Surface & Coatings Technology 205 (2010) 436–445

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Development of superhydrophobic coating on paperboard surface using the Liquid Flame Spray

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ARTICLE INFO

Article history:
Received 18 March 2010
Accepted in revised form 2 July 2010
Available online 27 July 2010

Keywords:
Superhydrophobic
Paperboard coating
On-line process
Titanium dioxide nanoparticle
Liquid Flame Spray

ABSTRACT

This paper introduces a new method for generating nanoscale coatings in a continuous roll-to-roll process at normal pressure. Nanostructured and transparent coating, based on titanium dioxide nanoparticles, was successfully deposited on-line at atmospheric conditions on pigment coated paperboard using a thermal spray method called the Liquid Flame Spray (LFS). The LFS coating process is described and the influences of process parameters on coating quality are discussed. Nanocoating was investigated by a field emission gun scanning electron microscope (FEG-SEM), an atomic force microscope (AFM), an X-ray photoelectron spectroscopy (XPS) and a water contact angle measurement.

The highest measured water contact angles on the nanocoated paperboard surface were over 160°. Falling water droplets were able to bounce off the surface, which is illustrated by high speed video system images. Regardless of the high hydrophobicity, the coating showed sticky nature, creating a high adhesion to water droplets immediately as the motion of the droplets stopped. Nanocoating with full coverage of the substrate was produced at line speeds up to 150 m/min. Therefore, the LFS coating has scale up potential to industrial level as an affordable and efficient method for coating large volumes at high line speeds.

1. Introduction

Paperboard is a highly versatile material with various favourable properties, e.g. biodegradability, renewability, mechanical flexibility and affordability. The complete utilisation of the versatility of paperboard requires the ability to control its surface properties. Comprehensive control of surface properties of paperboard, e.g. hydrophilicity and hydrophobicity, can benefit in the various converting processes of paperboard, including printing, extrusion coating, lamination, etc. [1]. The wettability (hydrophilicity) of paperboard surface can be increased with several industrial (roll-to-roll) surface modification techniques, like flame, corona discharge or atmospheric plasma treatments. These well-established surface modification techniques improve printability properties of paper [2] and enhance adhesion between polymers and paperboard or paper [3,4]. Generation of hydrophobic surface on cellulose based materials, e.g. on paperboard or paper, is more complicated, although several plasma and wet chemical techniques have been reported. Superhydrophobic surfaces have been created by fluorinating the paper using grafting and post-functionalisation [5] or by silane coating the paper through solution immersion process [6]. Plasma-assisted deposition of thin fluorocarbon [7–9], organosilicon [9] and hydrocarbon coatings [9] has also resulted in hydrophobic paper surfaces. Balu et al. [10] obtained superhydrophobic paper surface by combining plasma etching with PECVD (plasma enhanced chemical vapour deposition) of fluorocarbon film. However, for the paper or paperboard substrate, the plasma techniques are not yet utilised in large scale in packaging industry. The main limitation for the utilisation of plasma techniques in packaging industry is often the operating costs, because plasma deposition at vacuum or low pressure requires expensive vacuum chambers and pumps in order to create and contain the plasma process. Another drawback for vacuum or low-pressure systems and most of the wet chemical processes is that they are usually batch operations, which is not favoured in paper coating and lamination due to high-volume continuous roll-to-roll processes. Furthermore, fluoropolymers are widely used in superhydrophobic surfaces, but because of health issues they cannot be applied for example in food packaging.

Liquid Flame Spraying (LFS) is a thermal spraying method for generating and depositing nanosized (less than 100 nm) metal and metal oxide particles. Initially the LFS was developed as a method for glass colouring [11]. Nowadays the LFS is also utilised in fibre doping [12] and for coating various substrates, for example ceramic tiles [13] or metal surfaces [14]. The continuous nature of the LFS process and

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0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2010.07.003

the operating conditions at normal atmospheric pressure enable on-line roll-to-roll coating procedure to be used.

In the LFS process the precursors are in liquid form, diluted in water or alcohol, and are fed together with the combustion gases into a special designed spray gun. Instantly after exiting the burner nozzle the precursor solution is atomised to micron-sized droplets by the high-velocity gas flow. Liquid droplets evaporate in a hot and turbulent flame and subsequent reactions of the precursor vapour lead to formation of nanoparticles of desired material [15]. Afterwards nanoparticles grow larger in the flame by condensation, coagulation, coalescence and agglomeration [16–18]. The final particle size can be controlled, e.g. via total mass flow rate of the precursor (product of the precursor solution feed rate and its concentration) or by adjusting the collecting or depositing distance [19–22]. The main exhaust gases formed as by-products in the LFS process are normally water vapour and carbon dioxide. Low waste flows combined with relatively simple and inexpensive equipment make the LFS process comparatively cheap and environmentally friendly.

LFS coatings consisting of nanoparticles have a large fraction of surface molecules and hence high reactivity [16,23,24]. Added to this, the nanoscale roughness of the surface creates a unique topography for the nanocoating and enlarges its effective surface area. The properties of the LFS-made coatings may therefore vary remarkably from the properties of homogeneous coatings made of bulk materials. LFS coatings have potential to improve properties traditionally demanded for example from packaging materials, such as barrier and adhesion, but these coatings may also introduce totally new functional properties for the materials, including antibacterial, self-cleaning, non-sticking, non-wetting, superwetting, light protection, heat and wear resistance and electrical properties for example.

The range of suitable LFS precursors, i.e., metal salts and alkoxides in water or alcohol solution, is wide. Thus a large number of various coatings with unique properties can be produced using the LFS. Iron and manganese oxide, alumina, silica, titania, silver and palladium nanoparticles have been successfully produced in laboratory scale using the LFS [13–15,19–22]. Multi-component materials can also be produced by mixing different precursors together [25–28].

The LFS coating parameters (i.e. concentration and feed rate of the precursor solution, gas flows, burner distance and line speed) must be carefully adjusted in order to obtain the desired coating quality. For instance, the properties of nanoparticles are strongly related to particle size [16,23,24], thus incorrect coating parameters may change the coating composition and properties dramatically. It is widely known that both the chemistry and the topography of a surface affect water contact angle (CA) [29–34]. By adjusting the surface roughness in micro- or nanoscale the hydrophobicity of the surface can be enhanced. Furthermore, the combination of micro- and nanoroughness (hierarchical roughness) is an effective way to increase surface hydrophobicity. On flat surfaces the highest CAs achieved are normally around 120°, but proper roughness of the surface can raise the CA close to 180°. Even materials which are inherently hydrophilic (CA<90°) on a flat surface may show CAs of over 150°, if the surface is appropriately patterned [35,36]. Surfaces which have an extraordinary high CA are often called superhydrophobic, and the widely accepted criterion for superhydrophobicity is the CA value of over 150°.

Superhydrophobic surfaces have raised much interest during the last decade, and many research groups have dedicated themselves to the development and manufacturing of such surfaces [33–43]. Quite often, guidance and inspiration for producing superhydrophobic surfaces can be found from nature, for example leaves of lotus plant [44]. There are numerous ways to prepare superhydrophobic surfaces, e.g. plasma, laser and chemical etching, sol–gel methods, lithographical means, replicate templates, electrochemical methods and various spraying methods [33,45–47]. Usually superhydrophobic surfaces are prepared by patterning low-surface-energy material or by inducing a low-surface-energy layer on a patterned surface afterwards. Almost any substance can be used as a substrate for superhydrophobic surfaces, including fluorocarbons, silicones, hydrocarbons and metal oxides [33]. In recent years even fibre-based materials, such as paper, have been successfully modified to produce superhydrophobic surfaces [5,6,10,48], as mentioned above. Most of the artificially made superhydrophobic surfaces exhibit the lotus-effect, i.e., water droplets roll off easily from the surface. However, studying and manufacturing of sticky superhydrophobic surfaces has recently attracted increasing interest [10,45,48–51].

The main purpose of this work is to demonstrate the creation of a superhydrophobic surface on paperboard using a LFS on-line coating process. In addition, a goal is to understand the influences of various process parameters on the coating quality. Wettability of the nanocoated surface was studied by CA measurement and the behaviour of water droplets on the nanocoating was observed using high speed video system. The structure of the coating was investigated by field emission gun scanning electron microscope (FEG-SEM) and atomic force microscope (AFM). Chemical composition of paperboard and nanocoated surfaces was investigated by X-ray photoelectron spectroscopy (XPS). The nanocoating wear resistance and adhesion to paperboard surface were evaluated using simple abrasion and tape tests.

2. Materials and methods

Titanium dioxide (TiO_2) nanoparticles were generated and deposited directly on the pigment coated paperboard (200 g/m^2, Natura, Stora Enso, Skoghall mill Sweden) surface using the LFS. TiO_2 was selected as a coating material because it is well known from earlier studies [21,27], but also because of its non-toxicity. Precursor for the nanocoating was titanium tetraisopropoxide (TTIP, 97% pure, Aldrich). TTIP was diluted in isopropyl alcohol (IPA), so that two precursor solutions of separate concentrations (low concentration, LC$\approx$11.5 mg of pure Ti/ml and high concentration, HC$\approx$50 mg of pure Ti/ml) were obtained. The combustion gases used in this study were hydrogen (H_2) and oxygen (O_2). The reaction product of hydrogen–oxygen combustion is pure water, and the temperature in the flame is high enough to evaporate most of the precursor materials.

The LFS coating procedure was performed at the Tampere University of Technology (TUT) on the Paper Converting and Packaging Technology (PCPT) pilot line. At this stage of examinations only one burner was used, and hence the width of the highly hydrophobic coating was relatively narrow, ca. 50 mm. The LFS burner was installed inside a hood which was equipped with an air exhaust duct for purging unattached particles. The flame was pointed downwards and the web was running below the burner. A schematic picture of the experimental set-up is presented in Fig. 1.

The coating parameters which were varied were the concentration and the feed rate of the precursor solution, the burner distance and the line speed (Fig. 1). All the parameters affect the characteristics of the nanocoating, thus the desired end-use properties of the final coating must be taken into consideration when adjusting the coating parameters. Simultaneously, the type of the substrate and its limitations must also be taken into account. Furthermore, the volume and the ratio of the gas flows (H_2 and O_2) must be correctly chosen to obtain proper quality of the nanocoating.

The precursor solution was fed into a capillary needle in the middle of the burner by an infusion pump at a constant feed rate. Hydrogen was used as a combustion gas and an atomising gas, and it was fed into the flame through a circular channel immediately next to the precursor needle (Fig. 1). The other combustion gas, oxygen, was fed through the outer ducts, which form a circular ring around the precursor needle and the hydrogen flow channel. The volume flows for hydrogen and oxygen were 50 and 15 l/min respectively. The flow