

Nano-structured biphasic polymer film on the hair surface from PEGylated polymer latexes

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Accepted for publication July 29, 2003.

Synopsis

In this study, biphasic polymer latexes were synthesized by surfactant-free-emulsion polymerization of butyl methacrylate, poly(ethylene glycol) methyl ether methacrylate, and 2-(methacryloyloxy) ethyl trimethyl ammonium chloride. The latexes synthesized were composed of hydrophobic core phase and hydrophilic shell phase. Nano-structured film morphology could be obtained by annealing the biphasic polymer latexes between the two transition temperatures. It was found that the unique film morphology gave a viscoelastic property to the film. Scanning electron microscope and atomic force microscope images revealed that the biphasic polymer latexes deposited effectively onto the entire hair surface upon conditioning with 1 wt% polymer concentration in water. Consequently, they formed a smooth polymer membrane thereon, showing a high potential for a new hair cosmetic ingredient.

INTRODUCTION

Hair styling has been emphasized as a useful tool to express beauty. It has been required that the styling of hair should be performed conveniently, without causing any damage to the hair. Until recently, many different formulations, including hair-setting lotion, hair gel, hairspray, and blowing agents, have been developed and used widely.

Usually, the incorporation of polymers into the formulation is an area of particular interest for the achievement of intended physical properties in hair cosmetics. This has a big advantage in that we can easily get good holding power, prolonged curl retention, low stickiness, lack of flaking, gloss, transparency, a good feel, etc. (1–3). However, most of the polymers are dissolved in organic solvents, which causes an undesirable odor and incompatibility with other additives. To solve this problem, the incorporation of polymers with a form of latex has been proposed. Actually, Yahagi and Suzuki reported that

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a good styling effect on hair could be induced using submicron polymer particles (4,5). Also, according to some patents, polymer latexes having a low transition temperature deposit well onto the hair surface, finally forming a soft polymer film (6,7).

In this contribution, we introduce a useful hair treatment system in which biphasic polymer latexes are used to form a nano-structured film membrane on the hair surface. The biphasic polymer latexes are synthesized by controlling the compatibility between hydrophobic components and hydrophilic components in the polymer molecule (8,9). In order to exclude the effect of surfactants, the latexes are prepared by surfactant-free emulsion polymerization. This paper then investigates the effectiveness of the biphasic polymer latex system on the film property and the deposition efficiency on the hair surface.

EXPERIMENTAL

MATERIALS

Butyl methacrylate (BMA), poly(ethylene glycol) methyl ether methacrylate (PEG-MA, $M_w = 300, 1100, 2000 \text{ g} \cdot \text{mol}^{-1}$), 2-(methacryloyloxy) ethyl trimethyl ammonium chloride (METAC), and 2,2'-azobis(2-methyl propionamide) dihydrochloride (V-50) were purchased from Aldrich Chemical Co. The inhibitor in the monomers was removed using a removing column (Aldrich). Distilled deionized (DDI) water was used throughout the process.

SYNTHESIS OF BIPHASIC POLYMER LATEXES

The latexes were synthesized by surfactant-free emulsion polymerization. First, V-50 (0.2 g) and DDI water (360 g) were weighed into a four-necked round flask equipped with reflux condenser, nitrogen inlet apparatus, and mechanical stirrer. Under a nitrogen atmosphere, the reactor was submerged in a thermostated water bath and stirred with a rotation speed of 300 rpm at 75°C. After 10 min, the monomer mixture (40 g) composed of BMA, PEG-MA, and METAC was added to the reactor and polymerized for 10 h. The composition and designation of each sample are listed in Table I.

Table I
Polymerization Composition and Size Characteristics^a

Symbol ^b	Composition (wt%)			Avg. Dn (nm)	
	BMA	PEG-MA	METAC	DLS	TEM
PBMA	100	—	—	505	453
NAS300	80	20	—	475	386
NAS1100	80	20	—	450	347
NAS2000	80	20	—	330	298
NAS300-M5	75	20	5	287	244

^a 0.5 wt% V-50 as an initiator based on total monomer weight; 10 wt% solid content.

^b PBMA is the abbreviation of poly(butyl methacrylate). In the symbolization of NAS α -M β , α and β mean the molecular weight of PEG in PEG-MA and the concentration of METAC, respectively.

LATEX CHARACTERIZATIONS

The particle size of the latexes synthesized was measured by dynamic light scattering (DLS, Zetasizer 3000HS, Malvern, UK). Particle morphology was observed by a transmission electron microscope (TEM, JEOL 2010). Differential scanning calorimetry (DSC, TA Instruments, DSC 910) was used to determine the transition temperature. DSC traces were recorded from -100°C to 100°C , with a heating rate of $5^{\circ}\text{C}/\text{min}$ under N_2 flow. The mechanical properties of latexes were determined using an Instron universal tensile testing machine at room temperature. In the DSC and Instron measurements, the latex film was prepared by annealing the latexes at 50°C for two days in a Teflon square mold.

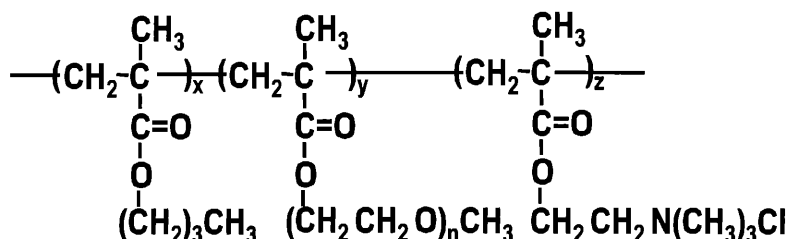
HAIR COATING PROCESS

The applicability of the biphasic polymer latexes to hair cosmetics was evaluated by observing their degree of deposition on the hair surface. A bundle of human hairs was impregnated in the diluted latex dispersion (1 wt% polymer content, pH 6.5). After being treated for 1 min, the hairs were dried fully at room temperature. In the case of thermal treatment, the dried hairs were annealed at 80°C for 10 min. The surface characteristics of the treated hairs were then observed by a scanning electron microscope (SEM, Hitachi S-4300). The more exact topography of the treated hairs was observed again with an atomic force microscope (AFM). In the AFM measurement, a latex-treated hair was adhered onto freshly cleaved mica. The sample was observed in air by using a commercial AFM (AutoProbe LS, PSI-LS) equipped with microfabricated V-shaped silicone nitride cantilevers (force constant: 0.05 mN/m) on a scanner using the contact mode.

RESULTS AND DISCUSSION

CHARACTERISTICS OF BIPHASIC POLYMER LATEXES

After surfactant-free emulsion polymerization, the biphasic polymer latexes obtained have a molecular structure composed of BMA, PEG-MA, and METAC units (Scheme 1). Figure 1 shows TEM images of the polymer latexes with the molecular weight of PEG in the absence of METAC. As the molecular weight of PEG increases, the latex size decreases gradually. This happens because the surface of the latexes is richly covered with PEG chains, which are responsible for the enhanced dispersion stability (8,9). Moreover, the surface activity is enhanced as a function of the length of the PEG chains (10). In



Scheme 1.

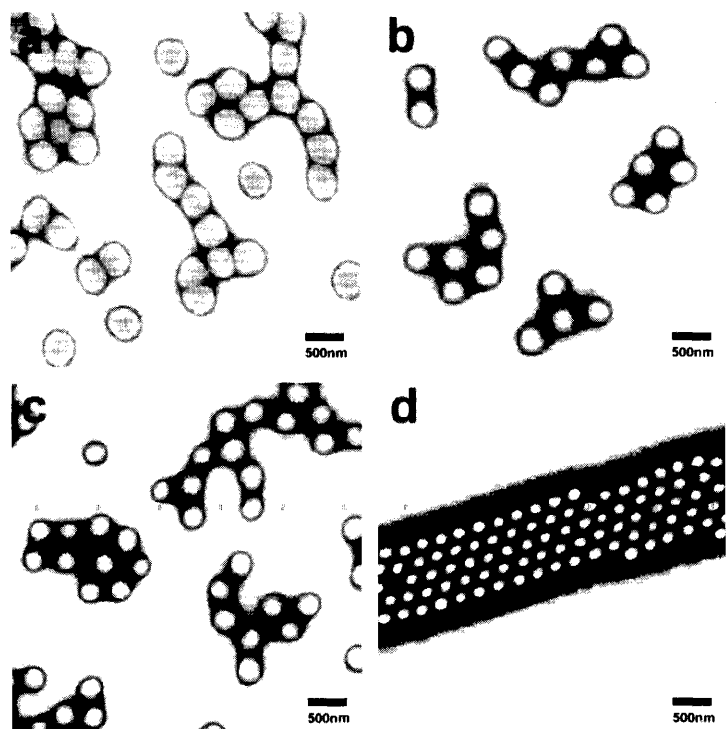


Figure 1. TEM images of biphasic polymer latexes: (a) PBMA. (b) NAS300. (c) NAS1100. (d) NAS2000.

DLS measurement, even though the effect of the PEG chains shows a similar trend, the latex sizes are somewhat larger than those determined by TEM measurement. This result is related to the effect of hydrodynamic volume. In the aqueous dispersion, the PEG-ylated latexes have a larger hydrodynamic volume, compared with non-treated latexes.

In order to examine the effect of a cationic monomer on the latex formation, the emulsion polymerization was carried out in the presence of 5 wt% of METAC. The latex size was remarkably reduced by incorporating the cationic group into the polymer backbone. This reveals that the cationic group makes a big contribution in improving the electrostatic stability of the latex particles (11). The composition and size characteristics measured are summarized in Table I.

FILM PROPERTIES OF BIPHASIC LATEXES

In order to examine the film property, the biphasic latexes were cast in a Teflon mold. The film prepared with the latexes containing $2000 \text{ g} \cdot \text{mol}^{-1}$ of PEG was very sticky due to the high molecular weight, resulting in a very soft continuous film phase. Therefore, considering basically the film properties, it was established that the molecular weight of PEG should be located between 300 and $1100 \text{ g} \cdot \text{mol}^{-1}$. In this consideration, the molecular weight of PEG was selected at $300 \text{ g} \cdot \text{mol}^{-1}$. Figure 2 shows the DSC thermograms of the biphasic latex films. PBMA and NAS300 films show only one transition temperature, at around 26°C . On the other hand, NAS300-M5 shows two transition temperatures at -57.5°C and 25.5°C , respectively. The results indicate that

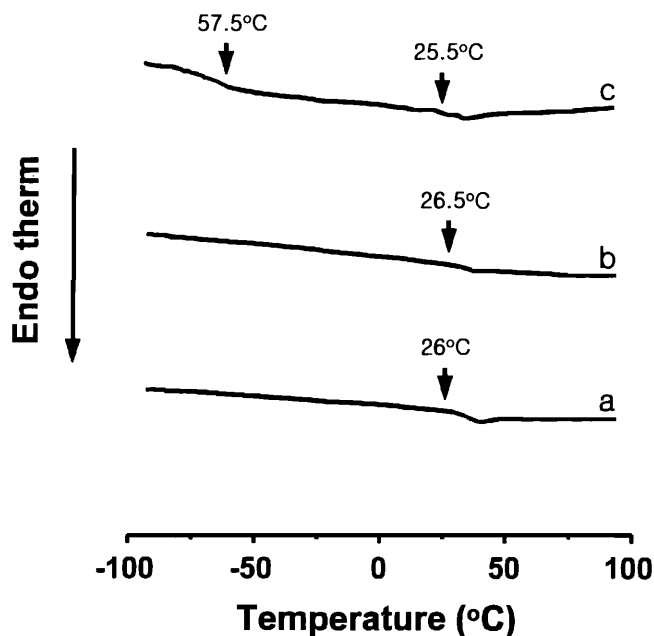


Figure 2. DSC thermograms of biphasic polymer latex films: (a) PBMA. (b) NAS300. (c) NAS300-M5.

the phase separation between PBMA and PEG was facilitated by the introduction of the cationic group into the polymer backbone. It has been known that in the polymer latex system, a high transition temperature contributes to the formation of films on the hair surface, while a low transition temperature exhibits a good deposition profile (7). It is then possible to say that the biphasic latex system having two transition temperatures can achieve the two functions simultaneously.

Figure 3 shows the mechanical property of biphasic polymer latex films. In the stress-strain curves, PBMA latex film shows a typical rigid polymer pattern. However, by adding PEG into the polymer composition, the tensile elongation increases; on the other hand, the tensile strength decreases steeply. That is, the property of PBMA latex film changes from brittleness to flexibility with the aid of soft PEG moiety. The incorporation of cationic groups slightly lowers tensile elongation, but the stiff property of PBMA latex film can be modified satisfactorily. In the analysis of mechanical property, it is evident that the biphasic latex film has viscoelasticity.

APPLICABILITY TO HAIR COSMETICS

To evaluate the ability to form a film on the surface of human hair, the biphasic latexes were deposited on the hair and the texture was examined with SEM. Figure 4 shows SEM images of latex films on the hair surface. It is clear that that the biphasic latexes readily covered the hair, resulting in a fine membrane on the hair surface. The coating ability was dependent on the functional group in the latexes. Especially, the cationic group played a crucial role in determining the degree of deposition of latexes on the hair surface. In the absence of the cationic group (NAS300), the deposition of biphasic latexes progressed partially (Figure 4b). However, in the presence of the cationic group (NAS300-

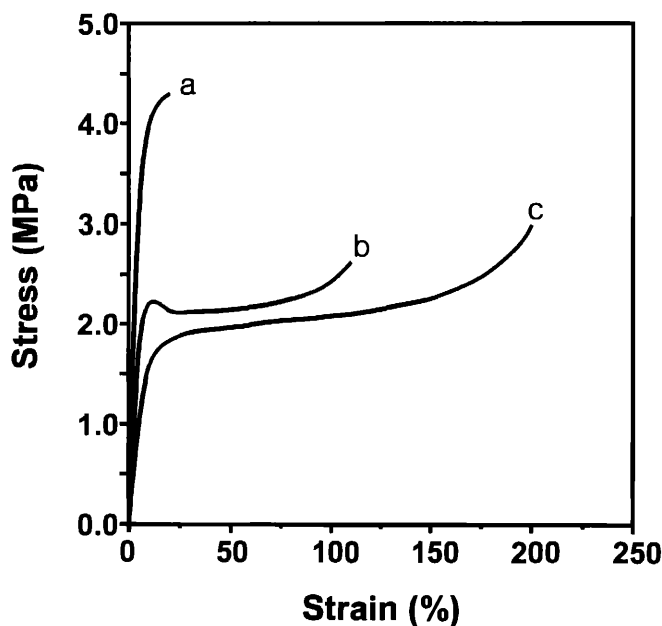


Figure 3. Stress–strain curves of biphasic polymer latex films: (a) PBMA. (b) NAS. (c) NAS-M5.

M5), the biphasic latex coated the entire hair (Figure 4c), which is attributed to the ion–ion interaction between hairs and positively charged latexes.

The topology of latex films on the hair surface was examined by AFM. Figure 5 shows the AFM images of the hair surface. A naked hair exhibits a rough surface because of the cuticles located in the exterior layer. However, after the hair was coated with NAS300-M5, it could be observed that the latexes deposited evenly on the hair surface and formed a film topology corresponding to a spherical cap structure. In addition, even after the film was annealed thermally at a high temperature, the spherical cap structure could be observed in the AFM images (Figure 5c). This film morphology was attributed to the limited interdiffusion between polymer chains, which was induced by the distinctly phase-separated latex structure. In general, the latex film is formed in three steps: water evaporation, particle deformation, and interdiffusion between particles (12,13). This process is largely influenced by several factors, such as the transition temperature of polymers, water resistance, and the surfactants (14–18). In addition to those factors, the compatibility between polymers also plays an important role in determining the final morphology of films (19). In our study, the biphasic polymer latex is composed of hydrophobic PBMA phase in the core and hydrophilic PEG and the cationic group in the shell. With reference to the topology shown in Figure 5, it can be said that PEG-rich shells were mixed selectively by the chain migration between adjacent particles and that the phase mixing between the hydrophobic PBMA core and the PEG-rich shell did not occur even at the high annealing temperature.

CONCLUSIONS

In this study, the biphasic polymer latexes composed of PBMA in the core and the

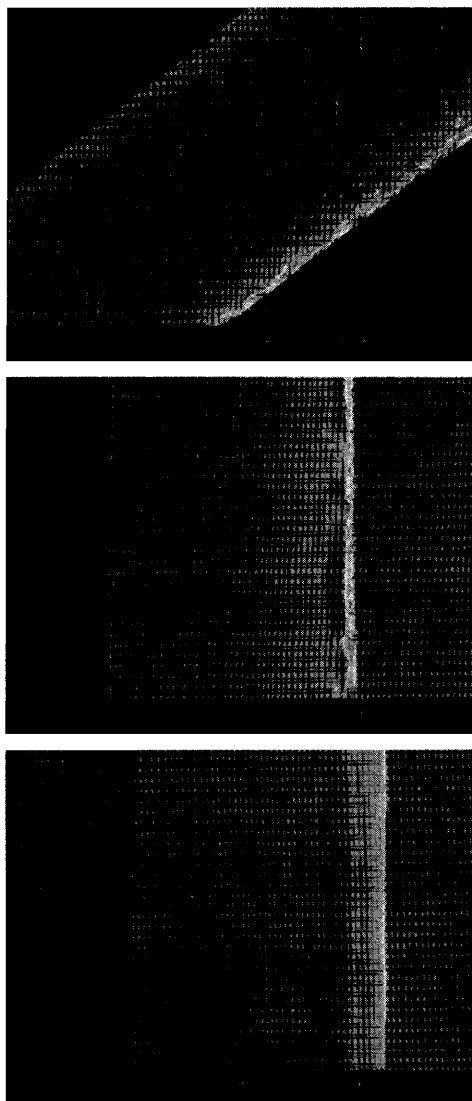


Figure 4. SEM images of human hairs treated with biphasic polymer latexes: (a) a naked hair. (b) a hair treated with NAS300. (c) a hair treated with NAS300-M5.

PEG/cationic group in the shell were synthesized by surfactant-free emulsion polymerization, and its applicability to a film former on the hair surface was evaluated. It was found that the PEG chains on the latexes help the formation of a stable latex dispersion. In the microscopic observations, the biphasic latexes show favorable deposition on the hair surface, forming a nano-sized spherical cap structure thereon. The biphasic polymer latexes considered in this study can give a viscoelastic property to human hairs, which is an important factor that determines the styling and feel of hair.

ACKNOWLEDGMENTS

This work was supported in part by the National Research Laboratory (NRL) program

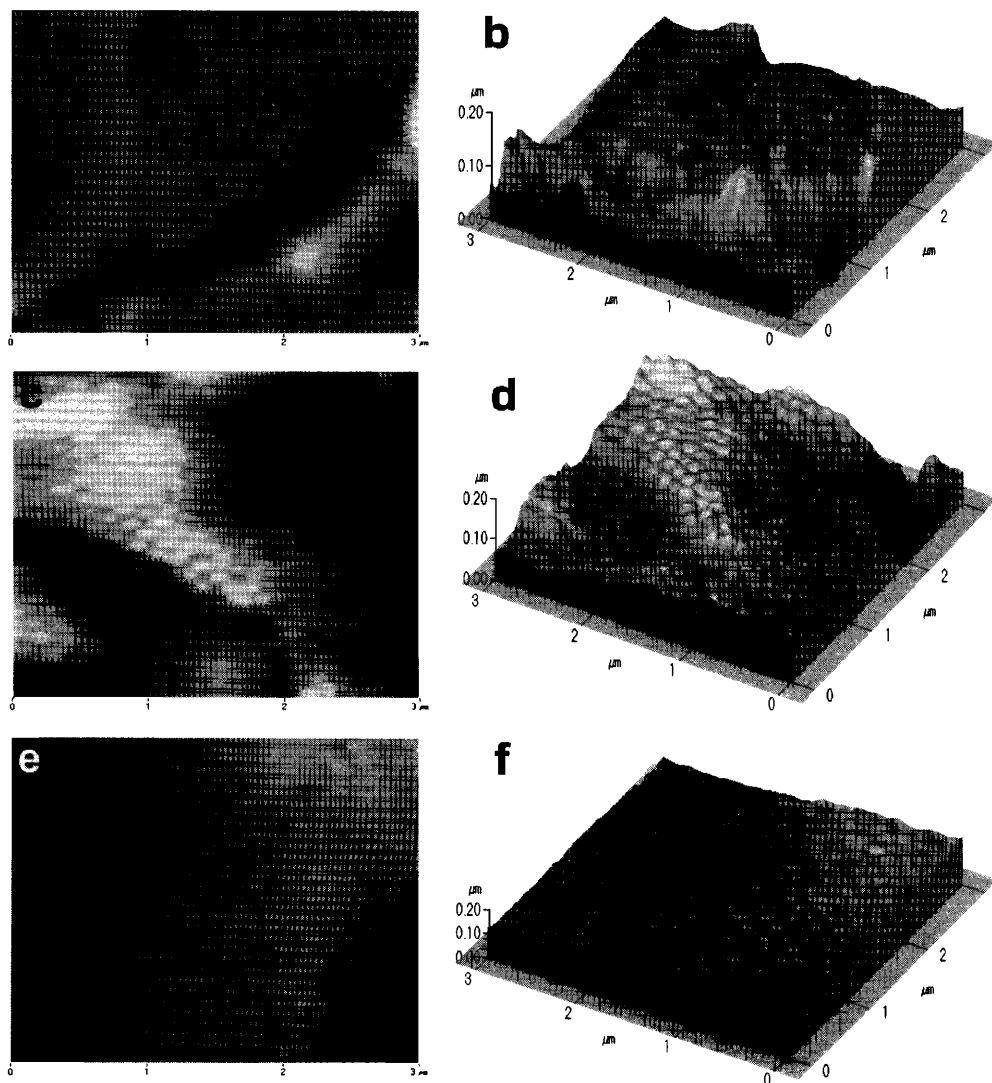


Figure 5. AFM images of human hairs treated with biphasic polymer latexes: (a,b) a naked hair. (c,d) a hair treated with NAS300-M5 at room temperature. (e,f) a hair treated with NAS300-M5 at 80°C for 10 min. Top view: a, c, e. 3D view: b, d, f.

(Project No. 2000-N-NL-01-C-270) of the Ministry of Science and Technology, South Korea. The authors express the deepest appreciation to all concerned with the development of Nanoaquasome™ from the biphasic polymer latexes.

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