

Facile Polymer Coating of Papers with Polymer Latices Containing a Hydrolysable Emulsifier

Y. Itoh, Ryo Akasaka, F. Sahara

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan

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ABSTRACT: Adsorption of polystyrene latices containing an alkali-hydrolysable cationic emulsifier on filter papers pretreated with sodium carbonate was examined. Hydrolysis of the emulsifiers synchronized with adsorption of the latices on the paper could fix, or coat, polystyrene on the paper surface rapidly and efficiently at room temperature, and little amounts of polymers were desorbed by rinsing. In contrast, a smaller amount of the latices

were adsorbed on the surface of the nonpretreated paper and most of them were desorbed from the surface by rinsing. The polymer-coated paper surface gained both water resistance and "quick drying." © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1653–1657, 2009

Key words: coatings; emulsion polymerization; latices; polystyrene; surfactants

INTRODUCTION

Water-based latex polymers are attractive for the uses in paints, adhesives, paper coatings, etc. because they are prepared using an environmentally friendly medium, water. Various components in the latices, however, may interfere with the "coalescence" of the individual latex particles, leading to reduced performances of the products. Many attempts to improve them are continued.^{1,2}

It has been recently reported that fibers in filter papers can be uniformly coated by cationic microlatices composed of polymethacrylates with a lower glass transition temperature (T_g), resulting in high resistance to water penetration.³ In the case, however, thermal annealing in the temperature range ($>100^\circ\text{C}$) much higher than the polymers' T_g is required as in preparation of latex films. This is probably because such emulsifiers, which stabilize the structure of latices and prevent their coalescence, increase the apparent T_g or minimum film formation temperature¹ of polymers. If the latices are unstabilized at lower temperature by losing the surface activity of the emulsifiers, the coalescence will be facilitated and thus polymers will adhere to the paper surface easily and

efficiently. Furthermore, the remaining "surfactant effects" on it such as ionic charge, hydrophilicity, and heterogeneity⁴ will diminish, improving performances of the coated paper.

In this context, cleavable surfactants that are converted to nonsurfactants under mild conditions⁵ will be suitable candidates for emulsifiers of polymer latices as coating materials. We have recently reported that an alkali-hydrolysable cationic surfactant, 1-tetradecyloxycarbonyltrimethylammonium chloride ($C_{14}B$), is hydrolyzed immediately and completely in dilute alkali solution ($\text{pH} > 10$) at room temperature to yield a nonsurfactant.⁶ We also demonstrated that $C_{14}B$ can be used as a cleavable emulsifier for emulsion polymerization of styrene (St), which precipitates emulsifier-free polymers quantitatively by addition of a small amount of alkali.⁶ Accordingly, if $C_{14}B$ in the polymer latices, which are adsorbed or aggregated on a substrate, is subjected to alkali hydrolysis, the resulting emulsifier-free polymers will coat the substrate surface at room temperature.

This study is focused on a facile polymer coating of papers with polystyrene (PSt) latices containing $C_{14}B$. Here, we used filter papers as substrates because of the followings: (1) Cellulose papers, of which surfaces are somewhat negatively charged, are compatible with cationic latices.³ (2) Highly water-permeable filter papers will also achieve very fast adsorption or aggregation of the latices on the surface. (3) Cellulose papers are relatively resistant to alkali,⁷ which will hold long-term stability after the coating processes including alkali hydrolysis of $C_{14}B$.

Correspondence to: Y. Itoh (yositoh@shinshu-u.ac.jp).

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EXPERIMENTAL

Materials

St (Wako Chemical, Osaka, Japan) was distilled under reduced pressure before use. C₁₄B was prepared and purified as reported previously.⁶

Emulsion polymerization

A typical polymerization procedure was as follows: To a mixture of St (6.25 g, 60 mmol), C₁₄B (0.21 g, 0.6 mmol), methyl yellow (0.031 g, 0.5 wt % of St) (Tokyo Kasei, Tokyo, Japan), and water (50 g) 2,2'-azobis (2-amidinopropane) dihydrochloride (0.049 g, 0.18 mmol) (Wako Chemical, Osaka, Japan) in water (5 g) was added and stirred at 60°C at 250 rpm for 3 h under nitrogen atmosphere. The polymer yield was determined to be 92% gravimetrically. The molecular weight was determined to be 5.0×10^5 by gel permeation chromatography.⁶ The mean diameter of the latex particles was determined to be 70 nm by dynamic light scattering.⁶ The corresponding PSt latices containing no dye, which had been prepared previously,⁶ was also used as references: polymer yield, 90%; molecular weight, 4.7×10^5 ; particle diameter, 72 nm.

Polymer coating of filter papers

For pretreatment of papers, three drops (0.24 mL) of water or aqueous NaCl or Na₂CO₃ solution (0.1M) was loaded on a quantitative filter paper (ADVANTEC, No. 5C; cut to a diameter of 25 mm) and air-dried overnight. The resulting papers are named nontreated, NaCl-treated, and Na₂CO₃-treated papers, respectively.

The pretreated papers were immersed in a 10 wt % of latex solution (10 mL) for 5 min at room temperature, rinsed in a lot of flowing water (5 L/min) for 1 min, and then air-dried overnight. The corresponding nonrinsed papers were also prepared as references. Adsorption amounts of the latices and/or polymers were determined gravimetrically and then normalized to that for the nontreated and nonrinsed paper (ca. 6 mg solid/60 mg paper). The amounts were also determined by measuring the concentration of methyl yellow in the latices and/or polymers as follows: each polymer (or latices)-coated paper was immersed in a 5 mL of *N,N*-dimethylformamide in 12 h at room temperature until methyl yellow was dissolved completely in the solution, and then the absorbance at 420 nm of the solution was measured with a Hitachi U-3210 spectrophotometer. The concentration of methyl yellow and then the amount of PSt latices and/or polymers (containing 0.5 wt % of methyl yellow) were determined by calibration with dye solutions of known concentration. The reproducibility of the data was within about ± 1 mg.

Measurements

Scanning electron microscope (SEM) images were taken by using a Hitachi S-5000 FE-SEM operated at 20 kV. All samples were sputter-coated with a thin overlayer of platinum-palladium before inspection.

Contact angles were measured by the static sessile drop method with a contact angle meter (Kyowa Interface Science, model CA-VP). After the immersing process, the rinsed or nonrinsed papers were wiped lightly with a paper towel, air-dried for a given time (0–4 h), and then their water contact angles were measured for one drop of water (1.5 μ L) at room temperature. The data for the initial contact angles were obtained within 10 s after contacting a water droplet on the sample. The reproducibility of the data was within about $\pm 20^\circ$.

RESULTS AND DISCUSSION

Preliminary investigation for coating method

As described in the Introduction section, PSt latices containing C₁₄B precipitate immediately in dilute alkaline solution (pH > 12), where C₁₄B in the latices can be completely hydrolyzed.⁶ Based on the result, preliminary investigations were carried out to find a suitable method for coating of filter papers with several bases such as NaOH, NH₃, N(CH₃)₃, and Na₂CO₃. The experiments revealed that simple addition of bases into the PSt-latex solution precipitated the polymer but scarcely coated the paper with it. We finally found that the paper pretreated by dropping aqueous Na₂CO₃ solution of a moderate concentration (ca. 0.1M) serves as an appropriate substrate for coating, leading to the highest adsorption amount of polymers. When the paper was pretreated with a higher concentration of Na₂CO₃ or a stronger base (e.g., NaOH), a lot of base in the paper was diffused and dissolved in the latex solution, precipitating the polymer aggregates immediately in the solution phase and decreasing the adsorption amount. Therefore, to perform the hydrolysis of C₁₄B in the latices synchronized with the adsorption of the latices on the paper, its pretreatment with a weak base of a moderate concentration seems to be suitable, though both pretreatment and coating conditions have not been optimized yet. Here, the adsorption and desorption efficiencies for the pretreated paper will be compared with those for the nontreated paper.

Adsorption of PSt latices on filter papers

To visualize the adsorption and desorption processes of latices, PSt latices containing 0.5 wt % of methyl yellow were prepared by a conventional method.⁶ The presence of the dye little influenced the

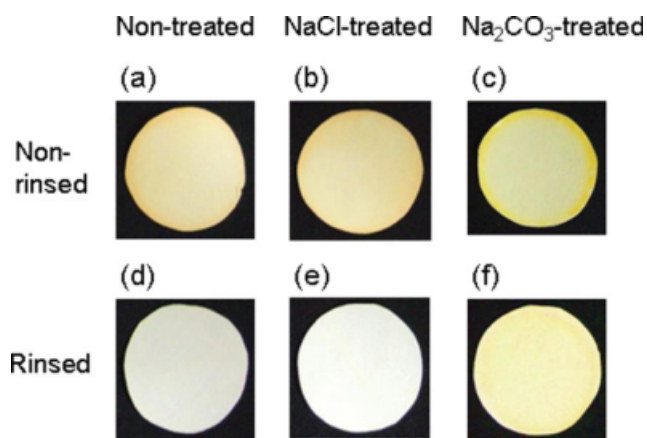


Figure 1 Photographs of PSt-C₁₄B latices-coated filter papers: (a) nontreated paper (nonrinsed); (b) NaCl-treated paper (nonrinsed); (c) Na₂CO₃-treated paper (nonrinsed); (d) nontreated paper (rinsed); (e) NaCl-treated paper (rinsed); (f) Na₂CO₃-treated paper (rinsed). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties of the latices (see Experimental section). Adsorption of the resulting PSt latices on filter papers was carried out by immersing the Na₂CO₃-treated or nontreated quantitative papers in the latex solution, rinsing them with water or not, and then air-drying. The paper pretreated with NaCl was also used to investigate the salt effect on the processes.

Figure 1 shows the photographs of the papers adsorbed with PSt latices. The latices could be adsorbed on the papers with and without alkali-pretreatment, resulting in the yellow colorization [Fig. 1(a–c)]. The relative adsorption amounts were determined gravimetrically and by measuring the concentration of methyl yellow in the latices and/or polymers photometrically. As shown in Table I, both data were almost consistent, indicating little release of the dye during the processes. Comparison of the amounts for the pretreatments showed that the values of the nonrinsed papers were almost the same as the nontreated and NaCl-treated papers and that

little concentration dependence of NaCl (up to 0.5M) on it was observed for the latter one. It should be noted that the Na₂CO₃-treated paper had a higher amount.

These results can be explained by the schematic illustrations in Figure 2. A simple physical adsorption of latices on the nontreated paper will occur and the morphology of the latices on the surface will change only limitedly [Fig. 2(a-1)]. A similar event will occur on the surface of the NaCl-treated paper. The little concentration effect of NaCl suggests that salting out of the latices which facilitates the latex aggregation, if it occurs, does not promote the adsorption process in the present salt concentration range (<0.5M). In contrast, the latices adsorbed on the Na₂CO₃-treated paper surface will be attacked immediately by Na₂CO₃ (strictly speaking, dissociated hydroxide ion) in the paper and the latex structure will be destroyed via hydrolysis of C₁₄B, facilitating the adhesion of the core polymer to the surface and then increasing the adsorption amount [Fig. 2(b-1)].

Desorption of PSt latices on filter papers

Rinsing the nontreated and NaCl-treated papers with water resulted in the decolorization [Fig. 1(d,e)] and the decrease in the adsorption amount (Table I), indicating desorption of the latices from the surfaces [Fig. 2(a-2)]. Higher value was obtained for the NaCl-treated paper, which further increased with the NaCl concentration (Table I). In this process, the salting out will resist the wash-down to some extent. It is important to note that apparently the Na₂CO₃-treated paper changes little by rinsing [Fig. 1(f)] and still retains the highest adsorption amount (Table I). This clearly indicates the strong adhesion of most polymers to the paper surface [Fig. 2(b-2)]. Because most latices will be destroyed at this stage, the salting-out effect of Na₂CO₃ (0.1M) on desorption of them seems to be minor.

TABLE I
Adsorption Amounts of PSt Latices for Pretreated Papers^a

| Filter paper | [Salt] (M) | Gravimetry ^b | | Photometry ^c | |
|--|------------|-------------------------|------------------------|-------------------------|--------|
| | | Nonrinsed | Rinsed | Nonrinsed | Rinsed |
| Nontreated | 0 | 1.0 | 0.1 | 1.2 | 0.1 |
| NaCl-treated | 0.1 | 1.0 (1.0) ^d | 0.4 (0.4) ^d | 1.1 | 0.3 |
| | 0.2 | –(1.0) ^d | –(0.8) ^d | – | – |
| | 0.5 | –(1.2) ^d | –(1.1) ^d | – | – |
| Na ₂ CO ₃ -treated | 0.1 | 1.6 | 1.6 | 1.6 | 1.6 |

^a Adsorption amounts are normalized to that for the nontreated and nonrinsed paper determined gravimetrically (1.0).

^b Determined gravimetrically.

^c Determined photometrically (see Experimental section).

^d Measured for PSt latices containing no methyl yellow.

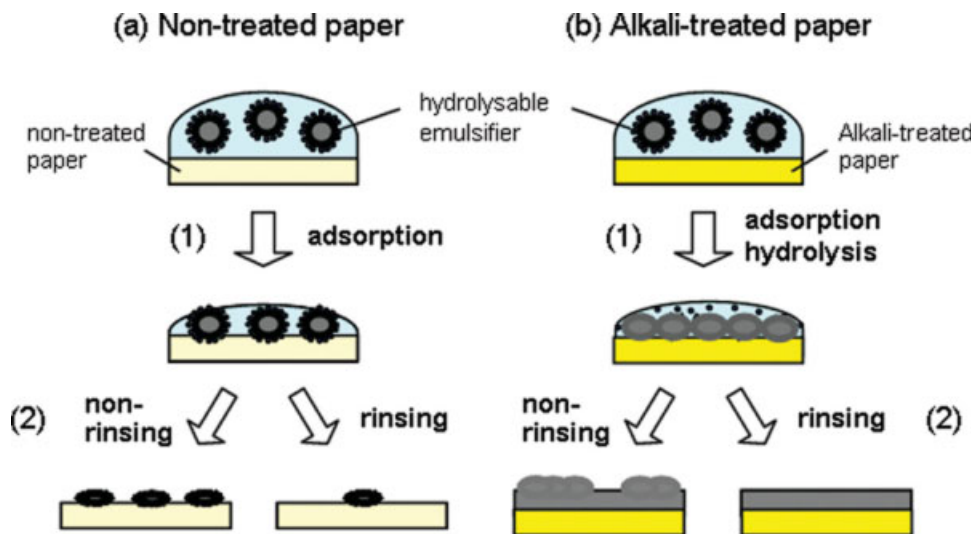


Figure 2 Schematic diagrams of coating processes for (a) nontreated and (b) alkali-treated papers: (1) adsorption of polymer-hydrolysable emulsifier latices on papers; (2) nonrinsing and rinsing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SEM images of coated papers

To verify the changes, the surface morphologies of the papers were investigated by SEM. SEM images for the nontreated and Na_2CO_3 -treated papers are shown in Figure 3 (magnification, $\times 5000$). Fibers in the nonrinsed papers appeared to have rough surfaces owing to the adsorption of latices and/or polymers [Fig. 3(a,b)]. By rinsing, the fiber in the nontreated paper returned almost to the one in the original paper due to desorption of the latices [Fig. 3(c)], whereas the one in the Na_2CO_3 -treated paper appeared to be still covered wholly with a large amount of polymers, forming a somewhat flat surface [fig. 3(d)]. These

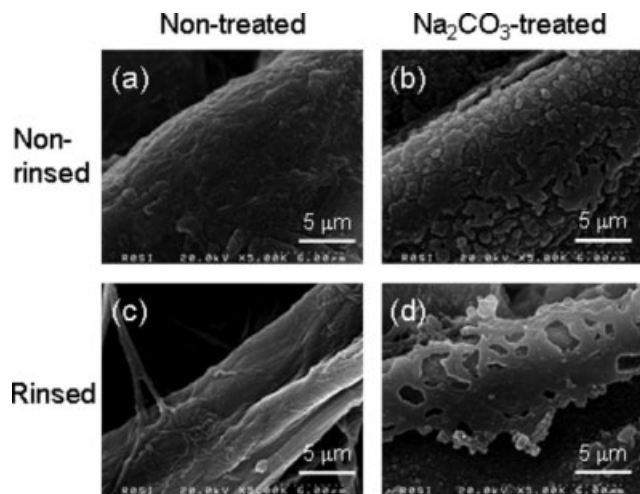


Figure 3 SEM images of PSt- C_{14}B latices-coated filter papers with a moderate magnification ($\times 5000$): (a) nontreated paper (nonrinsed); (b) Na_2CO_3 -treated paper (nonrinsed); (c) nontreated paper (rinsed); (d) Na_2CO_3 -treated paper (rinsed).

observations, thus confirm the adsorption and desorption of latices on the nontreated paper surface and the strong adhesion of polymers on the Na_2CO_3 -treated paper surface.

Such differences are more obvious in Figure 4 (magnification, $\times 50,000$). Although a great number of latex particles were adsorbed on the fiber in the nontreated paper before rinsing [Fig. 4(a)], the majority of them were removed by rinsing [Fig. 4(c)]. This result also confirms that the simple physical adsorption can fix little latices and polymers on the fiber. In contrast, the fiber in the Na_2CO_3 -treated paper before rinsing was covered with lumps of polymers with different sizes rather than the latex particles [Fig. 4(b)]. Although the hydrolysis yield of

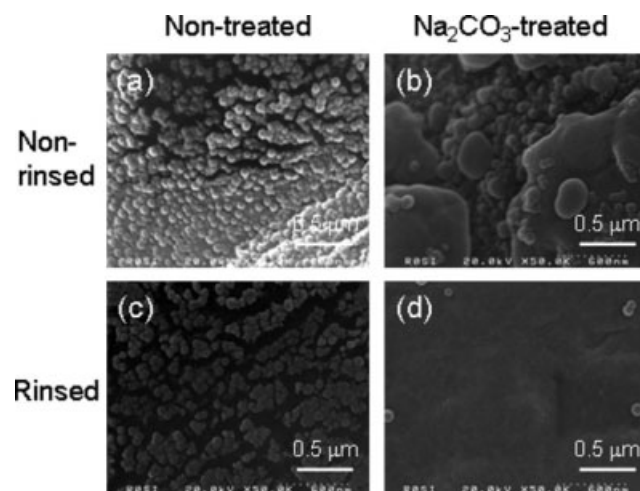


Figure 4 SEM images of PSt- C_{14}B latices-coated filter papers with a high magnification ($\times 50,000$): (a–d) see Figure 3.

TABLE II
Water Contact Angles for PSt Latices-Coated Papers^a

| Filter paper | 0 h | 1 h | 2 h |
|--|----------------------|----------------------|-----------------------|
| Nontreated | 0 | 0 | 0 |
| NaCl-treated | 0 (0) ^b | 0 (0) ^b | 50 (90) ^b |
| Na ₂ CO ₃ -treated | 30 (30) ^b | 80 (80) ^b | 110 (90) ^b |

^a Initial values (°) for rinsed papers as a function of air-drying time; measured within 10 s after the sample preparation.

^b Initial values for nonrinsed papers.

C₁₄B is not determined under the present condition, the majority of latex particles on the fiber surface will be destroyed immediately via the hydrolysis of C₁₄B at this stage, resulting in forming polymer aggregates and covering the surface [Fig. 2(b-2): nonrinsing]. By rinsing, the small lumps and the latex particles were removed almost completely, forming a flat surface [Fig. 4(d)]. The small aggregates which are not contacted (or entangled) directly with the fiber will be washed down [Fig. 2(b-2): rinsing]. In any event, it is evident that filter papers can be coated by PSt with high T_g (100°C)⁸ without any thermal annealing. Preliminary experiments also implied that polymers with a lower T_g [e.g., polybutylacrylate (−54°C) and polybutylmethacrylate (20°C)]⁸ can coat the paper more efficiently, giving very smooth surfaces.

Water resistance of paper surfaces

Water resistance and “quick drying” of the surfaces of the PSt-coated papers were estimated by measuring the initial water contact angle as a function of air-drying time after the sample preparation (Table II). Until 1 h air-drying, water droplets immediately penetrated into the nontreated and NaCl-treated papers before starting the measurement (within 10 s), and the initial contact angle for the NaCl-treated paper increased after 2 h drying, which still declined within 10 min after the measurement. In contrast, a

distinct initial value for the Na₂CO₃-treated paper, regardless of rinsing and nonrinsing, was recorded just after the sample preparation, which steadily increased in 2 h. It should also be noted that the value decreased only slightly (<10%) after the measurement. These results clearly indicate that the surface of the Na₂CO₃-treated paper is covered wholly by hydrophobic PSt and thus has both water resistance and quick-drying abilities.

CONCLUSIONS

We have presented a facile coating method with polymer latices. The advantage of the method is that not only the coating can be performed under very mild conditions, but also various polymers with different T_g can be used without thermal annealing. The coating with appropriate polymers may be easily applicable to quick-drying coatings, adhesives, paints, and so on. In particular, the high long-term stability of alkali-treated papers⁷ suggests potential utilities of the present method in papermaking and paper conservation processes.

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