Hydroplasticization Effect in Structured Latex Particles Film Formation

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Summary: Series of emulsion copolymers with structured particles were synthesized comprising copolymerized acrylic or methacrylic acid in the outer layer. All samples were based on particles, containing identical cores slightly crosslinked by allyl methacrylate and variable shells, weight ratio core/shell being constant 1/1. Each sample contained 10 wt% HEMA in the shell to achieve the film crosslinkability. In both series samples with different hardness and polarity (varible styrene/butyl acrylate ratio) of the shell layer were prepared. It was shown that the extent of particle swelling and hydroplasticization depends not only on the content of dissociated carboxylic groups, but also on the composition and crosslinking of the rest of polymer chain i.e. on its polarity and rigidity and on the origin of carboxylic groups. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar.

Introduction

Polymer colloids in aqueous media form a very important group of polymers, which find a whole series of technical applications. In „Low VOC“ or „Zero VOC“ water-borne coating compositions, the aqueous copolymer dispersions operate as a binder component. A typical group of latex binders comprises products with a core-shell structure, which have different compositions of their cores and shells. The problems connected with utilization the aqueous polymer dispersions in coating compositions comprises the questions connected with film-forming properties of originally discrete polymer particles and with their rheological properties as well. Both these aspects are to be studied paralelly, especially in such systems, which have a hydrophilic particle surface layer and belong to the group of the so-called „alkali-swellable“ polymer particles. Thanks to the hydrophilic nature of the surface layer and the dissociation of surface carboxylic groups, they can be, to a certain extent, plasticized with the surrounding water phase and can form films of sufficient quality even without any

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addition of organic coalescence aids. The rheological behavior, due to a change in the hydrodynamic particle volumes after the alkalization, is usually of strongly pseudoplastic character. The important aspect connected with the utilization of structured polymer particles in the coating system is the ability of discrete polymer particles to bind the pigments. The film formation and, consequently, the formulation principles have to be investigated together with alkali-swelling behavior of particles and together with the effect of particle swelling onto latex rheology. This study was focused on the effect of hydrophobic styrene concentration in the shell layer copolymer onto particle swelling and hydroplasticization.

Experimental

Materials: Monomers: Styrene (S) - technical grade, Kaučuk Kralupy, butyl acrylate (BA) - technical grade, acrylic acid (AA) - technical grade, Eastman, Sokolov, 2 - hydroxyethyl methacrylate (HEMA), N,N'-methylene*bis*acrylamide (MBA), allyl methacrylate (AMA), methacrylic acid (MAA) - technical grade, Roehm, Darmstadt, Disponil AES 60 - sodium salt of alkyl aryl polyoxyethylene sulfate, Henkel, ammonium persulfate - Air Products. Synthesized latexes were neutralized using 2-amino 2-methyl propanol (AMP-95), ANGUS.

Polymerization recipe: Latexes were produced in a 2500 ml glass reactor by semi-continuous non-seeded emulsion polymerization under nitrogen atmosphere at temperature 80 °C. The reactor charge was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion was fed into the stirred reactor at feeding rate about 10 ml/min. in three steps (1. seed preparation, 2. core preparation, 3. shell preparation). After that, during 2 hours of hold period the polymerization was completed.Two series of emulsion copolymers with structured particles were synthesized, the former comprising methacrylic acid, the latter acrylic acid in the outer layer. All samples were based on particles, containing identical cores slightly crosslinked by allyl methacrylate and variable shells, weight ratio core/shell being constant 1/1. Each sample contained 10 wt% HEMA in the shell to achieve film crosslinkability. In both series samples with different hardness and polarity (varible styrene/butyl acrylate ratio) of the shell layer were prepared.

Determination of the Minimum Film Forming Temperature (MFT): The minimum film forming temperature was measured using the MFT Tester (Synpo a.s. Pardubice). Minimum film temperature is defined to be the minimum temperature at which a film cast from dispersion becomes continuous and clear. The MFT Tester consists of a chromium coated copper slab in which a fixed temperature gradient is maintained by heating at one end (about 40 °C) and cooling at the other (about 0 °C). The polymeric emulsion was cast in a strip along this slab by a coating ruler with height of about 150 μm. The point at which the film becomes discontinuous when dry was observed, and this temperature was recorded as MFT. The slab is located in a box covered with a glass cover, in order to permit visual observation of the film during drying. Tests were carried out after a thermal equilibrium has been reached. Drying material was silica activated for 1 hour / 130 °C before the measurement.

Other analytical and testing methods used for characterization of latices and polymeric films: particle size - Coulter N4 Plus (Coulter Corp.), pH was measured using WTW 320 Ph-Meter, WTW G.m.b.H. Weilheim, Germany.

Results and Discussion

Swelling of the particle surface under alkaline conditions is important in the process of film formation form polymer dispersions. The alkali swollen latex particles are plasticized by the water phase this increases their viscosity and also enhances the ability of particles to undergo the process of coalescence. The extent of the particle hydroplastificization depends on the concentration of carboxylic groups an it is only effective at alkaline conditions. The effect of carboxylic groups content in styrene/butyl acrylate copolymer latex on changes in MFT at acidic and alkaline conditions is shown in Fig. 1.[1] The relationships document the increase in MFT with increasing content of acrylic acid due to increased Tg of copolymer. The particles need higher temperature to undergo the deformation necessary for a film formation *via* coalescence of particles. The sharp drop in MFT of samples with higher content of acrylic acid indicates their effective hydroplasticization under alkaline conditions. It is evident from the Fig. 1 that the minimum film formig temperature of the latex particles increased with incresing acrylic acid content as a consequence of increased T_g of the copolymer even at alkaline conditions. The MFT values of neutralized latexes, however, were lower than those of acidic ones. We investigated particles with shell layers based on butyl acrylate and styrene in different ratios, different concentrations of acrylic or methacrylic acid in the shell copolymer and different extent of the shell crosslinking by methylene-*bis*-acrylamide.[2, 3] All structured polymer particles contained a soft core based on butyl acrylate/styrene (wt. ratio

BA/S = 1.44) slightly crosslinked by allyl methacrylate and with a hard shell comprising 10 wt. % HEMA. The extent of particles hydroplasticization at alkaline conditions increased with

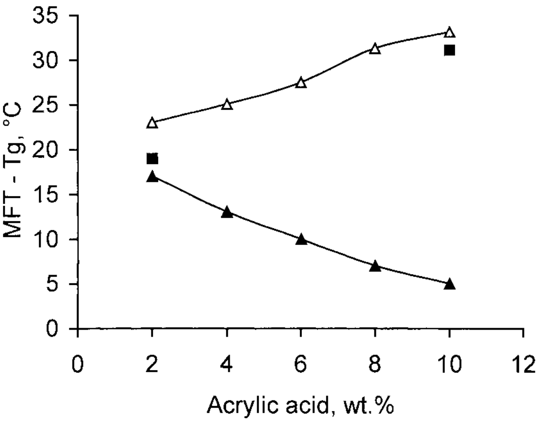

Figure 1. Effect of acrylic acid content in butyl acrylate/styrene/acrylic acid copolymer on T_g (■) and MFT in dependence on pH value. pH = 3 (▲), pH = 7,5 (△), wt. ratio butyl acrylate/styrene = 0.85 remained constant in all copolymers.[1]

lower concentration of styrene in the shell. The results were similar for samples with acrylic acid as well as methacrylic acid in the shell layer copolymer.

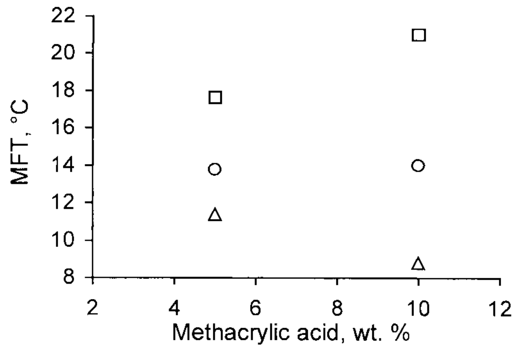

Figure 2. Effect of styrene and acrylic acid content in the BA/S/HEMA/AA/MBA shell layer copolymer on the minimum film forming temperature of neutralized structured core shell latexes. Shell composition BA/S/HEMA/MAA/MBA : HEMA = 10 wt. % , MBA = 1 wt. %, Styrene (△) = 35 wt. % , (○) = 40 wt. %, (□) = 45 wt. %.

As mentioned above, the extent of hydroplasticization depends not only on the content of dissocited carboxylic groups, but also on the composition of polymer chain and its polarity and rigidity. Thus, the hydroplasticization effect was not as high if the composition of butyl acrylate/styrene copolymer chain changed to higher content of styrene. This effect is illustrated in Figures 2 and 3. Here, the latexes comprising higher concentration of styrene in the shell layer of structured particles do not exhibit any drop in MFT as in the case of particles

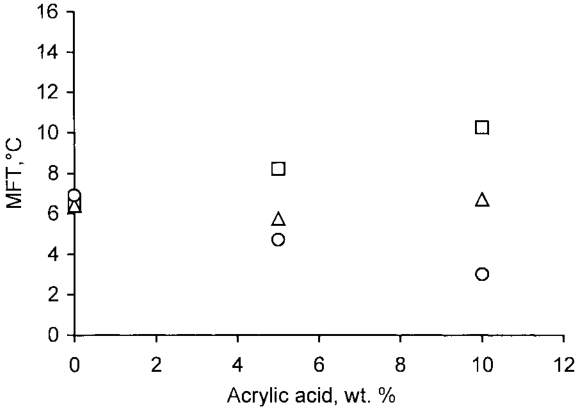

Figure 3. Effect of styrene and acrylic acid content in the BA/S/HEMA/AA/MBA shell layer copolymer on the minimum film forming temperature of neutralized structured core shell latexes. Shell composition BA/S/HEMA/AA/ : HEMA = 10 wt. % , Styrene (□) = 40 wt. %, (△) = 35 wt. % , (○) = 30 wt. %.

It is also evident from Fig. 4 that crosslinking of the shell layer with methylene-*bis*-acrylamide was accompanied by the increase of MFT of neutralized samples to values close to those of acidic non-croslinked particles as the crosslinking impedes swelling and, consequently, the hydroplasticization of the particle surface. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar and softer. Comparison of minimum film forming temperatures of structured polymer particles with variable content of styrene in the shells that were crosslinked with 1 % wt. methylene-*bis*-acrylamide was shown in Fig. 4.

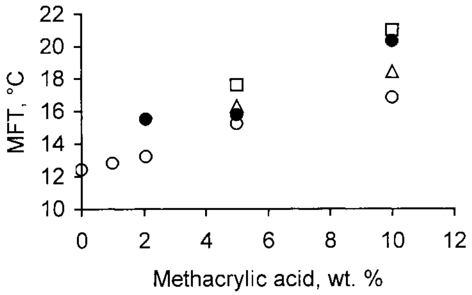

Figure 4: Effect of methacrylic acid and methylene-bis-acrylamide crosslinker content in the shell layer of structured core-shell particles on the minimum film forming temperature of neuralized (open points) and acidic (full points) latexes. Shell composition BA/S/HEMA/MAA/MBA : HEMA = 10 wt. % , S = 45 wt. %, MBA (●○) = 0 wt%, (△) = 0.5 wt. %, (□) = 1 wt. %

Effect of surface layer hydroplasticization on the latex viscosity.

Surface carboxylic groups usually cause an increase in viscosity after neutralization of particles due to particle swelling and also due to the elecroviscous effect.[3] Capillary viscometry indicated that the dependences of viscosity of different alkalinized latexes on their particle concentration considerably differ.[4] It could be assumed that during alkalinization of originally acid latexes, due to electrostatic interactions of ionized carboxylic groups, the effective hydrodynamic volume of latex particles (intrinsic viscosity $[\eta]$) increased, which manifested in an increase of the latex viscosity. A significant difference was found in the effect of copolymerized carboxylic groups from acrylic acid and of those from methacrylic acid as a result of different monomeric acids polarity and, consequently, different concentration of surface and burried carboxylic groups. The latex viscosity and the intrinsic viscosity of diluted latexes indicates the extent of particle swelling, i.e. the extent of particle hydroplasticization. The difference between the effects of carboxylic groups from acrylic acid and those from methacrylic acid copolymerized in the shell layer of structured particles is shown in Figures 5 and 6.

The hydrodynamic volume of latex particles was characterized by their intrinsic viscosities $[\eta]$ obtained by linear extrapolation of $\Phi/\ln \eta_r$ to zero volume fraction Φ of the latexes according to the Mooney equation[5] $\eta_r = \exp \{[\eta]\Phi/(1-\Phi/\Phi_c)$, where Φ_c is the volume fraction of particles at which viscosity reaches an infinite value (the volume fraction at maximum packing). The relative viscosity $\eta_r = \eta/\eta_s$, where η is the viscosity of latexes and η_s is that of the dispersion medium, was measured using an Ostwald capillary viscometer.

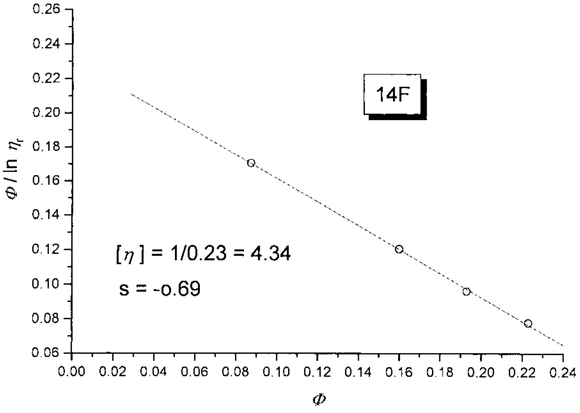

Figure 5 : Intrinsic viscosity of structured latex particles at pH = 8. Composition core//shell(wt. %): S/BA/MAA/AMA//S/BA/HEMA/MAA = 40/57.5/1.5/1//40/40/10/10. Mean particle diameter of acid particles 0.1 μm

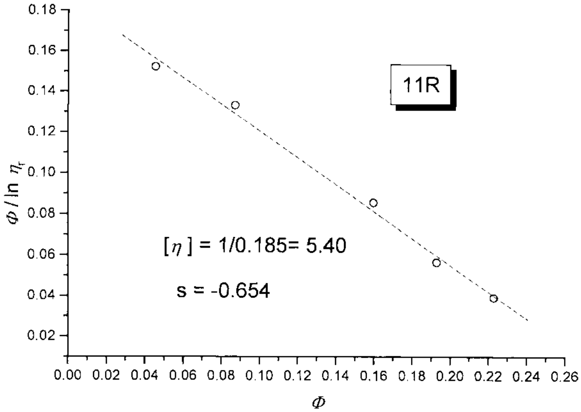

Figure 6 : Intrinsic viscosity of structured latex particles at pH = 8. Composition core//shell(wt. %): S/BA/AA/AMA//S/BA/HEMA/AA = 40/57.5/1.5/1//40/40/10/10. Mean particle diameter of acid particles 0.12 μm.

Similarly as in the case of minimum film forming temperature, the effect of styrene content in the shell layer on the particle surface hydroplasticization is also evident from viscosity measurements at higher solids content. Flow behavior of AMP-95 neutralized 40%solids latexes is shown in Figures 7 and 8. An increase in low-shear viscosity was found for latexes

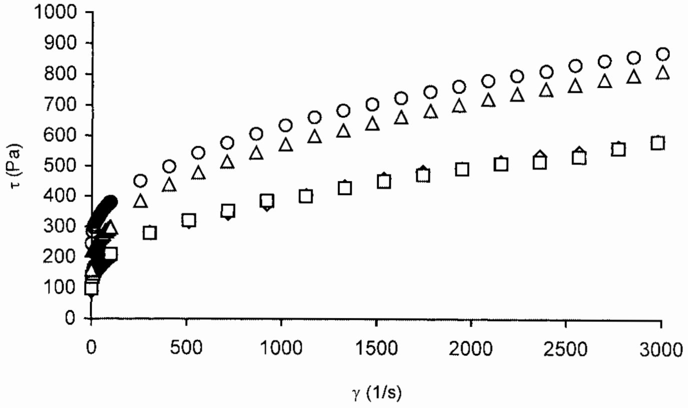

Figure 7: Effect of styrene content in the BA/S/HEMA/AA/MBA shell layer copolymer on the shear rate (γ) vs. shear stress (τ) relationship for neutralized latexes at 40 % solids. Shell composition BA/S/HEMA/AA/ : HEMA = 10 wt. %, AA = 10 wt. % and S = 45 wt. % (◇), S = 40 wt. % (□), S = 35 wt. % (△) and S = 30 wt. % (○).

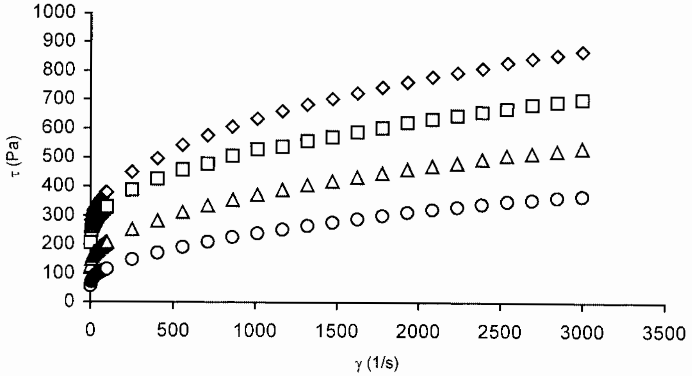

Figure 8: : Effect of MBA content in the BA/S/HEMA/AA/MBA shell layer copolymer on the shear rate (γ) vs. shear stress (τ) relationship for neutralized latexes at 40 % solids. Shell composition BA/S/HEMA/AA/ : HEMA = 10 wt. %, AA = 10 wt. %, S = 30 wt. %, MBA = 0 wt. % (◇), MBA = 0.5 wt. %. (□), MBA = 1.0 wt. % (△) and MBA = 1.5 wt. % (○).

containig 35 and 30 wt. % styrene in the shell layer. In the cases of styrene concentration 40 and 45 wt. % the the low-shear viscosity did not differe and were lower due to not so extensive swelling of polymer particles. The effect of swollen particles on the latex viscisity depends on the solids content, i.e. on the mutual particle distance. The higher solids, the higher effect of particle swelling on the rheology. Similarly, hindering of particle swelling by the particle surface crossllinking by MBA resulted in decrease in the low-shear latex viscosity at 40 wt. % solids as it shown in Fig. 8. [6]

Conclusion

The extent of hydroplasticization depends not only on the content of dissociated carboxylic groups, but also on the composition of polymer chain i.e. on its polarity and rigidity and on the origin of carboxylic groups. The effect of dissociated carboxylic groups on lowering the minimum film forming temperature was much more pronounced if the polymer chains were more polar. As the hydroplasticization is based on the particle surface swelling by water it also is accompanied by an increased latex viscosity. In latexes utilized as binders in water borne paints the functional groups, as they are e.g. carboxyl and hydroxyl ones, serve mainly as *loci* for crosslinking. Besides this, polar functional groups affect the most important application properties of water borne paint vehicles i.e. the film formation of the binder and the flow behavior of the paint.

Acknowledgement

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References

[1] D. Kubík, Diploma Thesis, University of Pardubice, 1995.
[2] M. Faltejsková, Diploma Thesis, University of Pardubice, 2001.
[3] Quadrat O.,Šňupárek J.: Progr. Org. Coat. **1990**, *18*, 207 .
[4] Šňupárek J., Quadrat O., Horský J., Kaška M.: The Effect of Hydrophilic Non-ionogenic Comonomers on Flow Properties of Carboxylated Latexs *in* Polymer Colloids: Science and Technology of Latex Systems (E. S. Daniels, E. D. Sudol and M. S. El-Aasser, Eds.), ACS Symposium Series 801, American Chemical Society / Oxford University Press, Washington, D.C., Chapter 6, 71 – 79, 2001.
[5] M. J. Mooney, *J. Colloid Sci.* **1951**, *6*, 162.
[6] P. Ritz, Diploma Thesis, University of Pardubice, 2002.