Monodisperse Micron-Size Polymer Core/Nanoparticle Pigment Shell Composite Particles Via Heteroaggregation

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ABSTRACT: A process for preparing monodisperse, micron-size composite particles consisting of a polymer core and a nanoparticle pigment shell is described. A heteroaggregation process employing uniform, stable micron-size polymer particles prepared by dispersion polymerization and unstable carbon black pigment particles proved successful for a variety of polymers including poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(n-butyl acrylate) (PBuA), and several functional copolymers. Sonication is applied to the mixture enabling the pigment to be broken into its primary particle size, allowing it to form a relatively uniform layer on the surface of the polymer particles by heteroaggregation when the sonication is removed. Attempts to encapsulate these pigment-coated particles by seeded polymerization resulted in only partial engulfment of the pigment particles in the surface. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 264–274, 2009

Key words: monodisperse particles; encapsulation; heteroaggregation; composite

INTRODUCTION

Encapsulated polymer particles of uniform size find use in a wide variety of applications including xerography, printing, cell labeling, and biological studies. Encapsulation of inorganic particles in a polymer has been tried using emulsion polymerization[1–4] and miniemulsion polymerization.[5–7] An alternative approach is to heteroaggregate inorganic (or organic) particles onto the surface of uniform-size polymer particles previously obtained by dispersion polymerization.

Several authors have used dispersion polymerization to encapsulate inorganic particles in conducting polymers like polypyrrol or polyaniline.[8–10] Also, Bourgeat-Lami and Lang obtained silica nanoparticles encapsulated in polystyrene (PS) via dispersion polymerization in aqueous ethanol medium.[11,12] However, in the previous works the dispersion polymerizations carried out in the presence of an inorganic pigment produced polydisperse particles that could not be used in applications in which a narrow distribution is required.

The aggregation of two stable systems, namely a polymer latex and a pigment dispersion using different methods has also been reported by several authors. Hou et al.[13] obtained pigmented nylon polymer particles by microencapsulation of carbon black by the change of the degree of mixing.

Depending on the relative importance of the three interactions in a polymer solution containing pigment particles (solvent-polymer, solvent-pigment, and pigment-polymer), two types of pigmented polymer particles were prepared: (1) particles with pigment enriched in the surface, and (2) particles with more fully encapsulated pigment. Xerox has developed several processes to synthesize toner particles by aggregation via temperature variation.[14] And in the work of Cairns et al.[15] submicrometer-size polypyrrole-polystyrene composite particles were obtained. The polypyrrole was deposited onto the latex surface and acted as a bridging flocculant leading to heteroaggregation.

Ultrasound has also been used to encapsulate particles. Dhas et al.[16] obtained zinc sulfide nanoparticles on silica microspheres by sonochemical formation of zinc sulfide and its deposition on the silica surface. Breen et al.[17] obtained ZnS-coated polystyrene core-shell particles through sonochemical deposition (using 250 nm carboxyl-modified polystyrene microspheres). Even though ultrasound has been used to obtain encapsulated particles, to our knowledge, there is no description in the literature of the formation of uniform, micron-size, composite polymer/inorganic particles by heteroaggregation using ultrasound.

In this investigation, processes to prepare uniform, micron-size polymer/pigment composite particles were investigated. Initially, screening studies included emulsion, suspension, and dispersion polymerizations, and heteroaggregation methods. No polymerization method was able to universally

TABLE I
Dispersion Polymerization Recipes and Particle Sizes of Monodisperse PMMA Latexes Prepared at 55°C

Ingredient	MMADP-1	MMADP-2	MMADP-3	MMADP-4	MMADP-5	MMADP-6
MMA (wt %)	10.0	10.0	10.0	10.0	10.0	10.0
Methanol (wt %)	85.9	85.9	77.4	85.9	73.0	68.7
DI water (wt %)			8.6		12.9	15.3
PVP K30 (wt %)	4.0	4.0	4.0	4.0	4.0	4.0
AIBN (wt %)	0.1	0.1	0.1	0.1	0.1	0.1
MAA (wt %)		0.1				
DMAEMA (wt %)				0.1		
Particle size (μm)	3.21	3.51	2.87	2.75	2.73	2.50
	2.89	2.98	2.79	2.89		
	2.86	3.14	2.80	2.82		
	2.87	3.11	3.02	2.55		
	3.06					

produce composite particles with narrow particle size distributions but instead was pigment specific. Subsequently, various heteroaggregation approaches were investigated including charge reversal via pH adjustment and addition of cationic water-soluble polymers. These were of only limited success. The work described herein was the most successful and proved relatively universal in terms of the pigments used. The use of carbon black as the pigment is described in this article with the goals of understanding the requirements for successful heteroaggregation and the subsequent irreversible attachment to the polymer particles.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, Sigma-Aldrich, >99%), styrene (S, Sigma-Aldrich, >99%), and butyl acrylate (BA, Sigma-Aldrich, >99%) monomers were purified of inhibitors by passing them through columns filled with an appropriate inhibitor removal packing material (Sigma-Aldrich). All other materials were used without further purification, including the alcohols, ethyl alcohol (190 proof, Pharmcoproducts Inc.), methyl alcohol (purified, EM Science); toluene (VWR Scientific); the azo-type initiators, 2,2′-azobis-(2,4-dimethyl-4-methoxy valeronitrile) (V-70, Wako) and 2,2′-azobis-(isobutyronitrile) (AIBN, Sigma-Aldrich); the redox system comprising *tert*-butyl hydroperoxide (*t*-BPO, Sigma-Aldrich), sodium formaldehydesulfoxylate (SFS, Anachemia), ferrous sulfate (FES, Fisher); stabilizers, polyvinylpyrrolidone (PVP K30 (viscosity-average molecular weight = 4×10^4), PVP K90 (viscosity-average molecular weight = 3.6×10^5)), poly(vinyl alcohol (PVA; degree of hydrolysis = 87–89%, molecular weight = 88,000, Acros); the acidic monomer, methacrylic acid (MAA, Sigma-Aldrich); the basic monomer, dimethylaminoethyl methacrylate (DMAEMA, Romtech Monomers); the crosslinker, allyl methacrylate (AMA, Sartomer); hydroxyethyl methacrylate (HEMA, Sigma-Aldrich); and glycidyl methacrylate (GMA, Sigma-Aldrich); and the water-soluble inhibitor copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, Sigma-Aldrich). Deionized (DI) water was used in all experiments. Carbon black (Mogul L, Cabot, Billerica, MA) was used as the pigment.

RESULTS

Polymer particles

Micron-size polymer particles were synthesized by dispersion polymerization of MMA, S (styrene), and BA (butyl acrylate). Carboxyl groups were incorporated by copolymerizing with methacrylic acid (MAA) (1 wt % respect to the main monomer) and amino groups by copolymerizing with DMAEMA (1 wt % respect to the main monomer).

The recipes used to prepare micron-size poly-(methyl methacrylate) (PMMA) latex particles with narrow size distributions are given in Table I. These are based on those reported by Shen et al.[18] The polymer particle dispersions were prepared by bottle polymerization. The ingredients were weighed into 8-oz glass bottles, purged with nitrogen, capped and sealed. The bottles were then placed in safety baskets supported on a rotor, and were tumbled end-over-end at 30 rpm in a constant temperature bath at 55°C. The reactions were carried out for 48 h. In all cases the conversions were >90%. The particle sizes as determined from scanning electron micrograph (JEOL 6300 F) images are reported in Table I. Multiple values are given for recipes that were repeated up to five times to obtain the required amount of particles for all the experiments. The distributions were narrow but were not characterized by statistical measurements of sufficient numbers of particles. This was not considered necessary relative to the goals of the work. Two additional latexes were prepared by replacing some of the MMA with 0.5 wt % HEMA (MMADP-7) and 0.5 wt % GMA (MMADP-8) in the recipe represented as MMADP-1.

Ingredient	SDP-1	SDP-2	SDP-3	SDP-4	SDP-5
S (wt %)	12.5	12.5	12.5	12.5	12.5
Ethanol (wt %)	85.5	85.5	85.5		85.5
Methanol (wt %)				85.5	
PVP K30 (wt %)	1.8	1.8	1.8	1.8	1.8
AIBN (wt %)	0.12	0.12	0.12	0.12	0.12
MAA (wt %)		0.1			
DMAEMA (wt %)			0.1		
AMA (wt %)					0.038
Particle size (μm)	1.32	1.48	1.38	1.28	1.39
	1.25	1.45	1.38	1.36	

The resulting particle sizes were 6.0 μm and 2.79 μm, respectively.

Similarly, polystyrene particles were prepared by dispersion polymerization according to the recipes given in Table II.[19] Polymerizations were carried out in the bottle polymerizer at 70°C for 24 h. Again, particle sizes for repeated experiments are reported. Smaller micron-size particles were obtained from these recipes.

Low T_g polymers were also prepared using *n*-butyl acrylate recipes reported in Table III.[20] The polymerizations were also carried out in the bottle polymerizer at 70°C for 24 h. Note that in these polymerizations, PVP K90 was used instead of PVP K30 as stabilizer, as it was shown[20] to be more suitable for this dispersion polymerization system. The particle sizes are reported as measured using an optical microscope (Nikon ECLIPSE TE300; 1000×) since the PBA particles were too soft for SEM examination.

Heteroaggregation experiments

To successfully carry out the heteroaggregation experiments, it was initially found that the polymer particle dispersions must first be cleaned of the stabilizer used in their preparation since without this procedure the pigment particles became stabilized without aggregating with the polymer particles. The

Ingredient	BADP-1	BADP-2	BADP-3	BADP-4
BA (wt %)	10.0	10.0	10.0	10.0
Methanol (wt %)	80.1	80.1	80.1	80.1
Water (wt %)	8.9	8.9	8.9	8.9
PVP K90 (wt %)	1.0	1.0	1.0	1.0
AIBN (wt %)	0.1	0.1	0.1	0.1
MAA (wt %)		0.1		
DMAEMA (wt %)			0.1	
AMA (wt %)				0.03
Particle size (μm)	2.23	2.61	2.72	2.91
	2.16	3.25	3.13	

Supernatant #	1	2	3	4	5	
Solids %	5.4	0.369	0.081	0.000	0.0088	
Sonication time (min)	20	40	60	80	100	120
Solids %	0.025	0.040	0.000	0.033	0.019	0.010

latexes were cleaned by first decanting the supernatant after sedimentation of the particles and then washing them with methanol in five successive sedimentation/decantation cycles. This washing procedure was found to be inadequate to remove sufficient stabilizer and subsequently, the latexes were sonified (Branson sonifier (Model 450); duty cycle of 50%; output power 5) several times until the excess stabilizer was removed. For example, Table IV reports the evolution of the weight percent solids content of the latex supernatant during this cleaning process, where the supernatant was collected five times by sedimentation/decantation followed by 6 cycles of sonification (20 min each) where the supernatant was also collected after sedimentation of the particles. It is clear that the sonification frees more of the stabilizer from the particles where it can be removed by decantation.

In the heteroaggregation procedure, dry pigment (5 wt % or varied based on polymer) was added to a previously cleaned latex dispersion in methanol (5 wt % solids) and sonified (duty cycle 50%; output power 5; 20 min). The dispersion mixture was cooled by an ice/water mixture during sonification to prevent excessive evaporation of the methanol.

Carbon black (Mogul L, Cabot) was used in the majority of the heteroaggregation experiments. Heebner characterized Mogul L by flow microcalorimetry.[21] It was found to have both strongly acidic and basic surface sites. Acidic sites were attributed to phenol and carboxylic acid groups whereas basic sites were attributed to quinone, ester, and lactone groups present on the carbon black. Mogul L is reported to have the following weight percentages of oxygen-containing groups in the surface: 4.4 wt % phenol, 14 wt % carboxyl, and 18 wt % 1-4 quinone groups.[22] Other reported characteristics are given in Table V.

Effect of the amount of carbon black

Heteroaggregation experiments were carried out to study the effect of the amount of carbon black added to a fixed amount of latex particles. Two PMMA homopolymer latexes with similar sizes of 2.87 (MMADP-1) and 2.86 μm (MMADP-3) were used in these experiments. Figure 1 shows SEM micrographs

| Pigment	Nature of the surface	Surface area $(m^2/g)^a$	Density (g/cm3)	pH[b]	Particle size (nm)
Mogul L	Furnace black oxidized grade	138	1.8	2–4	25

[a] Determined by nitrogen adsorption.
[b] In aqueous dispersion.

of the latexes aggregated with 1, 2, 2.5, 5, 10, and 15 wt % carbon black (with respect to the polymer) in methanol. In all cases, following the heteroaggregation, a black sediment was obtained with a clear supernatant. From Figure 1, it can be observed that even for the lowest amount of carbon black, the particles are fully covered by the pigment. For 1 and 2 wt % the images indicate a nonuniform layer of
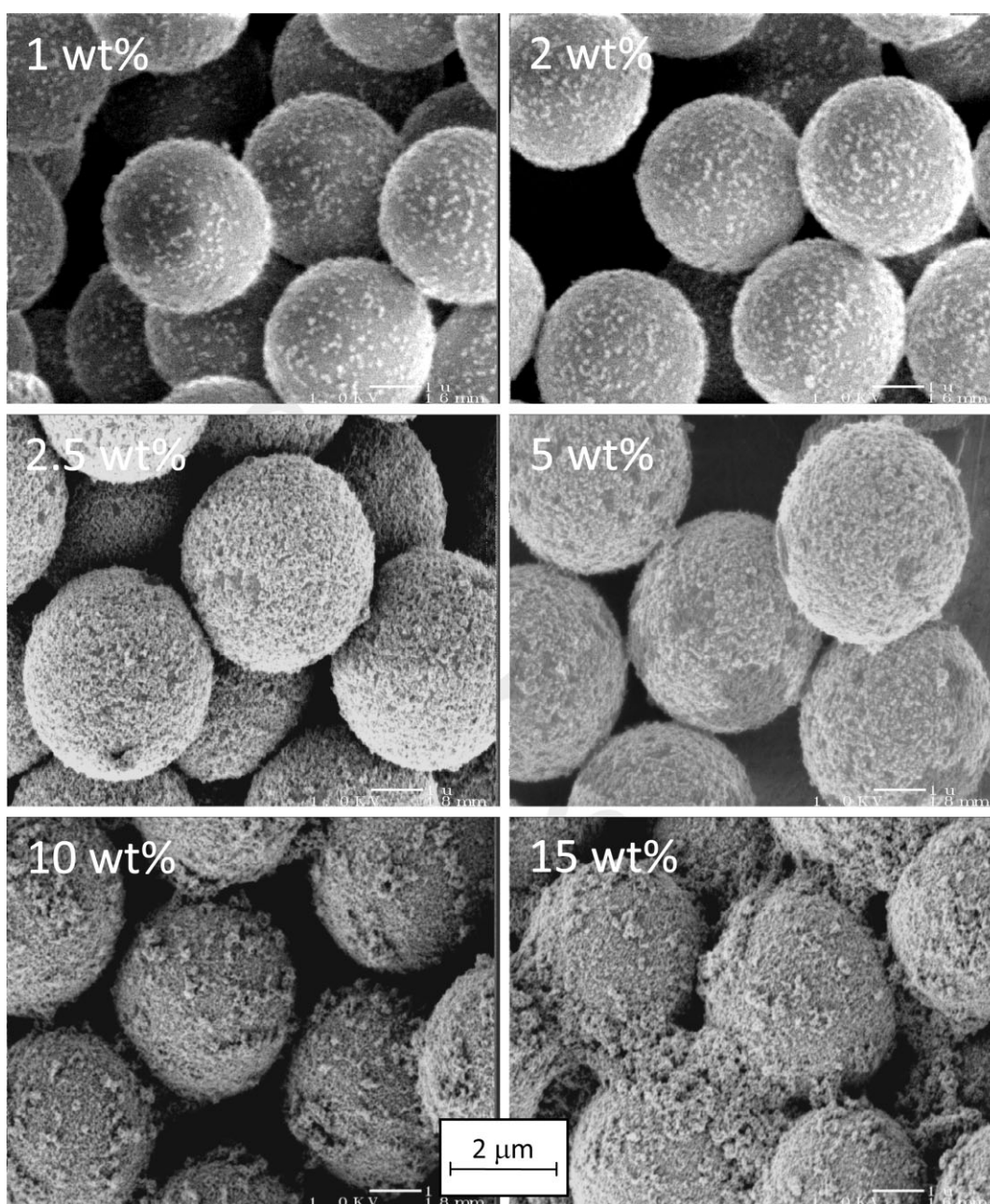
Figure 1 SEM micrographs of PMMA/carbon black heteroaggregated latexes prepared with different amounts of carbon black (wt % based on PMMA) in methanol; 5 wt % PMMA.
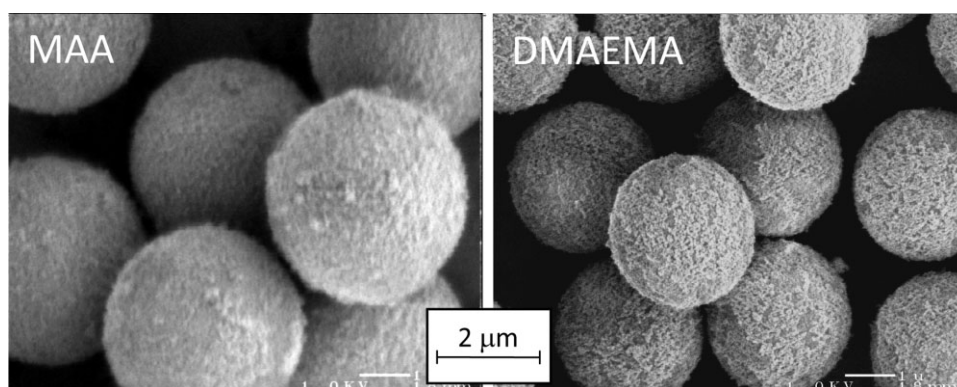
Figure 2 SEM micrographs of PMMA/carbon black heteroaggregated latexes prepared with particles functionalized with methacrylic acid (MAA) and dimethyl aminoethyl methacrylate (DMAEMA); 5 wt % PMMA and 5 wt % carbon black (based on PMMA).

carbon black, with small aggregates of carbon black attached to the PMMA particles surface. For 2.5 or 5 wt % carbon black the particles show a uniform layer of carbon black. However, increasing the amount to 10 wt %, it can be observed that some excess carbon black forms small aggregates on the surface of the particles. Further increasing the carbon black to 15 wt %, there is a large excess of carbon black that does not aggregate onto the surface of the particles.

Effect of the surface functional groups

PMMA particles prepared with different functional comonomers, namely methacrylic acid (MAA) (MMADP-2) and dimethylaminoethyl methacrylate (DMAEMA) (MMADP-4) were applied in heteroaggregation experiments with carbon black (5 wt % respect to the polymer) to investigate the effect of the chemical nature (acidic vs. basic) of the surface of the particles on the heteroaggregation. In all cases, a black sediment and clear supernatant were obtained after sonicating the latexes with carbon black. SEM images in Figure 2 indicate that, independent of the type of surface group, the particles were fully covered by a uniform layer of carbon black. No effect of the functional group type was observed in this system.

Effect of the dispersion medium

Several experiments were performed to check whether the continuous phase plays an important role in the heteroaggregation phenomenon. Previously cleaned PMMA particles were transferred to water and subjected to the aggregation procedure with 5 wt % carbon black (with respect to the polymer). The results obtained for heteroaggregation in methanol, ethanol, and water are shown in Figure 3 for homopolymer PMMA latexes. In all cases, a

black sediment and clear supernatant was obtained. It can be observed that when the heteroaggregation was carried in methanol or ethanol, a uniform layer of carbon black appears on the surface of the particles, while a less uniform layer appears when the heteroaggregation was carried in water. The same difference between methanol and water was found for particles prepared with MAA or DMAEMA.

Polystyrene

The heteroaggregation of carbon black on PS particles was also investigated. Several polystyrene particles (homopolymer (SDP-1), containing acidic (SDP-2) or basic groups (SDP-3)) were heteroaggregated with 5 wt % carbon black (based on PS) in methanol. Figure 4 shows the SEM micrographs of the heteroaggregated latexes. The carbon black shell is less uniform than that obtained for PMMA particles. Small aggregates of carbon black particles can be observed on the surface of the PS particles. For the homopolymer PS particles and those prepared with DMAEMA, black sediment and clear supernatant were obtained after sonication. However, for the latex prepared with MAA, black sediment and black supernatant were obtained. This result suggests that some species desorbs from the PS particles during sonification, and some of these adsorb onto the surface of the carbon black stabilizing it to some extent. This is despite the extensive cleaning procedure applied to the particles as described earlier.

Poly(*n*-butyl acrylate)

Heteroaggregation of PBA latexes (BADP-1, BADP-2, BADP-3, BADP-4) with carbon black was also carried out in methanol. In all cases, black sediment was obtained and only the particles prepared with DMAEMA (BADP-3) produced a black supernatant
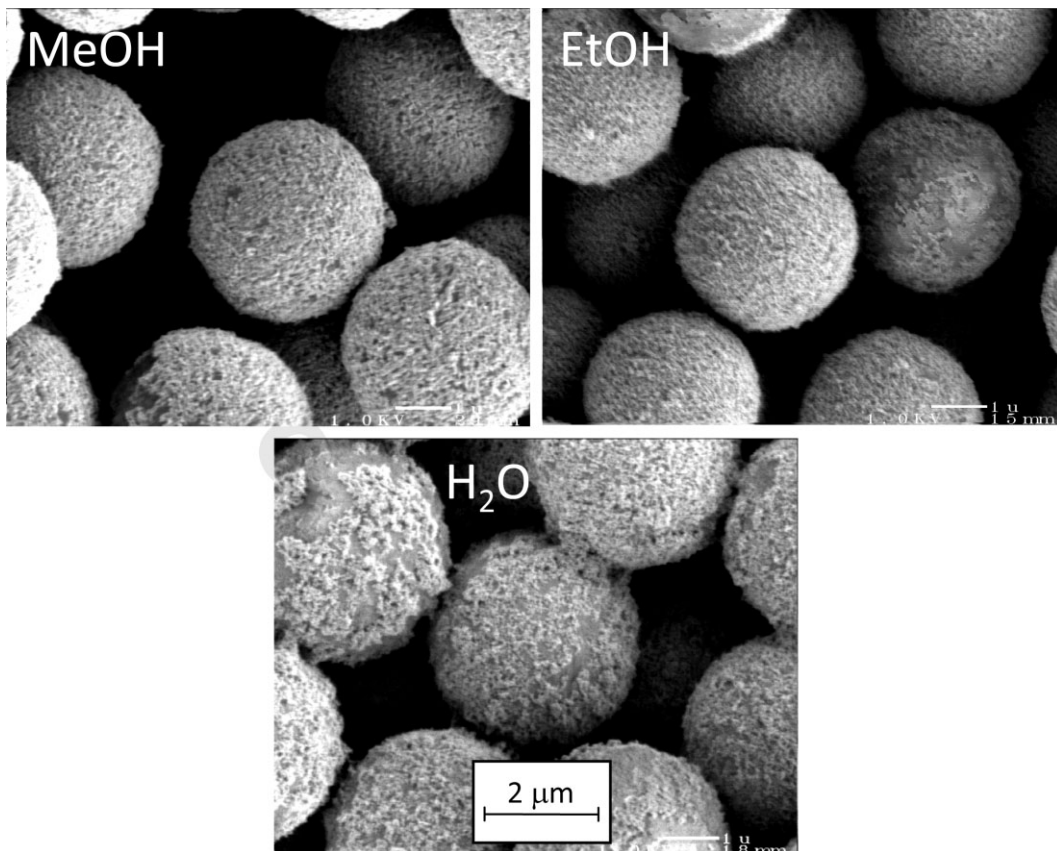
Figure 3 SEM micrographs of PMMA/carbon black heteroaggregated latexes in different media; 5 wt % PMMA and 5 wt % carbon black (based on PMMA).
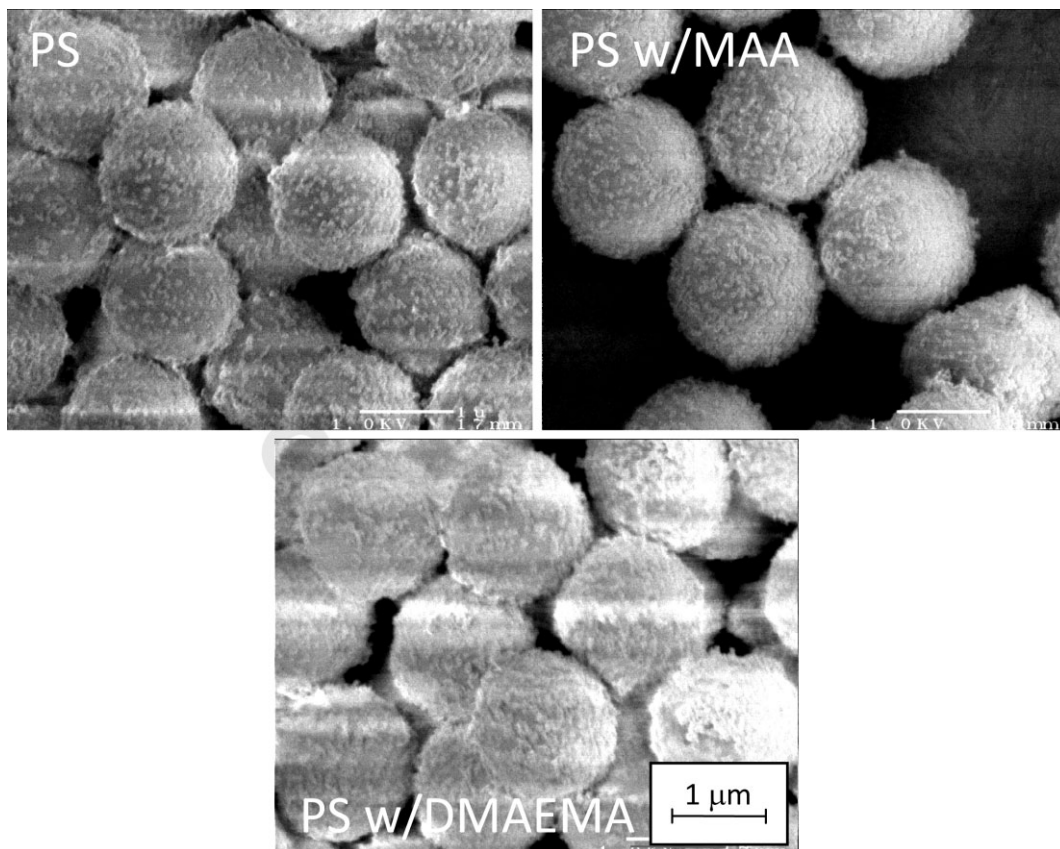
Figure 4 SEM micrographs of different composition PS latexes heteroaggregated with carbon black in methanol; 5 wt % PS and 5 wt % carbon black (based on PS).

following sonication, indicating again some desorption of a species able to stabilize the carbon black.

The PBA latexes were also transferred to water to try the heteroaggregation, but all the latexes coagulated upon transfer.

Other latexes

Micron size PMMA copolymer latexes prepared with HEMA (MMADP-7) and GMA (MMADP-8) were also applied successfully in heteroaggregation experiments with carbon black, although the 5% pigment on polymer was excessive for the large poly-(MMA-co-HEMA) particles (6 μm).

A number of submicron latexes (400 nm anionic PS, 344 nm cationic PS, 700 nm anionic PS) prepared by emulsion polymerization techniques were also tested but failed to produce particles where only the carbon black aggregated with the substrate particles. In these cases, heteroaggregation was either poor or the latexes coagulated during the preparation process.

Encapsulation

After establishing the conditions to successfully heteroaggregate the carbon black onto the surface of the micron-size polymer particles prepared by dispersion polymerization, methods were investigated to ensure that the pigment remained permanently attached to the surface of the polymer particles. This was done as it was noted that in the presence of any stabilizer, the pigment particles could become stabilized. This could be a consequence of adding the heteroaggregated system to another latex (such as a binder) containing a surfactant and subjecting the system to shear sufficient to remove the pigment from the surface of the particles. Two approaches were investigated: (1) swelling the polymer with a solvent such as toluene; and (2) performing seeded polymerizations of the aggregated particles. The first method was intended to plasticize the polymer, allowing it to engulf the pigment to some extent. The latter method could fix the pigment by overcoat-

ing (encapsulating) it with newly formed polymer and/or engulfing the pigment through the plasticizing effect of the monomer.

Dynamic swelling of aggregate composite latexes with toluene

The swelling of PMMA particles heteroaggregated with carbon black was carried out by the dynamic swelling method[23] under the conditions listed in Table VI. The dynamic swelling procedure was carried out in a three-neck reaction flask immersed in a water bath at 20°C and equipped with a Teflon stirring paddle. Heteroaggregated PMMA seed particles were dispersed in ethanol/water solutions containing PVA (poly(vinyl alcohol); degree of hydrolysis 87–89%, molecular weight 88,000, Acros) and different amounts of toluene. Then 53 g of an aqueous PVA solution (0.15 wt %) was fed to the dispersions via syringe pump. This procedure is intended to drive the solvent into the particles by reducing its solubility in the continuous phase.

Following swelling of the particles with toluene, the particles were again examined via SEM for evidence of engulfment of the pigment by the polymer. None was found. In fact, at the higher levels of toluene ($\geq$1 : 4 seed : toluene) it was clear that some of the carbon black had desorbed from the particles, also indicated by a black sediment in the swollen latex, where the swollen particles had creamed owing to their reduced density. This became more severe with increased toluene. Obviously, swelling the polymer did not lead to any improved compatibility between the pigment and polymer but rather seemed to reduce it. This suggests that the second technique, namely seeded polymerization of the PMMA particles, should be carried out with a polymer:monomer ratio not higher than 1 : 2.

Seeded polymerizations

In a second attempt to fix the pigment to the polymer, seeded polymerizations were carried out. Three

TABLE VI
Recipe for the Dynamic Swelling of PMMA Heteroaggregated Particles With Toluene

Ingredient	Initial charge (g)	Feed (g)
PMMA heteroaggregated with carbon black (MMADP-5)	0.26	–
Ethanol	15.5	–
PVA	0.06	0.0795
Toluene	(DS3) 0.26 (seed : toluene = 1 : 1)	–
	(DS4) 0.52 (seed : toluene = 1 : 2)	
	(DS5) 1.04 (seed : toluene = 1 : 4)	
	(DS7) 1.56 (seed : toluene = 1 : 6)	
Water	9.94	52.92

TABLE VII
Recipe for the Seeded Polymerization of PMMA
Particles Heteroaggregated with Carbon Black
(Reactions MMADS and SDS)

Ingredient	Initial charge (g)	Feed[a] (g)
Latex PMMA heteroaggregated with carbon black (MMADP-5)	0.26	–
Ethanol	15.5	–
Water	9.94	52.92
PVA	0.06	0.0795
MMA or S	1.04	–
V-70	0.052	–
$CuCl_2 \cdot 2H_2O$	0.13	–

[a] 53 of PVA aqueous solution (0.15 wt %) added over 3 hrs.

approaches were investigated, two by batch polymerization and one by semi-continuous polymerization. The first set of batch polymerizations employed the dynamic swelling procedure described previously whereas the second employed a more conventional seeded method.

Two reactions were carried out following dynamic swelling, one with MMA and a second with styrene. In reaction designated MMADS (MMA monomer via dynamic swelling), the procedure was as follows. The PMMA particles heteroaggregated with carbon black were swollen with monomer via the dynamic swelling method. The procedure was carried out under the conditions listed in Table VII. PMMA seed particles were dispersed in homogeneous ethanol/water solutions by dissolving the MMA (or S), 2,2'-azobis-(2,4-dimethyl-4-methoxy valeronitrile) (V-70, Wako) and poly(vinyl alcohol) (PVA, degree of hydrolysis 87–89%, molecular weight 88,000, Acros). Then 53 g of a PVA solution (0.15 wt %) was added to the dispersions at 20°C over 3 h. Cupric chloride

$(CuCl_2 \cdot 2H_2O$, Sigma-Aldrich) as a water soluble inhibitor was added to suppress the nucleation of submicron-sized polymer particles.

Once the dynamic swelling procedure was completed, the reaction mixture was transferred to a bottle, purged with nitrogen for 5 min, and then placed in a bottle polymerizer unit and the reaction was carried out at 30°C by end-over-end rotation at 30 rpm for 48 h.

Reaction SDS (styrene via dynamic swelling) was carried out following the same procedure but using S monomer instead of MMA.

After carrying out reaction MMADS for 48 h, SEM examination revealed that the particle diameter remained the same as before the polymerization. The MMA did not polymerize inside the particles and did not create a shell. The monomer polymerized mainly in the aqueous phase giving secondary particles with an average diameter of 230 nm as measured by dynamic light scattering (Nicomp, model 370).

Since styrene has a significantly lower water solubility, reaction SDS was carried out using it instead of MMA to reduce the extent of secondary nucleation. SEM images in Figure 5 confirm that the particles grew to a size $\sim$ 1.25 μm larger than the heteroaggregated seed particles, which is still less than the theoretical size indicating that secondary nucleation was not completely avoided by employing styrene. Although some pigment seems to be on the surface of the particles, microtoming is required to determine the internal morphology. Other images revealed that the particle size distribution was bimodal with a population of larger particles resulting from some limited aggregation of the seed particles. The recipe and polymerization conditions require some adjustment to eliminate this.

A series of seeded polymerizations, again using MMA as the main monomer, were carried out with
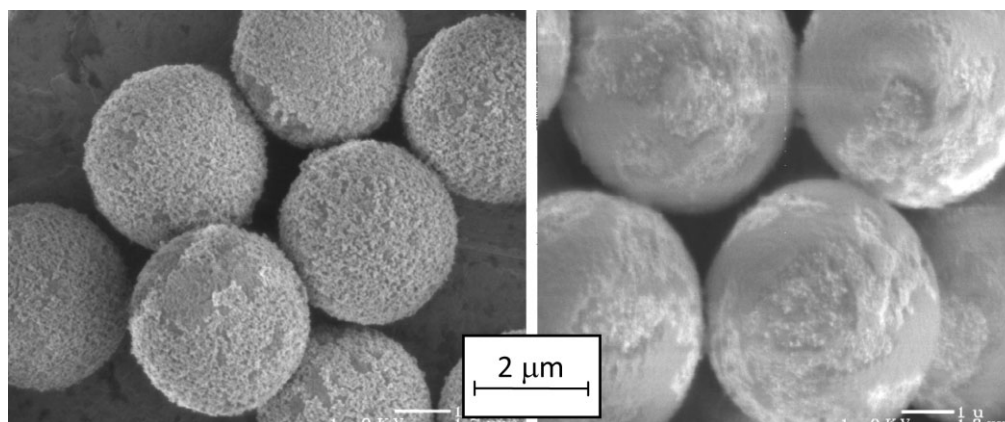
Figure 5 SEM micrographs of PMMA latex heteroaggregated with carbon black, before (a) and after (b) the seeded polymerization with styrene (reaction SDS).

TABLE VIII
Recipes for the Seeded Polymerization of PMMA Particles with and Without Heteroaggregated Carbon Black

Ingredient	MMASB-2 (MMASB-2CB)[a]	MMASB-3 (MMASB-3CB)[a]	MMASB-4 (MMASB-4CB)[a]
MMADP-3 (heteroaggregated with carbon black)	0.26	0.26	0.26
PVA, g	0.159 (0.3)[b]	0.159 (0.3)[b]	0.159 (0.3)[b]
MMA, g	0.208	0.208	0.208
HEMA, g	–	0.013	–
BuA, g	0.052	–	–
t-BPO, g	0.0522 (0.1)	0.0522 (0.1)	0.0522 (0.1)
SFS, g	0.0522 (0.1)	0.0522 (0.1)	0.0522 (0.1)
FES, g	0.0522 (0.1)	0.0522 (0.1)	0.0522 (0.1)
CuCl$_2\cdot$2H$_2$O, g	0.13 (0.24)	0.13 (0.24)	0.13 (0.24)
Water, g	53.341	53.341	53.341

[a] Two parallel reactions are represented by each column: using seed with and without carbon black (CB).
[b] Wt% based on water in parentheses.

the recipes given in Table VIII. Seed MMADP-3 (PMMA with no surface groups) was used with (designated by a CB suffix) and without heteroaggregated carbon black, the latter reactions serving as control experiments. BuA and HEMA comonomers were employed in reactions MMASB-2(CB) and MMASB-3(CB), respectively, in weight ratios of 80/20 MMA/BuA and 95/5 MMA/HEMA.

The procedure used in these polymerizations is as follows. First, the seed, stabilizer, and cupric chloride were mixed in a bottle for 24 h by end-over-end rotation. Then the monomer and t-BPO were added and the system again mixed overnight. The SFS and FES were added, the system was purged with nitrogen, capped, and sealed. The bottles were then placed in safety baskets supported on a rotor, and were rotated end-over-end at 30 rpm in a constant temperature bath at 45°C. The reactions were carried out for 48 h.

Figure 6 shows SEM micrographs of the particles obtained from reactions MMASB-2 and MMASB-2CB. In both images, the particles show varying degrees of a convoluted surface structure. The pigment is visible on the surface of the particles; this is likely to be the thermodynamically preferred location. Apparently, the seeded polymerization did not result in an "encapsulating layer" of polymer over the pigment particle surface. Similar results were found for the other two recipes as well.

The three latexes prepared by seeded polymerization with the heteroaggregated particles (MMASB-2CB, MMASB-3CB and MMASB-4CB) were sonified in the presence of additional PVP K30 to determine whether the carbon black was detachable from the surface of the particles as would be the case for the heteroaggregated seed. This would be indicated by a stable black supernatant (free carbon black stabilized by PVP) above the sedimented seed particles.
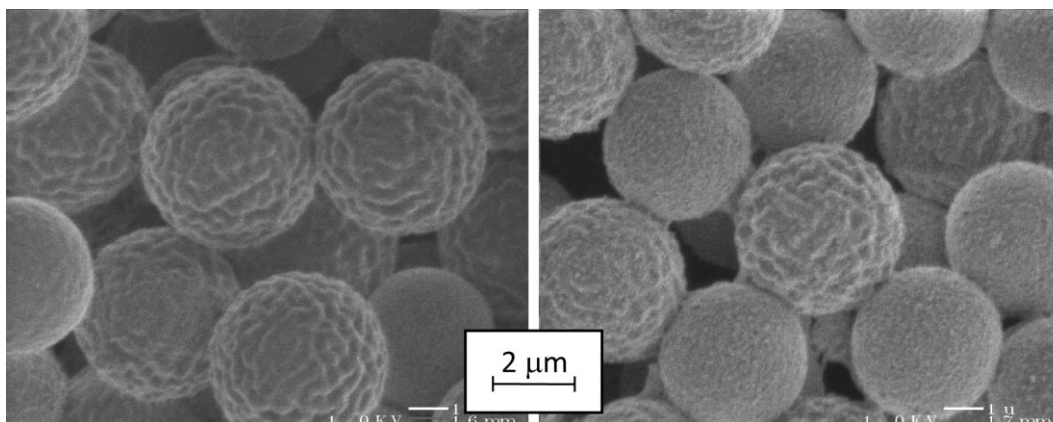
Figure 6 SEM micrographs of particles resulting from reactions (a) MMASB-2 and (b) MMASB-2CB.

TABLE IX
Recipe for Seeded Polymerization with MMA/HEMA of PMMA Particles Heteroaggregated with Carbon Black (Reaction MMASSB-4CB)

Ingredient	Initial charge (g)	Feed 1 (g)	Feed 2 (g)
MMADP-3 heteroaggregated with carbon black	1.0	–	–
PVA	0.159	–	–
MMA	0.95	0.95	–
HEMA	0.05	0.05	–
t-BPO	–	0.2	–
SFS	0.2	–	0.2
FES	0.2	–	0.2
$CuCl_2 \cdot 2H_2O$	0.2	–	–
Water	51.841	–	1.0

However, in all cases after sonicating the particles, the supernatant remained colorless. This indicates that the carbon black is irreversibly attached to the particles following the seeded polymerization process. Because the nanoparticles can still be seen, some partial engulfment by the polymer seems likely.

The final attempt at encapsulation was made by seeded semi-continuous polymerization. The recipe used is shown in Table IX. The seed was mixed with the PVA and the cupric chloride overnight. This was charged into a three neck, round bottom flask equipped with a mechanical stirrer with a Teflon stirring paddle, reflux condenser, and nitrogen inlet tube. The system was heated to 45°C, and the feed was started. One feed stream was composed of the monomers (MMA and 5 wt % HEMA) and the t-BPO, whereas the second feed stream was composed of the SFS and FES. These were fed over 30 min. Once the feeding was finished, the system was allowed to react for an additional 24 h.

SEM micrographs revealed that the particles did not increase in size indicating that secondary nucleation was extensive. A control reaction was carried out using seed particles with no carbon black and the results were similar; the diameter of the seed particles did not increase with the polymerization. The failure of the semi-continuous process, therefore, could not be attributed to the presence of the carbon black.

SUMMARY

A widely applicable shear-induced heteroaggregation process suitable for coating various types of micron-size polymer particles (PMMA (and copolymers), PS, and PBA) with nanosize pigments such as carbon black, has been investigated. Three requirements for the process have been defined: (1) the pigment must be broken down to its primary size by sonication; (2) the pigment must be unstable in the dispersion medium; and (3) the pigment must have affinity for the polymer substrate. Carbon black (Mogul L) could not be dispersed in methanol with sonication, the dispersion mixture quickly separating into an upper, transparent phase and a lower pigment phase. The heteroaggregation was successful using different polymer particles with varying properties. The mechanism of the attachment seems to be governed by the acid-base interactions between the surface sites of the particles and the carbon black. The Mogul L used in these experiments has strong acidic and basic groups in the surface that interact with the different polymers used.

Several procedures were investigated to permanently attach the pigment to the polymer particles: engulfment of the pigment by the polymer through swelling with a solvent or by creating a polymeric shell through seeded polymerization. The use of a solvent for the polymer such as toluene was not effective, and the carbon black particles remained in the polymer surface or detached themselves when relatively high amounts of toluene were added. Several batch and semi-continuous seeded polymerizations were carried out. The former method proved successful in permanently attaching the carbon black to the particles although the pigment could still be seen in the surface. Partial engulfment is considered to be the likely mechanism of attachment.

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