

Preparation of Core-Shell Latexes for Paper Coatings

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ABSTRACT: Novel core-shell latices with a partially crosslinked hydrophilic polymer core and a hard hydrophobic shell of polystyrene were prepared to improve optical properties of coated paper such as gloss and brightness. These core-shell latices were prepared by sequential addition of a monomer mixture of styrene, *n*-butylacrylate and methacrylic acid. Different crosslinkers were used to form the polymer core and in the second stage styrene to form the hard shell component. In addition, attempts were made to further improve optical properties by introducing a new polymerizable optical brightener, i.e., 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethenyl)benzene during polymerization either into the core or into the shell. The prepared core-shell latex particles were used as specialty plastic pigments for paper coating together with kaolin as the primary pig-

ment. The runability of paper coating formulation by either using a laboratory scale Helicoater or pilot scale JET-coating machine was very good. The produced coated papers were printed on both sides employing a heat set web offset (HSWO) printer to study the quality of image reproduction in terms of print gloss, print mottle, print through, etc. The core-shell latices improved the overall print quality. Furthermore, the results demonstrated that by optimizing polymer composition one can significantly enhance the optical properties and surface smoothness of coated paper. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1265–1270, 2009

Key words: emulsion polymerization; core-shell polymers; crosslinking; synthesis; dyes/pigment

INTRODUCTION

Core-shell latices, composed of a core covered by a shell, can be prepared by a two-stage emulsion polymerization or seeded emulsion polymerization. Colloidal stability can be difficult to obtain in a core-shell polymerization because the composition of the surface and the bulk change dramatically during the polymerization process. The advantage of core-shell latices is their ability to have a composition of different monomers in core and shell, and thereby giving the particle tailor-made properties for each application. Via core-shell polymerization it is also possible to get otherwise incompatible monomers into one particle or to add functionality either into the core or into the shell.^{1–8} There are many different morphologies of the core-shell structure: ideal core-shell, interface with a wavy structure, interface with a gradient of both core and shell, interface with microdomains and those with microdomains in the interface and an island structure as shell. There is a variety of analytical techniques for characterization of core-

shell particle morphology including transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), differential scanning calorimetry (DSC), dynamic light scattering (DLS), solid-state NMR and surfactant titration. Both thermodynamic and kinetic features are key factors controlling particle morphology. When core- and shell monomers are incompatible they can be polymerized by gradually varying the chemical composition of the shell when starting from the core-shell interface and moving towards the particle periphery.^{9–16}

Another type of interesting core-shell latex system for paper coating is the so-called hollow latex particles that contain a microvoid in their core. In paper coating hollow latex particles contribute to the improvement of opacity and gloss by scattering more light than the corresponding filled latex particles. The added opacity results from light being refracted at a number of sites as it passes through the hollow particle. One way of preparing hollow polymer particles is by polymerizing a crosslinked hydrophobic polymer shell around a hydrophilic polymer core, then drying and recovering particles. The volume of a core must be large enough so that it will leave a void upon drying and the shell must be strong enough to maintain its integrity.^{3,17–23}

One method of enhancing paper coating properties is by incorporating crosslinking agents into the latex formulations. Crosslinking generally improves physical properties of the polymer. Improvements

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are most significant above the glass-transition temperature. For example, thermal expansion and heat capacity are lowered, whereas the heat distortion temperature, tensile strength and refractive index are raised. Glass-transition temperature increases with increasing crosslink density.^{24–26} Latex with a high degree of crosslinking in paper coating color tends to reduce porosity and blister resistance, when on the other hand, binding strength increases and coating strength properties (such as dry pick, wet pick and wet rub resistance) will improve.⁴

Another way of adding value to the paper is incorporation of optical brightening agents (OBA) or fluorescent whitening agents (FWA). They can be used either in the pulp or in the coating. They absorb UV light and radiate the absorbed energy in the range of visible light thereby increasing the degree of whiteness experienced. The most common OBAs used in paper coating are diaminostillbene-based derivatives.^{27–29}

The aim of this work was to prepare a series of specialty core-shell latices with partially crosslinked hydrophilic polymer cores and hard hydrophobic shells to investigate whether the prepared plastic pigments would enhance optical properties and print quality of coated paper. To further improve paper we prepared latex containing a novel optical brightening agent. Runability of coating and printing processes was also one critical factor to be investigated. In addition, the most promising core-shell latex was evaluated in a pilot scale trial.

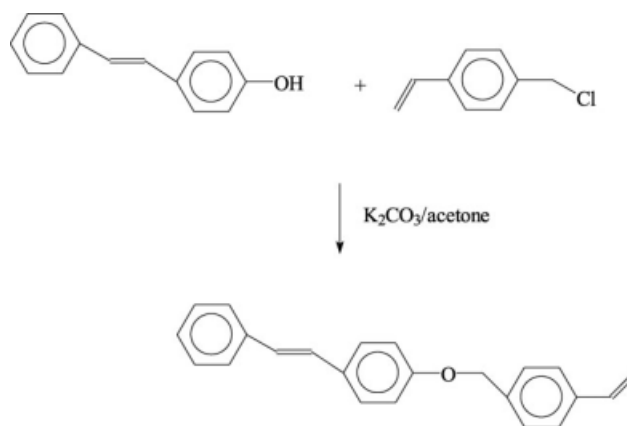
EXPERIMENTAL

Materials

All chemicals used for the preparation of the core-shell latices were of analytical grade, used as received from Aldrich if not otherwise stated. The crosslinking agents ethylene glycol dimethacrylate (EGDMA) and *N,N*-methylene bisacrylamide (MBA) were supplied by Acros. The optical brightening agent, 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)benzene, was synthesized as described in the following section. Potassium persulphate (KPS) was used as initiator, sodium 1,4-bis(2-ethylhexyl) sulfosuccinat (75% aq. solution) as surfactant, ammonia (NH₃ 25% aq. solution) and 1,2-benzisothiazol-3(2H)-one (Proxel) were used for stabilization and preservation.

Synthesis of 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)benzene

The synthetic route to 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)benzene is depicted in Scheme 1. 10,6 g of potassium carbonate (K₂CO₃) and 10 g of



Scheme 1 Synthesis of 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)benzene.

trans-4-hydroxystillbene in acetone were added to a round-bottom flask equipped with a reflux condenser. The mixture was allowed to react for one hour before gradually adding 7,7 g vinylbenzylchloride (VBC). The reaction was allowed to continue for 4 days at room temperature. The product was extracted with chloroform and water and then washed with water, hydrochloric acid (5%), sodium hydrogen carbonate, brine and ether until the solution was clear. After purification and drying 9,65 g (55%) of 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)benzene was isolated. The purified OBA showed the following characteristics: $T_m = 140$ – 146°C (DSC, TA instruments Q1000). NMR (Bruker 600 MHz); ¹H-NMR (C₆D₆, δ , ppm): 4.8 (s, 2H), 5.2 (t, 1H), 5.7 (t, 1H), 6.7 (m, 1H), 6.9–7.5 (m, 15H). ¹³C-NMR (C₆D₆, δ , ppm): 69.7, 113.8, 115.2, 125.5, 125.8, 126.5, 127.0, 127.3–128.0, 128.5, 128.7, 130.7, 136.8, 137.6, 138.0, 158.8.

Core-shell latex synthesis

Core-shell latices were synthesized by emulsion polymerization in a 1 L jacketed glass reactor with a mechanical stirrer, condenser and inlets for pre-emulsion and initiator. Core and shell pre-emulsions of water, surfactant and monomer(s) were prepared in a separate flask under magnetic stirring. The reaction vessel was heated with oil bath to 80°C. First water and surfactant were added to the reaction vessel and mixed at 50 rpm before starting simultaneous feeding of initiator solution and pre-emulsion. The core pre-emulsion was fed into the reactor within 1.5 h. During this time sodium hydrogen carbonate (NaHCO₃) was added to swell the core. Feeding of the shell pre-emulsion was started immediately after all of the first pre-emulsion had been introduced. Feeding of the second pre-emulsion took also 1.5 h. Stirring rate was gradually

TABLE I
Polymerization Recipes Used for Core-Shell Latexes. Paper Coating Formulations were made Using a Laboratory Scale Helicoater

Sample	S in shell (g) ^a	BA in core (g) ^b	MAA in core G ^c	Particle size (nm) ^d	Gloss %	PPS 10 (μm)	K and N	IGT (ms ⁻¹)
Reference	—	—	—	—	58.4	1.10	8.2	0.28
Latex 1	60	20	2	209	70.0	0.91	8.3	0.35
Latex 2	60	20	6	113	69.2	0.95	5.9	0.33
Latex 3	90	30	6	184	68.7	0.98	7.0	0.37
Latex 4	60	40	14	155	63.3	0.98	6.2	0.33
Latex 5	75	40	2	275	68.9	0.98	7.3	0.34
Latex 6	75	30	14	125	70.0	0.98	5.8	0.26
Latex 7	90	30	2	283	68.3	0.93	7.0	0.35
Latex 8	90	20	14	166	70.4	0.92	6.2	0.30
Latex 9	75	40	10	166	67.1	0.96	6.0	0.27
Latex 10	90	20	10	140	71.1	0.91	6.6	0.29

^a The amount (g) of styrene used in forming the shell.

^{b,c} The amount (g) of *n*-butylacrylate and methacrylic acid used in the production of the core.

^d Particle size was determined with a Malvern Zetasizer 1000/3000.

increased up to 200 rpm during the polymerization process. The reaction was allowed to continue for an additional hour after all pre-emulsions had been fed into the reaction vessel. Then the reaction temperature was cooled down and then the final terminating and preservation agents were added. The product was analyzed and used as such.

Coating color preparation

Coating color was prepared by using kaolin (Nugloss) as primary pigment, latex (Raisional SB 730) and sample latex, carboxyl methyl cellulose (CMC, FinnFix 30), calcium stearate, hardener and optical brightening agent (Blancophor P, 0.6 pph). Reference contained no additional core-shell latex. The components were mixed in the mentioned order and pH was regulated by sodium hydroxide (NaOH) to 8.5.

Laboratory trials

Coating colors were coated on one side 10 g/m² on LWC-paper (light weight coated, 39 g/m²). The experiment was carried out using a laboratory scale Helicoater. Then the samples were calendered with a laboratory calender.

Pilot trials

From the preliminary set of core-shell latices, the most promising candidate was up-scaled (SCALEUP 10) and used in pilot scale trials at Coating Technology Center in Raisio, Finland. The sample was coated at 10 g/m² on both sides on a 38 g/m² LWC-paper with a JET-coating machine and calendered in a nine nip supercalender. The coated papers were

then printed on both sides at heat set web offset (HSWO) printer at KCL, Keskuslaboratorio—Centrallaboratorium in Espoo, Finland. All four colors, cyan, magenta, yellow and black were used in printing.

Measurements

All the coated and printed papers were conditioned for 24 h at 23°C and 50% relative humidity before measurements. Measurements were performed according to valid TAPPI and/or SCAN paper testing standards.

RESULTS AND DISCUSSION

A series of core-shell latices with varying compositions were synthesized in accordance to the previously described method and recipes outlined in Table I. All of the produced latices were stable, uniform and their particle sizes varied in a range of 113 to 283 nm depending on the composition and the synthesis of the prepared latex. Figure 1 presents a transmission electron microscopy (TEM) image of core-shell latex taken with JEOL 100SX TEM instrument at Åbo Akademi University. The sample was first dried and then embedded in epoxide to support the sample. Then it was microtomed with a diamond knife into thin layers with a thickness of 20–100 nm and a slice was placed on a copper grid. The operation seems to have slightly distorted the particles. The preparation of the sample for TEM imaging is necessary but destructive and thus the image quality is not very high but we can still see darker edges and lighter center of the core-shell particle in the image.

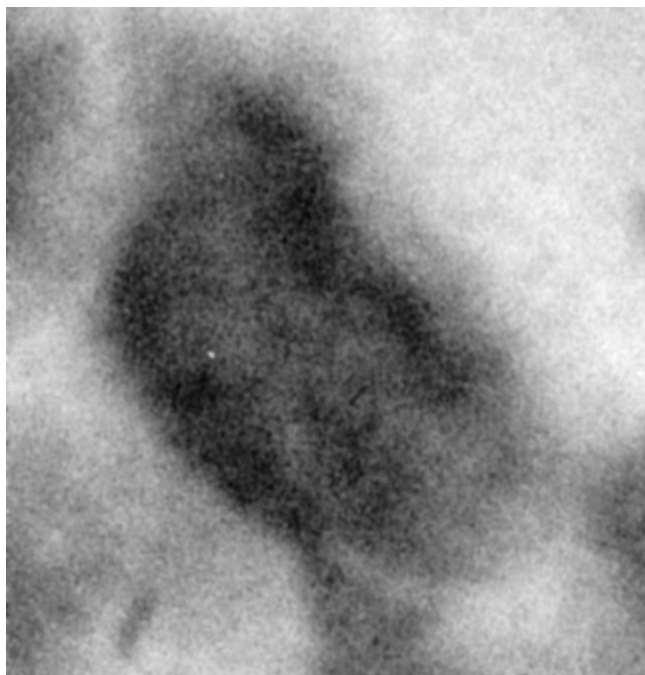


Figure 1 TEM image of a core-shell particle. The particle image is darker on the edges and lighter in the core.

The effect of NaHCO_3 in swelling of the core was investigated separately by preparing two additional latices. The recipes for both latices were identical except for that in the latter no NaHCO_3 was added, whereby the average particle size decreased from 345 nm to 164 nm. Thus, NaHCO_3 effectively swells the core. From selected latices coating colors were prepared. A coating color that did not contain any additional core-shell latex was used as reference. The coating colors were used to coat (10 g/m^2) LWC-paper on one side using a laboratory scale Helicoater and their paper performance characteristics were analyzed. The results are summarized in Table I.

For most of the core-shell dispersion formulations a significant improvement in gloss, IGT surface strength and surface roughness compared to the reference could be observed. The gloss value was measured according to TAPPI-T 480 standard at 75° angle of incident light and surface roughness was measured with Parker Print-Surf (PPS 10) according to SCAN-P 76 : 95 standard. It is generally known that the gloss of coated paper is largely dependent on surface smoothness: the smoother the surface the higher the gloss. In this case, however, as can be seen in Figure 2. the surface roughness values are not in full agreement with recorded gloss values.

Thus, we needed to also examine the effects of other parameters such as polymer composition and type of crosslinker that may also significantly contribute to the development of gloss. According to Taber et al.³⁰ for styrene-butadiene latices the gloss

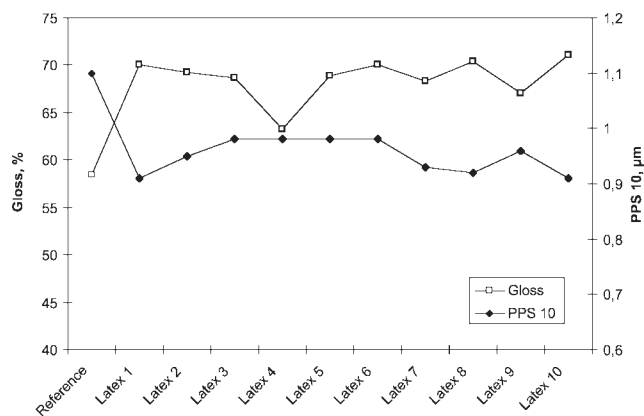


Figure 2 Gloss and PPS surface roughness of laboratory coated and calendered samples.

increases with increasing fraction of styrene units. From Table I it is also possible to examine the effect of monomer composition in core-shell latices on paper gloss. The results indicate that a similar trend as reported for styrene-butadiene latices can also be observed for these core-shell latices. Furthermore, on the contrary it seems that by decreasing the fraction of butyl acrylate units leads to higher gloss. Consequently, having a high fraction of styrene units and relatively low butyl acrylate in the core-shell dispersion has a beneficial impact on paper gloss.

Next we wanted to correlate the type of crosslinker used to various paper properties such as gloss, PPS surface roughness, brightness, K and N ink absorption and IGT surface strength. The following three crosslinkers were tested: ethylene glycol dimethacrylate (EGDMA), *N,N*-methylene bisacrylamide (MBA) and 1,1,1-trimethylol propane triacrylate (TMPTA). In all cases the amount of crosslinker used to partially crosslink the core was 0.33 w-% of crosslinker calculated from the total weight of all monomers in the recipe. The results are shown in Table II. The best gloss, brightness and smoothest surface were achieved with EGDMA, while the surface strength was weakest for EGDMA. TMPTA had the lowest gloss whereas MBA had the roughest surface. In general EGDMA seemed to exhibit the best balance of properties and was therefore chosen as the lead candidate for further testing in pilot trials.

TABLE II
Effect of Crosslinkers on Paper Properties

Crosslinker ^a	Gloss %	PPS 10 (μm)	K and N	IGT (ms^{-1})	Brightness %
EGDMA	61.20	1.20	12.1	0.14	75.9
MBA	60.30	1.40	11.1	0.17	69.2
TMPTA	56.80	1.27	12.3	0.17	69.9

^a 0.33 w-% crosslinker was used for crosslinking the core.

TABLE III
Viscosities for Pilot Coating Colours and Characteristics of Paper Samples Retrieved from the Pilot Test

Sample ^a	HAAKE A mPas	HAAKE B mPas	Brookfield 50 mPas	Brookfield 100 mPas	Z-strength (J/m ²) ^b	PPS 10 μm	Print gloss %
Reference SCALEUP10 (4pph)	20.1 21.6	21.3 22.5	1240 1390	782 832	346 341	1.90 1.74	63.8 66.6
SCALEUP10 (8pph)	20.7	21.6	1380	830	354	1.81	65.5

^a Core-shell latex in the pilot coating colour. The reference contained no additional core-shell latex.

^b Z-strength measured by Scott Bond method.

Pilot trials

Since latex 10 showed the most promising overall combination of properties in paper formulations in the preliminary test series, we decided to employ a slightly modified version of this recipe (using 2 g of MAA instead of 10 g and using 0.6 g of surfactant instead of 0.4 g) in an attempt to scale up the latex synthesis. The results from the pilot trials show that the latex (SCALEUP 10) could successfully be prepared in a quantity of 200 L. Two concentrations were tested: 4 pph (parts per hundred parts of main pigment by weight) and 8 pph in coating formulations using a coating that did not contain any additional core-shell latex as reference. The coating colors prepared had a solid content of 55% and in Table III the viscosity data is summarized.

Figure 3(a,b) show scanning electron microscopy (SEM) images of coated and calendered papers from the pilot trial. In the first SEM image [Fig. 3(a)] the paper contains no additional latex whereas the second paper [Fig. 3(b)] is coated with SCALEUP 10 (8 pph). Spherical latex particles seen on Figure 3(b) are ~ 290 nm in diameter. Pseudohexagonal plates larger than 1 μm in the micrographs are delaminated Nugloss kaolin pigments.

The pilot trials proceeded smoothly and the overall runability was excellent. Z-strength (Scott Bond), PPS-surface roughness, gloss, mottling, print through and print density were analyzed. Selected results are presented in Table III.

Z-strength diminished compared to the reference when we added 4 pph of SCALEUP 10 latex whereas it was increased in the case of using 8 pph of the same. PPS and print gloss were improved for the core-shell latex irrespective of concentration used, however, now the improvement was greater for the paper with lower concentration of SCALEUP 10 latex. The loss of gloss in papers with 8 pph compared to papers with 4 pph could partially be attributed to its rougher surface, i.e., a too high particle concentration cannot any more even out the surface. The optimal concentration of the sample latex is therefore dependent on the desired effects.

Addition of polymerizable optical brightening agent to core or shell

Finally we wanted to investigate whether SCALEUP 10 latex properties could be further enhanced by adding 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethynyl)-benzene type of optical brightener either into the core

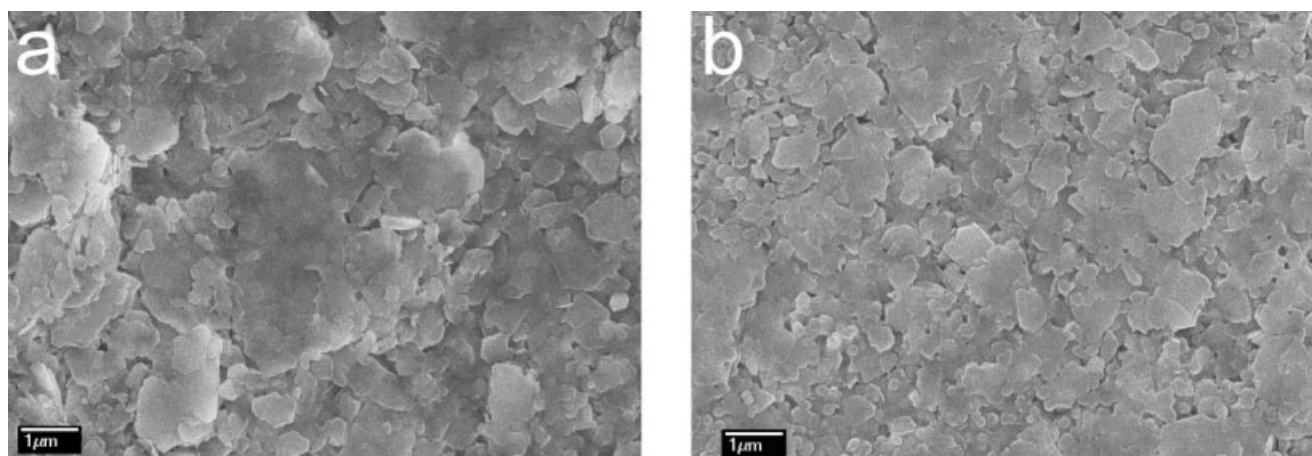


Figure 3 SEM images of coated and calendered pilot trial papers (a) without core-shell latex particles and (b) with 8 pph SCALEUP10.

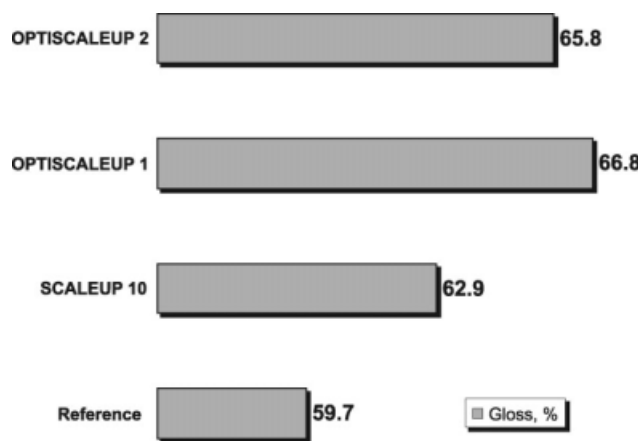


Figure 4 The effect of polymerizable optical brightening agent (1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylenyl)benzene) on gloss.

or shell. In OPTISCALEUP 1 the polymerizable OBA was polymerized into the core, whereas in OPTISCALEUP 2 into the shell. The results presented in Figure 4 indicate that addition of polymerizable OBA can further enhance paper gloss.

Concluding remarks

In summary, we have demonstrated that various partially crosslinked core-shell latices can be successfully prepared and used to improve paper print quality such as print gloss, print mottle, print through, etc. High styrene concentration and low butyl acrylate concentration in the latex contributed to high print gloss. Different crosslinkers: ethylene glycol dimethacrylate (EGDMA), *N,N*-methylene bisacrylamide (MBA) and 1,1,1-trimethylol propane triacrylate (TMPTA), also affected paper properties. Best balance of properties among the crosslinkers was achieved employing EGDMA. The latex performed well also in pilot scale trials. We were also able to incorporate a novel polymerizable optical brightener, i.e., 1-[(4-vinylphenoxy)methyl]-4-(2-phenylethylenyl)benzene into either the core or into the shell of the core-shell latex, whereby gloss could be enhanced even further.

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