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Ambient temperature self-crosslinking latices using low generation PAMAM dendrimers as inter-particle crosslinking agents

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ABSTRACT

This study focuses on one-component ambient temperature self-crosslinking latex coating compositions containing poly(amidoamine) (PAMAM) dendrimers in the role of eco-friendly crosslinking agents. Low generation amine-terminated PAMAM dendrimers of in the form of aqueous solution were added into acrylic latices containing diacetone acrylamide (DAAM) repeat units in their polymer structure. The latex storage stability and coating performance were evaluated and compared with the coating compositions containing the conventional adipic acid dihydrazide (ADH) crosslinking agent. It was found that the latices containing PAMAM dendrimers, exhibited a long-term storage stability and provided crosslinked coating films of high gloss, transparency and mechanical performance comparable to ADH-based self-crosslinking latices. Moreover, PAMAM-crosslinked coatings exhibited excellent water-whitening resistance.

1. Introduction

During the last decades, coating suppliers have been forced to move to waterborne technology due to increasing environmental regulations and legislative pressures. Therefore, waterborne colloidal polymers, i.e. "latices" prepared via emulsion polymerization are of particular interest and have been widely applied as binders for paints, inks and special coating materials for other applications. 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 [1–4]. 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 [5–10]. This chemistry, termed the keto-hydrazide reaction, is favored by 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 latices 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 [11], through wood paints and varnishes to paints for metal protection and decorative systems [12,13].

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 [14,15]. 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 [16–18]. 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 [19–21]. Particularly, low-generation PAMAM dendrimers (third generation or lower) have desired biological properties, such as nontoxicity and nonimmunogenicity for in vivo applications [22,23]. Thus, water soluble amino-functionalized PAMAM

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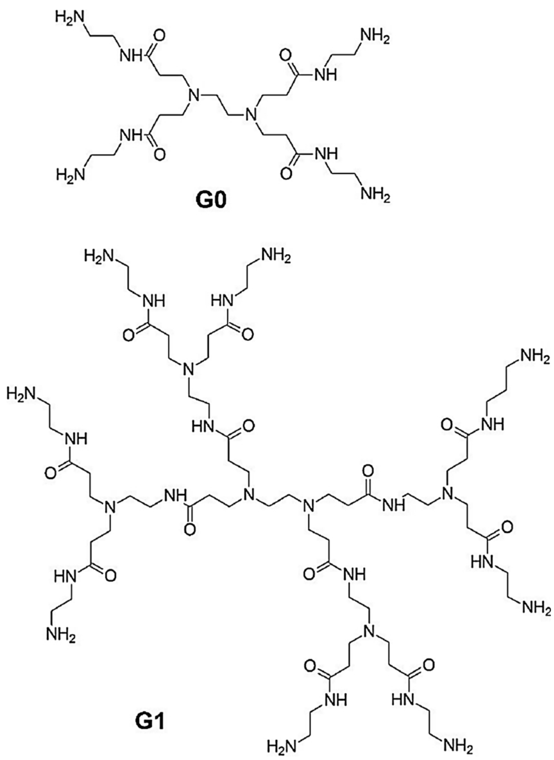

Fig. 1. Structure of PAMAM dendrimers of generation 0.0 (G0) and generation 1.0 (G1).

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 self-crosslinking of standard latices comprising DAAM repeat units within the polymer was provided by first and second generation PAMAM dendrimers, respectively. The latex stability and coating performance with emphasis on water sensitivity were evaluated and compared with the conventional ADH crosslinking agent.

2. Materials and methods

2.1. Materials

Amine-terminated poly(amidoamine) dendrimers (PAMAM) of generation 0.0 (G0) and generation 1.0 (G1) in as 20 wt.% methanol solutions were purchased from Sigma-Aldrich (Czech Republic). Their chemical formulas are illustrated in Fig. 1. After methanol evaporation, the PAMAM dendrimers were easily dissolved in distilled water to produce 10 wt.% aqueous solution. Adipic acid dihydrazide (ADH) crosslinker was purchased from TCI Europe (Switzerland). Model latices 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 FES 993 (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.

2.2. Preparation and characterization of self-crosslinking latices

Two standard latices were 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 C_0S comprised latex particles without intra-particle crosslinking. With a view to achieve enhanced properties of final coatings, the intra-particle crosslinking was introduced by copolymerizing AMA in the case of the latex sample labeled C_AS. To ensure the sufficient film-formation, the ratio of acrylic monomers forming latex particles was chosen to achieve the calculated T_g of the resulting polymer of approximately 15 °C (using the Fox equation [24]). The detailed composition of monomer feeds forming the latex sample C_0S was as follows: 43 g MMA, 53 g BA and 4 g MAA dosed in the first step and 38.5 g MMA, 52.5 g BA, 4 g MAA and 5 g DAAM dosed in the second step. In the case of the latex sample C_AS, the composition of monomer feeds in the first step consisted of 42 g MMA, 53 g BA, 4 g MAA and 1 g AMA, and the composition of monomer feeds in the second step was identical to C_0S sample.

The latices were produced in a 700 ml 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 2 ml/min in two steps. After that, during 2 h of hold period the polymerization was completed. The recipe of emulsion polymerization is shown in Table 1. The pH value of latices was adjusted to 8.5 by adding ammonia solution. The solids content of the latices was about 45 wt.%.

In order to produce G0 PAMAM-based one-component self-crosslinking latices, 10 wt.% water solution of G0 PAMAM dendrimer at the molar ratio G0 PAMAM:DAAM = 1:4 was added to the latex. Similarly, G1 PAMAM-based one-component self-crosslinking latices were obtained by adding 10 wt.% water solution of G1 PAMAM dendrimer at the molar ratio G1 PAMAM:DAAM = 1:8 to the latex. (The molecular weight of G0 PAMAM and G1 PAMAM is 517 and 1430 g/mol, respectively). Finally, the comparative ADH-based one-component self-crosslinking latices were produced by adding 10 wt.% water solution of ADH to the model latex at the molar ratio ADH:DAAM = 1:2. The self-crosslinking reaction of DAAM containing polymer with G1 PAMAM dendrimer and ADH, respectively, is depicted schematically in Fig. 2.

The minimum film-forming temperatures (MFFT) of all the prepared self-crosslinking latices and standard latices without any crosslinker were measured according to ISO 2115, using the MFFT-60 instrument (Rhopoint Instruments, UK). pH measurements were carried out at 23 ± 1 °C using a pH meter FiveEasy FE20 (Mettler-Toledo, Switzerland).

2.3. Monitoring of self-crosslinking reaction

The verification of the occurrence of G0 PAMAM- and G1 PAMAM-based self-crosslinking reaction was performed on dried coating films from the point of view of exploring their glass transition temperature (T_g), gel content and crosslinking density differences. The self-crosslinking based on PAMAM dendrimers was compared with ADH-based

Table 1
Recipe of emulsion polymerization.

Reactor charge:	
Water (g)	65
Disponil FES 993 IS (g)	0.5
Ammonium persulfate (g)	0.4
Monomer emulsion (1st step):	
Water	60
Disponil FES 993 IS (g)	7.4
Ammonium persulfate (g)	0.4
Monomers (g)	100
Monomer emulsion (2nd step):	
Water (g)	60
Disponil FES 993 IS (g)	7.4
Ammonium persulfate (g)	0.4
Monomers (g)	100