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Submicron Sized Hollow Polymer Particles: Preparation and Properties

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Summary: The considered method for obtaining hollow polymer particles is based on the following pathway: (1) preparation of a carboxylated core latex by emulsion copolymerization of acrylic monomers with methacrylic acid, (2) synthesis of a core-shell latex comprising a styrene (co)polymer shell, (3) neutralization of the core carboxylic groups with a base followed by the core ionization and hydration to a high degree, shell expansion and formation of water-filled hollows. A number of approaches to improve the hydrophilic core – hydrophobic shell compatibility and enlarge the hollow volume are considered. The synthesized hollow particles are of a submicron size with the relative hollow volume $V_{hol} : V_{part.} = 0.43 - 0.64$. Methods for cationic hollow particle latex preparation by anionic latex recharging with a cationic surfactant or acidic melamine resin are discussed. Recharging with a melamine resin is shown to afford hollow particles with an external polymer shell providing a high thermal stability of the particles.

Keywords: (co)polymerization; core-shell; hollows; particles; thermal stability

Introduction

Submicron sized hollow polymer particles with air filled hollows are known to be very effective light scattering materials. This property determines the general area of their application as a white pigment for obtaining coatings and polymeric composites. Since hollow polymer pigments are commonly produced as latices their application is particularly efficient for "water-borne processes" predominant in the pulp and paper industry and some branches of paint production. Hollow polymer pigments are featured by the following evident advantages over inorganic counterparts:

- low density in combination with high hiding power,
- good compatibility with polymeric binders,
- simplicity of compatibilization with water-borne polymeric binders.

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Hollow particle latices are known for more than 20 years and can be obtained using a wide variety of methods [1-5]. Presently the most promising results are achieved by Rohm & Haas Co. [4, 5]. This company has developed a process including the following three main stages:

1. Synthesis of a copolymer core latex containing the ionizing comonomer units;
2. Preparation of the particles with hydrophilic core - hydrophobic shell morphology by the (co)polymerization of styrene and/or other monomers in the presence of the core particles;
3. Ionization of the core copolymer at a temperature above T_g of the shell (co)polymer accompanied by a significant hydration of the core copolymer with its subsequent swelling, shell expansion and hollow formation.

The process often also involves some additional stages, i.e.:

- a seed latex synthesis in order to control the particle size;
- an intermediate shell preparation to afford the compatibilization of the hydrophilic core polymer and the hydrophobic shell polymer;
- preparation of an external shell to provide some specific properties of the particles.

However, the implementation of this approach and application of the resulting latices are complicated by certain problems, particularly relating to thermodynamic aspects of the hydrophilic core - hydrophobic shell compatibilization. In addition, the multistage nature of the process sometimes requires the synthesis interruption to separate the intermediate latex products and remove the coagulate.

Since hollow particles are usually prepared in the presence of anionic surfactants, they are negatively charged and consequently cannot be applied for obtaining pigmented compositions on the basis of thermosetting resins curable in the presence of acidic catalysts.

The application areas of hollow particles are also limited by the insufficient thermal stability of the shell usually synthesized from styrene (co)polymers.

This paper presents some approaches purposed to resolve the above problems.

Experimental

The following components were used for the latex preparation.

Monomers: methyl methacrylate (MMA), methacrylic acid (MAA), n-butyl acrylate (BA), ethylene glycol dimethacrylate (EGDM), styrene (ST), acrylonitrile (AN), divinyl benzene (DVB).

Surfactants: sodium dodecylbenzenesulfonate (SDBS), trimethyldodecyl ammonium chloride (TMDAC), trimethyldodecyl ammonium bromide (TMDAB).

Initiator: potassium persulfate (PP).

Ammonia solution was used for MMA-EGDM-MAA copolymer latex neutralization.

TEMPO is used as a radical inhibitor.

The latex syntheses were carried out in a glass reactor equipped with a reflux condenser, inlet for inert gas supply and two more inlets for feeding aqueous solutions of PP, SDBS and monomer mixtures via syringe pumps. Some of the trials were performed using a commercially available anionic hollow particle latex Ropaque HP-543 produced by Rohm & Haas Co. (solids 30 wt.%, particle size 500 nm).

Cationic melamine-formaldehyde resins (MFR) were prepared in the presence of HCl at various melamine:formaldehyde:HCl ratios at temperature 75-85 °C.

The latex particle size and morphology were examined using a Hitachi H-300 transmission electron microscope with a formvar-coated grid at an accelerating voltage 75 keV.

The ζ-potential was estimated by the macroelectrophoresis technique with Barton installation with latices having a concentration of 7% and with 0.025 N KCl solution as a side liquid. The ζ-potential was calculated according to the Helmholtz-Smoluchowski equation:

$$\zeta = \frac{4\pi\eta U_0}{D}$$

where η and D are the viscosity and dielectric permeability of the dispersion medium (water) equal to 0.1 cP and 81, correspondingly, and U_0 is the electrophoretic mobility of the particles determined according to the equation:

$$U_0 = \frac{U \times l}{E}$$

where U is the latex/side liquid boundary shift rate, E is the potential difference equal to 100 V in our experiments, and l is the distance between the electrodes (24 cm).

The synthesized hollow particles were also characterized with respect to their ability both to scatter light and to form white coatings. For these tests, the hollow-particle latex was mixed with the film-forming latex composed of a ST-BA-MAA (33.0/62.0/5.0 wt.%) copolymer or with etherified melamine resin. Coatings were made at ambient temperature on glass plates and with different surface concentrations (S) of the hollow pigment. The value S varied from

20 to 80 g/m^2. The efficiency of hollow particles as a polymeric pigment was estimated photometrically by measuring the contrast index *R* as the ratio between the reflection coefficients for a coated glass plate disposed on a black support with a reflection less than 1% and on a white support with a reflection 82%. The measurements were carried out at variable *S* values. The contrast index at a selected *S* was evaluated from the linear dependence of *R* versus *1/S*, that is, according to almost the same procedure as used for the determination of the contrast index of paints [6].

Results and discussion

Synthesis of hollow particle latices according to a three-step process without an intermediate shell formation stage.

One of the problems complicating the development of the considered process free of the intermediate shell formation stage is the preparation of core-shell particles as precursors for the hollow ones with the general difficulty relating to an extremely thermodynamically unfavorable hydrophilic core - hydrophobic shell morphology. Sometimes inverse or hemispherical structures are formed even in monomer starved conditions. Generally, a correct core-shell morphology can be obtained provided the shell monomers : core polymer weight ratio is high enough [7]. Indeed, the final hollow particles after the neutralization stage have a correct morphology if the shell polymer : core polymer weight ratio is 17.5 or higher (Figure 1a) while at lower ratios the particle structure is defective (Figure 1b).

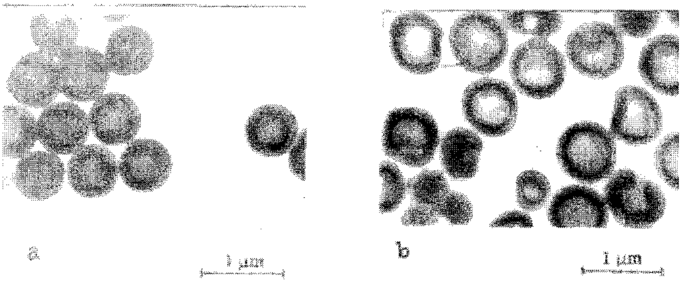


Figure 1. Electron micrographs of the hollow particles at various shell polymer (polystyrene): core polymer (MMA-MAA-EGDM copolymer 70:29.5:0.5 wt%) weight ratio: (a) – 17.5; (b) – 12.0. The neutralization stage is carried out using ammonia at 100°C. Other process conditions are described in [7].

Unfortunately, the approach involving a thick shell formation provides only particles with a relatively small hollow volume due to the complications at the shell expansion during the neutralization stage. The situation can be drastically changed by performing the process in the conditions simplifying the particle shell expansion at the final stage of the core carboxyl groups neutralization. For this purpose, some amount of styrene was added to the latex before neutralization to reduce T_g of the polymer and to provide the shell softening at temperatures below 100°C and promoting its expansion at the core polymer swelling [8]. In this case, the monomer acts as a temporary plasticizer. In order to prevent polymerization of the added styrene at neutralization, a small amount of an inhibitor was also added to the monomer. After completion of the neutralization, some more initiator was charged into the reaction system to polymerize the added styrene. The process recipe and conditions are summarized in Table 1. According to the analysis data (Table 2), the considered approach affords a marked increase of the relative hollow volume and improvement of the optical performances of the coating obtained using the hollow pigment.

Table 1. Recipe (g) and conditions of the process for hollow particle latex preparation free of the intermediate shell synthesis.

Components and conditions of the process	Stage			
	Carboxylated core latex	Core-shell latex	Neutralization	ST polymerization
Seed copolymer MMA-BA-MAA	5.52 (solid 1.25%)			
MMA	2.29			
MAA	0.985			
EGDM	0.017			
ST		55.7	5.57	
PP	0.029	0.728		0.415
SDBS	0.0056	0.294		
TEMPO			0.105	
Ammonia (10.4 wt%)			2.82	
Water	9.6	87.1		7.1
Process type	Semicontinuous	Semicontinuous	Batch	Batch
Temperature, °C	80	85	95	85
Time, min	180	120	60	40

Table 2. Hollow particle properties depending on the neutralization conditions.

Property	Neutralization in the presence of ST and TEMPO	Neutralization free of ST and TEMPO
Particle diameter, nm	870	640
Hollow diameter, nm	690	400
$V_{hol.}/V_{part.}$	0.50	0.24
Contrast index of the coating at $S = 40$ g/m^2	0.94	0.73

Another method for performing a three-step process without the shell thickness growth is based on the incorporation of a polar monomer (AN) units into the shell copolymer composition. This approach allows the reduction of the shell : core weight ratio up to 8. Geometrical parameters of the hollow particles with the shell comprising ST-AN-DVB (74:25:1 wt.%) as function of the shell:core weight ratio are summarized in Table 3. According to Figure 2, the particles are featuring with a perfect morphology.

Table 3. Geometrical parameters of the hollow particles as function of the shell : core weight ratio.

Shell : core weight ratio	Particle diameter d_{part}, nm	Hollow diameter d_{hol}, nm	Shell thickness, nm	$V_{hol} : V_{part}$
8.0	580	500	40	0.64
9.3	540	430	55	0.50
10.0	540	420	60	0.47
14.0	580	440	70	0.43

The core polymer composition and preparation conditions are described in Table 1
Other process conditions are described in [7].

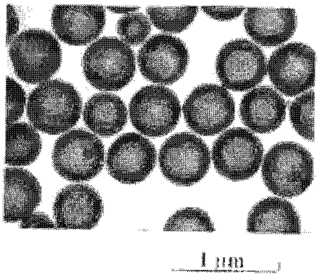


Figure 2. Electron micrograph of the hollow particles with ST-AN-DVB copolymer shell at shell : core weight ratio 8.0.

It should be noted that particles of this kind were obtained at quite high AN units contents in the shell polymer. Meanwhile, AN content can be significantly reduced by carrying out the process in the conditions providing with a variable shell composition along the shell radius, i.e. with a gradual decrease of AN content from the core-shell boundary to the outer surface of the particle. A schematic flow-chart of this process is illustrated in Figure 3. Since the reaction is performed under the monomer starved conditions an instantaneous monomer mixture composition in the vessel 2 corresponds to an instantaneous copolymer composition in the reactor 3.

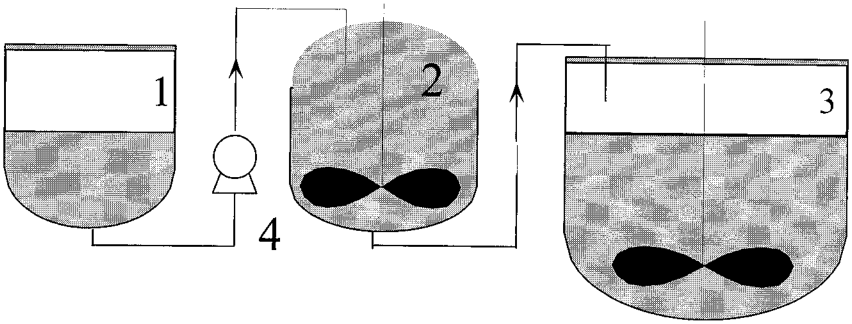


Figure 3. Flow-chart of the process with a changing monomer mixture fed into the reactor.

1 – vessel with a ST-DVB monomer mixture,
2 – vessel with a changing monomer mixture ST-DVB-AN,
3 – reactor,
4 – pump.

An instant monomer mixture composition fed into the reactor 3 and a final copolymer composition are calculated in accordance with the following equations:

$$a_{ST,\,DVB,\,AN} = \frac{q_{ST,\,DVB,\,AN}}{q_{ST} + q_{DVB} + q_{AN}} \cdot 100$$

$$A_{ST,\,DVB,\,AN} = \frac{Q_{ST,\,DVB,\,AN}}{Q_{ST} + Q_{DVB} + Q_{AN}} \cdot 100$$

$$q_{ST,\,DVB,\,AN} = (q^0_{ST,\,DVB,\,AN} - VC_{ST,\,DVB,\,AN})\, e^{-w\cdot t/v} + VC_{ST,\,DVB,\,AN}$$

$$Q_{ST,\,DVB,\,AN} = (VC_{ST,\,DVB,\,AN} - q^0_{ST,\,DVB,\,AN})\, e^{-w\cdot t/v} + C_{ST,\,DVB,\,AN}\, wt + q^0_{ST,DVB,\,AN} - VC_{ST,\,DVB,\,AN}$$

where $a_{ST,\,DVB,\,AN}$ – instant content of ST, DVB or AN in the vessel 2 (wt%), $A_{ST,\,DVB,\,AN}$ — ST, DVB or AN content in the final copolymer (wt%), $q_{ST,DVB,AN}$ and $q^0_{ST,\,DVB,\,AN}$ – amounts of ST, DVB or AN in the vessel 2 at any time (t) or at t = 0 (g), $Q_{ST,\,DVB,\,AN}$ – total amounts of ST, DVB or AN fed into the reactor at time t (g), $C_{ST,\,DVB,\,AN}$ - concentrations of ST, DVB or AN in the vessel 1 (g/cm^3), w – feeding volume rate (cm^3/min), t – feeding time (min).

AN gradient concentration depends on the initial conditions (Figure 4). Table 4 demonstrates the initial parameters of the process and properties of the product obtained in comparison with the latex prepared using a conventional procedure. These data show that AN content in the shell polymer can be decreased 3.5-fold without any deterioration of the latex properties.

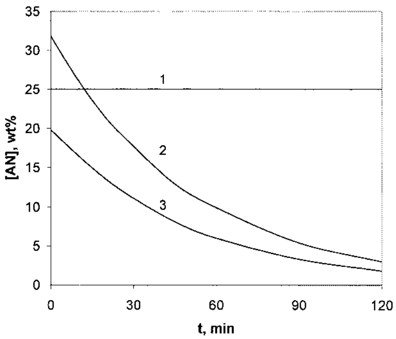


Figure 4. Plot of the instant AN concentration in the monomer mixture (vessel 2) versus time. The process conditions are summarized in Table 4.

Table 4. Process parameters and properties of the hollow particle lattices.

Trial No.	Monomer mixture composition in the vessel 1, g/cm^3			Amount of the monomers in the vessel 2 (t = 0), g			AN content in the vessel 2, wt%		Hollow particle latex properties			
	ST	DVB	AN	ST	DVB	AN	t=0	t=130 min	Total AN content in the shell polymer, wt%	Solids, wt%	D_{part} nm	Contrast index at S = 40 g/m^2
1	0.649	0.088	0.219	84.47	1.14	28.54	25.0	25.0	25.0	36.0	540	0.97
2	0.895	0.0101	0	76.53	0.86	35.80	31.6	2.38	11.0	39.2	480	0.95
3	0.895	0.0097	0	91.01	0.99	22.80	19.9	1.52	7.0	36.1	530	0.98

Notes: V = 130 cm^3, w = 2.55 cm^3/min, final core : shell weight ratio - 1:10,
core polymer MMA-MAA-EGDM (70.0:29.5:0.5 wt%),
polymerization temperature 80°C, neutralization temperature 100°C

Preparation of the latices with positively charged particles

The direct synthesis of cationic hollow particle latices including the amine containing core preparation (stage 1), e.g. by copolymerization of dimethylaminoethyl (meth)acrylate with other monomers and neutralization of amino-groups with an acid (Stage 3) is known to be not successful [5] since usually leads to a significant coagulate formation and consequently low solids of the latex (about 8 wt%). In addition, the production of large hollow volumes is impossible as the difference between the size of the initial amine core and the swollen core after the neutralization is too small [9].

The simplest way to prepare a cationic hollow particle latex is based on recharging of an anionic latex with a cationic surfactant. The most complicated problem relating to the particle recharging is maintaining the latex system colloidal stability at passing through the isoelectric state where the particles lose their electric charge.

Figure 5 shows the hollow particle charge. The possibility for recharging negatively charged particles is determined by several factors with one of the most important among them being the cationic surfactant ς-potential change as function of the added cationic surfactant amount. The system reaches the isoelectric state at the surfactant content about 2% relating to the polymer weight. However, the system becomes colloidally stable only provided the ς-potential exceeds +20 mV that can be attained in the case TMDAC content is higher than 3 wt%.

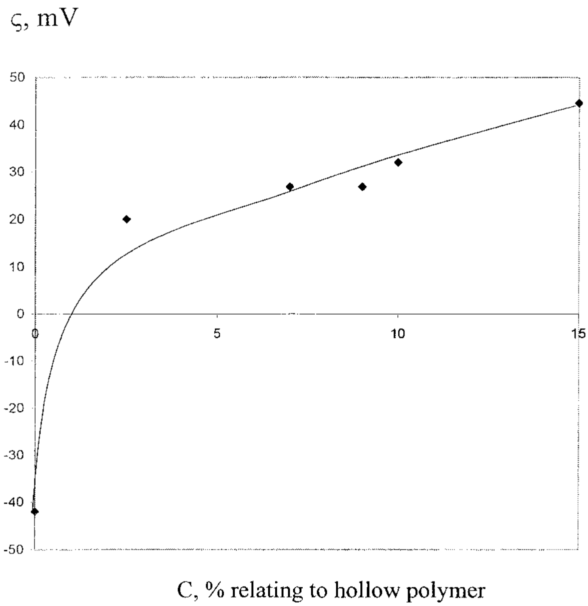


Figure 5. ς-potential of the hollow particle latex Ropaque HP-543 versus TMDAC concentration

Another important factor is the rate of the cationic surfactant introduction into the anionic hollow particle latex. To avoid a strong dilution of the latex concentrated (30-50 wt%) cationic surfactant solutions were used. The surfactant addition rate determines the duration of the system transition through the isoelectric state. If this period is too long the latex particles have enough time to join coagulation contacts leading to loss stability of the system. This is illustrated by data in Table 5. At slow surfactant addition, the latex undergoes a complete or partial coagulation despite the added surfactant amount is quite sufficient to attain the required ς-potential. The increase of the surfactant addition rate up to 2.0 $\mathrm{wt\%\cdot s^{-1}}$ (relating to the dry latex polymer) allows performing the process without any coagulum formation.

Table 5. Recharging conditions for anionic hollow particle latex Ropaque HP-543.

Surfactant type and concentration, wt%	Surfactant amount (relating to polymer), wt%	Surfactant addition rate, wt% · s^{-1}	Recharged latex properties		
			Solids, wt%	Coagulate, wt%	ς-potential, mV
TMDAC, 36.5	4.0	0.13	-	100	-
TMDAC, 36.5	4.0	0.80	22.4	27	+29
TMDAC, 36.5	4.0	2.00	30.8	no	+31
TMDAB, 50.0	5.0	2.50	31.2	no	+30
TMDAB, 50.0	7.0	3.50	31.2	no	+27
TMDAC, 36.5	9.0	4.50	30.8	no	+27

Performances of the initial anionic and recharged latices are summarized in Table 6. The particle diameter remains unchanged after recharging suggesting the absence of the particle aggregation. The coatings obtained from the synthesized latices also retain high level of their optical performances.

Table 6. Performances of the latices.

Property	Initial anionic latex	Recharged (cationic) latex
Solids, % wt.	30	30
TMDAC, %wt.	0	4
ς-potential, mV	–42	+31
Particle diameter, nm	500	500
Contrast index of the coating at S = 40 g/m^2	0.95	0.94

Preparation of latices with thermally stable particles

The thermal stability of hollow particles with a polystyrene shell can be improved [4] by the formation of an additional outer shell containing up to 50 wt% of a crosslinking comonomer (DVB). Nevertheless, this approach is limited in both the achieved thermal stability level and economic factors (expensive crosslinking comonomers). We suggested a method for obtaining hollow particles with an outer shell comprising a cheap thermosetting polymer [10]. The process includes the following stages:

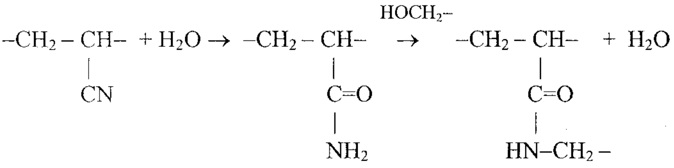
(a) preparation of an anionic hollow particle latex according to the above methods;

(b) synthesis of a melamine-formaldehyde precondensate in the form of an acid cationic colloid;

(c) mixing of the components obtained at stages (a) and (b) leading to the cationic precondensate deposition onto the surface of anionic hollow particles and their recharging. Details of the recharging are described in [10].

Thus the proposed method provides an effective approach simultaneously to two goals: improvement of the hollow particle thermostability and preparation of positively charged particles.

The preparation of melamine-formaldehyde resin acid colloids as recharging agents can be accomplished at a wide range of melamine:CH_2O:HCl molar ratios, however, the best values providing a colloidal stability and long shelf life for both the resin and the recharged latex are 1 : (5.6 – 7) : (0.42 – 0.69). The recharged latex behavior also depends on the shell type in the initial hollow particles. Provided the shell comprises ST-AN-DVB copolymer the recharged latex shelf life is more than 3 weeks if the weight ratio hollow polymer : MFR = 2.0. In the case the shell consists of polystyrene crosslinked with DVB (1 wt.%) instead of this copolymer the prepared cationic latex undergoes a similar gelation in a week. The cationic latex shelf life can be also achieved by its heating at 70-90°C after MFR addition. However, this procedure is only efficient for hollow particles containing a copolymer shell whereas for polystyrene shell an additional heating after the latex recharging leads to its fast coagulation. Perhaps, these phenomena could be attributed to the desorption or incomplete sorption of cationic MFR followed by the cationic prepolymer condensation in the aqueous phase. The formed large MFR molecules can bind the latex particles acting as a flocculant. In the case of copolymer shell, nitrile groups promote a covalent binding of MFR with the hollow particle surface as a result of the interaction between methylol groups in MFR with the copolymer, e.g. according to the following mechanism:



$$-\mathrm{CH_2}-\underset{\underset{\mathrm{CN}}{|}}{\mathrm{CH}}- + \mathrm{H_2O} \rightarrow -\mathrm{CH_2}-\underset{\underset{\underset{\mathrm{NH_2}}{|}}{\mathrm{C{=}O}}}{|}{\mathrm{CH}}- \xrightarrow{\mathrm{HOCH_2}-} -\mathrm{CH_2}-\underset{\underset{\underset{\mathrm{HN{-}CH_2}-}{|}}{\mathrm{C{=}O}}}{|}{\mathrm{CH}}- + \mathrm{H_2O}$$

The possibility or impossibility of such a reaction involving particles with a polystyrene shell can determine the difference between the behavior of these two latices. Heating of the recharged latex at 70-90°C accelerates MFR condensation and binding with the copolymer shell. Both of these factors reduce a possibility for MFR desorption thus enhancing the cationic latex stability and increasing the amount of the resin deposited onto the particle surface. Indeed MFR deposition at ambient temperature provides the initial anionic hollow particle diameter growth from 520 to 545 nm while an additonal heating at 70°C (2 hours) and 90°C (2 hours) enlarges the particle diameter up to 580 nm.

Thermal stability of the hollow particles with outer melamine shell was evaluated in accordance with the following simple procedure. First, the coatings were formed from the mixture of a hollow particle latex and methylated MFR on a glass substrate at ambient temperature within 24 hours. After the contrast index measurement the coating was annealed at 170°C for 75 min and the contrast index was measured again. The data obtained are summarized in Table 7.

Table 7. Contrast index of the coatings.

Hollow polymer / MFR weight ratio	ζ-potential of the particles, mV	Hollow polymer / binder weight ratio	Hollow polymer surface density, g/m^2	Contrast index	
				Before curing	After curing at 170°C
Anionic hollow particle latex	– 39	15 : 85	30	0.811	0.308
Anionic hollow particle latex	– 39	30 : 70	45	0.857	0.278
2.0	+ 33	15 : 85	25	0.718	0.725
2.0	+ 33	30 : 70	50	0.936	0.937
3.3	+ 26	15 : 85	25	0.721	0.718
3.3	+ 26	15 : 85	42	0.933	0.930
10.0	+ 22	15 : 85	25	0.875	0.366
10.0	+ 22	15 : 85	42	0.937	0.451

The initial anionic hollow particles free of the melamine shell undergo collapse at 170°C as indicated by a drastic drop of the contrast index (the coating became translucent indicating an abrupt decrease of the volume part of light-scattering centers, i.e. air-filled hollows). In contrast, the coatings based on hollow particles modified with MFR maintained their optical performances after heating. This allows us to suppose that the volume of air-filled hollows in the coating remains unchanged since rapid curing of the outer melamine shell prevents the internal copolymer shell collapse due to the following two factors:

1. covalent bonding of nitrile groups of the copolymer shell with the outer MFR shell;
2. certain affinity of ST-AN-DVB copolymer with MFR can promote the formation of an intermediate layer similar to an interpenetrating network.

An exception from this general trend is represented by the coatings formed using cationic latexes prepared at the ratio anionic hollow polymer : MFR equal to 10. Similar to the coatings obtained using anionic hollow particles in this case the contrast index also drastically drops after heating. This can be related to an insufficient strength of too thin melamine shell undergoing destruction as a result of stresses caused by the internal copolymer shell collapse.

Conclusion

The performed studies have demonstrated the efficiency of several methods for producing hollow particle latices according to a general approach involving three stages: carboxylated core latex preparation, core-shell latex synthesis, neutralization of the core polymer. The considered methods are free of the intermediate shell preparation and based on polar units incorporation into the shell polymer or performing a neutralization stage in the presence of the monomer as a temporary plasticizer. The methods afford the preparation of hollow particles with a high relative hollow volume.

The cationic hollow particle latices are prepared by recharging of anionic ones with cationic surfactants. The possibility of coagulum-free latex after recharging is determined by the cationic surfactant concentration and addition rate.

The recharging method is used for obtaining hollow thermostable particles. This approach is based on a cationic melamine resin deposition onto the surface of negatively charged hollow particles. Thus obtained hollow particles are suitable for the application in polymeric composites curable at elevated temperatures.

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