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Adjustable wettability of paperboard by liquid flame spray nanoparticle deposition

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ABSTRACT

Liquid flame spray process (LFS) was used for depositing TiO_x and SiO_x nanoparticles on paperboard to control wetting properties of the surface. By the LFS process it is possible to create either superhydrophobic or superhydrophilic surfaces. Changes in the wettability are related to structural properties of the surface, which were characterized using scanning electron microscope (SEM) and atomic force microscope (AFM). The surface properties can be ascribed as a correlation between wetting properties of the paperboard and the surface texture created by nanoparticles. Surfaces can be produced inline in a one step roll-to-roll process without need for additional modifications. Furthermore, functional surfaces with adjustable hydrophilicity or hydrophobicity can be fabricated simply by choosing appropriate liquid precursors.

1. Introduction

Wetting properties of surfaces are important in our everyday life. For example, in rain we need to use umbrellas, and coffee spilled on a table leaves a circular stain. Recently wetting phenomena have raised a growing interest in numerous industrial processes, and especially in research and development of new materials and surfaces, where knowledge and understanding of interactions on interfaces is crucial. The wetting properties of surfaces are governed by hydrophobicity and hydrophilicity phenomena, i.e. on hydrophilic surfaces water wets the surface whereas hydrophobic surfaces repel water and water forms sessile droplets.

Nature provides us with a number of examples of both hydrophilic and hydrophobic structures, which are typically difficult to reproduce by means of current engineering technologies. However, it is possible to mimic such formations in engineered structures (biomimetics) and one can apply nature's wisdom. Some natural structures have already been well characterized such as Lotus leaves with their superhydrophobic (extreme water repellent) and self-cleaning properties [1–3] or leafs of tropical herb Ruellia devosiana Makoy with superhydrophilic and oleophilic properties [4]. On the other hand, the Namib Desert beetle Stenocanora sp. combines both hydrophobic and hydrophilic structures for water collection from morning fog by specially patterned wings, which gather moisture from fog by hydrophilic regions and hydrophobic channels are then used to transport the gathered droplets. Such survival is amazing as the beetle species lives in one of the driest places in the world [5]. These are just some examples from a variety of highly adapted functional structures, which have inspired scientists and engineers in their work. As we can observe, nature provides information about surface wetting modifications ranging from superhydrophilic to superhydrophobic as well described by Ma and Hill [6].

Generally there are two factors affecting the wetting properties of a surface: chemical and physical properties of the surface [7,8]. Contact angle (CA) measurements are commonly used for wettability studies of surfaces as it provides a simple way to characterize surface energy, heterogeneity, and cleanliness of the surface. Contact angle was first introduced by Young [9] for smooth surfaces at the start of the 19th century. Later, the theory was expanded by Wenzel [7,10] and Cassie–Baxter [11] to cover also rough surfaces. For hydrophobic surfaces CA is greater than 90° and the surface is labeled to be superhydrophobic when contact angle exceeds 150°. At the other end of the spectrum, CA for a hydrophilic surface is less than 90°. The apparent contact angle can be strongly affected by roughness of solid surface as Quéré briefly discusses in the review article [12]. Relation between roughness and wetting phenomena seems to be the key issue for surface engineering, since some surface properties like water leveling/repellency or wicking on solid

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surface could not occur otherwise [12,13]. There are already known methods for controlling wetting properties, but they are mostly established for solid, smooth surfaces with rather low roughness. In the case of flexible materials, paper surface as a complex and porous network of wood fibres is more challenging and complex to modify. Recently atmospheric plasma or corona treatments as well as chemical vapour deposition and atomic layer deposition techniques have been investigated for surface modification of paper [14–17].

In this paper we demonstrate how to control the wetting properties of a paperboard by applying a liquid flame spray (LFS) process, which can be used for creating nanoparticles on a surface. Such a thermal spray process has a high velocity flame with the maximum temperature of 2600 °C, where a precursor dissolved in an organic solvent is injected. Hydrogen and oxygen act as combustion gases providing firstly nebulization of the organic solvent and atomization of the liquid precursor into the flame. The atomized droplets evaporate while the solvent burns into CO_2. The evaporated precursor molecules can either react chemically or decompose thermally, then re-condense to form nanoparticles of final material, which are then deposited on the surface to be modified. The major advantage of such process is the broad spectrum of metal or metal oxide nanoparticles, which can be created using different liquid precursors. A schematic picture of the LFS coating unit is presented in Fig. 1. For a detailed description of the process, see Refs. [18–22].

Here we present LFS as a novel coating method for paperboard, which, to our knowledge, this has not been systematically studied before. The purpose of this study is to correlate the changes in wetting properties of paperboard with nanosized TiO_x and SiO_x coatings produced by the LFS process. The paper is organized as follows: in Section 2 we present the experimental work and in Section 3 we show the changes in the CA induced by different nanoparticles. The changes in wettability are related to structural properties of the surface, which are characterized by using scanning electron microscopy and atomic force microscopy. Finally, the concluding remarks are presented in Section 4.

2. Experimental: materials and methods

In this study commercially available double pigment coated paperboard (200 g/m^2, Natura, Stora Enso, Skoghall, Sweden) was used as a substrate. Samples were prepared in a roll-to-roll process using coating and laminating pilot line at the Tampere University of Technology (Tampere, Finland) with a constant web speed of 30 m/min. Two different nanoparticle coatings were fabricated: TiO_x and SiO_x. For TiO_x coatings, the liquid precursor titanium (IV) isopropoxide (TTIP) was dissolved in isopropanol (IPA). The solution with a metal ion concentration of 11.9 mg/ml was fed into a nozzle with rate of 29.5 ml/min fixed at 15 cm distance from the substrate. According to the deposition model described by Mäkelä et al. [23], these process parameters lead to a deposition mass of 12.7 mg/m^2 and 415 particles/μm^2. SiO_x coatings were coated in the same way as TiO_x samples but with a different set of process parameters. Tetraethylorthosilicate (TEOS) precursor dissolved in IPA was used with a metal ion concentration of 15.9 mg/ml and a feeding rate of 15.2 ml/min with the nozzle-substrate distance of 20 cm.

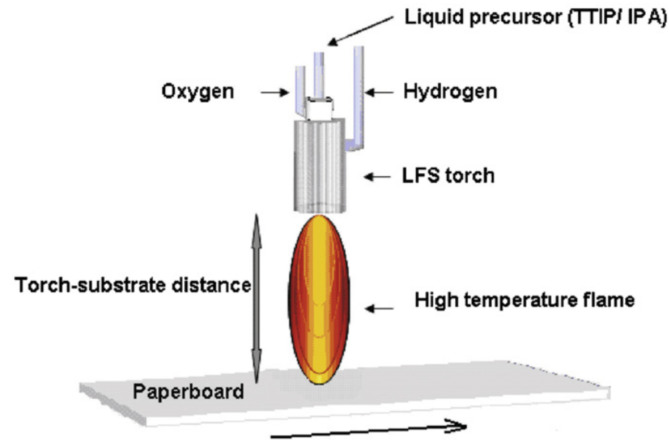

Fig. 1. Schematic picture of the liquid flame spray (LFS) set-up for coating paperboard. Hydrogen is used as a nebulizing gas.

Contact angle (CA) measurements were performed by a commercial contact angle goniometer KSV CAM 200 (KSV Instruments Ltd., Finland) with an automatic dispenser and motorized stage. The images of the droplets were captured by a digital CCD camera with a 55 mm zoom microscope lens with a blue LED light source, and then analyzed using the KSV CAM software supplied with the instrument. In this study 100 frames per second were taken during the first 10 s of each measurement and 1 frame per second

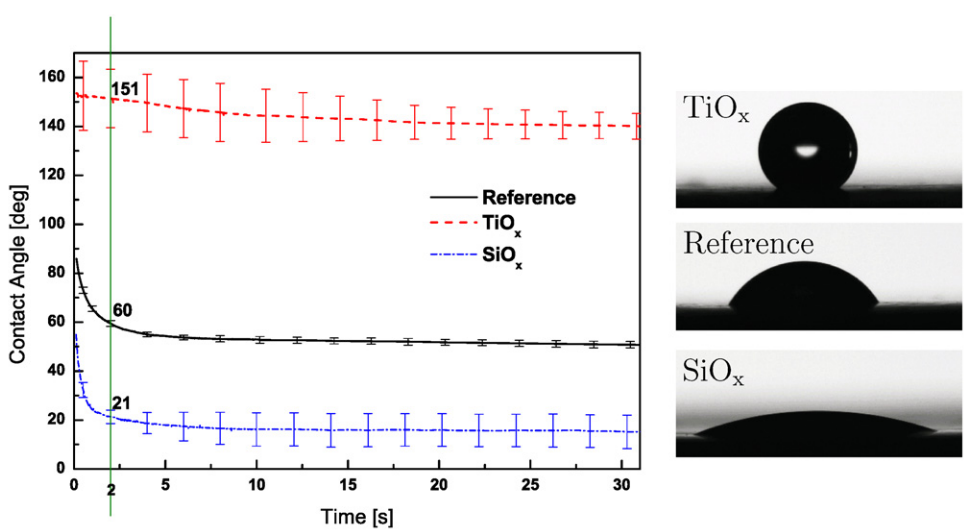

Fig. 2. Water contact angle (CA) for TiO_x (red) and SiO_x (blue) coatings as a function of time. The subfigures to the right display the captured images from the measurement at the 2.0 s. The error bars display standard deviation from three parallel measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)