



Studies on Preparation of Polymer Particles Containing Ethyleneurea Ring and Their Applications

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博士論文

Studies on Preparation of Polymer Particles
Containing Ethyleneurea Ring
and Their Applications

(エチレンウレア環を有する高分子微粒子の合成とその応用)

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Preface

Methacrylamide ethylethyleneurea was first presented as a useful chemical intermediate in the United States in 1950's. This compound reacts by the double bond with various compounds having reactive hydrogen. It also reacts by the amide group of ethyleneurea with formaldehyde to form useful condensates. Its polymers and copolymers by radical polymerization were useful in coating compositions such as textile finishing compounds, adhesives, paper treating agents and plasticizers. Many similar compounds have appeared on US patents for two decades ever since.

Those compounds have been used especially for waterborne coatings since 1970's. Quite a few improvements for waterborne paints were proposed with many functional monomers in those days. But what they call wet adhesion promoters were selected gradually. Because of their excellent performance in acrylic paints, 2-imidazolidinone, or ethyleneurea moiety, remains and is still known as the most potent wet adhesion promoting functional group.

Although methacrylamide ethylethyleneurea has succeeded commercially as a wet adhesion promoter, very little works are available in published literature on the mechanism of its wet adhesion performance.

The purpose of this doctoral work is to study how the monomer having ethyleneurea ring performs as a wet adhesion

promoter and to optimize this effect by utilizing various polymerization methods of polymer microspheres.

In **Part I** consisting of two chapters, the author takes his attention on properties of copolymer emulsions that contain small amount of ethyleneurea ring as a polymer component.

In **Chapter 1**, wet adhesion promoters for waterborne coatings will be surveyed and reviewed. To the author's knowledge, there is no published literature on this kind of a comprehensive review. Typical improvement methods and evaluation methods of wet adhesion promoters, and the proposed mechanisms of functions of ethyleneurea ring will be investigated.

In **Chapter 2**, copolymer emulsions with methacrylamide ethylethyleneurea and its application as a wet adhesion promoter will be examined. Comparison data with typical functional monomers of the wet adhesion for waterborne paints will be studied.

In **Part II** consisting of three chapters, the author takes his attention on production of the polymer particles with ethyleneurea ring and its optimized method of microsphere design.

In **Chapter 3**, the interaction between ethyleneurea ring and carboxyl group in polymer particles will be examined. Monomers having carboxyl group are usually used with wet adhesion promoters. Properties of the copolymer as well as the effect of the emulsion blend of particles with these functional

groups will be studied.

In **Chapter 4**, the synthesis of polymer particles with ethyleneurea ring and the wet adhesion properties will be studied. Clean polymer particles with surface oriented ethyleneurea ring will be prepared by emulsifier-free, seeded emulsion polymerization. And properties of the films from obtained polymer particles will be investigated.

In **Chapter 5**, the synthesis of polymer particles with ethyleneurea ring by starved feeding method and modification by crosslinking system will be studied. How to localize ethyleneurea ring more on the surface of particles and improvement of wet adhesion property will be investigated. A novel crosslinking system between ethyleneurea and dialdehyde will be studied on seeded composite particles with the evaluation of wet adhesion properties.

As mentioned above, through a series of work on polymer particles containing ethyleneurea ring, the author has reported his doctoral dissertation as the title of “**Studies on Preparation of Polymer Particles Containing Ethyleneurea Ring and Their Applications**”.

PART I

Properties of Polymer Emulsions Containing Ethyleneurea Ring

Chapter 1

Wet Adhesion Promoters for Waterborne Coatings

1-1 Introduction

It seems that the high-consumption industrial society that has pursued only economy and productivity has approached its turning point. We recognized that the compensation for the human evolution was tremendous, for example environmental pollution, carcinogens, greenhouse effects, and endocrine disrupters one after another. Science has just started taking measures to cope with this situation seriously.

As to the paint application, it is also indispensable to concern environmental issues for the future. Solvents themselves are not necessary to fulfill function of paints, so they tend to avoid emitting them excessively to the atmosphere.

The best option should be a waterborne coating which corresponds to the volatile organic compounds (VOC) control act. Waterborne paints have many advantages such as low cost, handiness (better handling of paint brush, faster drying than oily paint, or easier cleaning for paint tools), improvement of working surroundings (bad smells or health aspects), low risk for explosion or fire, and low-pollution problems.

For all that the replacement for solvent-based paint has been still slow. The major reason of that should be inferior

properties of waterborne paints to conventional paints.

“Wet adhesion” has been used as a technical term that indicates a property of polymer emulsion in western paint industry since 1960’s. It is the property how it withstands physical force such as abrasions or frictions under existence of water and keeps a perfect state as coating film. It is also criteria for the durability of coatings in rains or snowfalls when it is applied on exterior of houses, high humidity or splash of water in kitchen or bathroom when it is applied on interior walls, or washability of coating surface by brushing with a cleanser. In other words, it is simply that emulsion paints have been destined to have serious problem under those conditions basically because of water medium. The adhesion performance of waterborne coatings in wet condition was obviously inferior to solvent- based one.

Although wet adhesion promoters are applied widely for industrial use, there have been few literature that describe them totally and systematically. At the first chapter of the doctoral dissertation, wet adhesion promoters which are used as the most effective solution for this wet adhesion problems are summarized and discussed.

1-2 Waterborne Paints and Wet Adhesion Test Methods

As D.I.Y. (do it yourself) is a sort of culture in North America, they have a habit of painting walls of their house by

themselves. Therefore the market share of home-use paints in the whole paint products is fairly high.

Oil paints that had been used as typical home use-paints for wood have a good anti-soil property. However wet adhesion and permeability are not so good, they tend to blister on the interface between wood and coating film when they are exposed to rain or indoor condensation of dew.

Alkyd paints also have a low permeability, but have a good wet adhesion property. So alkyd-modified oil paints are used commonly for exterior application. Emulsion paints with easy handling and good permeability have been adopted as topcoats over conventional oil-based primers.¹⁾

There are several number of test methods and standards for wet adhesion property of emulsion paints such as Federal Specs., Canadian Government Test Method, ASTM, etc.²⁾ The common procedure in most of those methods is as follows.

- a) Test panels are pre-coated with high-gloss alkyd enamel, which is fully crosslinked.
- b) Emulsion paint is coated on the alkyd layer.
- c) Durability of coated film under exposure of water is evaluated.

Table 1 shows representative examples of those methods. Federal and Canadian standards for exterior and interior paints require resistance to several thousand cycles of scrubbing under wet condition. Generally when emulsion paints are over-coated on a panel pre-coated with alkyd enamels, exfoliation on the interface of undercoat and topcoat layers often occurs just by a

few dozens of scrubbing with cleanser under existence of water. To meet such hard requirements, wet adhesion promoters are used.

The circumstances are very different in Japan. We rarely use painted wood for exterior walls. There are few one-storied houses, so it is not easy to paint exterior walls by ourselves. The history of Japanese home-use paints has not been long compared with that of western countries.

Table 1 Characteristic of Wet Adhesion Test Methods

| | Description | Panel Preparation | Wet Conditions | Adhesion Test |
|-----|---|--|---|--|
| I | TTP-001511 Federal Spec. | Alkyd Enamel on ground glass, dried 3 days, baked 2hr at 200°C Test panel dried for 48hr | Cut test film | Underwater scrubbing for 3,500 cycles |
| II | TTP-001511 Modified | As in I. Embed cheese cloth in the latex film Dry for 24hr | Immerse in water for 1hr | Pull cheese cloth. It passes if latex-alkyd interface intact. |
| III | Wet Adhesion Abrasion Test- Interior Semi- Gloss | Alkyd Enamel on Lenata chart. Dried 6 days, Test paint dried for 7 days | Scrub to failure or 1,500 cycles with an abrasive soap solution | |
| IV | ASTM-2366-68 Moisture Blister Resistance for Exterior Paints | Two coats of test latex paints on cedar siding with 7 days drying after each coat | Expose panels in blister cabinet | Measure portion of panel showing blisters |
| V | 1GP-138 Canadian Government Test | Alkyd enamel on white pine panels. Dry for 7 days. Test latex to dry for 2hr | Expose in water spray chamber with 6 nozzles delivering 34.2L./hr for 1hr | Check blistering Scrub for 3,500 cycles |
| VI | JIS K5400, K5663 Washability Test | Synthetic resin emulsion paint on flexible panel or hard PVC sheet Dry 7 days | Scrub by weighted brush with 0.5% soap solution. | 500cycles for exterior paints, 100cycles for interior paints, and 100-300 cycles for home-use paints |

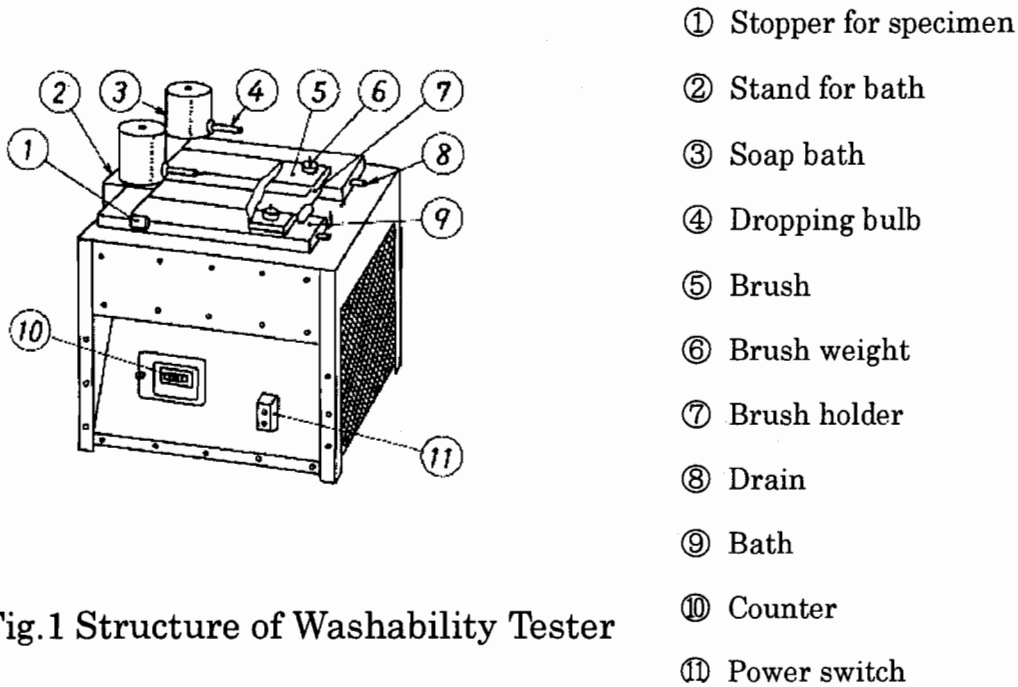


Fig.1 Structure of Washability Tester

- ① Stopper for specimen
- ② Stand for bath
- ③ Soap bath
- ④ Dropping bulb
- ⑤ Brush
- ⑥ Brush weight
- ⑦ Brush holder
- ⑧ Drain
- ⑨ Bath
- ⑩ Counter
- ⑪ Power switch

The market share of home-use paints in Japan is only around three percent. Japanese Industrial Standard (JIS) prescribes evaluation of washability as “coat a synthetic resin emulsion directly on flexible panel or polyvinylchloride sheet and scrub on the surface of coating by brush immersed soap solution”. Figure 1 shows structure of provided the washability tester by JIS K5400. “Washability” is defined as a resistance property of abrasion and damage for coated film when it is cleaned to remove stains. This is almost a synonym of “wet adhesion” in North American standards.

Table 2 shows the results of wet adhesion evaluation of commercialized emulsion paints in Japan, which is based on Wet Adhesion Abrasion Test for interior semi-gloss paints in North America (Table 1 III)³⁾. Top-coated emulsion paints were tested on

alkyd enamel undercoated panel by Gardner Scrub Test Machine. Unexpectedly all paints for bathroom could not withstand only 100 cycles. The paints for exterior wall were relatively better, but there were no paints that lasted over 1,000 cycles. There is a considerable gap on the levels of wet adhesion property between in North America and in Japan. The Japanese industry has not paid attention to wet adhesion promoters in Japan because of such a big difference of required property for emulsion paints.

Table 2 Results of Wet Adhesion Test for Commercial Waterborne Paints in Japan

| Type of emulsion paints | Gardner Scrub (cycles) |
|---------------------------------------|------------------------|
| Paint for Concrete Floor A | 260 |
| Paint for Concrete Floor B | 800 |
| Paint for Tin Roof | 350 |
| Paint for Construction | 230 |
| Multi-purpose Paint A | 730 |
| Multi-purpose Paint B | 6 |
| Paint for Wall and Bathroom A | 60 |
| Paint for Wall and Bathroom B | 38 |
| Paint for Wall and Bathroom C | 70 |
| Paint for Kitchen and Bathroom | 130 |
| Anti-mold Paint | 150 |
| Rust Preventive Paint A | 370 |
| Rust Preventive Paint B(quick-drying) | 700 |

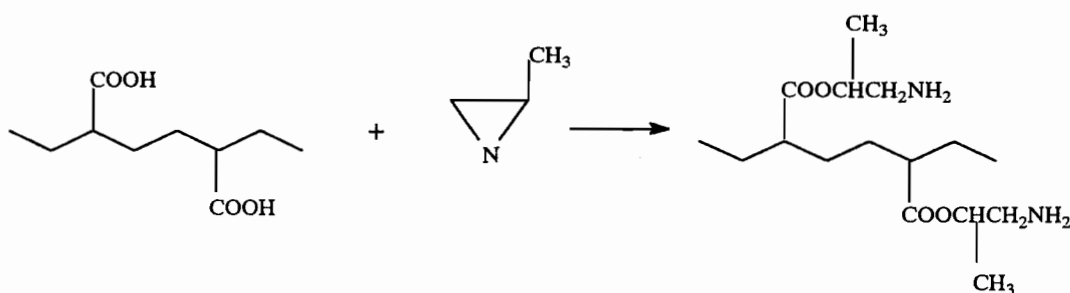
1-3 How to Improve Wet Adhesion Property

There are two industrial ways to improve wet adhesion

property as follows.

1-3-1 Introduction of functional group to polymer chain by graft reaction

The most typical way is the amination by post-added reactants to pre-introduced carboxyl or hydroxyl group on the surface of particles in latex. Aziridine ring such as ethyleneimine or propyleneimine is used for this modification.^{4,5)} Three-membered ring with nitrogen atom is very reactive, so ring-opening addition reaction occurs easily. Scheme 1 shows a addition reaction between carboxyl groups in polymer and propylene imine.



Scheme 1

This method gives a practical wet adhesion property, however yellowing problem after aging may occur originated in oxidation of amino groups which exist on the surface of polymer particles. Moreover aziridine is listed carcinogenic substance, therefore it is imposed restrictions on applications.

1-3-2 Introduction of polar group to polymer chain by copolymerization

Monomers with polar groups and an unsaturated group such as a vinyl group or an allyl group are copolymerized to introduce wet adhesion function into latex polymer backbone. These monomers are called "wet adhesion promoters" or "wet adhesion monomers". Amine, amide, and acetoamide have been used as introduced polar groups.⁵⁻¹⁰⁾ Table 3 shows typical examples of wet adhesion monomers.

(1) Amines

Dimethylaminoethylmethacrylate, 2-pyridine, and 4-pyridine had been used as wet adhesion promoters, but the effect of improvement was insufficient in general. The usage of those amine type monomers is usually 1 to 3% of total monomer amounts.

(2) Acetoacetates

Acetoacetates that give chelate compounds have also been used as wet adhesion promoters. However there are limitations to application conditions.

(3) Amides

Methylol modified diacetone acrylamide has been used, however amide type monomers were generally inferior to amine type one on the promotion of the wet adhesion properties. Although it has been known that some special compounds that have 2-imidazolidinone, namely, ethyleneurea group such as a methacrylamidoethylethyleneurea, a allyloxy-2-hydroxypropyl

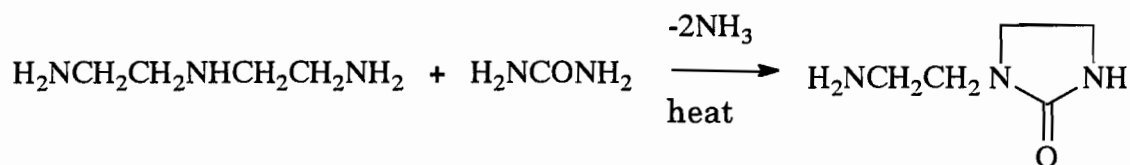
Table 3 Monomers which used for wet adhesion improvement

| Class | Typical monomers | |
|---------------|---|--|
| Amines | $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N} \end{array}$ 2-Vinyl pyridine | $\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N} \end{array}$ 4-Vinyl pyridine |
| | $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-CH}_2\text{CH}_2\text{-N}(\text{CH}_3)_2$ Dimethylaminoethyl methacrylate | |
| Acetoacetates | $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-CH}_2\text{CH}_2\text{O-COCH}_2\text{COCH}_3$ Acetoacetoxyethyl methacrylate | |
| | $\text{CH}_2=\text{CH-CH}_2\text{-NH-COCH}_2\text{COCH}_3$ Allyl acetoacetoamide | |
| Ethyleneureas | $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CONH-CH}_2\text{CH}_2\text{-N} \begin{array}{c} \diagup \\ \text{NH} \\ \diagdown \\ \text{O} \end{array}$ Methacrylamido ethylethyleneurea | |
| | $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-CH}_2\text{CH}_2\text{-N} \begin{array}{c} \diagup \\ \text{NH} \\ \diagdown \\ \text{O} \end{array}$ 2-Imidazolidinonyl ethyl methacrylate | |
| | $\text{CH}_2=\text{CH-CH}_2\text{-O-CH}_2\text{CH}(\text{OH})\text{-CH}_2\text{-NH-CH}_2\text{CH}_2\text{-N} \begin{array}{c} \diagup \\ \text{NH} \\ \diagdown \\ \text{O} \end{array}$ Allyloxy-2-hydroxypropylamino ethylethyleneurea | |
| Others | $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-CH}_2\text{CH}_2\text{-N} \begin{array}{c} \diagup \\ \diagdown \end{array}$ 2-(1-aziridine)ethyl methacrylate | |
| | $\text{CH}_2=\text{CH-CONH-C}(\text{CH}_3)_2\text{-CHCO-CH}(\text{CH}_2\text{OH})_2$ CH_2OH Trimethylol diacetone acrylamide | |

aminoethylethyleneurea show remarkable performance for promotion of a wet adhesion property, and have been widely used for industrial applications. The usage of those monomers is 0.5-2% of total monomer weight in emulsion polymerization. In case of containing amide group with ethyleneurea ring in the same molecule, the synergy effect of these groups is better on wet adhesion performance than that of ether or ester group with ethyleneurea ring.

1-4 Preparation and characteristics of methacrylamido ethylethyleneurea

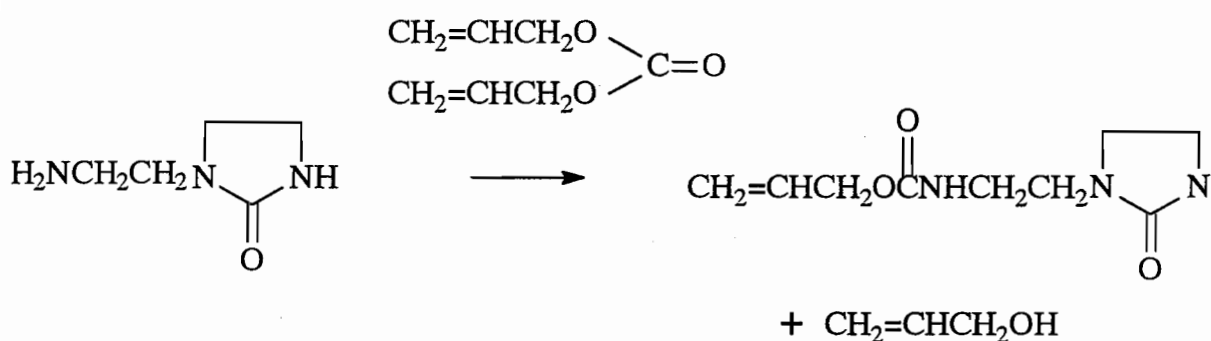
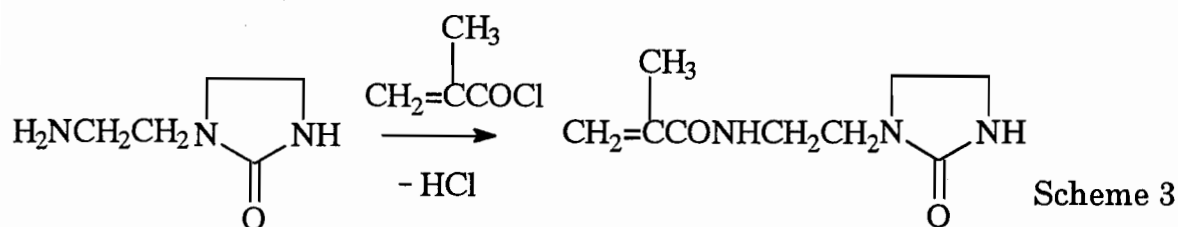
Ethyleneurea ring (2-imidazolidinone) is introduced by aminoethylethyleneurea (AEEU). AEEU is synthesized by condensation reaction of diethylene triamine and urea.¹²⁾ (Scheme 2)



Scheme 2

Hankins et al. synthesized methacrylamidoethylethylene urea from AEEU and methacrylic acid chloride, and also prepared a series of similar compounds.¹¹⁾ Scheme 3 shows reaction between AEEU and methacryloylchloride. Dixton et al

synthesized allylcarbamate derivatives by the reaction of AEEU and diallylcarbonate.¹²⁾ (Scheme 4)



Scheme 4

Those monomers that contain ethyleneurea ring are mixed with common vinyl monomers such as acrylates, methacrylates, vinylacetates, or styrene, and co-polymerized together by radical polymerization. N-(β -methacrylamidoethyl)-2-imidazolidone, namely, methacrylamidoethylethyleneurea (MAEEU) comes onto market as a mixture product with methacrylic acid and water, which is named SIPOMER WAM-II from RHODIA.

Obtained semi-gloss waterproof paint resisted over 2,000 scrub cycles on the wet adhesion test and no exfoliation was observed on the surface of coating layer. On the other hand, the control paint prepared by polymer emulsion without MAEEU was removed completely by only 85 scrub cycles by the same condition.^{15,16)} Figure 2 shows a photograph of the wet adhesion

test result.

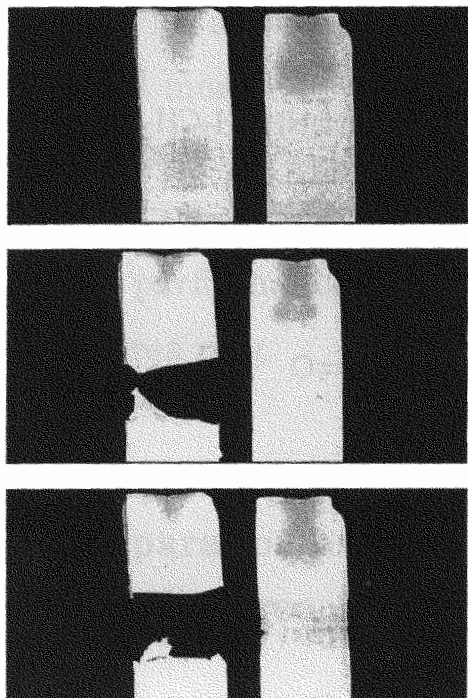


Fig.2 Wet Adhesion Test Result

Left: Control paint after 100 cycle scrubs

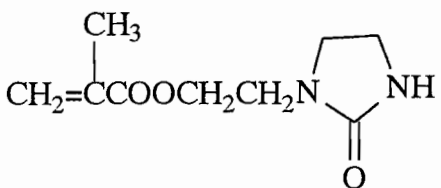
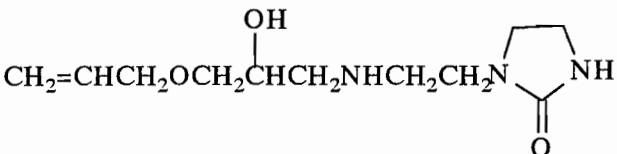
Right: Paint with MAEEU (1wt%) after 2,000 scrub cycles.

Kreis et al. synthesized various wet adhesion monomers, and prepared both of all-acrylic and vinyl acetate-acrylic polymer emulsions with these monomers. They evaluated wet adhesion performance of prepared waterborne paints blended with these latex by Gardner Scrub Test Machine.⁵⁾ Table 4 shows the representative data. A significant effect of ethyleneurea ring was observed in this work. Only 1.5 wt% of copolymerization of the monomers with ethyleneurea group changed wet adhesion property of coating film remarkably.

Lai compared difference of the effect for wet adhesion promoters¹⁶⁾ between MAEEU and N-(β -methacrylethyl)-2-imidazolidone, namely, ethylethyleneureamethacrylate (EUME).

Table 4 Wet adhesion promoters and those effect for waterborne acrylic and vinyl acetate-acrylic paints

(Comparison of number of scrub cycles by Gardner Scrub Test)

| Wet Adhesion Monomers (1.5phm in each latex) | All Acrylic Paint | Vinyl-Acrylic Paint |
|--|----------------------|------------------------|
| $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_2$ | 1,187 | 253 |
|  | >1,500 | 953 |
| $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}-\text{COCH}_2\text{COCH}_3$ | 251 | 83 |
| $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2-\text{NH}-\text{CONH}_2$ | 270 | 102 |
|  | >1,500 | >1,500 |

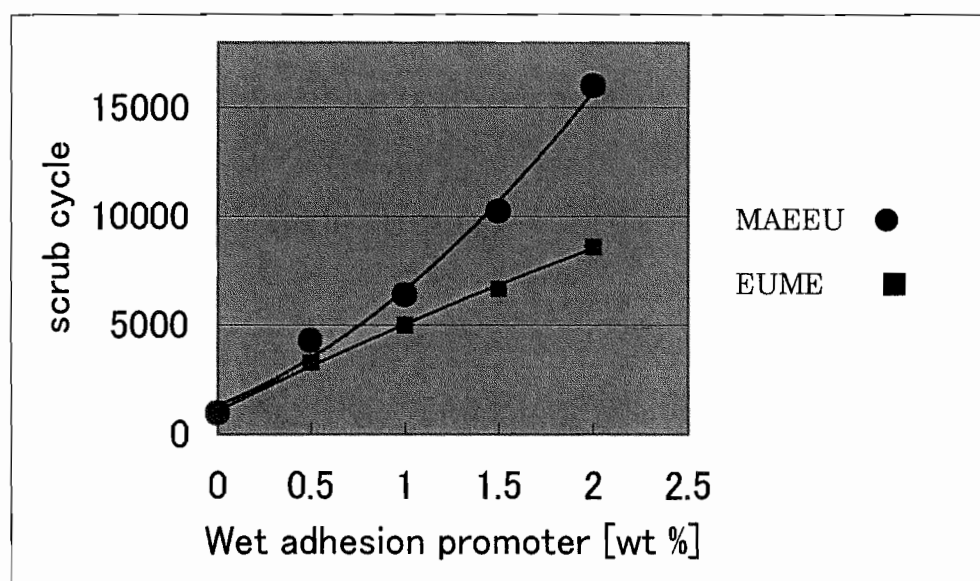


Fig. 3 Wet adhesion property vs wt % of wet adhesion promoters

Fig. 3 showed the result of wet adhesion test. MAEEU performed better than EUME. Inter- or intra-molecular hydrogen bonds with amido group and ethyleneurea group may intensify interaction of polymer chains. (Figure 4)

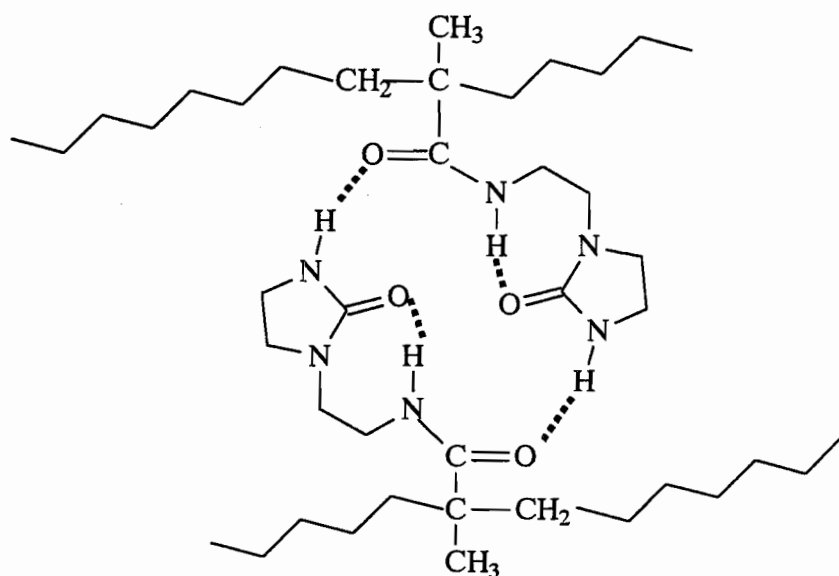


Fig. 4 Intra- and inter-hydrogen bonding

The mechanisms of effects of ethyleneurea ring accounting for the wet adhesion property have been considered as follows.

a) Dipole moment

Table 5 shows dipole moment of typical molecules. The ethyleneurea ring has a extremely large dipole moment that is 4.5 Debye units. This figure is larger than H_2O , acetone or formamide. It causes their strong interaction with negatively charged surface like a alkyd resin coating or pigments. Figure 5

shows each bond moment in ethyleneurea group.

Table 5 Dipole moment of molecules (Debye) ¹⁷⁾

| | | | |
|----------------------|------|---|-----|
| CHCl ₃ | 1.06 | CH ₃ COCH ₃ | 2.9 |
| CH ₃ Cl | 1.87 | C ₆ H ₅ NH ₂ | 1.5 |
| H ₂ O | 1.85 | C ₆ H ₅ OH | 1.5 |
| CH ₃ OH | 1.7 | HCONH ₂ | 3.7 |
| CH ₃ COOH | 1.7 | Ethyleneurea | 4.5 |

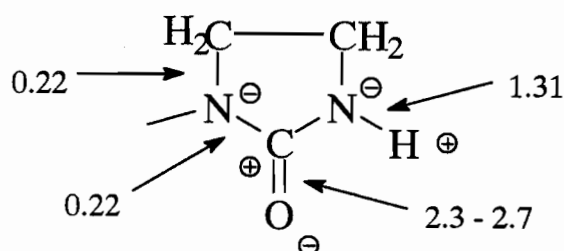


Fig.5 Bond moment of ethyleneurea ring (Debye)

b) Interface tension

A modification of the polymer particles by hydrophilic functional group can lower the interface tension between polymer latex and pigments. The improved wetting and the penetrating properties make the contact between the two surfaces easier and make the affinity of them stronger.

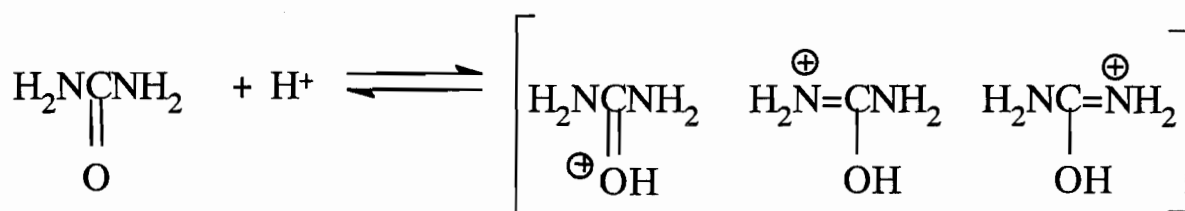
c) Hydrogen bond

The carbonyl and imino groups in ethyleneurea ring form hydrogen bond networks with carbonyl or hydroxy groups on the interface of substrate.

d) Coulomb force

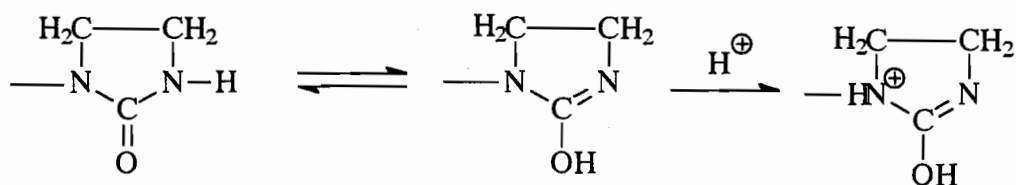
It was said that cationic charged amino groups by protonation incorporate with anionic charged surface of substrate such as pigments or alkyd resin coated layer. It is an interaction by the Coulomb force.

Nitrogen atom of amido is usually hardly protonated. Urea itself is weak base. But it forms salt with strong acid. Basicity of urea is stronger than common amides because the cationic ion of urea can be stabilized by resonating molecule structures. (Scheme 5)



Scheme 5

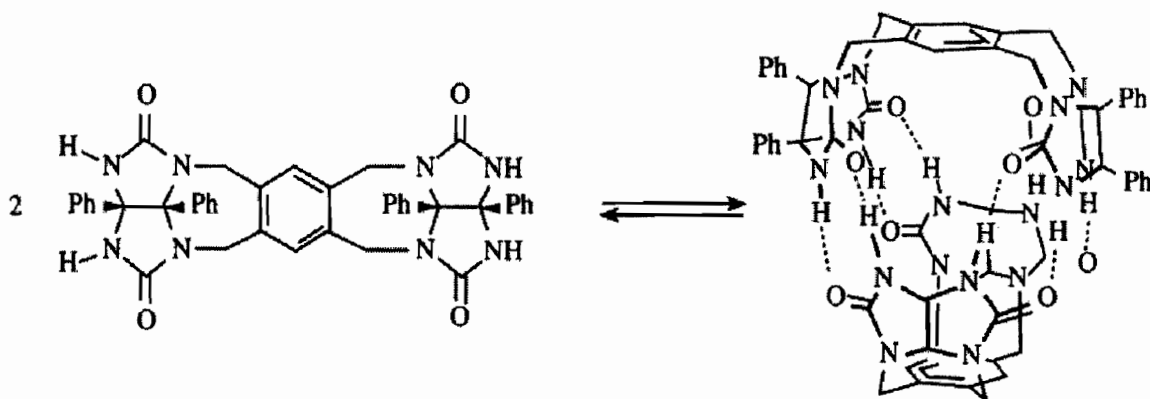
Cationization of ethyleneurea ring may also be explained as follows. 2-imidazolidinone and 2-oxy-2-imidazoline are referred to as keto-enol tautomers. (Scheme 6) This enol structure allows protonation of ethyleneurea ring.



Scheme 6 Tautomerism and protonation of ethyleneurea ring

e) Others / formation of super molecular

There are several cases to apply intermolecular force by similar structure to 2-imidazolidinone for supramolecular design. The self-organization capsule by Rebek et al. is a case of supramolecular combined two same molecules like a stitched tennis ball.¹⁸⁾ The hydrogen bonds between two bicyclic ethyleneurea frameworks are utilized successfully to stitch two unit molecules. (Scheme 7)



Scheme 7 Tennis ball-like self organization capsule

Hydrogen bond network between nucleic acid bases of DNA is conceivable as an illustration of interaction between cyclic carbonyl groups and N-H bonds. (Scheme 8)

Urea is also easy to form hydrogen bond network. Urea itself forms clathrate with many guest compounds such as n-alkanes, fatty acids, halogenated hydrocarbons and so on. For example, it is known that urea forms hexagonal system crystal with existence of octane molecule.¹⁹⁾ This hexagonal lattice of urea has a hollow whose diameter is 520nm. And octane

molecule is encapsulated in the cavity. This clathrate compound is one of typical supermoleculars, and this fact also supports strong hydrogen bond formation of urea structure.

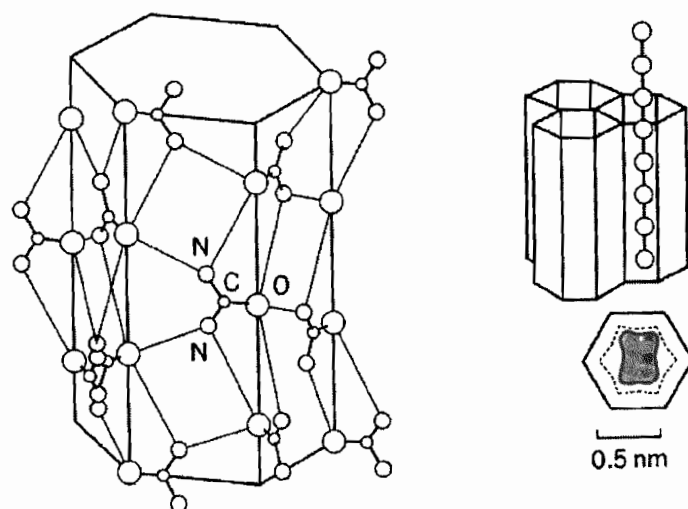
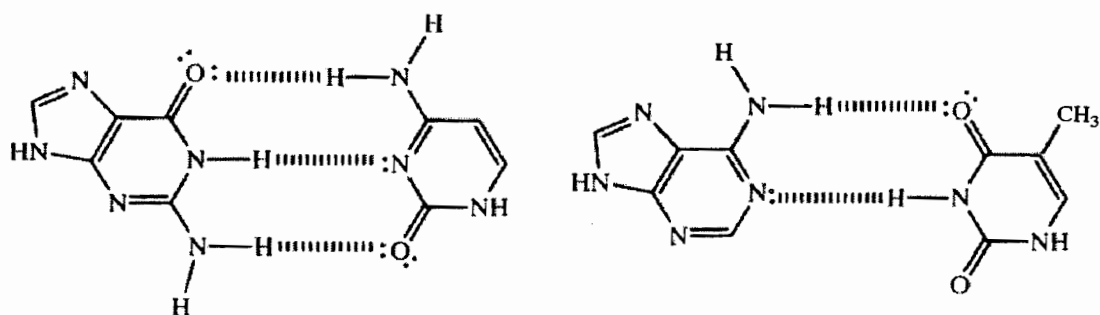


Fig. 6 Hexagonal lattice of urea; Clathrate of uear and octane



Scheme 8 Hydrogen bond of Guanine and Cytosine, Adenine and Thymine

There is much room for examining mechanism of such particular functions of ethyleneurea, not only the approach from

wet adhesion property but also from polymer colloids or molecular design.

Manufacturers are still continuing efforts to develop new generation of monomers with ethyleneurea ring. Washability of paints has not been regarded so important in Japan. However, they are trying to apply those monomers for improvement of pressure sensitive adhesives, adhesion to metals, crosslinking agents, paper coatings, and surface modification of films, etc. Those approaches may accelerate substitution from solvent-based products to waterborne one, and consequently contribute to take measures to environmental issues.

1-5 Conclusion

Typical wet adhesion monomers are introduced from the point of view of improvement for water resist paints in this chapter. The author reviewed and investigated past studies on wet adhesion promoter with ethyleneurea ring. But proposed mechanisms of wet adhesion did not seem to clarify enough the peculiarity of methacrylamide ethyleneurea for this kind of application. In other word, it is valuable to prove it for developing further applications.

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Chapter 2

Copolymer Emulsion with Methacrylamide Ethylethyleneurea and Its Application

2-1 Introduction

As described in Chapter 1, paint films are required to remain on the surface of substances even in wet or high moisture circumstances. Basically solvent-based paints have good water resistance property, so most walls of exterior of house, kitchen and bathroom are painted with solvent-based paints.

However, as the regulation of volatile organic compounds (VOC) becomes tighter because of the growing concerns on environmental issues, waterborne emulsion paints have come to be considered more important.

It is well known that surfactants in a latex have important functions such as emulsification of monomers, providing fields for initiation of emulsion polymerization and stabilizing polymer particles after polymerization. But these surfactants migrate on the surface of formed film and cause bad affection to water resistance. Also emulsion paints usually show poor durability when those surfaces are washed with cleanser.

“Washability” is the word which is prescribed in Japanese industrial standard (JIS) K5400 and means durability for abrasion and damage of such a washing process with cleansers to

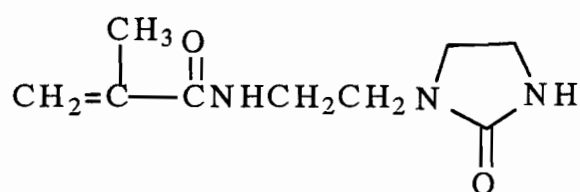
remove stains from painted surface.

In the Western countries, various methods which are a selection of pigments, dispersing agents and compatibilizers have been tried to improve the wet adhesion property. But those trials based on paint ingredients had not performed well. Emulsion-free emulsion polymerization would be a preferable method, but it alone was not enough.

The most effective way to improve this was to introduce a special monomer, which is called "wet adhesion promoter", to the backbone of polymer chain at emulsion polymerization process.

In this chapter, studies about the introducing effects of a representative wet adhesion promoter, methacrylamideethyl ethyleneurea (MAEEU), in emulsion polymerization of acrylate, vinylacetate/acrylate, and styrene/ acrylate will be discussed.

Figure 1 shows structure and properties of MAEEU, that is N-(β -methacrylamidoethyl)-2-imidazolidone.



| | |
|--------------------|-----------|
| Molecular weight: | 197 |
| Melting point: | 115-117°C |
| Tg of homopolymer: | 87±3°C |

Fig.1 Structure of methacrylamideethylethylene urea

2-2 Experimental

Materials

Methylmethacrylate (MMA), Butyl acrylate (BA), Methacrylic acid (MAA) were used without further purification. N-methylol methacrylamide, glycidyl methacrylate, 2-hydroxyethyl methacrylate, were also used as received. The composition of SIPOMER WAM-II is 50% of MAEEU, 20% of MAA, and 30% of water with 2000ppm of hydroquinone as an inhibitor. Commercial grade Polyoxyethylene (40mol) octylphenol ether (IGEPAL CA-897) and Ammonium salt of polyoxyethylene (4mol) nonylphenol ether sulfate (RHODAPEX CO-436) was used as received. Analytical grade ammonium persulfate (APS) as an initiator was recrystallized. Deionized water was used.

Preparation of polymer particles

Anionic emulsions were prepared by emulsion feeding polymerization method. The polymerization conditions were listed on Table 1. The kettle charged water was heated to 80°C. 20 % of initiator solution (16ml) was added, then immediately 10 % of monomer emulsion (50 ml) was added and held for 10 min. Remaining initiator and monomer emulsion was fed dropwise for 3 h. respectively while maintaining temperature at 78~82°C. After addition temperature was raised to 85°C and maintained for 1 h., then cooled down to below 30°C. pH of emulsion was adjusted to 8-9 by ammonium hydroxide and coagulum was filtered through 100 mesh cheese-cloth.

An emulsion without SIPOMER WAM-II was prepared as a control with the same condition. Several polymer emulsions were also prepared with typical functional monomers instead of MAEEU. Tested monomers were N-methylol methacrylamide (N-MMAm), glycidyl methacrylate (GMA), 2-hydroxyethyl methacrylate (2-HEMA).

Table 1 Monomer composition and formulation of Emulsion

Kettle Charge

| | |
|-----------------|---------|
| Deionized water | 156.6 g |
|-----------------|---------|

Emulsion of Monomers

| | |
|-----------------|--------|
| Deionized water | 96.0 g |
|-----------------|--------|

| | |
|-----------------------|--------|
| RHODAPEX CO-436(58%)* | 12.8 g |
|-----------------------|--------|

| | |
|------------------------|-------|
| IGEPAL CA-897 (70%) ** | 1.6 g |
|------------------------|-------|

| | |
|--------------------|---------|
| Methylmethacrylate | 189.0 g |
|--------------------|---------|

| | |
|---------------|---------|
| Butylacrylate | 189.0 g |
|---------------|---------|

| | |
|------------------|-------|
| Methacrylic acid | 4.8 g |
|------------------|-------|

| | |
|--------------------------------|-------|
| <i>Functional monomers</i> *** | 8.6 g |
|--------------------------------|-------|

Initiator Solution

| | |
|-----------------|--------|
| Deionized water | 80.0 g |
|-----------------|--------|

| | |
|---------------------|------|
| Ammonium Persulfate | 1.6g |
|---------------------|------|

* Ammonium salt of polyoxyethylene (4) nonylphenol ether sulfate,

** Polyoxyethylene (40) octylphenol ,

*** GMA, N-MMAm, 2-HEMA, or MAEEU

Preparation of semi-gloss paints

The formulation of semi-gloss paint is showed on table 2. Each ingredient was added in the order of listed and the mixed paint was agitated until it became smooth and uniform by a disperse-mill.

Table 2 Composition of the Semi-gross Paint

| | |
|--|-------------------|
| 1) Water | 287.5 g |
| 2) BEVALOID 6755 * ¹ | 12.5 g |
| 3) IGEPAL CTA-639W * ² | 6.5 g |
| 4) CELLOSIZ WP-4400 (3 %aq.)* ³ | 2.5 g (Thickener) |
| 5) BEVALOID 6001* ⁴ | 4.3 g (Defoamer) |
| 6) Tiumium dioxide | 687.5 g |
| 7) Ethylene glycol | 186.5 g |
| 8) Prepared polymer emulsion | 681.25g |
| 9) Ethylene glycol | 46.5 g |
| 10) Ammonium monophosphate | 2.5 g |

*¹ BEVALOID 6755: Sodium salt of polyacrylic acid (Dispersing agent)

*² IGEPAL CTA-639W: Polyoxyalkylene nonylphenol ether(Dispersing agent)

*³ CELLOSIZ WP-4400: Carboxy methyl cellulose (Thickener)

*⁴ BEVALOID 6001:Mineral oil based defoaming agent

Wet Adhesion Test (Washability)

a) Apparatus

Erichsen washability and scrubbing resistance tester Model 494, steel plate: dull black, glass base plate, coating rod,

high gloss oil-based enamel (tinted), and abrasive type scrub medium conformance with ASTM methods D2486 and D3450 supplied by the Lenata Company were used.

b) Preparation before the test

High gloss, oil based enamel was coated as $75\mu\text{m}$ thick film on a steel plate. It was dried at room temperature for seven days. After the simultaneous coating of the prepared paints using the latex with and without SIPOMER WAM-II were made across and perpendicular to the gloss enamel near center of the plate. Other paints from emulsions with different functional monomers were coated by the same way. These coatings were dried at room temperature for seven days. The coated plate was taped to a glass base plate and mounted in the Erichsen Tester. A brush was soaked in a 2% solution of IGEPAL CA-720, polyoxyethylene (16mol) nonylphenol ether for 30 min. The brush was then removed and excess detergent was shaken off. 10g of scrub medium was spread evenly over the brush bristles. The brush was mounted in the holder of the Tester. The panel was wetted with 5g of water in the brush path.

c) Testing procedure

After each 250 cycles, 10 g of scrub media was added. The brush was remounted and 5 g of water was added in the path of the brush to continue the test. The number of cycles needed to fully remove the paint film in a continuous line across all of the test paints was recorded. The results of the paints using latices

with/without SIPOMER WAM-II were compared. Before testing the next panel, the brush was rinsed and pre-soaked in a 2% solution of IGEPAL CA-720 solution for 5 min.

Swelling Diameter Test (SDT)

Films of about 0.5mm thickness were prepared from each emulsion on a polypropylene board (8 x 12.5cm). Cast emulsions were dried at room temperature for 24 h. and cured at 100 °C for 1 h.. Cured films were cut by circle of 15mm diameter. Those specimens were immersed into tetrachloro ethylene for 1 hr, then measured diameter (d) of swelling circle of films and observed condition. SDT was calculated by the following scheme.

$$SDT (\%) = (d-d_0)/d_0 \quad d_0 = 15 \text{ (mm)}$$



2-3 Results and Discussion

Preparation of polymer emulsion

Table 3 showed the property of prepared polymer emulsion. The conversion rate of emulsion with 1% of MAEEU was 98.9%, and it had good mechanical, freeze-thaw, and high temperature stabilities.

Table 3 A recipe of polymerization incorporating MAEEU

| | |
|-----------------------------------|----------------------|
| Deionized water | 85.0 g |
| Nonoxynol-4sulfate ammonium salt* | 3.3 g |
| Octoxynol-40 ** | 0.4 g |
| Monomers (MMA/BA/MAA) | 99.0 g (48.5/48.5/2) |
| Methacrylamidoethylethyleneurea | 1.0 g |
| Ammonium persulfate | 0.4 g |

Emulsion feeding method, polymerization temperature 80°C

*RHODAPEX CO-436 (58%) (RHODIA)

**IGEPAL CA-897 (70%) (RHODIA)

The property of the polymer emulsion above

| | |
|-----------------------------------|------------|
| Solid | 53.3 % |
| Wet coagulum | < 0.05 % |
| Viscosity | 200 mPa·s |
| Thaw-freeze stability | > 5 cycles |
| High temperature stability (50°C) | > 30 days |

Wet Adhesion Test

Figure 2 showed the result of the wet adhesion test. The white paint with control latex peeled off only by 85 scrub cycles. On the other hand, the white paint with 2 wt% of SIPOMER WAM-II co-polymerized latex was still intact after 3,000 scrub cycles.

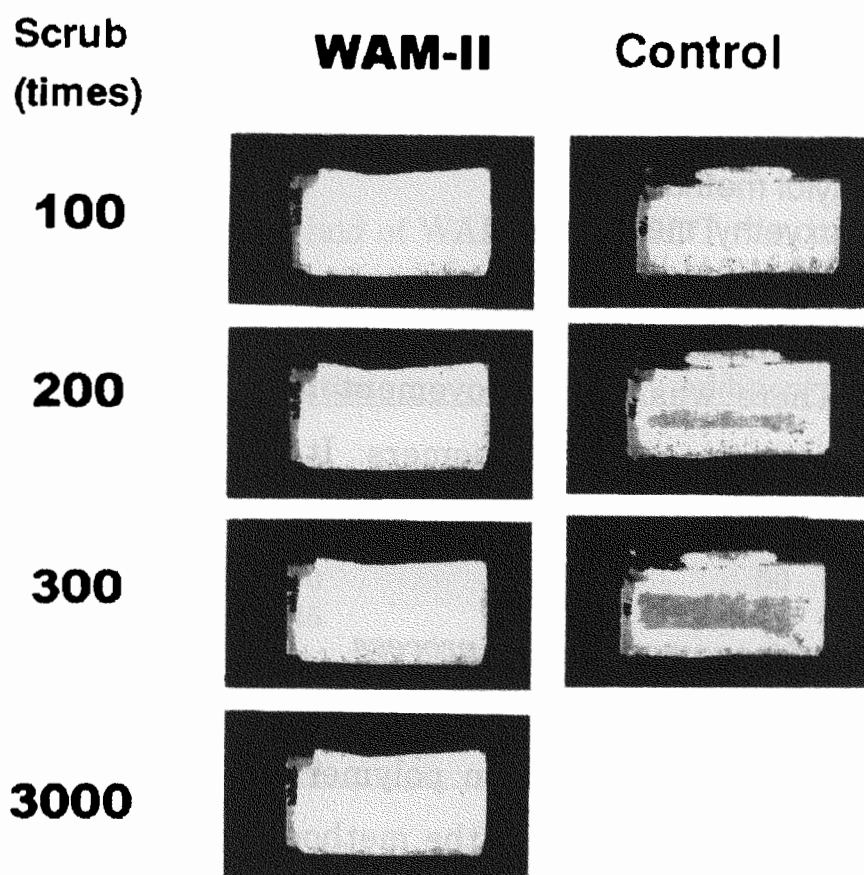


Fig. 2 Wet adhesion test for paint with SIPOMER WAM-II and control

Several polymer emulsions were prepared with typical functional monomers such as N-methylol methacrylamide, glycidyl methacrylate, 2-hydroxyethyl methacrylate. The dosage was 2%, as same as amount of SIPOMER WAM-II of Table 1. The same emulsion polymerization method and the same formulation as table 2 were used to prepare each paint. Table 4 shows the results of washability test for these paints.

Table 4

Incorporation effect of functional monomers vs. wet adhesion

| Functional monomers in binder emulsion | Wet adhesion scrub cycles |
|--|---------------------------|
| Glycidyl methacrylate | 220 |
| N-methylol methacrylamide | 70 |
| 2-Hydroxyethyl methacrylate | 250 |
| SIPOMER WAM-II | >3,000 |

There was no improvement for wet adhesion properties with these functional monomers. It is clear that the effect of MAEEU is significantly peculiar.

Effect of monomer feeding process

Three different feeding methods of SIPOMER WAM-II was investigated with emulsion polymerization by emulsion feeding method. Pre-addition was the method that WAM-II added to the initial kettle charge with deionized water. Post-addition was the method that WAM-II added at once to the reactor when the feeding of monomer emulsion was finished. And simultaneous addition was a typical emulsion feeding method of mixture with WAM-II and other monomers.

Table 5 shows the SDT result on different addition methods of WAM-II on emulsion polymerization. The film of non-crosslinked copolymer of MMA/BA/MAA dissolved in tetrachloroethylene. The simultaneous addition of WAM-II with base monomers imparted the best result for solvent resistance. The post-addition of WAM-II did not show any improvement for

this SDT test. The wet adhesion scrub test results were also correlated with those test results. The simultaneous and pre-addition showed better performance than post-addition. The post-addition had no improvement as compared to control.

Table 5 addition method of WAM-II and SDT results

| | Control No-addition | Pre-addition | Simultaneous -addition | Post-addition |
|------------------------|------------------------|--------------|---------------------------|---------------|
| <i>Kettle charge</i> | | | | |
| D.I.water | 96 | 95 | 95 | 95 |
| WAM-II | | 1 | | |
| <i>Monomer Em.</i> | | | | |
| BA | 50 | 50 | 50 | 50 |
| MMA | 45 | 45 | 45 | 45 |
| MAA | 1 | 1 | 1 | 1 |
| WAM-II | 0 | | 1 | |
| Na DBS(33%) | 8 | 8 | 8 | 8 |
| D.I. Water | 50 | 50 | 50 | 50 |
| <i>After M-feeding</i> | | | | |
| WAM-II | | | | 1 |
| SDT (%) | dissolved | 150 | 100 | dissolved |

WAM-II should be introduced when it mixes with base monomers and interacts with carboxyl group well. But on the pre-addition or post-addition cases, both of functional groups are hard to crosslink each other. Because MAEEU is a water soluble monomer.

Combining effect of MAEEU containing emulsion

A polymer emulsion which contains 4 wt% per total monomer of SIPOMER WAM-II was prepared by emulsion feeding method. Table 6 shows effect of blended emulsion with a

commercial poly(vinylacetate-acrylic) emulsion and the results when it was used as a binder for a white mat paint. On this case, 10-20% addition of copolymer of MAEEU also improved the wet adhesion properties of the white paint significantly.

Table 6 Wet adhesion of blended binder for paints

| Paint binder | 1 | 2 | 3 |
|---|------|-------|-------|
| PVAc-acrylate latex (parts) | 100 | 90 | 80 |
| Acrylic latex with 4% of WAM-II (parts) | 0 | 10 | 20 |
| Wet adhesion scrub cycles | <100 | 1,400 | 2,500 |

2-4 Conclusion

Using a commercially available wet adhesion promoter, SIPOMER WAM-II, that is mixture of methacrylamide ethylethyleneurea (MAEEU) and methacrylic acid, wet adhesion property has studied on this chapter. SDT result showed addition of MAEEU in monomer emulsion formed a kind of crosslinking between polymer chain during emulsion polymerization process. But the effect of ethyleneurea ring incorporation to copolymer emulsion was superior to typical crosslinking monomers. Also it was found that blend of emulsion with ethyleneurea to control emulsion improved wet adhesion property.

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PART 2

Synthesis and Evaluation of Polymers Containing Ethyleneurea Ring

Chapter 3

Interaction Between Ethyleneurea Ring and Carboxyl Group in Polymer

3-1 Introduction

Complex formations between synthetic polymers, such as poly(acrylic acid) and poly(ethyleneoxide), or poly (acrylamide) and poly(acrylic acid), are well known as a reversible reaction . It is considered that pH- and temperature-sensitive interpolymer was formed through hydrogen bonding and hydrophobic interaction between these polymers ¹⁾. This behavior is interesting as not only a model of complex between biopolymers such as enzyme and substrate, or antigen and antibody but also a application for drug delivery system.

In the previous chapter, the author confirmed that the film from MAEEU copolymer emulsion showed superior wet adhesion properties on the alkyd resin coated layer. This effect could be due to interaction between ethyleneurea ring in polymer particles and carboxyl group or hydroxy group in alkyd resin.

In this chapter, copolymer of MAEEU and methacrylic acid was prepared by solution polymerization. Also, polymer particles with ethyleneurea ring, carboxyl group and both of them were prepared respectively, and interaction of those particles by blend of these emulsions was studied to clarify mechanism of MAEEU

functions.

3-2 Experimental

Materials

A commercial monomer mixture of MAEEU and methacrylic acid was used as received. (SIPOMER WAM-II, RHODIA, see Table 1) SIPOMER β -CEA, is used as received. (mixture of β -carboxyethyl acrylate 40wt%, acrylic acid 20wt%, and further polyester oligomers) 2-Propanol, tetrachloroethylene, sodium hydroxide were used as received. Analytical grade of potassium peroxide was recrystallized before use. Deionized water was distilled before use. Calcium hydroxide, $\text{Ca}(\text{OH})_2$, was used as received. Sodium salt of dodecylbenzene sulfonate, RHODACAL DS-10 (RHODIA), was used as received.

Table 1 Typical properties of SIPOMER WAM-II

| | | |
|------------------|---------------------|------------------|
| MAEEU | 50% | (mol ratio 1.00) |
| Methacrylic acid | 20% | (mol ratio 0.92) |
| Water | 30% | |
| MEHQ | 1,000 ppm | |
| Appearance | Clear, amber liquid | |
| Viscosity | 20 mPa·s | |
| Color (Gardner) | 5 | |
| pH(10% aq) | 4 | |

Preparation of MAEEU-methacrylic acid co-polymer

Table 2 shows recipe for the preparation of copolymer of MAEEU and methacrylic acid. Copolymer solution was prepared at 80°C for 2 h. under nitrogen atmosphere. Then a solution of NaOH was added dropwise to copolymer solution to neutralize carboxyl group. Water was distilled as azeotropic mixture with 2-propanol from neutralized solution ²⁾. Obtained dark brown gel was re-precipitated by 2-propanol and filtrated. After drying, light brown solid was obtained.

Table 2 Recipes of Preparation of P(MAEEU/MAA)

| <i>Solution polymerization</i> | |
|--------------------------------|---------|
| MAEEU | 40.0 g |
| Methacrylic acid | 16.0 g |
| 2-Propanol | 168.0 g |
| Deionized water | 76.0 g |
| KPS | 1.0 g |
| <i>Neutralization</i> | |
| NaOH (flake) | 7.2 g |
| Deionized water | 95.3 g |

Refining of MAEEU

MAEEU was separated and refined from commercial grade SIPOMER WAM-II. Aqueous solution of Ca(OH)₂ was added to

SIPOMER WAM-II to remove methacrylic acid. This mixture was kept in refrigerator for one day, then generated precipitation of calcium methacrylate was removed by filtration. Obtained solution was dark brownish liquid which was 37% solid content. MAEEU was recrystallized from acetone, and identified by FT-IR and H-NMR.

Preparation of polymer particles

The copolymer particles with refined MAEEU was prepared by emulsion polymerization under usual condition which is listed in Table 3.

Table 3 Recipes of Emulsion polymerization with MAEEU

| | EU-1 | CE-1 | WA-1 |
|-----------------------------|------|------|------|
| Butyl acrylate | 49 | 49 | 49 |
| Methylmethacrylate | 49 | 49 | 49 |
| MAEEU (37%) | 1.1 | | |
| SIPOMER WAM-II | | | 2 |
| B-Carboxyethyl acrylate | | 2 | |
| Dodecylbenzene sulfonate Na | 3 | 3 | 3 |
| Ammonium persulfate | 0.2 | 0.2 | 0.2 |
| Deionized water | 146 | 147 | 147 |

Emulsion feeding method 80°C, 4h., solid content 40%

The obtained two kinds of polymer particles were mixed well (EU-1 and CE-1, WA-1 and CE-1) at various molar fractions and subjected to further experiments.

Swelling Diameter Test (SDT)

Films of about 0.5mm thickness were prepared from each emulsion on a polypropylene board (8 x 12.5cm). The cast emulsions were dried at room temperature for 24 h. and cured at 100 °C for 1 h.. Cured films were cut by circle of 15mm diameter. Those specimens were immersed into tetrachloroethylene for 1 h., then measured diameter (d) of swelling circle of the film and observed condition. SDT was calculated by the following scheme.⁴⁾

$$\text{SDT (\%)} = (d-d_0)/d_0 \quad d_0 = 15$$

Viscoelasticity

Dynamic mechanical spectroscopic studies were carried out under tensile conditions with a dynamic viscoelastic analyzer (Seiko Instruments Inc., EXSTAR DMS 6100) at 1-10Hz and at a heating rate of 5°C/min.

3-3 Results and Discussion

MAEEU-Methacrylic acid co-polymer

The water-absorbing capacity of obtained copolymer P(MAEEU-MAA) was 33 g/g-polymer. And the shape of water-absorbed gel was similar to original dried polymer. (Fig. 2) It indicates that copolymer of MAEEU and MAA is highly cross-linked.

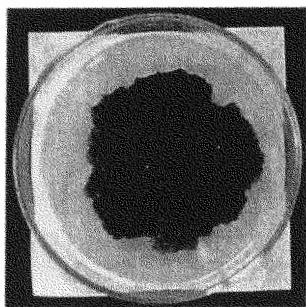


Fig.1 Copolymer gel (wet)

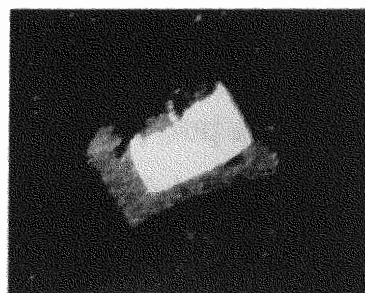
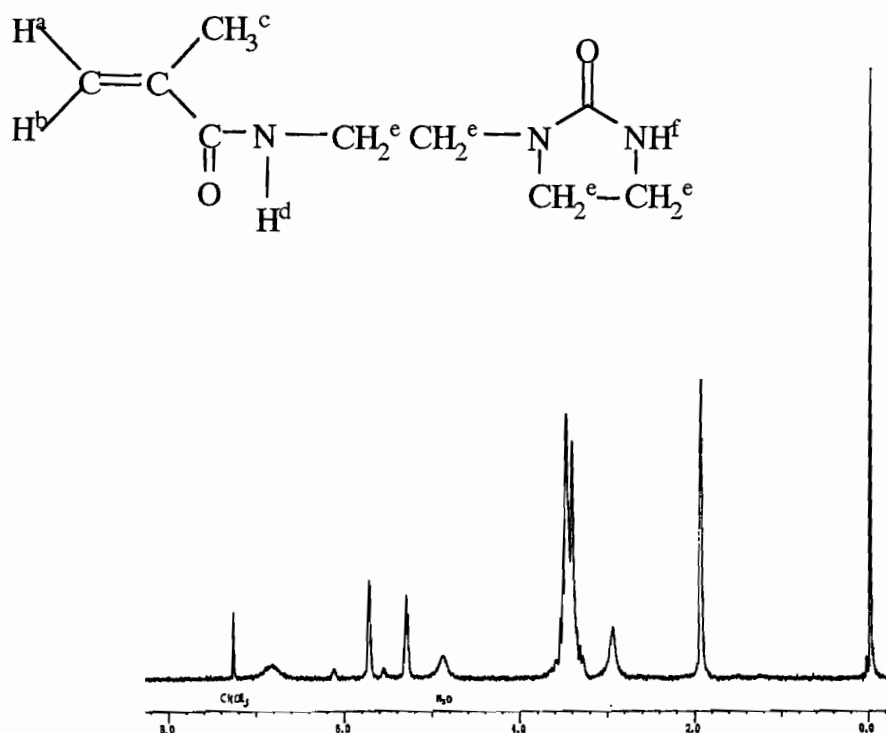


Fig. 2 Water-absorbed gel
(White portion is filter paper)

¹H-NMR of MAEEU (in CDCl₃)



| | | | | |
|----------|---|--------------------------------|---|--|
| δ | c | 1.9 (3H, s, -CH ₃) | e | 3.5 (8H, m, CH ₂ -CH ₂) |
| | d | 4.9 (1H, H-N<) | b | 5.3 (1H, H-C=) |
| | a | 5.7 (1H, H-C=) | f | 6.9 (1H, H-N<) |

Swelling Diameter Test (SDT)

P(BA-MMA-MAEEU) polymer particles (EU-1) and P(BA-MMA- β -CEA) polymer particles (CE-1) were blended at various ratio and measured SDT by tetrachloroethylene. (Table 4) The major component of SIPOMER β -CEA is 2-carboxyethyl acrylate, that is dimer of acrylic acid, and Tg of its homopolymer is 37°C. It is much lower than that of acrylic acid (107°C). So it does not make a coating film harder like as acrylic acid. Figure 3 shows that almost equimolecular quantity of ethyleneurea and carboxylic acid imparts the highest solvent resistance. Very similar results were obtained by blending of P(BA-MMA-WAM-II) polymer particles (WA-1) and P(BA-MMA- β -CEA) polymer particles (Table 5).

Figure 4 also shows almost equimolecular quantity of ethyleneurea and carboxylic acid imparts the highest solvent resistance. Those results support the existence of interaction between ethyleneurea ring and carboxyl group.

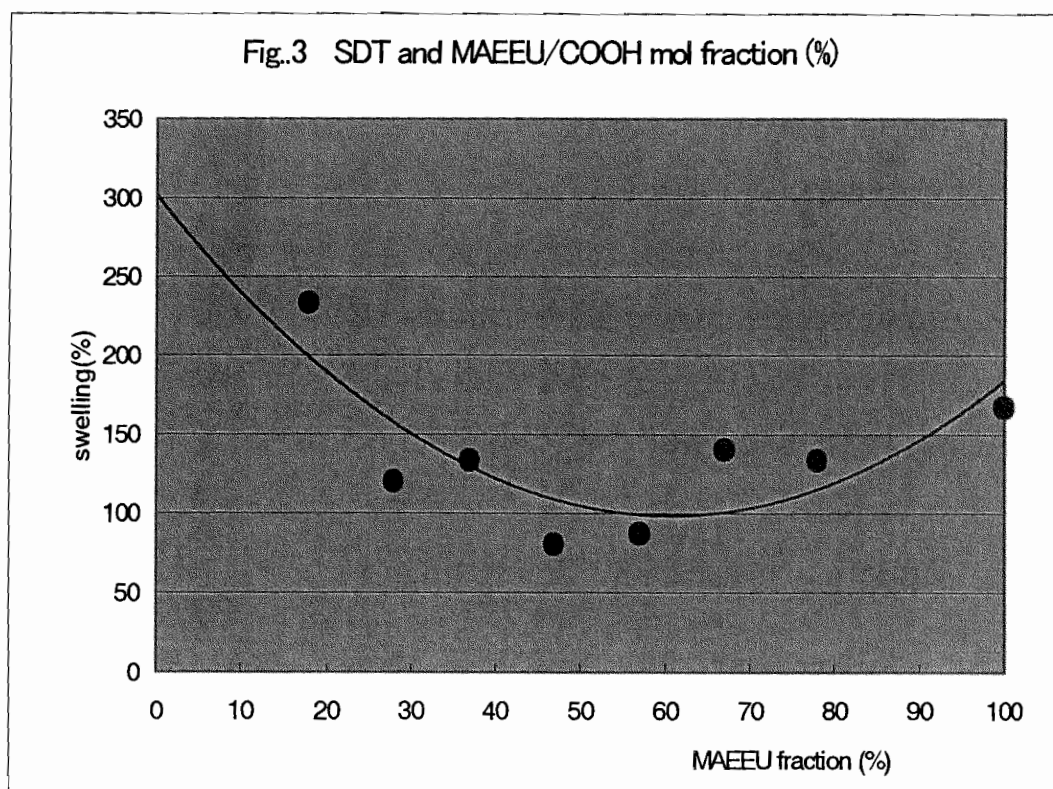
Table 4 SDT test results and mol ratio of MAEEU/-COOH

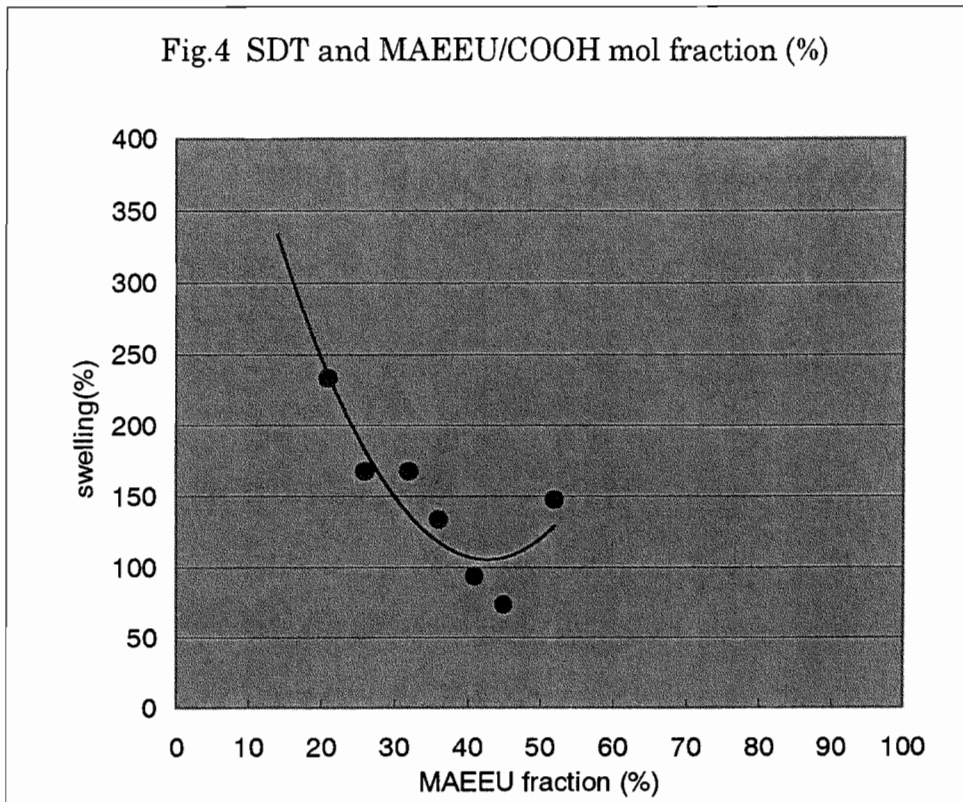
| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| EU-1(1.1%) | 100 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 0 |
| CE-1(2.0%) | 0 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 100 |
| MAEEU/COOH molar fraction(%) | 100/0 | 78/22 | 67/33 | 57/43 | 47/53 | 37/63 | 28/72 | 18/82 | 0/100 |
| SDT (%) | 167 | 133 | 140 | 87 | 80 | 133 | 120 | DS* | DS* |

Table 5 SDT test results and mol ratio of MAEEU/-COOH

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| WA-1(2.0%) | 100 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 0 |
| CE-1(2.0%) | 0 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 100 |
| MAEEU/COOH molar fraction(%) | 52/48 | 45/55 | 41/59 | 36/64 | 32/68 | 26/74 | 21/79 | 14/86 | 0/100 |
| SDT (%) | 147 | 73 | 93 | 133 | 167 | 167 | DS* | DS* | DS* |

DS*: Dissolved in solvent





Dynamic Viscoelasticity

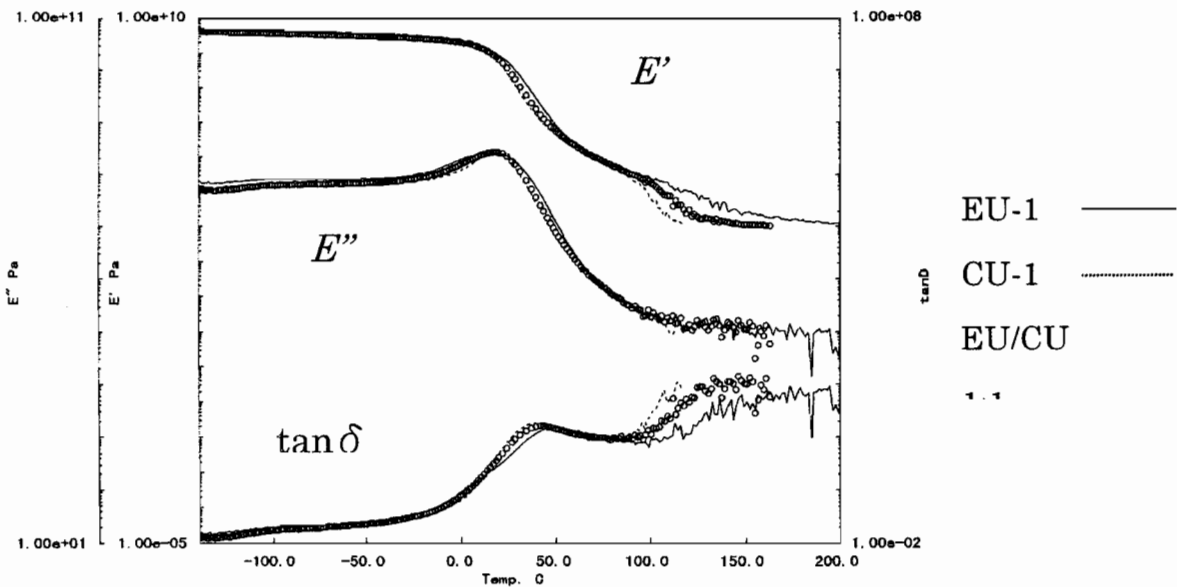


Fig. 5 Dynamic viscoelasticity of films from copolymer emulsions and blended emulsion

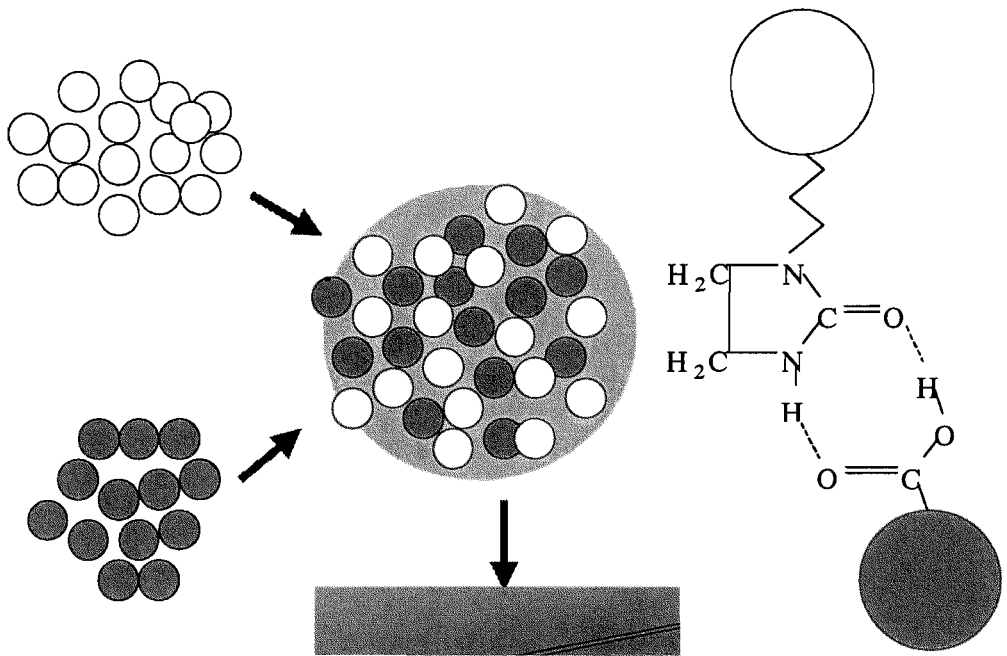
The storage modulus E' , loss modulus E'' and loss tangent $\tan \delta$ of blended emulsion film (EU-1/CU-1 50/50) was observed as just in between that of EU-1 and that of CU-1.

3-4 Conclusion

The following conclusions were derived from the results and discussions.

- 1) The cross-linkage between ethyleneurea ring and carboxyl group occurred not only in polymer solution but also in emulsion particles mixture.
- 2) Most effective molecular ratio of MAEEU/COOH was about 1:1.
- 3) Wet adhesion property of SIPOMER WAM-II may be improved by reduction of MAA. (If cross-linking between the paint with WAM-II and alkyd paint layer is more important.)
- 4) This result suggests possibility of room temperature cross-linking system.

Effect of Emulsion Blend



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Chapter 4

Synthesis of Polymer Particles with Ethyleneurea ring and the Wet Adhesion Properties

4-1 Introduction

A sort of specialty monomers is commercially used for emulsion polymerization system to improve adhesion property of waterborne paints in wet condition. It is known that these wet adhesion monomers achieve significant improvement to durability of coating layer for washing. Methacrylamideethyl-ethyleneurea is one of the most effective wet adhesion monomers when it is introduced to the binder emulsion of waterborne paints.

In the present chapter, co-polymer emulsions with n-Butyl methacrylate and MAEEU were synthesized by emulsion-free emulsion polymerization. Then films were prepared respectively from these emulsions, and effects of introduction of ethyleneurea ring on wet adhesion properties were investigated.

4-2 Experimental

Materials

n-Butyl methacrylate (BMA, Nacalai Tesque Inc.) was purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Methacrylamide

ethylethyleneurea (MAEEU) was separated from SIPOMER WAM-II (RHODIA) which is commercialized as a mixture of MAEEU (50%), methacrylic acid (20%), and water (30%). Calcium chloride and water were added to SIPOMER WAM-II, then kept in refrigerator for one night (16h.). The resulting calcium methacrylate was removed by filtration. MAEEU was recrystallized from acetone. (white powder, mp 114.5-117°C) Analytical grade of potassium persulfate (KPS, Nacalai Tesque Inc.) as an initiator was recrystallized. Deionized water (resistivity : $5 \times 10^6 \Omega \cdot \text{cm}$) was distilled before use .

Table 1 Recipes of emulsifier-free emulsion polymerization for preparation of P(BMA / MAEEU) particles

| Ingredients | MAEEU contents (mol %) | | | |
|-----------------------|------------------------|-------|-------|-------|
| | 0 | 0.25 | 0.5 | 1.0 |
| BMA (g) | 80.0 | 14.95 | 14.90 | 14.80 |
| MAEEU (g) | 0 | 0.05 | 0.10 | 0.20 |
| KPS (g) | 0.80 | 0.30 | 0.30 | 0.30 |
| Water (g) | 720 | 285 | 285 | 285 |
| Dh ^{b)} (nm) | 390 | 423 | 514 | 562 |

a) In flask: N₂; 70°C; 10h.; stirring rate 300rpm

b) Hydrodynamic diameter measured by DLS

Preparation of polymer particles

The copolymer particles of P(BMA-MAEEU) was prepared by emulsifier-free emulsion polymerization under condition which is listed in Table 1. Prescribed amount of BMA, MAEEU, KPS, and water were charged in a four-neck flask, then polymerized at

70°C under nitrogen atmosphere.

Table 2 Recipes of emulsifier-free seeded emulsion copolymerizations for preparation of PBMA / P(BMA-MAEEU) particles

| Ingredients | MAEEU contents (mol %) | | |
|------------------------------------|------------------------|------|------|
| | 0.25 | 0.5 | 1.0 |
| PBMA Particles ^{b,c)} (g) | 3.49 | 3.48 | 3.45 |
| BMA (g) | 17.4 | 17.4 | 17.2 |
| MAEEU (g) | 0.06 | 0.13 | 0.27 |
| KPS ^{d)} (g) | 0.26 | 0.26 | 0.26 |
| Water (g) | 330 | 330 | 330 |
| Dh ^{e)} (nm) | 720 | 724 | 870 |

a) N₂; 70°C; 24h.; stirring rate, 160rpm

b) Produced by emulsifier-free emulsion copolymerization

c) Hydrodynamic diameter measured by DLS, 390nm

d) First, 0.175g of KPS was added and 18h. later the remains (0.085g) as aqueous solution was added.

e) Hydrodynamic diameter measured by DLS

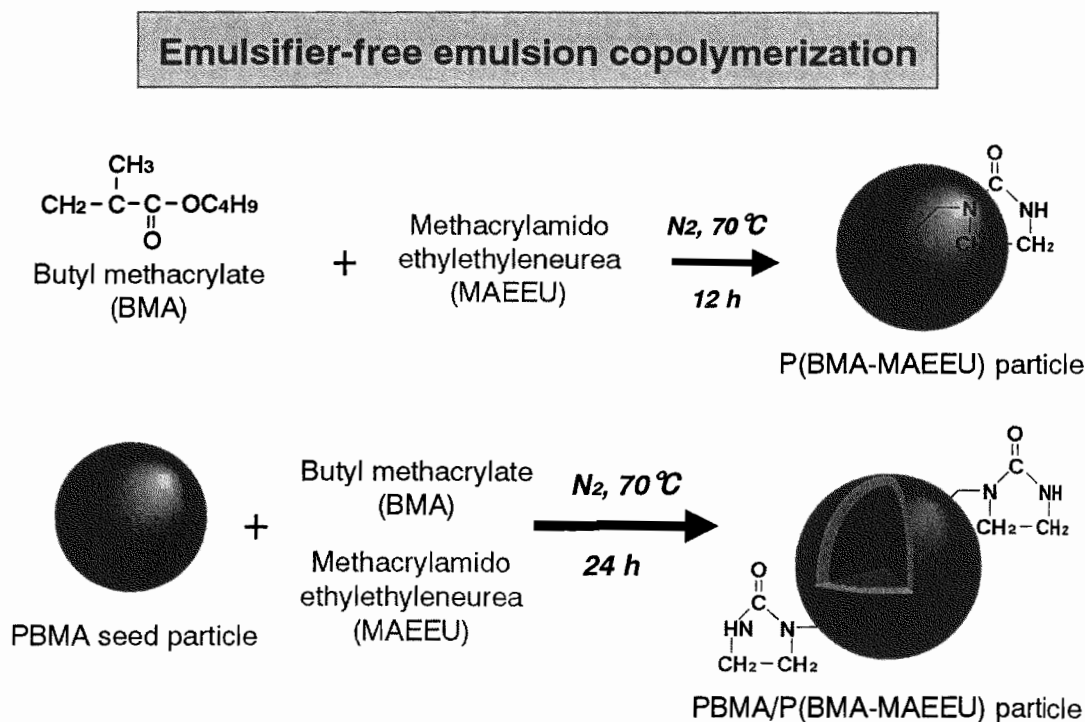
The particles of PBMA/P(BMA-MAEEU) were also prepared by emulsifier-free seeded emulsion polymerization under condition listed in Table 2. Poly(butyl methacrylate) particles used as seed particles were prepared by the same procedure of emulsifier-free emulsion polymerization under condition on Table 3 at 80°C.

Table 3 Recipes of emulsifier-free seeded emulsion copolymerization for preparation of PBMA seed particles

| Ingredients | | |
|------------------|------|-----|
| BMA | (g) | 80 |
| KPS | (g) | 0.8 |
| Water | (g) | 720 |
| Dh ^{c)} | (nm) | 390 |

- a) In flask : N₂; 70°C; 10h.; stirring rate, 120rpm
 b) Produced by emulsifier-free emulsion polymerization
 c) Hydrodynamic diameter measured by DLS

Fig.1 Preparation of MAEEU Copolymers



Observation of particles by electron microscope

P(BMA-MAEEU) particles and PBMA/P(BMA-MAEEU) particles were observed with a transmission electron microscope (TEM, Nippon Electron Inc. JEM2010CX) and taken photographs.

Film formation

Before the film formation, polymer particles were washed three times by a centrifuge instrument. Films with a wet thickness of about $100\ \mu\text{m}$ were prepared from each emulsion by casting on an alkyd resin coated steel plate and dried for 24 h. at 40°C . And also a film of P(BMA-MAEEU) copolymer particles

Fig.2 Procedure of cross-cut adhesion test

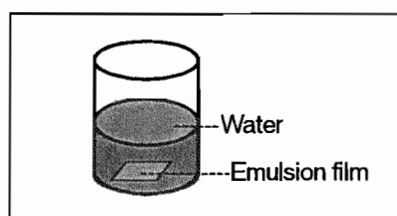
Experiment procedures for the measurements of wet adhesion

P(BMA-MAEEU), PBMA/P(BMA-MAEEU) emulsion

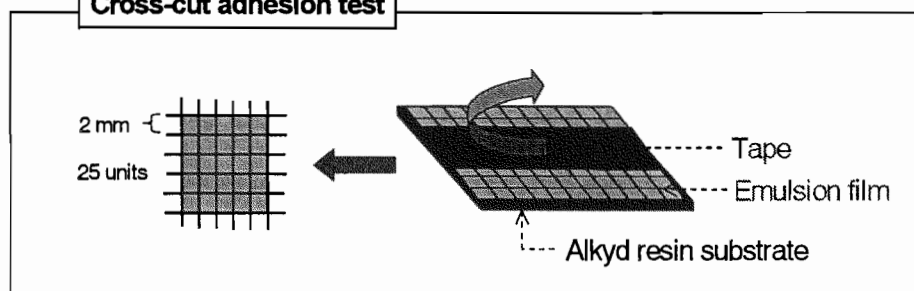
↓
Casting on Alkyd resin substrate
(Film thickness: $100\ \mu\text{m}$)

↓
Drying at 40°C for 1 day

↓
Annealing in water for 1 day



Cross-cut adhesion test



with post-added sodium dodecylsulfate (SDS) was prepared to investigate an effect of typical emulsifier.

Evaluation of wet adhesion property by cross cut adhesion test

Obtained emulsion films on the alkyd resin coated plate were immersed in water for one day at 25°C, then films were cut to 25 squares (5 x 5) with 2mm intervals between each lines. After that pressure sensitive adhesive tape (Nitto Electric Inc.) was put on the surface of films and was stuck by 2kg roller (one round trip). The exfoliation test have been done several times, counted remained number of square, and described its percentages for 25 squares. (JIS K5400 method)

Determination of MAEEU by elementary analysis

Emulsion particles were washed three times by centrifuge, and dried 3 days under reduced pressure. MAEEU was determined from nitrogen contents in particles by automatic high sensitive nitrogen-carbon-hydrogen analyzer (Shimadzu SUMIGRAPH NCH-21)

Evaluation of Minimum film formation temperature (MFT)

Emulsion particles were washed three times by the centrifuge, diluted to 1×10^{-4} wt% as solid content with 10mM KCl aqueous solution, and adjusted pH with HCl or KOH aqueous solutions. Each ζ -potential was measured by electrophoresis light scattering instrument (Otsuka electronics LEZA-600).

4-3 Results and Discussion

Preparation of polymer particles

Figure 3 shows time-conversion curve of emulsifier-free emulsion polymerization with 1 mol% of MAEEU. The polymerization rates were relatively slow, however almost 100% monomer converted to polymer in 10 h.. The more MAEEU was used, the hydrodynamic diameter increased and more coagulation was generated.

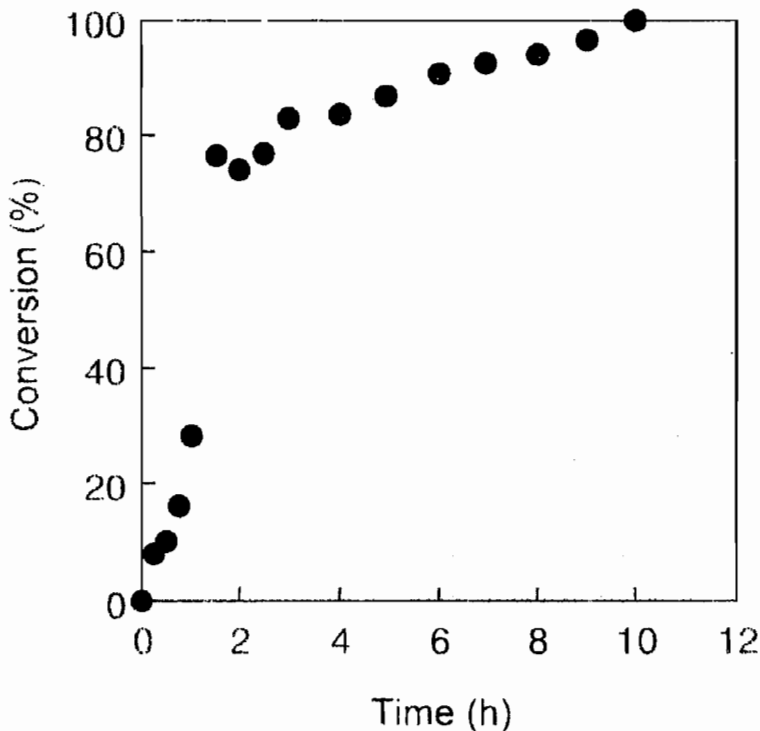


Fig.3 Time-conversion curve for emulsifier-free emulsion polymerization of BMA and MAEEU (1 mol%)

Figure 4 shows relationship of MAEEU concentration and the gel fraction at 5-10 wt% of total monomer concentration. At 10 wt% monomer concentration, even 1 mol % of MAEEU with 99 mol % of BMA was not stable, gel fraction was 30 wt%. At 5 wt% monomer concentration, practically 2 mol% of MAEEU introduction was almost the upper limit.

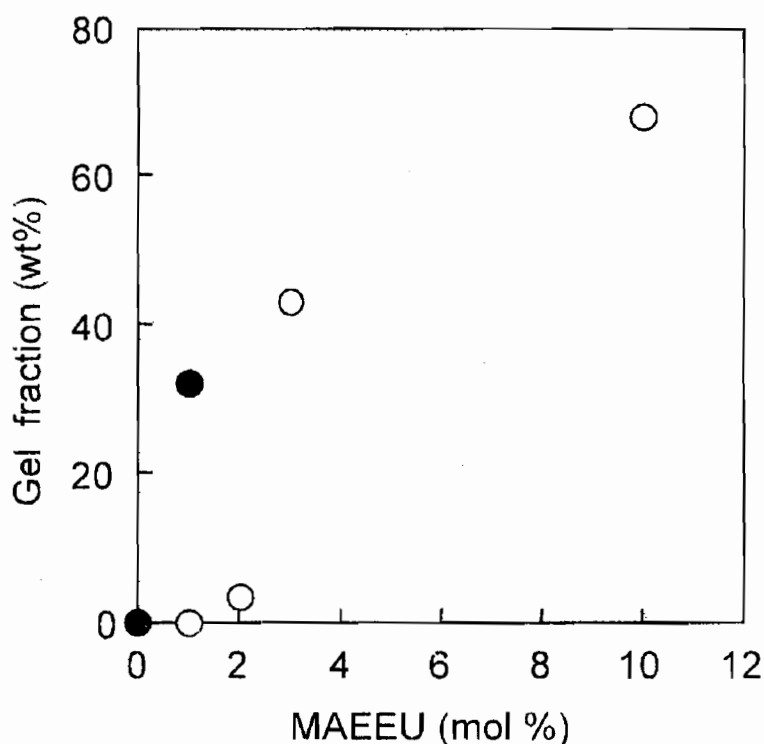


Fig.4 Relationship between the MAEEU concentration and the gel fraction during emulsifier-free emulsion copolymerization of BMA and MAEEU at 70°C for 10 h. in serum. Monomer concentrations, 5 wt%(○), 10 wt%(●)

Observation of particles by electron microscope

Figure 5 shows TEM photographs of particles of P(BMA-MAEEU) with 0.5 %mol MAEEU concentration and that of PBMA/P(BMA-MAEEU). Particles coalesced with each other because of low glass transition point, however it was stable in emulsion phase. The particle size is fairly monodisperse. Seeded particles are much larger than simple copolymer particles.

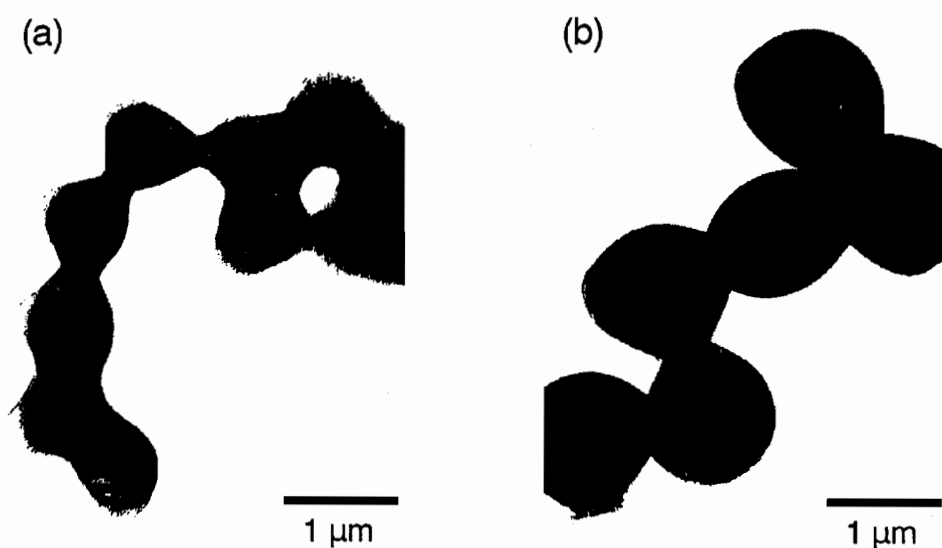


Fig. 5 TEM photographs of (a) P(BMA-MAEEU) and (b) PBMA/P(BMA-MAEEU) particles: MAEEU content 0.5 mol%

Effects of an emulsifier for wet adhesion

Figure 6 shows cross cut test results of emulsion films from emulsifier-free P(BMA-MAEEU) particles and copolymer particles with post added SDS. The wet adhesion property

decreased with increasing addition amount of SDS. Especially it dropped sharply in the vicinity of the critical micelle concentration (c.m.c.) of SDS, which is $1.2-3.6 \times 10^{-3}$ mol/l. It is clear that emulsifier affects wet adhesion properties, therefore emulsifier-free emulsion polymerization must be very useful to improve wet adhesion.

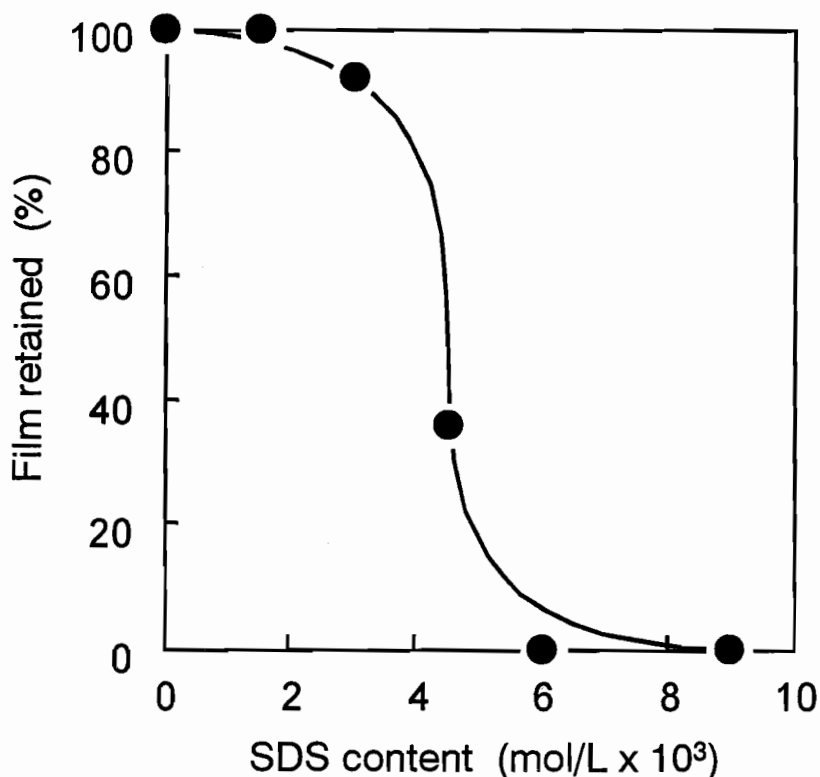


Fig. 6 Relationship between SDS content and film retained after the 10 times cross-cut adhesion test for P(BMA-MAEEU) emulsions (MAEEU, 1.0 mol%) films after soaking in water at 60°C for 2 days

Evaluation of wet adhesion property

Figure 7 shows cross cut test results of films from a P(BMA) emulsion and P(BMA-MAEEU) copolymer emulsions. The film from P(BMA) homopolymer remained few parts on the plate, however the film from copolymer particles with 1 mol% of MAEEU did not peel off from the plate at all, after this peeling test. The more MAEEU introduced to particles, the more film parts remained on the plate (0-1.0 mol %).

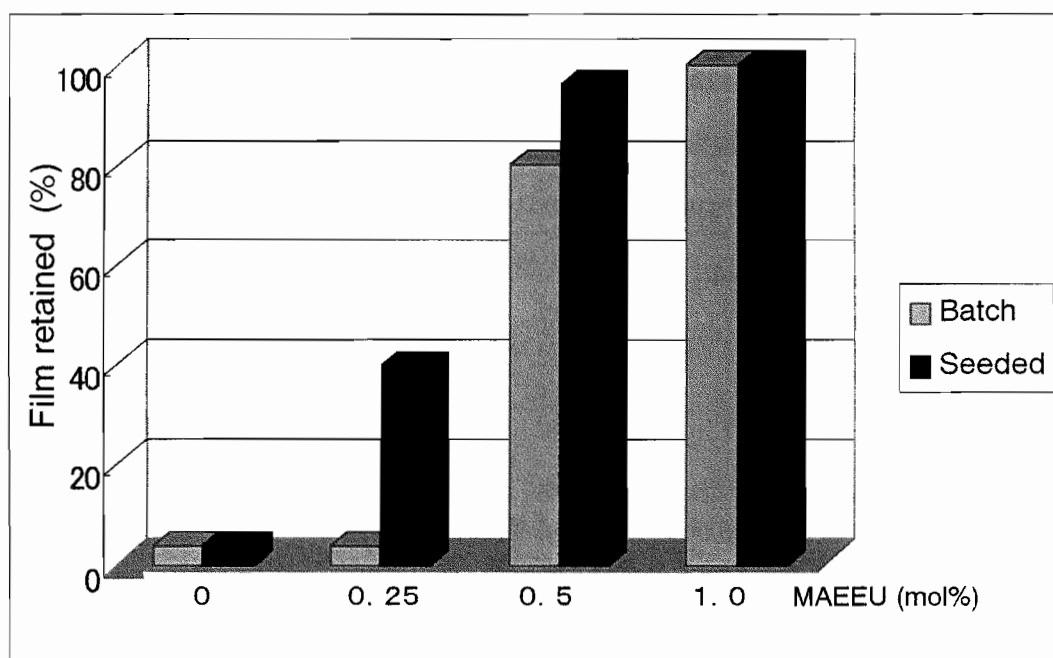


Fig.7 Relationships between MAEEU contents and cross-cut wet adhesion test for the films prepared from P(BMA-MAEEU) emulsions (Batch) and PBMA/P(BMA-MAEEU) emulsions (Seeded)

Films from PBMA/ P(BMA-MAEEU) seeded polymer emulsion shows similar results. But the seeded polymers imparted better wet adhesion properties than the batch copolymers on the same concentration range of MAEEU (0.25-0.5 mol %).

These suggest that introduction of MAEEU improves wet adhesion properties remarkably. And seeded polymerization procedure should make MAEEU localize more on the surface of particles.

Determination of MAEEU by elementary analysis

Table 4 shows the elementary analysis result of P(BMA-MAEEU) copolymer particles and PBMA/P(BMA-MAEEU) seeded polymer particles. Approximately 30% of used MAEEU monomer

Table 4 Elemental analysis of P(BMA-MAEEU) and PBMA/P(BMA-MAEEU) particles

| MAEEU contents mol% before copolymerization | MAEEU contents (mol%) | |
|--|-----------------------|-------------------|
| | P(BMA-MAEEU) | PBMA/P(BMA-MAEEU) |
| 0.25 | 0.1 | 0.05 |
| 0.5 | 0.2 | 0.2 |
| 1.0 | 0.4 | 0.3 |

was copolymerized into particles in both of cases. A comparison of these results showed that MAEEU amount in the seed polymer particles was less than that in the copolymer particles at the same level of used MAEEU concentration.

Evaluation of surface potential of particles by ζ -potential measurements

Figure 6 shows the ζ -potential of PBMA seed particles, P(BMA/ MAEEU) copolymer particles and PBMA/P(BMA-MAEEU) seed polymer particles, respectively, used 0.5 mol % of MAEEU at various pH range. P(BMA) particles have a negative electric charge because of the effect of sulfuric end group from the

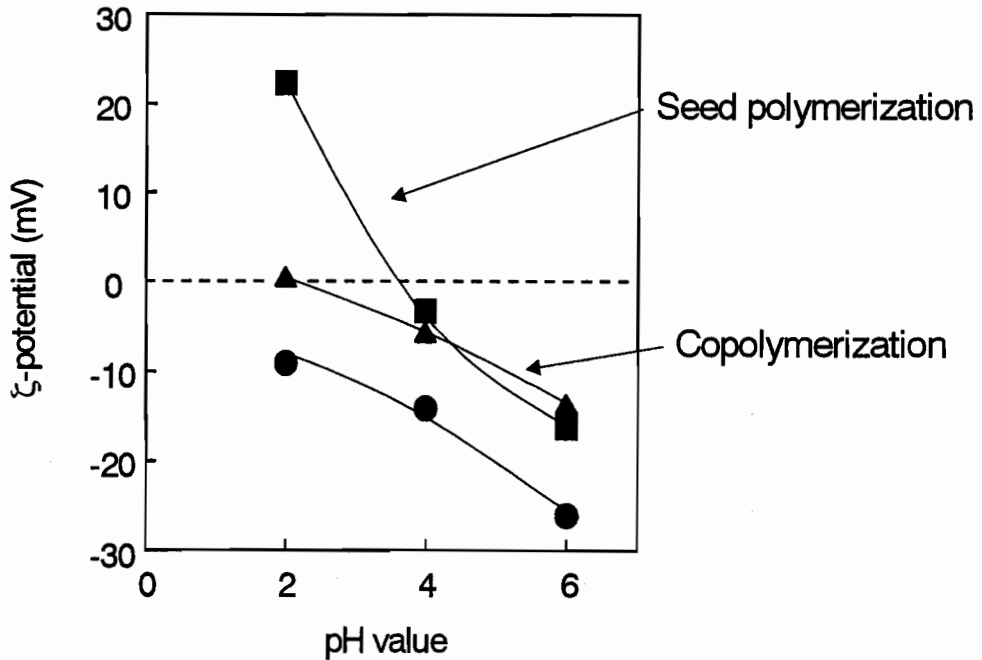


Fig. 6 Relationships between pH value and z-potential of PBMA (●), P(BMA-MAEEU) (MAEEU, 0.5 mol%) (▲), PBMA/P(BMA-MAEEUEU) [MAEEU in P(BMA-MAEEUI), 0.5 mol%] (■)

initiator. On the other hand the surface charge of P(BMA/MAEEU) copolymer particles shifted to the positive side obviously. In case of PBMA/P(BMA-MAEEU) seeded polymer particles, the ζ - potential became more positive especially lower pH range (at pH 2). These positive shifts must be caused by cationization of ethyleneurea ring under acid condition. This results support that it is possible to orient ethyleneurea ring on the surface of particles by seeded emulsion polymerization.

Evaluation of minimum film formation temperature (MFT)

Figure 7 is a photograph of evaluation of MFT with prepared emulsion. MFT of P(n-BMA) is about 31 °C, and that of 2 mol% of MAEEU co-polymer is about 37°C. Emulsions with

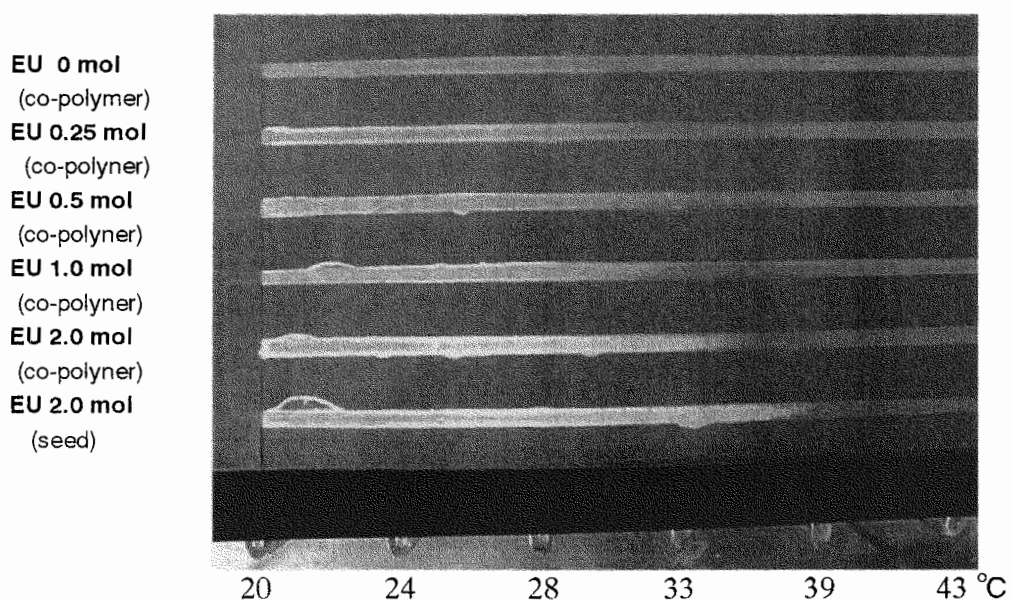


Fig.7 Photograph of MFT of emulsion with various MAEEU(EU) contents and comparison of co-polymer and seeded polymer

higher MAEEU content tend to shift MFT higher, in spite of the condition that the amount of functional monomer was not so large. Seeded copolymers tend to have a higher MFT than co-polymers with the same of MAEEU mol%.

MFT and glass transition temperature (Tg) are correlated. Tg of P(n-BMA) is 20°C and P(MAEEU) is 87°C. Tobolsky scheme gives theoretical Tg as follows.

$$1/Tg = w_a/Tg^a + w_b/Tg^b$$

The theoretical Tg of copolymer is calculated by this scheme.

$$1/Tg = 0.98/20 + 0.02/87$$

$$Tg = 21.1$$

That is, Tg of P(MAEEU/BMA) (2/98) increased only 1.1 °C from that of p(n-BMA). However MFT of P(MAEEU/BMA) (2/98) increased significantly from that of p(n-BMA). This result strongly suggested the orientation of MAEEU portion on the surface of particles. Also seeded polymerization method made such an orientation of the hydrophilic monomer on the surface more effectively.

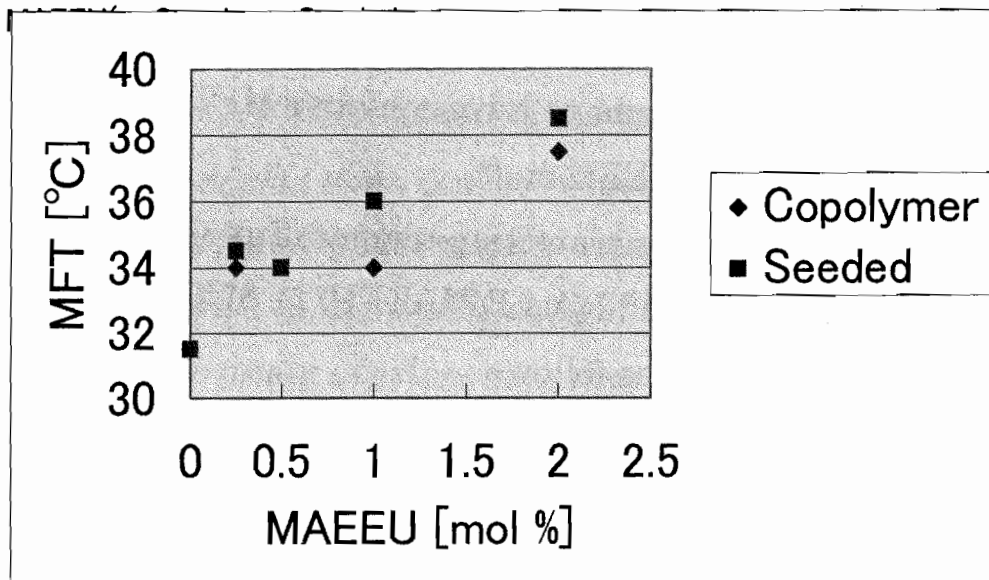


Fig. 8 MFT vs. mol% of MAEEU in polymer particles

4-4 Conclusion

Emulsifier-free clean polymer particles was successfully prepared with surface oriented ethyleneurea ring by emulsifier-free, seeded emulsion polymerization. The films from obtained polymer particles showed significant wet adhesion properties.

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Chapter 5

Synthesis of Polymer Particles with Ethyleneurea Ring by Starved Feeding Method and Modification by Crosslinking System

5-1 Introduction

One of the strong points of polymer microsphere is the flexibility for various designs of internal structure. Especially composite polymer particles are suitable to modify the surface of particles that is essential for an adhesion properties of water-borne coatings.

In Chapter 4, utilizing the seeded polymerization method, the core-shell composite polymer particles having an ethylene-urea-rich shell were produced. These particles showed good wet adhesion properties.

In this chapter, co-polymer emulsions with n-Butyl methacrylate and MAEEU will be synthesized by emulsion-free emulsion polymerization with starved feeding method to localize ethyleneurea ring more on the surface of particles. And the effect for wet adhesion properties will be studied.

To improve mechanical properties of waterborne coatings, crosslinking system is widely used in industrial application.¹⁾ The reaction of urea group and dialdehyde is considered as a candidate of a new ambient temperature crosslinking system.

The effect of addition of dialdehyde, glyoxal, to composite polymer particles with ethylene ring will be studied and discussed.

5-2 Experimental

Materials

n-Butyl methacrylate (BMA, Nacalai Tesque Inc.) was purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Methacrylamide ethylethyleneurea (MAEEU) was separated from SIPOMER WAM-II (RHODIA) which is commercialized as a mixture of MAEEU (50%), methacrylic acid (20%), and water (30%). Calcium chloride and water were added to SIPOMER WAM-II, then kept in refrigerator for one night (16h.). The resulting calcium methacrylate was removed by filtration. MAEEU was recrystallized from acetone. (white powder, mp 114.5-117°C) Analytical grade potassium persulfate (KPS, Nacalai Tesque Inc.) as an initiator was recrystallized. Deionized water (resistivity : $5 \times 10^6 \Omega \cdot \text{cm}$) was distilled before use. 40% aqueous solution of Glyoxal (Nacalai Tesque Inc.) was used without further purification.

Preparation of polymer particles by starved monomer feeding method

The seed particles of PBMA were prepared by emulsifier-free emulsion polymerization. Prescribed amount of BMA, MAEEU, KPS, and water were charged in a four-neck flask, then

polymerized at 70°C under nitrogen atmosphere. The particles of PBMA/P(BMA-MAEEU) with starved feeding method were prepared under condition listed in Table 1 from the seed PBMA particles by emulsifier-free seeded emulsion polymerization. First, 0.175g of KPS was added and 7h. later the remains (0.085g) as a aqueous solution was added. BMA was added at the rate of 2.5 g/h for 7 h.. And 1.58 wt% of MAEEU aqueous solution was added at the rate of 0.5 g/h for 7h..

Table 1 Recipes of emulsifier-free seeded emulsion copolymerization for preparation PBMA /P(BMA- MAEEU) particles utilizing starved-feed monomer addition method

| Ingredients | MAEEU contents (mol %) | | |
|------------------------------------|------------------------|------|------|
| | 0.25 | 0.5 | 1.0 |
| PBMA Particles ^{b,o)} (g) | 3.49 | 3.48 | 3.45 |
| BMA ^{d)} (g) | 17.4 | 17.4 | 17.2 |
| MAEEU ^{e)} (g) | 0.06 | 0.13 | 0.27 |
| KPS (g) | 0.26 | 0.26 | 0.26 |
| Water (g) | 330 | 330 | 330 |
| Dh ^{f)} (nm) | 744 | 771 | 757 |

a) In flask: N₂; 70°C; 12h.; stirring rate 220 rpm

b) Produced by emulsifier-free emulsion polymerization

c) Hydrodynamic diameter measured by DLS; 440nm

d) BMA was added at the rate of 2.5 g/h for 7h.

e) 1.58 w% of MAEEU aqueous solution was added at the rate of 0.5 g/hr for 7h.

f) Hydrodynamic diameter measured by DLS

Crosslinking System

Normal feeding method as control: at 70°C for 24h., stirring rate 160rpm, BMA and MAEEU added at once. First, 0.175g of KPS was added and 18h. later the remains (0.085g) as a aqueous solution was added.

Starved feeding method: First, 0.175g of KPS was added and 7h. later the remains (0.085g) as a aqueous solution was added. Simultaneously BMA was added at the rate of 2.5 g/h for 7 h.. 1.58 wt% of MAEEU aqueous solution was also added at the rate of 0.5 g/h for 7h..

Before the film formation, particles were washed three times by a centrifuge instrument. Various amount of glyoxal; 1/1, 1/1, and 1/5 and as mol ratio of MAEEU/glyoxal; were added to seeded PBMA/ P(BMA- MAEEU) emulsions both of normal feeding and starved feeding methods after cleaning of particles.

Evaluation of wet adhesion properties by cross cut adhesion test

Obtained emulsion films on the alkyd resin coated plate were immersed in water for one day at 25°C, then films were cut to 25 squares (5 x 5) with 2mm intervals between each line. After that pressure sensitive adhesive tape (Nitto Electric Inc.) was put on the surface of films and was stuck by 2kg roller (one round trip). The exfoliation test have been done several times, counted remained number of square, and described its percentage for 25 squares. (JIS K5400 method)

5-3 Results and Discussion

Starved Feeding Method

Figure 2 and Figure 3 showed relationships between MAEEU contents and film retained after the 100 times cross-cut wet adhesion test for prepared from PBMA/P(BMA-MAEEU) emulsions (seeded) and PBMA/P(BMA-MAEEU) emulsions (starved-fed). Starved feeding method showed better wet adhesion properties even MAEEU contents was only 0.25 mol%. This result suggests that ethyleneurea ring localized more on the surface of polymer particles.

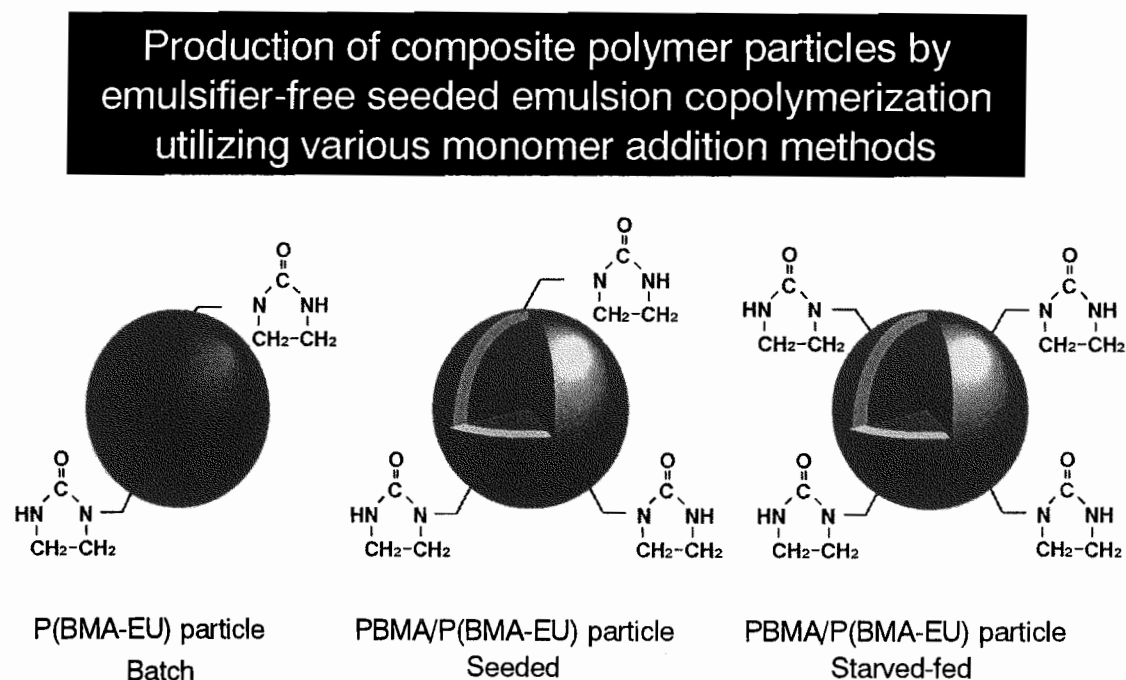


Fig. 1 Control for surface of particles with polymerization methods

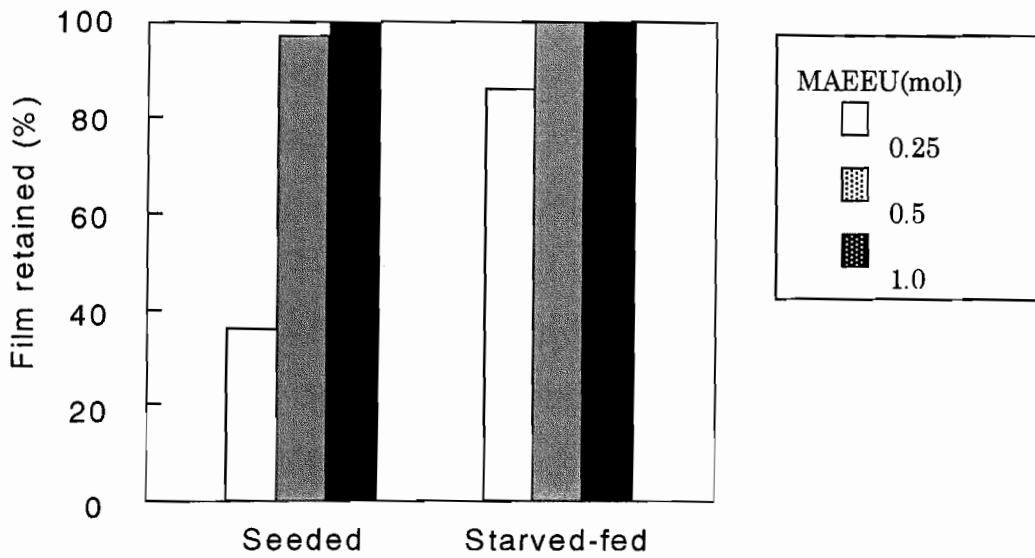


Fig. 2 Percentage of film retained after the 100 times cross-cut adhesion test for the films prepared from PBMA/P(BMA-EU) emulsions (Seeded), PBMA/P(BMA-EU) after r.t. water immersion.

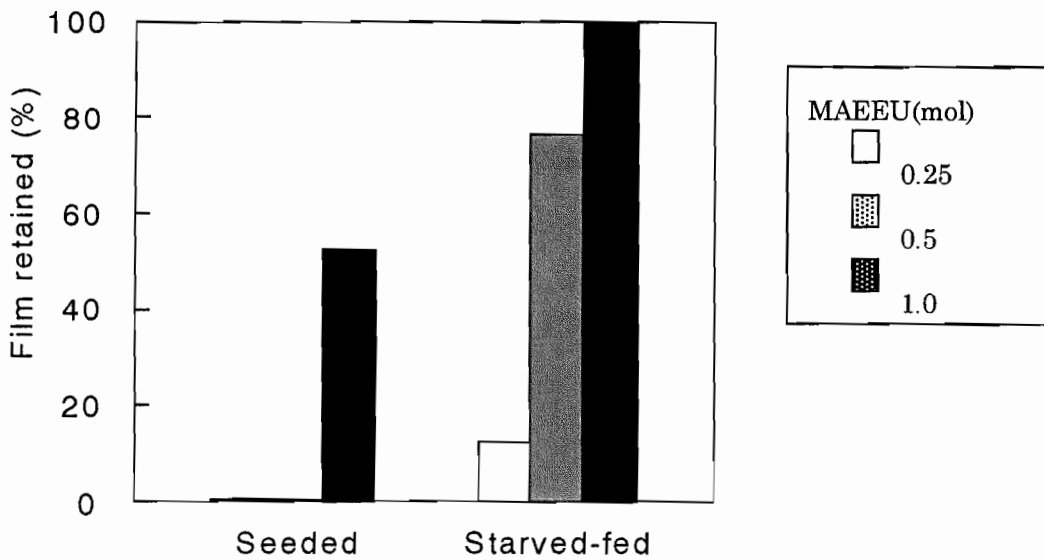


Fig. 3 Percentage of film retained after the 5 times cross-cut adhesion test for the films prepared from PBMA/P(BMA-MAEEU) emulsions produced using difference of monomer addition methods (Seeded batch, Starved-fed). After 40°C water immersion

All of previous wet adhesion properties were tested on the pre-coated alkyd enamel paint that has ester and hydroxy group as functional groups.

Fukuzumi et al . proposed for the improvement of wet adhesion property for acrylic emulsion film on steel plate by MAEEU ²⁾ for industrial application. They found that combination of MAEEU, vinyl compound with carbonyl group and bihydrazide group showed further improvement for wet adhesion.

Figure 4 demonstrated wet adhesion properties on the stainless steel plate. Even on the metal substrate, polymer particles produced by seeded and starved-fed polymerization method performed good adhesion.

The staved-fed particles presented better result than seeded particles with normal feeding method.

Oxydation layer exist on the surface of metal and it generates water dissociative adsorption layer and oxyhydroxy metal layer ³⁾. These layers may play important role for the interaction between polymer particles with MAEEU and metal surface.

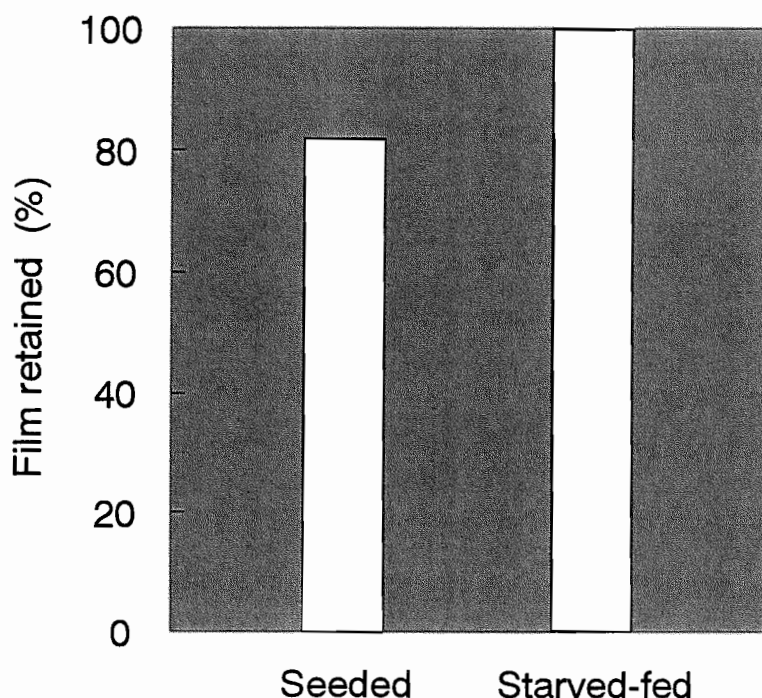
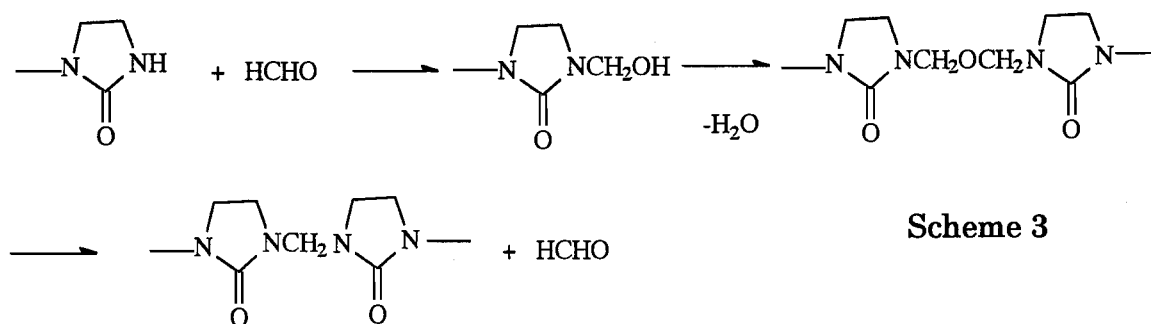
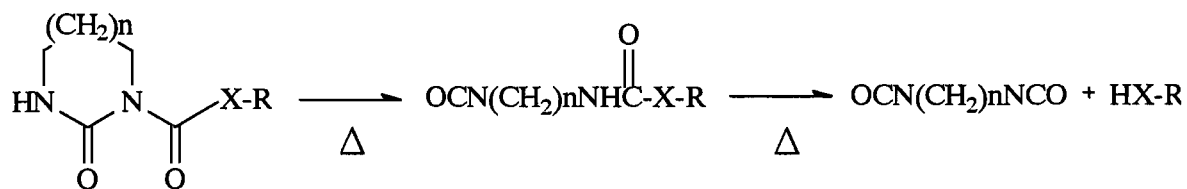
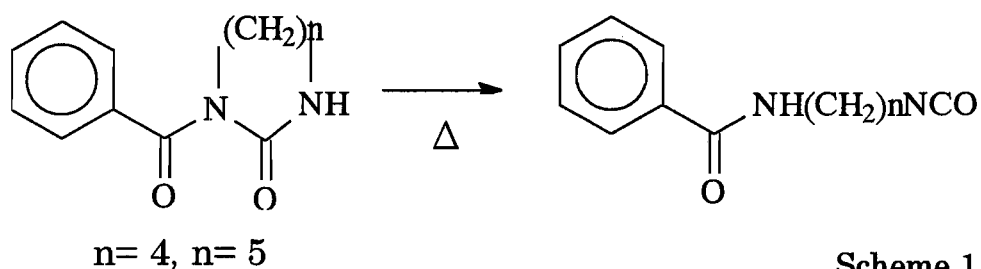


Fig. 4 Percentage of film retained after the 100 times cross-cut adhesion test for the films on the stainless steel prepared from PBMA/P(BMA-MAEEU) emulsions produced using difference of monomer addition methods (Seeded batch, Starved-fed).

Crosslinking System

Cyclic urea can be regarded as masked isocyanate. The seven- and eight-membered ring, that is tetramethyleneurea and pentamethyleneurea, undergo easily ring opening by heating. (Scheme 1) Carbonyl ethyleneurea, which is prepared from ethylene diisocyanate, also undergoes ring-opening reaction by heating and forms isocyanate or diisocyanate derivatives. (Scheme 2) ^{4, 5)} However five- and six-membered ring without neighboring carbonyl group, that is ethyleneurea and

trimethyleneurea, are very stable and do not appreciably dissociate upon heating.⁶⁾ Therefore crosslinking reaction by covalent bond should not occurred between MAEEU and another functional group even at high temperature.



Influence of crosslinking agent on wet adhesion and tensile strength of film from composite particles

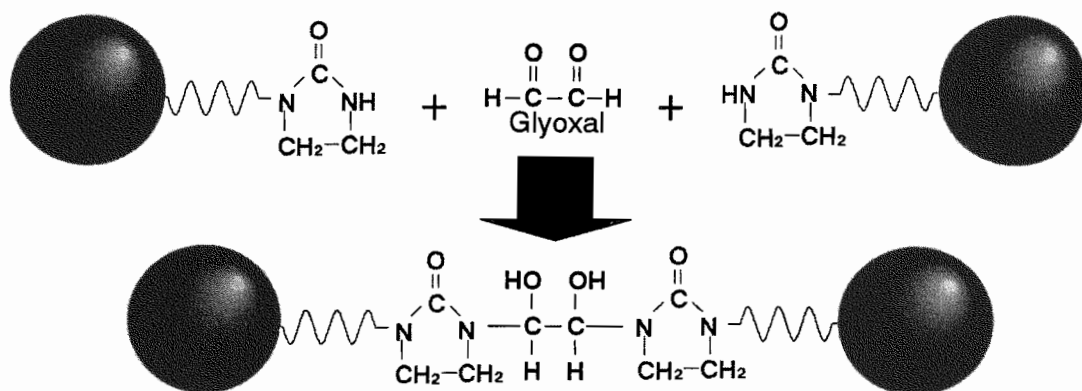
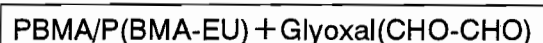


Fig. 5 Schematic diagram of the new crosslinking system

The reaction of 2-imidazolidinone, that is ethyleneurea, with formaldehyde was investigated in detail by C. Shimasaki et al⁷⁾. 1,3-bis(hydroxymethyl)-2-imidazolidinone was easily isolated. Polycondensation reaction of 1,3-bis(hydroxymethyl)-2-imidazolidinone is effective crosslinking system. However it generates harmful formaldehyde as a byproduct.

Baumstark et al . proposed new crosslinking system of urea group containing dispersions with dialdehyde at ambient temperature ⁸⁾. A schematic diagram of this system was illustrated in Fig. 5.

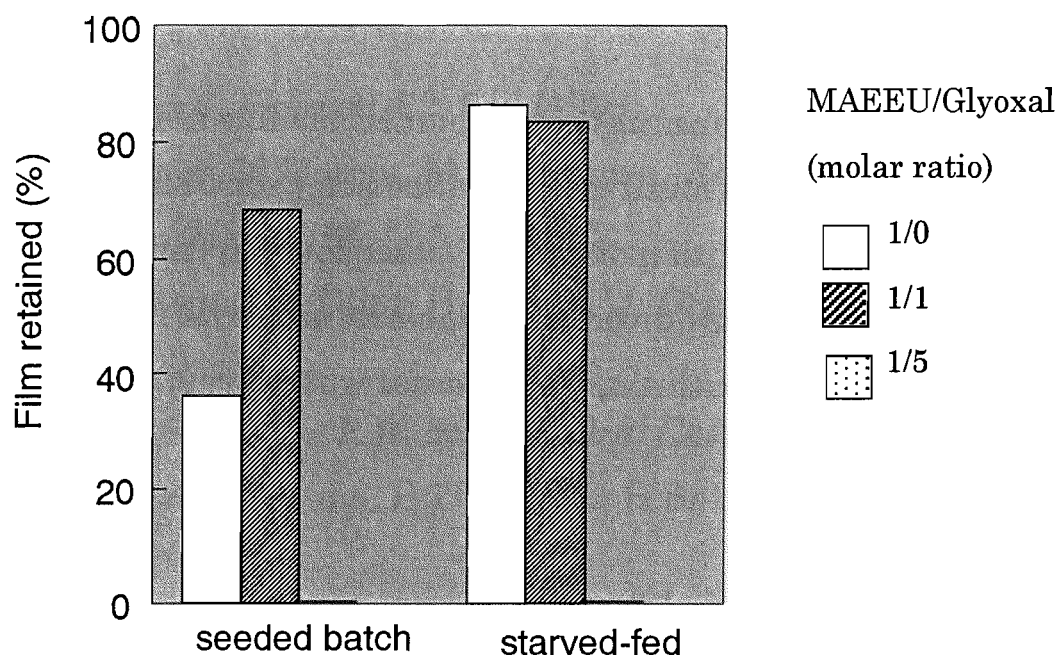


Fig. 5 Percentage of film retained after the 100 times cross-cut adhesion test for the films prepared from PBMA/P(BMA-MAEEU) emulsions (MAEEU content=0.25mol%) produced by different monomer addition methods

Figure 6 also showed the relation between glyoxal/MAEEU molar ratio and area of film retained under wet adhesion test. The Equimolar addition of glyoxal to seeded polymer particles with MAEEU improved the wet adhesion properties significantly. A large excess of glyoxal addition hindered wet adhesion properties.

This results indicates that the combination of ethyleneurea ring and dialdehyde could improve the wet adhesion properties as a ambient temperature crosslinking system at suitable molar ratio.

5-4 Conclusion

Starved feeding method on emulsifier free seeded emulsion polymerization improved wet adhesion properties effectively.

Post addition of glyoxal to seeded polymer emulsion with MAEEU also improved wet adhesion properties more. It would be an efficient crosslinking system for waterborne coatings.

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Summary

In present work, the preparation of polymers having ethyleneurea ring as well as properties of those polymers were studied. A series of results are described as follows.

Part I is concerned with the wet adhesion promoters and properties of copolymer emulsion that contains small amount of ethyleneurea ring as a polymer component.

In **Chapter 1**, wet adhesion promoters for waterborne coatings was surveyed and reviewed. Evaluation methods and typical methods for improvement of wet adhesion, functions and the proposed mechanism of ethyleneurea ring were investigated. Typical wet adhesion monomers were introduced and past studies on wet adhesion promoter with ethyleneurea ring were summarized. But proposed mechanisms of wet adhesion did not seem to clarify enough the peculiarity of methacrylamide ethylethyleneurea.

In **Chapter 2**, copolymer emulsions with methacrylamide ethylethyleneurea and its application as wet adhesion promoters was examined. Comparison data with typical functional monomers for wet adhesion was studied. Using a representative wet adhesion promoter, wet adhesion property was studied. Swelling diameter test result showed addition of MAEEU in monomer emulsion formed a kind of crosslinking between polymer chain during emulsion polymerization process. But the effect of ethyleneurea ring incorporation to copolymer emulsion

was superior to typical crosslinking monomers. Blend of emulsion with ethyleneurea also improved control emulsion's wet adhesion properties.

Part II is concerned with production of polymer particles with ethyleneurea ring and its optimized properties.

In **Chapter 3**, the interaction between ethyleneurea ring and carboxyl group in polymer particles was examined. Property of the copolymer as well as the effect of emulsion blend of these functional groups was studied. The crosslinkage between ethyleneurea ring and carboxyl group occurred not only in polymer solution but also in emulsion particles mixture. It was clarified that most effective molecular ratio of MAEEU/COOH was about 1:1. This result suggested possibility of room temperature cross-linking system

In **Chapter 4**, the synthesis of polymer particles with ethyleneurea ring and wet adhesion properties was studied. Emulsifier-free clean polymer particles with surface oriented ethyleneurea ring were prepared by emulsifier-free, seeded emulsion polymerization. And properties of the films from obtained polymer particles were investigated. Emulsifier-free, clean polymer particles with surface oriented ethyleneurea ring were successfully prepared. The films from obtained polymer particles showed significant wet adhesion properties.

In **Chapter 5**, the synthesis of polymer particles with ethyleneurea ring by starved feeding method and modification by crosslinking system were studied. Starved feeding method of

MAEEU for seeded composite particles localized ethyleneurea ring more on the surface of particles and improved wet adhesion properties. Furthermore it was found that post addition of glyoxal to seeded polymer emulsion improved wet adhesion properties. It would be a desirable crosslinking system for film forming at room temperature.

As mentioned above, through a series of work on polymer particles containing ethyleneurea ring, it is concluded that polymer particle design to localize ethyleneurea ring on the surface of particles has many potential applications in industrial areas.

Publication List

Chapter 1

Wet Adhesion Promoters for Waterborne Coatings

M. Matsuda

Journal of the Adhesion Society of Japan

Vol.37, 24 (2001)

Chapter 2

Improvement of Washability for Waterborne Coating

M. Matsuda, T. Sugitani and H.B.Go

The Finish and Paint, 591, 35 (1999)

Chapter 3

Interaction between Ethyleneurea Ring and Carboxylic Acid Group

M. Matsuda

Colloid Polymer Science, In Preparation

Chapter 4

Synthesis of Polymer Particles with Ethyleneurea Group and the Wet Adhesion Properties

M. Okubo, M. Matsuda, A. Terada, and S. Kondo

Preprints of The 39th Annual Meeting of Adhesion Society of Japan (2000) p.33

Colloid Polymer Science, in preparation

Chapter 5

Synthesis of Polymer Particles with Ethyleneurea Ring by Starved Feeding Method and Modification by Crosslinking System

M. Okubo, M. Matsuda, A. Terada, and Y. Kagawa
Colloid Polymer Science, in preparation

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