Water Stability of Hydrophobic Organosilicon Coatings Deposited on Cellulosic Materials by Atmospheric Pressure Dielectric Barrier Discharge

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Abstract: Organosilicon coatings have recently received a lot of interest in the food and packaging industry. Yet, the water stability, an important criterion for the food industry, of such coatings needs to be optimized. In this study, organosilicon coatings are produced on a 3-layer stack of paper by an atmospheric pressure DBD operating with He and TMCTS as plasma gas and precursor, respectively. The penetration depth of plasma modification as well as the water stability of the coatings were investigated.

Keywords: organosilicon, cellulosic material, stability, penetration.

1. Introduction

About one trillion single-use plastic bags are used annually across the world. These bags, however, have been demonstrated to have an extreme destructive impact on the ecological environment. On the other hand, paper products would leave much less environmental foot print and hence has gained attention in different industries such as textiles [1], food and packaging [2], sensors [3], etc. Paper is obtained from the mechanical pressing of cellulose pulp and subsequent dry outs. However, due to their hydrophilic nature, paper products are at the risk of degradation in humid conditions. Thus, extensive research has been devoted to increasing the hydrophobicity of cellulosic materials specifically through surface modification procedures [4-6].

In this regard, modifying surfaces with plasma is considered as one of the most efficient methods to enhance the surface hydrophobicity. In comparison to wet chemical approaches, plasma processes offer dry and low-temperature medium with which a wide variety of substrate materials, even thermosensitive materials such as paper, can be treated. These techniques are considered economical and ecological friendly due to low consumption of chemicals and the absence of solvents. Furthermore, for the food industry application, the coatings must remain stable in solutions. Additionally, some work in the literature indicate that plasma can penetrate thought the porosity of multiple layers in polyester fabrics [7]. This penetration process demonstrates its importance in the batch processing of porous paper in industrial applications.

In this study, a hydrophobic surface is developed using an atmospheric pressure dielectric barrier discharge with helium as working gas and tetramethylcyclotetrasiloxane (TMCTS), as the precursor for plasma enhanced chemical vapour deposition of functional organosilicon coatings. The penetration depth of plasma species into a 3-layer stack of porous paper and its relation to water stability of the layers were established.

2. Experimental procedure

Experiments were performed in a plane-to-plane DBD housed in a vacuum chamber. The DBD cell was formed by two electrodes (2.5 cm × 5.5 cm) made of metallized paint (Pt-Ag alloy) deposited on alumina plates (635 µm thick). The gap between the electrodes was set to 1 mm using two glass slides. Each paper substrate was folded in a way to form a 3-layer assembly. Then the latter was stuck to the lower electrode with the help of kapton tapes on each side to prevent any gas diffusion from the substrate edges. Thus, any observed penetration of the treatment is presumably through the paper layers. The gases, i.e. He as a carrier gas and TMCTS, were introduced to the reactor through a diffuser located at one side of the chamber. **Erreur ! Source du renvoi introuvable.** shows the schematic of dielectric barrier discharge reactor used in this study.

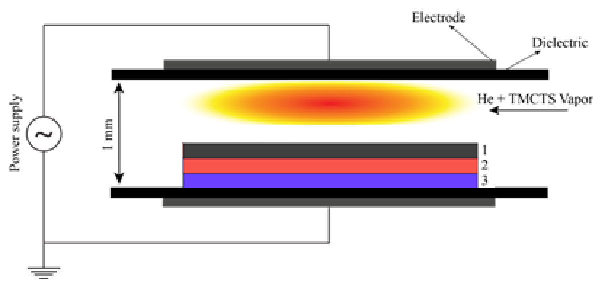

Figure1 Schematic of the dielectric barrier discharge reactor used for the deposition of organosilicon coatings. The substrate is shown colour-coded for the sake of clarity.

In this work the flow rates of 4.5 L/min and 120 g/h for the He and the organic precursor were used, respectively. The chamber was continuously pumped down to maintain atmospheric pressure. A sinusoidal voltage ($2kV_{pp}$, 20kHz) was then applied to the electrodes to ignite the plasma. The voltage and the current were measured high voltage probe (Tektronix P6015A) and a wide-band terminated current transformer (LILCO Ltd. 13W5000), respectively. The oscilloscope (Tektronix DPO5204B) recorded all the voltage and current waveforms during the deposition.

A JSM-7600F scanning electron microscope manufactured by JEOL was used to acquire SEM images. This microscope uses a field emission gun and has a resolution of 1.4 nm at 1 kV and 1 nm at 15 kV. The samples were coated with 2 nm of gold prior to SEM observations to prevent distortion and charging effects.

The static contact angle of the coatings was measured using a contact angle goniometer (OneAttension Theta, Biolin Scientific) connected to a video camera system and computer software (Attension) following the Sessile drop method. A single droplet with a volume of approximately 15 µL was deposited on the surface for 5 minutes to evaluate the static contact angle and absorption rate of the samples. The samples were then immersed in deionized water for 20 hours at room temperature. Subsequently, the absorption test was repeated to investigate the aging of the wetting properties after the immersion of the coatings. In this regard, the contact angle and volume of the droplet were recorded every 60 seconds for a total duration of 5 minutes.

3. Results and discussion

Figure -2 shows the applied voltage (V_a) and the measured current (I_m) versus time obtained from a He/TMCTS plasma with a paper sample placed on the bottom electrode. The measured current curve exhibits multiples current peaks linked to the different discharge breakdowns and visible in a typical homogeneous regime [8]. Therefore, all the depositions were performed under the homogeneous regime.

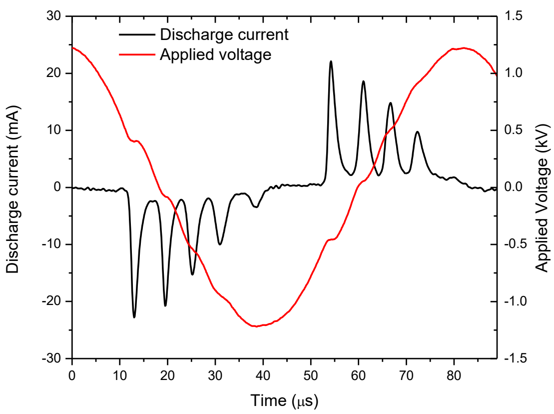

Figure -2 Current-voltage characteristic of He-TMCTS discharge in presence of a 3-layer paper stack

The paper samples were treated for 30 minutes in a homogeneous discharge using an appropriate gas mixture of He and TMCTS. The scanning electron microscopy micrographs of the plasma deposited surfaces were acquired to analyze the morphology of the films on the paper substrates. Figure -3a shows a SEM image of an untreated kraft paper. As a result of mechanical processing during preparation, the surface is rough and cellulose microfibres are clearly visible. Figure -3b confirms the lumped-feature of the plasma deposition the surface of the microfibres .

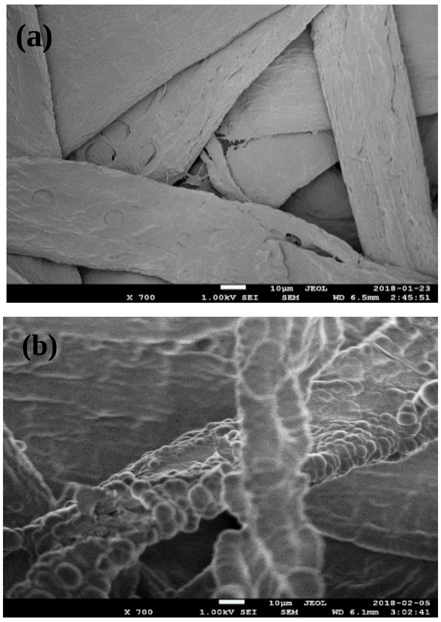

Figure -3 SEM images of a) untreated kraft paper, b) kraft paper substrate covered by organosilicon coating

The static and dynamic water contact angle values were also measured on all layers of the stack, **Erreur ! Source du renvoi introuvable.**. The contact angle values seem to be almost constant on all layers (~135°) and indeed much higher compared to that of the untreated kraft paper. This increase in wettability is in agreement with the data reported in the literature [9].
Thus, it is indicated that the plasma modification is effective not only on the first layer but also it could sequentially penetrate even to the layers underneath. The time for the droplets to be fully absorbed on the surface is referred to water absorption time. In terms of water absorption, all the layers showed the same behaviour and the water droplets stayed on the surface for the duration of 300s. To investigate the water stability of the 3 layers of the stack, each layer was individually immersed in de-ionized water for 22 hours at room temperature. Subsequently, the samples were dried out at ambient air and their static and dynamic contact angles were again

examined. In this regard, the contact angle and volume of the droplet were recorded every 60 seconds for a total duration of 5 minutes. The results show that the contact angle and water-absorption time remained intact for the layers 1 and 2 even after 22h water immersion. Nevertheless, the values reduced in the case of layer 3. The results suggest that water immersion partially remove the coating from the surface. However, different layers exhibit different degrees of removal. This can be explained by different chemical and mechanical stability of the coatings. These results are in a good agreement with the static and dynamic contact angle studies after water immersion where the contact angle and water absorption time were largely reduced.

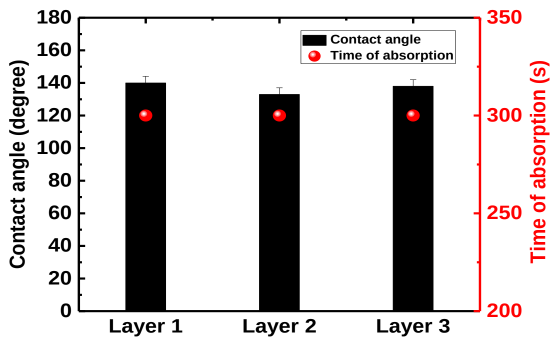

Figure 4 Static contact angle values and water-absorption time of all layers after plasma treatment

4. Conclusion

Over the range of experimental conditions studied here, we have shown that the helium/TMCTS atmospheric pressure dielectric barrier discharge was able to penetrate to 3 layers of kraft paper and led to a hydrophobic deposition. After plasma treatment, all the layers exhibited almost the same values of water contact angle and water-absorption time. Nevertheless, after 22h immersion in water, the wettability was gradually decreased as the layer got deeper due to some coating removal. Hence, it can be concluded that the water stability of each layer depends on its position from the first layer.

Acknowldegments

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5. References

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