-free acrylic emulsions or the acrylic resins **obtained from them** are called ACn (x:y) where n denotes the sample number corresponding to the above monomer composition (x:y) of acrylic resin; MMA: *n*-BA= x: y as AC1 (35:65), AC2 (50:50), and AC3 (65:35). The NC emulsions are also named NCn-X by using the sample number (n) expressing its monomer composition of the acrylic resin (identical with the n of ACn) and its silica content (X) as NC2-1 (silica: acryl=35: 100 (w/w)), NC2-2 (silica: acryl=50: 100), and NC2-3 (silica: acryl=60:100). The same abbreviations are used for the films prepared from the emulsions, although we sometimes add a term, emulsion or film, after the abbreviation for easier understanding. The acrylic emulsion AC2 used for preparing NC2-X is currently utilized as the main component of the ordinary acrylic wall paints,²⁸ whereas the acrylic compositions of AC1 and AC3 for preparing NC1-X and NC3-X are softer and harder, respectively, consisting of different *n*-BA compositions.

As we reported before, the NC emulsions can be prepared by using a reactive nonionic surfactant NE-10 having a lower cloud point (T_c) of 40 °C in the pre-polymerization step. This surfactant is first mixed with colloidal silica at temperature lower than the T_c, and it is then allowed to deposit by raising the temperature to 60 °C that is significantly higher than the T_c. During this process the depositing surfactant mostly sediments on the surface of the silica nano-particles to make an over-coat layer that can accommodate monomer layer in the initial pre-polymerization. Table S1 compares the typical preparations of acrylic emulsions in the presence and absence of NE-10, which were selected from our data previously reported.²⁷ It was evident that the acrylic emulsion finally obtained without adding a nonionic surfactant in the initial pre-polymerization (Run No.1) consisted of both large (158 nm in average

diameter) and small particles (35 nm in average diameter) because of the presence of the un-coated silica particles (20-30 nm in average diameter). In this particular case, only an anionic surfactant SDS was used as the emulsifier which ought to have no specific interaction with silica particles. Use of the other anionic surfactants such as sodium dodecylbenzenesulfonate (NEOPELEX G-15, Kao Corp.), sodium alkyl diphenyl ether disulfonate (PELEX SS-H, Kao Corp.), sodium polyoxyethylene alkyl ether sulfate (EMAL D-3-D, Kao Corp.), and ammonium lauryl sulfate (LATEMUL AD-25, Kao Corp.) gave similar results. Even by using a nonionic surfactant having higher T_c such as ADECA REASOAP NE-30 ($T_c > 100\text{ }^{\circ}\text{C}$, abbreviated as NE-30), bi-modal size distribution of the emulsion particles was observed. The single modal size distribution of the emulsion particles was obtained only in the presence of NE-10 or other nonionic surfactants showing low T_c in which each silica nano-particle was enveloped to form a core-shell nano-particle. The use of the reactive surfactant NE-10 was effective for increasing the emulsion stability and not essential for constructing the acryl-silica core-shell structure in the NC emulsion. The related unreactive nonionic surfactants showing low T_c were also effective for preparing the hybrid NC emulsion.

Figure 1 compares the changes in solution states of an original colloidal silica solution (A: free of NE-10), an aqueous solution of NE-10 (B), and a NE-10-containing colloidal silica solution (C) with temperature variation. The colloidal silica (A) showed no change in appearance with the temperature change, keeping a colloidal state of white in color. In contrast, the solution of NE-10 turned turbid on warming at $60\text{ }^{\circ}\text{C}$, and gel-like precipitates sedimented on the bottom part of the test tube when kept at $60\text{ }^{\circ}\text{C}$ for 16 h because of the insoluble nature of the nonionic surfactant above T_c . The precipitates, however, were quickly re-dissolved by cooling to room temperature. The colloidal silica containing NE-10 became highly cloudy on warming at $60\text{ }^{\circ}\text{C}$ and separated into two layers. The bottom layer consisted

of both NE-10 and colloidal silica particles, forming a soft gel. This phase-separated feature was not broken even when the system was cooled down to room temperature, i.e., below T_c . These results indicated that the surfactant NE-10 depositing above T_c included the silica particles together and precipitated as gel. This gel state, once formed, did not turn to sol again even at higher temperature. The same behavior was also observed by using a non-reactive nonionic surfactants as EMULGEN 108 (a polyoxyethylene lauryl ether obtained from Kao Corp. $T_c = 40\text{ }^{\circ}\text{C}$), but not by using nonionic surfactants showing higher T_c such as EMULGEN 120 ($T_c = 98\text{ }^{\circ}\text{C}$) and 130K ($T_c > 100\text{ }^{\circ}\text{C}$), both non-reactive polyoxyethylene lauryl ether-type made by Kao Corp. as well as by using reactive-type NE-30 ($T_c > 100\text{ }^{\circ}\text{C}$). With these nonionic surfactants, the surface deposition is not possible.

All the above results strongly suggest that the nonionic surfactant such as NE-10 works as a specific emulsifier in the initial stage of polymerization to generate an organic thin layer on each of the colloidal silica particle that can efficiently allow the formation of NC composite emulsions.

Figure 1. Temperature-dependent solution states of a colloidal silica (A: 33.4 wt-% in solid

content), an aqueous solution of NE-10 (B: 5 wt-%-concentration), and a mixed solution (C) of colloidal silica (33.4 wt-%) and NE-10 (12 wt-%). The arrow shows the interface below which sediments are present.

Film-forming ability of the NC emulsions and film transparency

Each of the NC emulsions obtained in the preceding section was fabricated into a film by the ordinary casting method using a polyethylene substrate. Table 1 summarizes the film-forming abilities of the NC emulsions. It is suggested here that the film formation depends on the balance of the softness related with the glass transition temperature (T_g) of the acrylic resins and the hardness related with the silica content.

Table 1. Film forming ability of the nano-composite emulsions. ^{a)}

Silica content		MMA: <i>n</i> -BA=35 :65 (w/w)				MMA: <i>n</i> -BA=50: 50 (w/w)			
		NC film		BL film		NC film		BL film	
Silica : Acryl (wt: wt)	(vol-%)	Sample	Film forming ability ^{b)}	Sample	Film forming ability ^{b)}	Sample	ability ^{b)}	Sample	ability ^{b)}
0 : 100	0	AC1	-(s)			AC2	+		
35 : 100	15	NC1-1	-(s)	BL1-1	-(s)	NC2-1	+	BL2-1	+
50 : 100	20	NC1-2	-(s)	BL1-2	-(s)	NC2-2	+	BL2-2	+
60 : 100	23	NC1-3	+	BL1-3	+	NC2-3	+	BL2-3	±
85 : 100	29	NC1-4	+	BL1-4	+	NC2-4	-(b)	BL2-4	-(b)
100 : 100	33	NC1-5	+	BL1-5	+	NC2-5	-(b)	BL2-5	-(b)
125 : 100	38	NC1-6	+	BL1-6	+	NC2-6	-(b)	BL2-6	-(b)
150 : 100	43	NC1-7	+	BL1-7	±	NC2-7	-(b)	BL2-7	-(b)
175 : 100	47	NC1-8	-(b)	BL1-8	-(b)				
200 : 100	50	NC1-9	-(b)	BL1-9	-(b)				

^{a)} The sample emulsion was cast on a glass plate and dried at *°C for * h.

^{b)} +: The film was successfully prepared.

±: The film was somewhat brittle, but it could be peeled off from the glass plate to obtain a crack-free film.

-(s): The substance was soft and sticky.

-(b): The film was too brittle to peel off from the glass plate.

The T_g values of AC1 (MMA:*n*-BA=35:65), AC2 (50:50), and AC3 (65:35) were -4 °C,

21 °C, and 43 °C, respectively, as determined by the DSC analysis of the polymers. A general decreasing tendency of T_g with increasing the n-BA content coincides with the order of softness of the acrylic resins²⁹. Since the AC1 was a gummy material, even NC1-1 and NC1-2 having low silica contents did not form self-supporting films. In these cases, the resulting films were too soft and sticky to be peeled off from the substrate. When the silica content was further increased, the films became enough rigid to be self-supporting. Thus, transparent films were successfully obtained from NC1-4 ~ NC1-7 in which the silica-to-acryl composition increased from 85 for NC1-4 to 150 (wt/wt%) for NC1-7. Above this composition, the film became too brittle to be crack-free, and NC-8, for example, having a silica-to-acryl composition of 175 (wt/wt%), could not be fabricated into a transparent film even on a glass plate.

On the other hand, AC2 consisting of a harder polyacrylate ($T_g = 21$ °C) gave a transparent self-supporting film in silica-free state. The NC emulsions NC2-1, NC2-2, and NC2-3 could also be fabricated into similar transparent films whose silica-to-acryl compositions were in a range of 35-60 (wt/wt%), whereas no crack-free film was obtained from NC2 having a silica content higher than 60 (wt/wt%) because of the brittle nature. In the NC3 series consisting of harder polyacrylate, it was impossible to peel off a crack-free film in any of the silica-acryl compositions, although the as-formed films NC3-1~ NC3-3 having a silica-to-acryl composition up to 60 (wt/wt%) were all transparent (data are not involved). Even in the film of NC3-1 having the lowest silica-to-acryl composition of 35 (wt/wt%) crack formation attended when peeled off from the substrate. Since the hardest polymer AC3 ($T_g = 43$ °C) gave a brittle film, its involvement of silica nano-particles only enhanced the fragileness of the resulting film.

For comparison, simple silica-acryl blend emulsions were also prepared by mixing the AC emulsions and colloidal silica AT-50. Both the blend emulsions and their cast films

are abbreviated as BLn-X where n and X denote the aforementioned sample number and silica content, respectively, as those of NCn-X. The film forming ability of BLn was not so different from that of NCn at most of the acrylic compositions and silica contents. Significant difference was observed only for the blend films BL1-7 and BL2-3 having higher silica contents, which became more brittle than the corresponding NC films (NC1-7 and NC2-3) (Table 1).

Figure 2 compares the appearances of the NC1 and BL1 films having identical silica contents. The size of the glass substrate used for the film casting was $100 \times 150 \text{ mm}^2$, and the average thickness of the film formed was 40~45 μm . While the BL1 film became translucent with white edges at a low silica-to-acryl composition of 125 (wt/wt%) and whole white above this composition, the NC1 film turned white in color at a silica-to-acryl composition as high as 200 (wt/wt%). Since the whitening is attributed to the aggregation of silica particles, the NC structure ought to be effective for suppressing the particle aggregation. It is because each silica particle is separated from each other with the core-shell structure. It is noteworthy that the volume content of silica is 47 % in the transparent NC1-8 film while it reaches 50 % in the white NC1-9 film. In the latter film, therefore, the amount of organic matrix may be below a critical level, making it difficult to keep the homogeneity of the hybrid particles. Consequently, the film forming ability of the NCn emulsions is strongly influenced by the silica content and the related soft/hard balance of the resultant composite films.

As we reported elsewhere, the core-shell structure of NC emulsion is effective for preventing the aggregation of silica particles and for homogeneous distribution of silica particles in making its cast film. In the present NC emulsion, however, no covalent bonding is present between the silica surface and acrylic resin, and the silica particles are sometimes excluded out of the acrylic shells during the drying process of the cast films to form local

aggregation structure. Probably, the cage of the silica particle is not strong because of the rubbery nature of acrylic resin consisting of higher n-BA compositions and the covering of the silica surface with the surfactant NE-10. In fact, the FE-SEM photo of the surface of a **NC1-4** film indicated several particles agglomerated in several parts (shown by arrows in Figure S1 (a)). The TEM image also indicated such agglomeration, although the size of the agglomeration or the number of particles in direct aggregation is not so large (Figure S1 (b)) as that observed in the blend film prepared by mixing colloidal silica and acrylic emulsion. This difference in particle agglomeration causes the different properties of the cast films prepared from NC and BL emulsions.

Figure 2. Comparison of the appearances of NC1 and BL1 films.

Tensile properties of NCn films

We evaluated the mechanical properties of the NCn films obtained above and compared with those of the corresponding BLn films. **Figure 3** compares the representative stress-strain curves (S-S curves) of the NC1 and BL1 films. Since the basic polyacrylate AC1 of NC1 and BL1 was gummy at room temperature, its tensile properties could not be measured. Both NC1 and BL1 films involving silica nano particles became stronger with increasing the silica content. As indicated in **Figure 3a** (enlarged), the yield strength and strain of the BL1 films became higher and lower, respectively, with increasing the silica content (from BL1-4 to BL1-7). The NC-1 films also exhibited similar behaviors, but their yield strength and yield strain were higher and lower, respectively, compared to those of the corresponding BL1 films having identical silica contents. NC1-4 showed much higher elongation than NC1-6 in spite of having a similar yield stress. Interestingly, each of the NC1 films showed a plateau region above the yield point, and the NC1-4 film containing 29 vol% of silica indicated a wide plateau region extending to over 400 % in strain, while the NC1-7 film containing 43 vol% of silica showed a very limited plateau region (c.a. 1 %). Since no plateau region was shown by the BL1 films, this elastic behavior shown above the yield point ought to be characteristic of the NC1 films in which the nano-particles are distributed more homogeneously with smaller particle agglomeration.

Figure 3. Stress-strain curves of NC1 and BL1 films. The left (a) is the enlarged view of the right (b).

The tensile modulus, elongation, and strength of the NC1 and BL1 films are plotted as a function of silica content in Figure 4 (The numerical data are summarized in Table S2). Evidently, both the modulus and strength dramatically increased with increasing the silica content in both NC and BL films, while their elongation at break decreased oppositely. Little difference was observed in the tensile modulus and strength of the NC1 and BL1 films having identical silica contents. The increased mechanical properties can reasonably be attributed to the reinforcement effect of silica particles.

Figure 4. Changes in (a) tensile modulus, (b) elongation, and (c) strength as a function of silica particle content for NC1 (□) and BL1 (●) films. The error bars are for average differences from the averaged values.

Figure 5 compares the representative S-S curves of the NC2 and BL2 films. Note that the base acrylic polymer AC2, having a T_g at 21 °C (by DSC), showed a typical strain-stress behavior of the ordinary plastic films; the stress gradually increased from its yield point to its fracture point that reached 450 % in elongation. Both the NC2-3 and BL-2-3 films involving silica particles also showed similar behaviors, but their modulus became much higher and the elongation became lower.

Figure 5. Stress-strain curves of the NC2, BL2, and AC2 films. The left (a) is the enlarged view of the right (b).

As plotted in **Figure 6** (The numerical data are summarized in **Table S3**), the tensile modulus increased with increasing the silica content while the elongation decreased oppositely, while the tensile strength was not much influenced by the silica content. Little difference was observed between the tensile properties of NC2 and BL2, probably because the hard or plastic

nature of the matrix resin AC2 reflected them.

Figure 6. Changes in (a) tensile modulus, (b) elongation, and (c) strength as a function of silica particle content for NC2 (□) and BL2 (●) films. The error bars are for average differences from the averaged values.

The above results revealed that only NC1-4 showed an interesting plastic region in the S-S curve. The drop of stress of the NC1 and BL1 films ought to be caused by the crazing taking place between the silica particles and the matrix polymer around the yield point. The silica particles in NC1-4 film, however, still retains strong interaction with the matrix even passing the yield point, probably because the nano-size silica particles may be involved in the entanglement of polymer chains and the silica-acrylic polymer chain interaction is to be maximum at this silica content as Espiard et al. suggested before.⁸ In the corresponding BL1 films, on the other hand, the dispersion state of the silica particles is not homogeneous, and the stress is likely to be concentrated on silica-poor parts after the yield point, causing the decreased stress with strain. In other words, the higher stress after the yield point of NC1 is another evidence for the well-dispersed state of silica particles in NC1.

Dynamic mechanical properties of NC films

Figure 7 shows typical DMA curves of the NC1 films. Evidently, the storage modulus (E') of the NC films became larger with increasing their silica content, particularly above T_g of the acrylic resin which was determined to be 10 °C from the peak of $\tan \delta$ curves (Figure 7b). Note that that the $\tan \delta$ value decreased with increasing the silica content although no T_g change was recorded with it. The reinforcement effect of silica is therefore clearly shown for the NC1 films.

Figure 7. Temperature dependences of storage modulus (a) and loss tangent (b) of the NC1 films

Figure 8 shows the DMA curves of the NC2 and the related films. Different from the above polymer (AC1), the acrylic polymer AC2 exhibited a typical glassy feature in the DMA curve; E' dropped sharply around 50 °C correspondingly to the glass-rubber transition. From the $\tan \delta$ peak, the T_g of AC2 was determined to be 54 °C (Figure 8b). The E' of NC2 containing silica particles was higher than that of AC2, especially, above the T_g . For example, the E' values of NC2-1 and NC2-3 were about 3.7 MPa and 19 MPa, respectively, at 80 °C, while that of AC2 was about 1.0 MPa. Below T_g , however, the increase in modulus of NC2 was rather limited (from 1.6 GPa of AC2 to 2.8 GPa of NC2-3 at -20 °C). No clear T_g change was also shown here. Similar hybridization effects on the T_g and E' changes were ever reported for butyl acrylate/styrene copolymer containing nano silica particles.³⁰ For the simple blend films BL2, the effect of nano silica on the E' change was much smaller, and the E' change exhibited irregular peaks (see Figure 8 for BL2-3), which may be attributed to the

inhomogeneous distribution or the large local aggregation of the particles in the blend films.

Figure 8. Temperature dependences of storage modulus (a) and loss tangent (b) of the AC2-based films

Thermal resistivity of the NC films

Typical TGA curves of the NC1, NC2, and the related films are compared in Figure S2. The thermal data involving the temperatures of 5 ($T_{5\%}$) and 10 wt% losses ($T_{10\%}$) are determined from these curves and summarized in Table 2. Both AC1 and AC2 started to decompose around 300 °C and almost lost their weight at 410 °C in nitrogen atmosphere. They showed similar $T_{5\%}$ and $T_{10\%}$ values both in nitrogen and in air, although the values were slightly lower in air. On the other hand, the $T_{5\%}$ and $T_{10\%}$ of NC1-3 in nitrogen were 308 and 335°C, respectively, whereas those of NC2-2 were 349 and 364°C, respectively. NC1-3 showed a considerably faster initial weight loss. In air, the same values ($T_{5\%}$ and $T_{10\%}$) of NC1-3 and NC2-2 were (277 and 294°C) and (275 and 285°C), respectively, being even lower than those of AC1 and AC2 in air, although the residual weights of NC1-3 and

NC2-2 at 500 °C were as high as 36-37 wt% and 32-33 wt%, respectively. These residual weights were almost coincident with their silica contents, 38 and 33 wt%, respectively, indicating that silica components had remained without decomposition up to 500 °C. Since silica particles (involved in Figure S2a) showed a small weight loss (4.7 wt% at 100°C and 6.0 wt% at 500 °C) due to the silanol condensation at surface, their weight loss may have contributed to the relatively fast weight losses of NC1-3 and NC-2-2. Assuming that the silica particles have no special effect on the thermal degradation of the acrylic polymer, an ideal TGA curve of NC1-3 could be predicted by combining the TGA curves of AC1 and silica particles with their weight fraction considered. Figure 9 compares the real TGA curves of NC1-3 with the predicted curves. Evidently, the weight loss of NC1-3 was lower than the predicted below 300 °C. We think that this behavior may be attributed to the homogeneous dispersion state of the particles by which the silanol condensation among the silica nano-particles can be reduced. In the NC1, the silica surface must effectively be covered with nonionic surfactant, suppressing the rate of silanol condensation.²⁸ Above 300 °C, in return, NC1-3 showed larger weight loss than predicted, especially under nitrogen. Probably, the acidic silanol groups on the silica particles may have accelerated the decomposition of acrylic matrix. It was also shown here that the decomposition proceeds much faster in air than in nitrogen.

The initial weight losses of AC2 at 100 and 200 °C in nitrogen reached 0.7 and 0.9 %, respectively, which were significantly higher than the corresponding values of AC1 (Figure S2b). We think that the higher T_g of AC2 may have hindered the migration of water through the film during the drying process to increase the water content in the resulting film.

Table 2. TGA data of nano-composite films.

Sample	Silica content (wt%)	In N ₂					In air				
		Weight loss (wt%)		T _{5%} ^{a)} (°C)	T _{10%} ^{b)} (°C)	residual weight at 500°C (%)	weight loss (wt%)		T _{5%} ^{a)} (°C)	T _{10%} ^{b)} (°C)	residual weight at 500°C (%)
		at 100°C	at 200°C				at 100°C	at 200°C			
silica	100	---	---	---	---	---	4.0	5.0	192	>500	94
AC1	0	0.2	0.3	347	363	2.5	0.3	0.6	297	310	1.5
NC1-3	38	0.9	1.3	308	335	37	0.9	1.4	277	294	36
AC2	0	0.7	0.9	350	368	2.7	0.6	2.1	297	307	0
NC2-2	33	0.7	1.1	349	364	33	0.8	2.5	275	285	32
BL2-2	33	1.1	1.5	348	365	34	2.9	4.2	266	283	32

^{a)} Temperature at 5% weight loss.

^{b)} Temperature at 10% weight loss.

As shown in **Figure 9**, the weight loss of NC2-2 below 250 °C was lower than the predicted one. The residual weights of NC2-2 at 500 °C were 33 % in nitrogen and 32 % in air, which were coincident with its silica content, 33 %, again. Evidently, the corresponding blend film BL2-2 exhibited higher weight losses than NC2-2, suggesting the silanol condensation induced among the silica particles in agglomeration in the film. Consequently, the homogeneity of the NC films in terms of particle distribution is very efficient for the decreased weight loss below 300 °C or increasing the thermal stability.

As described in the preceding paper, a white paint prepared by using NC1-type hybrid emulsion showed characteristic anti-flaming property.²⁹ This property must be attained not only by its low organic content but also by the continuous formation of moisture upon heating.

Figure 9. Comparison of the real TGA thermograms of NC1-3 and the theoretically predicted ones from those of AC1 and silica particles in nitrogen and in air.

CONCLUSION

Various NC films were prepared from hybrid emulsion incorporating nano-size silica particle in the emulsion core. Among them, NC1-3~6 containing 60-150 wt/wt % silica relative to acrylic resin were found to have both stiffness and toughness enough to be utilized for practical purposes such as paint resins. DMA analysis supported their relatively high tensile modulus at high temperature. TGA analysis also assured their heat-resistance up to 250 °C, although the incorporated silica slightly accelerated thermal decomposition of the acrylic resin above 250 °C in air. It was confirmed that the NC films are generally superior to the BL films directly prepared by mixing colloidal silica and

acrylic emulsion in terms of the homogeneity of particle distribution in the cast films as well as of the mechanical strength at high temperature. The transparency of the NC films was excellent, being very important for application of these materials to proper color decoration.

It was also revealed that the nonionic surfactant NE-10 is allowed to sediment on the colloidal silica surface above its clouding point, forming of an organic thin layer that can work as the site for monomer absorption and polymerization.

Contrary to the conventional acrylic emulsion whose solid part is almost exclusively derived from the petroleum resources, the solid part of the present NC emulsion contains up to 60 wt% of silica. The usage of such a new composite material as architectural paint is effective for reducing the consumption of the petroleum resources in the field of paint industry. The reduction of organic content in paints is also efficient for reducing the emission of CO₂ by their incineration after use, considering that paints, once processed, cannot be recycled.

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