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ORIGINAL CONTRIBUTION

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An effective cross-linking of polymer layer on monodisperse, poly(maleic anhydride-styrene)-modified colloidal silica particles and properties of the composite

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Summary The cross-linkings of the surface polymer layer on mono disperse, poly(maleic anhydride-styrene)-modified silica particles by the reaction with diisocyanate were studied. The extent of cross-linking was estimated by the weight decrease by immersing the particles in the buffer solution of pH 2.0, 4.0 and 9.0 at a room temperature for 24 h. The reaction of the polymer-modified silica with 1,6-diisocyanatohexane afforded relatively stable composite particles which lost less than 5 wt% of the polymer in aqueous solution in the pH range 2.0–9.0. The diisocyanate was a preferable cross-linker to 2,4-diisocyanatotoluene in terms of stability in acidic or basic aqueous solution. The flexibility of the cross-linker molecule possibly plays an important role in the cross-linking reaction. The carboxyl and amino groups were formed by treating the cross-linked composite particles with diluted HCl solution; 5–6 and 0.5–1.1 μmol g^{-1}, respectively. The cross-linked composite particles exhibited the characteristic property of ζ-potential, -44 to -47 mV and -102 to -107 mV in a neutral aqueous solution and ethanol, respectively.

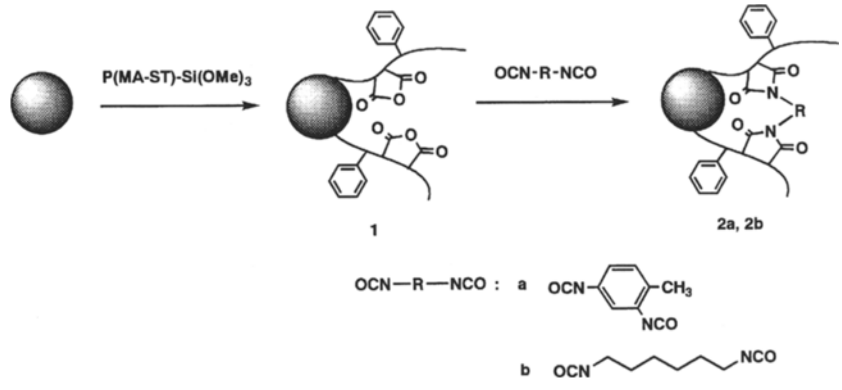
Key words Cross-linking of polymer layer – composite particles – poly(maleic anhydride-styrene) – monodisperse colloidal silica – surface modification

Introduction

Fabrication of physical and chemical properties on ultrafine particles is promising in new developments in materials chemistry [1–3]. We have been functionalizing monodisperse inorganic colloidal particles, mainly silica, by polymer modification. If it is possible to control surface potential or hydrophobicity by modification of colloidal particles by polymeric materials, the modified particles have potential for new applications of composite materials; for instance, two- or three-dimensional particle-arrayed substrate [2, 4–6].

In this regard, we have developed effective modification methods of monodisperse colloidal silica [7–11], in which the modification using polymeric silane coupler is useful and convenient. But, the procedure usually gives the composite particles having a shortcoming for the stability in acidic or basic atmosphere, because of hydrolysis cleavage of Si–O–Si bonds between the silica and the polymer. A previous paper [1] described an effective polymer modification procedure in which the reaction of the colloidal silica with trimethoxysilyl-terminated poly(maleic anhydride-styrene) coupling agent (P(MA-ST)-Si(OMe)$_3$), followed by cross-linking with di- or tri-ols and di- or tri-amines, gave an efficient polymer coating and simultaneous formation of carboxyl or amino group, respectively. However, the reactions with the alcohols and the amines did not make sufficient cross-linking among polymer chains and lost 9–12 wt% of the bound polymer after

Scheme 1 Modification of colloidal silica by poly(maleic anhydride-styrene) and cross-linking by diisocyanate



immersing the cross-linked composites in the pH 4.0 buffer. In this study, improvements of the linkage in the polymer layer on poly(maleic anhydride-styrene)(P(MA-ST))-modified silica using the reaction of maleic anhydride moiety with the diisocyanate as a cross-linker, as shown in Scheme 1, and the characteristic properties of the resulting particles were investigated.

Experimental

Materials

Monodisperse colloidal silica suspended in aqueous ethanol, containing 27 wt% SiO_2 of 140 nm diameter and 23 wt% H_2O, was kindly offered by Catalysts & Chemicals Ind. Ltd. A polymeric coupling agent of P(MA-ST)-$Si(OMe)_3$ with number-average molecular weight (M_n) of 9000 was prepared by the method described previously [10].

Measurements

Infrared spectra were recorded with a diffuse reflectance method on a JEOL-JIR5500. Spectrophotometric absorption was measured on a JASCO V-520S. Scanning electron micrographs (SEM) were taken by a JEOL-JCX733. Particle size distribution was measured by a dynamic light-scattering method on Ohtsuka DLS-700S using ethanol solvent.

Preparation of composite **1**

The reaction of the colloidal silica with the polymeric coupler and successive isolation of composite **1** were carried out by the method described previously [10].

Reaction of composite **1** with diisocyanate

A typical run was carried out as follows. To suspension of composite **1** (0.4 g) in 30 cm^3 dry *N*,*N*-dimethylformamide (DMF) was added 0.8 g 1,6-diisocyanatohexane and 0.05 cm^3 dry triethylamine. The mixture was kept at 70 °C for 12 h in a nitrogen atmosphere. Centrifugal separation from aqueous methanol solution (90 vol%) three times, methanol and acetone, and successive drying under reduced pressure gave the composite **2b**.

Determination of bound polymer

The amount of bound polymer to silica was estimated from the weight loss during a temperature elevation from 100 °C to 800 °C, after keeping a 100 °C for 1 h, by the thermal gravimetric analysis.

Determination of carboxyl group on the particles

A mixture of 20 mg composite particles, 15 mg *N*,*N'*-dicyclohexylcarbodiimide and 5 cm^3 chloroform was stirred at 4 °C for 2 h. After 10 mg *p*-nitrophenol was added to the suspension, the mixture was kept stirred at 4 °C for 12 h. A centrifugation from the acetone suspension and drying under vacuum gave the esterated particles. The surface carboxyl group was estimated by the concentration of *p*-nitrophenolate ($\varepsilon = 18\,000$ at 400 nm) in the supernatant, which was obtained by a centrifugation after the treatment of the particles (10 mg) with 5 cm^3 diluted aqueous ammonia (4%).

Determination of amino group on the particles

To suspension containing the composite particles (30 mg) in 20 cm^3 ethanol, 10 cm^3 0.1 M picric acid ethanolic solution was added. The suspension was oscillated by ultrasonic wave irradiation and the resulting particles was separated from 20 cm^3 dichloromethane solution by a centrifugation five times. The paste was again suspended in 5% *N*,*N*-diisopropylethylamine dichloromethane solution (5 cm^3) by ultrasonic wave irradiation and the picrate anion on the composite was transferred into the solution as *N*,*N*-diisopropylethylammonium picrate. A centrifugal separation of the picrate from the particles was repeated three times and the total volume of the solution was adjusted to 50.0 cm^3 with dichloromethane. The amino group was estimated by the absorbance of the picrate in the solution at 358 nm ($\varepsilon = 14\,500$).

Measurements of ζ-potential and isoelectric point

ζ-potential of suspended particles in the pH 7.0 buffer (M/30 KH_2PO_4 + M/30 Na_2HPO_4) consisted of 0.1 M NaCl or in ethanol was measured by a light-scattering electrophoresis on Ohtsuka ELS-800. The isoelectric point was determined from the ζ-potential in the buffer solution from pH 2.0 to 5.0 that consisted of 0.1 M NaCl; the buffer was prepared from M/15 Na_2HPO_4 and M/30 citric acid.

Results and discussion

Cross-linking with diisocyanate

The reaction of succinic anhydride or maleic anhydride with an isocyanate is known to form the cyclic imide under a mild condition, which is relatively stable in a weak acidic or basic atmosphere. It has been also reported that the imide group behaves as a relatively stable cross-linkage segment in polyurethane [12]. If the polymer chains on P(MA-ST)-modified silica particles were linked to each other via covalent bond, like putting a net around silica particles, the polymer layer was protected by the linkage from pealing out of the polymer chains through the hydrolysis of the siloxane bond in an acidic or basic atmosphere. Thus, we examined the cross-linking between the polymer chains of P(MA-ST) on the silica surface employing the reaction of maleic anhydride moiety on composite **1** with 1,6-diisocyanatohexane or 2,4-diisocyanatotoluene. In Fig. 1, the time dependence of weight increase on silica particles by the reaction with the diisocyanates is shown. The amount of bound polymer attained mostly constant value, 37 mg g^{-1}, after 24 h in the reaction with 2,4-diisocyanatotoluene, while the amount increased with the time even after 48 h in the reaction with 1,6-diisocyanatohexane. In the latter case, oligomers formed by the polymerization of the diisocyanate are probably grafted on composite **1**. The oligomers presumably consisted of 1,3-diazacyclobutan-2,4-dione or cyanurate group made by dimerized or trimerized cyclization of the isocyanate group, respectively [13]. In the reaction with 2,4-diisocyanatotoluene, the formation of the oligomers seems to be difficult, because of the steric hindrance of 2-position-NCO group. The formations of maleimide group on composites **2a** and **2b** by the cross-linking reaction of maleic anhydride moiety with the diisocyanate were confirmed by the appearance of IR absorption bands at 1712 and 1730 cm^{-1}, respectively (Fig. 2), which were assignable to stretching vibrations of carbonyl groups. The extent of cross-linking using the isocyanate was estimated by the weight decrease on the silica particles after immersing the composite in each aqueous solution of pH 2.0, 4.0 and 9.0 at room temperature. In Figs. 3 and 4, the weight decreases of the composites **2a** and **2b** by the acid and the base treatments are shown. The weight decrease, which reflects the cross-linking among P(MA-ST) chains using 1,6-diisocyanatohexane, were almost of less than 5 wt% by the treatment at pH 2.0, 4.0 and 9.0. Since the weight decrease of composite **1** after immersing the particles in the pH 4.0 buffer was 33 wt% [11], the result indicated that the degree of cross-linking among the P(MA-ST) chains bound to the silica was considerably high. The weight decrease at each pH condition is mostly independent of the reaction time in the cross-linking. Therefore, these results suggest that the reaction for 6 h is enough to cross-link P(MA-ST) chains. On the other hand, the reaction with 2,4-diisocyanatotoluene led to relatively larger weight decreases by the acid or base treatment than the reaction

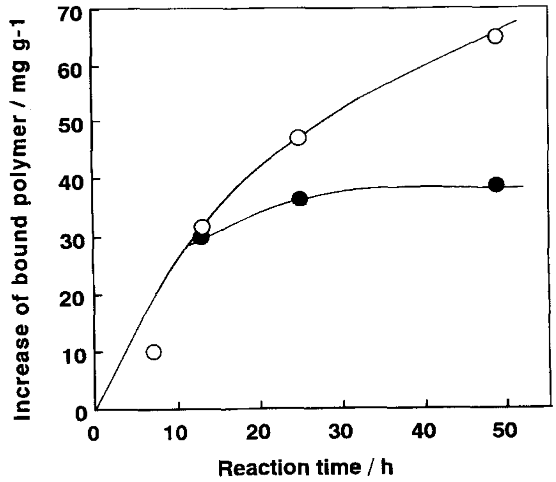


Fig. 1 Time dependence of bound polymer to silica in the reaction with 1,6-diisocyanatohexane (○) and 2,4-diisocyanatotoluene (●). The reactions were carried out by using composite **1** (0.2 g) and diisocyanate (0.2 g) in dry DMF (15 cm^3)

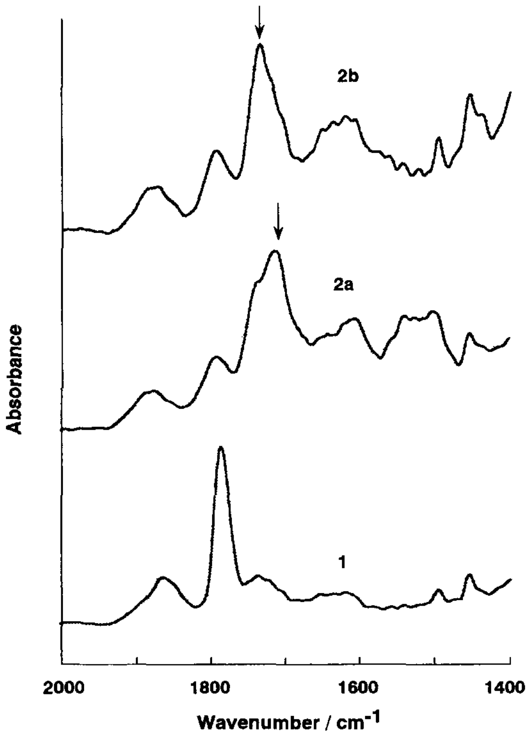


Fig. 2 IR spectra of composite **1**, **2a** and **2b**

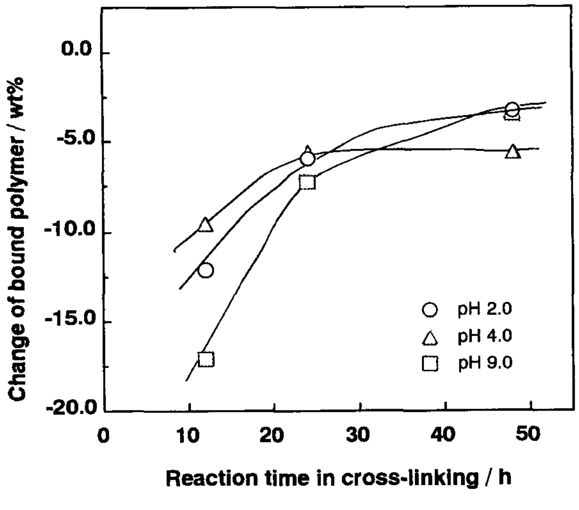


Fig. 3 Changes of bound polymer on composite **2a** by the acid or base treatment with the reaction time in the cross-linking

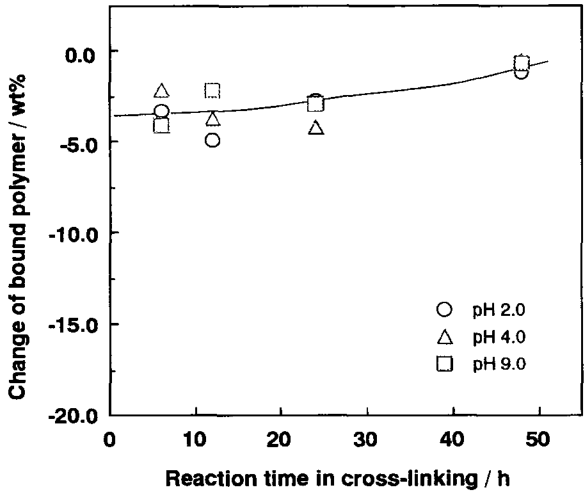


Fig. 4 Changes of bound polymer on composite **2b** by the acid or base treatment with the reaction time in the cross-linking

with the 1,6-diisocyanatohexane. In this case, the weight loss by the treatment in the each buffer solution decreased with time in the cross-linking reaction and attained 4–5 wt% in the reaction for 48 h. Although aromatic isocyanates is generally more active than aliphatic ones [14], 2-position-NCO group of 2,4-diisocyanatotoluene shows less reactivity with a functional group such as hydroxyl or amino group, because of steric hindrance due to methyl group [15]. Also, the rigid structure of the cross-linker probably makes the reaction of both side-isocyanate groups difficult. These results suggest that high flexibility of 1,6-diisocyanatohexane molecule give efficient cross-linking among the polymer chains. In any case, the present cross-linking procedures improved the linkage among P(MA-ST) chains and afforded more stable polymer-modified particles in aqueous solution in the pH range 2–9, as compared to the particles prepared by the reaction of P(MA-ST)/SiO_2 with di- or tri-ols and di- or tri-amines [11]. A dynamic light-scattering analysis of composites **2a** and **2b** showed that both composite particles had narrow size distribution, as shown in Fig. 5, and that the aggregation of the particles did not take place during the cross-linking reaction.

Concentration of surface carboxyl and amino groups

The composites **2a** and **2b** also had both maleic anhydride and amino groups on the surface. The existence of these groups were observed by the IR absorption bands at 1860 and 1781 cm^{-1}, assignable to C=O bond stretching vibrations of carbonyl group, and the bands at 3300–3400 cm^{-1}, assignable to N–H bond stretching vibrations, respectively. The amino group possibly comes from hydration of the isocyanate group which did not participate in the cross-linkage. Therefore, hydration of the anhydride and the isocyanate group on composites **2a** and **2b**, separated using chloroform after the reaction with the

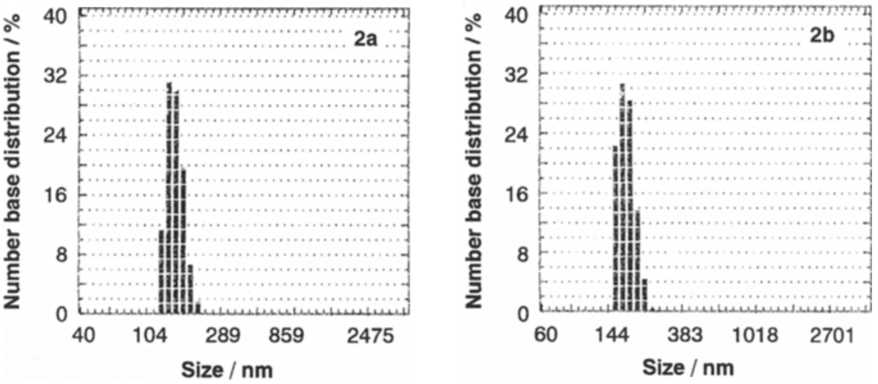
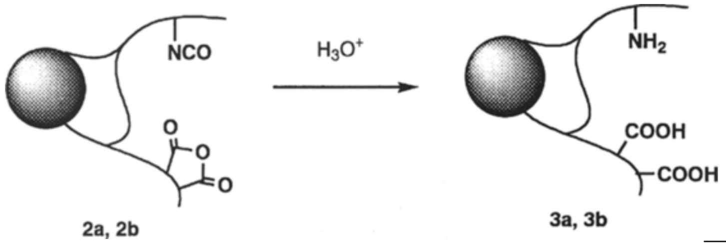


Fig. 5 Particle size distributions of composite **2a** and **2b**, measured in ethanol

diisocyanate, would simultaneously form carboxyl and amino groups on the composites **3a** and **3b**, as follows:



(1)

The hydrations of the surface groups on the composites **2a** and **2b** were carried out by immersing the particles in 0.01 M hydrochloric acid at room temperature for 24 h. The carboxyl group was determined by the esterification with *p*-nitrophenol. Thus, the group refers to the functional one, which is able to bind a secondary modifier. The composites **2a** or **2b** derived from the cross-linking with respective 1,6-diisocyanatohexane or 2,4-diisocyanatotoluene had the carboxyl group of 5–6 μmol g^{-1} (Table 1). In our previous study [11], we have reported that the cross-linking reactions of P(MA-ST)-modified silica, composite **1**, with diols leads to weight increase of 10–13 mg g^{-1} and to the carboxyl group formation of 1.0–1.3 μmol g^{-1}. Therefore, the present cross-linking is an effective method for derivation of the carboxyl group.

The reaction of composite **1** with each diisocyanate cross-linker also gave the amino group of 0.5–1.1 μmol g^{-1} (Table 1). The longer the reaction time was in the cross-linking using the respective diisocyanate, the higher was the amino group concentration. The result indicated that unreacted isocyanate end group increased with the reaction time. Also, the amount of the amino group would give an information about the extent of cross-linking. For example, the reaction of composite **1** with 1,6-diisocyanatohexane for 12 h afforded a weight increase of 9.7 mg g^{-1} (Table 1), which corresponded to 5.8 μmol g^{-1} of the diisocyanate. Therefore, it is suggested that about 81% of the isocyanate takes part in cross-linking among the surface polymer chains, on assuming perfect conversion of unreacted isocyanate group to amino group.

Properties of composites 1, 3a and 3b

The present polymer modification and cross-linking are expected to elaborate specific surface properties to colloidal silica. In Table 2, ζ-potentials and isoelectric points of the original colloidal silica, composites **1**, **3a** and **3b** are listed. The original colloidal silica exhibited ζ-potential of -51 mV in pH 7.0 buffer solution, but showed extremely small value (0.1 mV) in ethanol and partially aggregated. The composite **1** exhibited the potential of -37 mV in the

Table 1 Carboxyl and amino groups on composite **3a** and **3b**[a)]

Composite	Bound polymer[b)] [mg g^{-1}]	CO_2H [μmol g^{-1}]	NH_2 [μmol g^{-1}]
3a	81 (12)	4.9	0.5
	93 (24)	5.0	1.8
3b	72 (6)	5.9	0.7
	77 (12)	5.3	1.1

[a)] The composites **3a** and **3b** were derived from composite **1** containing of 67.3 mg g^{-1} polymer.
[b)] The values in parentheses are the reaction time in hour in the reaction of composite **1** (0.4 g) with the isocyanate (0.8 g) in dry DMF (30 cm^3).

Table 2 Properties of colloidal silica, and composites **1**, **3a** and **3b**

Particles	ζ-potential [mV]		Isoelectric point
	In pH 7.0 buffer	In EtOH	
Colloidal silica	− 51	0.1	2.1
1	− 37	− 111	1.3
3a	− 44	− 102	2.7
3b	− 47	− 107	2.5

pH 7.0 buffer. On composite **1**, silanol group was reduced by the first modification, so that the composite was expected to have higher ζ-potential in aqueous solution than the original silica. Therefore, the polymer chains on composite **1** probably shrink in the buffer solution and the property arises from the unreacted silanol groups. Interestingly, the composite **1** gave ζ-potential of −111 mV in ethanol, which resulted from the polymer modification. According to the Gouy–Chapman theory [16–18], the measurement of ζ-potential in organic solvent generally gives evaluation of a large value, because of lower dielectric constant as compared to water solvent. Hence, negatively large ζ-potential of composite **1** in ethanol might be due to charging of P(MA-ST), which was partially hydrolyzed to form carboxyl group. Both composites **3a** and **3b** showed the potential of − 44 and − 47 mV in pH 7.0 buffer, respectively, being lower than composite **1**. Probably, the carboxyl group formed contributes to lowering the potential. The ζ-potentials of composite **3a** and **3b** in ethanol were −102 and −107 mV, respectively, which were similar to the composite **1**. The isoelectric points of composites **3a** and **3b** were respectively 2.7 and 2.5, which were slightly higher than that of the composite **1**. The amino group formed by the hydrolysis of unreacted isocyanate group probably contributes to the elevation of the isoelectric point. However, these results suggest that the cross-linking and successive hydrolysis does not remarkably affect the surface properties of composite **1**, especially ζ-potential.

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