



Water sensitivity of fluorine-containing polyacrylate latex coatings: Effects of crosslinking and ambient drying conditions

Jana Machotová^{a,*}, Eva Černošková^b, Jan Honzík^a, Jaromír Šňupárek^a

^a Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

^b Joint Laboratory of Solid State Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

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ABSTRACT

In this study, fluorine-containing polyacrylate latexes comprising different levels of copolymerized perfluoroethyl groups were prepared by the two-stage emulsion polymerization of 2,2,2-trifluoroethyl methacrylate, methyl methacrylate, butyl acrylate and methacrylic acid as main monomers, where the fluorine-containing monomer was copolymerized only into the second stage polymer. The effects of keto-hydrazide self-crosslinking and its combination with pre-coalescence and ionic crosslinking, respectively, on coating wettability, water absorption and water whitening were investigated. For the keto-hydrazide self-crosslinking, diacetone acrylamide was copolymerized into the second stage polymer to provide sites for the subsequent reaction with adipic acid dihydrazide. The pre-coalescence crosslinking of latex particles was introduced by copolymerizing allylmethacrylate during the synthesis and the ionic crosslinking was provided by the addition of a commercial zinc complexing agent. The influences of ambient conditions during the film-forming process in terms of temperature and relative humidity differences on coating wettability were evaluated. Further, changes of coating wettability as a function of water exposure duration were tested. The results showed that the highest level of hydrophobicity at the same amount of copolymerized 2,2,2-trifluoroethyl methacrylate could be achieved in the case of non-crosslinked latex films dried at elevated temperatures, whereas the highly crosslinked latexes combining pre-coalescence crosslinking and keto-hydrazide self-crosslinking provided the most water whitening-resistant coating films.

1. Introduction

A common drawback of latex coatings is their water sensitivity, usually connected with water whitening, loss of adhesion and poor durability. Normally, when latex particles dry to form a continuous clear film, the liquid water evaporates while ionically-charged components such as surfactants, initiators and buffers remain trapped in interstitial areas of the film and become a driving force for the migration of water into interstitial areas. This migration results in increased water absorption and water whitening of coating films. Nevertheless, the hydrophilic components are usually the essential part of standard commercial products; therefore, the efforts to enhance water resistance of latex coatings by means of polymer structure changes are being highly encouraged. Among them, fluorination and crosslinking have been the traditionally used approaches.

Fluorinated polyacrylate latexes with special surface properties, such as low surface tension and related hydrophobicity, good adhesion

to matrices and environmental protection value have attracted the attention of many investigators [1–4]. Up to date, fluorinated acrylate polymer emulsions with various structures, such as graft [5], random [6], and core-shell [7–11] have been synthesized by conventional emulsion polymerization, mini emulsion polymerization, seeded emulsion polymerization, and other synthetic polymerization techniques. However, the relatively high market price of fluorinated monomers limits their use and the challenge is how to minimize the amount of fluorinated monomers whereas the reasonable properties of the resulting products still can be maintained. One possible strategy to achieve cost-effectivity and increased coating hydrophobicity is to prepare latexes using a two-stage synthesis producing core-shell particles consisting of fluorine-free core and fluorine-rich shell [12–16]. The presented results reveal that while the weight fraction of fluorine-containing compounds in the polymer is decreased considerably, the physical and chemical properties still can be kept [17,18].

The fluorine-containing groups in fluorinated polymers have the

* Corresponding author at: Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic.

E-mail address: jana.machotova@upce.cz (J. Šňupárek).

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tendency to orientate toward air-film interface during film formation to minimize the interfacial energy resulting in materials with increased hydrophobicity [19,20]. However, the fluorine groups can migrate to the inside of coating films when the environment surrounding the film changes, such as being immersed into water [21,22]. This phenomenon may lead to decrease in some properties of fluorinated latex films, such as water resistance [23]. If the fluorinated groups are fixed on the surface of latex particles, this problem might be resolved [9].

Besides fluorination, increasing crosslinking density is an effective tool to improve water resistance [24], solvent resistance [25] and mechanical properties [26,27] of water borne emulsions used as coatings and adhesives. Methods for increasing crosslinking density include pre-coalescence (intra-particle) crosslinking of latex particles achieved during polymerization and post-coalescence (inter-particle) crosslinking proceeding during latex film formation. Pre-coalescence crosslinking often results in rigid latex particles that may suffer from poor deformability and suppressed chain interpenetration during the coalescence stage. Post-crosslinking refers to a chemical reaction designed to occur during or shortly after latex film-formation. Among different post-crosslinking reactions, the keto-hydrazide self-crosslinking via the reaction between carbonyl groups in diacetone acrylamide (DAAM) repeat units and hydrazide groups from adipic acid dihydrazide (ADH) has been shown to be particularly effective [28–33]. The water soluble ADH is added to the latex after its preparation and as a result, the one-component self-crosslinking latex providing a long-term storage stability and a rapid crosslinking at ambient temperature is easily obtained. Therefore, these latexes are popular in a wide range of applications, starting from paints for the building industry through wood paints and varnishes to paints for metal protection and decorative systems.

The paper focuses on the combined effects of crosslinking and ambient conditions during the film-forming process on water sensitivity and wettability of fluorine-containing polyacrylate latex coating films. The presented work also aims to demonstrate the optimal composition based on the self-crosslinking latex system with the emphasis on sparing the fluorinated monomer consumption while maintaining the desired water-repellent properties.

2. Experimental

2.1. Materials

Latexes were synthesized of 2,2,2-trifluoroethyl methacrylate (TFEMA), methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), allyl methacrylate (ALMA) and diacetone acrylamide (DAAM). All the monomers were purchased from Sigma-Aldrich (Czech Republic). Disponil FES 993 (BASF, Czech Republic) was used as the surfactant and ammonium persulfate (Penta, Czech Republic) was utilized as the initiator of the polymerization reaction. Adipic acid dihydrazide (ADH) was utilized as the crosslinker and was purchased from Sigma-Aldrich (Czech Republic). Aqueous suspension of ZnO nanoparticles (trade name nZ-BOCH 202) having the ZnO content of 40 wt.% was used as the ionomeric crosslinking agent and was kindly obtained from Bochemie (Czech Republic). All the chemicals were utilized as received without any further purification.

2.2. Preparation and characterization of latexes

Four series of polyacrylate latexes were synthesized by the semi-continuous two-stage emulsion polymerization comprising a variable content of acrylic monomers (see Table 1). The weight ratio of first stage/second stage polymer was 1/1, which means a thickness of the second stage polymer layer of about 20% of the particle radius in the case of a full phase separation. The nature of acrylic monomers forming first stage and second stage polymers was chosen to achieve a calculated T_g (using the Fox equation [34]) of approximately 10 °C. In the case of all series, TFEMA was copolymerized with the monomers

designed to form the second stage polymer and its concentration was gradually increased. In the series A, no crosslinking was introduced into latex films. In the series B, the latexes were designed to provide the keto-hydrazide self-crosslinking during the film-formation. The series C was represented by latexes that were able to produce highly crosslinked films by means of the combination of both the pre-coalescence crosslinking and the keto-hydrazide self-crosslinking. In the series D, the latexes were designed to provide both the keto-hydrazide self-crosslinking and the ionomeric crosslinking (complexing) during the film-formation. The pre-coalescence crosslinking of latex films was achieved by covalent intra-particle crosslinking of emulsion copolymers during their synthesis using ALMA. For the keto-hydrazide self-crosslinking, a constant amount of DAAM was copolymerized into the second stage polymer to provide sites for the subsequent interfacial covalent crosslinking by the reaction with ADH added during latex coating formulation. The ionomeric interfacial crosslinking was performed by the addition of a commercial zinc complexing agent in the amount of 3 wt.% (based on solids) to the latex after its neutralization and ADH addition. Carboxyl functionalities were introduced into the structure of first stage and second stage polymers by copolymerization with a constant amount of MAA for three reasons: firstly, to improve the colloidal stability of latexes; secondly, to ensure the acid catalysis of keto-hydrazide crosslinking; and thirdly, to enable the ionomeric crosslinking via zinc metal ions.

The latexes were produced in a 700 mL glass reactor by the semi-continuous two-stage emulsion polymerization under starved conditions in nitrogen atmosphere at 85 °C. This procedure ensured relatively homogeneous latex particles of statistical copolymers. The recipe of emulsion polymerization is shown in Table 2. 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. first stage polymer preparation, 2. second stage polymer preparation). After that, during 2 h of hold period at 85 °C the polymerization was completed. The pH was adjusted to 8.5 with ammonia solution. To ensure the keto-hydrazide self-crosslinking of latexes, a 10 wt.% aqueous solution of ADH in the amount corresponding to the molar ratio ADH:DAAM = 1:2, was added to the latex under agitation. The solids content of final latexes was about 35 wt.%.

The average particle sizes of latex particles in the water phase were determined by dynamic light scattering experiments performed using a Coulter N4 Plus instrument (Coulter, Corp., UK). All the DLS measurements were conducted at 25 °C. The structure of prepared polymers with the emphasis on the evidence of crosslinking reactions was investigated by means of a Fourier transform infrared (FT-IR) spectroscopy on a Nicolet iS50 instrument (Thermo Fisher Scientific, USA). The measurements were performed on a built-in all-reflective diamond ATR in the range from 4000 cm^{-1} to 500 cm^{-1} using the resolution of 2 cm^{-1} (64 scans per spectrum). The degree of crosslinking introduced into latex coating films was evaluated from the point of view of gel content changes. Specimens for the FT-IR spectroscopy and gel content measurements were prepared by pouring and drying the latexes on silicone substrates. The specimens were first air-dried at room temperature (RT, 23 ± 1 °C) for a month and then vacuum-dried at 30 °C for 2 weeks. The gel content was determined according to CSN EN ISO 6427 using a 24-h extraction with THF in a Soxhlet extractor. Around 1 g of the dried latex sample was put into the thimble. After the extraction, the thimble was dried in an oven at 75 °C for 12 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.

2.3. Evaluation of wettability of latex coatings

Wettability studies involved the measurements of water contact angles using an optical tensiometer Attension Theta (Biolion Scientific, Finland) by the sessile drop method. An automatic micropipette was used to accurately dispense the volume (1 μL) of water. The time

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