Water-Redispersible Low-T_g Acrylic Powders for the Modification of Hydraulic Binder Compositions

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ABSTRACT: Water-redispersible, low-T_g acrylic polymer powders are obtained in a free-flowing form by spray drying the structured aqueous dispersions. Powder sticking and caking phenomena are minimized thanks to the heterogeneous particle morphology achieved through a sequential polymerization technique. Redispersibility is reached by the presence of functional monomers containing acid groups, properly distributed in the polymer particles. The influence of the different synthesis parameters on the drying and redispersion processes is discussed. The acrylic powders developed here are well suited for the modification of Portland cement mortars, giving performances comparable to their corresponding "mother" latices. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1781–1787, 1999

Key words: acrylic powders; redispersibility; sequential polymerization; mortars

INTRODUCTION

Polymeric powders are used in several industrial fields. One of the most promising segments of this class of products concerns redispersible powders. In the presence of water and mechanical energy, these materials are easily reemulsified in the water phase, performing similarly to the "mother" latices.[1,2] This property can be achieved through the use of specific protective colloids, such as for poly(vinyl acetate)-based powders or, as in our case, by the presence of ionizable functional groups distributed in the polymer particle.

Redispersible powders find application in the formulation of coatings, cement admixtures, adhesives,[2–4] and microencapsulating agents for pharmaceuticals.[5,6] Especially in the field of polymer-modified hydraulic cement compositions, there is a growing trend toward the replacement of latex additives with redispersible powders.[7] Polymer resins bring several technical improvements to cement-based compounds such as better workability, higher tensile and flexural strengths, waterproofness, and good adhesion to different substrates.[8,9] One of the main advantages offered by redispersible powders over ordinary latices is their ability to be dry-mixed with hydraulic binders, aggregates, and other ingredients for the manufacturing of monocomponent formulations ready to use at the job site. Additional benefits are lower packaging and distribution costs, lesser environmental impact, and no need for protection against freezing and bacterial attack.

The preparation of powders from thermoplastic polymers with a low glass transition temperature (T_g < room temperature) is complicated by the high tackiness of the formed products. Particle

sticking can occur either during the drying process or during storage, under the influence of heat, pressure, and humidity. The recovery of such materials is possible only by using large amounts of external additives, as fillers and protective colloids, which surround the individual polymer particles, reducing their tendency to agglomeration.[10,11]

The sequential polymerization technique allows the creation of heterogeneous polymeric structures.[12] In particular, the synthesis of polymer particles characterized by a gradient of composition going from a soft nucleus, with a low T_g, to a harder external shell, with a high T_g, permits the recovery of powders even from elastomeric materials using the traditional drying methods.[13]

This article describes the preparation of low-T_g acrylic redispersible powders through an ordinary spray-drying process. Polymer dispersions are synthesized using a two-step emulsion polymerization process. Successively, they are atomized and transformed into free-flowing powders which are able to redisperse easily in water. The obtained powders are particularly useful for the formulation of one-pack hydraulic binder compositions with characteristics equivalent to their corresponding "mother" latices.

EXPERIMENTAL

Preparation of Latices

Commercial polymerization-grade reagents were used as received in all the syntheses. Materials include methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and acrylic acid (AA) from Atochem and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) from Lubrizol. The emulsion polymerizations were carried out in a 2-L thermostated glass reaction vessel fitted with a stirrer, reflux condenser, thermometer, dry nitrogen inlet, and dropping funnels.

The syntheses were conducted at 80°C using a two-step semicontinuous process with a preemulsion feed. The monomer weight ratio between steps 1 and 2 was fixed at 2:1, while the distribution of the hard and soft monomers in the two polymerization stages was varied in order to obtain polymers with different T_g's and degrees of functionalization. The acid monomer and the chain-transfer agent [n-dodecylmercaptan (NDM) from Fluka] were preferably located in the second preemulsion feed. Some experiments were carried

out with a classical one-step semibatch procedure for the prepartion of unstructured latices having identical monomeric compositions. The amounts of the initiator [potassium peroxidisulfate (KPS) from Carlo Erba] and surfactant [sodium dodecyl sulfate (SDS) from Cesalpinia Chemicals] were constant in all the trials. The polymerization pH was kept low (pH < 3) to reduce the tendency of acid monomers to polymerize in the aqueous phase. All the syntheses were carried out to more than 99.5% completion, giving rise to 40% solids latices. As an example, in Table I is reported the polymerization recipe for the preparation of latex PL 110.

Preparation of Powders

A laboratory spray-drying apparatus (Lab Plant Model SD04) equipped with a 0.7-mm static nozzle was used for the preparation of 50–100-g samples. Latices were neutralized with calcium hydroxide (Carlo Erba) to pH 8–10, optionally formulated with 5–10% weight by the weight of calcium carbonate (Microcal FM 150, from ECC), and diluted to a solid content of about 30%, suitable for the introduction into the spray-drying chamber via a peristaltic pump. Inlet temperatures of 110–130°C, outlet temperatures of 75–85°C, and feeds of 300–350 g/h were typical in our process. In some cases, the latices were spray-dried directly into the acid form.

Characterization of Latices and Powders

Table II gives information on the monomer composition, the type of functionalization, the structure, and the glass transition temperature of synthesized latices. Table III contains information about the formulation process and the characteristics (bulk density, redispersibility, pH of reconstituted latices) of the experimental powders. The bulk density was measured in accordance with ASTM B213. The water redispersibility was evaluated using the following qualitative procedure: One gram of dry powder was stirred for 5 min with 100 mL of deionized water and the resulting mixture was transferred into a sedimentation tube; the formation of a latex phase was observed and the amount of sediment measured after 1 and 24 h was used for the evaluation of the product water redispersibility. A good redispersibility, noted as "+++," is obtained when a latex phase without sediment is still present 24 h after the redispersion process. The powder is classified as

Table I Typical Recipe for Two-step Emulsion Polymerization (Latex PL110)

	Chemicals	Weight (g)	Feed Rate (mL/min)
Initial reaction charge	DI Water	700.0	
	SDS (30%)	1.7	
	Preemulsion 1	30.0	
	KPS (5%)	30.0	
Preemulsion 1	DI Water	175.0	6.0
	SDS (30%)	20.0	
	BA	368.0	
	MMA	152.0	
	MAA	1.5	
Initiator solution 1	DI Water	60.0	0.4
	KPS	0.8	
Preemulsion 2	DI Water	90.0	3.0
	SDS (30%)	8.0	
	BA	45.0	
	MMA	190.5	
	MAA	22.5	
	NDM	1.5	
Initiator solution 2	DI Water	40.0	0.2
	KPS	0.5	
Total		1907.0	

not redispersible, noted as "−," if it gives rise to sediment formation and a clear upper phase already after 1 h. The contemporary presence of a sediment and a latex phase after 24 h represents different degrees of redispersibility, noted as "+" and "++."

Preparation and Characterization of Polymer-modified Mortars

For the preparation of polymer-modified mortars, an ordinary Portland cement type 425 and a standardized multigranular sand with particle size from 0.1 to 2.0 mm and a specific gravity

Table II Latice Composition, Structure, and Characterization

Latex	BA/MMA (w/w)	Acid Monomer		Polymer Type	T_g (°C)[a]	T_g (°C)[b]
		Type	Concentration (meq/g of Polymer)			
PL 130	1.1	AMPS	0.18	Random	0	+16
PL 136	0.65	"	0.15	Sequential	+20	+15, +90
PL 124	1.1	"	0.18	"	0	−6, +88
PL 118	1.2	"	0.36	"	0	−10, +85
PL 140	0.63	MAA	0.15	Random	+20	
PL 122	1.2	"	0.46	"	0	+17
PL 137	0.63	"	0.15	Sequential	+20	
PL 120	1.4	"	0.18	"	−10	−18, +85
PL 110	1.2	"	0.36	"	0	−7, +89
PL 138	0.62	AA	0.15	"	+20	
PL 123	1.1	—	0.00	"	0	

[a] Fox equation (medium value).
[b] DSC, Perkin–Elmer Model Pyris 1 (20°C/min).

Table III   Polymer Powder Preparation and Characterization

Powder	Latex	Acid Type	Ca(OH)$_2$	CaCO$_3$ (%)	Bulk Density (g/L)	Redispersion	pH
PW 71	PL 136	AMPS	—	—	325	+++	2.1
PW 85	PL 118	AMPS	—	—		+++	2.0
PW 72	PL 137	MAA	—	—	323	+	3.2
PW 83	PL 110	MAA	—	—		+	
PW 73	PL 138	AA	—	—	360	+	3.0
PW 80	PL 123	—	—	—		−	
PW 70	PL 130	AMPS	Yes	10	<200	++	8.0
PW 68	PL 124	AMPS	"	5	330	+++	8.5
PW 58	PL 118	AMPS	"	"	347	+++	10.5
PW 74	PL 136	AMPS	"	"	408	+++	8.6
PW 75	PL 137	MAA	"	"	396	++	7.9
PW 81	PL 140	MAA	"	10	<200	+	8.1
PW 82	PL 122	MAA	"	"	<200	++	8.5
PW 84	PL 110	MAA	"	5	246	+++	10.6
PW 76	PL 138	AA	"	"	403	++	7.8

+++: very good; ++: good; +: sufficient; −: not redispersed.

of 2.68 g/cm^3 were used. A typical repairing mortar recipe was chosen for the evaluation of the developed powders' properties. A sand cement ratio (s/c) of 3 and a polymer cement ratio (p/c) ratio of 0.07 were applied in all the preparations. The water level was adjusted to achieve a proper flow for the application (w/c = 0.50–0.55); a suitable amount of a defoamer (Lumiten EP 3108, from BASF) was added to the mixture to obtain wet densities over 2.1 kg/dm^3. Fresh mortars were evaluated in terms of the initial flow (slump test according to UNI 7044) and the wet density (by measuring the mass required to fill a 400-mL cup). Specimens of 4 × 4 × 16 cm were prepared for the mechanical characterization and the water-absorption determinations after 7 days of immersion. A standard curing procedure (28-day water im-

mersion) for the unmodified mortars and a 28-day wet-curing procedure (23°C, 50% RH) for the polymer-modified specimens were applied.[8] The adhesion on standard concrete slabs was evaluated according to UNI 9532. The results of fresh and hardened mortar characterization are summarized in Table IV.

RESULTS AND DISCUSSION

As evidenced by the DSC traces (presence of two transitions), heterogeneous polymer particles characterized by a BA-rich soft nucleus (T_g < 10°C) and a harder thin shell (T_g > 85°C) are obtained when a sequential polymerization technique is adopted. Latices prepared with a standard one-step polymerization process show DSC

Table IV   Application of Powders in Polymer-modified Mortars

Mortar	Units	1	2	3	4	5
Powder		—	PW58	PW84		
Latex					PL118	PL110
Initial flow	(mm)	16.5	200	195	210	200
Wet density	(kg/dm^3)	2.250	2.125	2.170	2.100	2.150
Compressive strength	(MPa)	38.0	30.0	36.0	32.0	34.0
Flexural strength	(MPa)	7.5	9.0	9.2	8.5	9.0
Adhesion	(MPa)	1.5 A	2.3 C	2.5 C	2.5 C	2.5 C
Water absorption	(%)	5.5	5.0	4.1	4.2	4.0

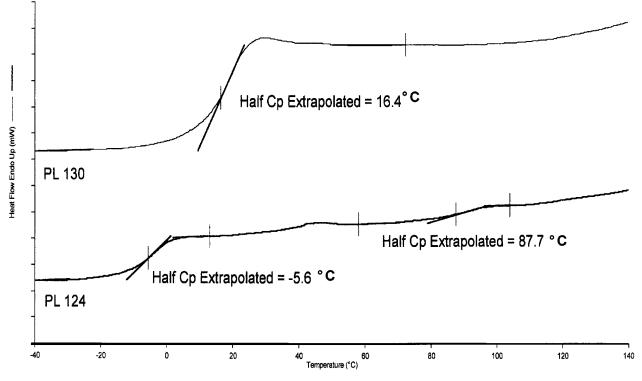A = adhesive failure; C = cohesive failure.

Figure 1 DSC curves for latices PL 130 (standard polymerization technique) and PL 124 (sequential polymerization technique).

profiles characterized by only one transition (Table II and Fig. 1). This behavior is typical for a random copolymer with a homogeneous composition. The analysis of the drying process gives us another tool to differentiate the structure of polymer particles. In fact, the sequentially polymerized latices, thanks to their hard external shell, are easily transformed into free-flowing powders with higher yields without requiring large amounts of $CaCO_3$ as an anticaking agent. On the contrary, the spray-drying process of low-T_g random polyacrylate water dispersions ($T_g < 20°C$) with the same chemical composition is more difficult. The corresponding powders present important aggregation phenomena, have very low bulk densities, and can be collected only in the presence of $CaCO_3$ (Table III, PL 130, 140, 122). These results provide a good correlation between the scheme of the synthesis and the polymer structure. Further details on the drying process and the relationships between the synthesis criteria and the powder formation were reported elsewhere.[13]

Water redispersibility is achieved by the incorporation of monomers bearing acid groups into the polymer chain. The effect of the type of func-

tional monomer used, its concentration, and distribution into the polymer structure on the powder behavior is discussed below. Three acid monomers were evaluated: the first containing strong acid groups (AMPS, $pK_a \approx 1$) and the others with weaker acid groups (MAA, $pK_a = 4.66$, and AA, $pK_a = 4.25$).

Effect of Latex Structure

A comparison between the latices obtained by the one-step polymerization (PL 140/MAA content = 0.15 meq/g; PL 130/AMPS content = 0.18 meq/g) and those prepared with the sequential polymerization technique (PL 137/MAA content = 0.15 meq/g; PL 124/AMPS content = 0.18 meq/g) was made. As evidenced in Table III, the structured polymer powders show a better water redispersibility with respect to the corresponding "random" polymers. In particular, random MAA-containing products are not fully redispersible, unless the acid content becomes relatively high, as in product PW 82, derived from latex PL 122 (MAA content = 0.46 meq/g). In fact, in spite of the MAA high water solubility, during random polymerization, a part of the acid monomer is

buried inside the latex particles[15,16] and the concentration of acid groups present on the surface of the particles is insufficient to give good water redispersibility. The powder obtained from the desiccation of latex PL 123 is obviously not redispersible due to the absence of polar acid groups.

Effect of Acid Type

The use of AMPS allows one to obtain powder redispersions at a lower acid group molar concentration. The comparison between similar polymers containing the same amount of acid groups (0.15 meq/g), —SO_3H in the former (PL 136) and —COOH in the latter (PL 137 and 138), points out that the carboxylic function gives a lower redispersibility efficiency and poorer stability of the reconstituted latices. Carboxylated powders perform better at a higher acid-group concentration (PL 110). The formation of larger amounts of water-soluble oligomers can provide an explanation of the good stability given by AMPS functionalization.

Effect of pH

Carboxylated polymers become water redispersible only after neutralization with strong bases like calcium hydroxide. The free —COOH groups' ionization degree is too low to guarantee the reemulsification in an acid environment. The —SO_3H-functionalized powders redisperse easily also without acid-group salification. The high acid strength in this case is sufficient to promote the redispersion process even at low pH values (Table III, compare PW 71, 72, and 73 with PW 74, 75, and 76, respectively).

Application of Powders as Cementitious Mortar Modifiers for Concrete Repair.

The results summarized in Table IV show that the redispersible polymer powders (PW 58 and 84) perform similarly to the original latices (PL 118 and 110). All the main advantages expected from a mortar polymer modification such as better flexibility, lower water uptake, and good adhesion on a concrete substrate are fully achieved. Inferior compressive strengths showed by polymer-modified mortars, independently if a latex or a powder has been used, are a consequence of the wet density reduction due to air inclusion during mixing operations. Surfactants, usually present as minor ingredients in any emulsion recipe, can give rise to foam development in the phase of mortar preparation.

CONCLUSIONS

Sequential copolymerization allows one to obtain acrylic latices which are readily transformed into powders by a spray-drying process. This technique is particularly useful for low-T_g (< 20°C) powder preparation where a random polymerization procedure leads to sticky products almost unobtainable in a spray-drying desiccation.

The reemulsification process is achieved by the use of acid-functionalized monomers. A well-designed distribution of such monomers into the polymer particles permits a powder redispersibility at a lower acid content.

AMPS-containing polymers have excellent water redispersibility in comparison with MAA/AA-functionalized powders. Similar redispersion properties are obtained with a lower molar content of a —SO_3H monomer with respect to the carboxylated monomer. The neutralization process is not important for the redispersibility of AMPS-functionalized powders, making them applicable also in neutral or acid environments (noncementitious applications).

The low-T_g acrylic powders developed here are useful for the preparation of one-pack flexible cementitious compounds. The use of a powder instead of a latex gives equivalent performances and results which are advantageous either from an economical point of view (reduced transport costs due to the lack of water) or from an end-user point of view (easier handling, lower risk of dosage mistakes).

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