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Property study of structured self-crosslinking acrylic latex binder: effect of molar mass and particle design

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Abstract

In the present contribution, the optimization of coating properties of structured self-crosslinking latexes based on diacetone acrylamide and adipic acid dihydrazide crosslinking system by varying particle design and molar mass was investigated. Latexes were prepared by the semi-continuous non-seeded emulsion polymerization of methyl methacrylate, butyl acrylate, diacetone acrylamide and methacrylic acid as main monomers. Two series of latex particles of hard-core/soft-shell or soft-core/hard-shell

design were synthesized with a predominant soft phase. In both series, molar mass of the soft phase was gradually reduced by isooctyl 3-mercaptopropionate included in the synthesis. The results show that desired coating properties can be tailored successfully by varying the molar mass and particle design. Better properties exhibited coatings drawdowned from latexes of soft-core/hard-shell particle design. A moderate reduction of molar mass of emulsion copolymers caused a significant improvement of adhesion and blocking resistance, obviously due to enhanced coalescence leading to favoured inter-particle diffusion of copolymer molecules of reduced molar mass.

Keywords: Emulsion polymerisation; Core–shell latex; Molar mass; Keto-hydrazide crosslinking

1. Introduction

Currently, environmental and legislation pressure has driven coating industries to produce coatings with minimum content of volatile organic compounds (VOCs). Hence, waterborne latexes represent a promising alternative to organic solvent-based systems in coatings applications. Acrylic latexes are frequently used binders due to their low cost, and easy preparation. However, their performances such as relatively poor water resistance, surface tackiness and unsatisfactory film hardness limit their practical application in many fields. Therefore, conventional acrylic latex paint compositions are usually based on polymers with relatively high glass transition temperature (T_g) and coalescing agents that are VOCs. In order to reduce the level of VOCs and to improve the performance of latex coatings, the applications of structured core–shell latexes [1–4] and crosslinking chemistry in emulsion polymers [5–9] have attracted a considerable interest in recent years.

The use of structured core–shell latex particles in which two or more different polymers coexist allows an optimal combination of properties from both components. This largely depends on the morphological features of the latex particles; hence, the investigation of latex particle morphology and factors controlling it has been the goal of many scientists [10–12]. Structured polymeric materials exhibit properties that are often superior to those of their component homopolymers due to their morphological structure. Core–shell particles are often designed with the low T_g polymer forming a shell around the high T_g core [13]. In this hard-core/soft-shell morphology, the low T_g shell facilitates film-formation while the high T_g core enhances the mechanical properties of the film. Li et al. [14] evaluated the effect of different glass transition temperatures of core and shell phases finding that latexes with a high T_g core and a low T_g shell can coalescence better than the representatives with a low T_g core and a high T_g shell. When the traditional morphology is inverted, the high T_g polymer forms a shell around the soft, low T_g core [15]. The soft-core/hard-shell morphology has received less attention due to the fact that the high T_g shell not only limits polymer inter-diffusion across particle boundaries, but also restricts the mobility of the soft polymer in the particle core [16]. However, Santos et al. found [17] that core–shell latex particles with poly(*n*-butyl acrylate) cores and poly(methyl methacrylate) shells in the content of 20 wt. % formed films with good mechanical strength at room temperature. This combination of coalescent free film formation and good mechanical properties was attributed to inclusions of soft cores in a continuous matrix of deformed tough shells.

Among different crosslinking reactions, the keto-hydrazide self-crosslinking has been studied extensively [18–22]. The latexes based on diacetone acrylamide (DAAM) and adipic acid dihydrazide (ADH) self-crosslinking system can get cured rapidly at room temperature and do not need any additional crosslinker to be added before use. The reaction between the carbonyl functionalities of DAAM and hydrazide groups of

ADH proceeds rapidly at ambient temperature and is favored by the loss of water and the simultaneous decrease in pH arising from the evaporation of ammonia or amines during the film forming process [23]. The network formation mechanism based on the keto-hydrazide crosslinking reaction is depicted schematically in Fig.1. Nevertheless, 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 [24]. In order to obtain increased mechanical properties, chemical resistance, and high cohesive and adhesive strength, an emulsion coating polymer requires a balance between chemical inter-particle crosslinking and polymer chain mobility resulting in sufficient inter-diffusion during the particle coalescence phase. The compromise between these two antagonist properties can be tailored by a proper design of latex particles. Hence, a precise control of particle design is particularly important in the case of self-crosslinking latexes [25–27].

In our recent work [28] we focused on the effect of molar mass of shell polymer on coating properties of keto-hydrazide self-crosslinking latexes based on core–shell microgel particles. We have found that the reduction of molar mass of shell polymer improved significantly coalescence of latex particles resulting in decreased minimum film forming temperature and enhanced water resistance. As the self-crosslinking latexes based on DAAM and ADH crosslinking system are usually composed of core–shell particles with DAAM repeat units localized in the shell layer, the influence of structured particle design and morphology should be explored in particular. Nevertheless, no investigations on the influence of particle design concerning the self-crosslinking latexes have been published to the best of our knowledge so far and this lack of information has motivated the present work. This study assesses the combined effects of particle morphology, glass transition temperature and molar mass on coating properties of self-crosslinking latexes, confronting especially fundamental

characteristics of emulsion copolymers with end-use properties of coating films. These properties included minimum film-forming temperature, hardness, adhesion, blocking resistance and water sensitivity. The attention is focused on the optimization possibility of desired coating properties of self-crosslinking latexes as well.

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) and diacetone acrylamide (DAAM). All the monomers were purchased from Sigma–Aldrich Czech Republic). Disponil FES 993 (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, Lach-Ner Company, Czech Republic) was used as the solvent for molar mass distribution measurements. All the chemicals were utilized as received without any further purification.

2.2. Latex preparation and characterization

Two series of hard-core/soft-shell and soft-core/hard-shell latex particles, respectively, with a predominant soft phase were synthesized comprising a variable content of acrylic monomers (see Table 1). The core/shell weight ratio was 1/3 for the series of hard-core/soft shell particles and 3/1 for the series of soft-core/hard-shell particles. The nature of acrylic monomers was chosen to achieve a calculated target glass transition temperatures (using the Fox equation [29]) of soft and hard phases of

approximately 5 and 25 °C, respectively. Molar mass of the soft phase was gradually reduced by isooctyl 3-mercaptopropionate included in the synthesis. The shell layer included 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 MAA into all the prepared copolymers.

The latexes were produced in a 700 ml glass reactor by the semi-continuous non-seeded emulsion polymerisation 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 2 ml/min in two steps (1. core preparation, 2. shell preparation). After that, during 2 hours of hold period the polymerisation was completed. The recipe of emulsion polymerisation 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, a 10 wt.% aqueous solution of ADH, in the amount corresponding to the molar ratio ADH:DAAM = 1:2, was added to the aqueous dispersion with agitation. The solids content of final latexes was about 45 wt.%.

The apparent viscosity of final latexes was measured according to CSN ISO 2555 using a Brookfield viscometer, Model DV-1 at 100 rpm at 23 °C. The average particle sizes of latex particles 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 polymer dispersion was approximately 0.05 wt.% of solids and for each sample, averaged values of ten measurements were collected. 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.

2.3. Molar mass determination

In our recent paper [30] we compared and discussed the molar mass determination of structured emulsion copolymers by means of size exclusion chromatography (SEC) and asymmetric flow field flow fractionation (A4F), respectively, both separation methods being coupled with a multi-angle light scattering detector (MALS). It is known that SEC fails in case of polymer samples containing large branched macromolecules that elute abnormally or ultra-high molar mass fractions that can be degraded by shearing forces in SEC columns. On the contrary, the separation in A4F-MALS is not affected by stationary phase and is not limited by molar mass. Our results revealed that SEC-MALS was convenient for the characterization of low molar mass latex copolymers without crosslinked structure, whereas A4F-MALS was proved as a very efficient technique for the characterization of high molar mass emulsion copolymers and core–shell microgels as well. Based on this experience, the molar masses of latex copolymers were determined by means of either A4F-MALS or SEC-MALS, taking as the main criterion for the choice of the proper separation method the value of mass recovery of the given separation column. (Mass recovery is defined as the ratio of the amount of polymer sample eluted from the SEC column to the amount of polymer sample injected into the column.) Reduction in the mass recovery in the case of A4F separation indicates the penetration of oligomeric fractions through the semi-permeable membrane, whereas lowering the SEC column mass recovery suggests filtering out of ultra-high molar mass fractions of branched or crosslinked

macromolecules by the SEC column. Thus, higher-molar-mass samples characterized by almost full A4F column mass recovery and lowered SEC column mass recovery (below 90 %) were evaluated using A4F-MALS, whereas lower-molar-mass samples exhibiting a reduction in A4F mass recovery higher than 5 % and SEC mass recovery values close to 100 % were evaluated using SEC-MALS.

In the case of A4F-MALS, an instrumental setup consisted of an A4F system Eclipse 3+ (Wyatt Technology Corporation), a HELEOS MALS photometer and an Optilab rEX refractive index (RI) detector (both Wyatt Technology Corporation). The review of theoretical principles as well as the details of the A4F instrumentation can be for example found in the recent reference [31]. Both MALS and RI detectors operated at 658 nm. The instrumental set-up was completed with a Waters 2487 dual wavelength Absorbance detector that was set to the operating wavelength of 254 nm. A long channel with a wide 350 mm spacer and a regenerated cellulose 5 kDa membrane was used for the A4F separation using linear cross flow gradient from 3 mL/min to 0.1 mL/min within 15 min, followed by 30 min isocratic step at 0.1 mL/min and 10 min at zero mL/min. Elution and focusing steps (2 min each) preceded the injection + focusing step (3 min) that was followed by additional 10 min focusing. That means the elution started at 17 min.

In the case of SEC-MALS, an instrumental setup consisted of a set of two PL gel Mixed-B 300 mm x 7.5 mm columns (Agilent, USA), an Agilent 1100 Series HPLC pump and the same detectors as used for A4F. Tetrahydrofuran (THF) was used as the mobile phase for both SEC and A4F experiments at SEC flow rate and A4F detector flow rate of 1 mL/min. Samples of latexes without ADH were injected as solutions in THF in the volume of 100 μL and the concentration of about 0.2 % w/v. All prepared solutions were filtered with 0.45 μm filter before the injection into SEC columns or A4F channel. The data acquisition and processing were carried out by ASTRA 6 software

(Wyatt Technology Corporation). The MALS data were processed using Berry light scattering formalism. The *dn*/*dc* of copolymers was calculated based on the *dn*/*dc* values of parent homopolymers and the weight fractions of monomers in a given copolymer. The calculation of molar mass was performed assuming chemical homogeneity of the prepared copolymers. Although this assumption may not be completely fulfilled it must be taken in order to get molar mass from the MALS detector.

2.4. Gel content and glass transition temperature measurements

For the glass transition temperature (T_g) and the gel content measurements, specimen were prepared by pouring the latexes into a silicone mould. Films were formed by water evaporation at room temperature for a month. The T_g of the dried microgel copolymers was determined by means of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). The measurements were carried out at the heating rate of 10 °Cmin^{-1} with N_2 atmosphere. The testing temperature range was -80 to 120 °C. The gel content of emulsion copolymers was determined according to CSN EN ISO 6427 using a 24-hr extraction with tetrahydrofuran in a Soxhlet extractor. Around 1 g of the sample was dried in a desiccator overnight, and put into the thimble. After the extraction, the thimble was dried in an oven at 75 °C for 6 h, cooled in a desiccator overnight, and the gel content was calculated from the initial and final weights, assuming that the gelled material remained in the thimble.

2.5. Coating preparation and evaluation

The coating films with a wet thickness of 120 μm were cast on glass panels by drawdowning the self-crosslinking latexes using a blade applicator. No coalescing solvents were used. After curing at room temperature (23 °C) and 50 % relative humidity for 1 month, the resulting films were evaluated for their hardness, adhesion,

water absorption and blocking resistance. The hardness of test films was measured by the pendulum hardness tester with “Persoz” pendulum (BYK-Gardner, Germany) following CSN EN ISO 1522. The adhesion was evaluated by means of the pull-off test according to ISO 4624 using COMTEST®OP3P (Proinex Instruments, Czech Republic). All experiments were carried out at room temperature (23 ± 1 °C).

For evaluating the water absorption, specimens were prepared by pouring the latexes into a silicone mould. Films were air-dried at room temperature (23 °C) for a month. The water absorption by the latex films was measured by immersing samples in distilled water at 23 °C for 30 days. The water absorption, A is given by $A = 100(w_t - w_0)/w_0$, where w_0 is the sample weight before immersion and w_t is the sample weight after immersion in water. The swollen films were carefully removed from water, and water from the film surface was removed by touching the polymer with a filter paper. For each sample, five specimens of the approximate dimensions 20 × 20 × 0.75 mm^3 were tested and averaged values of the results were collected.

The coatings were evaluated for their blocking resistance as well. The blocking resistance was determined by drawdowning a 120 μm wet film on two individual glass panels. After drying for 5 h, 24 h and 10 days at room temperature (23 °C) and 50 % relative humidity, the individual samples were stacked face-to-face and a pressure corresponding to 2.98 kPa was applied for 24 h. The face-to-face samples were then released from each other and the surface damage was evaluated and ranked by degree: 1 – no blocking (films fall apart spontaneously); 2 – blocking in spots; 3 – blocking in small areas (under 1 cm^2); 4 – blocking in larger areas (over 1 cm^2); 5 – impossible separation of films.

3. Results and discussion

3.1. Molar mass versus particle design

Two series of structured latex particles differing in particle design were synthesized to have a predominant soft phase. Latexes of series A were based on hard-core/soft-shell particles, whereas latexes of series B were designed as soft-core/hard-shell particles. Compositions of the latexes are presented in Table 1.

Molar mass distribution curves obtained from A4F-MALS for emulsion copolymers of series A and B copolymerized at the CTA content 0, 0.1, and 0.25 wt.% in the soft phase are presented in Fig. 2. It can be seen clearly for both series that increasing the CTA content in the composition of monomer feeds forming the soft phase resulted in a shift of molar mass distribution curves to lower values. When performing polymerization without the CTA addition (curves 1, 2), a significant amount of high molar mass structures (of molar masses in the order of magnitude of 10^7 g/mol) represented by branched or even crosslinked molecules was formed due to inter-molecular chain transfer to polymer as a result of BA copolymerization [32]. The cumulative molar mass distribution curves indicate as well that all the given samples exhibited a pronounced content of low molar mass fractions below (10^5 g/mol), the content of low molar mass fractions in latex samples being increased with rising concentration of CTA in the soft phase of latex particles.

In order to get correct molar mass determination, the higher molar mass samples exhibiting no pronounced amount of oligomeric fractions that could penetrate through the semi-permeable membrane in A4F column were evaluated using A4F-MALS. Thus, the molar mass averages (especially M_n that reflects mainly the fractions with lower molar mass) obtained for these samples are believed to not be overestimated. On the contrary, the lower molar mass samples containing no significant amount of ultra-high molar mass macromolecules prone to shear degradation in SEC columns were evaluated using SEC-MALS. Hence, the molar mass averages (especially M_w) should not be underestimated and can be considered correct. The conditions for the choice of the

proper separation technique are given briefly in the text above and are discussed in more detail in the reference [30] as well.

The values of number-average molar mass, weight-average molar mass and dispersity (M_n, M_w, M_w/ M_n, respectively) of emulsion copolymers obtained from SEC-MALS and A4F-MALS, respectively, as a function of CTA content are shown in Table 3 and the weight average molar mass as the function of CTA is demonstrated also in Fig. 3. It was found for both series that increasing the CTA content in the composition of monomer feeds forming the soft phase resulted in a considerable decrease in the molar mass averages and dispersity of emulsion copolymers. The effect of molar mass reduction was manifested more significantly in the case of the weight-average molar mass which was strongly affected by the presence of high molar mass fractions. In the case of both series of latex copolymers, it is evident that a sharp drop in molar mass occurred particularly by using 0.1 and 0.25 wt. % of CTA, while at higher contents of CTA, the further molar mass regulation was influenced only slightly. Nevertheless, comparing the series A and B differing in particle design in terms of the location of the soft phase, a significant difference in molar mass at the same CTA content in the soft phase can be observed. Higher molar mass emulsion copolymers of broader dispersity were formed for the hard-core/soft-shell morphology of emulsion copolymers of series A (based on emulsion copolymers of soft shell layer with reduced molar mass).

Although the emulsion polymerization was performed at starved conditions ensuring an almost immediate reaction and conversion of supplied monomers, the covalent attachment of shell monomers, oligomers and macromolecules to core polymer may have occurred to some extent. This finding suggests swelling of the pre-formed core structures of latex particles by monomers fed in the second stage of emulsion polymerization (shell preparation) and polymerization of these monomers inside the core structure. During the shell preparation, shell monomers are believed to react

predominantly with each other, but the existing unemployed core polymers may participate in the shell polymerization owing to intermolecular chain transfer to polymer. Moreover, interpenetration and entangling between core and shell polymers may take place as well, depending on mobility, flexibility and polarity of core and shell copolymers. As a result, higher molar mass emulsion copolymers were probably formed in the case of hard-core/soft-shell morphology, which enables easier interpenetration and subsequent covalent bonding of incipient flexible shell copolymers chains onto the finished and more rigid core macromolecules.

Hence, it can be assumed that the referred prepared latex particles do not exhibit a clearly defined core–shell morphology, but may be considered rather as single-phase particles formed in a two-step process where swelling of the pre-formed core structures by shell monomers is followed by polymerization of these monomers with or without the active participation of the existing core polymers, the latter being highly influenced by mobility of the nascent shell polymer chains.

3.2. Properties of latexes and emulsion copolymers

All the tested self-crosslinking latexes exhibited negligible amount of coagulum (0.1 – 0.5 %) and were stable for over 12 months. Their composition and characteristic properties (particle size and viscosity) are listed in Table 1. The results showed that neither the viscosity nor the latex particle size was affected by particle design (consisting in different location of the predominant soft phase in latex particles) and also by the amount of the added CTA (more precisely by the molar mass of emulsion copolymers). Nevertheless, the MFFT values of the self-crosslinking latexes were shown to be influenced significantly by particle design and molar mass of emulsion copolymers, a demonstration is given in Table 3 and Fig. 4. It was expected that decreasing the molar mass of emulsion copolymers would result in a drop in MFFT

values owing to higher mobility and plasticization effect of low molar mass polymer molecules leading to enhanced coalescence at lower temperatures. This expectation was shown to be fulfilled only partly. Comparing the self-crosslinking latexes without molar mass regulation (A0 and B0) with latexes synthesized using the low concentration of CTA in monomer feeds forming the soft phase (A1, A2 and B1), the molar mass decrease of emulsion copolymers reaching the average M_w about 7.10^5 g/mol was shown to be connected with a slight elevation of MFFT values. This phenomenon is probably related to enhanced interpenetration, entangling and covalent bonding between core and shell polymers inside distinct latex particles, which was facilitated by increased mobility of lower molar mass polymer chains and resulted in formation of more rigid polymeric structures less susceptible to deform and interpenetrate during coalescence of latex films.

MFFT results also show that self-crosslinking latexes of series A based on hard-core/soft-shell particles exhibited lower MFFT values than latexes of series B based on soft-core/hard-shell particles. This finding let us assume that in spite of a significant interpenetration of core and shell phases during the synthesis, latex particles cannot be considered conclusively as single-phase particles of uniform statistical composition, however, a considerable gradient of chemical composition may occur along the latex particle diameter replicating the designed particle morphology (given predominantly by the composition of monomer feeds). Thus, the coalescence of particles designed as soft-core/hard-shell morphology was shown to be worsened.

Further, gel content of emulsion copolymers of both series, without and with the addition of ADH crosslinker into the aqueous dispersion was determined and the results are presented in Table 3. It was shown that samples A0 and B0 polymerized without CTA addition contained a small amount of gel as a result of inter-molecular chain transfer reactions. Gradual decrease in molar mass resulted in drop in gel content and

when reducing the molar mass below 7.10^5 g/mol, the gel was not formed any more. The phenomenon of decreased gel content with reduced molar mass was confirmed in the case of copolymer samples crosslinked with ADH as well. Nevertheless, the ADH-crosslinked copolymers exhibited markedly higher values of gel content in comparison with corresponding copolymers without ADH-crosslinking as a result of increased network density owing to keto-hydrazide crosslinking. It was shown as well that the samples of series A comprised more gel in comparison with samples of series B at the same CTA content in the soft phase. This effect is associated with higher molar mass of copolymers of series A and can be attributed to enhanced interpenetration and chemical bonding of nascent soft and flexible shell copolymer chains to finished core macromolecules resulting in increased gel formation. In the case of soft-core/hard-shell particle design, the inter-molecular chain transfer reactions were apparently suppressed due to lower mobility of nascent less flexible shell copolymer chains of higher T_g.

The effects of molar mass of emulsion copolymers and particle design on glass transition temperature of emulsion copolymers were investigated as well. It was shown that only one T_g was detected for all the prepared samples which suggests the formation of single-phase latex particles. Similarly to MFFT, the T_g of latex copolymers decreased with reducing their average molar mass with the exception of samples A1, A2 and B1 which exhibited higher T_g than samples A0 and B0 (having the highest molar mass copolymers of series A and B, respectively). A possible explanation for this fact was given in the previous text and probably consists in an increased extent of interpenetration between core and shell polymers due to enhanced mobility of less molar mass chains. In this way, physical entanglements could have been formed and subsequently might have been fixed into the polymer structure by the proceeding polymerization. Hence, the segmental mobility of the final macromolecular structure was decreased causing the elevation T_g.

The comparison of copolymers of series A and B at the same CTA content demonstrates the effect of particle design and morphology on glass transition temperature of emulsion copolymers. The copolymers of series A exhibited lower T_g than copolymers of series B, which correlates well with MFFT measurements. Enhanced hindering of segmental mobility in the case of soft-core/hard-shell particle design may be caused by more compact arrangement and increased attractive intermolecular forces of distinct macromolecules in latex particles, nevertheless further investigation of this phenomenon is needed. It can be observed as well that T_g values of copolymers after crosslinking with ADH were increased in contrast to copolymers without ADH-crosslinking, which reveals again clearly that the keto-hydrazide crosslinking reaction occurred during the film-formation of all the studied self-crosslinking latexes leading to intra- particle crosslinking (occurring between diacetone acrylamide groups within the same particle) or inter-particle crosslinking (occurring at the interface between particles).

3.3. Properties of coatings

It is known that latexes based on multiphase particles combining hard high T_g and soft low T_g phases are typically used to fulfill specific coating requirements, like increased blocking resistance [33]. Moreover, the self-crosslinking latexes are usually designed as core–shell latexes with DAAM repeat units incorporated into the polymer backbone of the shell layer, therefore the effects of particle design confronting polymer composition, T_g and molar mass on end-use coating properties should be explored in particular in the case of these coating binder systems.

The combined effects of particle design and molar mass of copolymers on hardness, adhesion, water absorption and blocking resistance of coating films drawdowned from self-crosslinking latexes are presented in Table 4 and Figs. 5-8. For

the sake of simplification, only the values of M_w are given. It should be noted that all the self-crosslinking latexes were able to form high-quality transparent films at ambient temperature and dry film thickness of the coatings was approximately 50 μm. It can be observed that all the investigated coating properties were influenced significantly by molar mass of emulsion copolymers and particle design. As expected, hardness of latex films (see Fig. 5) was deteriorated with lowering the average molar mass of copolymers in the case of latexes of both series due to plasticizing effect of low molar mass copolymers. This effect can be explained by the increased number of polymer chains ends having greater free volume. The exception are the coating samples A1, A2 and B1 which exhibited higher hardness than coatings A0 and B0 (based on the highest molar mass copolymers of series A and B, respectively). This finding corresponds to elevated T_g of these copolymers and its possible explanation based on more compacted molecular arrangement and attractive intermolecular forces has been given in the text above. It was also found that there was no significant difference in final hardness when comparing the particle design of both series, nevertheless, the samples of series B showed higher hardness at the similar average molar mass of copolymers, which is in a good accordance with T_g results and has been discussed previously.

Further, it was shown for latex coatings of both series that the adhesion measured using the pull-off test increased sharply with reducing the molar mass of emulsion copolymers (see Fig. 6). This finding obviously relates to increased number of low molar mass fractions ensuring favoured coalescence and also adhesion of final coating films to a substrate. It was demonstrated as well that reducing the weight average molar mass below ca. 150.10^3 g/mol lead to a decrease in pull-off strength. This phenomenon is probably associated with a loss of film cohesion owing to a pronounced shortening of the polymer chain length, which resulted in decreased number of chain inter-particle entanglements and gel forming chain crosslinks leading to deterioration of

latex coating cohesion. Surprisingly, the results of pull-off test also revealed that coatings cast from latexes of series A (based on particles of hard-core/soft-shell design) exhibited lower adhesion in contrast to coatings of series B (based on particles of soft-core/hard-shell design) at the comparable weight average molar mass of emulsion polymers. This effect can be attributed to higher concentration of more polar MMA building blocks in outer layer of latex particles in the case of series B, but more probably, to better cohesion of the coating films based on latexes of series B due to increased attractive intermolecular forces of distinct macromolecules in latex particles leading to favoured film cohesion.

The results of water absorption are depicted in Figure 7. It is evident that water sensitivity of latex coating films increased with lowering the molar mass of emulsion copolymers until reaching the weight average molar mass of about 3.10^5 g/mol in the case of the series A, and about 1.10^5 g/mol for the series B. The films based on emulsion copolymers of even lower molar mass (A5, B4 and B5) exhibited a sharp drop in water absorption. The water sensitivity of latex films is closely linked to coalescence quality: films made of well coalesced particles usually suffer from large water uptake after a long-term immersion in water, because the closed film structure hinders the extraction of emulsifiers and other water soluble components by water, which causes a greater water uptake due to osmotic pressure [34]. Hence, it can be assumed that lowering the molar mass of emulsion copolymers provided higher water sensitivity as a consequence of better coalescence of particles caused by favoured inter-diffusion of low molar mass polymer chains. On the contrary, the following reduction of polymer chain length resulted in worse coalescence due to suppressed formation of inter-particle entanglements and crosslinks. When comparing the water sensitivity from the point of view of particle design, it was shown that the soft-core/hard-shell designed particles (series B) provided films of lower water sensitivity, probably as a consequence of worse

coalescence. This phenomenon is in a good accordance with MFFT results and as discussed previously, may suggest a considerable gradient of chemical composition in latex particles replicating the designed particle morphology based on soft core surrounded by hard shell.

In addition to that, the pronounced effect of particle design on final coating properties was manifested in the case of blocking resistance (given in Fig. 8). The self-crosslinking latexes of series B (soft-core/hard-shell particle design) provided films of higher blocking resistance than the latexes of series A. This finding reveals again the existence of composition inhomogeneity inside latex particles approaching two-phase core–shell morphology. Thus, the particles of soft-core/hard-shell design were shown to exhibit enhanced blocking resistance owing to higher concentration of high T_g polymers in upper layers of latex particles. It should be mentioned that all the tested self-crosslinking latexes provided films that could be separated from each other even after 5 hours-long drying. Naturally, the blocking resistance was improved with increasing drying time in most cases, but the maximal blocking resistance was achieved already after 24-hours-long film drying. It was found for both series of latexes as well that the blocking resistance of coating films could be improved significantly by molar mass reduction of emulsion copolymers. The coatings based on A2, A3 or B1, B2 latexes exhibited improved blocking resistance in comparison with coatings cast from A0 or B0 latexes. This effect may be associated with better particle coalescence and T_g elevation of emulsion polymers, which has been already discussed in the text above.

4. Conclusions

In this study, we focused on the combined effects of particle morphology, glass transition temperature and molar mass on coating properties of self-crosslinking latex binders based on keto-hydrazide crosslinking system. We aimed to describe empirically

the optimization possibility of desired coating properties as well. The latexes were prepared by the semi-continuous emulsion polymerization of acrylic monomers. Two series of latex particles of hard-core/soft-shell or soft-core/hard-shell design were synthesized with a predominant soft phase. In both series, molar mass of the soft phase was gradually reduced by isooctyl 3-mercaptopropionate included in the synthesis. The results of molar mass measurements demonstrated that higher molar mass emulsion copolymers were formed at the same CTA content in the soft phase in the case of the hard-core/soft-shell particle design, obviously due to easier interpenetration and subsequent covalent bonding of incipient flexible shell copolymers chains onto the finished and more rigid core macromolecules. It was shown that only one T_g was detected for all the prepared emulsion copolymers which indicates the formation of single-phase rather than core–shell particle morphology. The copolymers of hard-core/soft-shell particle design exhibited lower T_g than copolymers of soft-core/hard-shell particle design. Enhanced hindering of segmental mobility in the case of soft-core/hard-shell particle design may be caused by more compact arrangement and increased attractive intermolecular forces of distinct macromolecules in these latex particles. Similarly to T_g, MFFT values of the self-crosslinking latexes were shown to be affected by particle design and molar mass of emulsion copolymers. The latexes based on hard-core/soft-shell particles exhibited lower MFFT values than latexes of based on soft-core/hard-shell particles, which suggests a considerable inhomogeneity of chemical composition along the latex particle diameter replicating the designed particle morphology.

The results of measurements of coating properties revealed that hardness of latex films was decreased with lowering molar mass of emulsion copolymers due to plasticizing effect of low molar mass copolymers. The exception represented the coating samples with slightly reduced molar mass which exhibited higher hardness than coating

based on the highest molar mass copolymers. This effect was shown to be in a good accordance with elevated T_g and MFFT of these copolymers and its possible explanation can be related to more compacted molecular arrangement resulting in less flexible polymer chains. Further, it was found that the initial reducing the molar mass of emulsion copolymers provided better adhesion and blocking resistance of coating films on one side, but increased water sensitivity on the other side, probably as a consequence of better coalescence of particles caused by favoured inter-diffusion of shorter polymer chains. The results also revealed that coatings cast from soft-core/hard-shell latexes exhibited lower water sensitivity, better adhesion and blocking resistance in contrast to coatings based on particles of hard-core/soft-shell design at the comparable molar mass of emulsion polymers obviously owing to higher concentration of high T_g polymers in the upper layer of latex particles.

Acknowledgements

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Table 1

Composition and characteristics of self-crosslinking latexes based on structured particles differing in particle design and chain transfer agent concentration in monomer feeds

Sample	Composition of monomer feeds (g) MMA/BA/MAA/DAAM/CTA		CTA content [a] (wt. %)	Viscosity (mPa.s)	Particle size in water phase (nm)
	Core	Shell			
Series A: Particles of hard-core/soft-shell in weight ratio 1/3, molar mass variation of shell					
A 0	30/19/1/0/0	68/75/3/4/0	0.0	26.2	115
A 1	30/19/1/0/0	67.95/74.9/3/4/0.15	0.1	20.0	123
A 2	30/19/1/0/0	67.82/74.8/3/4/0.38	0.25	24.2	101
A 3	30/19/1/0/0	67.65/74.6/3/4/0.75	0.5	27.1	96
A 4	30/19/1/0/0	67.25/74.25/3/4/1.5	1.0	34.7	102
A 5	30/19/1/0/0	66.5/73.5/3/4/3	2.0	30.1	99
Series B: Particles of soft-core/hard-shell in weight ratio 3/1, molar mass variation of core					
B 0	75.75/71.25/3/0/0	26.5/18.5/1/4/0	0.0	23.9	106
B 1	75.70/71.15/3/0/0.15	26.5/18.5/1/4/0	0.1	18.6	117
B 2	75.57/71.05/3/0/0.38	26.5/18.5/1/4/0	0.25	20.1	100
B 3	75.40/70.85/3/0/0.75	26.5/18.5/1/4/0	0.5	22.4	111
B 4	75.0/70.5/3/0/1.5	26.5/18.5/1/4/0	1.0	32.0	94
B 5	74.25/69.75/3/0/3	26.5/18.5/1/4/0	2.0	29.2	104

[a] CTA content is related to the total amount of monomer mixture (including CTA) forming soft core and soft shell phase, respectively.

Table 2

Recipe of emulsion polymerisation of self-crosslinking latexes of series A and B

	Series A	Series B
Reactor charge:		
Water (g)	80	80
Disponil FES 993 IS (g)	0.5	0.5
Ammonium persulfate (g)	0.4	0.4
Monomer emulsion (core):		
Water	37.5	112.5
Disponil FES 993 IS (g)	3.65	10.95
Ammonium persulfate (g)	0.2	0.6
Monomers including CTA (g)	50	150
Monomer emulsion (shell):		
Water (g)	112.5	37.5
Disponil FES 993 IS (g)	10.95	3.65
Ammonium persulfate (g)	0.6	0.2
Monomers including CTA (g)	150	50

Table 3

Effect of chain transfer agent concentration and particle design on molar mass averages (M_n, M_w), dispersity and glass transition temperature of emulsion copolymers and minimum film-forming temperature of self-crosslinking latexes

Sample	CTA content [a] (wt. %)	M_n (10^3g/mol)	M_w (10^3g/mol)	M_w/M_n	Without ADH		
					Gel content (wt. %)	T_g (°C)	Gel con
Series A: Hard-core/soft-shell particles, molar mass variation of shell							
A 0	0.0	240	5,641 [b]	23.5	5.5	20.9	
A 1	0.1	159	1,370 [b]	8.6	1.4	23.3	
A 2	0.25	122	746 [b]	6.1	0.2	22.8	
A 3	0.5	88	359 [b]	4.1	0.0	19.7	
A 4	1.0	91	291 [c]	3.2	0.0	18.3	
A 5	2.0	76	204 [c]	2.7	0.0	14.7	
Series B: Soft-core/hard-shell particles, molar mass variation of core							
B 0	0.0	221	2,592 [b]	11.7	1.1	25.8	
B 1	0.1	134	749 [b]	5.6	0.3	27.8	
B 2	0.25	103	328 [b]	3.2	0.0	25.6	
B 3	0.5	74	163 [c]	2.2	0.0	23.4	
B 4	1.0	56	111 [c]	2.0	0.0	22.7	
B 5	2.0	27	46 [c]	1.7	0.0	18.9	

Table 4

Comparison of final properties of ADH-crosslinked coating films cast from self-crosslinking latexes based on structured particles differing in molar mass and particle design

Sample	M_w (10^3g/mol)	Hardness (%)	Adhesion (MPa)[a]	Water absorption (%)
Series A: Hard-core/soft-shell particles, molar mass variation of shell				
A 0	5,641	37.8	0.35	49.4
A 1	1,370	41.6	0.49	53.4
A 2	746	39.6	0.62	55.1
A 3	359	36.3	0.73	69.4
A 4	291	34.4	0.83	74.5
A 5	204	25.8	0.94	41.7
Series B: Soft-core/hard-shell particles, molar mass variation of core				
B 0	2,592	39.7	0.49	42.7
B 1	749	40.8	0.76	45.7
B 2	328	39.5	0.94	51.1
B 3	163	35.3	1.48	71.6
B 4	111	32.4	1.12	30.3
B 5	46	24.0	0.84	27.2

[a] Maximal stress achieved during testing.

[b] Water absorption after a 30-days-long immersion in distilled water at 23 °C.

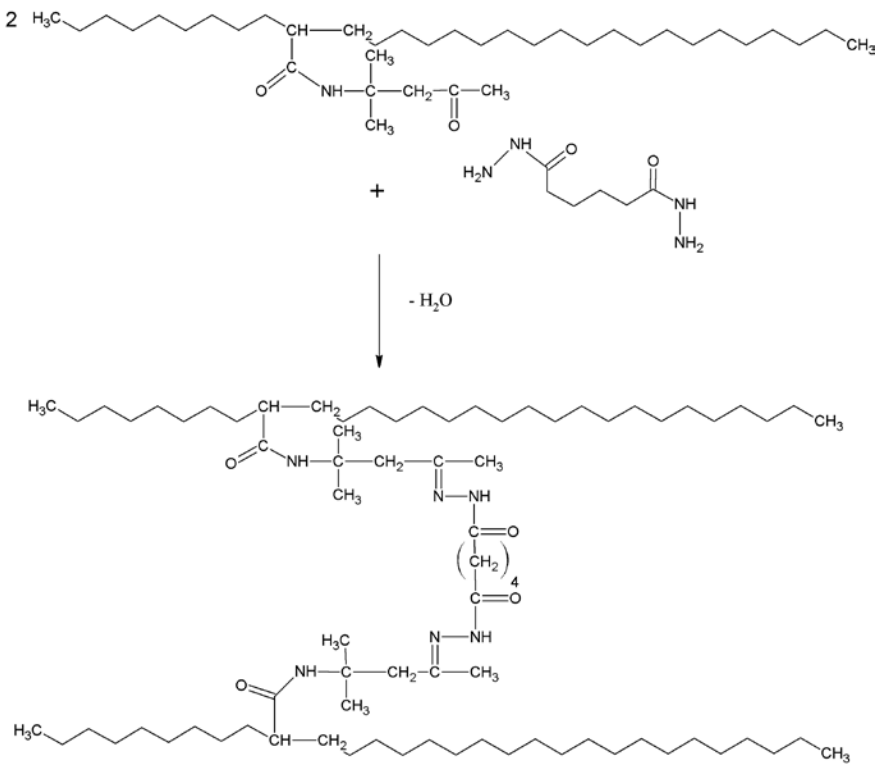

Fig. 1

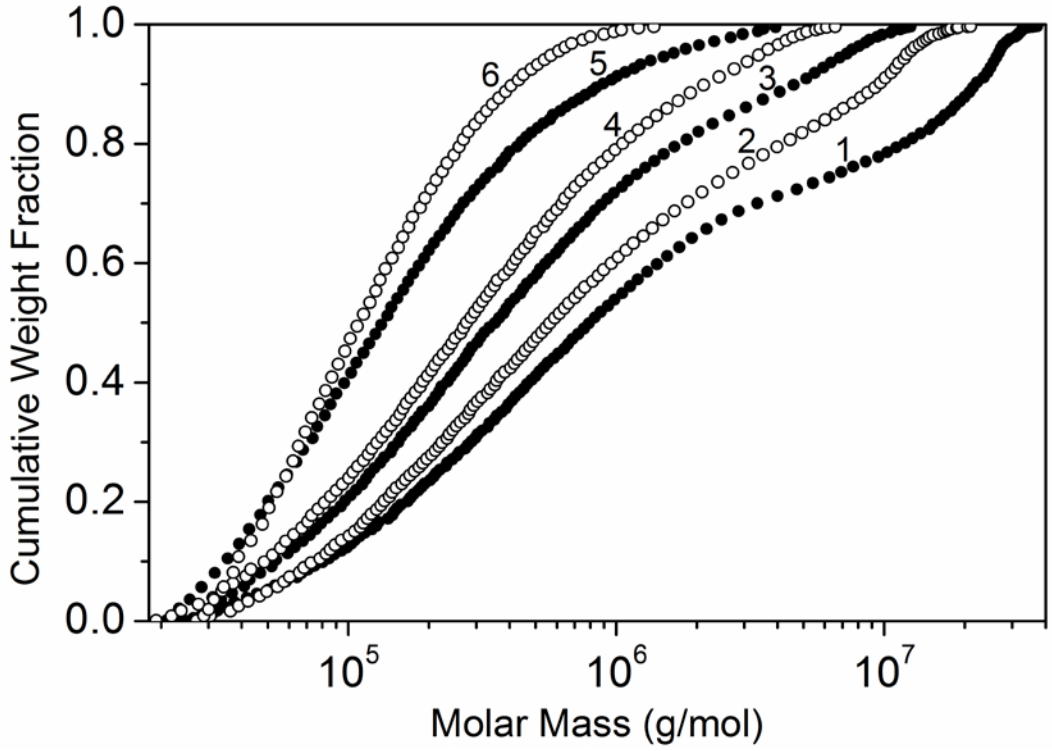
Cumulative Weight Fraction
Molar Mass (g/mol)
1.0
0.8
0.6
0.4
0.2
0.0
10^5
10^6
10^7
1
2
3
4
5
6

Fig. 2

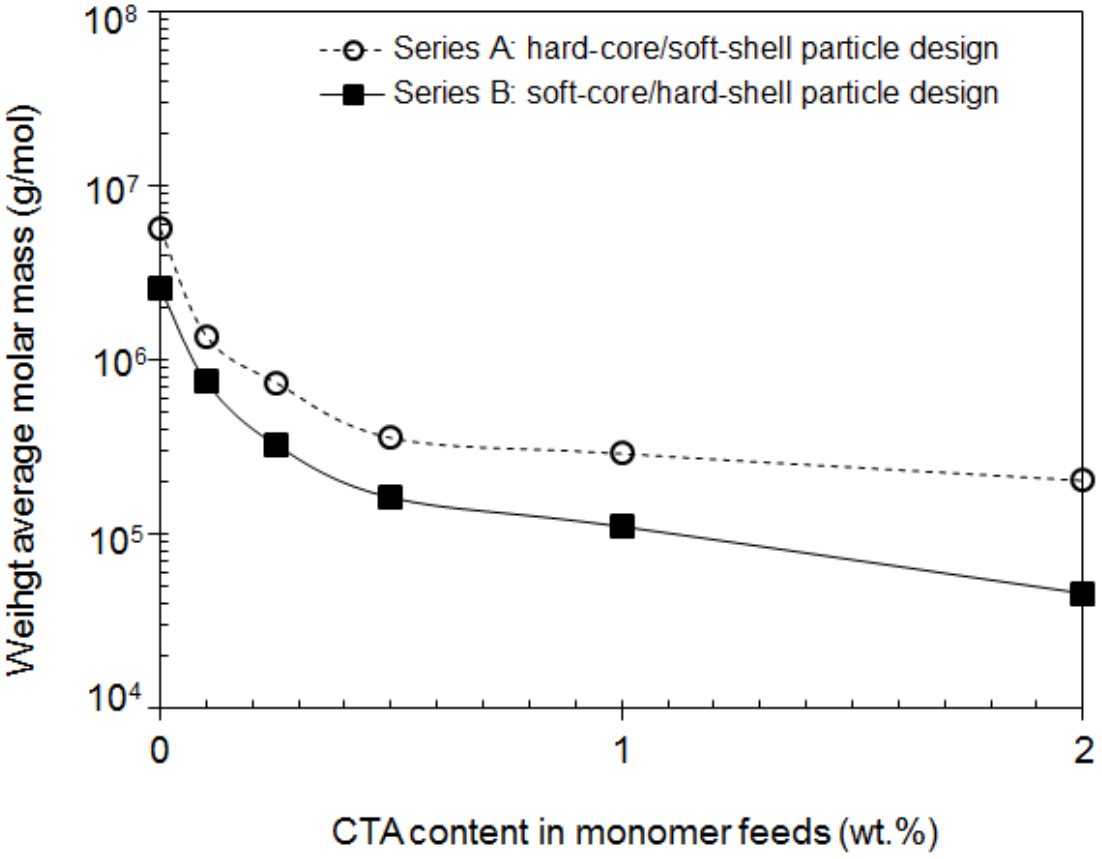
Series A: hard-core/soft-shell particle design
Series B: soft-core/hard-shell particle design
Weihgt average molar mass (g/mol)
10^8
10^7
10^6
10^5
10^4
0
1
2
CTA content in monomer feeds (wt.%)

Fig. 3

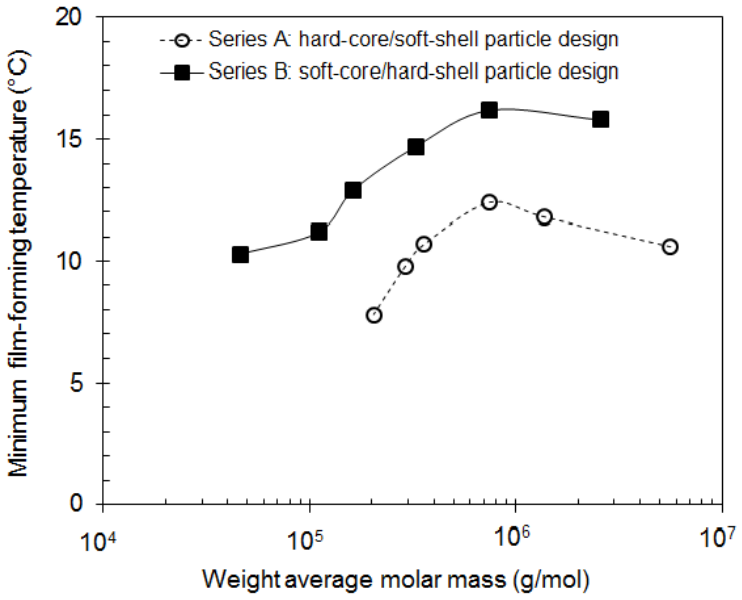
Series A: hard-core/soft-shell particle design
Series B: soft-core/hard-shell particle design
Minimum film-forming temperature (°C)
20
15
10
5
0
10^4
10^5
10^6
10^7
Weight average molar mass (g/mol)

Fig. 4

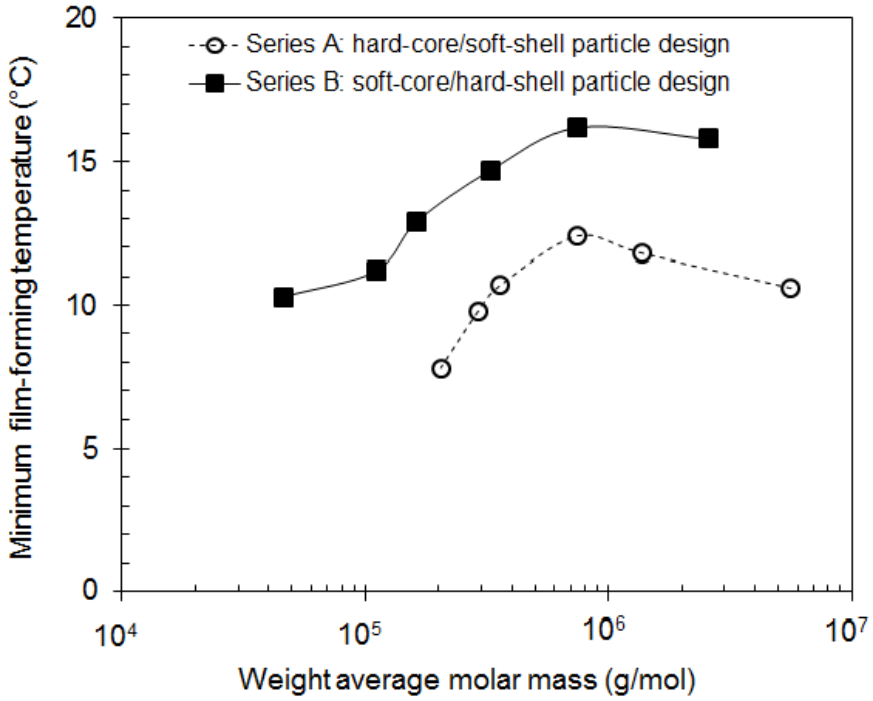
Series A: hard-core/soft-shell particle design
Series B: soft-core/hard-shell particle design
Minimum film-forming temperature (°C)
20
15
10
5
0
10⁴
10⁵
10⁶
10⁷
Weight average molar mass (g/mol)

Fig. 5

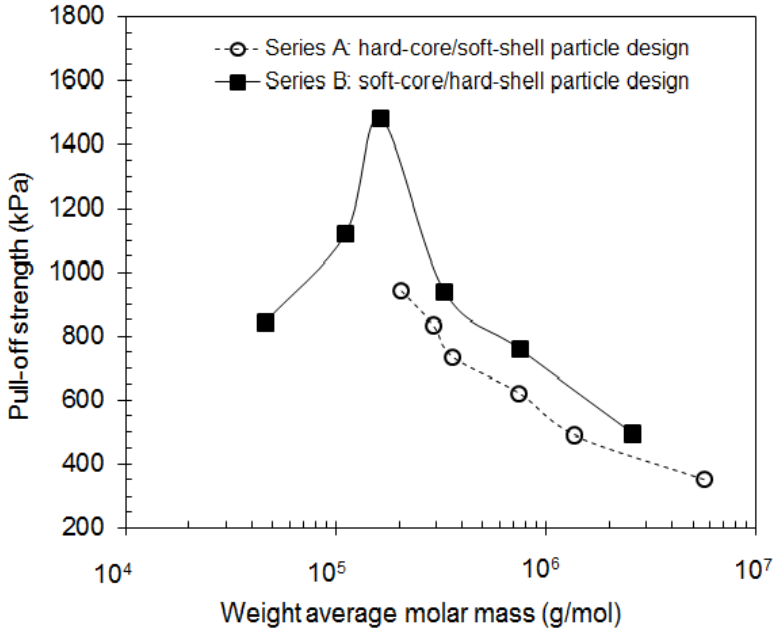
Series A: hard-core/soft-shell particle design
Series B: soft-core/hard-shell particle design
Pull-off strength (kPa)
1800
1600
1400
1200
1000
800
600
400
200
10⁴
10⁵
10⁶
10⁷
Weight average molar mass (g/mol)

Fig. 6

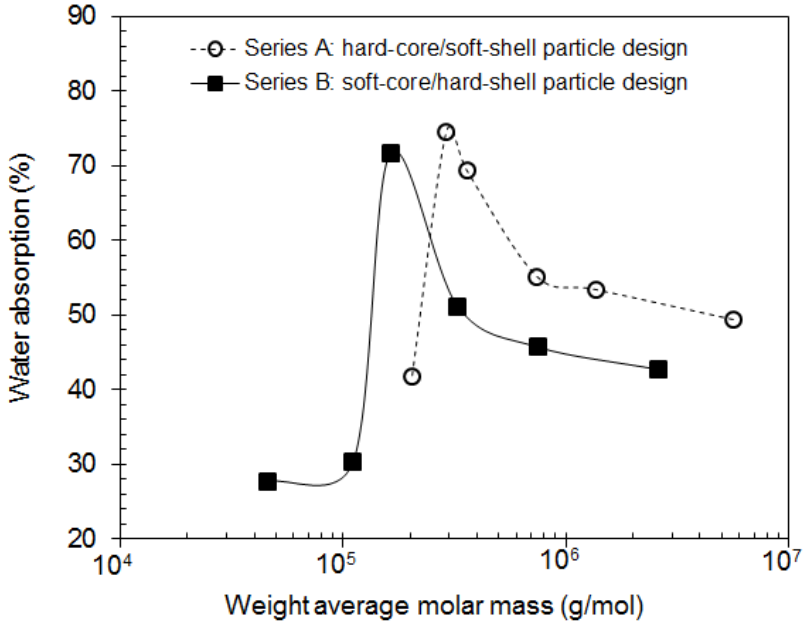
Series A: hard-core/soft-shell particle design
Series B: soft-core/hard-shell particle design
Water absorption (%)
Weight average molar mass (g/mol)
90
80
70
60
50
40
30
20
10^4
10^5
10^6
10^7

Fig. 7

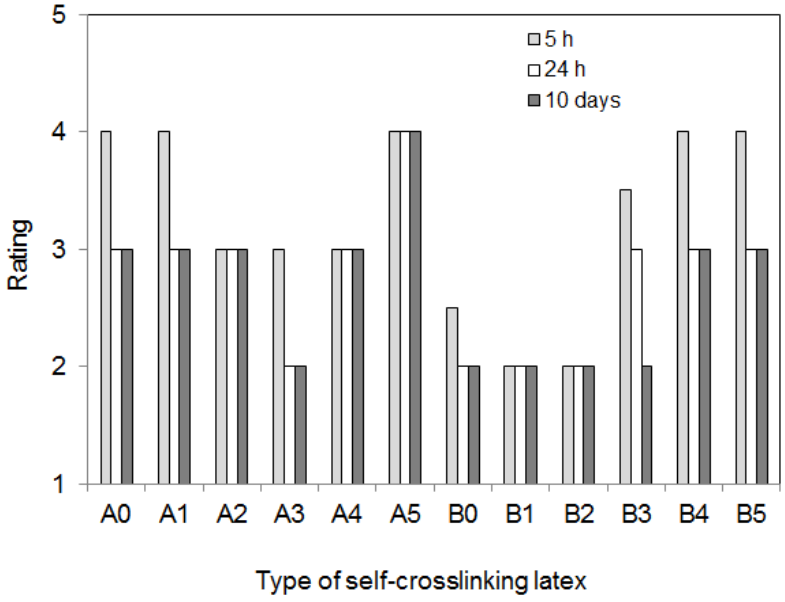
5 h
24 h
10 days
Rating
Type of self-crosslinking latex
5
4
3
2
1
A0
A1
A2
A3
A4
A5
B0
B1
B2
B3
B4
B5

Fig. 8