

Emulsion Polymerization of Co-polymers Having Both Hydrophilic and Hydrophobic Side Chains and Their Adhesion Properties

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ABSTRACT

We have studied on the surface and adhesion properties for acrylic terpolymers, having both hydrophobic and hydrophilic side chains, synthesized via solution polymerization. In order to develop a waterborne material, we tried to synthesize these terpolymers via emulsion polymerization. The polymeric emulsion synthesized was mainly composed of methyl methacrylate (MMA), methoxy-polyethyleneglycol methacrylate (MPEGMA) having hydrophilic side chains and methoxypolypropyleneglycol methacrylate (MPPGMA) having hydrophobic side chains. The viscosities of this series increased with an increase in the content of the co-monomer such as MPEGMA and MPPGMA. This behavior resulted in the increase in the diameter and heterogeneity of the emulsion particle via AFM observation. Furthermore, the tensile adhesion strength and 90-degree peel strength of the adhesive of these polymeric emulsions were measured. In the case of polymeric emulsion composed of the same content of both hydrophilic and hydrophobic component, the adhesion property showed the highest value. However, since the adhesion properties as a practical applicable adhesive were poor, some improvements were required. When the composition above was modified with butyl acrylate (BA), the improvement effect on adhesion strength was accepted. In particular, 90-degree peel strength increased up to a maximum of 400% of the original value.

INTRODUCTION

We^[1-5] have studied on the surface properties for comb-like polymers having hydrophilic and/or hydrophobic side chains and their applications to the functional polymeric materials, via X-ray photoelectron spectroscopy (XPS), dynamic contact angle (DCA) and so on. Co-polymers mainly composed of methyl methacrylate (MMA), methoxypol-

ethyleneglycol methacrylate (MPEGMA) as a hydrophilic component and methoxypolypropyleneglycol methacrylate (MPPGMA) as a hydrophobic component were synthesized by the radical polymerization in an organic solvent. From these studies, it was shown that the various functionalities were originated from the molecular mobility of their side chains based on each surface free energy, and the coexistence of hydrophilic

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and hydrophobic side chains results in the high environmental responsibility.

Recently, since the organic solvent used for the polymeric material is harmful to a human body and the pollution to environment, the usage is restricted. Accordingly, the poly-merization manner and usage style for the polymeric material should be necessary to convert from a solvent solution-type into an aqueous solution-type. Although the aqueous type polymer is mainly synthesized using emulsion polymerization, this polymerization technique is more complex than organic solution polymerization as known well. Therefore, the precise control for a polymerization is considerably difficult. Especially, the reaction of the macromonomer having hydrophilic or hydrophobic side chain used for a study mentioned above will be further complicate because of the high molecular weight and the difference of the polarity.^[6] On the other hand, a macromonomer has also been reported to be acting as an emulsifier or a dispersant in particular co-polymerization system.^[7] The emulsions are easy to handle because of aqueous dispersed fluid in spite of a high molecular weight. Especially, since emulsion series-adhesives do not essentially have any healthy damage by VOC (Volatilized Organic Compound), it will be suitable and useful for a practical application.^[8]

In this study, we synthesized amphiphilic co-polymers by means of emulsion polymerization instead of radical solution polymerization. Subsequently, we tried to apply these polymeric emulsions to the adhesives. The properties of emulsion were estimated via utilizing atomic force microscope (AFM), the tensile adhesion and the 90-degree peel test as the adhesion property and so on.

EXPERIMENTAL

Materials

Monomers used for emulsion poly-merization were methyl methacrylate (MMA), styrene (St), acrylic acid (AA), methoxypolyethyleneglycol methacrylate (MPEGMA), methoxypolypropyleneglycol methacrylate (MPPGMA) and polydimethylsiloxane methacrylate (PDMSMA). MPEGMA, MPPGMA and PDMSMA were macromonomers having comparatively long side chains of hydrophilic (MPEGMA) or hydrophobic (MPPGMA, PDMSMA) component. The chemical structures of these macromonomers were shown in Figure 1. MMA, St, AA and monomers (butyl acrylate (BA), vinyl acetate (VAc)) used for the other usage were commercially available grade and were purified with ordinary method. MPEGMA and MPPGMA were supplied by Shin-Nakamura Chemicals Co. and PDMSMA was supplied by Shin-Etsu Chemical & Industry Co., and were used as received. The molecular weight and the number of repeating unit in side chains of MPEGMA, MPPGMA and

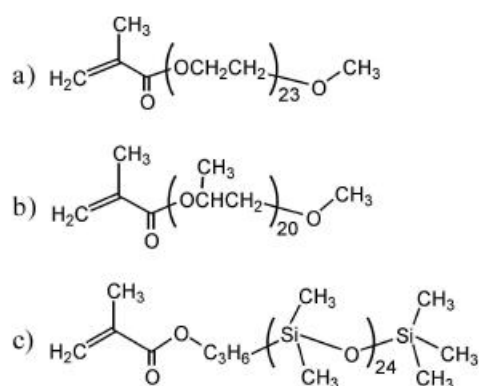


Figure 1. Chemical structure of monomers a) Methoxypolyethyleneglycol methacrylate (MPEGMA), b) Methoxypolypropyleneglycol methacrylate (MPPGMA), c) Polydimethylsiloxane methacrylate (PDMSMA).

Table 1. Characteristics of Monomers MPEGMA, MPPGMA and PDMSMA Determined by GPC and ¹H-NMR.

Monomer	M _n ($\times 10^{-2}$)	M _w / M _n	Number of repeating units	Surface tension at 25°C (mN/m)
MPEGMA	10.4	1.08	21.4	43
MPPGMA	9.24	-	14.2	31
PDMSMA	20.1	-	24.1	22

PDMSMA were shown in Table 1. In addition, the surface tensions of side chain in macromonomers were also listed in the Table.⁽⁹⁾ These characteristics were determined by Gel Permeation Chromatography (GPC, TOSOH-8020) with the polystyrene standard and Proton-NMR (Varian 400 MHz NMR) using chloroform-d₁ as a solvent.

Two kinds of surfactant were used for the emulsifiers of emulsion polymerization. Poly (oxyethylene) polycyclic phenyl ether sulfuric acid ester salt (Newcol-707SF) as an anionic emulsifier and ethylene oxide/propylene oxide/ethylene oxide tri-block co-polymer (Pruronic-F68, MW=8350) as a nonionic emulsifier were supplied by Nippon Nyukazai Co. and Asahi Denka Kogyo Co., respectively. These emulsifiers were used without further purifications.

Emulsion Polymerization

Co-polymers used in this study were prepared by emulsion polymerization utilizing the dropping mode. Following three types of co-polymers composed of four monomers were synthesized: MMA/MPEGMA/MPPGMA/AA, MMA/MPEGMA/PDMSMA/AA and St/MPEGMA/PDMSMA/AA. The feed amounts of comonomers MPEGMA and MPPGMA (or PDMSMA) were adjusted to 5~35 wt% corresponding to an amount of MMA or St, varying from 60 to 90 wt%. Furthermore, in order to increase the cohesive forces of this polymeric system, 3 wt% of AA of gross monomer weight was

added. The polymerization was carried out as follows: at first, monomer emulsion was prepared: monomers were poured successively from lower polarity into 2 wt% of aqueous solution of the emulsifiers (Newcol-707SF and Pruronic-F68); stirring by homogenizer (ULTRA Turrax T25), after all of the monomers were poured, the chain transfer agent (1-dodecanethiol) to control the coagulations and aqueous solution of the initiator (ammonium peroxodisulfate, APS) were also added it; then, the monomer emulsion was dropped at constant speed for 3 hours using peristaltic pump into water preheated at 78~82°C; after the dropping was over, it was matured keeping at 78~82°C for 2~5 hours; at this time, the polymerization was stopped. All of the water used was de-ionized.

Synthesized emulsions were adjusted to pH7~8 by aqueous ammonia and then, filtered through the 200-mesh screen. MMA/MPEGMA/MPPGMA/AA, MMA/MPEGMA/PDMSMA/AA and St/MPEGMA/PDMSMA/AA obtained by the above polymerization were abbreviated as MP_x-y, MS_x-y and SS_x-y, respectively. Suffix x and y indicates monomer content (wt%) of hydrophilic (MPEGMA) and hydrophobic (MPPGMA or PDMSMA) component, respectively.

Characterization and Adhesion properties of Polymeric Emulsion

Characterization for the polymeric emulsions was carried out via the measurement of viscosity and the non-volatile content, and the observation of surface morphology. The viscosity was determined by Rotational Viscometer (Brookfield RVT) according to Japanese Industrial Standard (JIS) K 6828. The non-volatile content was also determined according to the same standard as the above as follows. The dish made of aluminium foil containing about 2 g (w₁) of polymeric emulsions was dried in the oven

for 60 minutes at 104–106°C and weighed (w_2). After that, the non-volatile content was calculated by $w_2/w_1 \times 100$. After dilution of polymeric emulsion by 100 volume times of de-ionized water, it was poured on the glass plate and dried, then the surface morphology was observed by Atomic Force microscope (AFM, SPA 300 Seiko Instruments). Topographic images were recorded in the contact mode under ambient conditions. Si_3N_4 cantilevers with nominal force constant 0.09 N/m were used for measurement in contact mode. Scanning range and frequency was 500–10,000 nm and 1–2 Hz, respectively.

Adhesion properties for the polymeric emulsion were estimated by the measurement of the tensile and the 90-degree peel adhesion strength according to JIS A5536. The specimen for the tensile test was prepared by adhering the attachment (l:40 mm, w:40 mm) made of stainless steel SUS304 on the floor tile made of polyvinyl chloride (PVC) having the same area as the attachment with epoxy adhesives. The tensile adhesion strength was measured at 1 mm/min in tensile rate using TENSILON Testing Machine (Orientec Co.).

Next, the specimen for the peel test was the floor sheet (l:200 mm, w:25 mm) made of PVC. The 90-degree peel adhesion strength was measured at 200 mm/min in peel rate using AGS-1000A type Peel Testing Machine (Shimadzu Co.).

RESULTS AND DISCUSSION

Characterization of Polymeric Emulsion

The non-volatile content, the viscosities and the features of polymeric emulsions are shown in Table 2. Their non-volatile content were indicated the nearly same value as the theoretical value in all of the series. The

Table 2. Properties of Polymeric Emulsions.

Polymeric emulsion	Non-volatile content (%) (Calc.)	Viscosity (mPa·s)	Feature
MP5-5	31.5(42.8)	3.8	Latex
MP10-10 ^{#1}	36.9(41.6)	23	Latex
MP10-10 ^{#2}	33.0(38.8)	11×10^1	Latex
MP12.5-12.5	32.0(42.6)	16×10^3	Creamy
MP15-15	33.0(42.8)	14×10^3	Creamy
MP0-30	30.0(42.6)	8.0	Latex
MP20-20	38.0(41.8)	-	Coagulation
MP25-5	37.0(42.6)	-	Coagulation
MP30-0	38.0(42.6)	-	Coagulation
MS5-5	36.8(42.8)	5.6	Latex
MS10-10	31.0(41.6)	15	Latex
MS15-15 ^{#3}	37.5(42.6)	36×10^1	Creamy
MS15-15 ^{#4}	39.5(42.6)	20×10^2	Creamy
SS5-5	31.0(42.8)	13	Latex
SS10-10	38.3(41.6)	52	Latex
SS15-15	36.7(42.6)	-	Coagulation
SS20-20	32.0(41.8)	-	Coagulation

Conditions of Polymerization: #1 CTA (Chain Transfer Agent) 2%, AT (Aging Time) 2 hrs. #2 CTA 1%, AT 5 hrs. #3 CTA 2%, AT 2 hrs. #4 CTA 1%, AT 2 hrs.

viscosities in MP series increased with an increase in co-monomer (MPEGMA and MPPGMA) content. MP20-20, MP25-5 and MP30-0 were coagulated, while only MP0-30 showed a low viscosity. We consider that the abrupt increase in viscosity was due to the aggregation of hydrated polyethyleneglycol (PEG) segments in an aqueous phase. In addition, the similar behavior was also observed in MS and SS series.

The topographic 3-D images for the surfaces of polymeric emulsion with lower viscosity via AFM are shown in Fig. 2a-2d. The particles on each surface had a narrow particle size distribution, and their diameters were 0.2–0.3 μm . However, the larger particles than 1 μm were observed locally in Figure 2c (MS15-15). This suggests that the increase in comonomer content results in the high heterogeneity of the polymeric particle. In general, it has been thought that in the case of emulsion polymerization

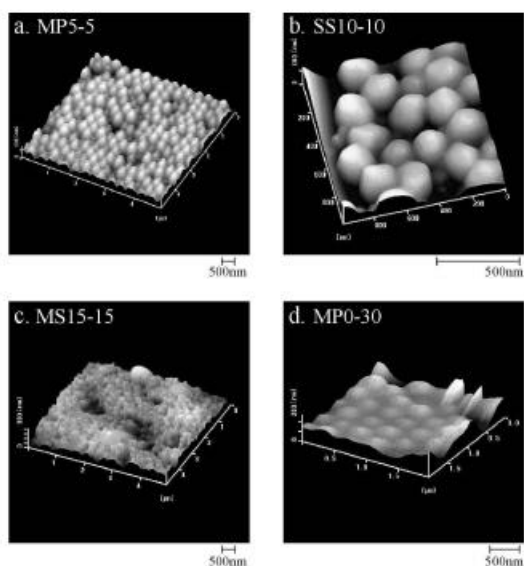


Figure 2. Surface topographic 3-D images of four types of low viscosity emulsions via AFM.

using a hydrophobic macromonomer such as MPPGMA, it is difficult to polymerize smoothly due to the difficulty of the diffusion of monomer into the micelle. In contrast, a polymerization of MP0-30 including only MPPGMA proceeded normally as shown in Figure 2d. The topographic images for the surfaces of polymeric emulsion with higher viscosity and coagulum via AFM are shown in Figure 3a-3d. As shown in both Figure 3b and 3c, the particle size of polymeric emulsion was large and the particle was connected with each other. In addition, the particles in Figure 3c were not spherical shape. From this fact, it was shown that an increase in MPEGMA content, maintaining low content of MPPGMA resulted in a distortion of the particle shape. It was also clear that the growth of the polymeric particles was inhibited by not MPPGMA but hydrophilic MPEGMA. On the other hand, although MP15-15 had a considerably large particle size and narrow size distribution, any coagulum could not be observed in this system. The polymeriza-

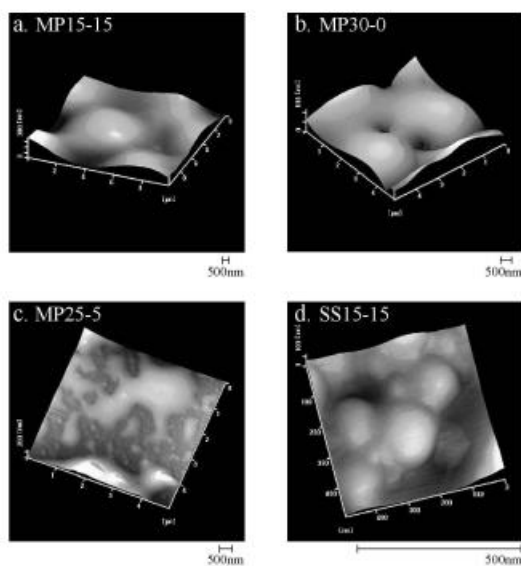


Figure 3. Surface topographic 3-D images for a high viscosity emulsion or coagulated emulsions via AFM.

tion of the system, having the same content of MPEGMA and MPPGMA, could be proceeded easily.

Adhesion Properties of Polymeric Emulsion

The tensile adhesion and 90-degree peel strength of the polymeric emulsions, which did not coagulate, are shown in Table 3. Since the polymeric emulsions synthesized in this study correspond to the vinyl-copolymerized resin emulsion (A:) or acryl resin emulsion (B:) prescribed by JIS A 5536, the required adhesion strength for these adhesives is 0.2 N/mm^2 (A:, B:) as a tensile adhesion strength, 20.0 N/25mm (A:) or 10.0 N/25mm (B:) as a 90-degree peel strength.

Only the tensile adhesion strength of MP series adhesives exceeded the above standard. MP15-15 adhesive showed the highest tensile adhesion strength (0.9 N/mm^2) and the highest 90-degree peel strength (7.0 N/25mm) in MP series. As described in

Table 3. Adhesion Properties of Polymeric Emulsions that Did not Coagulated.

Polymeric emulsion	Tensile adhesion strength (N/mm ²)(kgf/cm ²)	90-Degree peel strength (N/25mm)(kgf/25mm)
MP5-5	0.1[1.2]	1.0[0.10]
MP10-10	0.2[1.9]	1.8[0.18]
MP12.5-12.5	0.8[7.4]	5.5[0.56]
MP15-15	0.9[8.3]	7.0[0.71]
MP5-25	0.5[4.5]	2.5[0.26]
MP0-30	0.3[2.8]	3.5[0.36]
MS5-5	0.2[1.6]	0.5[0.050]
MS15-15	0.2[1.5]	1.3[0.13]
SS5-5	0.1[0.98]	1.0[0.10]
SS10-10	0.1[0.98]	1.0[0.10]

section 3.1, this emulsion showed the best emulsion properties.

On the other hand, the adhesion strengths in MS and SS series were considerably low. This is due to extremely low intermolecular cohesion energy of PDMS side chain. That is low intermolecular cohesion energy. From these results, it was shown that the adhesion properties in MP series were better than that of MS and SS series. However, the adhesion strength in MP series is lower than practically applicable adhesion strength for the similar type of adhesives yet. Especially the lowness of 90-degree peel strength is a problem. Thus, it is necessary to modify the toughness of this system.

Effect of Modification of Polymeric Emulsion on Adhesion Properties

In order to improve the adhesion properties of the MP series, emulsion copolymerization containing vinyl acetate (VAc) or butyl acrylate (BA) as a co-monomer was carried out. As is well known, PVAc and PBA are beneficial because a low glass transition temperature (T_g) is shown. The tensile adhesion strength and 90-degree peel strength of the adhesive of synthesized emulsions are shown in Table 4. Although

Table 4. Adhesion Properties of Polymeric Emulsions Modified with Butyl Acrylate (BA) or Vinyl Acetate (VAc).

Polymeric emulsion	Modifier (wt%/Mo.)*	Tensile adhesion strength (N/mm ²)(kgf/cm ²)	90-Degree peel strength (N/25mm)(kgf/25mm)
MP10-10	BA 5	0.30[2.6]	2.9[0.30]
	BA 10	0.40[4.3]	5.9[0.60]
	VAc 10	0.10[1.3]	1.0[0.10]
MP15-15	BA 5	1.1[11]	17[1.7]
	BA 10	0.80[8.2]	28[2.9]
	VAc 10	0.70[6.5]	3.9[0.40]
	VAc 20	0.80[7.7]	2.9[0.30]

* Monomer gross weight(g)

the adhesion strength of synthesized emulsion modified with VAc did not increase, co-monomer BA could be improved it significantly in both MP10-10 and MP15-15. In particular, in MP15-15 adding 10 wt% of BA, 90-degree peel strength increased up to 28 N/25mm to 7 N/25mm of original value. This value was higher than practical applicable peel strength. Accordingly, it is clear that an addition of BA contributed to the improvement of the toughness. The effect of the improvement on adhesion strength between VAc and BA would be caused by the difference in the T_g of PVAc and PBA. The official value of T_g of PVAc and PBA is approximately 30°C and -50°C, respectively. This suggests that since the T_g of PVAc is somewhat higher than room temperature, the modulus of the synthesized emulsion having PVAc segment did not decrease so much. Contrarily, it is considered that because PBA shows sufficiently low T_g, the modulus of the synthesized emulsion having PBA segment decreased so as to become adaptable toughness.

CONCLUSIONS

Co-polymers having both hydrophilic and

hydrophobic side chain were synthesized by emulsion polymerization. Good emulsion-properties were shown in particular compositions up to 30 wt% of the sum of hydrophilic MPEGMA and hydrophobic MPPGMA content. From experimental results of emulsion-properties and adhesion strength, we found that the polymeric emulsion composed of the same content of both hydrophilic and hydrophobic component such as MP15-15 was best for application to the adhesive.

In order to improve the lowness of 90-degree peel strength, co-monomer such as butyl acrylate (BA) or vinyl acetate (VAc) was introduced into emulsion polymerization system. When the MP10-10 and MP15-15 were modified with BA, both the tensile adhesion strength and 90-degree peel strength could be improved significantly.

On the other hand, the parameter, which has a bad influence on adhesion properties, is not only mechanical properties of the adhesive but also surface properties of that. We think that the low adhesion properties of these adhesives are responsible for the emulsifier. Therefore, we are just trying to use a novel polymeric emulsifier.

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