

Preparation and Characterization of Poly(butyl acrylate)/Poly(methyl methacrylate) Composite Latex by Seeded Emulsion Polymerization

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Abstract: As model waterborne acrylic coatings, mono-dispersed poly(butyl acrylate-methyl methacrylate) copolymer latexes of random copolymer and core/shell type graft copolymer were prepared by seeded multi-staged emulsion polymerization with particle size of 180~200 nm using semi-batch type process. Sodium lauryl sulfate and potassium persulfate were used as an emulsifier and an initiator, respectively. The effect of particle texture including core/shell phase ratio, glass transition temperature and crosslinking density, and film forming temperature on the film formation and final properties of film was investigated using SEM, AFM, and UV in this study. The film formation behavior of model latex was traced simultaneously by the weight loss measurement and by the change of tensile properties and UV transmittance during the entire course of film formation. It was found that the increased glass transition temperature and higher crosslinking degree of latex resulted in the delay of the onset of coalescence of particles by interdiffusion during film forming process. This can be explained qualitatively in terms of diffusion rate of polymer chains. However, the change of weight loss during film formation was insensitive to discern each film forming stages-I, II and III.

Keywords: composite latex, seeded emulsion polymerization, film formation.

1. Introduction

One of the major applications of acrylic emulsion polymers is for waterborne coatings. The film formation process in waterborne coatings is the most important step to the development of final performance of waterborne coating systems. It has been known that the characteristics of waterborne coatings such as film forming behavior and the final properties of coated films are largely

dependent on the latex particle morphology.

Composite latex particles of different morphology can be prepared by multi-staged emulsion polymerization techniques where a second stage monomer is polymerized in the presence of preformed first polymer particles[1-3]. During the course of multi-staged emulsion polymerization, the equilibrium morphology of composite latex particles is mainly governed by thermodynamic factors, and kinetic factors

also affect the final morphology which is dependent on thermodynamic factors[4-6].

The film forming process can be understood in terms of three consecutive stages such as evaporation of the water leading to close packing of latex particles (stage-I), deformation of the particles into polyhedrons under the action of surface and capillary forces (stage-II), and coalescence of the particles due to the result of interdiffusion of polymer chains across of the particle boundaries[7-9].

In this study, the behavior of model composite acrylic latex during film formation is investigated using n-butyl acrylate as soft phase and methyl methacrylate as hard phase monomers. Various particle morphology including random copolymer particle and core/shell type particle is obtained by seeded multi-staged emulsion polymerization. The film formation behavior of those model latexes is traced by the measurement of cumulative water loss and by the change of tensile strength and failure energy during the consecutive stages of film forming process. The change of UV transmittance during film formation is also examined.

2. Experimental

2.1. Materials

The monomers, methyl methacrylate (Junsei Chemical Co., MMA) and n-butyl acrylate (Junsei Chemical Co., BA), were used after purification by 2N NaOH solution to remove the inhibitor. After this treatment, these monomers were washed with distilled water several times. Sodium lauryl sulfate (Aldrich Chemical Co., SLS) was used as an emulsifier and potassium persulfate (Sigma Chemical Co., KPS) was used as an initiator.

2.2. Synthesis of Composite Latex Particles

Semi-batch type seeded emulsion polymerization reaction was performed in a

1000 ml jacket reactor and purged with nitrogen gas during polymerization. The reactor was equipped with a mechanical stirrer, reflux condenser, thermocouple, and nitrogen gas inlet tube. Agitation speed was fixed at 200 rpm and the reaction temperature was controlled at 75° C. The PMMA-PBA random copolymer, PMMA/PBA core/shell, and PBA/PMMA core/shell of various PMMA/PBA phase ratio from 3/7(w/w) to 7/3(w/w) were obtained.

2.3. Film Formation and Preparation of Specimen

The petri dish filled with the prepared latex was placed in the drying chamber under the controlled temperature and humidity. The cumulative water loss was measured during drying time and the film was taken out of chamber at the fixed time interval and dumbbell-type specimen (4 mm x 0.6 mm x 17.5 mm) for the tensile test were obtained by a punch cutter immediately. Tensile properties and UV transmission of those specimen was measured using a UTM (Lloyd, LR-5K) and a UV spectrophotometer (Helios, Alpha UVA 083717), respectively.

2.4. Characterization

A light scattering apparatus (Malvern, Zetasizer 3000HS) and a scanning electron microscopy (Leica, SEM 440) were used to analyze the particle size and size distribution of latex particles. Coagulation temperature of latex was measured to evaluate the film forming temperature indirectly. The glass transition temperature of latex was measured by DMA (TA Instruments, Model 2980). The surface of film was examined with an atomic force microscopy (Autoprobe, CP).

3. Results and Discussion

3.1. Characterization of Latex

The size and size distribution of

prepared latex obtained in our experiment are presented in Table 1. It indicates that the final latex has narrow particle size distribution without generation of new particles during the second stage of emulsion polymerization.

Fig. 1 presents the coagulation temperature of prepared latex as a function of composition for the different structure of latex, which is closely related to minimum film forming temperature of latex. Generally the coagulation temperature of latex increases with the increasing composition of MMA. This result satisfies the general behavior of predicted glass transition temperature of shell phase for core/shell type latex or random type latex.

3.2. Film Forming Behavior

Fig. 2 depicts a set of cumulative water loss data from films dried at 30 °C for different amounts of crosslinker (0.0, 0.25, 0.5, 1.0 wt.%). Rapid water loss is observed for the first 100 minutes and later the rate of weight loss is reduced gradually. We believe that the rapid water loss is a consequence of stage-I of film forming process and the period of reduced rate of water loss approaching zero corresponds to stage-II and stage-III. However, no significance difference of cumulative weight loss pattern for different amounts of crosslinker is observed. This is

interpreted as reflecting the fact that the crosslinking density within the latex particle has little effect on the water evaporation which mainly occurs outside of the particles.

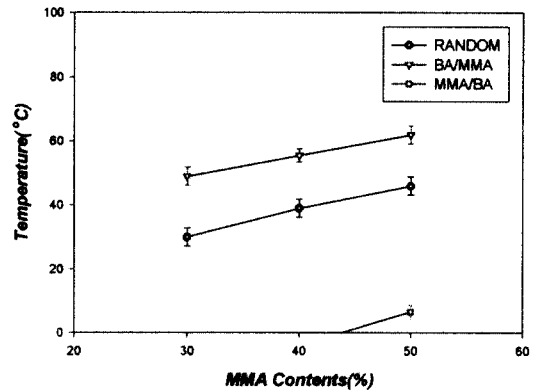


Fig. 1. Effect of particle morphology of latex on the coagulation temperature.

We immediately punched the specimen from the films obtained at given interval of drying time during entire course of film forming periods. The specimens were then subjected to tensile tests immediately. The stress-strain curves can be integrated to yield the failure energy which describes the toughness of the material. Those failure energy data from films dried at 30 °C for different amounts of crosslinker are given in

Table 1. Particle Size and Particle Size Distribution of Prepared Latex (MMA/BA=5/5)

Type of Latex	Seed Latex Size (Dw)	Final Latex Size (Dw)	PDI (Dw/Dn)
PBA/PMMA core/shell type	98.3 nm	190.4 nm	1.05
PMMA/PBA core/shell type	98.3 nm	191.6 nm	1.03
PMMA-PBA random type	98.3 nm	190.9 nm	1.05

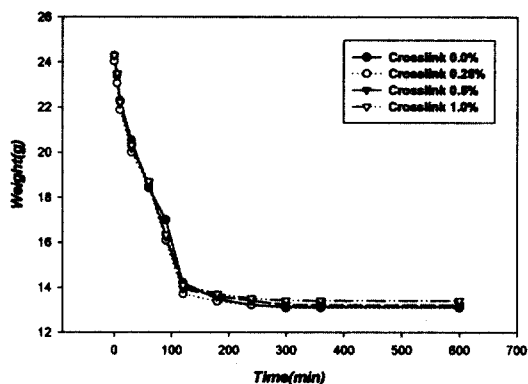


Fig. 2. Weight loss behavior of latex during film formation.

Fig. 3. No failure energy can be expected during film forming stage-I, very weak failure energy might be maintained in stage-II, and real toughness of films will begin to develop during stage-III. As shown in Fig. 3, toughness of films already begins before 100 minutes of drying time for the lower crosslinked samples (0.0 and 0.25 wt.%). Toughness of higher crosslinked films (0.5 and 1.0 wt.%), however, starts to develop after 160 minutes of drying time. It has been known that the failure energy of film is largely dependent on the length of the interdiffusion path[9, 10]. It also has been known that the length of the diffusion path is proportional to $t^{1/2}$ which can be expected from the de Gennes reptation theory[11]. It is revealed that the full failure energy is achieved at about an interdiffusion length which corresponds to the order of magnitude for the radius of gyration of the polymer molecules. It is found in Fig. 3 that higher crosslinking degree of latex resulted in the delay of the onset of coalescence of particles and the time for full toughness development during film forming process. This can be explained qualitatively in terms of change of diffusion rate for crosslinked polymer chains.

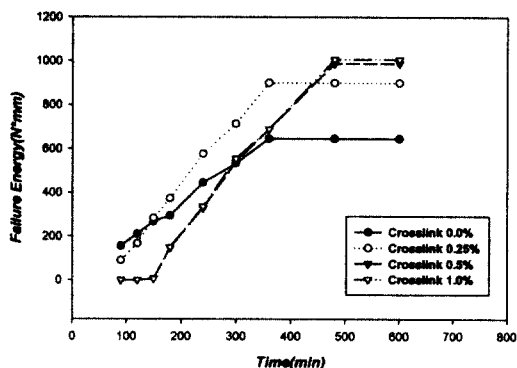


Fig. 3. Effect of crosslinking density on tensile fracture energy of films during film formation.

In addition, we monitored the turbidity change of films during drying using UV spectrophotometer as shown in Fig. 4. Turbidity data measured by UV absorption are closely related with the failure energy data. In the case of the latex with 0.25 wt.% crosslinker, optically homogeneous film is obtained after drying for 300 minutes. The latex with 1.0 wt.% crosslinker needs at least 500 minutes to be an optically homogeneous film.

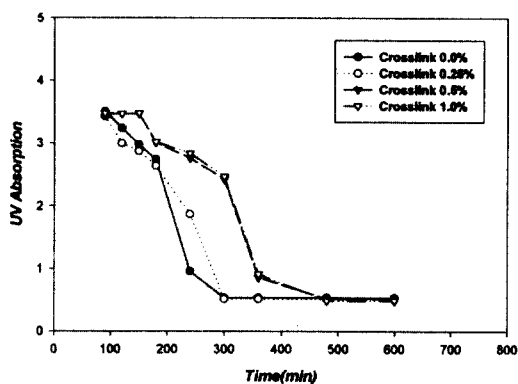
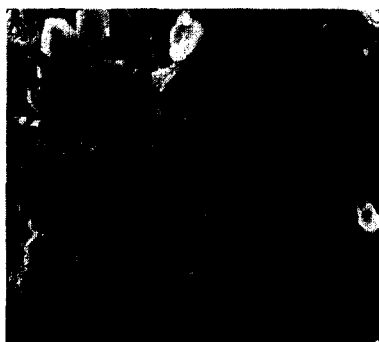
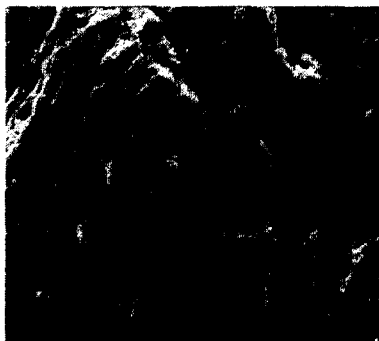


Fig. 4. Effect of crosslinking density on UV absorption of films during film formation.

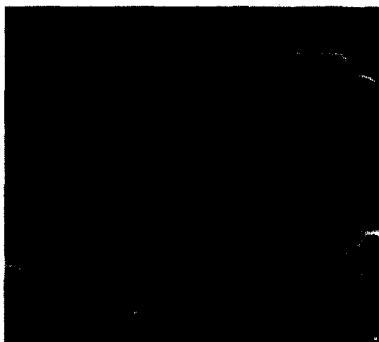
Fig. 5 shows SEM micrographs of fracture surface obtained after tensile test for the films of 0.5 wt.% crosslinker. SEM micrograph of the film dried for 90 minute indicates a heterogeneous fracture surface that reveals individual latex particle clearly.



(a) 100 minute



(b) 180 minute



|10µm| (c) 500 minute

Fig. 5. SEM micrographs of fracture surface obtained after tensile test for various drying time.

Upon further drying for 150 minutes, the fracture surface of the film shows a partial coalescence of particles due to the interdiffusion of polymer chains at the boundary of deformed particles. The fracture surface of film dried for 300 minutes whose toughness is developed fully, reveals a homogeneous structure of surface.

4. Conclusions

The film formation behavior of model PMMA-PBA latex was traced simultaneously by the weight loss measurement and by the change of tensile properties and UV transmittance during the entire course of film formation. It was found that the increased crosslinking degree of latex resulted in the delay of the onset of coalescence of particles by interdiffusion and the time for full toughness development during film forming process. This can be explained qualitatively in terms of change of diffusion rate for crosslinked polymer chains. It was found that failure energy data were in good accordance with turbidity data measured by UV absorption, and both data clearly discern each film forming stages-I, II and III.

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