

UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Chemistry and Technology of Macromolecular Materials

Adéla Rückerová

**Smart Coating Binders Based on Structured Self-crosslinking
Latexes**

Theses of the Doctoral Dissertation

Pardubice 2020

Study program: **Chemistry and Technology of Materials**

Study field: **Surface Engineering**

Author: **Adéla Růckerová**

Supervisor: **prof. Ing. Andréa Kalendová, Dr.**

Year of the defense: 2020

References

RÜCKEROVÁ, Adéla. *Smart Polymer Coating Binders Based on Structured Self-crosslinking Latexes*. Pardubice 2020. 228 pages. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Chemistry and Technology of Macromolecular Materials. Supervisor prof. Ing. Andréa Kalendová, Dr.

Abstract

The thesis with the title „Smart coating binders based on structured self-crosslinking latexes“ is focused on study, preparation, characterization and application of one-component polymeric binders for waterborne coatings. The latexes were prepared using the emulsion polymerization technique. The functionalized compounds can be covalently linked in the structure of latex-particles, which causes the intra-particle crosslinking resulting in microgel particles or the subsequent inter-particle crosslinking reaction. Ideal candidates for achieving this effect from this group of compounds are phosphazene derivatives, which can act as intra-particle crosslinking agents and also as flame retardants in the resulting coatings. A section of the thesis is also dedicated to the so-called flash rust creation and elimination. The phenomenon occurs frequently when a latex paint is applied on metal substrates. This phenomenon can be eliminated by the incorporation of a relatively low amount of nano-sized zinc oxide in latex binders during their polymerization, which results in improvement of mechanical and optical properties of the resulting coatings. Properties of coatings prepared this way were also modified by replacing the conventional ADH – inter-particle crosslinker for the novel 0G PAMAM dendrimer.

Abstrakt

Práce s názvem „Inteligentní polymerní pojiva na bázi strukturovaných samosíťujících latexů“ se zabývá studiem, přípravou, hodnocením a aplikací jednosložkových pojiv vodou ředitelných nátěrových hmot připravovaných technikou emulzní polymerace. Do struktury latexových částic lze kovalentně navázat funkcionalizované sloučeniny, které zapříčiňují vznik polymerní sítě uvnitř těchto částic, popř. umožňují následné mezičásticové síťování po přidání síťující složky. Deriváty *cyklo*-trifosfazenu například mohou sloužit jako vnitročásticové síťovadlo, a jejich přítomnost navíc snižuje hořlavost takto připravených nátěrových povlaků. Dále byla pozornost věnována vzniku a eliminaci tzv. bleskové koroze, jejíž výskyt bývá při nanášení vodných pojiv na kovové substráty velmi častý. Zakomponováním již velmi malého množství nanočástic oxidu zinečnatého do latexového pojiva v průběhu jeho přípravy, lze tento jev dostatečně eliminovat a tím zlepšit jak mechanické vlastnosti nátěrů, tak jejich vzhled. Vlastnosti takto připravených nátěrových povlaků byly také modifikovány za použití alternativního mezičásticového síťovadla poly(amido)aminunulté generace místo konvenčního dihydrazidu kyseliny adipové.

Keywords

Emulsion polymerization, latex, flame retardant, phosphazene, zinc oxide, flash rust, 0G PAMAM

Klíčová slova

Emulzní polymerace, latex, oxid zinečnatý, retardér hoření, fosfazen, blesková koroze, 0G PAMAM

Table of Contents

Introduction.....	6
Aims of the thesis	8
1 Experimental	9
1.1 Materials.....	9
1.2 Optimalization of HACTP.....	9
1.2.1 Latex preparation and characterization	9
1.2.2 Preparation and characterization of latex coatings	11
1.3 Investigation of the effect of G0 PAMAM as inter-particle crosslinking agent	12
1.3.1 Preparation of selfcrosslinking latexes	12
1.3.2 Characterization of self-crosslinking reaction.....	12
1.3.3 Polymer characterization.....	13
1.3.4 Preparation and characterization of coatings.....	14
2 Results and discussion.....	16
2.1 Evaluation of latexes with copolymerized HACTP.....	16
2.2 Evaluation of coatings containing HACTP.....	16
2.2.1 Evaluation of flame stability of coatings with HACTP.....	17
2.3 Evaluation of polymers considering inter-particle crosslinkers	18
2.3.1 Evaluation of latex coatings.....	19
2.3.2 Flash rust resistance	22
3 Conclusion.....	24
List of References	25
List of Published Works	28

Introduction

Traditional solvent-based coatings are being substituted by environmentally friendly waterborne coatings offering a wide application range of products, starting from paints and plasters for the construction industry, through wood paints and varnishes to paints for metal protection and decorative systems [1,2]. However, properties such as quick drying, adhesion strength, water resistance and mechanical properties of the latter category of products are generally inferior to those of paints or plasters and there are continues attempts to improve those properties [3–6]. The film formation of conventional latex coatings primarily relies on coalescence of thermoplastic polymeric particles to provide mechanical properties and chemical resistance. Coalescence is a result of physical entanglement of polymeric molecules, and consequently it is not an adequate substitute for the chemical crosslinking. Hence, the cross-linking technology has frequently been incorporated into latex coatings to improve their performance [7,8]. For special applications, increased flame stability of coating materials may be desired. To enhance special safety properties in terms of reduced flammability, the incorporation of derivatives of halogeno-*cyclo*-phosphazenes into the polymer backbone may offer solutions. These compounds exhibit unusual thermal properties, such as flame retardancy and self-extinguishability [9,10].

During the endothermic thermal decomposition of phosphazene-based polymers, phosphate, metaphosphate, and polyphosphate compounds are generated and a nonvolatile protective barrier layer on the polymer surface is formed, cutting off the supply of oxygen [11,12]. The typical reaction of HCCTP is a nucleophilic substitution. The nucleophile, being able to pass its free electron toward the attacking electrophilic phosphorus atom, belongs usually to the group of amines, alcoholates, alcohols, or thiols. Several derivatives of HCCTP have already been synthesized and used as flame retardants and antioxidants in polymers [13-16]. In the present work, we concentrated on the synthesis of a new flame retardant using nucleophilic substitution of HCCTP with allylamine. The resulting hexaallylamino-*cyclo*-triphosphazene (HACTP) was incorporated into acrylic polymers during the emulsion polymerization and the latexes were further used for the development of low VOC thermosetting transparent coating systems. The final coating properties were evaluated with emphasis on the flame stability measured using dual-cone calorimeter measurements.

However, the performances of common latex coatings such as quick drying, adhesion strength, water resistance, and mechanical properties are usually inferior to solvent-based coatings. One approach to improve the balance in the properties of latex coatings against solvent-based coatings is to introduce intra-particle crosslinking and/or inter-particle self-crosslinking chemistry in emulsion polymers [8, 17-19]. Currently, self-crosslinking via the reaction of a carbonyl pendant group on the polymer backbone with some diamine, especially where that diamine is the adipic acid dihydrazide (ADH), has attracted a tremendous amount of research activity [7, 20, 21]. This chemistry, termed the keto-hydrazide reaction, is favored due to the loss of water and the simultaneous decrease in pH arising from the evaporation of ammonia or amines during the film forming process. The ADH-based self-crosslinking latexes can get cured rapidly at ambient temperature and do not need any additional crosslinker to be added before

use, therefore they have been shown to be suitable for a wide range of applications, starting from paints for the building industry [22-24]. Nevertheless, according to WKG Germany safety rating, ADH represents a highly water polluting substance. Hence, efforts trying to replace ADH by an environmental friendly and effective crosslinking agent are particularly important. One promising way may be achieved by using poly(amidoamine) (PAMAM) dendrimers which are a specific family of dendritic polymers, based on an ethylenediamine core and an amidoamine repeat branching structure [25, 26]. These substances are synthesized from cheap raw materials and their size and surface functionality (amine, carboxyl, methylester) can be varied by the number of controlled repetitive additions of monomer units giving rise to different generations [27-29]. Due to unique properties including well-defined molecular structure, spherical shape and water solubility, PAMAM dendrimers have found numerous applications in chemical, biological and physical processes [30-32]. Particularly, low-generation PAMAM dendrimers (third generation or lower) have desired biological properties, such as nontoxicity and nonimmunogenicity for in vivo applications [33, 34]. Thus, water soluble amino-functionalized PAMAM dendrimers of lower generations have attracted our attention as the potential pro-ecological crosslinkers for self-crosslinking latex coating compositions containing diacetone acrylamide (DAAM). The present work deals with low generation amine terminated PAMAM dendrimers as the promising and environmentally friendly inter-particle crosslinking agents for ambient temperature one-component self-crosslinking waterborne coatings. The latex stability and coating performance with emphasis on water sensitivity were evaluated and compared with the conventional ADH crosslinking agent.

Another handicap of latex coatings is flash rust (flash corrosion). Flash rust is a rapid, widespread corrosion that occurs during initial coating application, especially when aqueous coating films reside on the steel surface. For this reason, corrosion inhibitors are typically used to hinder the formation of a passivation layer by insulating coating electrically or making the coating impermeable to fight electrochemical reactions [35-37]. Recently, inorganic nanoparticles like silica [38] and cerium oxide [39] have been successfully applied in formulations of anti-corrosion coatings. Zinc oxide nanoparticles have been reported to impart the flash corrosion resistance as well. Being added into aqueous alkyd dispersion, improved corrosion resistance and mechanical properties of coatings were observed [40]. Surface-treated ZnO nanoparticles were incorporated in the course of latex synthesis by means of mini-emulsion polymerization, and binder coating systems with increased flash rust protection were obtained [41].

Herein, we report on the easy preparation of stable self-crosslinking acrylic latexes containing surface-unmodified ZnO nanoparticles and low-generation amine-terminated PAMAM dendrimers. The incorporation of ZnO nanoparticles was performed during the latex synthesis by the conventional emulsion polymerization technique. PAMAM dendrimers as aqueous solutions were added into latexes containing diacetone acrylamide repeat units in their polymer structure. Latex storage stability and coating performance with emphasis on water sensitivity, chemical resistance and flash rust resistance were evaluated and compared with a model zinc oxide-free self-crosslinking latex based on a conventional cross-linking agent (ADH).

Aims of the thesis

The main topic of the work was to prepare coating binders for water-based coatings with many improved properties, specifically latexes with microgel structure with decreased flammability, decreased hydrophobicity, improved chemical resistance and reduced occurrence of flash corrosion during application on metal substrates.

The first goal was to prepare water dispersions as coating binders using methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA) and diacetone acrylamide (DAAM). DAAM was added in the shell structure of latex particles to find the optimal inter-particle crosslinking density by the reaction with ADH.

The second goal was to optimize the amount location of hexaallylamino-*cyclo*-triphosphazene in latex particles due to the intra-particle crosslinking of latex particles and due to the flammability decrease of final latex coatings.

The third goal was to incorporate nanoparticles of zinc oxide into the latexes during the polymerization because of the mechanical and chemical resistance increase and due to the flash rust occurrence elimination during the film-formation process on steel substrates.

The fourth part was to optimize the amount of 2,2,2trifluorethyl methacrylate in the structure of latex particles to provide coatings with increased hydrophobicity and even lower flammability.

The fifth goal was to find a novel inter-particle crosslinking agent instead of conventionally used ADH. Due to the environmental risks of ADH, the low generation ethylene core amine terminated PAMAM dendrimer is offered as more eco-friendly inter-particle crosslinking agent.

1 Experimental

1.1 Materials

Hexaallylamino-*cyclo*-triphosphazene (HACTP) was prepared using hexachloro-*cyclo*-triphosphazene purchased from Sigma-Aldrich (Czech Republic). Amine-terminated poly(amidoamine) dendrimers of generation 0 (0G PAMAM) was prepared according to Esfand a Tomalia in the methanolic solution. After methanol evaporation, the PAMAM dendrimer was easily dissolved in distilled water to produce 10wt.% aqueous solution. Adipic acid dihydrazide (ADH) crosslinker was purchased from TCI Europe (Switzerland). Surface-unmodified ZnO nanoparticles having the average particle size below 100 nm were obtained from Sigma-Aldrich (Czech Republic). Model latexes were synthesized of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), allyl methacrylate (AMA) and diacetone acrylamide (DAAM). All monomers were purchased from Sigma-Aldrich (Czech Republic). Disponil FES993 (BASF, Czech Republic) was used as the emulsifying agent and ammonium persulfate (Lach-Ner Company, Czech Republic) was used as the initiator of the polymerization.

1.2 Optimization of HACTP

1.2.1 Latex preparation and characterization

Latexes of functionalized core-shell particles bearing in the structure a flame retardant were synthesized by the semi-continuous non-seeded emulsion polymerization comprising a variable content of acrylic monomers. The prepared HACTP was shown to be readily soluble in the utilized acrylic monomers and was incorporated into shell structure of latex particles in the amount of 0 – 1 wt.% based on the shell structure polymer content. The structure of HACTP is shown in Figure 1.

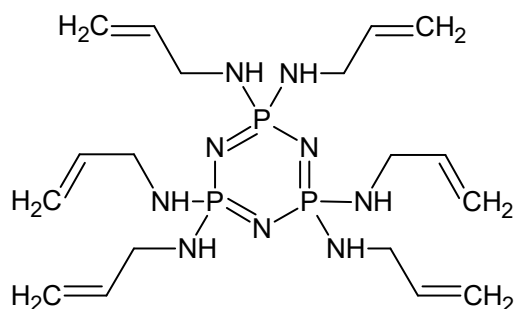


Figure 1 Structure of hexaallylamino-*cyclo*-triphosphazene.

The nature of acrylic monomers forming core and shell phases was chosen to achieve a calculated T_g (using the Fox equation [42]) of approximately 2 °C. The detailed composition of monomer feeds forming the latex sample “S” was as follows: 43g MMA, 53g BA and 4g MAA dosed in the first step and 38.5g MMA, 52.5g BA, 4g MAA, 5g DAAM and 0 - 1 g HACTP dosed in the second step. To enable the subsequent inter-

particle crosslinking with a hydrazide-based crosslinking agent (ADH), DAAM was incorporated in polymer particles to introduce ketone carbonyl functional groups. The ADH/DAAM self-crosslinking reaction is shown in Figure 2.

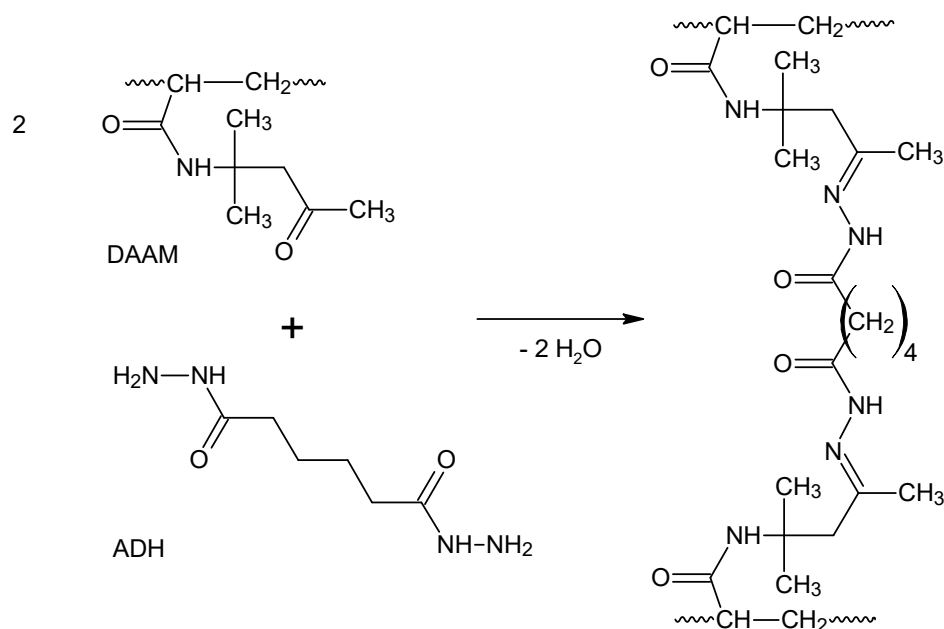


Figure 2 The inter-particle crosslinking reaction of DAAM and ADH.

The latexes were produced in a 700ml glass reactor under nitrogen atmosphere at 85°C. 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 the feeding rate about 2ml/min in two steps. After that, during 2h of hold period the polymerization was completed. The recipe of emulsion polymerization is shown in Figure 3. The pH value of latexes was adjusted to 8.5 by adding ammonia solution. The solids content of the latexes was about 45wt.%. 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). All the DLS measurements were conducted at 25°C. The concentration of the measured polymer dispersion was approximately 0.05 wt% of solid. For the glass transition temperature (T_g) and the gel content measurements, specimens were prepared by pouring the latexes into a silicone mold. Films were formed by water evaporation at room temperature for a month. The T_g of the dried latex copolymers was determined by means of differential scanning calorimetry (DSC) using a Pyris 1 DSC instrument (PerkinElmer, USA). The measurements were performed at the heating rate of 10°C min⁻¹ under N₂ atmosphere. The testing temperature range was 80 to 120°C. The gel content of microgel copolymers 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 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.

Figure 3 Recipe of emulsion polymerization.

Reactor charge	[g]
Water	65
Disponil FES 993 IS	0.5
Initiator (0.4 g (NH ₄) ₂ S ₂ O ₈ + 15 ml H ₂ O)	15.4
Monomer emulsion 1st step	[g]
Water	60
Disponil FES 993 IS	7.4
Monomers	100
Initiator (0.4 g (NH ₄) ₂ S ₂ O ₈ + 15 ml H ₂ O)	15.4
Monomer emulsion 2nd step	[g]
Water	60
Disponil FES 993 IS	7.4
Monomers	100
Initiator (0.4 g (NH ₄) ₂ S ₂ O ₈ + 15 ml H ₂ O)	15.4

1.2.2 Preparation and characterization of latex coatings

The coating films with a wet thickness of 120 μm were cast on glass and metallic panels by drawing the thermosetting coating systems using a blade applicator. The film formation process was performed by leaving the films at room temperature (23°C) for 14 days. The resulting coating films based on latex particles containing variable amount of HACTP in their shell structure were evaluated for their gloss, hardness, adhesion, impact resistance, chemical resistance, and flame stability. The dry film thickness was determined using a three-point instrument (BYK-Gardner, Germany); in the case of films prepared on glass panel, thickness of specimen on metallic panels was measured by the SAUTER TE 1250-0.1 F Digital Coating Gauge (SAUTER, Germany). The gloss of coatings was measured by a micro TRI-gloss μ instrument (BYK-Gardner, Germany) using a gloss-measuring geometry 60°. The hardness of test films was measured by the pendulum hardness tester “Persoz” pendulum (BYK-Gardner, Germany) following the CSN EN ISO 1522. The adhesion was determined using the crosscut tester (Elcometer Instruments, UK) following the CSN ISO 2409. The impact resistance was evaluated according to CSN EN ISO 6272 using the Elcometer 1615 Variable Impact Tester (Elcometer Instruments, UK) and the chemical resistance was determined by methyl ethyl ketone rubbing following ASTM D 4752. All experiments were performed at room temperature (23 ± 1°C).

For evaluating the flame stability using the dual-cone calorimeter (Fire Testing Technology, UK), specimens of the approximate dimensions 80×50×4 mm³ were prepared by pouring the coating systems into a silicone mold. Films were air-dried at room temperature (23°C) for 14 days and then vacuum dried at 30° C for 5 days. The measurements were done in a sample holder suitable for testing thermally thin materials. The center of a measured sample was situated at 6 cm from the lowest part of the cone heater. The heat release rate was calibrated by burning methane. The cone radiancy 25 kW.m⁻² corresponds to a cone temperature of 680 °C.

1.3 Investigation of the effect of G0 PAMAM as inter-particle crosslinking agent

1.3.1 Preparation of self-crosslinking latexes

Two standard latexes bearing in the structure the optimal 0.75 wt.% amount of the flame retardant (HACTP), were also synthesized by the technique of semi-continuous non-seeded emulsion polymerization using variable content of acrylic monomers. To enable the subsequent inter-particle crosslinking with a suitable amine- or hydrazide-based crosslinking agent, DAAM was incorporated in polymer particles to introduce ketone carbonyl functional groups. The latex sample labeled Fin did not contain nanosized ZnO and latex labeled FinZn contained 3 wt.% of ZnO nanoparticles (theoretical content applied on the polymer content). To ensure the sufficient film formation properties, the ratio of acrylic monomers forming latex particles was chosen to achieve the calculated T_g of the resulting polymer of approximately 2°C (using the Fox equation [44]). The detailed composition of monomer feeds forming the latex sample Fin was as follows: 43g MMA, 53g BA and 4g MAA dosed in the first step and 38.5g MMA, 52.5g BA, 4g MAA, 5g DAAM and 0.75 g HACTP dosed in the second step. In the case of the latex sample FinZn, the composition of monomer feeds in the first and in the second step was identical to Fin sample with adding 3 wt.% of *nano*-ZnO (theoretical concentration based on polymer content).

The latexes were produced using the same procedure as in the case of optimization of HACTP. Only for the preparation of the latex FinZn, the above mentioned procedure included the preparation of well dispersed ZnO aqueous suspension. Firstly, ZnO nanopowder was mixed with water and emulsifier that were designated for the preparation of second step monomer emulsion. To destroy agglomerates formed by individual ZnO nanoparticles to a great extent, a proper dispersing using an ULTRA-TURRAX T25 disperser (IKA, Germany) at 14,000 rpm was performed for 20 min followed by ultrasonic treatment for 1 h. Then, the fine *nano*-ZnO suspension was gently mixed with monomers designed for the preparation of second step monomer emulsion (using a stirrer at low speed for 1 min). Finally, the resulting second step monomer emulsion containing ZnO nanoparticles was dosed to the reactor immediately.

In order to produce G0 PAMAM-based one-component self-crosslinking latexes, 10 wt.% water solution of G0 PAMAM dendrimer at the molar ratio 0G PAMAM:DAAM=1:4 was added to the latex. (The molecular weight of 0G PAMAM is 517). The 0G PAMAM/DAAM reaction is shown in Figure 4. Finally, the comparative ADH-based one-component self-crosslinking latexes were produced by adding 10 wt.% water solution of ADH to the model latex at the molar ratio ADH:DAAM=1:2.

1.3.2 Characterization of self-crosslinking reaction

The self-crosslinking reaction of DAAM containing polymer with 0G PAMAM dendrimer and ADH, respectively, is depicted schematically in Figures 2 and 4. The minimum film-forming temperatures (MFFT) of all the prepared self-crosslinking latexes and standard latexes without any inter-particle crosslinker were measured according to ISO 2115, using the MFFT-60 instrument (Rhopoint Instruments, UK). pH

measurements were carried out at $23 \pm 1^\circ\text{C}$ using a pH meter FiveEasy FE20 (Mettler-Toledo, Switzerland). The storage stability of the (*nano*-ZnO particles containing and without them) one-component self-crosslinking latexes comprising different crosslinking agents was symbolized by storing the latexes at 50°C for 50 days and was evaluated according to particle size and zeta potential of latex particles. The apparent viscosity of latexes was measured at 25°C using a Brookfield LVDV- E Viscometer (Brookfield Engineering Laboratories, USA) at 100rpm according to CSN ISO 2555. The average particle sizes and zeta potentials of latex particles dispersed in water phase were detected by dynamic light scattering (DLS) performed by using a Coulter N4 Plus instrument (Coulter, Corp., UK). The concentration of solid polymer in the water phase was about 0.05wt.% and the measurements were performed at 25°C .

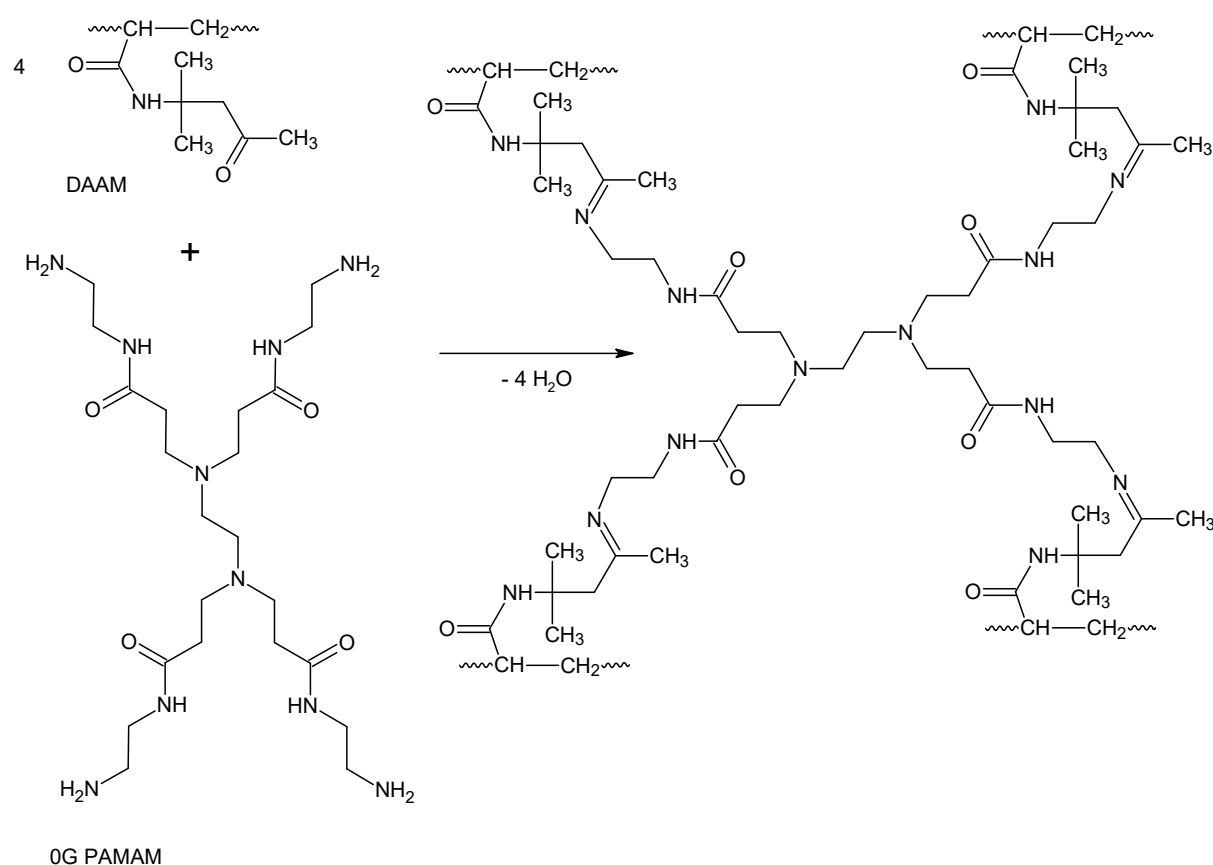


Figure 4 The self-crosslinking reaction of DAAM and 0G PAMAM.

1.3.3 Polymer characterization

The verification of the occurrence of 0G PAMAM based self-crosslinking reaction was performed on dried coating films from the point of view of their glass transition temperature (T_g), gel content and crosslinking density differences. The self-crosslinking based on PAMAM dendrimers was compared with ADH-based self-crosslinking and not self-crosslinked. The specimens for the measurements were prepared by pouring and drying the latexes on silicone substrates. The specimens were first air-dried at room temperature ($23 \pm 1^\circ\text{C}$) and 50% relative humidity for a month and then vacuum-dried at 30°C for 2 weeks. The thickness of dry films was approximately 1mm. The glass transition temperature (T_g) of dried latex polymers was measured by means

of differential scanning calorimetry using a Pyris 1 DSC instrument (Perkin-Elmer, USA). The measurements were performed under N₂ atmosphere at the heating rate of 10°C/min from -80°C to 120°C and the second heating curve was used for T_g determination. The gel content of dried latex polymers was determined by the extraction in a Soxhlet extractor with THF for 24h according to CSN EN ISO 6427. The crosslinking density was evaluated from swelling experiments performed on dry gel polymer samples (around 0.2 g) which were immersed in toluene at 25°C for one week. A swelling time of one week was chosen as the basis of the test results on several samples which showed no significant changes after one week of immersion in toluene. At the end of the immersion period the sample was removed, rapidly blotted with tissue and transferred to the weighing bottle to obtain the swollen weight of the sample. Eqs. (1)–(4) employing the theory of Flory and Rehner [43] were used to calculate the average molecular weight between crosslinks (M_c) and the crosslinking density (expressed as moles of crosslinks per cm³ of polymer network), as given in the following:

$$M_c = \frac{V_1 \rho_p [\phi^{\frac{1}{3}} - \frac{\phi}{2}]}{-[\ln(1 - \phi) + \phi + \chi \phi^2]} \quad (1)$$

$$\phi = \frac{W_p \rho_s}{W_p \rho_s + W_s \rho_p} \quad (2)$$

$$\chi = 0,34 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (3)$$

$$\text{Crosslinking density} = \rho_p / M_c \quad (4)$$

where V_1 is the molar volume of toluene (106.3cm³/mol); ρ_p is the density of polymer that was calculated to be 1.11g/cm³ for the BA/ MMA/MAA (53/43/4 by weight) copolymer from 1.06, 1.18 and 1.015g/cm³ for poly(BA), poly(MMA) and poly(MAA), respectively; ϕ is the volume fraction of the gel polymer in the swollen gel; W_p and W_s are the weight fractions of the gel polymer and solvent (toluene) in the swollen gel, respectively; ρ_s is the density of solvent (0.8669g/cm³); χ is the polymer and solvent interaction parameter; δ_1 is the solubility parameter of polymer that was calculated to be 9.18 (cal/cm³)^{1/2} for the BA/MMA/MAA (53/43/4 by weight) copolymer from 9.0, 9.3 and 9.8 (cal/cm³)^{1/2} for poly(BA), poly(MMA) and poly(MAA), respectively [26,27]; and δ_2 is the solubility parameter of toluene, 8.9 (cal/cm³)^{1/2}.

1.3.4 Preparation and characterization of coatings

The self-crosslinking latexes were applied on glass and metallic panels using a blade applicator. The thickness of wet coating films was 120µm. No coalescing agents were used. The coatings were air-dried at room temperature (23 ± 1°C) and 50% relative humidity for 30 days, although in practice, a procedure of 5 days-long drying at room temperature has been shown to provide coatings that exhibit properties close to the results presented below. The coating films were evaluated for their gloss, hardness, adhesion, impact resistance, chemical resistance and water absorption. The gloss of coating films was determined by a micro TRI-gloss µ instrument (BYK-Gardner,

Germany) using a gloss-measuring geometry 60°. The hardness of coatings was measured by a pendulum hardness tester “Persoz” (BYK-Gardner, Germany) according to CSN EN ISO 1522. The adhesion of coating films to glass substrate was determined according to CSN ISO 2409 using a cross-cut tester (Elcometer Instruments, UK). The impact resistance was evaluated using an Elcometer 1615 Variable Impact Tester (Elcometer Instruments, UK) following CSN EN ISO 6272. The chemical resistance was determined by methyl ethyl ketone rubbing following ASTM D 4752. All experiments were performed at room temperature ($23 \pm 1^\circ\text{C}$).

For the water absorption evaluation, specimens were prepared by pouring the self-crosslinking latexes into a silicone mold. Films were air-dried at room temperature (23°C) for a month. The water absorption expressed in terms of water uptake by latex films was measured by immersing specimens of the approximate dimensions $20 \times 20 \times 0.75 \text{ mm}^3$ in distilled water at 23°C . The water absorption, A is given by $A = 100(w_t - w_0)/w_0$, where w_0 is the initial weight before immersion and w_t is the weight after immersion in distilled water during the specified time. The soaked film was removed from water and the surface of the film was carefully dried by touching the polymer with filter paper.

For evaluating the flame stability using the dual-cone calorimeter (Fire Testing Technology, UK), specimens of the approximate dimensions $80 \times 50 \times 4 \text{ mm}^3$ were prepared by pouring the coating systems into a silicone mold. Films were air-dried at room temperature (23°C) for 14 days and then vacuum dried at 30°C for 5 days. The measurement was performed the same way as it was written below but now with the respect to different types of inter-particle crosslinking agents.

The flash rust resistance was evaluated subjectively on coating films cast on steel substrates (medium carbon steel with 0.5% C) which were obtained from Labimex (Czech Republic). Coatings were air-dried at room temperature ($23 \pm 1^\circ\text{C}$) and at $50 \pm 5\%$ relative humidity for 24 h before the flash rust evaluation.

2 Results and discussion

2.1 Evaluation of latexes with copolymerized HACTP

Latexes with the amount of coagulum (0.42 – 1.18 wt.%) were synthesized by the semi-continuous non-seeded emulsion polymerization process with varying levels of HACTP molecules in the shell compositions and were stable for over 1 year. The prepared latex copolymers were studied from the point of view of particle size in water phase, glass transition temperature, and gel content with respect to HACTP concentration in the shell structure of latex particles. These characteristic properties are listed in Table 1. Diameters of core-shell particles were between 120.8 and 125.4 nm. The DLS results showed further that the latex particle size was not affected significantly by the amount and location of HACTP in emulsion copolymers. Nevertheless, T_g and gel content values were shown to be influenced by the content of HACTP in latex particles. Although the pendant allyl double bonds of HACTP were supposed to remain partly unreacted (because of steric hindrance effects and lower reactivity in comparison to vinyl groups of acrylic monomers) and therefore the cross-linking ability of the phosphazene derivative was believed to be suppressed, the glass transition temperature and gel content of emulsion copolymers were found to be increased compared with HACTP-free copolymers. The relatively high gel content determined for emulsion copolymers S0.5 – S1 (containing HACTP- cross-linked shell structure) can be explained that the HACTP can generate network and but they can also occur the chain transfer reactions at radical polymerizations of alkyl acrylates which are responsible for the formation of branched or even cross-linked macromolecules. It was found further that the gel content was increased with the growing content of HACTP in shell structures. This leads us to conclude that in the process of emulsion polymerization of common acrylic monomers, HACTP was proved to act as an efficient intra-particle cross-linker leading to the formation of latex particles of microgel structure.

Figure 5 Characterization of latexes.

Sample	pH	Viscosity [mPa.s]		Particle size [nm]	T_g [°C]	Sol content [hm.%]	
		before alkalization	after alkalization			- ADH	with ADH
C0	1.93	27.05	1143	120.8	13.8	69.2	42.3
S0.5	2.4	6.04	11.76	121.3	18.3	22.1	11.3
S0.75	2.51	11.22	30.72	125.3	19.5	19.2	9.3
S1	2.61	20.28	30.35	125.4	21.8	18.5	5.5

2.2 Evaluation of coatings containing HACTP

One-component coating films based on self-crosslinking aqueous coating systems with the HACTP-modified emulsion microgels were prepared and their properties were tested. All the coating systems were able to form high-quality transparent films. Dry film thickness of the coatings was approximately 60 μm . The effect of HACTP on final

coating properties is presented in Table 6. A slight increase of hardness of coating films was observed with the increasing content of HACTP in the shell layer of microgel particles. This fact can be attributed to increased network density of resulting polymer materials. It was shown further that all the tested coatings exhibited high gloss and superior adhesion to glass and steel substrates. Also, the impact resistance of the resulting coatings were shown to reach maximum values suggesting the formation of cross-linked and elastic polymer materials in which sufficient coalescence of latex particles. It was found as well that HACTP amount slightly improved the chemical resistance. It can be said that the presence of HACTP did not deteriorate all the above-mentioned coating characteristics in comparison with the HACTP-free coatings.

Figure 6 Properties of coatings containing HACTP derivative.

Sample	Gloss [rel.%]	“Persoze” hardness [rel.%]		MEK resistance [s]	Impact resistance [cm]	Adhesion
		after 24 hours	after 14 days			
S0	80.4	17.26	19.31	20.5	> 100	0
S0.5	81.8	24.59	31.04	28.8	> 100	0
S0.75	83.7	31.15	33.41	33.2	> 100	0
S1	84.7	34.36	37.20	35.4	> 100	0

2.2.1 Evaluation of flame stability of coatings with HACTP

Our interest was focused on the evaluation of flame retardancy of the prepared phosphazene derivative in the resulting coatings, the effect of HACTP amount inside latex particles on combustion of self-crosslinking coatings was studied as well. The results obtained from measurements using dual-cone calorimeter are presented in Figure 7. It was found that the coatings comprising HACTP exhibited lower values of mean heat release rate and mean effective heat of combustion. This phenomenon is amplified with the increasing HACTP content, which indicates a slower flame spread due to incorporated HACTP, the lowest value was reached at S0.75. Decreased values of total smoke release during combustion of samples containing HACTP may reflect a more efficient oxidation of hydrocarbon chains in the presence of the phosphorus compound. It is assumed that the phosphorus atom reacts in the gas phase where the PO• radical is playing the main role. In the case of values of total oxygen consumed, no significant effect of HACTP presence was proved. Nevertheless, one of the most important criteria of the flammability evaluation is the maximum average rate of heat emission that decreased markedly by the 0.75 wt.% content of HACTP (contained in the shell structure of latex particles) in the tested coating materials. These results lead us to conclude that HACTP did act as a flame retardant in the investigated coating materials. The flame stability was influenced mainly by the HACTP content. It was investigated that the highest flame retardation was reached by incorporation of 0.75 wt.% of HACTP in the shell structure of latex particles and another increase was not shown as effective.

Figure 7 Flammability of coatings with HACTP derivative.

Sample	HRR [kW.m ⁻² .g ⁻¹]	EHC [MJ.kg ⁻¹]	TSR [m ² .m ⁻² .g ⁻¹]	MARHE [kW.m ⁻² .g ⁻¹]	TOC [g.g ⁻¹]
C0	36.16	29.20	83.75	36.25	1.78
S0.5	29.09	29.07	76.26	26.14	1.73
S0.75	11.13	27.23	26.95	9.76	1.60
S1	30.78	27.01	80.38	35.36	1.65

2.3 Evaluation of polymers considering inter-particle crosslinkers

The results of MFFT measurements are listed in Figure 8. In comparison with latexes Fin and FinZn without any inter-particle crosslinker, the corresponding 0G PAMAM-self-crosslinking latexes were found to exhibit significantly decreased MFFT values. On the contrary, ADH-containing self-crosslinking latexes were shown to possess higher MFFT than the corresponding standard latexes. The considerable drop in MFFT values in the case of latexes containing 0G PAMAM dendrimer is desirable (indicating good application properties) and may be associated with enhanced hydroplasticization of polymer due to the presence of highly alkaline amidoamine dendrimers. PAMAM crosslinker probably caused permanent neutralization of carboxylic groups during the film-formation (in comparison with conventional ADH-crosslinked latex compositions that turn acid after ammonia evaporation resulting in protonated carboxylic groups). Thus, softening of polymer chains comprising ionized carboxylic groups during the whole process of film-formation was probably achieved resulting in MFFT decrease.

The inter-particle crosslinking of air-dried coating films cast from latexes containing different inter-particle crosslinking agents was verified from the point of view of T_g and gel content enhancement. The number average molecular weight between crosslinks (M_c) and the crosslinking density of coating film samples were determined too. For the comparison, coating films based on the standard latexes without any crosslinker were tested as well. Figure 8 shows results of T_g , gel content and crosslinking density measurements with respect to the inter-particle crosslinker type in a given coating composition. 0G PAMAM-crosslinked coatings were found to exhibit decreased glass transition temperatures, compared with coatings crosslinked with the conventional ADH. Both crosslinkers possessed higher glass transition temperatures in comparison with coating materials cast from the corresponding standard latexes without any crosslinker.

When comparing both series of latexes, the latexes containing zinc oxide nanoparticles were shown to provide densely crosslinked materials, which can be assigned to ionic cross-linking due to zinc metal ions. Although the network of ionic cross-linking is thought not to be as strong as a covalently crosslinked network, the ionic cross-linking was shown to withstand THF treatment during Soxhlet extraction. We can conclude that 0G PAMAM dendrimer worked as the effective inter-particle cross-linking agents comparable to the conventional ADH cross-linker and the presence of zinc oxide nanoparticles increased the network density of resulting materials considerably.

Figure 8 Properties of polymers considering different crosslinking agents.

Sample	Sol [hm.%]	T_g [°C]	$MFFT$ [°C]	M_c [g.mol ⁻¹]	Crosslinking density [mol.cm ⁻³]
Fin	19.2	10.47	6.8	59167.8	1.77×10^{-5}
Fin + ADH	9.3	19.51	9.3	17590.5	6.01×10^{-5}
Fin + 0G PAMAM	12.2	12.86	4.4	23220.5	4.42×10^{-5}
FinZn	9.9	12.56	9.6	25073.9	4.25×10^{-5}
FinZn + ADH	1.8	13.63	12.7	11845.1	8.63×10^{-5}
FinZn + 0G PAMAM	5.6	13.20	8.4	21905.7	4.73×10^{-5}

The attention was also paid on the stability in the case of the PAMAM containing self-crosslinking one-component latexes. Hence, we focused our research on storage stability testing as well. The stability of latexes was evaluated according to changes of the average particle size and zeta potential before and after storing at 50 °C for 50 days. The results of the measurements are summarized in Figure 9. No significant changes of all the tested properties were observed after the storing, which proves a good stability of the novel one-component self-crosslinking compositions based on 0G PAMAM inter-particle crosslinkers.

Figure 9 Results of storage stability.

Sample	Viscosity [mPa.s]		pH	Particle size [nm]	Zeta potential [mV]	
	before alkalization	after alkalization			beginning	after 2 months
Fin	11.22	30.72	2.51	125.3	-38.6	-41.9
Fin + ADH	-	-	-	130.7	-42.1	-45.6
Fin + 0G PAMAM	-	-	-	126.3	-39.3	-43.1
FinZn	23.34	28.19	6.13	157.6	-37.1	-40.4
FinZn + ADH	-	-	-	156.2	-40.2	-42.9
FinZn + 0G PAMAM	-	-	-	155.4	-38.7	-42.8

2.3.1 Evaluation of latex coatings

The effect of inter-particle self-crosslinking using 0G PAMAM and ADH as crosslinking agents on properties of the resulting coatings is shown in Figure 10. The thickness of dried coating films was about 50 μm and all prepared coatings were transparent without any surface defects. It was shown that all tested coating films exhibited high gloss without any significant difference depending on the inter-particle crosslinker type. High gloss of a given latex film suggests a good coalescence without

any phase separation during the film-formation or premature particle aggregation in the dispersion. Further, mechanical properties of the 0G PAMAM- and ADH-crosslinked coatings were evaluated. The 0G PAMAM-crosslinked coatings based on both types of standard latexes (Fin and FinZn) were found to show increased initial and final hardness values in contrast to the non-crosslinked coatings. When comparing latexes regarding to ZnO nanoparticles presence, the results indicated clearly that the coatings containing ZnO nanoparticles (imparting ionic cross-linking) exhibited significantly improved MEK resistance. Moreover, the 0G PAMAM-based coatings showed as high adhesion to glass substrate and impact resistance as the ADH-based coating films. Hence, it is evident that the self-crosslinking latexes using 0G PAMAM dendrimers as the intra-particle crosslinkers provide high quality coatings of similar properties compared to the conventional ADH-based systems.

Figure 10 Properties of coatings considering different crosslinking agents.

Sample	Gloss [rel.%]	“Persoze” hardness [rel.%]		MEK resistance [s]	Impact resistance	Adhesion
		1 day	30 days			
Fin	85.1	16.62	22.48	20	> 100	0
Fin + ADH	83.7	31.15	32.51	33,2	> 100	0
Fin + 0G PAMAM	82.5	20.84	27.18	156	> 100	0
FinZn	79.9	10.0	14.36	> 300	> 100	0
FinZn + ADH	77.8	21.2	23.90	> 300	> 100	0
FinZn + 0G PAMAM	76.9	15.42	21.19	>300	> 100	0

Our interest was also focused on the evaluation of flammability of the prepared self-crosslinking latex coatings, on the effect of inter-particle crosslinking agent. The results obtained from measurements using dual-cone calorimeter are presented in Figure 11. It was found that the coatings based on the Fin-composition exhibited lower values of mean heat release rate in case of use ADH inter-particle crosslinking agent and mean effective heat of combustion by the use of both crosslinking agents. FinZn-based coatings exhibited lower values of mean heat release rate and mean effective heat of combustion after crosslinking with both types of inter-particle crosslinking agents. In the case of values of total oxygen consumed, no significant effect of crosslinkers presence was proved. Nevertheless, one of the most important criteria of the flammability evaluation is the maximum average rate of heat emission that decreased slightly by the presence of both crosslinker in the tested coating materials. These results lead us to conclude that the copolymer composition plays the main role in the flammability but the 0G PAMAM and ADH as crosslinking agents also mildly did act as a flame retardant in the investigated coating materials. It was investigated that the highest flame retardation was reached by FinZn coating binders with incorporation of 0.75 wt.% of HACTP in the shell structure of latex particles and 0G PAMAM as crosslinking agent.

Figure 11 Flammability evaluation of coatings considering different crosslinking agents.

Sample	HRR [kW.m ⁻² .g ⁻¹]	EHC [MJ.kg ⁻¹]	TSR [m ² .m ⁻² .g ⁻¹]	MARHE [kW.m ⁻² .g ⁻¹]	TOC [g.g ⁻¹]
Fin	24.22	30.03	49.79	14.22	1.7
Fin + ADH	11.13	27.23	26.95	9.76	1.6
Fin + 0G PAMAM	34.10	26.78	56.89	12.86	1.5
FinZn	19.35	27.72	52.89	12.34	1.5
FinZn + ADH	18.22	27.67	49.30	11.69	1.4
FinZn + 0G PAMAM	15.28	28.25	34.25	9.48	1.1

A common drawback of latex coatings is their water sensitivity, usually connected with water-whitening, loss of adhesion and poor durability. Therefore, the efforts to enhance water resistivity of latex coatings by means of polymer structure changes are still being encouraged and the novel 0G PAMAM-based self-crosslinking coating compositions were tested from the point of view of their water sensitivity (expressed in terms of water absorption) as well. The results of water absorption measurements are illustrated in Figs. 13 and 14. We can observe similar water absorption trends with respect to the inter-particle crosslinker type for both series of latex coatings (based on latexes Fin and FinZn, differing in the absence / presence of *nano*-ZnO). The coatings without any inter-particle crosslinker exhibited the lower water absorption after a short-term contact with water and concurrently, they showed the most pronounced water uptake after a long-term water exposure. The PAMAM dendrimer provided films with a considerably low long-term water absorption, but these films suffered from a higher short-term water absorption. It can be assessed that the short-term water absorption seemed to depend mainly on the polarity of macromolecular structure; the more polar the utilized crosslinker (ADH < G0 PAMAM), the higher the early water absorption. Concerning the long-term water absorption, the reason for the reduced water uptake in the case of crosslinked latex films is associated most likely with the enhanced stiffness of crosslinked polymer, which restricts the influx of water and does not allow water domains to grow. Nevertheless, suggesting a comparable crosslinking density, the explanation of decreased water absorption of PAMAM crosslinked films in contrast to ADH-crosslinked ones is still challenging. The literature survey revealed that latex coatings composed of amide-based acrylic monomers and polyamine additives exhibited increased water resistance. Therefore, we suppose that a higher level of amine and/or amide functionalities in the resulting polymer structure provided an improved water resistance of coatings.

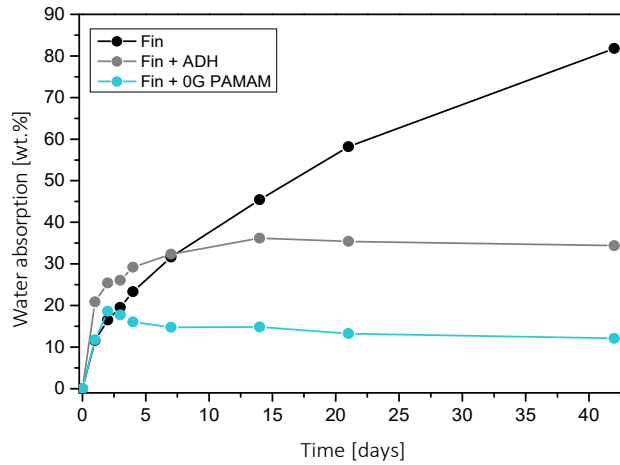


Figure 12 Water absorption into coatings cast from the latex Fin.

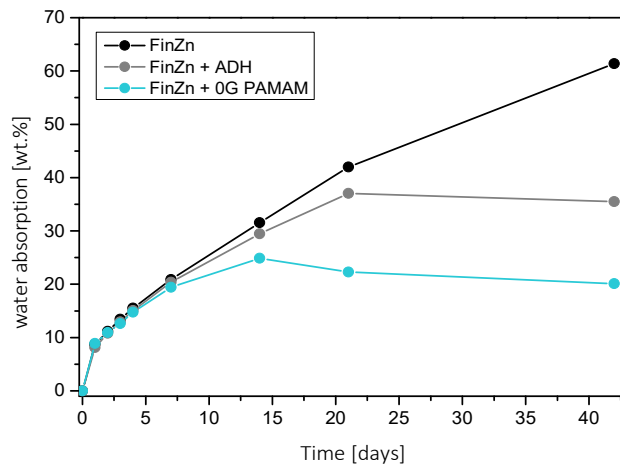


Figure 13 Water absorption into coatings cast from the latex FinZn.

2.3.2 Flash rust resistance

The appearance and course of flash rust are affected by a series of factors (relative humidity and temperature during the film formation process, the type and the pH value of the coating polymer composition) which can show a synergic action. The flash rust appearance on coated steel panels is demonstrated in Figure 15 and 16. It is evident that the coating compositions using 0G PAMAM dendrimer as the inter-particle cross-linkers provided significantly improved flash corrosion resistance, where the flash rust appeared to a less extent. It is worthy of attention that the series of coating compositions containing ZnO nanoparticles did show a significant trend to flash rust inhibition. Hence, it can be also stated that the effect Zn^{2+} ions did play a significant role. We suppose that the flash rust manifestation was affected particularly by the pH value of the given coating composition after ammonia evaporation. The flash rust resistance was observed in case of latex compositions providing alkalinity in the vicinity of steel substrate during the drying out of a coating film.

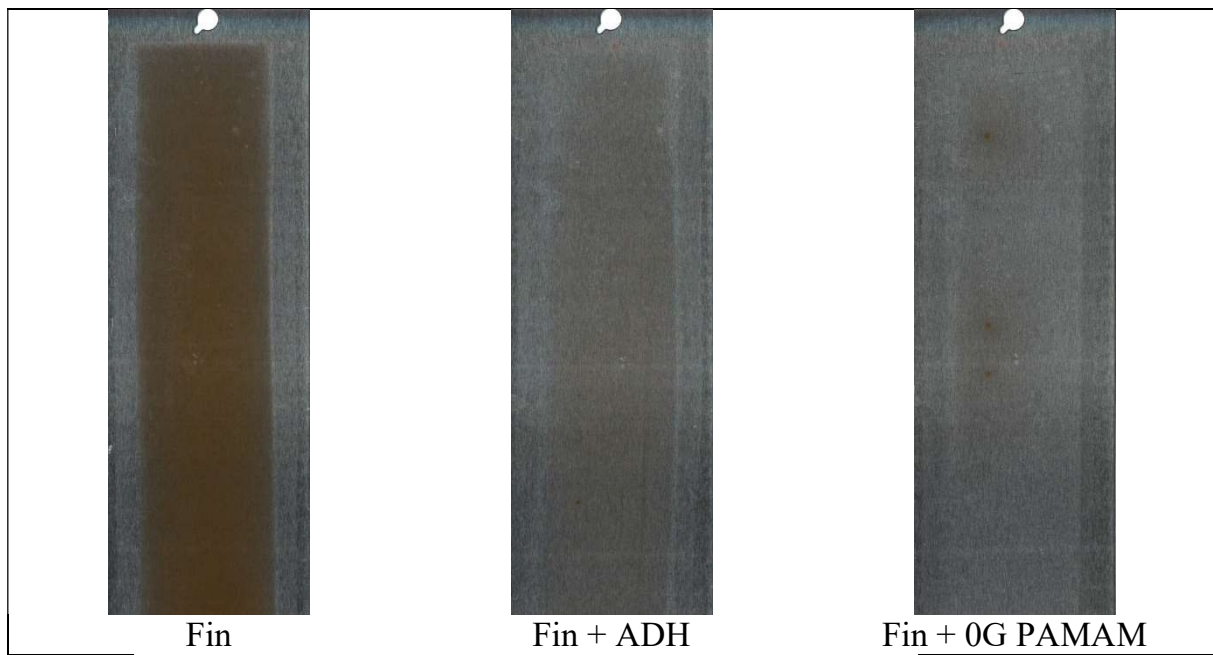


Figure 14 Photographs of coated metallic panels: coating cast from latex Fin.

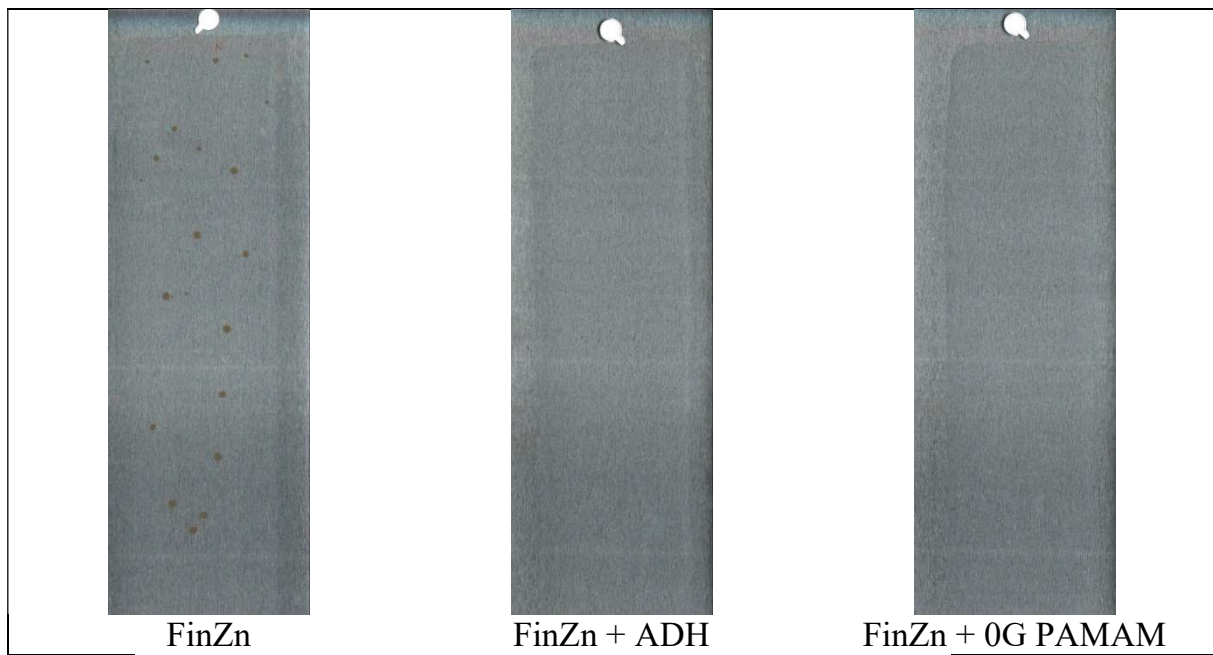


Figure 15 Photographs of coated metallic panels: coating cast from latex FinZn.

3 Conclusion

The phosphazene derivative was incorporated into the macromolecular structure of acrylic polymers through the emulsion polymerization technique proceeding at standard conditions. During the emulsion polymerization of acrylic comonomers, HACTP performed the function of an efficient intra-particle cross-linker leading to the formation of latex particles of microgel structure. In addition to that, the basic objective of this work was to evaluate the flame retardancy of the prepared phosphazene derivative in the aqueous coatings based on the HACTP-modified emulsion microgels. The presence of HACTP was found to cause a slower flame spread during the material combustion without affecting transparency, flexibility, toughness, and adhesive properties of resulting coatings.

The second goal of the work was to investigate one-component ambient temperature self-crosslinking latex coating compositions containing amine-terminated 0G PAMAM dendrimer, as the inter-particle crosslinker and ZnO nanoparticles as the flash rust inhibitors. The latexes containing 0G PAMAM dendrimer did not suffer from a short-term storage stability. The ZnO nanoparticles incorporation was shown to impart solvent resistance of coatings due to ionomeric cross-linking. Moreover, these coating compositions were shown to possess decreased MFFT values and provided crosslinked coating films of high gloss, transparency and mechanical performance comparable to the conventional ADH-based self-crosslinking latexes. It was found as well that an excellent water resistance performance could be achieved by introducing the combination of ZnO-based ionomeric cross-linking and PAMAM-based self-crosslinking into latex coating compositions. Moreover, the coating compositions using PAMAM cross-linkers provided significantly improved flash rust resistance. With respect to given facts, the PAMAM-based one-component self-crosslinking latexes could be binders for exterior and interior material protection including steel.

List of References

1. ITOH, Y., AKASAKA, R. Hydrolysable emulsifier-containing poly(meth)acrylate lattices for paper coating. *Int. J. Polym. Mater. Polym. Biomater.* 2014, 63, 137-142.
2. PERUZZO, P.J., ANBINDER, P.S., PARDINI, O.R., VEGA, J., COSTA, C.A., GALEMBECK, F., AMALVY, J.I. Waterborne polyurethane/acrylate: Comparison of hybrid and blend systems. *Progr. Org. Coat.* 2011, 72, 429-437.
3. STEWARD, P.A., HEARN, J., WILKINSON, M.C. An overview of polymer latex film formation and properties. *Adv. Colloid Interface Sci.* 2000, 86, 195-267.
4. BAL, A., GUCLU, G., İYİM, T.B., OZGUMUS, S. Effects of nanoparticles on film properties of waterborne acrylic emulsions. *Polym.-Plast. Technol. Eng.* 2011, 50, 990-995.
5. XU, H., YANG, D., GUO, Q., WANG, Y., WU, W., QIU, F. Waterborne polyurethane-acrylate containing different polyether polyols: Preparation and properties. *Polym.-Plast. Technol. Eng.* 2012, 51, 50-57.
6. LIU, J., MA, J., BAO, Y., ZHU, Z. Synthesis and application of polyacrylate/nano-SiO₂ composite leather finishing agent with polymerizable surfactant. *Polym.-Plast. Technol. Eng.* 2012, 51, 1460-1467.
7. ZHANG, J.D., YANG, M.J., ZHU, Y.R., YANG, H. Synthesis and characterization of crosslinkable latex with interpenetrating network structure based on polystyrene and polyacrylate. *Polym. Int.* 2006, 55, 951-960.
8. HOLUB, P. One-component systems yield good properties. *Eur. Coat. J.* 2004, 10, 21-28.
9. ZÁRYBNICKÁ, L., BAČOVSKÁ, R., VEČEŘA, M., ŠŇUPÁREK, J., ALBERTI, M., RYCHLÝ, J., KALENDA, P. Synthesis of curing agent for epoxy resin based on halogenophosphazene. *J. Appl. Polym. Sci.* 2016, 133, 42917-42926.
10. ALLEN, C.W. Regio- and stereochemical control in substitution reactions of cyclophosphazenes. *Chem. Rev.* 1991, 91, 119-135.
11. LEVCHIK, G.F., GRIGORIEV, Y.V., BALABANOVICH, A.I., LEVCHIK, S.V., KLATT, M. Phosphorus-nitrogen containing fire retardants for poly(butylene terephthalate). *Polym. Int.* 2000, 49, 1095-1100.
12. GU, J.W., ZHANG, G.Ch., DONG, S.L., ZHANG, Q.Y., KONG, J. Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. *Surf. Coat. Technol.* 2007, 201, 7835-7841.
13. GU, X.J., WEI, H., HUANG, X.B., TANG, X.Z. Synthesis and characterization of a novel curing agent for epoxy resin based on phosphazene derivatives. *J. Macromol. Sci. A.* 2010, 47, 828-832.
14. SUN, J., WANG, X.D., WU, D.Z. Novel spirocyclic phosphazene-based epoxy resin for halogen-free fire resistance: Synthesis, curing behaviors, and flammability characteristics. *ACS Appl. Mater. Interfaces* 2012, 4, 4047-4061.
15. YOU, G., CHENG, Z., HAO, P., HE, H. Research progress on synthesis and application of cyclotriphosphazene-based flame retardants. *Chin. J. Appl. Chem.* 2014, 31, 993-1009.
16. HE, Y., SU, S. Flame retardant resin composition without halogen and its application. PCT Int. Appl. 2014 (WO 2014089934 A1 20140619).

17. NAKAYAMA, Y. Development of novel aqueous coatings which meet the requirements of ecology-conscious society: novel cross-linking system based on the carbonylhydrazide reaction and its applications, *Prog. Org. Coat.* 2004, 51, 280-299.
18. GUO, T.Y., LIU, J.Ch., SONG, M.D., ZHANG, B.H. Effects of carboxyl group on the ambient self-crosslinkable polyacrylate lattices, *J. Appl. Polym. Sci.* 2007, 104, 3948-3953.
19. LAI, X., SHEN, Y., WANG, L. Preparation and properties of self-crosslinkable polyurethane/ silane hybrid emulsion, *J. Polym. Res.* 2011, 18, 2425-2433.
20. KOUKIOTIS, Ch., SIDERIDOU, I.D. Mechanical properties of films of latexes based on copolymers BA/MMA/DAAM and BA/MMA/VEOVA-10/DAAM and the corresponding self-crosslinked copolymers using the adipic acid dihydrazide as crosslinking agent, *Prog. Org. Coat.* 2010, 69, 504-509.
21. KOUKIOTIS, Ch. G., KARABELA, M.M., SIDERIDOU, I.D. Mechanical properties of films of latexes based on copolymers BA/MMA/DAAM and BA/MMA/VEOVA-10/DAAM and the corresponding self-crosslinked copolymers using the adipic acid dihydrazide as crosslinking agent, *Prog. Org. Coat.* 2012, 75, 106–115.
22. WANG, R.M., WANG, J.F., WANG, X.W., HE, Y.F., ZHU, Y.F., JIANG, M.L. Preparation of acrylate-based copolymer emulsion and its humidity controlling mechanism in interior wall coatings, *Prog. Org. Coat.* 2011, 71, 369-375.
23. ZHANG, S.F., HE, Y.F., WANG, R.M., WU, Z.M., SONG, P.F. Preparation of emulsifier-free acrylate cross-linkable copolymer emulsion and application in coatings for controlling indoor, *Iran. Polym. J.* 2013, 22, 447-456.
24. ZHANG, S.F., LIU, F.R., HE, Y.F., WANG, R.M., SONG, P.F. Waterborne polyurethanepolyacrylic ester hybrid emulsion for humidity-controlling coatings, *Arab. J. Sci. Eng.* 2014, 39, 23-30.
25. TOMALIA, D.A., BAKER, H., DEWALD, J., HALL, M., KALLOS, G. , MARTIN, S., ROECK, J., RYDER, J., SMITH, P. A new class of polymers: starburst-dendritic macromolecules, *Polym. J.* 1985, 17, 117-132.
26. TOMALIA, D.A. Birth of a new macromolecular architecture: dendrimers as quantized building blocks for nanoscale synthetic polymer chemistry, *Prog. Polym. Sci.* 2005, 30, 294-324.
27. BOSMAN, A.W., JANSSEN, H.M., MEIJER, E.W. About Dendrimers: structure, physical properties, and applications, *Chem. Rev.* 1999, 99, 1665-1688.
28. YANG, H., MORRIS, J.J., LOPINA, S.T. Polyethylene glycol–polyamidoamine dendritic micelle as solubility enhancer and the effect of the length of polyethylene glycol arms on the solubility of pyrene in water, *J. Colloid Interface Sci.* 2004, 273, 148-154.
29. TORIGOE, K., SUZUKI, A., ESUMI, K. Au(III)–PAMAM interaction and formation of Au–PAMAM nanocomposites in ethyl acetate, *J. Colloid Interface Sci.* 2001, 241, 346-356.
30. LIU, M., KONOL, K., FRÉCHET, J.M. Water-soluble dendritic unimolecular micelles: their potential as drug delivery agents, *J. Control. Release* 2000, 65, 121-131.

31. ENDO, T., YOSHIMURA, T., ESUMI, K. Synthesis and catalytic activity of gold–silver binary nanoparticles stabilized by PAMAM dendrimer, *J. Colloid Interface Sci.* 2005, 286, 602-609.
32. MILHEM, O.M., MYLES, C., MC KEOWN, N.B., ATTWOOD, D., D'EMANUELE, A. Polyamidoamine Starburst® dendrimers as solubility enhancers, *Int. J. Pharm.* 2000, 197, 239-241.
33. ROBERTS, J.C., BHALGAT, M.K., ZERA, R.T. Preliminary biological evaluation of polyamidoamine (PAMAM) Starburst dendrimers, *J. Biomed. Mater. Res.* 1996, 30, 53-65.
34. KESHARWANI, P., JAIN, K., JAIN, N.K. Dendrimer as nanocarrier for drug delivery, *Prog. Polym. Sci.* 2014, 39, 268-307.
35. REINHARD, G., SIMON, P., RAMMELT, U. Application of Corrosion Inhibitors in Water-Borne Coatings. *Prog. Org. Coat.* 1992, 20, 383-392.
36. DEL AMO, B., ROMAGNOLI, R., DEYÁ, C., GONZÁLEZ, J.A. High Performance Water-Based Paints with Non-Toxic Anticorrosive Pigments. *Prog. Org. Coat.* 2002, 45, 389-397.
37. REINHARD, G. Formulation of Water-Borne Dispersions for Corrosion-Protective Primers. *Prog. Org. Coat.* 1990, 18, 123-145.
38. YEON, S.J., MIJEONG, H. Multi-Functional Hybrid Coatings Containing Silica Nanoparticles and Anti-Corrosive Acrylate Monomer for Scratch and Corrosion Resistance. *Nanotechnology* 2011, 22, 025601, 1-10.
39. MONTEMOR, M.F., FERREIRA, M.G.S. Analytical Characterization of Silane Films Modified with Cerium Activated Nanoparticles and its Relation with the Corrosion Protection of Galvanised Steel Substrates. *Prog. Org. Coat.* 2008, 63, 330-337.
40. EL SAEED, A.M., EL-FATTAH, M.A., AZZAM, A.M. Synthesis of ZnO Nanoparticles and Studying its Influence on the Antimicrobial, Anticorrosion and Mechanical Behavior of Polyurethane Composite for Surface Coating. *Dyes Pigments* 2015, 121, 282-289.
41. CHIMENTI, S., VEGA, J.M., AGUIRRE, M., GARCÍA-LECINA, E., DÍEZ, J.A., GRANDE, H.J., PAULIS, M., LEIZA, J.R. Effective Incorporation of ZnO Nanoparticles by Miniemulsion Polymerization in Waterborne Binders for Steel Corrosion Protection. *J. Coat. Technol. Res.* 2017, 14, 829-839.
42. FOX, T.G., FLORY, J.P. Jr. Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight. *J. Appl. Phys.* 1950, 21, 581-591.
43. FLORY, P.J., REHNER, J. Statistical mechanics of cross-linked polymer networks II. Swelling. *J. Chem. Phys.* 1943, 11, 521-526.

List of Published Works

MACHOTOVÁ, Jana, ZÁRYBNICKÁ, Lucie, RÜCKEROVÁ, Adéla., BAČOVSKÁ, Radka, RYCHLÝ, Jozef, IMRAMOVSKÝ, Aleš. Synthesis and Application of Hexaallylamino-cyclo-triphosphazene as Flame Retardant in Latex Coatings. *Polymer-Plastics Technology and Engineering*, 2017, 56(5), 563-571.

MACHOTOVÁ, Jana, RÜCKEROVÁ, Adéla, BOHÁČIK, Peter, PUKOVÁ, Kateřina, KALEDOVÁ, Andréa, PALARČÍK, Jiří. High-performance one-pack ambient cross-linking latex binders containing low-generation PAMAM dendrimers and ZnO nanoparticles. *Journal of Coatings Technology and Research*, 2018, 15(5), 1167-1179.

RÜCKEROVÁ, Adéla, MACHOTOVÁ, Jana, SVOBODA, Roman, PUKOVÁ, Kateřina, BOHÁČIK, Peter, VÁLKA, Roman. Ambient temperature self-crosslinking latices using low generation PAMAM dendrimers as inter-particle crosslinking agents. *Progress in Organic Coatings*, 2018, 119, 91-98.

RÜCKEROVÁ, Adéla, MACHOTOVÁ, Jana. Vodou ředitelné nátěry s novými kovalentně vázanými retardéry hoření. *Chemické listy*, 2017, 111(8), 541-544.

RÜCKEROVÁ, Adéla, MEDUNOVÁ, Michaela, MACHOTOVÁ, Jana, KALEDOVÁ, Andréa, BAČOVSKÁ, Radka, VEČEŘA, MIROSLAV. Síťování vodou ředitelných nátěrů za použití retardéru hoření. *Chemické listy*, 2018, 112(7), 450-453.

RÜCKEROVÁ, Adéla, MACHOTOVÁ, Jana, MEDUNOVÁ, Michaela, PUKOVÁ, Kateřina, KALEDOVÁ, ANDRÉA. Fluorine containing latex coatings prepared using phosphazene-based flame retardant as an efficient crosslinking agent. *Scientific Papers of the University of Pardubice*, 2018, 24, 159-165.