

COATING BINDERS BASED ON STRUCTURED SELF-CROSSLINKING LATEXES

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Abstract

This work is focused on self-crosslinking latexes synthesized by the technique of emulsion polymerization. The prepared water dispersions of acrylic copolymers contain microgel particles of core-shell structure. The variability of properties of the resulting latexes is the advantage of this type of coating binders. Crosslinking ensuring the microgel structure of latex particles was achieved by hexaallylamino-*cyclo*-triphosphazene which also aims to reduce the flammability of the resulting polymer. Because of the double bonds present in hexaallylamino-*cyclo*-triphosphazene molecule, this kind of flame retardant can be incorporated into the structure of microgels by radical copolymerization like other monomers. Diacetone acrylamide was bonded together with the monomers in the shell structure of microgel particles. Keto- functionalities of diacetone acrylamide repeat units ensure the interfacial crosslinking reaction with adipic acid dihydrazide after water evaporation during film-formation. Thus, the interpenetrating network can be generated.

Introduction

Because of the increasing pressure on environmental protection the self-crosslinking latexes were synthesized using the technique of emulsion polymerization. Acrylate monomers, redox initiator, emulsifying agent and water were used as starting substances. The prepared water dispersions of acrylic copolymers contain particles of core-shell structure. The variability of properties of the resulting latexes is the advantage of this type of coating binders. This kind of latexes can be used as water based one-component coating system. Crosslinking ensuring the microgel structure of latex particles was achieved by hexaallylamino-*cyclo*-triphosphazene which also aims to reduce the flammability of the resulting polymer^[1-3]. Hexaallylamino-*cyclo*-triphosphazene is a tawny crystalline substance, which is prepared by the reactions of white crystalline hexachloro-*cyclo*-triphosphazene and allylamine in medium of tetrahydrofuran. Because of the double bonds present in hexaallylamino-*cyclo*-triphosphazene molecule, this kind of flame retardant can be incorporated into the structure of microgels by radical copolymerization like other monomers, as shown in Figure 1^[4-6].

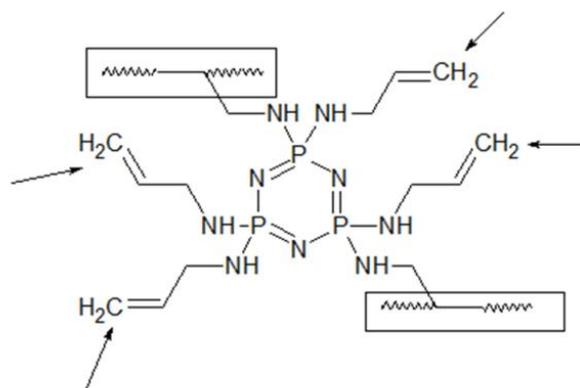


Figure 1. Principle of crosslinking emulsion copolymers by using hexaallylamino-*cyclo*-triphosphazene

Diacetone acrylamide was bonded together with the monomers in the shell structure of microgel particles. The film forming usually runs through coalescence of microgel particles, wherein the gradual deformation of spherical particles into a continuous coating film proceeds. The deformation of latex particles occurs because of evaporation of water from the coating. The coatings made only by coalescence don't have enough mechanical properties and chemical resistance. This disadvantage can be inhibited by making an interparticle

network. The interparticle network is made by using various resins. Reactive groups present in resins can react with different functional groups that are engaged in latex particles. The final film is usually formed at high temperatures. This way of making interparticle crosslinking can be eliminated by using diacetone acrylamide together with other monomers during the synthesis of latexes. Then the water solution of adipic acid dihydrazide is added to the finally made latexes. Keto- functionalities of diacetone acrylamide repeat units ensure the interfacial crosslinking reaction with adipic acid dihydrazide after water and amines evaporation during film-formation, as shown in Figure 2. Thus, the interpenetrating network can be generated. It is the condensation reaction which is splitting off the water. This reaction is acid catalyzed, therefore of using of methacrylic acid during latex synthesis is convenient^[7-8].

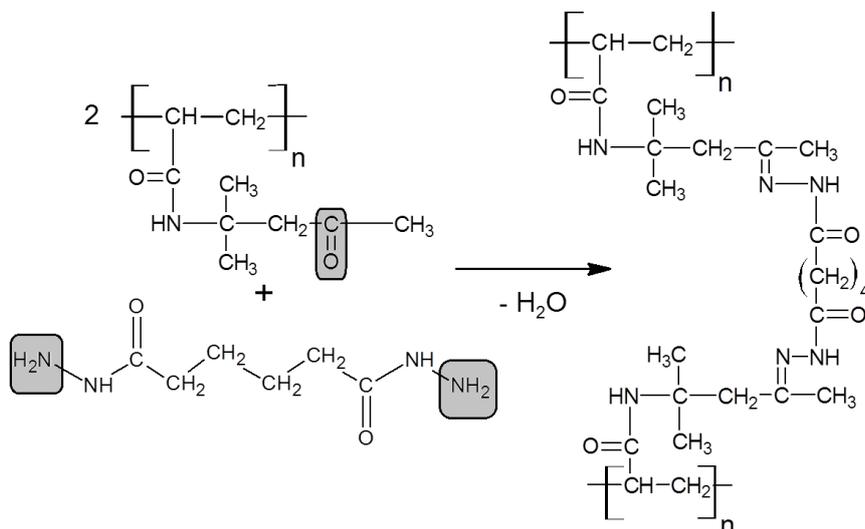


Figure 2. Crosslinking reaction of keto-funktionalities of diacetone acrylamide and amino groups of adipic acid dihydrazide

Discussion and result analysis

Gel content

The increasing concentration of hexaallylamino-*cyclo*-triphosphazene is supposed to have the positive effect on the flammability of coating systems and also should increase the crosslinking density of microgel particles and their gel content. The gel content of the microgel particles was investigated by Soxhlet extraction in tetrahydrofuran. The microgel particles whose core and shell structures were crosslinked by using hexaallylamino-*cyclo*-triphosphazene contained the highest proportion of gel. With the increasing amount of hexaallylamino-*cyclo*-triphosphazene smaller amounts of low molecular sol fraction were extracted. This fact shows that the microgel particles contained higher proportion of polymer gel. The shell structures of microgel particles contained different amounts of diacetone acrylamide, which should influence the inter-particle crosslinking and mechanical and chemical properties of final coating films. The amount of hexaallylamino-*cyclo*-triphosphazene varied from 0 to 1 wt.% and the amount of diacetone acrylamide varied from 0 to 10 wt.% (based on total amount of monomers forming core and shell, respectively).

Stability of latexes

Amount of coagulum can be considered as a criterion of stability of water dispersion. Coagulum is in this case the solid component which was formed in the reactor during the polymerization. The increasing amount of hexaallylamino-*cyclo*-triphosphazene and diacetone acrylamide was shown to affect the stability of the polymer dispersion during the synthesis. The dependence of the amount of coagulum formed during the synthesis on the amount of diacetone acrylamide comonomer in the shell structure of latex particles is shown in Figure 3. The lowest amount of coagulum was found in the case of latexes of microgel particles comprising 0.5 wt.% or 0.75 wt.% of hexaallylamino-*cyclo*-triphosphazene and 5 wt.% of diacetone acrylamide in the shell structure. In the case of utilizing 0.5 wt.% of hexaallylamino-*cyclo*-triphosphazene in the core structure or simultaneously in core-shell structure, the stability during the synthesis of latexes was decreased.

Hence, the latexes of microgel particles comprising 0.5 wt.% or 0.75 wt.% of hexaallylamino-*cyclo*-triphosphazene covalently bonded in the shell structure were found as the most stable.

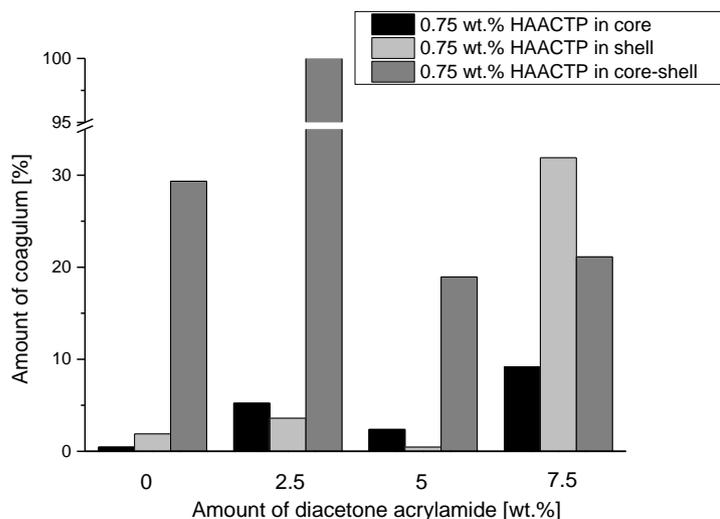


Figure 3. Amount of coagulum depending on the diacetone acrylamide concentration in the shell structure of latex particles

Coatings

Coating films based on the prepared water dispersions were coated on glass and steel substrates. Thus prepared coatings were left to dry out for 30 days at room temperature. The resulting coating films showed after 30 days of drying transparent character, high gloss, excellent adhesion to both types of substrates and enhanced chemical resistance. The hardness of coating films was measured after 24, 48, 72 hours and after 30 days. The hardness was determined using the method of pendulum damping by Persoz. Relatively high hardness of coating films was reached after 24 hours of drying at room temperature, as shown in Figure 4. The hardness of coating films depends on interparticle crosslinking of latex particles. The interparticle network is arising due the reaction of diacetone acrylamide and adipic acid dihydrazide. Therefore, the hardness of the coatings increased with the increasing amount of the embedded diacetone acrylamide in the structure of microgel particles.

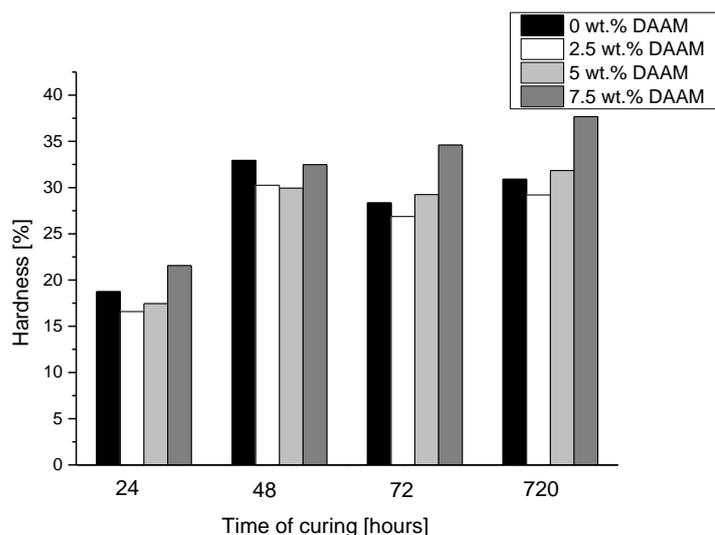


Figure 4. Hardness of coatings depending on the duration of curing and the amount of diacetone acrylamide (DAAM) in the shell structure of microgel particles

Hexaallylamino-*cyclo*-triphosphazene should have the crosslinking feature and should also affect the flame stability of the coatings. Flammability and flame stability were monitored by the combustion in cone calorimeter. The flammability was expressed in terms of mean heat release rate, mean effective heat of combustion, total heat release, total oxygen consumed, total smoke release, maximum average rate of heat emission (MARHE). It was shown that values of MARHE were decreased by using the increasing amount of hexaallylamino-*cyclo*-triphosphazene, see Figure 5. The increasing amount of hexaallylamino-*cyclo*-triphosphazene caused the drop in amounts of released smoke as well. Both these factors indicate the enhanced flame stability of coating materials containing hexaallylamino-*cyclo*-triphosphazene during the combustion process, as shown in Figure 6.

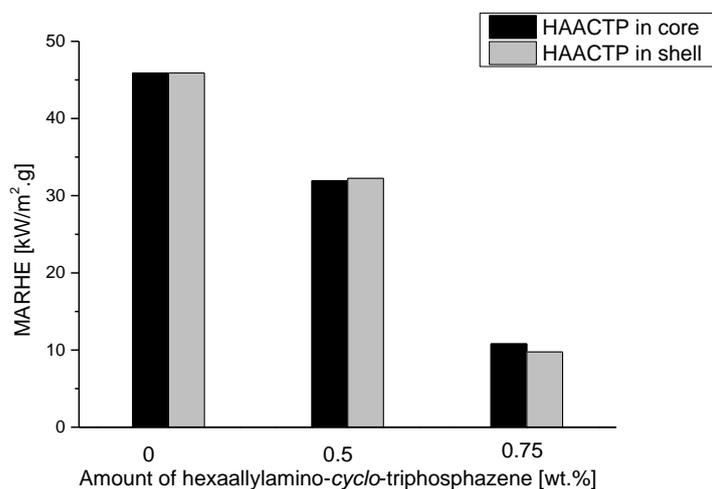


Figure 5. Maximum average rate of heat emission (MARHE) depending on the amount of hexaallylamino-*cyclo*-triphosphazene in microgel particles

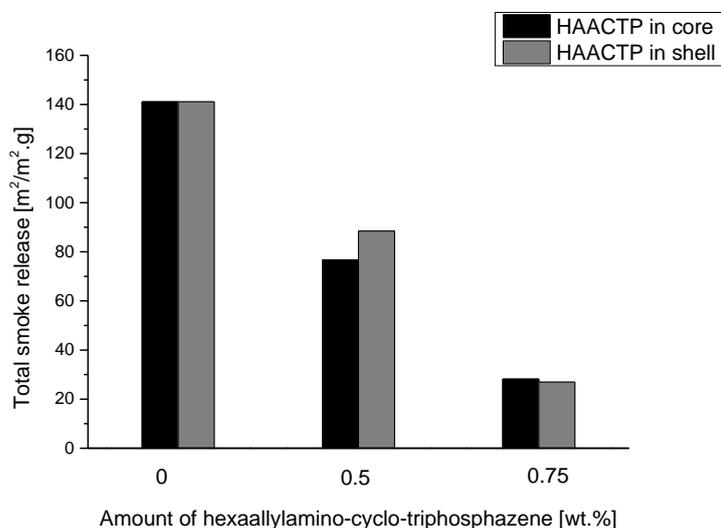


Figure 6. Total smoke release depending on the amount of hexaallylamino-*cyclo*-triphosphazene

Conclusion

During the process of emulsion polymerization the hexaallylamino-*cyclo*-triphosphazene was successfully incorporated in the latex particles. The subsequent interparticle network inside coating films was achieved by the condensation reaction of dicitone acrylamide and adipic acid dihydrazide. Thus prepared latexes show good storage stability. Latex coatings can be considered as a one-component water-based coating systems. By using hexaallylamino-*cyclo*-triphosphazene are coating systems with covalently bonded flame retardant. This kind of coatings exhibits properties like transparency, good mechanical properties, excellent adhesion to different surfaces and sufficient chemical resistance. Such coatings have increased flame resistivity, they real application can be primary in interior accommodations specially as transparent varnishes for wood surfaces.

Acknowledgement

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