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Lotus-like paper/paperboard packaging prepared with nano-modified overprint varnish

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ABSTRACT

Paper/paperboard has great advantages over plastics as packaging material in terms of cost and sustainability. However, the application of paper/paperboard packaging is limited due to their inferior water resistance performance. Here we report a functional overprint varnish prepared with the aim to significantly abate the wettability of the printed packaging. The prominent water repellency of the varnish is rendered by its unique nano-structured morphology, a technology bio-mimicking lotus surface. The frost formation on the applied packaging is also inhibited. Moreover, the transparency and the application process of the varnish are retained. We expect such varnish has high potential for expanding the application field of paper/paperboard packaging, especially for uses requiring a strict standard of water resistance.

1. Introduction

Papers and paperboards are extensively used in various industries. The primary consumption of this kind of material is for producing various types of flexible, semi-rigid, or rigid packaging [1]. In addition to its effective cost and high application flexibility, paper/paperboard is also considered as the most environmentally friendly material for packaging, in view of its natural sourcing and easy recyclability. As a result, paper and paperboard are the largest-used packaging material throughout the world, by weight. The global paper packaging market in 2011 is reported to be worth 236 billion US dollar [2].

Paper and paperboard are sheet materials comprising an interlaced network of cellulose fibers, which is intensely vulnerable to water or moisture owing to its hydrophilic nature. In many cases, an additional barrier material such as aluminum or plastic [3–5] is incorporated to improve their performance and function. However, this laminated paper/paperboard packaging is not only more expensive but also less recyclable than those made only by paper [1]. Besides the metallic or plastic film, over-print varnish is another widely used protection technology, which is very cost-effective and very easy to apply. However, varnish does not have as good water repellency as film. In an effort to enhance the water-resistance, hydrophobic polymer has been utilized to produce the over-print varnish, or wax/silicone additive has been incorporated. Although the performance of such varnish is good, neither of the methods is able to render the printed paper packaging completely waterproof like a lotus leaf.

The mechanism underlying the super-hydrophobic properties of the lotus leafs was unveiled more than two decades ago [6]. Since then, mimicking such natural phenomenon to prepare the lotus-like surface has aroused intense interest both in academia and in industry, as the surface has demonstrated self-cleaning [7], water repellency [8], stain repellency [9], anti-bacteria [10], and many other superior benefits [11,12]. However, most of the reported technologies of preparing such surfaces are highly complicated and very difficult to be applied in industrial scale. That is probably why only rarely have packaging materials, to the best of our knowledge, been reported to be modified to have the lotus-like surface.

Nevertheless, if lotus-like superhydrophobic modification can be further applied to paper or paperboard packaging, to utilize its unique lotus-like properties, such as water and moisture-repellent, anti-frost formation, it will provide better packaging appearance benefits with less water/moisture/frost damage. In addition, it could also eliminate the usage of plastic coating on paper package and thus reduce environmental impact by yielding fully recyclable paper packages.

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Here we report a novel technical route to hydrophobically modify an over-print varnish with fumed silica. The optimized formulation capable of imparting the lotus-like property to paper and paperboard packaging has been identified.

2. Experimental

2.1. Materials

Waterborne varnish (07-1449-LT705) was supplied by Weilburger® (Germany). Silica nano-particles (AEROSIL® R812S, average particle size 7 nm, specific surface area 220 m^2/g) were purchased from Evonik Degussa. Decamethylcyclopentasiloxane (D5) and polydimethylsiloxane (PDMS, BP-9400) were supplied by Dow Corning and Bluestar Silicones (Shanghai) Co., Ltd., respectively. Nonionic surfactant p-octyl polyethylene glycol phenyl ether (OP) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All these materials were used as received without any treatment.

2.2. Functionalization of waterborne varnish

The modifying agent for the varnish was prepared by mixing four components (D5, R812S, BP-9400 and OP), with the mass ratio of D5/R812S/BP-9400/OP at 57:3:9:1. The final waterborne varnish was prepared through adding the modifying agent into commercial varnish with various mixing proportions, under vigorous stirring. The detailed preparation procedure as used was as follows. Firstly R812S nanoparticles were dispersed into D5 silicone oil, and then BP-9400 was added into this mixture, which was then blended with the commercial varnish. Finally, the modified varnish was obtained after OP was added dropwise with a buret and then stirring for a further 10 min.

2.3. Application of the varnish onto printed paperboard

Before usage, the modified varnish was homogenized evenly by a 10-min ultra-sonication. Afterward, it was applied onto an offset printed paperboard (15 cm × 15 cm) with an anilox roller.

2.4. Characterization

ATR (attenuated total reflectance) spectra were recorded on a Nicolet 6700 FT-IR spectrometer of Thermo Electron Corporation. The observation of the morphology of the samples was carried out with a field emission scanning electron microscope (FESEM, HITACHI S-4800). Rheological behavior of the modified varnish was investigated with an Anton Paar Physica MCR301 instrument. The static water contact angles were measured on a KRÜSS DSA100 Drop Shape Analyzer (KRÜSS, Germany) using a 5 μL triply distilled water droplet at ambient temperature.

2.5. Performance test

Three aqueous liquids, including distilled water, mud slurry and ink, were dripped onto the paper surfaces laid on a slope with a 20-degree angle, to test the water resistance. The durability of the performance was examined with a peristaltic pump dripping water, from 10 cm above, for 2 h at a constant rate of 1 drop per second.

The anti-frosting experiment was conducted in a cabinet which automatically opened and closed its door according to a pre-set program. Two pieces of paper (20 cm × 16 cm) coated with the original and the modified varnish, respectively, were stuck onto the inner wall of the cabinet, which was set to be closed for 300 s and then open for 10 s before closed again, simulating real using conditions. In order to fully frost the paper, the cabinet ran the open-close loop program for 5 h before remaining closed at −15 °C for another 19 h.

3. Results and discussion

The fabrication process of the lotus-like printed paper packaging is illustrated in Fig. 1. Hydrophobic nanoparticles (R812S) and silicone polymer (PDMS, BP9400) are homo-genously dispersed in a solvent (D5 silicone oil) to prepare the modifying agent [13], and subsequently the dispersion is emulsified into a waterborne over-print varnish. During a normal printing process, the particles and the PDMS are deposited onto the paper packaging, so modifying the surface to be superhydrophobic.

A very important feature of a lotus-like, e.g. superhydrophobic, surface is the micro-/nano-structured morphology. Therefore, the process to fabricate such kind of morphology is of critical importance for preparing the superhydrophobic surface. A widely used

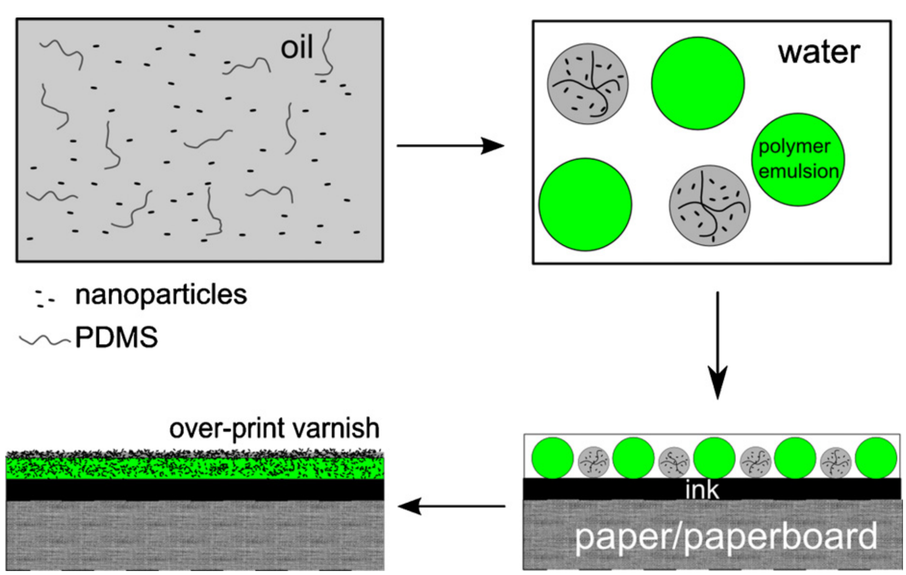

Fig. 1. Schematic illustration of the fabrication process of the lotus-like paper packaging via modifying the overprint varnish with hydrophobic nanoparticles and silicone polymer.