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Paperboard as a substrate for biocompatible slippery liquid-infused porous surfaces

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Abstract: Slippery liquid-infused porous surfaces or SLIPS were first introduced in 2011 by Wong et al. who reported a bioinspired self-repairing surface with remarkable slippery properties. Generally, production of these surfaces includes fossil-based or expensive materials and processes that are available mainly in laboratory scale. In this study, slippery surfaces with sliding angles of less than 10° are obtained using fibre-based material – paperboard – that is commercially available in large-scale and also cheap compared to substrates generally used in this field. The hierarchical nanostructure that is a necessary condition for appropriate droplet mobility was obtained by the liquid flame spray method. This method is fast, scalable, has a variety of optimization parameters and can be utilized in roll-to-roll technology that is traditional in paper industry. In this work, paperboard serves not only as a substrate, but also as a reservoir for the lubricant, thus it is important to evaluate the affinity of the material for the oils and estimate the capillary movement. Therefore, Cobb and Klemm methods were used when choosing a paperboard material. In addition to synthetic oils, rapeseed oil was also utilized as a lubricant, which potentially leads to eco-friendly and recyclable slippery liquid-infused porous surfaces.

Keywords: capillary movement; liquid flame spray; lubricant imbibition; paperboard; slippery liquid-infused porous surfaces.

Introduction

Recently, much attention has been paid to functional materials. Nowadays the material should have not one, but several functions in order to meet modern needs. For the packaging materials, for example, the main function is preservation of the product and possibility of easy transportation. Thus, the strength and barrier properties of the material are positioned in priority. However, progress does not stand still and some new functions are added to the standard ones, e. g., the functions of “intellectual” packaging, which can signal the quality of the product. Special attention is also paid to such properties as hydrophobicity/oleophobicity of the material. Along with superhydrophobic materials (contact angle exceeds 150°), slippery liquid-infused porous surfaces (SLIPS) that possess self-cleaning properties are actively studied (Wong et al. 2011). This remarkable property can work, e. g., inside the package, providing a more efficient or complete removal of the product (Mukherjee et al. 2018). In case of slippery lubricant-infused surfaces, a drop of liquid does not stick to the object, but is sliding on the surface even at a slight inclination, removing contaminations (Lafuma and Quéré 2011, Wooh and Butt 2017). Thus, such surfaces can reduce product waste and contribute to optimal material recycling.

Slippery liquid-infused porous surfaces are known to be bioinspired self-repairing system with unique properties, such as water repellence, dropwise condensation (Anand et al. 2012, Rykaczewski et al. 2014), repellency to ice and frost (Kim et al. 2012, Chen et al. 2013, Wilson et al. 2013, Manabe et al. 2014, Qiu et al. 2014, Juuti et al. 2017), inhibition of corrosion (Qiu et al. 2014, Wang et al. 2015, Yang et al. 2015) and biofouling (Epstein et al. 2012, Wang et al. 2015, Manna et al. 2016). SLIPS can be described as solid-liquid systems, consisting of a nanotextured substrate and a lubricant distributed in its structure. Lubricants generally include ionic liquids (Anand et al. 2012), vegetable or synthetic oils, such as silicone oil, perfluorinated oil, cottonseed (Mukherjee et al. 2018) olive or coconut oils (Manna and Lynn 2015). A variety of materials can be utilized as a substrate, including polymer mem-

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branes, silicon films, fabrics (Shillingford et al. 2014), metals (Kim et al. 2012, Wilson et al. 2013, Wang et al. 2015) and even paper (Glavan et al. 2014). The most important component of the SLIPS concept is a nanostructure on surface of the substrate. A hierarchical structure is fabricated on the substrate, providing key functions of SLIPS (Wong et al. 2011, Kim et al. 2013). This feature is responsible for special wetting properties, and it allows retaining a sufficient amount of lubricant. Lubricant should have a chemical affinity to the substrate and form a continuous film on the top of nanostructure.

Recent papers describe a variety of techniques for imparting the required nanostructure to the surface, including growing of nanofilaments (Artus et al. 2006), lithography (Pokroy et al. 2009) or anodization (Wang et al. 2015). These techniques enable fabricating the SLIPS with excellent characteristics, such as hydrophobicity and high mobility of water droplets on the surface. Nevertheless, most of these methods include technologically complicated procedures that are incompatible with roll-to-roll production. As known, roll-to-roll processes are considered an essential part of the paper and packaging industry. Therefore, this study deals with a liquid flame spray (LFS) technique, which is compatible with roll-to-roll production (Teisala et al. 2010, Stepien et al. 2011), imparting functional properties to the surface, achieving the hierarchical structure necessary for SLIPS (Teisala et al. 2013a). Depending on the future function of the coating, various chemical substances can be deposited in liquid flame spraying method; silver oxide, for example, provides antibacterial properties to the surface (Brobbey et al. 2017), and silicon oxide provides hydrophilic properties (Aromaa et al. 2012b).

The main advantages of LFS coatings include self-healing properties (Teisala et al. 2013b), high line speed in roll-to-roll process (Teisala et al. 2010, Mäkelä et al. 2011, Haapanen et al. 2019), relatively low cost (Haapanen et al. 2019) and a variety of optimization parameters (Mäkelä et al. 2011). On the other hand, due to relatively high temperatures of the deposition, the use of LFS for heat sensitive materials can be challenging.

This study describes binary TiO_2/SiO_2 coating obtained by combining titanium and silicon containing precursor. LFS coating of TiO_2 provides superhydrophobic properties for paper substrate (Teisala et al. 2010, Stepien et al. 2011). At low concentrations, silica does not switch the wettability (Haapanen et al. 2015), but it positively affects the durability of structure and its wear resistance (Stepien et al. 2013a).

Most studies deal with films and membranes as a substrate for SLIPS (Wong et al. 2011, Daniel et al. 2013, He et al. 2017, Niemelä-Anttonen et al. 2018). However, paper and paperboard, being a porous medium, are promising materials for slippery surfaces. Paper provides a number of functional properties; it is textured, bio-based, easy to tailor, commercially available, suitable for roll-to-roll manufacturing and for surface treatment. In addition, the use of paper or paperboard as a substrate potentially makes it possible to solve a problem that is important for SLIPS system – depletion of lubricant. When the layer of lubricant is depleted on the surface, additional portions can come from the substrate media, which acts as a feeding layer due to the capillary phenomena. Thus, the aim of this study is choosing optimal paper material, which will have poor affinity to water, but will have appropriate oil capacity to serve as a lubricant reservoir. Selected grade is processed with TiO_2/SiO_2 nanoparticle coating to achieve hierarchical structure on the surface. Obtained system is impregnated with lubricant to create SLIPS. In fact, utilizing not only synthetic, but also vegetable oils, it was possible to fabricate SLIPS, which are completely based on eco-friendly materials. Finally, slippery behaviour of produced structures is studied, determining sliding angles and hysteresis.

Materials and methods

Materials

The following commercially available paperboard materials were investigated in this research (Figure 1):

Ensocoat by Stora Enso, a coated solid bleached sulfate (SBS), with a three-layer fibre structure of chemical pulp, a double-pigment coating on the top and one layer coating on the reverse side (dark surface layers on Figure 1). Grammage is 275 g/m².

MetsäBoard Classic FBB, a double blade coated folding boxboard (FBB), hard sized, with three-layer fibre structure of bleached chemical and bleached mechanical pulp. Grammage is 250 g/m².

Cupforma Natura by Stora Enso, a bleached cup board (BCB) with multilayer construction of bleached sulphate pulp, while the middle layer contains chemi-thermomechanical pulp. Grammage is 260 g/m².

Distilled water was used for Cobb and Klemm tests, and pure Milli-q water – for contact angle measurements. Silicone oils (PDMS) of different viscosities were purchased from Sigma-Aldrich. Commercial cooking rapeseed oil was used as biocompatible lubricant (JSC Rukola).

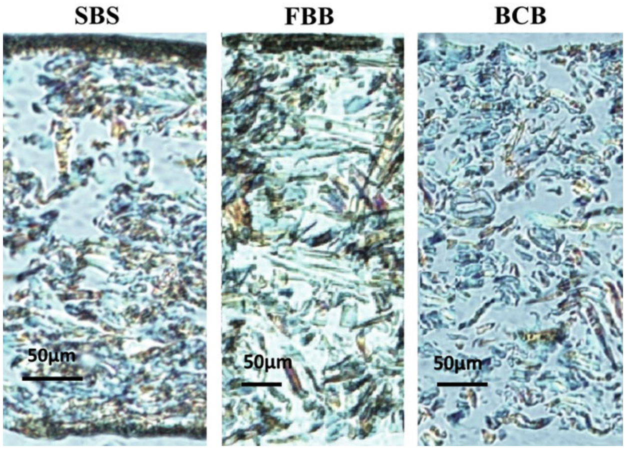

Figure 1: Cross section of paperboard materials.

Methods

In this research, two separate approaches were performed for slippery liquid-infused porous surfaces characterization. First one is traditional for this field: static water contact angles measurement and dynamic experiments where advancing, receding and sliding angles were determined.

The second approach combines several techniques widely used in paper industry, including Cobb and Klemm methods. These techniques are aimed at examining of the capillary phenomena that occur in the process of impregnation the porous substrate with lubricant. Both Cobb and Klemm methods were performed at ambient conditions of 23 °C and 50 % relative humidity.

Determination of water absorptiveness. Cobb method

Cobb measurements provide information about the amount of liquid that can be absorbed by substrate. As a rule, in such measurements water is used as a liquid, but in this study, the method was modified to evaluate the lubricant capacity of the substrate. A weighted sample was mounted inside the device and water or tested lubricant is poured into the cylinder (Figure 2A). In the end of exposure time, the liquid should be quickly removed, and the specimen should be weighted again. In this research, several exposure periods were used to estimate the speed of imbibition. According to the measurement procedure (ISO 535:2014) the excess liquid from the surface of studied material was removed using blotting paper and a 10 kg metal roller. Thus, only the mass the liquid, that was inside the bulk of the material, is taken into consideration.

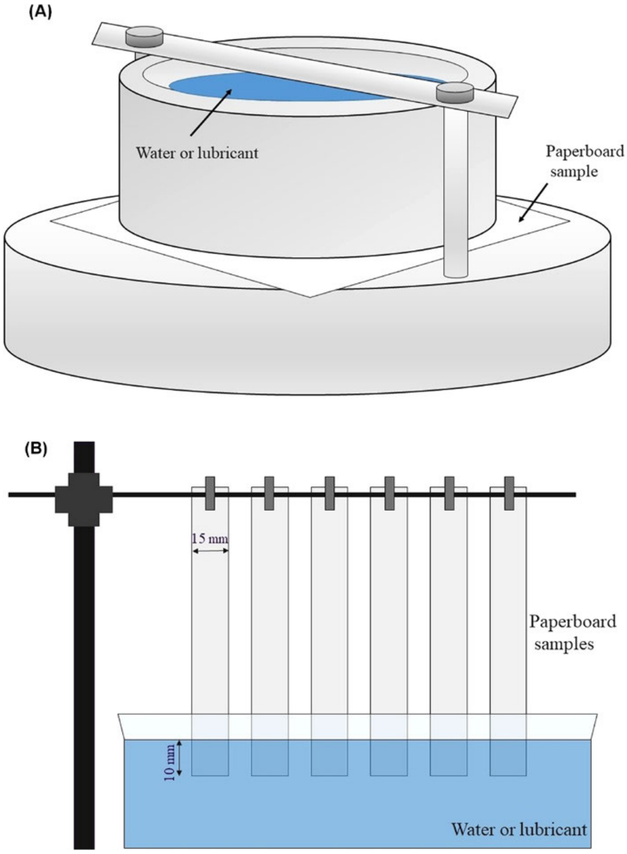

Figure 2: Schematic illustration of the setup: (A) Determination of water absorptiveness, (B) Determination of capillary rise.

Determination of capillary rise. Klemm method

This method examines liquid transport in a porous media for the selected system lubricant/substrate (ISO 8787:1986). A strip of the test material is vertically placed in a reservoir with the liquid at a depth of 10–15 mm (Figure 2B). After 10 minutes, the height of capillary rise is evaluated. Applied to SLIPS, this technique allows evaluating the affinity of the lubricant to the substrate and making assumptions about the speed of imbibition or depletion of the lubricant layer. In contrast to the earlier described Cobb method, in this case absorption occurs through the side cut of the material, thus eliminating the effect of the coatings that may have some repelling properties.

Liquid flame spray coating

Superhydrophobic titanium dioxide (TiO_2)–silicon dioxide (SiO_2) nanoparticle coating was generated on paper-

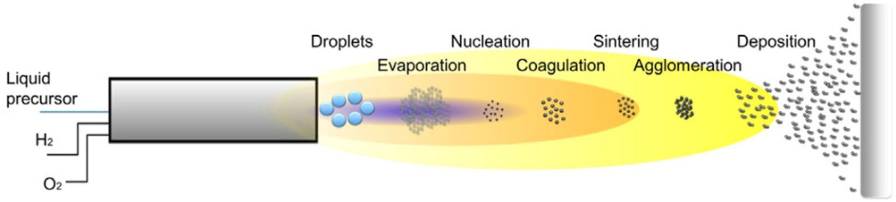

Figure 3: Schematic picture of the Liquid Flame Spray coating process (Haapanen et al. 2015).

board using liquid flame spray equipment. The ratio of oxides in the coating was controlled by the ratio of precursors in the feed solution.

The deposition process is shown schematically in Figure 3.

A detailed description of the coating process, as well as utilized chemical composition, was given in previous publications (Mäkelä et al. 2011, Haapanen et al. 2015). Briefly, a liquid precursor, an organic compound containing the deposited material, is supplied to the nozzle with a certain feeding rate. Combustion gases (O_2, H_2), in addition to the burning function itself, transfer the precursor to aerosol state. Due to the high flame temperature, the organic precursor decomposes forming an oxide, after that occur coagulation, sintering, agglomeration and deposition processes. LFS method allows the possibility of applying several layers of nanocoating if necessary.

The driving force of the liquid flame spraying method is thermophoresis, i. e. the particles are transported to the surface due to the temperature gradient between the flame and the material being coated (Mäkelä et al. 2011). A different thickness and structure of the nanocoating can be achieved by varying the process parameters. For example, by reducing the gap between the substrate and the nozzle, the agglomeration process can be limited, thus decreasing the size of the particles being deposited. In the liquid flame spraying process, various metal oxide particles can be deposited, ranging from 2 to 100 nanometers (Haapanen et al. 2015). By changing the feeding rate or the concentration of the precursor, the size of the flame can be controlled, which is important in case of heat-sensitive substrates. In general, it is necessary to maintain a balance between the tendency to deposit a considerable amount of particles and the thermal sensitivity of the material (Haapanen et al. 2019).

Another parameter that can be adjusted is the liquid precursor composition; it is possible to use a single-component solution or a mixture of several compositions. The composition of the coating for this research was 70 % TiO_2–30 % SiO_2 and 90 % TiO_2–10 % SiO_2. Here and throughout the percentages for the composition are atomic, i. e. refer to Ti and Si. Homogeneous and hierarchical structure of the fabricated surface was controlled by the processing parameters: precursor concentration (50 mg atomic Ti/ml), feed rate (12 ml/min), burner distance (6 cm), line speed (50 m/min). The substrate passed through the burner with the flame 3 or 5 times, creating 3 or 5 layers respectively.

Contact angle and sliding angle measurement

The static water contact angle and the droplet sliding angle were measured using a KRUSS Drop Shape Analyzer – DSA100 at ambient conditions of 23 °C and 50 % relative humidity. It is important that there is the perceptible difference in water droplet moving mechanism for two cases – tilted superhydrophobic surface and tilted lubricant impregnated nanotextured surface. In the first case, a droplet rolls down, whereas on the lubricated surface it mostly slides. It is also visible that the rolling off process is usually fast and takes milliseconds, while the sliding process is much slower. For this reason, the tilting speed for the experiment was relatively low (10° per minute), in order to not to overlook the moment of motion of the water droplet. Sliding or roll-off angle was determined as an angle at which the surface should be tilted for the beginning of the constant motion of the droplet. Hysteresis was determined as the difference between advancing and receding water contact angles on tilted surface before the beginning of the constant motion of the droplet. The droplet volume was 6 µl for static contact angle measurements and 10 µl for the experiments with tilting. The number of independent measurements for experiments with tilting was 10 or more.

SEM imaging

For SEM (Scanning Electron Microscope) imaging (LEO 1530 Gemini, Zeiss) the samples were sputter-coated with

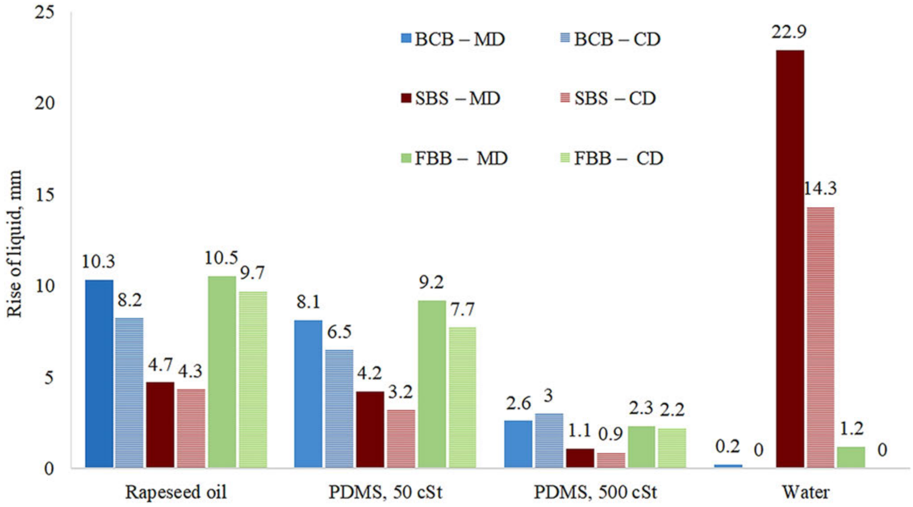

Figure 4: Capillary rise of liquid in paperboard samples in machine direction (MD, solid bars) and cross-machine direction (CD, patterned bars).

7 nm thick Pt layer to reduce the surface charging. The side view on paper was made by fracturing the sample that was precooled in liquid nitrogen. SEM imaging was performed in Max Planck Institute for Polymer Research, Mainz, Germany.

Results and discussion

Lubricant imbibition

Three grades of commercially available paperboards with similar grammage were taken as substrates in this study. For being suitable as a substrate, material should meet the following criteria: be poorly moistened with water, but at the same time provide an easy transport of lubricant. All types of paperboard used in this study are hydrophobic and oleophilic. Static water contact angle for FBB is 95° (±2°), for SBS is 93° (±2°) and BCB is 122° (±2°). Also, paperboards showed significant affinity to oils with contact angles less than 10°. The droplet of oil is quickly spreading, forming a continuous film on the top of the surface. Although the LFS coating has its own pores and texture, it is supposed that it will not affect the lubricant capacity or transport due to its low thickness. Thus, oil absorption studies were performed on paperboard without any LFS coating. Figure 4 shows the capillary rise values obtained by the Klemm method. According to the standard, rise of liquid is evaluated visually to the nearest millimetre. Therefore, it can be assumed that the error of the presented data is ±1 mm.

Apparently, the capillary rise of water for BCB and FBB samples is extremely low. The capillary rise of oils is significant, moreover, for silicone oil with a low viscosity the capillary rise increases. It is also visible that for the machine direction all values are greater. The reason of this phenomenon is probably the orientation of the fibers during paper production process. SBS is wetted with water relatively fast, while capillary rise of oils is insufficient. Thus, it can be summarized that BCB and FBB have a certain affinity for the lubricants used, which will potentially ensure the quick movement of the lubricant inside the structure, preventing depletion.

An important characteristic of SLIPS system is the amount of oil that the substrate can absorb, in other words, its lubricant capacity. To determine this characteristic, the Cobb method was used, which allows evaluating the mass of liquid that is absorbed by 1 m^2 of substrate over a certain period of exposition time (Figure 5).

The amount of water absorbed by the bleached cup board sample is quite low compared to the amount of lubricants, probably because of its hydrophobic surface. Static water contact angle for BCB is 122° (±2°). Paper typically is a hydrophilic material, owing to the fact that it is made of cellulose, but due to a special sizing treatment, its surface can be hydrophobic. Hydrophobic sizing treatment is usually implemented to protect the raw edge in such boards, which can be exposed to liquids. As a result, water quite slowly penetrates into the BCB structure through the pores; this explains the low speed of the absorption process. In contrast, oil readily impregnates BCB sample; the major part of lubricant was absorbed already in 30 seconds (Figure 5). When increasing the exposure

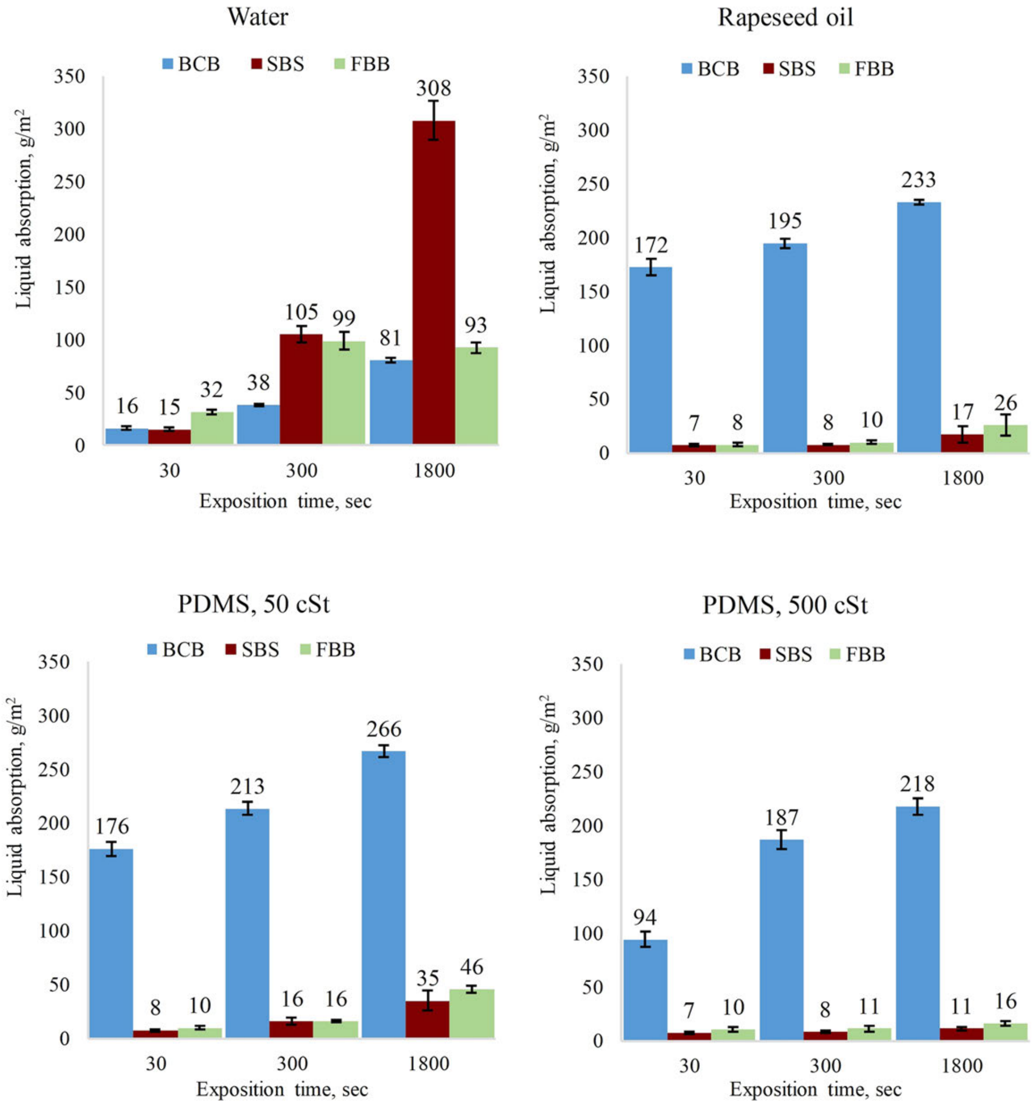

Figure 5: Liquid absorptiveness of paper samples.

time up to 5 or 30 minutes, the weight gain mainly refers to the spread of oil through the internal capillaries beyond the boundaries of the studied area. For viscous lubricant, PDMS 500 cSt, the imbibition rate slightly decreases, thus for high viscosity oils the exposure time should be increased.

The surface of FBB and SBS has certain properties that diminish the absorption of lubricant. The penetration occurs through the pores in the pigment coating, and oil presumably flows through tortuous path. For these samples, after a considerable exposure time, the mass of absorbed lubricant was still minimal. With a short exposure time, the amount of absorbed oil was insignificant and visually imbibition was practically not observed. The FBB sample shows quite poor lubricant absorptiveness despite the fact that capillary rise performance is significant. The reason is probably in the different kind of contact area: in Klemm method a side cut of the sample contacts with the liquid, i. e., the exposed fibers provide capillary rise. In contrast, in Cobb method, the front part of paperboard sample is exposed to the liquid, therefore, the penetration occurs through the pores in the pigment coating.

For BCB specimen, where the surface is not coated, lubricants easily penetrate into the structure, similar to the Klemm capillary rise experiments.

Based on the experimental results, we can conclude that BCB samples are more suitable as a substrate for obtaining lubricant-infused slippery surface. In this case, the main emphasis was put on the easy transport of the lubricant in the paper structure. Pigment coatings on the

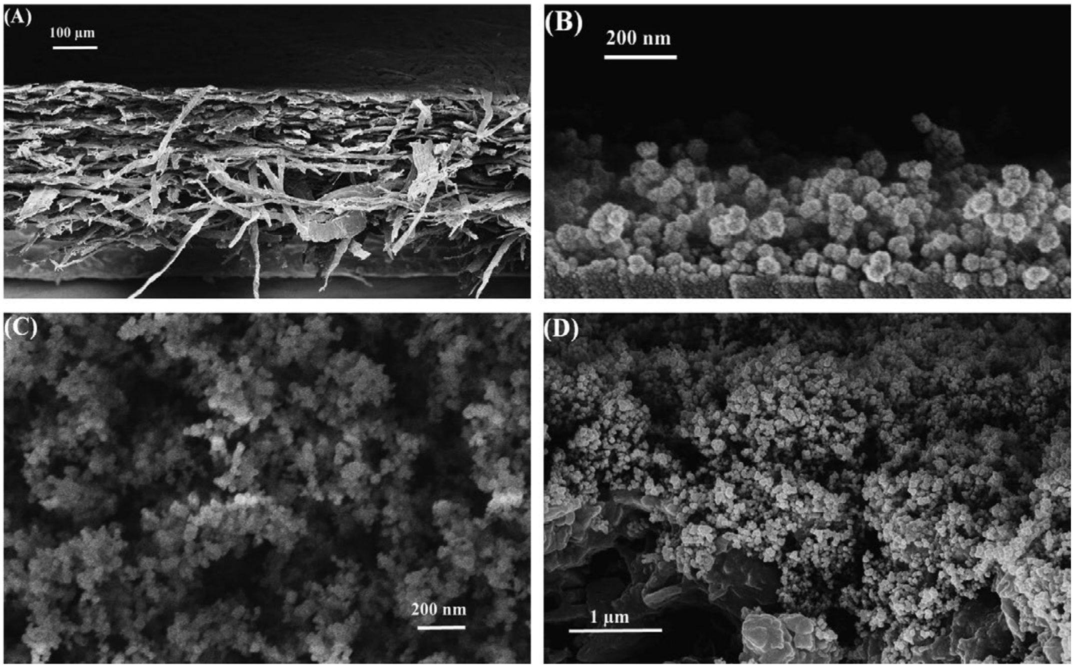

Figure 6: SEM images: (A) Bleached cup board (cross section), (B) LFS nanocoating 70 % TiO_2–30 % SiO_2 on glass slide (cross section), (C) LFS nanocoating 70 % TiO_2–30 % SiO_2 on paperboard (top view), (D) LFS nanocoating 70 % TiO_2–30 % SiO_2 on paperboard (inclined).

surface of the FBB and SBS samples in some way prevent the efficient imbibition of samples with lubricant. On the contrary, BCB samples showed a significant affinity to oils and poor water transport. FBB and SBS samples have relatively smooth surface because of the pigment coating. In contrast, slightly rough and fibrous surface structure of the BCB paper substrate can add one more level to the hierarchical roughness to enhance hydrophobicity (Teisala et al. 2012). Therefore, liquid flame spraying process was performed on BCB paper samples, and then a lubricant was impregnated into the structure for obtaining slippery liquid-infused porous surface.

Surface imaging of LFS nanocoating

Liquid flame spray coating on BCB is imaged in Figure 6. The structure of the coating is hierarchically rough: the particles create the nanostructure, their agglomerates form the submicrometer scale structure, and the paperboard surface has its own roughness itself. The structure of such fibrous material as paperboard is not smooth, so it is challenging to estimate the thickness of the nanocoating, which was applied by liquid flame spraying. Therefore, the same coating in identical conditions was fabricated on the glass slide. The observed thickness was about 400 nm for 3 layers and 500 nm for 5 layers.

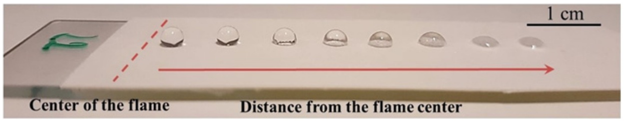

Figure 7: Wetting gradient on BCB with LFS coating.

Wetting and slippery performance

Static water contact angles and roll-off angles were measured for LFS coated bleached cupboard before and after lubricant impregnation. For both mixtures 70 % TiO_2–30 % SiO_2 and 90 % TiO_2–10 % SiO_2 a superhydrophobic structure was achieved. However, during contact angle measurement a gradual change in wetting properties was detected for all the samples (Figure 7). The volume of the water droplets here is 6 µl.

The part of the specimen that was closest to the flame center has the optimal properties (contact angles 150–160° and roll-off angles 3° (±2°)) and with increasing distance from this spot, the CA significantly diminishes.

Typically, the reason for this phenomenon is the insufficient amount of proper chemical composition on the surface of LFS generated coating. Titanium oxide and silicon oxide are hydrophilic themselves, but during LFS processing some special carbonaceous compounds are formed on top of the coating (Aromaa et al. 2012a, Stepien et al. 2012, 2013b). In other words, the reason of the superhydrophobicity of LFS coated paper is the combination of the oxide nanostructure with a complex of various organic compounds that are produced during spraying process. Apparently, these compounds are generated due to evaporation or decomposition of the components of the substrate material at elevated temperature. Thus, the substrate material has a significant effect on the final properties of the LFS coating (Stepien et al. 2013b). Various grades of paper and paperboards have different raw materials, sizing reagents, pigment coating components e. g. fillers or binders. In order to obtain the appropriate composition of carbonaceous compounds on the surface of titania, it is necessary to adjust the processing parameters (precursor concentration, feed rate, burner distance and line speed) for each new substrate material. However, in this study, there was no task to solve the optimization problem. Applying the LFS coating process, a hierarchical structure was obtained as it was imaged in SEM pictures (Figure 6). The BCB substrate with this texture on top was impregnated with oils to obtain a SLIPS system. For these experiments 5 layer structure was used.

During SLIPS preparation procedure, several droplets of lubricant were placed on the surface of BCB with LFS coating. Lubricant was spreading through the substrate quite fast as it was observed in the oil imbibition experiments (i. e. Cobb and Klemm methods). Excess liquid was carefully removed with blotting paper. In contradistinction to Cobb measurements, a metal roller was not used, because this would certainly damage the nanostructure on the surface. The formation of the minor wetting ridge was detected on several samples, but visually no excess lubricant on the surface was observed. However, according to publications the overfilling does not affect the value of the sliding angle (Muschi et al. 2018). The sample was tilted until the beginning of constant droplet motion as imaged at Figure 8. The volume of the water droplets here is 10 µl.

Figure 9 shows the values of the sliding angles and hysteresis for the slippery surfaces with various lubricants.

Static water contact angle for SLIPS with silicone oil is 109° (±2°), and with rapeseed oil 86° (±4°). Low contact angle value for rapeseed oil is probably the result of its polarity. Water, being a polar liquid, does not repel significantly from the surface covered with rapeseed oil. However, rapeseed oil provides good sliding properties and that allows the use of eco-friendly vegetable oil in SLIPS system. All the studied lubricants provide sliding angles less than 10°, even in case of using the viscous silicone oil. Thus, on the surface of paperboard there was a sufficient amount of lubricant to provide the sliding of the droplet at low tilting angles. According to publications, the viscosity of the oil has a greater effect on the speed of the droplet (velocities vary inversely with lubricant viscosity), because gravitational energy of the sliding droplet is mainly spent on viscous dissipation in the wetting ridge around the base of the droplet (Smith et al. 2013).

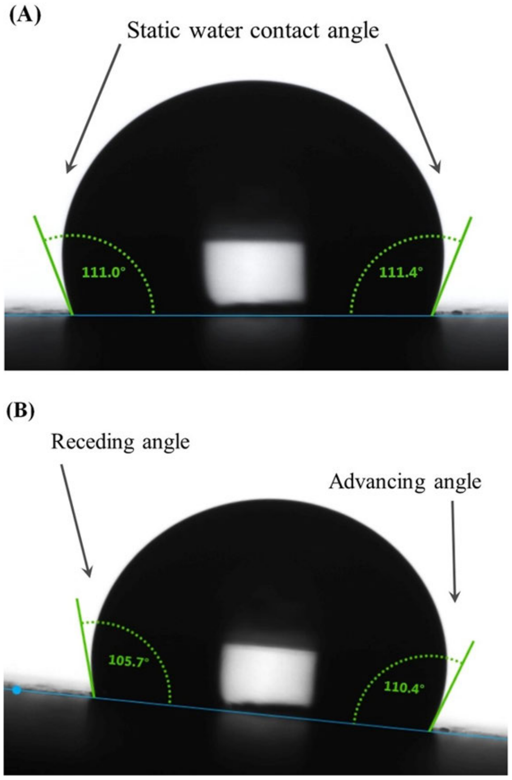

Figure 8: Tilting experiment of water droplet on SLIPS: (A) initial condition, tilting angle is 0°, (B) start of sliding with tilting angle 6°.

Error bars for these experiments are quite significant. The reason for this is probably a certain inhomogeneity of the coating, and in addition, the paper itself is not smooth. Uneven impregnation with oil, which is rather difficult to determine visually, can also be the reason. Also, some protuberant parts of the surface can have poor lubricant coverage, thus creating a “pinning point”.

Both studied compositions – 70 % TiO_2–30 % SiO_2 and 90 % TiO_2–10 % SiO_2 provide efficient sliding properties for SLIPS system. As a reference system, slippery surface was attempted to be fabricated using PDMS and BCB without LFS coating and this sample does not exhibit similar slippery properties even with an excessive amount of lubricant. In that case, water droplets are pinned to the surface of the lubricated sample and do not slide even at large inclinations.

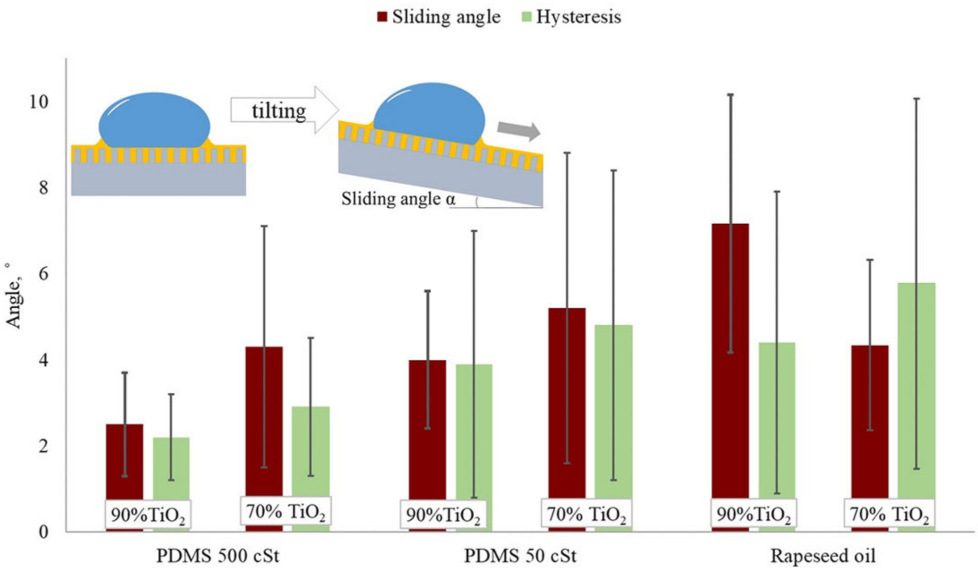

Figure 9: Sliding angles and hysteresis for the slippery surfaces with various lubricants.

Conclusion

This study investigated three samples of commercially available paperboard to be utilized as a substrate for SLIPS: coated solid bleached sulfate – SBS, double blade coated folding boxboard – FBB, and bleached cup board – BCB. The affinity for the studied lubricants and water, as well as the capillary movement of these liquids inside the samples, was evaluated. The optimal properties were shown by the BCB sample, which absorbs a large amount of lubricant, and at the same time, it provides certain repellence effect for water. Imbibition process for this paperboard is quite fast, which is beneficial for upscaling or future production. Less than a minute is required to achieve full oil capacity for this sample. However, the viscosity of the lubricant should be considered – for viscous oils the exposure time should be increased. Complete imbibition of the substrate is important for the concept of a feeding layer that can replenish depleted lubricant on the surface. To obtain superhydrophobic hierarchical surface, the TiO_2–SiO_2 nanoparticle coating, generated by LFS method, was applied to BCB sample. Despite the uneven distribution of superhydrophobic properties described earlier, a considerable amount of nanoparticles was observed on the surface of the paperboard. After imbibition with lubricants, SLIPS were obtained with sliding angles less than 10 degrees. It is noteworthy that rapeseed oil also provided good sliding properties, along with silicone oils, which are conventionally used in this field. This study shows the potential of paperboard as a substrate and rapeseed oil as a lubricant for slippery surface fabrication. Such system would be beneficial in terms of being biocompatible and recyclable, providing alternative and sustainable approach.

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