PROPERTIES OF COATINGS BASED ON SELF-CROSSLINKING LATEXES CONTAINING NANOPARTICLES OF ZINC OXIDE

VLASTNOSTI NÁTĚRŮ NA BÁZI SAMOSÍŤUJÍCÍCH LATEXŮ OBSAHUJÍCÍ NANOČÁSTICE OXIDU ZINEČNATÉHO

Adéla Rückerová, Jana Machotová, Kateřina Puková

University of Pardubice, Institute of Chemistry and Technology of Macromolecular Materials, Studentská 95, 532 10, Pardubice

Summary

The paper deals with the synthesis and properties of water polymer dispersions. Latexes were prepared by emulsion polymerization with adding zinc oxide during the polymerization in the amount from 0 to 6 wt.%. The paper describes preparation and characterization of latex coatings as well. The real amount of zinc oxide in the prepared water-borne coatings is correlated with optical properties of the coatings. The creation of flash rust was shown to be inhibited by the application of the coatings on steel substrates.

Key words: anticorrosive coatings, emulsion polymerization, latex, zinc oxide

Water dispersions of copolymer microgel particles were prepared by emulsion polymerization. Composition of copolymer microgel particles consisted of methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (KMA) and diacetone acrylamide (DAAM) as starting main monomers. Microgel particles are structured as core-shell particles, wherein the shell of microgel particles was crosslinked by adding hexaallylamino-*cyclo*-triphosphazene. [1-2] Additionally, an interparticle crosslinking called keto-hydrazide crosslinking was performed after draw-downing the coating films. [3] Nanoparticles of zinc oxide were added in various amounts to the polymer system during the synthesis, specifically to the emulsion of monomers comprising the shell structure of microgel particles. The zinc oxide was added to the polymer system in order to inhibit the creation of flash rust. Creation of flash rust after the application of water based coatings on steel substrates is a frequently referred phenomenon. [4-7]

Synthesis and characterization of latexes

Emulsion consisting of water, acrylic monomers mixture, initiator and emulsifier was added into a heated reactor. This emulsion formed the core of core-shell microgel particles. After 15 minutes of post-polymerization, the emulsion of monomers creating the shell of microgel particles was added dropwise. First, water with the emulsifying agent and nano-powder of zinc oxide was allowed to the exposure of ultrasonic waves for 20 minutes, then the mixture was mechanically dispersed using a disperser for 15 minutes. After that, the aqueous phase containing zinc oxide was stirred with a

mixture of monomers and the initiator. The resulting zinc oxide-containing monomer emulsion was added dropwise to the reactor and the polymerization of shell layer of polymer particles proceeded. After cooling the polymer dispersion at 23°C, latexes were characterized in terms of the amount of coagulum formed during the polymerization. The amount of coagulum indicates the stability of polymer system. Besides, the Brookfield viscosity, pH and the minimal film-forming temperature were measured.

Characterization of coating films

The prepared latexes were casted on glass-, steel- and silicone substrates. Monitored properties of the coatings were investigated after 30 days of drying at 23°C. The coatings applied on glass substrates were evaluated in terms of their appearance, gloss and surface hardness using pendulum damping by Persoz. The hardness was measured after 24, 48 and 72 hours of drying and after 30 days. The dried films formed on silicone substrates were tested from the point of view of their noncombustible share. By this method, the real content of solid zinc oxide in polymer film was examined. Coating films prepared on silicone substrates were removed from the substrate and weighed in porcelain cups which were burned at 600°C before. Prepared samples were combusted in an oven at 600°C up to achieving constant weight of incombustible residues. After weighing of incombustible residues the real content of zinc oxide in the coating film was calculated.

Discussion

The amount of coagulum shows the stability during the emulsion polymerization. The lowest amount of coagulum was reached by using 0.5 wt.% of hexaallylamino-*cyclo*-triphosphazene in the shell structure of microgel particles and also in the case of 5 wt.% of diacetone acrylamide relative to the amount of monomers. Structure of hexaallylamino-*cyclo*-triphosphazene is shown in Figure 1.

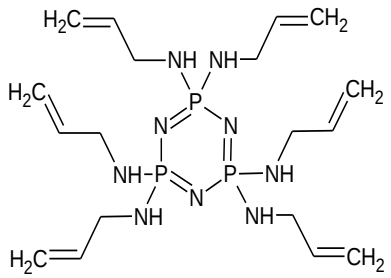

Figure 1. Structure of hexaallylamino-*cyclo*-triphosphazene

Therefore, the formulation with 0.5 wt.% of hexaallylamino-*cyclo*-triphosphazene was chosen as the most appropriate microgel composition and latexes containing this amount of hexaallylamino-*cyclo*-triphosphazene with various concentration of zinc oxide ranging from 0,5 wt.% to 6 wt.% were

synthesized with the particle size of 40 - 100 nm. It was found that the amount of coagulum increased with increased amount of zinc oxide that was added to the polymer system. The coagulum contained a certain amount of zinc oxide, so the actual amount of zinc oxide within the latex is not consistent with the quantity added during the synthesis. The quantity of coagulum in various polymer systems is shown in Figure 2. For determining the real amount of zinc oxide, the amount of incombustible residues in the coating film without zinc oxide was deducted.

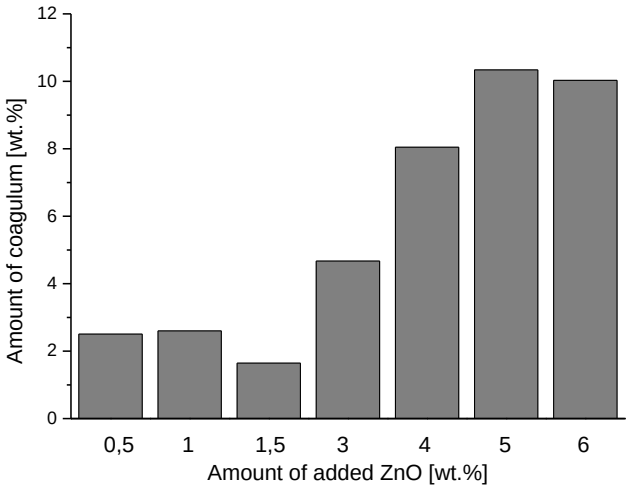

Figure 2. Amount of coagulum depending on the theoretical zinc oxide concentration in latex

In the case of the prepared self-crosslinking latexes, the film formation is achieved by two simultaneous processes: the coalescence of microgel particles and interparticle crosslinking via diacetone acrylamide and adipic acid dihydrazide reaction. Also the formation of ionic bonds between Zn^{2+} ions and COO^- groups belonging to methacrylic acid takes place there. This kind of bonds affects the film forming and also coating properties. The highest amount of zinc oxide in the coating film was achieved by preparing the latex with 4 wt.% of zinc oxide, as shown in Figure 3. It was shown that higher amount of added zinc oxide does not affect properties of the coatings, because the major amount of zinc oxide was excluded from the polymeric system with the coagulum.

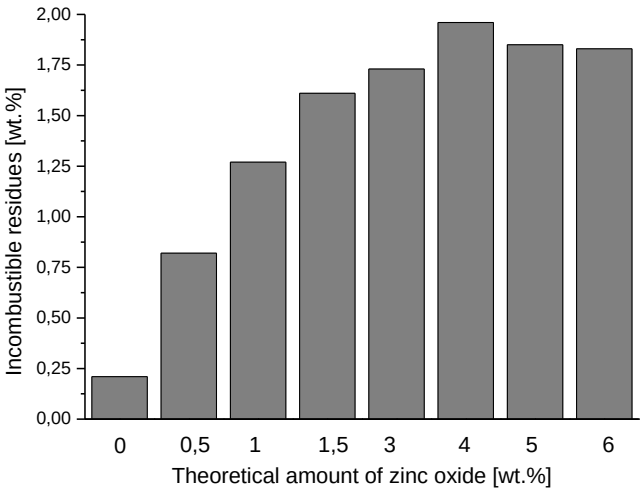

Figure 3. Amount of incombustible residues depending on the theoretical zinc oxide concentration in the coating film

The prepared coatings were evaluated for their l appearance. The coating films were transparent and clear, without any surface defects. Only the coating prepared with 4 wt.% of zinc oxide exhibited surface cracks and haze. This phenomenon could be caused by a higher minimum film-forming temperature of this coating related to the high amount of zinc oxide nanoparticles. This phenomenon was confirmed by measuring the minimum film-forming temperature. The value of minimum film-forming temperature depended on the concentration of the added zinc oxide, as shown in Figure 4. It is evident that the coating system prepared with 4 wt.% of zinc oxide reached the highest value of 14.9 °C.

Considering the inadequate appearance of coating films based on latexes prepared with 4 wt.% of zinc oxide, this coating system is not very convenient for practical use. This polymeric system exhibited also the highest amount of coagulum and the highest value of minimum film-forming temperature. Hence, it would be appropriate to use maximum 3 wt.% of zinc oxide for coatings for further research.

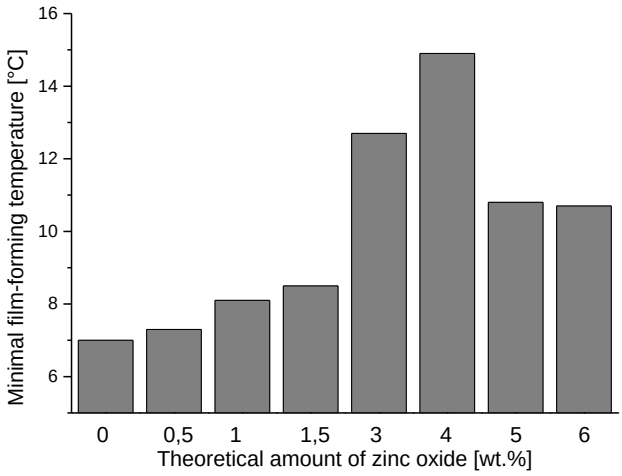

Figure 4. Value of minimum film-forming temperature depending on the theoretical zinc oxide concentration in the coating film

Conclusion

Latex coatings were prepared by emulsion polymerization that was altered by a simultaneous addition of zinc oxide to the polymeric system during the polymerization. The amount of coagulum formed during polymerization increased with the increasing amount of zinc oxide added to the polymeric system. Therefore, it is appropriate from an economical viewpoint to use maximal 3 wt.% of zinc oxide (related to monomers) during the polymerization. This claim was supported by optical properties of coating films. Higher amount of zinc oxide than 3 wt.% caused turbidity of coating films and mechanical defects of coatings.

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