

Study on Water Resistance of Paper Treated with Polyacrylate Microlatex

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ABSTRACT: Polyacrylate microlatexes were synthesized by microemulsion polymerization of acrylic monomers in the presence of cationic emulsifiers using a modified process. Paper treated with some of the polyacrylate microlatexes showed good water resistance. Paper's water resistance and its relation to the glass transition temperature (T_g) of the copolymer, the particle size of the microlatex, and the

emulsifier were studied. It was found that paper fiber can be uniformly coated by cationic microlatexes with polymers of lower T_g , resulting in higher resistance to water penetration. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 962–966, 2005

Key words: monomers; glass transition; copolymerization; water resistance; coating

INTRODUCTION

From the late 20th century, as a basic material, paper has been used in more and more realms. Often, certain chemical additives are required in the papermaking process to provide paper with resistance to diffusion and penetration of aqueous liquid.¹ Different kinds of chemical additives are either added into pulp or used for paper surface treatment.

Chemicals, such as modified rosins, alkyl ketene dimmer (AKD), and alkenyl succinic anhydride (ASA), are used for pulp treatment to increase the hydrophobic property of the paper fiber surface.^{2–6} But modified rosins are usually not very effective, while AKD and ASA have limited application due to high cost. For surface treatment, polymeric solutions or emulsions such as polyvinyl alcohol (PVA), copolymer of styrene and maleic anhydride (SMA), polyurethane (PU), and polyacrylamide (PAM) are usually employed. By forming a layer of polymer film on the whole paper sheet, the water resistance of paper is enhanced.^{1,7} However, the effectiveness of these polymer additives for improving water resistance is hardly satisfactory, and the consistency of paper fibers' hydrophobicity is rather poor.

Microemulsion polymerization, first reported by Stoffer and Bone in 1980,^{8,9} has been gaining interest in recent years for its small particle size, strong pene-

trability, and good film-forming ability. Some monomers, including acrylates and styrene, can be polymerized and form a stable polymer microemulsion.¹⁰ It is conceivable that in papermaking, polymer microemulsion can penetrate into paper fiber. However, it is still not clear whether and how the polymer microemulsion interacts with paper fiber and in consequence affects the hydrophobicity of paper fiber.

This study is focused on the interaction between the polymer microemulsion and the paper fiber. Microlatexes of methyl methacrylate (MMA) and butyl methacrylate (BMA) copolymers of different composition were synthesized using a modified microemulsion polymerization process. The fiber surface property and the water resistance of paper treated with microemulsions, and their relation to a series of factors such as microlatex particle size, the type of emulsifier, and the glass transition temperature are discussed and reported.

EXPERIMENTAL

Materials

AR grade MMA and BMA (Shanghai Reagent Co., Shanghai, China) were distilled under reduced pressure before use. AR grade octodoltrimethylammonium bromide (OTAB) (Shanghai Jingwei Co., Shanghai, China) and AR grade sodium dodecylsulfate (SDS) (Shanghai Research Institute of Special Chemistry and Materials) were used as received. Potassium persulfate (KPS) (Shanghai Reagent Co.) was purified by recrystallization from water. De-ionized water was used for all experiments. Whatman Grade2 filter paper with the weight of 97g/m² was purchased from Fuyang Special Paper CO. LTD.

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TABLE I
Monomer Component of Microemulsion
and Tg of Polymer Microlatex

Sample no.	1	2	3	4	5	6
MMA(g)	30	20	15	10	6	0
BMA(g)	0	10	15	20	24	30
Diameter of polymer microlatex(nm)	31.7	21.2	39.7	26.2	40.4	40.8
Tg (°C)	128	82.8	70.3	61.1	55.4	48.5

Microemulsion polymerization process

In the present study, Ming's modified microemulsion polymerization process was used,¹¹ by which the microemulsion with higher polymer content could be prepared through continuous addition of monomer to a pre-emulsified system. The pre-emulsion was prepared with 80g of water, 5g of monomer, and a given type and amount of emulsifier in a 250-mL 4-neck flask. The flask was equipped with a reflux condenser, a thermometer, an addition funnel, a stir bar, a N₂ inlet, and a N₂ outlet. When the reaction mixture was heated to 75°C, a solution of 90mg of KPS in 5g of water was added while N₂ bubbled through the flask. The polymerization was carried out under mild stirring. After 0.5 h the remaining 25g of monomer was continuously and slowly added into the polymerizing microemulsion in 40 min, which is defined as dropping time. When the addition is complete, the flask was kept at 75°C for 1 h.

Water resistance test

The water resistance test used Chinese national standards GB 5554-85 (Method for determination of water repellency of water proofing agents-Spray test) and AATCC Test Method 22-2001 (Water Repellency: Spray Test) as references. A microemulsion was diluted with de-ionized water to a solid content of 24 wt %, in which a sheet of filter paper was immersed. The

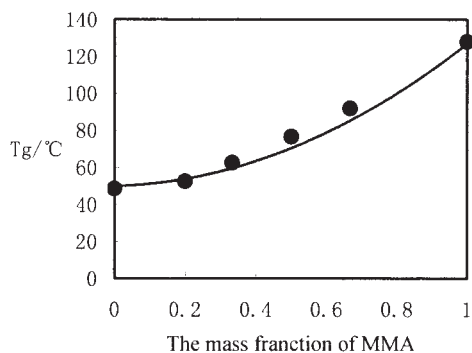


Figure 1 Tg of Poly(MMA-co-BMA) (the line was computed according to the FOX equation).

TABLE II
Water Resistance of Paper Fiber Treated with Polymer
Microemulsion at Different Baking Temperatures

	1	2	3	4	5	6
90°C	N	N	N	N	N	N
100°C	N	PN	PN	Y	Y	Y
120°C	N	PN	Y	Y	Y	Y
140°C	PN	Y	Y	Y	Y	Y
160°C	PN	Y	Y	Y	Y	Y

N: no water resistance; BPN: most of the sample is penetrated; PN: part of the sample is penetrated; Y: no water penetration in 1 hr.

mass ratio of the diluted microemulsion to the filter paper was 1 : 50. After the filter paper was dried at the given temperature and time, it was laid to float in a water container with pH test paper on top of the filter paper. The pH test paper changed color when water penetrated through the filter paper and made contact to it. The time needed for the color to change was recorded as a measure of water resistance.

Particle size determination

The Z-average diameters of the microlatex particles were determined by dynamic light scattering on L and G Microtrac Particle Analyzer 9200 (Leeds and Northrup Co.). Microlatex samples were diluted with deionized water to about 0.1 wt % of polymer concentration.

Glass transition temperature measurement

Microemulsions of different copolymer compositions were demulsified with methanol to separate polymer from water. The precipitates were washed repeatedly with methanol and water, and then dried in a vacuum oven at 50°C for 24 h. The glass transition temperatures (Tg) of those copolymers were measured on a Pyris 1 Differential Scanning Calorimeter (DSC) (Perkin-Elmer Co.) at the heating rate of 10°C/min in the range of 20 to 200°C.

SEM observation of paper surface

The compatibility between microlatex and paper fiber was studied via the observation of coverage of polymer film on fiber surface using a scanning electron microscope (SEM) (Hitachi HU-11B).

RESULTS AND DISCUSSION

Effect of polymer Tg on water resistance of paper treated with microemulsion

Emulsifier OTAC was used in microemulsion polymerization of MMA and BMA of different ratios. As

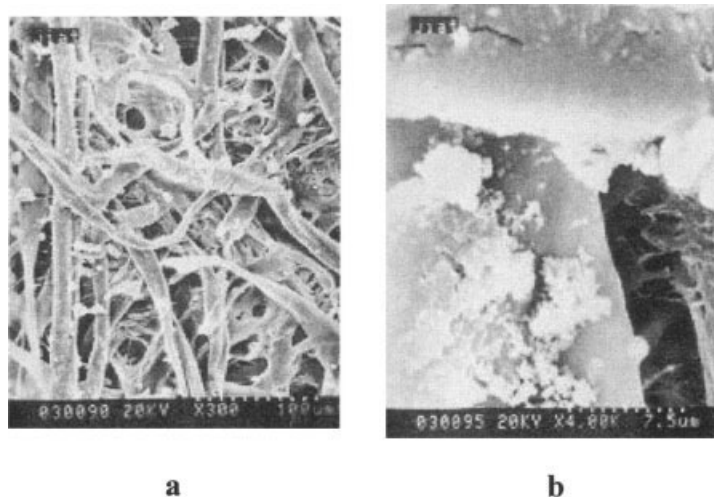


Figure 2 SEM picture of the paper fiber treated with PMMA microemulsion (No. 1) and baked at 160°C: (a) $\times 300$, (b) $\times 4000$.

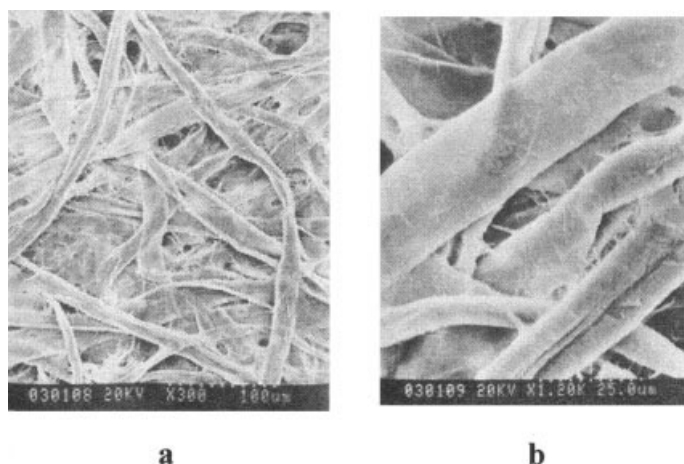


Figure 3 SEM picture of the paper fiber treated with Poly(MMA-co-BMA) microemulsion (No. 3) and baked at 160°C: (a) $\times 300$, (b) $\times 1200$.

shown in Table I, polymer T_g decreases as the content of BMA increases. The change of copolymers' T_g with their composition can be described by the Fox equation¹²:

$$1/T_g = W_A/T_{gA} + W_b/T_{gB},$$

where T_g represents the glass transition temperature of a copolymer. T_{g_i} and W_i are T_g and weight fraction of its component. Glass transition temperatures obtained from our experiment (solid points in Fig. 1) are close to the theoretical value calculated from the Fox equation (the curve in Fig. 1). This indicates the reaction is essentially a random copolymerization

T_g s of MMA and BMA homopolymer obtained from microemulsion polymerization are higher than those reported.¹³ This is probably due to the formation of crystallization-like order structure in particles of

TABLE III
Effect of OTAC Content on the Size of Polymer Microlatex*

Sample no.	4	7	8	9
Emulsifier content (g)	4.0	3.3	2.1	0.9
Polymer size (nm)	26.2	31.9	45.8	86.1

* The monomer composition is MMA : BMA = 10 : 20.

TABLE IV
Effect of Latex Particle Size on Water Resistance

	4	7	8	9
90°C	N	N	N	N
100°C	Y	PN	BPN	BPN
120°C	Y	Y	BPN	BPN
140°C	Y	Y	BPN	PN
160°C	Y	YN	Y	PN

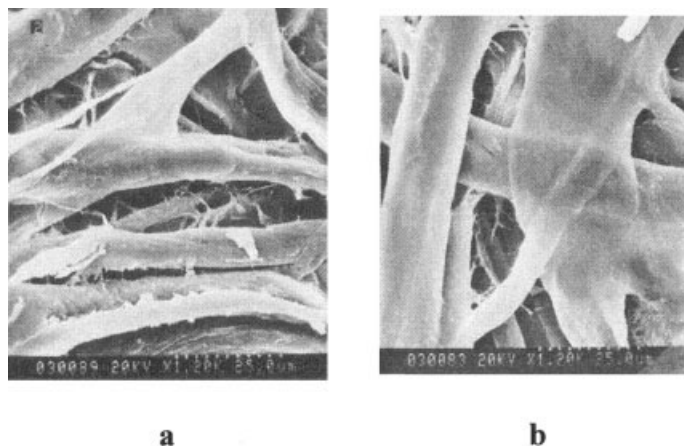


Figure 4 SEM picture of the paper fiber treated with Poly(MMA-co-BMA) microemulsion of different particle sizes and baked at 160°C: (a) emulsion No. 9, $\times 1200$, (b) emulsion No. 4, $\times 1200$.

nanometer-scale after the microemulsion polymerization.^{11,14,15}

Table II listed water resistance of paper treated with microemulsions of different polymer compositions at various baking temperatures. It can be seen that at a given baking temperature, paper treated with polymers of lower T_g results in better resistance to water penetration; while for a given polymer composition, the strength of water resistance of treated paper is highly dependent on baking temperature. Polymers of lower T_g are prone to thermo flow at lower baking temperatures, which has a positive effect on film formation on paper fiber. On the other hand, the formation of polymer film is also benefited from higher baking temperatures. Our study found that the best baking temperatures are in the range of 40 to 50°C higher than polymers' T_g.

SEM observation confirmed that the water resistance of paper treated with the microemulsion was related to the formation of polymer film on paper fiber surface. For example, dried at 160°C, some of the MMA homopolymer aggregate to form grains (Fig. 2). The polymer film was not evenly formed on the fiber surface. There are areas where paper fiber was hardly covered by the polymer and hence remained hydrophilic and susceptible to water penetration. On the other hand, at the same experimental condition, paper fiber treated with MMA-BMA copolymers was uni-

formly covered by polymer membrane (Fig. 3), which in turn rendered better water resistance.

Effect of microemulsion particle size on water resistance

The particle size of copolymer microlatex can be controlled by adjusting the amount of emulsifier added to the reaction. Table III enumerates the average diameters of copolymer microlatex synthesized with different amounts of emulsifiers at the given MMA to BMA ratio of 10 : 20. It is clear that as the amount of emulsifier decreases, the particle size increases and the system gradually transfers from microemulsion to conventional emulsion. Table IV presents the effect of microemulsion particle size on water resistance of the treated paper. It can be seen that the smaller the particle size is, the higher water resistance the treated paper has. The cause of this effect may be two-fold. First, the large amount of emulsifier used for producing smaller particle size also brings in a large amount of positive charges, which improve the polymer compatibility with paper fiber. Secondly, microlatexes of smaller size can film better on fiber surface. This is also in agreement with SEM observation. After baking the microlatex synthesized with less emulsifier and of particle size 86.1nm agglomerated and spalled on the

TABLE V
Particle Size and T_g of Microlatex Synthesized with Different Emulsifier Content*

Sample no.	Y1	Y2	Y3	Y4	Y5
Emulsifier content (g)	2.8	2.3	1.3	1.0	0.3
Microlatex size/nm	44.9	45.8	73.8	73.8	136.9
T _g /°C	64.6	62.1	67.0	64.6	51.4

* The monomer composition is MMA: BMA = 10:20

TABLE VI
Water Resistance of the Paper Fiber Treated with Emulsions Prepared Using SDS

	Y1	Y2	Y3	Y4	Y5
90°C	N	N	N	N	N
100°C	BPN	BPN	BPN	BPN	N
120°C	BPN	BPN	BPN	PN	N
140°C	BPN	BPN	PN	PN	PN
160°C	PN	PN	Y	Y	Y

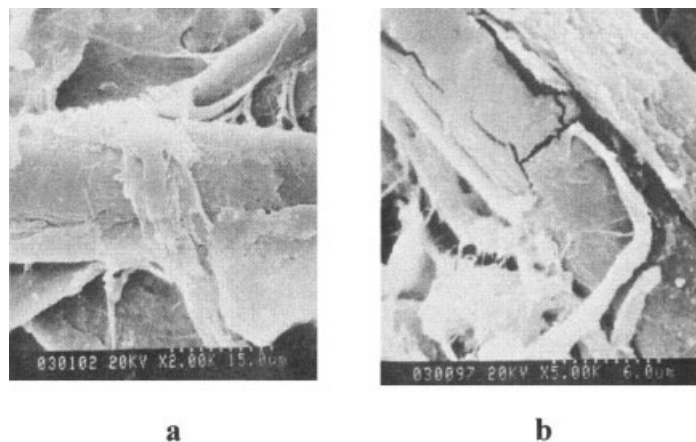


Figure 5 SEM picture of the paper fiber treated with Poly(MMA-co-BMA) microemulsion prepared using anionic emulsifier SDS (Y1) and baked at 160°C: (a) $\times 2000$, (b) $\times 5000$.

surface of paper fiber, whereas uniform film was formed on the fiber surface of paper treated with the microlatex of particle size 26nm (Fig. 4).

Effect of different types of emulsifier on water resistance of paper fiber

There are two types of ionic emulsifier: cationic emulsifier and anionic emulsifier. They can bring positive and negative charges, respectively, to the surface of microlatex. OTAC, used in most of our experiments, is a cationic emulsifier. To investigate the dependency of paper water resistance on charge type, SDS, a typical anionic emulsifier, was used to prepare a series of microemulsions. The polymerization process was the same as that for OTAC, except for the amount of emulsifier used. The amount of emulsifier, the particle size, and the water resistance of papers treated with microemulsions prepared with anionic emulsifiers were compiled in Table V and Table VI. The results show that the particle size of microlatex decreases with the increase of the amount of emulsifier added. When the amount of anionic emulsifier exceeded 2.3g, microemulsion was produced, resulting in small particle size ($<50\text{nm}$). Their glass transition temperatures were similar to that of latex emulsified by OTAC. Nevertheless, as shown in Table VI, papers treated with microemulsion prepared with anionic emulsifier did not have strong water resistance in comparison to papers treated with microemulsion made with cationic emulsifier. A SEM picture (Fig. 5) showed that parts of paper fiber were not covered by polymer film and there were also cracks within the film. This is because negatively charged papers have a repulsive effect towards microlatex particles of the same electric charge, resulting in poor film formation.

CONCLUSION

Acrylic microemulsion synthesized using cationic emulsifier, when used as a paper surface treat-

ment agent, provides paper with strong water resistance. The polymer's glass transition temperature highly affects both the film formation process on the fiber surface and the fiber's water resistance. To achieve better water resistance the coated paper should be dried at a temperature of 40 ~ 50°C higher than the Tg of the polymer. In addition, the water resistance of the treated paper is closely related to the particle size of microemulsion. Small particle size is beneficial to film formation and therefore enhances water resistance. As to microemulsions prepared with anionic emulsifier, the water resistance of coated paper is usually unsatisfactory due to the poor compatibility between paper fiber and the latex particles.

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