

# Quick-drying, protective coating of papers with poly(methacrylate) latices containing alkali-hydrolysable emulsifiers

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**Abstract** Surfaces of filter papers pretreated with sodium carbonate were coated with poly(methacrylate) latices containing alkali-hydrolysable or non-hydrolysable cationic emulsifiers by a simple drop-coating method and their surface properties were investigated. Determination of fixed amounts of polymers and observation of the paper surfaces suggest that glass transition temperature of the polymers and hydrolysability of the emulsifier are dominant factors for the coating. The latices of poly(2-ethylhexyl methacrylate) containing the hydrolysable emulsifier could coat the paper surface almost perfectly and smoothly, making it quick-drying and water repellent.

**Keywords** Coatings · Emulsion polymerization · Latices · Cleavable surfactant · Hydrolysis

## Introduction

Water-based polymer latices prepared through emulsion polymerization have become most important materials because of not only environmental concerns but also potential applications in industrial fields [1–3]. For their utilization in paints, adhesives, paper coatings, textile finishes, etc., several processes including coalescence of latex particles, their adherence to substrates, and formation of polymer films must be performed satisfactorily. However, emulsifiers and other additives in latices or latex dispersions may hinder the above processes and still remain in the final products, decreasing the product performances such as water repellency, quick-drying, insulation, adhesive, and mechanical and other surface

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properties [3, 4]. To overcome these problems, surfmers (surface-active monomers), water-soluble monomers, or polymeric surfactants as emulsifiers are being replaced with traditional surfactants [5–7] and functional monomers and surfactants such as silicone- and fluorine-containing ones [8–11] are being studied in both industry and academia. In such cases, the effects of emulsifiers and other additives were diminished but not inhibited. For the significant advance, elimination of surface-active or water-soluble species from the final products should be essential and desirable. In this context, cleavable surfactant seems to be one of promising candidates for emulsifiers of polymer latices [12].

We have recently succeed in preparation of emulsifier-free polystyrene, poly(methacrylate)s, and poly(acrylate)s by conventional emulsion polymerization using an alkali-hydrolysable cationic emulsifier, (1-tetradecyloxy)carbonylmethyl)trimethylammonium chloride ( $C_{14}B$ ) followed by simple addition of a weak base [13, 14]. Based on the fact that cellulose fibers and papers can be polymer coated easily with cationic polymer latices [15, 16], we have also proposed a novel method for paper coating using the above  $C_{14}B$ -containing latices [17, 18]. It was demonstrated that cellulose fibers in filter papers pretreated with dilute sodium carbonate ( $Na_2CO_3$ ) can be polymer coated rapidly without any thermal annealing by dipping the paper in the latex dispersion. We also found that poly(methacrylate)s and poly(acrylate)s with a lower glass transition temperature ( $T_g$ ) such as poly(butyl methacrylate) and poly(butyl acrylate) can coat the fiber surfaces efficiently to make them flat and hydrophobic. These are attributable to coalescence of the latex particles induced by hydrolysis of the emulsifier just on the fiber surfaces and to the subsequent adherence of polymers to them. It should be noted that such surface modification was not observed or markedly diminished for the latices containing a conventional, or non-hydrolysable, emulsifier, cetyltrimethylammonium chloride (CTAC), because of its residual effect on the film formation. In such case, the coating requires thermal annealing at a temperature higher than 100 °C [16, 18].

By the above dip-coating method, however, the porous surface of filter paper was coated imperfectly by the small quantity of polymers, indicating only a limited modification: the surface became somewhat hydrophobic but little water repellent [17, 18]. For further improvement in the paper performances, the paper surface should be wholly coated with polymers.

In this study, a drop-coating method is employed to develop the protective coating of filter papers with the latices of poly(methacrylate)s with different  $T_g$ . We find that the paper surface can be coated almost perfectly and smoothly with poly(2-ethylhexyl methacrylate) (PEHMA), which gains both quick-drying and water repellency.

## Experimental

### Materials

2-Ethylhexyl methacrylate (EHMA) was purchased from Tokyo Kasei (Tokyo, Japan) and distilled under reduced pressure before use. All other chemicals were

those reported previously [13, 14, 17] or commercially available, and purified by the usual methods. The “bulk” PEHMA was prepared by conventional bulk polymerization as reported previously [14].

### Emulsion polymerizations

The latices of PMMA and PBMA were prepared according to the previous method [14]. Emulsion polymerizations of EHMA were also carried out, where the concentrations of the contents [EHMA, 2,2'-azobis(2-amidinopropane) dihydrochloride (AIBA) and CTAC or C<sub>14</sub>B] were decreased to half for the other systems to avoid the coagulation of latices. Characterizations of the polymers and polymer latices were carried out as described in the previous articles [13, 14]. The experimental conditions and data are summarized in Table 1. The resulting latex dispersions were used for the following experiments as they were.

### Polymer coating of filter papers

A drop-coating method was used to prepare coatings on filter papers as follows: a quantitative filter paper (ADVANTEC, No. 5C; thickness, 0.22 mm; cut into a rectangle of 25 × 50 mm) was pretreated by loading a 1 mL of aqueous Na<sub>2</sub>CO<sub>3</sub> solutions (0.2 M) on it and air-drying it overnight at room temperature. A 2.5 mL of the latex dispersion was loaded gently on the above Na<sub>2</sub>CO<sub>3</sub>-pretreated paper, which was allowed to stand for 1 h at room temperature, and then decanted away. The coatings were also done for the bare (non-treated) filter papers. The papers were rinsed in a lot of flowing water (5 L/min) for 1 min to remove the latices or their aggregates adsorbed simply physically on the paper surface as much as possible, and air-dried overnight. The corresponding non-rinsed papers were also prepared. The adsorbed and/or fixed amount of the latices and/or polymers was determined

**Table 1** Emulsion polymerizations of alkyl methacrylates using C<sub>14</sub>B and CTAC as emulsifiers

Polymer	Emulsifier	Conversion (%)	$M_w^a$ ( $\times 10^5$ )	Particle diameter (nm)	PDI <sup>b</sup>
PMMA	C <sub>14</sub> B	91	13	65	0.04
PMMA	CTAC	97	– <sup>d</sup>	68	0.05
PBMA	C <sub>14</sub> B	93	9.3	66	0.06
PBMA	CTAC	86	– <sup>d</sup>	70	0.02
PEHMA <sup>c</sup>	C <sub>14</sub> B	97	20	95	0.01
PEHMA <sup>c</sup>	CTAC	100	– <sup>d</sup>	95	0.04

Monomer = 60 mmol; surfactant = 0.6 mmol; initiator = 0.18 mmol; polymerization temperature = 60 °C; polymerization time = 1 h

<sup>a</sup> Determined by viscosity measurement: Ref. [14]

<sup>b</sup> Polydispersity index of particle diameter: Ref. [13]

<sup>c</sup> EHMA = 30 mmol; surfactant = 0.3 mmol; initiator = 0.09 mmol; polymerization temperature = 70 °C; polymerization time = 1 h

<sup>d</sup> Not determined

gravimetrically for more than three pieces of papers, which was defined conveniently as the quantity of the total weight of the polymer/latices-coated paper minus the weight of the bare filter paper per square centimeter ( $\text{g/m}^2$ ): the reproducibility of the data was about 20%.

## Measurements

The molecular weights ( $M_w$ s) of PEHMA were determined by viscosity measurements [14]. The intrinsic viscosity  $[\eta]$  was estimated by extrapolation of the plot of reduced viscosity and polymer concentration to the concentration of zero.  $M_w$  was then calculated from Mark–Houwink equation:  $[\eta] = K \cdot M_w^a$ . The parameters ( $K$ ,  $a$ ) used here were  $K = 6.30 \times 10^{-3} \text{ mL/g}$  and  $a = 0.707$  in tetrahydrofuran at 30 °C [19].

Surface morphologies of the papers were observed by means of scanning electron microscopy (SEM) with a Hitachi S-5000 FE-SEM or a Hitachi SEM SU1510 operated at 5–15 kV [17]. All samples were sputter coated with a thin overlay of platinum–palladium before inspection.

The paper thickness was measured with a screw micrometer (MITUTOYO PB-1B; error  $\pm 4 \mu\text{m}$ ).

Contact angles were measured by the static sessile drop method at room temperature [17]. The initial contact angle ( $\theta_0$ ) was obtained within 10 s after contacting a water droplet to the sample surface. Quick-drying of the polymer-coated paper surfaces was estimated by recording the  $\theta_0$  value as a function of air-drying time (1–24 h). The test was repeated four times and the average value was used. The  $\theta_0$  value of the PEHMA cast film was also determined.

Water repellencies of the polymer-coated papers were estimated by the water-immersion and water-penetration tests. The water-immersion test was as follows: A piece of the polymer-coated paper ( $25 \times 50 \text{ mm}$ ) was immersed in ultrapure water at room temperature for 48 h and then dried under vacuum. The corresponding non-immersed papers were also prepared. After a water droplet was contacted to the sample surface, the contact angle ( $\theta$ ) was recorded every 5 min until the droplet penetrated into the paper. The test was repeated four times and the average value was used. The water-penetration test was carried out as follows: a piece of the polymer-coated paper was cut into a 13-mm diameter circle and mounted in a membrane filter holder (ADVANTEC, KS-13), and a glass syringe filled with 10 mL of ultrapure water was connected to the holder top. The load of 1 N was applied to the top of the syringe and then the penetration time of the whole water through the paper was recorded at room temperature. The test was repeated three times and the average time was recorded as the penetration time.

## Results and discussion

### Coating of polymer latices on filter papers

All polymer latices used in this study were stable and monodisperse [polydispersity index of particle diameter (PDI)  $< 0.1$ ] [13], as reported previously (Table 1)

**Table 2** Fixed amounts of polymer latices and thicknesses of the coated layers for Na<sub>2</sub>CO<sub>3</sub>-treated filter papers

Polymer	Polymer/CTAC		Polymer/C <sub>14</sub> B	
	Amount (g/m <sup>2</sup> )	Thickness (μm)	Amount (g/m <sup>2</sup> )	Thickness (μm)
PMMA	1.1	11	1.8	17
PBMA	1.1	22	0.7	9
PEHMA	2.6	6	4.1	15

The papers are rinsed with water

[13, 14]. Although, the particle diameters for the PEHMA latices (95 nm) were slightly larger than for PMMA and PBMA ones (ca. 70 nm), the solution properties and their influences on the coating seem not to be much different.

When the Na<sub>2</sub>CO<sub>3</sub>-pretreated papers were coated with the polymer latices by the dip-coating method, the fixed amount of them on both surfaces of the paper and/or inside it after rinsing was 4 g/m<sup>2</sup> at the highest: less than 20% of the polymer latices charged was only available [18]. On the other hand, the present drop-coating method increased the fixed amount up to 5 g/m<sup>2</sup> on one surface of the paper: an unexpectedly small yield, not more than 25% of the latices charged, was obtained and the paper thickness increased by 5–25 μm (Table 2). Most of the polymer latices and aggregates accumulated or weakly adsorbed on the surfaces as well as the latices dispersed in the solution may be removed away by rinsing.

During the coating process under this condition, the latex dispersions penetrated partly through the non-pretreated papers, but did not through the Na<sub>2</sub>CO<sub>3</sub>-pretreated ones, indicating the strong electrostatic interaction between the latex surfaces and Na<sub>2</sub>CO<sub>3</sub> [18]. No apparent change was observed for the PMMA/CTAC latex dispersion during the process, whereas a small size of aggregates in aqueous phase and a slightly bigger size of them on the paper surface appeared for the PBMA/CTAC and PEHMA/CTAC latices, respectively. The lower  $T_g$  values of the latter polymers will lead to some coalescence of the polymer latices: the literature values are 105, 20, and –10 °C for PMMA, PBMA, and PEHMA, respectively [20]. Most of the latex particles and aggregates for the PMMA/CTAC and PBMA/CTAC latices, however, were washed down, resulting in the low fixed amounts (Table 2).

When coated with the C<sub>14</sub>B-containing latices, the coalescence of latex particles induced by hydrolysis of C<sub>14</sub>B facilitated both coagulation in the aqueous phase and adhesion to the paper surfaces. In fact, a large amount of bigger solid particles for the PBMA/C<sub>14</sub>B and PEHMA/C<sub>14</sub>B latices appeared on the paper surfaces. However, the majority of the “PBMA/C<sub>14</sub>B” solid particles were washed down because of the “weak bonding” with the surfaces, decreasing the fixed yield to even less than that of the PBMA/CTAC latices (Table 2). This is in contrast with the previous result that the higher fixed amount was obtained for the PBMA/C<sub>14</sub>B latices by a dip-coating method [18]. On the other hand, the PEHMA/C<sub>14</sub>B latices easily adhered to the surface and thus formed film on it, increasing the yield. As described above, however, the coating efficiency was still low (<25%). It is

interesting to note that, despite the low fixed amount, the PEHMA/C<sub>14</sub>B-coated paper surface became water repellent still during the coating process (i.e., in a wet state). Therefore, the combination of polymers with a lower  $T_g$  and a hydrolysable emulsifier (C<sub>14</sub>B) is most likely suitable for quick-drying and protective coating.

The thickness of the coated layer could not be measured by SEM images because of little contrast and large surface roughness, and then estimated roughly by measurement with a screw micrometer. As shown in Table 2, the thickness was not correlated with the fixed amount, suggesting the adsorption and adhesion of polymer latices to different places (surface or inside) of the paper with different bonding strengths and quantities.

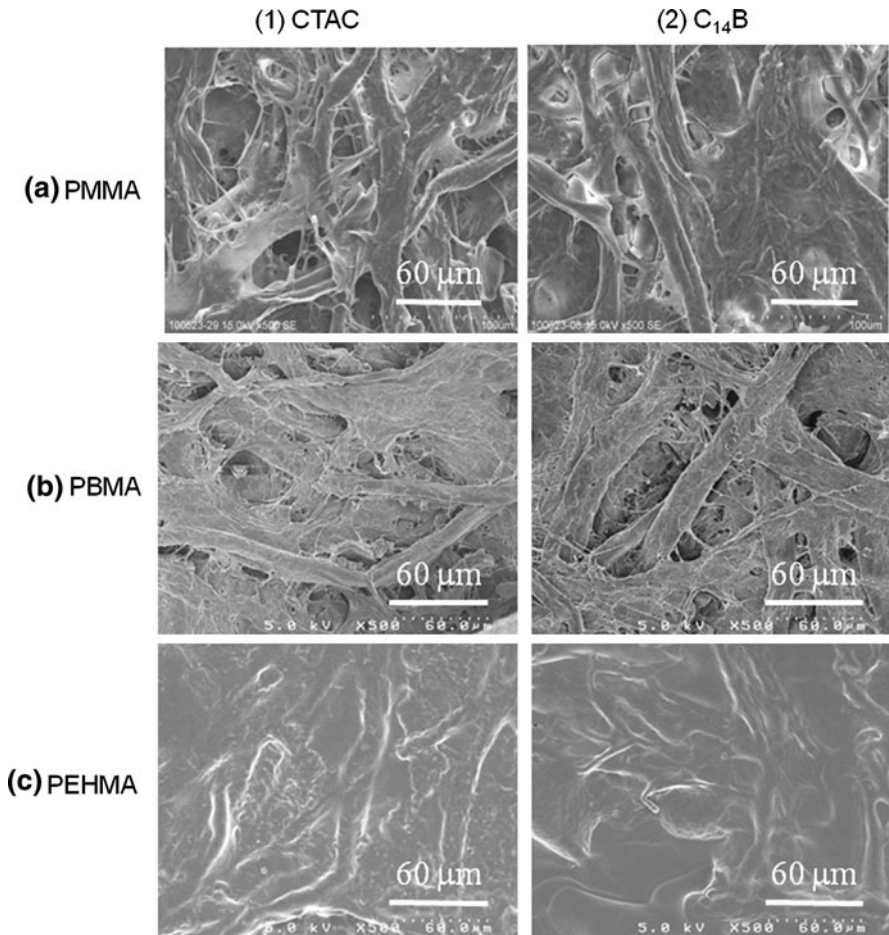
In this experiment, the polymer latices were coated on the papers pretreated with 0.2 M Na<sub>2</sub>CO<sub>3</sub>. Using a higher concentration of Na<sub>2</sub>CO<sub>3</sub> (>0.5 M) or a stronger alkali such as NaOH, the majority of the polymer/C<sub>14</sub>B latices coagulated in the aqueous phase and then the fixed amount further decreased. This is because a lot of the alkalis (solid) dissolve and disperse in the bulk aqueous solution before reacting with the latices approaching the paper surface, leading to dispersion of a large amount of “weakly bound” solid particles in the solution or their accumulation on the surface which will be easily washed down.

#### SEM images of polymer-coated papers

SEM images of the coated papers after rinsing are shown in Figs. 1 (magnification,  $\times 500$ ) and 2 (magnification,  $\times 5,000$ ). The paper and fiber surfaces were coated partially with the PMMA and PBM latices, reflecting the low fixed amounts (Table 2). In contrast, the paper surfaces were coated almost perfectly and smoothly with the PEHMA latices, reflecting the very low  $T_g$  value of PEHMA. A distinct difference, however, was not observed between the PEHMA/CTAC- and PEHMA/C<sub>14</sub>B-coated paper surfaces.

#### Wetting and protective properties

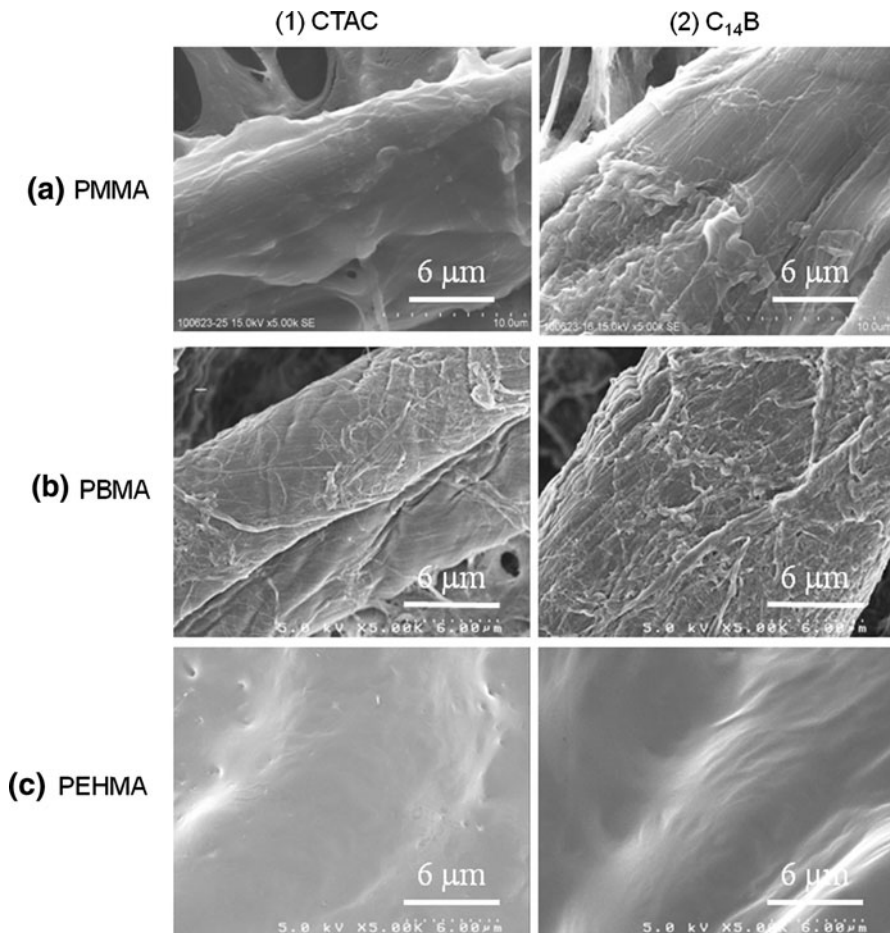
For applications of polymer latices in waterborne coatings, the drawbacks of quick-drying and water repellency must be improved [3, 4]. Quick-drying of the polymer-coated paper surfaces was estimated by measuring the initial water contact angle ( $\theta_0$ ) as a function of air-drying time at room temperature after the sample preparation (Fig. 3). Some scattered plots might be due to an alteration in the surface roughness. The bare and Na<sub>2</sub>CO<sub>3</sub>-pretreated papers themselves were water permeable, always showing the contact angle of zero: a water droplet penetrated through the papers within 10 s. The surfaces of the polymer/CTAC-coated papers were gradually dried with a drying time (Fig. 3a). It is apparent that the required drying time and the  $\theta_0$  value for the dried surface were dependent on hydrophobicity of the polymers and their surface coverage: PEHMA > PBMA > PMMA. For reference, the water contact angles for the polymer cast films were determined to be 99°, 83°, and 72° in that order [14]. Similar trends were observed for the PMMA/C<sub>14</sub>B- and PBMA/C<sub>14</sub>B-coated papers (Fig. 3b). It should be noted that the surface of the PEHMA/C<sub>14</sub>B-coated paper dried immediately after the sample



**Fig. 1** SEM images of polymer-coated filter papers with a low magnification ( $\times 500$ ): (1) polymer/CTAC-coated paper; (2) polymer/ $C_{14}B$ -coated paper; **a** PMMA; **b** PBMA; **c** PEHMA; the papers are rinsed with water

preparation, indicating the high  $\theta_0$  value still at time zero. As described above, the hydrolysis of  $C_{14}B$  will make the PEHMA-coated surface hydrophobic and thus water repellent immediately.

Water repellency of the paper surfaces was estimated by measuring the time-course of water contact angle ( $\theta$ ) for the dried surfaces of the polymer-coated papers before and after immersion in pure water for 48 h (Fig. 4). A water droplet immediately penetrated into the PMMA- and PBMA-coated papers because of the poor coating (i.e., a little fixed amount) (Table 2). On the other hand, the  $\theta$  values for the PEHMA/CTAC-coated paper were recorded up to 30 and 10 min before and after immersion, respectively (Fig. 4a). A rapid decrease of the angle for the immersed sample indicates the loss of some of the coated polymer layer from the paper surface. Although, the SEM images imply the coverage of the whole surface

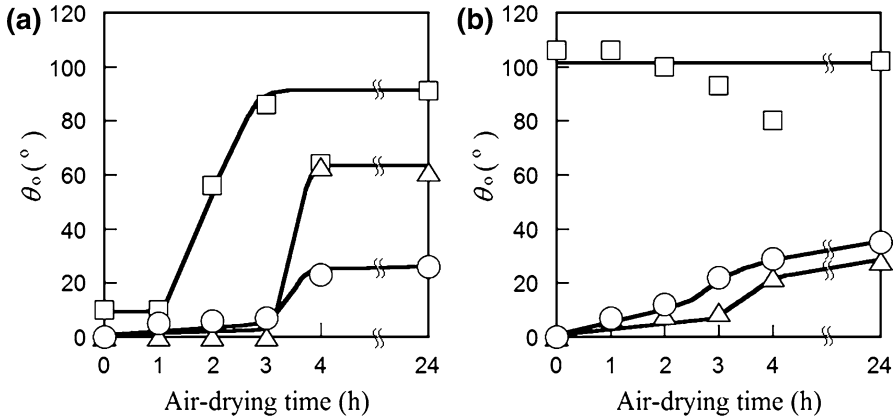


**Fig. 2** SEM images of polymer-coated filter papers with a high magnification ( $\times 5,000$ ): (1) polymer/CTAC-coated paper; (2) polymer/ $C_{14}B$ -coated paper; **a** PMMA; **b** PBMA; **c** PEHMA; the papers are rinsed with water

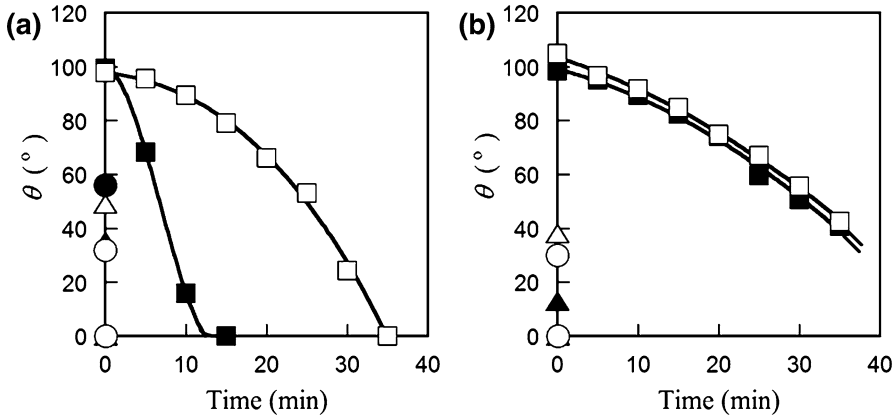
and little defects on it (Figs. 1c-1, 2c-1), the persistence of CTAC in the coated layer may allow water to easily contact the surface, ripping the layer and thus decreasing the water repellency. In contrast, the PEHMA/ $C_{14}B$ -coated papers continued to have a higher angle over 40 min and little immersion effect was observed (Fig. 4b). Thus, the coating of PEHMA/ $C_{14}B$  lattices was found to be more protective.

Water repellency of the polymer-coated papers was also estimated by the water-penetration test. The penetration times are listed in Table 3. As expected from the above water-immersion test, 10 mL of water penetrated through the PMMA- and PBMA-coated papers within a few minutes and the PEHMA/CTAC-coated paper had some resistance to the penetration. It should be emphasized that the PEHMA/ $C_{14}B$ -coated paper perfectly inhibited the penetration under this condition.





**Fig. 3** Dependence of air-drying time (h) on initial water contact angle ( $\theta_0$ ) for polymer-coated papers: **a** polymer/CTAC-coated paper; **b** polymer/C<sub>14</sub>B-coated paper; circle PMMA; triangle PBMA; square PEHMA; the papers are rinsed with water



**Fig. 4** Time course (min) of water contact angle ( $\theta$ ) for polymer-coated papers before and after immersion in pure water for 48 h: **a** polymer/CTAC-coated paper; **b** polymer/C<sub>14</sub>B-coated paper; circle PMMA; triangle PBMA; square PEHMA; open symbol before immersion; closed symbol after immersion; the papers are rinsed with water

**Conclusions**

This study has demonstrated that by a drop-coating method filter paper surfaces can be easily coated with poly(methacrylate)s at room temperature using polymer/C<sub>14</sub>B latices and that the latices of PEHMA with a low  $T_{ig}$  coat the whole surface smoothly. It is notable that the paper surface can gain quick-drying and water repellency just after the simple coating without any thermal annealing. Therefore, this method with “hydrolysable” polymer latices has potential utilities in polymer coating systems. However, the coating yield was unexpectedly found to be still low, not more than 25% of the polymer latices charged, and the water-penetration test

**Table 3** Penetration time (min) of pure water through polymer-coated filter paper

Polymer	Polymer/CTAC	Polymer/C <sub>14</sub> B
PMMA	0.9	4.4
PBMA	1.7	2.8
PEHMA	170	>500

Passage time (min) of 10 mL of pure water

showed that the water repellency is imperfect (i.e., impermanent). Our preliminary experiments for optimization of the coating conditions such as concentrations of alkali, emulsifier, and latices and coating procedures suggest the accomplishment of the “quantitative” coating and the improvement of mechanical properties, which will be published in the near future.

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