



Permanently antimicrobial waterborne coatings based on the dual role of modified poly(styrene-co-maleic anhydride)

William J. Cloete, Lehani Verwey, Bert Klumperman *

Stellenbosch University, Department of Chemistry and Polymer Science, Private Bag X1, Matieland 7602, South Africa

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ABSTRACT

Poly(styrene-*alt*-maleic anhydride) was successfully (partially) modified with *N,N*-dimethylaminopropylamine to yield the corresponding *N*-substituted maleimide with dangling tertiary amine functionality. The remaining maleic anhydride units were ammonolyzed to create a water-soluble polymer. This polymer was used as a polymeric surfactant in the emulsion copolymerization of styrene and *n*-butyl acrylate. The tertiary amine-functional polymer was further shown to possess antibacterial and antifungal properties. When post-added to a poly(styrene-co-butyl acrylate) latex, the antimicrobial activity was not homogeneously present on a coating film made from the latex. However, when the tertiary amine-functional polymer was used as surfactant in the preparation of the latex, the antimicrobial activity was homogeneous and consistent over the entire coating surface.

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1. Introduction

Biocides are widely used in the coatings industry to prevent or inhibit bacterial growth in storage containers as well as after application on substrate surfaces [1]. The current use of low molar mass biocides is a source of major concern since biocides leach out of the final products or substrate films and result in residual toxicity in fresh water systems such as rivers, dams and ground water sources [2,3]. Due to its mode of operation it is also prone to lead to biocide resistant bacteria. Low molar mass biocides are typically made up of halogens, metal ions, organo-metalic compounds as well as quaternary ammonium salts [4–6] and comprise all biocides that are not polymeric in nature. They are often impregnated into a polymer matrix, and use the water absorbed by the matrix as a vehicle to leach out and kill bacteria on the material surface and nearby surroundings [7,8]. Due to intrinsic properties of the high molar mass polymeric material, the matrix stays intact and only mild swelling may occur. High level toxicity of species such as organo-tin compounds (e.g. tributyl-tin) has

resulted in banning of its use in antifouling coatings for marine applications [9,10]. The use of organo-tin compounds has been phased out over the last couple of decades, but trace amounts at toxic levels to microorganisms in harbors still remain a cause for concern. Contemporary use of silver and copper ions pertaining to the activity of the Ag^+ and Cu^{2+} ions against a wide range of bacteria saw these type of biocides gain increased popularity [11,12]. In the case of temporary medical and surgical implants, the short time of antimicrobial activity is not a problem. However, the impregnation and leaching from latex coatings is not ideal given the call for long term antimicrobial activity in coatings. It would be ideal to have polymeric biocides that strongly adsorb to individual particles and upon film formation remain distributed throughout the entire film. Examples of these are described in a review by Kenawy et al. [13] and work done by Tiller and Fuchs [14]. As a result of large scale chain entanglement, polymeric biocides used in a latex would eventually form part of the bulk system and allow for antimicrobial activity over a longer period of time due to no leaching of the active ingredients. “Fresh” biocide moieties will also be continuously exposed as degradation of the binder film proceeds. In principle permanently antimicrobial coatings can easily

* Corresponding author. Tel.: +27 21 808 3988.

E-mail address: bklump@sun.ac.za (B. Klumperman).

be achieved by suitably functionalizing or modifying a polymeric species to produce a water soluble macromolecular biocide [15]. Another environmental concern is the endocrine disrupting nature of surfactants such as APEOs (alkyl phenol ethoxylates) capable of mimicking steroids and hormones. They are widely used as emulsifiers in the production of primary dispersions and latex binders via emulsion polymerization. The surfactant does not form part of the final coating and leaches along with the continuous water phase upon drying of the coating film. Polymeric biocides and surfactants integrated into the film would be unable to leach from the final substrate film. Wastewater treatment would also be much simpler because macromolecular species can easily be removed from wastewater by means of a suitable flocculent [16]. Most polymers produced from vinyl monomers such as styrene or acrylates, are fairly inert and do not allow for any further modification. However, copolymerization of a stable monomer with one that allows for further modification produces polymeric species that can easily be functionalized, post-polymerization. For example, the copolymer poly(styrene-*alt*-maleic anhydride) [SMA], contains maleic anhydride (MANh) units that are highly reactive towards nucleophilic addition reactions by various amine compounds [17]. SMA is a strongly alternating copolymer and, depending on the excess of styrene (STY) relative to MANh in the monomer mixture, a block of STY of varying chain length can be incorporated towards the end of the reaction by using controlled living radical polymerization [18]. SMA undergoes self-emulsification after incorporation of a suitable nucleophile via the maleic anhydride units in the polymer chain to introduce specific functional groups into the polymer chain [19].

Various tertiary amine and quaternary ammonium compounds show a great degree of antimicrobial activity [20]. Amine-functionalized SMA incorporated into synthetic latexes can provide a means to obtain permanently antimicrobial latexes and coatings. In this study we show that incorporating amine-functionalized SMA in a synthetic latex leads to (1) latexes with inherent antimicrobial and antifungal properties that remain stable over time and (2) that the amine functionalized SMA can replace low molar mass surfactants in *ab initio* emulsion polymerization systems.

2. Materials and methods

2.1. Reagents

SMA1000 (Sartomer; alternating copolymer 1:1 styrene to maleic anhydride, $M_n = 2351$ g/mol, $D = 1.99$), 3-dimethylamino-1-propylamine (Fluka, 98%), acetone (Sasol, 98.5%) and ethyl acetate (chemically pure, Kimix), *N,N*-dimethylformamide (DMF) [Saarchem, 99%], diethyl ether (Merck Chemicals, 99%), 1-bromodecane (Aldrich, 98%), methanol (Sasol, chemically pure) and pyrene (Sigma, 99%) were used as received. Styrene (STY) and butyl acrylate (BuA) monomer were obtained from Freeworld Coatings Research Centre at Stellenbosch and purified by distillation under reduced pressure after removal of inhibitors by washing with KOH(aq) and NaOH(aq) respectively

and drying over MgSO₄-anhydrous. The water soluble initiator, KPS (potassium persulphate) [Sigma-Aldrich, 99%], was used along with SDS (sodium dodecyl sulphate) [Saarchem, 90%] as surfactant. Milli-Q deionised water was used as continuous phase in all reactions.

2.2. Characterization

2.2.1. Fourier transform infrared spectroscopy (FT-IR)

The polymer samples were compressed into translucent discs after mixing with KBr. The spectra were recorded using a Nexus FT-IR spectrophotometer and presented as an average of 32 scans, running the instrument in transmission mode under N_{2(g)} purging, with a resolution of 4.0 cm⁻¹.

2.2.2. Size Exclusion Chromatography (SEC)

For SEC, the instrument included a Waters 1515 isocratic pump, a Waters inline degasser AF, a Waters 717 plus auto sampler with a 100 µL sample loop, a Waters 2487 dual wavelength absorbance UV detector, a Waters 2414 refractive index detector at 30.0 °C. SEC measurements were performed on a set of two PLgel columns (Polymer Laboratories) 5 µm Mixed-C (300 × 7.5 mm) connected in series along with a PLgel guard column (50 × 7.5 mm). THF (stabilized by 0.125% BHT) was used as mobile phase at a flow-rate of 1.00 mL/min. Sample concentrations were 1.0 g/L and injection volumes were 100 µL. The columns were calibrated with polystyrene standards from Polymer Laboratories (Church Stretton, Shropshire, UK). Data processing was performed by Breeze version 3.30 SPA (Waters) software.

2.2.3. Dynamic light scattering (DLS)

DLS was done at the Freeworld Coatings Research Centre, Stellenbosch, on a Malvern Instruments ZetaSizer Nano-S equipped with a He-Ne laser operating at a wavelength of 633.0 nm and the scattered light was detected at an angle of 90°. The instrument was externally calibrated with 200 nm poly(styrene) spherical particles.

2.2.4. Transmission Electron Microscopy (TEM)

The particle morphology of the polymer latex was investigated by means of TEM analysis using a Leo912 Omega TEM (Zeiss, Oberkochen, Germany) operated at 120 kV. The latex (1 µL) was diluted with DDI water (1 mL) so as to obtain a translucent solution and 3 µL of the solution was transferred onto a piece of parafilm. Staining agent (2% aqueous uranyl acetate) was added to the solution and subsequently transferred to a carbon-coated 200 mesh copper grid. Excess sample was removed by means of blotting with a piece of filter paper and left to dry at room temperature before the imaging was done.

2.2.5. Inoculation of films in bacteria medium

Films of 75 µm were cast on a microscope slide, employing the STY/BuA latex with the 85% SMI (styrene maleimide copolymer, SMI-85) added in 5 wt% of the total solids content and dried in a sample drying oven @ 60 °C. The slides were then placed in a petri dish along with the bacteria *Lactobacillus sakei* (Gram positive), in a suitable

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