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Effect of molar mass on film-forming properties of self-crosslinking latexes based on structured acrylic microgels

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ABSTRACT

The influence of molar mass of the shell layer of latex particles having core–shell morphology on film-forming and final coating properties of self-crosslinking latexes based on keto-hydrazide crosslinking system was investigated. Structured latex particles were prepared by the semi-continuous non-seeded emulsion polymerization of acrylic monomers. The particle core was slightly crosslinked to prevent the copolymers forming the core phase from migration into the shell phase. The molar mass of copolymers forming the shell phase was gradually reduced by isooctyl 3-mercaptopropionate chain transfer agent included in the synthesis of the shell layers. The results confirmed theoretical predictions and revealed that even a slight amount of chain transfer agent added during the synthesis achieved a substantial lowering of minimum film-forming temperature and reduction of water sensitivity of latex coatings.

1. Introduction

Nowadays, environmental and legislation pressure has forced coatings industries to develop environmentally friendly coatings with less or ultimately zero VOCs (volatile organic compounds). Therefore, waterborne polymers, i.e., “latexes”, prepared via emulsion polymerization are of particular interest. Colloidal polymer particles may be tailored to exhibit a desired morphology, composition, particle size distribution, functional reactive groups and molar mass. However, common latex coatings have relatively poor water resistance and unsatisfactory film hardness, which limits their practical application in many fields. In order to improve their properties, the applications of the core–shell structured latexes, intra-particle crosslinking and self-crosslinking chemistry in emulsion polymers have been studied substantially in recent years [1–6].

The incorporation of crosslinking chemistry in waterborne coatings is recognized to provide a particularly effective means of enhancing the mechanical strength, chemical stability, and solvent resistance of the final film [7–11]. Recently, a system based on the reaction of a carbonyl pendant group on the dispersed polymer backbone with a diamine, especially where the diamine is the adipic acid dihydrazide (ADH), has been the subject of increased interest [12–19]. This chemistry, termed the keto-hydrazide reaction, offers the advantage of fast, ambient-temperature crosslinking in functionalized acrylic latex, when the dihydrazide is incorporated in the aqueous phase of the latex. Among the carbonyl functionalized monomers, diacetone acrylamide (DAAM) has attracted the most significant attention [20,21].

The molar mass distribution can strongly influence many physical properties of an emulsion coating polymer (e.g., glass transition temperature T_g, gel content, extent of polymer chains inter-diffusion during the coalescence period) [22]. In order to possess increased final coating properties, a balance between chemical crosslinking and polymer chain mobility resulting in sufficient inter-diffusion and entanglement of polymer chains during the particle coalescence stage has to be maintained [23]. By introducing the self-crosslinking chemistry in emulsion polymers, the physical and chemical integrity of latex films is enhanced, while the film formation process may be complicated. As a result, a precise control of latex copolymer particles structure from the point of view of the molar mass and its distribution is particularly important in the case of self-crosslinking latexes. By varying the molar mass of emulsion copolymers, desired film properties like hardness, or minimum film-forming temperature can be tuned. To the best of our knowledge, no investigations on the dependence of molar mass on film-forming and fundamental coating properties of

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Table 1
Composition and characteristics of self-crosslinking latexes based on structured microgels.

Sample	Composition of monomer feeds (wt.%) MMA/BA/MAA/AMA/DAAM/CTA		Viscosity (mPa s)	Particle size in the water phase (nm)	MFFT (°C)
	Core	Shell			
L0	48.5/48.5/1.5/1.5/0/0	47.5/47.5/1.5/0/3.5/0	18.0	116	13.3
L0.1	48.5/48.5/1.5/1.5/0/0	47.45/47.45/1.5/0/3.5/0.1	16.5	112	12.7
L0.75	48.5/48.5/1.5/1.5/0/0	47.12/47.13/1.5/0/3.5/0.75	11.2	108	9.2
L1.5	48.5/48.5/1.5/1.5/0/0	46.75/46.75/1.5/0/3.5/1.5	14.9	113	8.1
L2.5	48.5/48.5/1.5/1.5/0/0	46.25/46.25/1.5/0/3.5/2.5	12.3	107	5.2

self-crosslinking latexes were performed. This lack of information has motivated this present work.

The aim of the present study was to explore the film-forming and final coating properties of self-crosslinking latexes in relation to the molar mass distribution of the copolymer forming shell layer of structured acrylic microgels. The strategy was to have structured particles composed of an internally crosslinked core (to prevent the copolymers forming the core phase from migration into the shell phase) and a shell layer comprising DAAM repeat units (to provide for interfacial crosslinking by reaction with ADH added during latex formulation). The molar mass distribution of the copolymer forming the shell phase was systematically varied by the chain transfer agent included in the synthesis of shell layers and was determined using the size exclusion chromatography (SEC) combined with a multi-angle light scattering (MALS) detector.

2. Materials and methods

2.1. Materials

Self-crosslinking latexes investigated in this research work were synthesized of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), diacetone acrylamide (DAAM), and allyl methacrylate (AMA). All the monomers were purchased from Roehm (Germany). Disponil FES 993 IS (BASF, Czech Republic) was used as a surfactant and ammonium persulfate (Lach-Ner Company, Czech Republic) was utilized as an initiator of the polymerization reaction. Isooctyl 3-mercaptopropionate (Sigma–Aldrich, Czech Republic) served as a chain transfer agent (CTA). Adipic acid dihydrazide (ADH) was utilized as the crosslinker and was purchased from Sigma–Aldrich, Czech Republic. Tetrahydrofuran (THF, Sigma–Aldrich, Czech Republic) was used as the SEC carrier. All the chemicals were utilized as received without any further purification.

2.2. Latex preparation and characterization

Water dispersions of structured microgel particles were synthesized comprising a variable content of acrylic monomers (see Table 1). The core/shell weight ratio of the samples was 2/3, which means a shell thickness of about 26% of the particle diameter. The nature of acrylic monomers forming core and shell phases was chosen to achieve a calculated T_g (using the Fox equation [24]) of approximately 6–8 °C. A slight cross-linking inside the latex particle core was achieved by a controlled amount of AMA. The level of isooctyl 3-mercaptopropionate CTA included in synthesis of each of the shell layers was systematically varied. The shell layer included a constant amount of DAAM repeat units to provide ketone carbonyl functionalities for interfacial crosslinking by reaction with ADH added during latex formulation. To improve the colloidal stability of latexes and to ensure the acid catalysis of keto-hydrazide crosslinking reaction, carboxyl functionalities were introduced into the structure of core and shell layers by copolymerization with a constant amount of MAA into all the prepared copolymers.

Table 2
Recipe of emulsion polymerization.

Reactor charge	
Water (g)	80
Disponil AES 60 (g)	0.5
Ammonium persulfate (g)	0.4
Monomer emulsion (core)	
Water	50
Disponil AES 60 (g)	5.84
Ammonium persulfate (g)	0.32
Monomers (g)	80
Monomer emulsion (shell)	
Water (g)	90
Disponil AES 60 (g)	8.76
Ammonium persulfate (g)	0.48
Monomers (g)	120

For comparison and better interpretation of results, water dispersions of copolymers (without core–shell structure) having the identical composition as the shell layer of microgel particles (see Table 1, the composition of monomer feeds is listed in the column shell) were synthesized according to the procedure mentioned above. However, the step of core preparation was avoided. The recipe of emulsion polymerization remained similar as provided in Table 2, only a difference in avoiding the monomer emulsion forming core was obeyed. Similarly, the latex of copolymers having the identical composition as the core phase of microgel particles was synthesized, avoiding the step of shell preparation.

The latexes were produced in a 700 ml glass reactor by the semi-continuous non-seeded emulsion polymerization under nitrogen atmosphere at 85 °C. This procedure ensured relatively homogeneous latex particles of statistical copolymers. The reactor charge was put into the reactor and heated to the polymerization temperature. Then the monomer emulsion was fed into the stirred reactor at feeding rate about 10 ml/min in two steps (1. core preparation, 2. shell preparation). After that, during 2 h of hold period the polymerization was completed. The recipe of emulsion polymerization is shown in Table 2. The latex was cooled to room temperature and filtered to remove any coagulum. The pH was adjusted to 8.5 with ammonia solution. To produce self-crosslinking latexes of structured microgel particles, a 10 wt.% aqueous solution of ADH, in the amount corresponding to the molar ratio ADH:DAAM = 1:2, was added to the aqueous core–shell microgel dispersion with agitation.

The apparent viscosity of final latexes was measured by CSN ISO 2555 using a Brookfield viscosimeter, Model DV-1 at 100 rpm at 23 °C. The average particle sizes of structured microgels in the water phase were obtained from dynamic light scattering (DLS) experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). The DLS measurements were conducted at 25 °C. The concentration of the measured microgel dispersion was approximately 0.05 wt.% of solids. The minimum film-forming temperature (MFFT) was measured using the MFFT-60 instrument (Rhopoint Instruments, UK) according to ISO 2115. The MFFT is defined as the minimum temperature at which a film cast from the polymer dispersion becomes continuous and clear.