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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

Christos G. Koukiotis, Maria M. Karabela, Irini D. Sideridou*

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki GR-54124, Greece

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ABSTRACT

The purpose of this investigation was to determine the mechanical properties of films of latexes based on the copolymers butyl acrylate (BA)/methyl methacrylate (MMA)/diacetone acrylamide (DAAM) and BA/MMA/vinyl neo-decanoate (VEOVA-10)/DAAM and the corresponding self-crosslinked copolymers using the adipic acid dihydrazide (ADH) as crosslinking agent. These copolymers were synthesized by a modified semi-continuous microemulsion copolymerization. During the copolymerization various emulsifier systems, stabilizing systems and monomer compositions were used. The static tensile strength of films of all copolymers prepared was determined. Also, the prepared films were tested by dynamic mechanical analysis (DMA) for the determination of storage modulus (E'), loss modulus (E''), tangent delta ($\tan\delta$) and glass transition temperature (T_g). The mechanical properties of films were improved by the addition of the crosslinking agent ADH. Furthermore, the use of polymerizable emulsifier during the preparation of latexes caused an improvement of mechanical properties of the films, in comparison with mechanical properties of the films of latexes which prepared without polymerizable emulsifier.

1. Introduction

Aqueous acrylic polymer emulsions are friendly to the environment and as time goes by, they tend to replace solvent based binders in several coatings and adhesive applications to protect our health and to ensure safety. In our previous study stable latexes of butyl acrylate (BA)/methyl methacrylate (MMA)/diacetone acrylamide (DAAM) copolymers and BA/MMA/vinyl neo-decanoate (VEOVA-10)/DAAM copolymers were prepared by a starve-fed emulsion polymerization [1]. The structures of the monomers used are shown in Fig. 1. VEOVA-10 is the vinyl ester of Versatic ester of Versatic 10 (or neo-decanoic acid) a synthetic saturated monocarboxylic acid of highly branched structure containing 10 carbon atoms [2]. R_1 and R_2 are (branched) alkyl groups containing in total 7 carbon atoms. This unique highly branched carbon rich structure provides the monomers with a hydrophobic nature and a strong resistance to saponification. DAAM that can be prepared by the reaction of acrylonitrile, acetone and sulfuric acid is a very water-soluble monomer (solubility > 100 g/100 g water) [3].

The main disadvantages of classic acrylic polymer emulsions are poor solvent resistance, surface tackiness at high temperatures and brittleness at low temperatures caused by their thermoplastic nature. Various crosslinking methods that have been developed to overcome these disadvantages can be categorized as bicomponent crosslinking methods or monocomponent crosslinking methods. Crosslinking reactions between hydrazides and carbonyl moieties at ambient temperatures were described in literature [4–8]. The most common dihydrazide, adipic dihydrazide (ADH) derived from the reaction of adipic acid with hydrazine hydrate is a water-soluble and odorless compound with low toxicity [9,10]. These properties make ADH suitable for modern low volatile organic contents (VOCs) water based crosslinking systems that are friendly to the environment and safe to use. DAAM after emulsion copolymerization appears on the surface of the latex particles and provides the carbonyl moieties that can react with the water-soluble adipic dihydrazide (ADH) after evaporation of water and during the formation of the film. The crosslinking reaction of particles with ADH which is added in the latex after polymerization is shown in Fig. 2.

The purpose of this investigation was to determinate the mechanical properties of films of the copolymers BA/MMA/DAAM and BA/MMA/VEOVA-10/DAAM and the corresponding self-crosslinkable copolymers using the ADH as crosslinking agent. The static tensile strength of films of the prepared copolymers was determined. Also the films of the prepared copolymers were tested by dynamic mechanical analysis (DMA) for the determination of storage modulus (E') loss modulus (E''), $\tan\delta$ and glass transition

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* Corresponding author. Tel.: +30 210 2310 997825; fax: +30 210 2310 997769.
E-mail address: siderid@chem.auth.gr (I.D. Sideridou).

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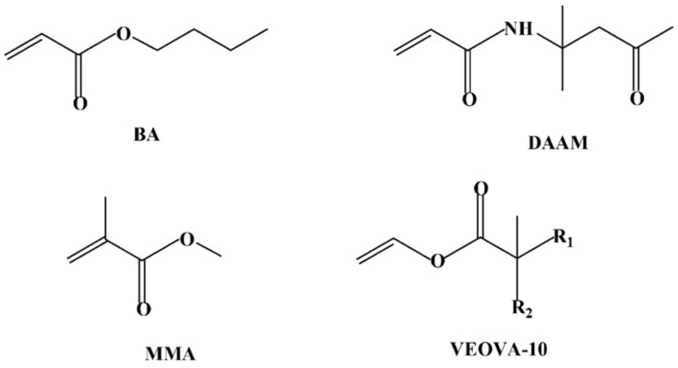

Fig. 1. Chemical structure of the monomers used in the synthesis of copolymers.

temperature (T_g). The effect of the type of emulsifier system, the type of stabilizing system and the monomer composition used during the preparation of copolymers on their mechanical properties was studied.

2. Experimental

2.1. Materials

Butyl acrylate (BA), 99.5% (stabilized with 15 ppm MEHQ), methacrylic acid (MAA), glacial 99.5% (stabilized with 200 ppm MEHQ), and acrylic acid (AA), glacial 99.5% (stabilized with 200 ppm MEHQ), were received from BASF (Ludwigshafen, Germany). Methyl methacrylate (MMA), 99.9% (stabilized with 100 ppm MEHQ), was supplied from Degussa Röhm GmbH (Darmstadt, Germany). Vinyl neo-decanoate, (VEOVA-10), was supplied from Hexion Specialty Chemicals B.V. (Rotterdam, The Netherlands), while adipic dihydrazide (ADH) and diacetone acrylamide (DAAM) were provided from DSM Exclusive Synthesis/Intermediates (Linz, Austria). Ammonium persulfate (99.9% technically pure) was used as initiator and was provided from Evonik Degussa Initiators GmbH (Pullach, Germany). Sodium hydroxymethanesulfonate (Rongalit C) was supplied from BASF (Ludwigshafen, Germany) and tert-butylhydroperoxide, 70% solution in water (TBHP, Trigonox® A-W70 trade name) was received from Akzo Nobel Polymer Chemicals BV (Amersfoort, The Netherlands); they were used as redox systems to maximizing the conversion and producing latexes with very low VOCs, which are more friendly to the environment. BA, MMA and VEOVA-10 were checked for purity with GC analysis. The used surfactants are listed in Table 1.

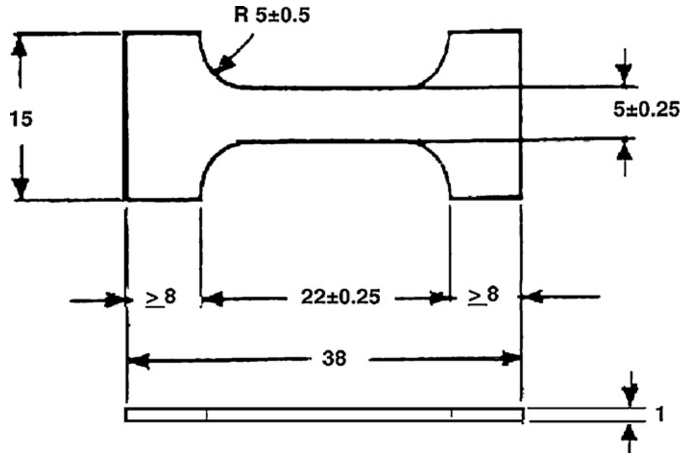

Fig. 3. The test dump-bell specimen. All dimensions are in mm (ASTM D 1708).

All the reagents were used as received without further purification. Water was deionized by passage through a set of three columns (an active carbon bed and two ion exchange columns in the row) to a final conductivity less than 6 μS.

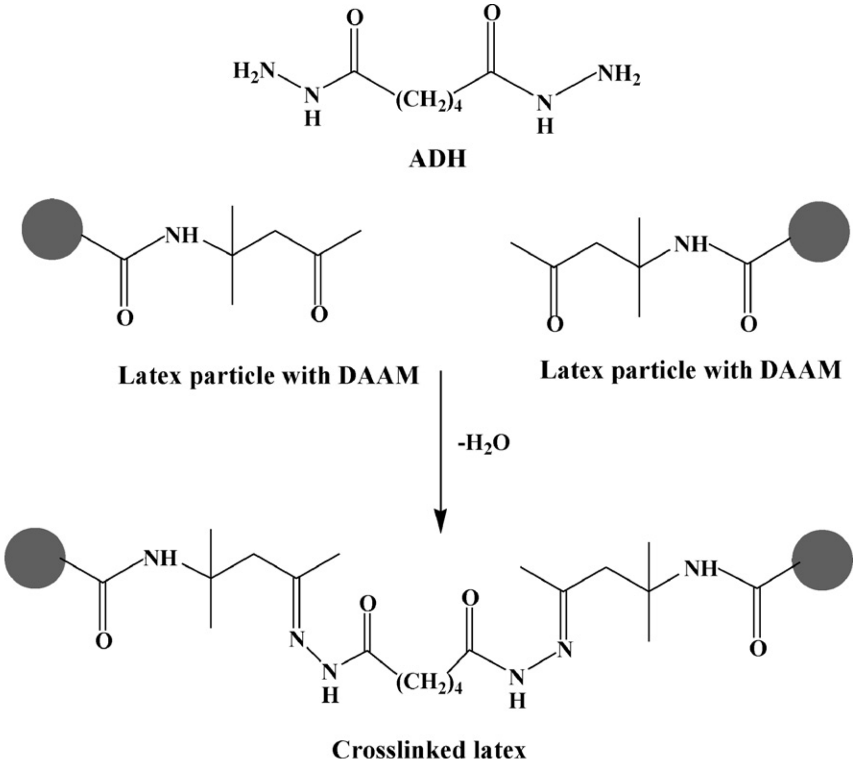

Fig. 2. Crosslinking reaction of DAAM latex particles with the crosslinking agent ADH.