

## Development of VOC-free, high- $T_g$ latex binders by a high-temperature water-extended latex technology

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**Abstract** The potentiometric titration of carboxylated methyl methacrylate latexes prepared with varying amounts of methacrylic acid showed that only very small amounts of their total acids copolymerized were neutralized at room temperature until the acid level was well above 10%. However, it was found that all the acids copolymerized were completely titrated either in a 50/50 water/ethanol mixture at room temperature or in water at high temperatures near their backbone polymer  $T_g$ s, regardless of their acid contents, as predicted from the existing theories on the alkali-swelling of carboxylated latexes. It was also found that these high-temperature alkali-swollen latex particles remained in the swollen state even after they were cooled down to room temperature and became film-forming at much lower temperatures. This discovery led to a new technology coined as a high-temperature water-extended latex technology. This new technology enabled us to develop VOC-free water-extended latexes of high- $T_g$  polymers that would exhibit good film formation at ambient temperature and turn into hard and non-blocking latex films and latex-bound pigmented coatings upon drying. Particularly, when fugitive bases were used for neutralization at high temperatures, the resulting water-extended latexes became hard, non-blocking, and water-resistant binders upon drying.

**Keywords** High-temperature alkali-swelling, Water-extended latexes, Water plasticization, Latex film formation, VOC-free water-plasticized latexes

### Introduction

Since the alkali-swelling of carboxylated latex particles<sup>1-4</sup> has been extensively studied by both industrial and academic scientists in the past, it has been well understood that their alkali-swelling increases with increasing acid content and hydrophilicity of backbone polymers and decreases with increasing  $T_g$  of backbone polymers and crosslink density of the whole polymers. According to these understandings, lightly carboxylated latex particles of high- $T_g$  polymers would not swell upon neutralization at room temperature, but would swell at high temperatures near their polymer  $T_g$ s. Indeed, they were alkali-swellaible at high temperatures; however, it was surprising to find out that these high-temperature alkali-swollen latex particles remained in their swollen state even after they were cooled down to room temperature. Also, it was found that these high-temperature water-extended latexes showed much lower minimum film formation temperatures (MFFT) than those of their original lightly carboxylated, high- $T_g$  latexes. This discovery was coined as a high-temperature water-extended latex technology.<sup>5</sup>

Latexes for clear film and coating applications are required to be film-forming at ambient temperature, but their dry films and coatings must be hard and non-blocking. Therefore, high- $T_g$  latexes are currently formulated with co-solvents or coalescing aids to achieve good film formation at ambient temperature and revert to hard polymer films and coatings after drying. Although this approach satisfies these mutually opposing requirements, its consequence is to release volatile organic components (VOCs) into the atmosphere. For this reason, there is a strong need for developing VOC-free latexes of high- $T_g$  polymers, which can satisfy these opposing requirements. It was thought that the aforementioned high-temperature water-extended latex technology might be able to fill

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this need. Water had been already recognized as a non-VOC plasticizer for hydrophilic (i.e., polar) polymer latexes.<sup>6–11</sup> For example, polyvinyl acetate latexes are well known to form continuous films at room temperature, although their dry latex polymer  $T_g$ s are well above room temperature.<sup>8–10</sup> Their unique film-forming behaviors are attributed to water plasticization, sometimes referred to as hydroplasticization. This study was aimed at developing VOC-free latexes of high- $T_g$  polymers that would exhibit good film formation at ambient temperature and turn into hard, non-blocking, and water-resistant latex films and latex-bound pigmented coatings upon drying, along with the release of fugitive bases. This article describes the discovery of a high-temperature water-extended latex technology and the development of VOC-free, high- $T_g$  latex binders by this technology.

## Experimental

Two series of carboxylated methyl methacrylate copolymer latexes were prepared by a seeded semicontinuous emulsion polymerization process. All latex samples under study were made by using a recipe shown in Table 1.

The first series of lightly crosslinked, carboxylated methyl methacrylate (MMA) latexes was prepared with varying amounts of methacrylic acid (MAA) from zero to 30 parts by weight and 0.5–1 part allylmethacrylate (AMA) as a crosslinking monomer by a seeded

semicontinuous emulsion polymerization process in a jacketed 4-L stainless steel reactor. Crosslinking was intended to keep the distributions of copolymerized carboxylic groups uniform both before and after their neutralization at high temperatures. Following the recipe shown in Table 1, a polystyrene seed latex of 25 nm in diameter at 28% polymer solids was used at 0.463 part seed polymer per 100 parts monomers to make the final latex particles of 150 nm in diameter. The polymerization temperature was 90°C. The monomer feed was added over 4 h, the aqueous feed containing 0.75 part sodium persulfate, 1.0 part Dowfax 2A1 (sodium alkyl diphenyl oxide disulfonate from The Dow Chemical Company), and 0.15 part sodium hydroxide per 100 parts monomers was added over 4.5 h, and the overall polymerization time was 5 h. The total monomers and solids, including the seed, were 40% by weight. The reactor latex samples were steam-stripped, and then each latex sample was formulated with a small amount of biocides at its reactor pH 2.5–3.5. Their particle sizes were monodisperse at about 150 nm. These latexes were evaluated to study the effect of latex medium (water vs a 50/50 water and ethanol mixture) on their potentiometric acid titrations at room temperature, the effect of temperature on the alkali-swelling of lightly carboxylated, high- $T_g$  polymer latexes, the swelling ratios of high-temperature water-extended latex particles at room temperature, and the deformability of high-temperature water-extended latexes. All these evaluations were carried out as a function of %MAA, alkali-swelling temperature at a constant % neutralization, and % neutralization at a constant temperature, respectively.

The second series of carboxylated methyl methacrylate (MMA)-ethyl acrylate (EA) copolymer latexes was prepared with varying ratios of methyl methacrylate/ethyl acrylate and 5 parts methacrylic acid per 100 parts monomers by a seeded semicontinuous emulsion polymerization process in a jacketed 8-L glass-lined stainless steel reactor. These latexes were prepared and post-formulated exactly in the same way as described above for the first series of lightly crosslinked, carboxylated MMA latexes, except that they were made at 50% solids. Their particle sizes were also 150 nm. These latex samples were tested for the feasibility of developing VOC-free, high-temperature water-extended latexes of high- $T_g$  polymers that would have good film formation at ambient temperature and turn into hard, non-blocking, and water-resistant latex films and latex-bound pigmented coatings upon drying, along with the release of fugitive bases such as ammonia.

**Table 1: A recipe used for the preparation of all the latexes under study**

<i>Seeded semicontinuous emulsion polymerization recipe</i>
<i>Reactor charges</i>
$W_w$ parts D.I. water for desired latex %solids
$W_s$ part seed latex polymer of $D_s$ for desired final particle size, $D_f$
0.02 part chelating agent (e.g., Versnex 80)
<i>Monomer feed (4 h)</i>
100 Parts monomers
<i>Aqueous initiator/surfactant feed (4.5 h)</i>
30 parts D.I. water
0.75 part sodium persulfate
1.0 part surfactant (e.g., Dowfax 2A1)
0.15 Part NaOH
<i>Polymerization conditions</i>
Polymerization temperature: 90°C
Total polymerization time: 5 h

$W_s = 100 \times (D_s/D_f)^3$  for  $D_s \ll D_f$ , where subscripts, s and f, stand for seed and final latex particles, respectively

Versnex 80 is pentasodium diethylene-triaminepentaacetate from The Dow Chemical Company

Dowfax 2A1 is sodium alkyl diphenyl oxide disulfonate from The Dow Chemical Company

## Results and discussion

A series of lightly crosslinked, carboxylated methyl methacrylate (MMA/MAA/AMA) latexes made with varying amounts of MAA from zero to 30 parts at the

interval of 5 parts and 0.5 part AMA was potentiometrically titrated with a NaOH solution for their copolymerized acids at room temperature in both water and a 50/50 water and ethanol mixture. Their potentiometric titration results are shown in Fig. 1. As can be seen from Fig. 1, only very small amounts of the acids copolymerized were titratable in water on the latex samples containing 5 and 10 parts MAA, whereas all their copolymerized acids were neutralized in the mixture of water and ethanol (50/50), regardless of their acid contents. In water, only surface acids of the latex particles made with less than 15% MAA were shown to be titratable, but the 50/50 mixture of water and ethanol softened the sample latex particles so that all the acids incorporated into them became accessible to titration. These results are consistent with our current understanding on the alkali-swelling of carboxylated latexes.

Figure 2 shows the swelling ratios of lightly cross-linked, carboxylated methyl methacrylate [MMA/MAA/AMA (91.5/7.5/1)] latex particles neutralized with 110% NaOH as a function of swelling temperatures and determined at room temperature by a viscosity method described below. The ratios of the swollen particle volumes to the original particle volumes were calculated from the viscosity data measured by a capillary viscometer. The Einstein equation for the relative viscosity of dispersions,<sup>12,13</sup>  $\eta_r = 1 + 2.5\phi$ , was used to semiquantitatively estimate the volume fraction ratios of the swollen to the original disperse phase within its valid disperse volume fractions up to about 0.04. This method could have been made more accurate by measuring the viscosity of the

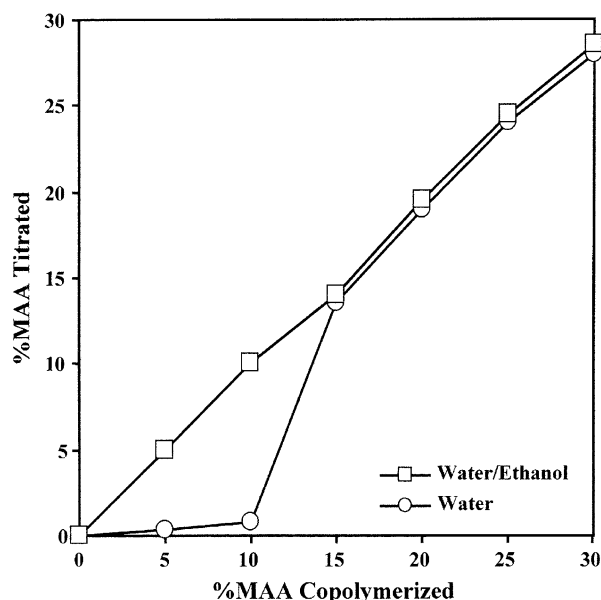


Fig. 1: The potentiometric acid titration of MMA/MAA/AMA(0.5) copolymer latexes made with varying amounts of MAA at the interval of 5 parts in water (open circle) and a 50/50 water/ethanol mixture (open square) at room temperature

continuous phase and obtaining more accurate relative viscosities, but since dilution of the samples was high enough, it was thought that assuming the medium viscosity to be that of water would be adequate for our studies. It can be seen from Fig. 2 that the swelling ratio increased with increasing neutralization temperature. Lower swelling at lower neutralization temperatures was due to either the stiffness of the backbone chains or a partial neutralization or the combination of both. Although the swelling ratios at the actual neutralization temperatures were not determined, they were expected to be much greater than those measured at room temperature. The dotted curve in Fig. 2 represents the swell ratios estimated at the neutralization temperatures. During this experiment, it was discovered that the deformation of the swollen particles increased with increasing swelling ratio upon drying. This discovery has become the basis of a new high-temperature water-extended latex technology. It was also found that the high-temperature alkali-swollen latexes of high- $T_g$  polymers cooled down to room temperature would expand with increasing temperature. Indeed, they turned out to be environmentally responsive particles, which would reversibly swell and de-swell with increasing and decreasing temperatures, respectively.

Figure 3 shows the swelling ratios of lightly cross-linked, carboxylated methyl methacrylate [MMA/

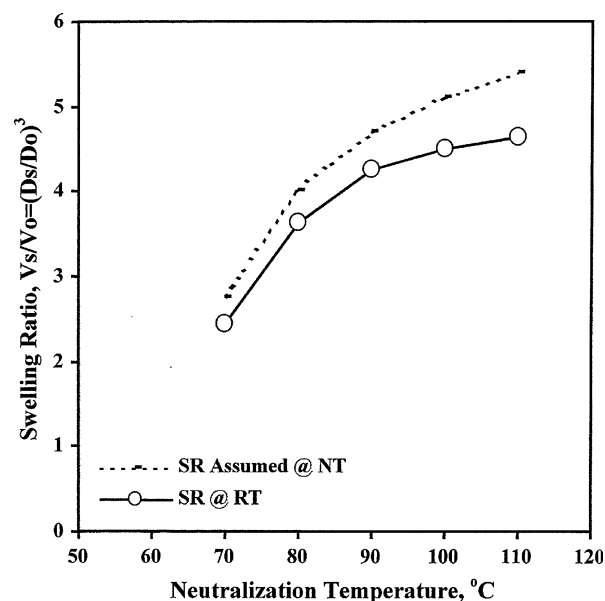


Fig. 2: The swelling ratios of MMA/MAA/AMA (91.5/7.5/1) latex particles neutralized with 110% NaOH as a function of swelling temperatures and determined by a viscosity method based on the Einstein equation<sup>12,13</sup> at room temperature, along with the estimated swelling ratios at the neutralization temperatures: The solid curve stands for the swelling ratios cooled down to and measured at room temperature and the dotted curve for the estimated swelling ratios at the neutralization temperatures (NTs)

MAA/AMA (92/7.5/0.5)] latex particles neutralized at 105°C as a function of % NaOH neutralization and determined at room temperature by both a viscosity method at the respective neutralization pH and hydrodynamic chromatography (HDC)<sup>14</sup> at pH 3. As can be seen from Fig. 3, the swelling ratio increased with increasing % neutralization, as expected, however, it will be interesting to note that their swelling ratios measured by HDC at pH 3 were shown to be dependent on the extent of their high-temperature swelling. Acidification caused more swollen particles to de-swell more. The behavior that the more highly water-extended particles are the more susceptible to environmental changes such as pH, temperature, etc. is quite unique to the high-temperature water-extended latexes whose swelling depends on both the degree of neutralization and the neutralization temperature, unlike the behavior of low  $T_g$  alkali-swella-ble latexes.

Figure 4 shows the MFFT's of MMA/EA/MAA latexes made with varying MMA/EA ratios from 55/40 to 85/10 at 5 parts MAA neutralized as a function of % neutralization with  $\text{NH}_4\text{OH}$  at 80°C for 1 h. Their copolymer  $T_g$ s were measured by a differential scanning calorimeter (DSC) and shown in Fig. 4, along with their compositions. Their wet latex  $T_g$ s were measured by a MicroCal MC-2 scanning calorimeter<sup>11</sup> and found to decrease with increasing degree of neutralization at high temperatures, strongly indicating that their MFFT's would be lowered. It can

be seen from Fig. 4 that the MFFT's of acrylic latexes whose  $T_g$ s ranged from 50 to 100°C and higher were substantially lowered, when they were neutralized with  $\text{NH}_4\text{OH}$  at 80°C for an hour and cooled down to room temperature. Remarkably, those high-temperature water-extended acrylic latexes whose polymer  $T_g$ s were below 70°C became film forming well below room temperature. Furthermore, ammonia was released upon drying during film formation and the water-extended latexes were then reverted to their original high- $T_g$  polymers in the acid form, thus resulting in water resistant, hard, and non-blocking latex films and latex-bound pigmented coatings. Although their antiblocking and water-resistant properties are not reported in this article, it is well understood that hard, high- $T_g$  polymer films are non-blocking as well as that the water resistance of latex films made from carboxylated latexes is better, when they are neutralized with fugitive bases rather than with permanent bases. Therefore, it is quite clear from Fig. 4 that the newly discovered high-temperature water-extended latex technology would enable us to develop VOC-free, high- $T_g$  latex binders. However, it is also clear that their antiblocking and water resistance should be optimized to meet the requirements for their intended end-use applications. Additionally, this technology can be combined with various ways to interfacially crosslink carboxylated latexes.<sup>15</sup>

It would be interesting to speculate about some potential applications of this high-temperature water-extended latex technology beyond the development of VOC-free latex binders for a variety of coating applications. This technology should enable us to

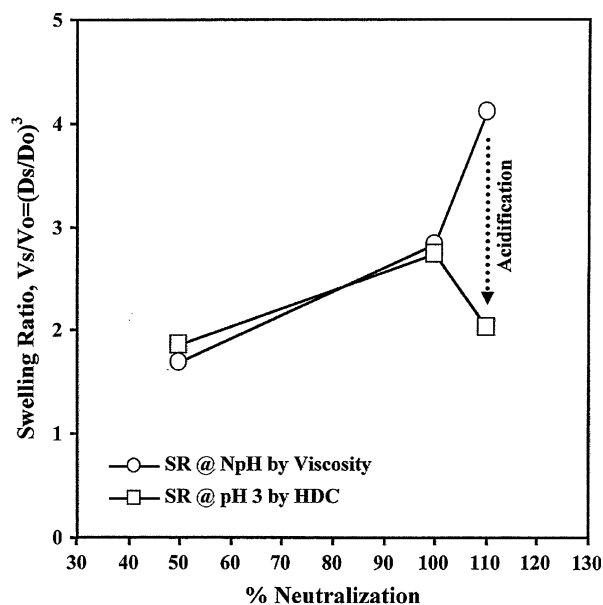


Fig. 3: The swelling ratios of MMA/MAA/AMA (92/7.5/0.5) latex particles neutralized at 105°C as a function of % NaOH neutralization and determined at room temperature by a viscosity method based on the Einstein equation<sup>12,13</sup> at the neutralization pH and hydrodynamic chromatography (HDC)<sup>14</sup> at pH 3, respectively: The open circles stand for the swelling ratios measured at the respective neutralization pHs by a viscosity method and the open squares for the swelling ratios measured at pH 3 by HDC

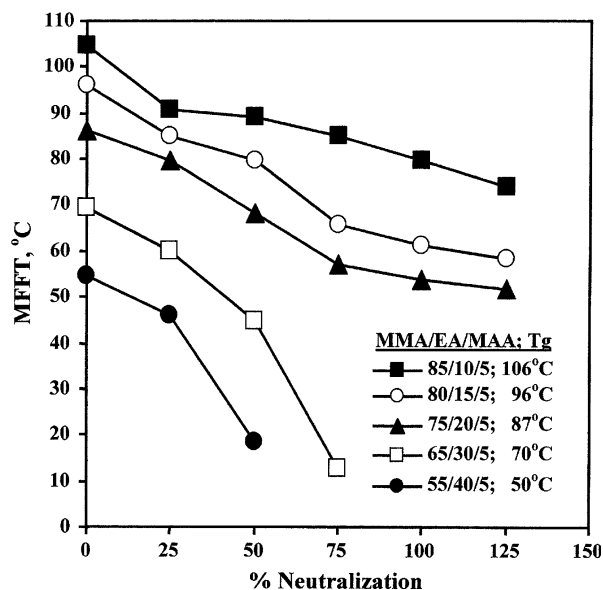


Fig. 4: The minimum film formation temperatures (MFFT's) of MMA/EA/MAA latexes made with varying MMA/EA ratios and 5 parts MAA neutralized as a function of % neutralization with  $\text{NH}_4\text{OH}$  at 80°C for 1 h and cooled down to room temperature

develop stiff paper coating latexes which would significantly improve the stiffness of coated papers, so papermakers would be able to reduce their base paper weights. Heat gelation of various dispersions can be achieved by adding small amounts of high-temperature water-extendable base latexes or their partially extended latexes into them, along with some additional bases. Furthermore, structured composite latexes containing both high-temperature water-extendable and non-extendable polymers can be prepared to form many different particle morphologies,<sup>16</sup> such as core-shell, inverted core-shell, microdomain, and interpenetrating polymer network structures, which would exhibit many unique properties upon neutralization at high temperatures.

## Conclusion

It was discovered that lightly carboxylated, high- $T_g$  polymer latexes could be made into water-extended latexes by neutralizing them at high temperatures near their backbone polymer  $T_g$ s. These water-extended latexes exhibited good film formation at ambient temperature and turned into water-resistant, hard, and non-blocking polymer films and latex-bound pigmented coatings upon drying, along with the release of fugitive bases. Thus, it is quite clear that these newly discovered high-temperature water-extended latexes would enable us to develop VOC-free high- $T_g$  latex binders for a variety of coating applications. It was also found that high-temperature water-extended latex particles of high- $T_g$  polymers cooled down to room temperature exhibited reversible behaviors of swelling and de-swelling in response to temperature and pH. These findings led to a high-temperature water-extended latex technology, which could offer us a wide range of potential applications.

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