

NANOSTRUCTURED POLYMER COATINGS FOR CONTROLLING THE WETTABILITY OF FIBROUS SURFACES

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ABSTRACT

In this research we present a new approach for modifying and functionalizing the surface properties of fibrous substrates, especially cellulose-based products, by the deposition of organic nanoparticle coatings. The partial imidisation of high-molecular weight poly(styrene-maleic anhydride) in presence of ammonium hydroxide results in a stable water-borne dispersion of nanoparticles with sizes of 50 to 100 nm. The hydrophobic properties of coated paper surfaces are governed by a unique combination of chemical (degree of imidisation) and topographic (porosity and roughness) effects: it has been found that the contact angle increases at a higher degree of imidisation and higher surface roughness. As such, maximum advancing contact angles in the range of 140 to 150° and receding contact angles of 50° can be obtained on paper surfaces.

Key Words: Cellulose, Nanoparticles, Hydrophobicity

1. INTRODUCTION

The control over wetting and barrier properties of fibrous substrates, especially cellulose-based products such as paper and cardboard, finds high interest for improving the printing qualities and is important for the manufacturing of a new generation of packaging materials. Common techniques for creating hydrophobic paper and improving barrier properties rely on wet-end fiber treatments using organic sizing agents or the application of multi-component coatings containing binding agents and specific additives. The hydrophobicity of paper surfaces can be modified by graft polymerization (1), oxygen-plasma treatment (2), plasma-assisted coating deposition (3), chemical vapour deposition (4), pentafluorobenzoylation (5), esterification (6), or silylation (7) of the cellulose fibers. Other techniques include internal and/or surface sizing additives (8), or coating applications using modified starches (9). In combination with specific inorganic fillers (e.g., clay, delaminated talc, aluminiumhydroxide) and polymer films or waxes (e.g. extruded polyethylene, fluoropolymers), the entire weight of traditional paper coatings takes about 10 to 30% of the paper sheet.

New trends for enhancing the functionality of paper(-board) surfaces are driven by the need for reducing the coating weight and replacing chemicals such as fluorine-based additives (10), silanes (11), waxes and organic solvents. The implementation of nanotechnology and integration of macro-, micro-, nanostructures at paper surfaces is aimed as a tool for tailoring the performance of paper substrates or fibrous substrates in general. In this research, a novel generation of organic nanoparticles will be presented that can be applied as a coating from water-borne dispersions without the need of additional surfactants. The deposition of nanoparticles at the surface of fibrous substrates increases the specific surface area, while they change the capillary properties of the surface by reducing the macroscopic pore sizes and eventual formation of additional binding with the fibers.

2. EXPERIMENTS

2.1 Materials

Two grades of high-molecular weight poly(styrene-maleic anhydride) copolymer (SMA) were used as ground pellets: (i) the SMA-1 copolymer has molecular weight $M_w = 80000$ g/mol and contains 26 mol-% maleic anhydride and 74 mol-% styrene groups, and (ii) the SMA-2 copolymer has a weight molecular weight of $M_w = 65000$ g/mol and contains 28 mol-% maleic anhydride and 72 mol-% styrene groups.

The SMA materials were converted into partially imidised poly(styrene-co-maleimide) nanoparticles, denoted as SMI-1 and SMI-2 respectively, by reaction in a double walled, oil-heated reactor of 1 liter under continuous stirring. About 140 g SMA was charged together with an equivalent amount of ammonium hydroxide (25 % aqueous solution) as such that the molar ratio of maleic anhydride monomers (MA) to ammonium hydroxide was 1:1.01. Water was added until a total volume of 700 ml was obtained without further addition of emulsifiers. During reaction, the viscosity profile was recorded as the electric power needed to drive the stirrer at a constant speed of 50 rpm. When admitting the ammonium hydroxide solution at a temperature of approximately 90°C and a reaction pressure of 1 bar, the SMA dissolves in the reaction mixture (anhydride ring opening) thereby forming a viscous gel. The reactor was subsequently heated until the reaction mixture had a temperature of approximately 150°C and the reaction pressure was increased to approximately 6 bar in order to prevent boiling of the reaction mixture. The initiation of imidization reaction and formation of nanoparticles was observed after a reaction time of approximately 5 hours, characterized by a sudden drop in viscosity. After a total reaction time of approx. 6 hours, the reaction mixture was cooled down to room temperature. The obtained dispersions of SMI nanoparticles in water have white colour and are stable without further addition of surfactants or stabilizing agents.

2.2 Methods

The nanoparticles were applied as a coating on standard grade paper by using a K303 Multi-coater from RP-Print Coat Instruments, Ltd. The coatings were dried for 2 min at 100°C and stabilized for at least one day. Supplementary heat treatments to the coated papers were applied in a hot-air oven at temperatures between 100 and 250°C for 6 hours.

The morphology of the paper coatings was investigated by scanning electron microscopy on a FEI SEM XL30 (LaB6 filament) and FEI Dualbeam (FEG-SEM) apparatus. The topography of the nanoparticle coatings was studied with an atomic force microscopy (AFM) in AC tapping-mode, using PicoScan 2500 PicoSPM II Controller (PicoPlus, Molecular Imaging) with a silicon probe of $k = 40$ N/m and 300 kHz resonant frequency. The average surface roughness (R_a) was calculated on a $2 \mu\text{m} \times 2 \mu\text{m}$ standard scan size that was flattened by image processing procedures. The variation on roughness values is about $\pm 2 \mu\text{m}$. The chemical composition and degree of imidisation of the nanoparticle coatings was determined from FT-Raman spectroscopy, using a Perkin Elmer Spectrum GX equipment. The spectra were collected with a Nd:YAG laser power of 500 mW at a 4 cm^{-1} resolution and averaged over 64 scans. The spectra for coated paper surfaces were corrected with a spectrum of uncoated paper surfaces. The static and dynamic contact angles were measured on a Krüss drop shape analysis system (DSA 10 Mk2) by placing a constant drop volume of 4 μl (static)

or by increasing the drop volume from 0 to 7 μl at a rate of 6 $\mu\text{l}/\text{min}$ (dynamic). The drop shapes were geometrically determined from Laplace-Young (static) or tangent (dynamic) fitting procedures. The variation on contact angles is about $\pm 2^\circ$.

3. RESULTS

3.1 Morphology and topography

The scanning electron microscopy images (Figure 1) show that the nanoparticles form a non-continuous coating, offering the coated paper a micro-to-nano structured morphology with increased gloss and better water repellency than uncoated papers. As observed by optical microscopy, the coatings are glassy and transparent own to its nanometer-scale composition and amorphous structure. Also after thermal heating below the glass transition temperature of 190°C (SMI-1) or 203°C (SMI-2), the polymer coatings do not flow into a continuous film and remain nano-structured.

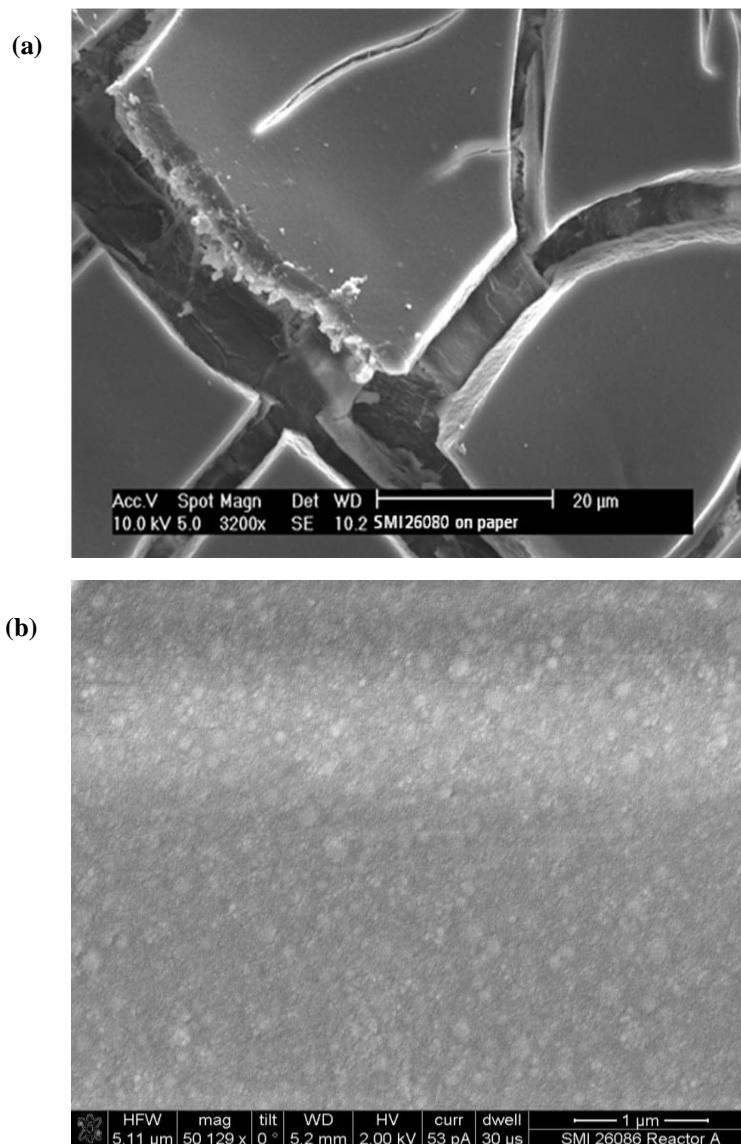


Figure 1. Scanning electron microscopy of SMI-1 coatings on paper surface, (a) SEM magnification 3200 x, (b) FEI-SEM magnification 50000 x.

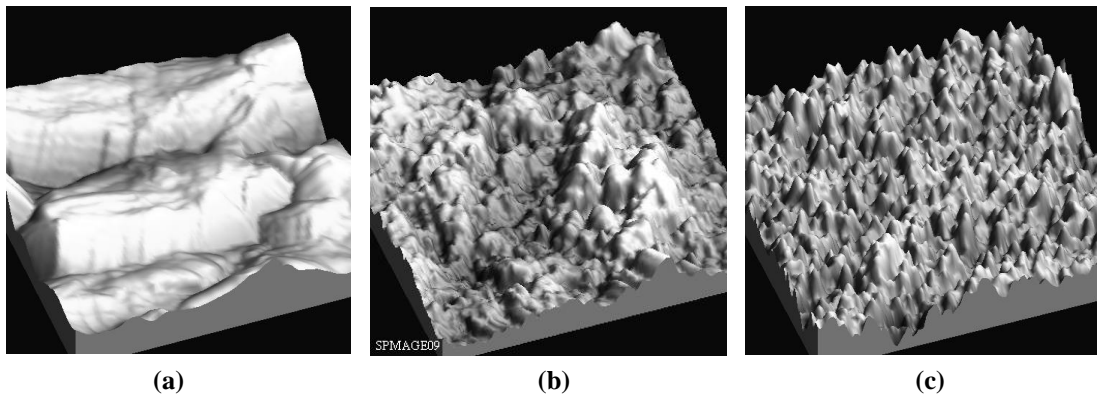


Figure 2. Atomic force microscopy on a standard surface size of $2\ \mu\text{m} \times 2\ \mu\text{m}$, (a) uncoated paper, (b) SMI-1 coated paper, (c) SMI-2 coated paper.

The atomic force microscopy (Figure 2) scans indicate differences between the uncoated paper surface, showing bare cellulose fibers and microfibrils, and the coated paper surfaces, showing a completely covering nanostructured layer with particle sizes of 90 – 105 nm (SMI-1) or 85 – 100 nm (SMI-2).

3.2 Spectroscopy

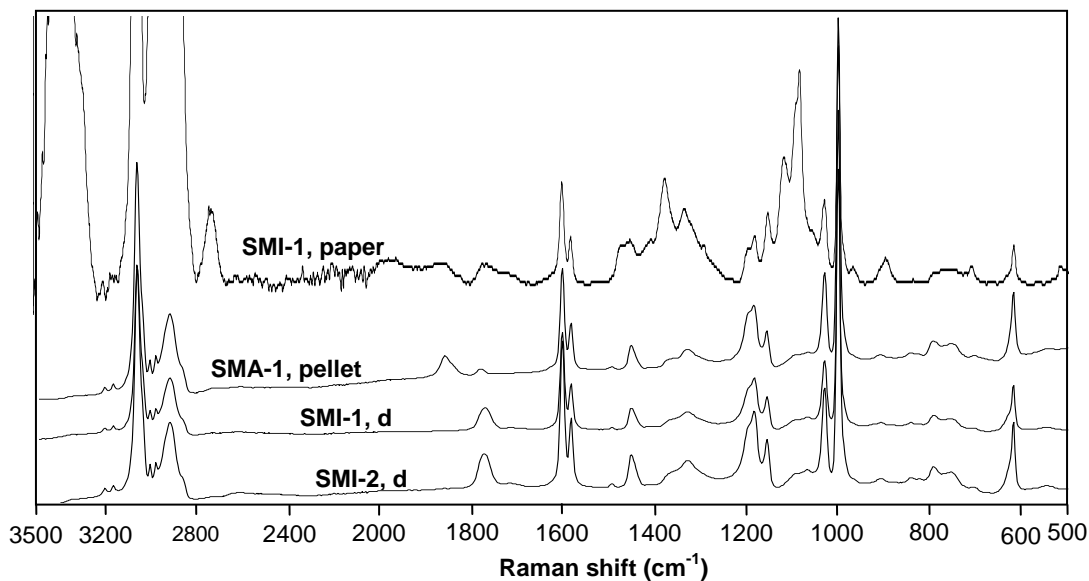


Figure 3. FT-Raman spectra of SMA-1 (pellet), SMI-1, d (in water dispersion), SMI-2, d (in water dispersion) and SMI-1, paper (absorbed on paper).

The characteristic Raman shifts for SMI nanoparticles absorbed on cellulose surfaces are: 3000 (w; ν_{NH}); 3060, 2916 (m; ν_{St}); 1857 (m; $\nu_{\text{C=O, anhydride}}$); 1777 (w; $\nu_{\text{C=O, anhydride}}$); 1765 (m; $\nu_{\text{C=O, imide I}}$); 1602 (s; ν_{St}); 1583 (m; ν_{St}); 1452 (m; ν_{St}); 1329 (m; $\nu_{\text{imide II}}$); 1184 (m; ν_{St}); 1156 (m; ν_{St}); 1031 (s; ν_{St}); 1000 (vs; ν_{St}); 900-750 (w, ν_{aromatic}); $620\ \text{cm}^{-1}$ (m; ν_{st}). The degree of imidisation relatively to the styrene amount is calculated from the intensity ratio of $1765\ \text{cm}^{-1}$ to $1602\ \text{cm}^{-1}$ bands. As such, the maximum theoretical imide content is 35 % for SMI-1 and 39 % for SMI-2. It is observed that the imide content of the dispersed nanoparticles is lowest (24 % for SMI-1 and 26 % for SMI-2), while it increases after drying (28 % for SMI-1 and 32

% for SMI-2) and it is somewhat lower after adsorption on paper surfaces (25 % for SMI-1 and 29 % for SMI-2). The latter indicates additional interactions between the nanoparticles and the cellulose fibers, attributed to the formation of hydrogen bonds as revealed from a strong increase in C-OH stretching bands. After thermal heating of the coated papers, further imidisation was observed to a maximum degree of 30 % for SMI-1 at 135°C and a maximum degree of 37 % for SMI-2 at 135°C.

3.3 Contact angle measurements

The static contact angles are $\theta^* = 104^\circ$ for uncoated paper, and increase to 115° for SMI-1 or 127° for SMI-2 coated paper. The dynamic advancing contact angles are 120° for SMI-1 and 138° for SMI-2, respectively. The differences in static and dynamic advancing contact angles indicate the role of chemical and topographical structuring of paper surfaces. After thermal heating of the coated papers, the maximum dynamic advancing contact angles are 133° for SMI-1 and 150° for SMI-2 at 135°C, in parallel to the previously noted maximum degree of imidisation, corresponding to a receding contact angle of 43° (SMI-1) to 52° (SMI-2).

More in general, the chemical and topographical influences on contact angle measurements can be modeled according to the Wenzel model (Figure 4): the equilibrium contact angle θ^* on a rough nanostructured surface (corresponding to the measured dynamic advancing contact angles) relatively to the equilibrium contact angle θ on a smooth surface (obtained by extrapolation) can be explained by introducing the roughness parameter r , according to $\cos \theta^* = r \cos \theta$. The effect of the surface roughness is expressed by relating the roughness parameter r to the average surface roughness (Ra) as determined from AFM scans. The effect of chemical surface composition is expressed by the degree of imidisation as determined from Raman spectroscopy. The increase in contact angle with higher degree of imidisation is evidenced by contact angle measurements on non-imidised flat SMA coatings ($\theta = 58^\circ$). The wettability of the SMI nanoparticle coatings turns from hydrophobic into hydrophilic for imide contents below 20%.

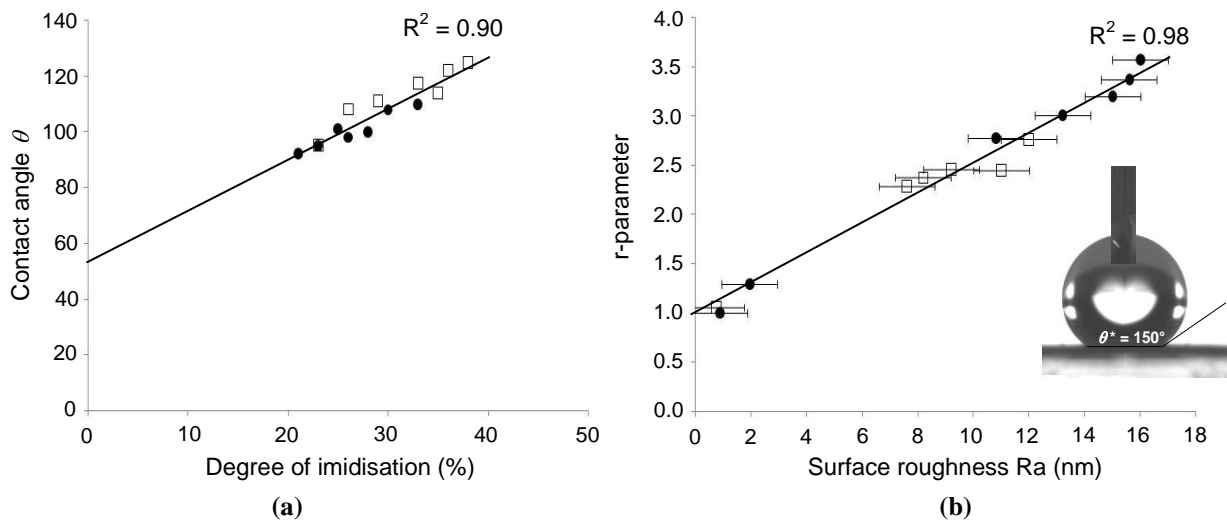


Figure 4. Calculation of the wetting parameters for SMI-1 (●) and SMI-2 (□) fitting into the Wenzel model, (a) equilibrium contact angle on virtually flat surface as a function of the degree of imidisation, (b) r-parameter as a function of the measured surface roughness (inset: maximum obtained advancing contact angle).

4. CONCLUSIONS AND OUTLOOK

In this work, the synthesis of partially imidised nanoparticles from high-molecular weight poly(styrene maleic anhydride) was presented. The nanoparticles are obtained as a stable water-borne dispersion and are favourably applied as a non-film forming coating onto cellulose-based substrates, offering good mechanical and thermal resistance. The wetting properties of the coated paper substrates can be controlled by varying the imide content and average surface roughness. Hydrophobic paper surfaces with a maximum advancing contact angle of $\theta_a = 150^\circ$ and receding contact angle of $\theta_r = 52^\circ$ were achieved. These nanoparticle coatings serve as a unique and ecological replacement for chemical treatments hydrophobizing fibrous substrates.

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