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Fluorine containing latex coatings prepared using phosphazene-based flame retardant as an efficient crosslinking agent

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The paper is focused on the use of phosphazene derivative in latex coatings. Hexaamino-cyclo-triphosphazene can act as a low-molecular-weight hardening agent for latex copolymers if the shell structure of latex particles contains molecules of glycidyl methacrylate. The coatings containing the fluorine atoms and hexaamino-cyclo-triphosphazene exhibited transparent character, high gloss and convenient mechanical properties. The incorporated phosphazene caused the increase of heat resistance of coatings in terms of the decrease of the heat emission during the material combustion.

Keywords: Core-shell; Phosphazene; Cone-calorimeter, Emulsion polymerization

Introduction

In this century, the abundance of harmful substances in the air has reached new limits; therefore, there is a tendency to develop and practically use the water-based coatings in the industry to eliminate volatile organic compounds (VOCs). Water-based coatings do not contain VOC and they could be useful as interior and exterior

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coatings for wood and metal substrates as well. Latex coatings can offer comparable mechanical, optical and adhesion properties, together with chemical and water resistance as many solvent-borne coatings [1–4].

The film formation by ordinary latex coatings takes place via coalescence, which is a process of physical sintering of thermoplastic particles. This pathway is not a sufficient compensation of the chemical crosslinking of coating films; therefore, the chemical crosslinking is also usually used in preparation of water-based coatings. The chemical crosslinking is necessary for attaining better mechanical and chemical properties and such features are usually ensured by functionalized monomers incorporated in the structure of polymeric systems; the most frequently used being carboxy-, hydroxyl- or glycidyl groups that enable the reaction with different types of crosslinking agents [5–7].

For special applications, additives based on halogen carbohydrates or amino derivatives of *cyclo*-triphosphazene could be incorporated in water-based coating systems to improve the flame stability during the material combustion [8,9]. Triphosphazenes have a cyclic structure containing alternating nitrogen and phosphorus atoms, when each of the latter bears two substituents. This type of substances exhibit unusual thermal properties, preventing combustion of materials or showing a self-extinguishing effect. The basic member of the phosphazene family is hexachloro-*cyclo*-triphosphazene (HCCTP) and its derivatives are often used for preparing other *cyclo*-triphosphazenes that can act as flame retardants and antioxidants for some polymeric materials [10–12].

This work is focused on optimizing the amount of hexaamino-*cyclo*-triphosphazene (HACTP) in latex copolymers in terms of the increased crosslinking density of latex coatings, increased flame stability, and improved mechanical properties.

Materials and methods

Materials

Latexes investigated in this work were prepared using 2,2,2-trifluoroethyl methacrylate (TFEMA), butyl acrylate (BA), methacrylic acid (MAA), and glycidyl methacrylate (GMA). All the monomers were obtained from Rohm (Germany). Disponil FES 993 was used as emulsifying agent and sodium carbonate for pH stabilization. The Hexaamino-*cyclo*-triphosphazene (HACTP) used for inter-particle crosslinking was synthesized from hexachloro-*cyclo*-triphosphazene (HCCTP) purchased from Sigma-Aldrich.

Preparation of latexes

Water dispersions containing core-shell latex particles were prepared with the aid of the technique of semi-continuous emulsion polymerization. TFEMA, BA, and MAA were used as the main co-monomers for latex synthesis. GMA was incorporated in the shell structure of latex particles to initiate the interparticle crosslinking reaction after adding a low-molecular-weight crosslinking agent, in this case, hexaamino-*cyclo*-triphosphazene (HACTP). TFEMA/BA/MAA were used for formation of the core structure in the weight ratio 58/40/2. For the shell structure, the weighted ratio of MMA/BA/MAA/GMA was determined as 46/42/2/10. HACTP is a white water-soluble crystalline substance being added in the form of 10 wt. % water solution to the final latex.

Latexes were prepared in the glass reactors under inert nitrogen atmosphere. The batch was placed into the reactor and heated at 85 °C. Afterwards, the mixture of monomers, initiator, water, buffer solution, and emulsifying agent dosed in the reactor over the course of 90 minutes. By this emulsification, a typical core structure of latex particles was formed. After completing the core, the mixture forming the shell structure of latex particles was added into the reactor dropwise for 90 min. After two hours-lasting polymerization, the final latex was cooled down to 25°C and the pH value adjusted from about 7.5 to 8.5 using 10% ammonia solution. The solid content of latex was about 45 wt. %. The HACTP was added to the final latex in the form of 10 wt. % water solution. HACTP was added to the latexes in molar ratio 0:1, 0,5:1, 1:1, 3:1 and 6:1 in relation to GMA contained in the shell of latex particles. The scheme of the resultant crosslinking reaction is shown in Fig. 1.

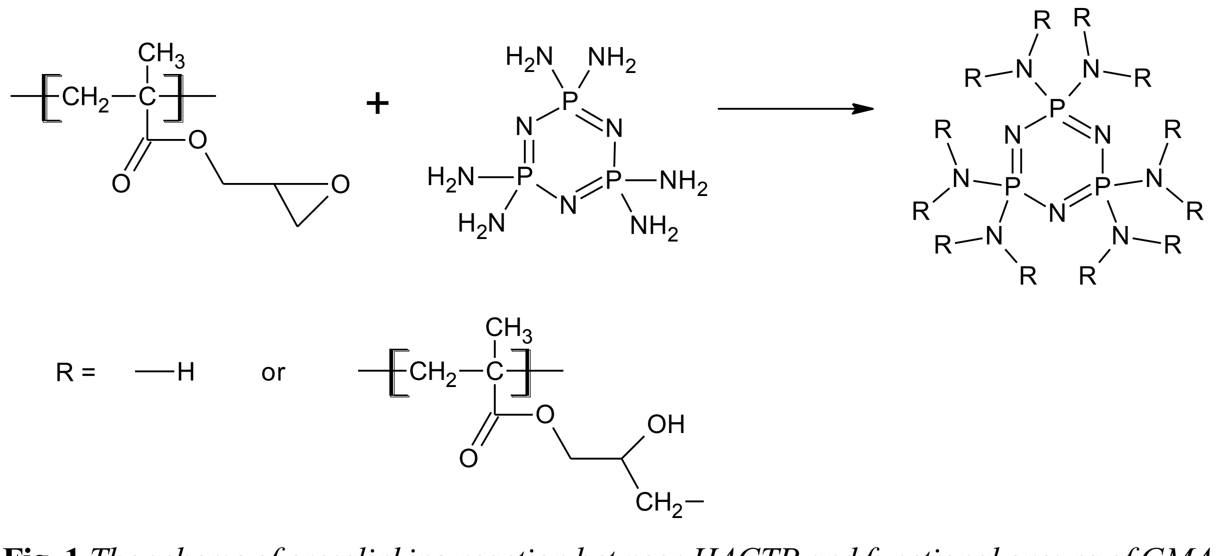

Fig. 1 *The scheme of crosslinking reaction between HACTP and functional groups of GMA*

The different ratios of the corresponding components were tested to find out the optimal ratio with respect to the mechanical and optical properties and the decreased flammability.

Preparation and characterization of latex coatings

Latexes with the added low-molecular-weight hardening agent HACTP were used for coatings preparation. All the latexes were evaluated with regard to minimum film-forming temperature (MFFT) in terms of varying amount of the hardening agent. The coating systems prepared in this way were poured in silicone molds and let dry at room temperature for 14 days. Completely dried polymeric samples were characterized using the method of differential scanning calorimetry (DSC) with a heating ratio of 10 °C min^{-1} in the temperature range from –80 up to 120 °C for determination of the glass transition temperature (T_g). The amount of polymeric gel was measured using THF extraction in a Soxhlet extractor operated for 24 hours. Around 1 g of the sample tested was weighted into the extraction thimble and let effect the THF on the sample. Then, the thimble was dried and weighted. Dried polymeric samples before and after extractions were tested using inductively coupled plasma optical emission spectrometry (ICP-OES). In this way, the amount of elementary phosphorus was determined and the crosslinking and covalently linking of HACTP proved. Flammability of the samples resp. coatings was tested by controlled burning in a cone-calorimeter (Fire Testing Technology, UK). The weight of the samples was about 8 g. By burning the heat release rate (HRR), the effective heat of combustion (EHC), the maximum rate of average heat emission (MARHE), and total oxygen consumed (TOC) were detected. The latex coatings were deposited on glass substrates with the wet thickness 120 μm and so prepared coatings left to dry for 7 days followed by testing on gloss and hardness. The gloss of the coatings was measured on black mat surface by the geometry set to 60°, whereas the hardness specified according to the norm CSN EN ISO 2409 using the pendulum damping method "Persoz".

Results and discussion

Characterization of the prepared latexes and their coatings

The real polymeric solid content of prepared latexes reached about 42 wt. %. Water-based coatings were prepared from latexes containing core-shell latex particles. Their shell structure contained copolymers with glycidyl groups being able to react with amine groups coming from HACTP. The coatings were studied from a point of view of mechanical and optical properties; namely, when the presence of HACTP did not affect the transparency and gloss of the final coatings.

Results of such measurements are shown in Table I. As seen, the increasing amount of HACTP has affected the minimum film-forming temperature in sense of the increasing MFFT.

It was shown that the increasing amount of HACTP enhanced the inter-particle crosslinking density in the polymeric system. Coatings whose latex particles were not covalently linked with phosphazene molecules reached the MFFT about 7 °C. A six-fold excess of hardening agent has led to the MFFT increasing up to 13.4 °C, which suggests us the formation of inter-particle crosslinking.

On the other hand, the increase is not so extreme and should not affect the utility properties. The gel content, as a material typically related to the glass transition temperature, increased with the increasing amount of HACTP from 89 up to 93 wt. %. More pronounced crosslinking of the tested systems exhibited a lower loss of low-molecular sol due to a higher crosslinking density — revealed by the DSC analysis — that had influenced mobility of the polymeric chains and their segments. The resulting glass transition temperatures are also shown in Table I. By the investigation of gloss, it was shown that the presence of low-molecular hardener did not affect the final gloss of these coatings because all dried coatings under study had reached a high gloss and transparent character. The increasing amount of hardener affected the hardness of the coatings deposited on glass substrates, when the system SP6 containing the highest amount of HACTP reached the highest increase of coating hardness.

The gel fraction was obtained by extractions in THF and analyzed using ICP-OES method. The resulting amounts of phosphorus are shown in Table II. It is evident that the amount of elementary phosphorus corresponds to the amount of phosphazene derivative added into the coating system.

Table 1 *The phosphorus amount, mechanical and film properties of coatings with different HACTP amount*

Item	HACTP : GMA [wt. %]	MFFT [°C]	T_g [°C]	Gel content [wt. %]	Amount of phosphorus after sample extraction [mg kg^{-1}]	Gloss [%]	Hardness [%]
SP0	0:1	7	17.20	89.9	0	80.2	17.5
SP0,5	0,5:1	9.1	18.85	90.1	519	80.4	17.7
SP1	1:1	9.8	17.40	91.2	1041	80.8	19.2
SP3	3:1	11.8	18.91	92.8	4122	80.7	19.7
SP6	6:1	13.4	17.20	93.2	7466	80.9	20.6

The attention was also paid to the ability of the coatings to prevent burning or slow down the process of burning by incorporating the HACTP into the latex coatings. The values measured in cone-calorimeter are shown in Table 2. It is clear from the results that HACTP has caused the decrease of the heat release rate (HRR) during the burning process.

The effective heat of combustion has also decreased with the increasing amount of HACTP in latex coatings. In relation to the decrease of a maximum rate of the average heat emission (MARHE) with the increasing amount of HACTP, it can be said that HACTP in the latex coatings has acted as a flame retardant.

Table 2 *Results of coatings combustion in the cone–calorimeter*

Item	HRR [kW m^{-2} g]	EHC [MJ kg^{-1} g]	TOC [g g^{-1}]	MARHE [kW m^{-2} g]
SP0	41.93	3.09	1.69	35.14
SP0,5	35.21	2.78	1.71	33.62
SP1	34.46	2.63	1.64	31.76
SP3	28.68	2.53	1.53	31.06
SP6	27.11	2.49	1.42	30.68

Conclusions

The aim of the study was to examine hexaamino-*cyclo*-triphosphazene as a low-molecular-weight hardener for acrylic copolymers. If the glycidyl methacrylate is incorporated into the shell structure of the latex particles, free amino groups can react with glycidyl functionalities in an additional reaction mode. This way of performing inter-particle crosslinking positively affects both mechanical and optical properties. Moreover, the covalently linked HACTP has been shown to work as a flame retardant of the coatings prepared from emulsion copolymers. The presence of HACTP in studied coatings has caused the decrease of heat release rate (HRR) and the maximum rate of average heat emission (MARHE). Due to the resultant fine transparency, the prepared latex compositions can be recommended as the coatings of choice for interior applications.

References

[1] Bal A., Güçlü G., İyim T.B., Özgümüş S.: Effects of nanoparticles on film properties of waterborne acrylic emulsions. *Polymer-Plastics Technology and Engineering* **50** (2011) 990–995.

[2] Liu J., Ma J., Bao Y., Zhu Z.: Synthesis and application of polyacrylate/ nano-SiO_2 composite leather finishing agent with polymerizable surfactant. *Polymer-Plastics Technology and Engineering* **51** (2012) 1460–1467.

[3] Xu H., Yang D., Guo Q., Wang Y., Wu W., Qiu F.: Waterborne polyurethane-acrylate containing different polyether polyols: Preparation and properties *Polymer-Plastics Technology and Engineering* **51** (2012) 50–57.

[4] Steward P.A., Hearn J., Wilkinson M.C.: An overview of polymer latex film formation and properties. *Advances in Colloid and Interface Science* **86** (2000) 195–267.

[5] Ferrell P.E., Gummeson J.J., Hill L.W.: The reactions of amines with melamine formaldehyde crosslinkers in thermoset coatings. *Journal of Coatings Technology* **67** (1995) 63–69.

[6] Zhang J.D., Yang M.J., Zhu Y.R., Yaung H.: Synthesis and characterization of crosslinkable latex with interpenetrating network structure based on polystyrene and polyacrylate. *Polymer International* **55** (2006) 951–960.

[7] Guofeng Q., Guozhang M., Caiying H., Jianbing W., Tingfa Y., Ruofei Z., Hui Z., Xiaogang H.: Effects of glycidyl methacrylate content and addition sequence on the acrylic latexes with carboxyl groups. *Journal of Coatings Technology and Research* **13** (2016) 973–980.

[8] Rückerová A., Machotová J.: Vodou ředitelné nátěry s novými kovalentně vázanými retardéry hoření: (in English: Water based coatings with covalently linked novel flame retardant). *Chemické listy* **111** (2017) 541–544.

[9] Ocelka T., Oceánský J., Kotlík B., Kačer P.: Sampling methods for fire retardants. *Chemické listy* **111** (2017) 156–162.

[10] Kubota S., Ito O.: Aminophosphazenes cured epoxy resins – carbon fiber composites, in Mizumachi H. (Ed): *Adhesion Science and Technology, Proceedings of the International Adhesion Symposium.* Gordon and Breach Science Publishers, Yokohama 1994, p. 578.

[11] Fox T.G., Flory P.J.: Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. *Journal of Applied Physics* **21** (1950) 581–591.

[12] Bakhshi H., Zohuriaan-Mehr M.J., Bouhendi H., Kabiri K.: Effect of functional monomer GMA on the physical-mechanical properties of coatings from poly(BA-MMA) latexes. *Journal of Materials Science* **46** (2011) 2771–2777.