

Impact of Temperature and Humidity on Superhydrophobicity of Polyurethane/Organoclay Nanocomposites

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ABSTRACT

This work investigates temperature, humidity and humidity hysteresis effects on the superhydrophobic performance of polyurethane/organoclay nanocomposites. An experiment was conducted to measure the contact and averaged sliding angles of the nanocomposite throughout a temperature cycle ranging from 20°C to -2°C at both high and low humidity conditions. Results from a high humidity test show a slight decrease in superhydrophobicity at freezing temperatures as well as humidity hysteresis effects at the end of the temperature cycle. The presence of these effects were still detected in a low humidity test but was discovered to be less significant. Results also show a reduction in contact angle values when relative humidity levels were reduced from above 85% to close to 0%. This was hypothesized to be partially due to a minor degradation in nanocomposite surface structure.

Keywords: superhydrophobic, nanocomposites, temperature, humidity, humidity hysteresis, contact angle

1 INTRODUCTION

Inspired by the lotus leaf, researchers have successfully fabricated synthetic surfaces with high water contact angles ($>150^\circ$) and low sliding angles [1], [2]. These superhydrophobic surfaces can be applied in a variety of areas such as anti corrosion/fouling surface applications as well as drag reduction in marine and fluid powered systems. Due to its ability to repel supercooled water, recent preliminary investigations also show that a superhydrophobic coating is able to reduce both ice accumulation and adhesion on a surface [3]–[6]. The ice-phobic nature of these surfaces provides an attractive solution to current icing problems that can occur on applications such as aircraft, power lines and wind turbines.

However, the performance of a superhydrophobic surface in natural icing conditions is still not well understood. An effective anti-icing superhydrophobic surface will depend not only on its ability to maintain superhydrophobicity at freezing temperatures but at different humidity levels as well [7]. Yin *et.al.* [8] studied the effect of temperature on a sandblasted

nano-SiO₂ superhydrophobic surface at high humidity conditions (RH $>$ 80%) and discovered that static water contact angles decreased as test conditions fell below freezing temperatures. Similar observations were made by Karmouch *et.al.* [9] on a nanostructured polytetrafluoroethylene (PTFE) surface at low humidity. Measurements showed that the contact angle hysteresis of the surface increases when subjected to temperatures below 5°C. The decrease in superhydrophobic performance was attributed to water condensation on the surface where micro-droplets penetrate into the gaps of the nanostructures, triggering a transition of a Cassie-Baxter to a Wenzel state. However, an investigation by Mockenhaupt *et.al.* [10] on a superhydrophobic *Brassica* leaf showed that at isothermal conditions (temperature of the superhydrophobic surface and water droplet are equivalent) and at low humidity conditions, the sliding angle of the surface did not change significantly.

According to the authors knowledge, there has not been any publications which have examined the effect of humidity as well as humidity hysteresis effects on superhydrophobic polyurethane/organoclay nanocomposite coatings. Therefore, in this work, the effects of varying temperature and humidity on the superhydrophobicity of these surfaces were investigated. An experiment was designed to systematically measure the static water contact angles and sliding angles of the nanocomposites at isothermal conditions for a full temperature cycle of 20°C to -2°C at both high and low humidity levels to quantify the humidity and humidity hysteresis effects.

2 MATERIALS AND METHODS

2.1 Nanocomposite Fabrication

Precursor solutions were first created, followed by spray casting and then thermosetting to produce the final nanocomposite coatings. First, as-received dimethyl dialkyl C14-C18 amine functionalized montmorillonite clay particles (Nanoclay, Nanocor Inc., USA) were first dispersed in ethyl alcohol at room temperature.

Waterborne perfluoroalkyl methacrylic copolymer (PMC) (30% wt polymer, 70% wt water; Dupont) was then added slowly to the solution and blended with vortex mixing. Separately, a moisture-cured polyurethane (MCPU) was also dispersed in ethyl alcohol. The

MCPU was a one-component liquid formula comprising of 25% diphenyl-methane-diisocyanate and 75% polyurethane pre-polymer (hexanedioic acid, polymer with 1,6-hexa-nediol and 1,1-methylenebis 4-isocyanato-benzene). This type of polyurethane formula is commonly found in many commercially available adhesives such as Titebond and Gorilla. Finally, the alcohol/organoclay/PMC suspension was blended into the MCPU solution, creating a Pickering emulsion. The final blend was stirred using a vortex mixer for 15 minutes until the mixture was in a homogenous and stable state.

To create the nanocomposite coatings from this precursor solution, the slurries were spray cast onto aluminum substrates using an internal mix, double-action airbrush atomizer (model VL-SET, Paasche). The substrates were coated with a single spray application from a distance of approximately 30 cm above the substrate for a “dry” spray and then heat cured at 100°C overnight.

2.2 Experimental Set-Up and Process

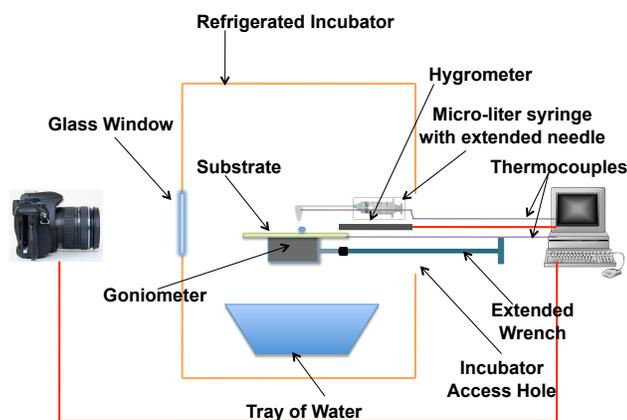


Figure 1: Schematic of the experiment for high humidity conditions

The nanocomposite substrate was placed on a manual goniometer stage (Thorlabs GN-05) and attached onto a breadboard. Water droplets were deposited on the surface of the substrate using a deflected tip needle (Sigma Aldrich Z116157) attached to a 2ml micro-liter syringe (Gilmont GS-1200). This entire set-up was placed within a microprocessor controlled refrigerated incubator (Sanyo MIR-154) with a temperature range of -10°C to 60°C and an accuracy of 0.2°C (Figure 1). An extended wrench was positioned through the incubator access hole to meet the lead screw of the goniometer for the acquisition of sliding angle measurements.

For high humidity experiments, a tray of water was placed in the incubator to increase the relative humidity within the chamber. For a low humidity experiment, desiccants (EMD Chemicals, DX0017) were

placed within the incubator for moisture absorption. The level of humidity near the substrate was monitored using a hygrometer (Control Company Model 4185). In addition, thermocouples were used to measure the substrate and water temperatures, respectively. Water contact angle measurements of the nanocomposite surface was performed by capturing digital images of the water droplet through the incubator glass window using a digital SLR camera (Canon T2i, macro lens MP-E). The images were then analyzed using a B-spline snake approach pioneered by Stalder *et.al.* [11] as a plug-in program within the Image-J software.

The data acquisition process begins at 20°C, during which the nanocomposite substrate, water and test chamber air temperature were confirmed to be isothermal before a 10 μ L water droplet was deposited on the surface of the substrate for contact angle measurements. The process of tilting the goniometer stage to obtain the sliding angle was repeated three times so that an averaged value was acquired. The entire data acquisition process was then repeated until a full temperature cycle (ranging from 20°C to -2°C) was completed.

To correctly assess the hysteresis effects of the contact and sliding angle, extra care was taken to ensure that the humidity levels at temperatures during the second half the temperature cycle (-2°C to 20°C) closely resembles the humidity levels acquired during the first half of the temperature cycle (20°C to -2°C). This requires occasional adjustment of the target temperature so that the intended level of relative humidity can be reached.

3 RESULTS AND DISCUSSION

The superhydrophobic performance of the nanocomposite coating was quantified before being subjected to temperature and humidity tests. Figure 2 shows the image of a 10 μ L water droplet resting on the nanocomposite superhydrophobic surface. Image analysis of this picture shows that the contact angle of the water droplet was 162.3°. Average value for the sliding angle of the surface was 4.6°.

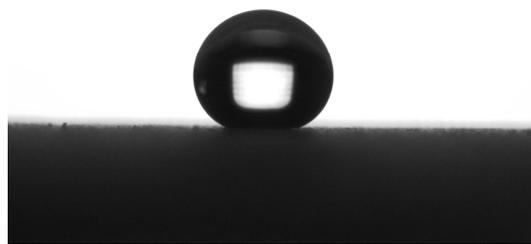


Figure 2: Image of a 10 μ L water droplet on the nanocomposite surface at ambient conditions

The experiment was initiated at a temperature of 20°C and the direction of the temperature cycle is represented by the arrows shown in Figure 3. The humidity levels were consistently maintained at over 85% throughout the entire temperature cycle. It can be observed that contact angle decreased from 167° to 159° as temperature was reduced from 20°C to 0°C. The decrease in contact angle was due to the condensation of the highly saturated air on the micro and nano-asperities of the nanocomposites, therefore increasing the wettability of the surface.

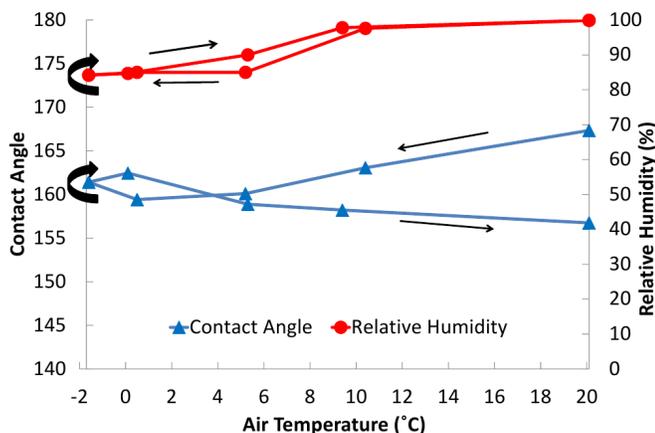


Figure 3: Water contact angle measurements for a complete temperature cycle at high humidity

During the second half of the temperature cycle, the first few points of contact angle measurements closely resembles the values previously acquired in the first half of the temperature cycle. However, even though the relative humidity of the air in the test chamber at all points of measurement were matched to within 5%, the contact angle continues to decrease after 5°C and diverges from the initial point of measurement at 20°C by 10°. This pattern of divergence suggests that there was a presence of contact angle path dependency. This also indicated that high humidity conditions will not only induce adverse effects on the surface superhydrophobicity by increasing wettability of the surface but also introduce humidity hysteresis effects into the performance of the surface when exposed to humid air for extended periods of time. Hysteresis effects were also present in sliding angle measurements. As shown in Figure 4, averaged sliding angles increased from 3.9° to 7.5° during the second half of the temperature cycle during which the test chamber was heated from 5°C back to 20°C.

In the low humidity experiment, relative humidity values were successfully controlled to be less than 10% throughout the entire temperature cycle. The contact angle was measured to be 157° at 20°C and remained

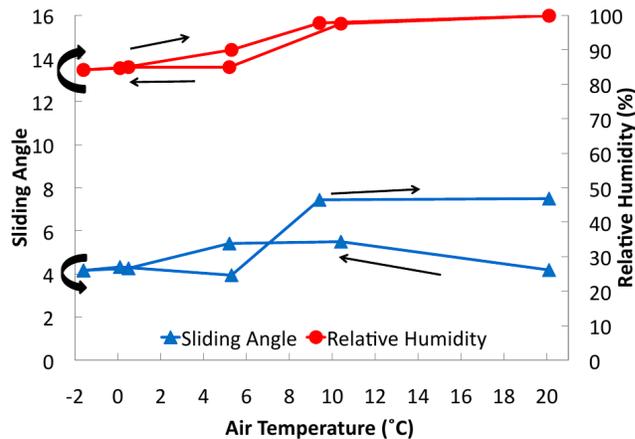


Figure 4: Sliding angle measurements for a complete temperature cycle at high humidity

within the uncertainty range of 3°C throughout the cooling process until 0°C (Figure 5). Contact angle measurements from the second half of the temperature cycle decreased from values obtained from the first half but remained close to a constant value with no sign of divergence. Characterization of the averaged sliding angles across the temperature cycle shown in Figure 6 depicted a similar trend. Increase in sliding angle measurements were detected at 20°C. However, values from all other points of measurement in the temperature cycle remain constant with uncertainty.

This suggests that slight humidity hysteresis as well as condensation effects resulting from changes in surrounding temperatures were still present. However, the combined result from both of these effects was still minor as compared to the effects from high humidity. In fact, the presence of high humidity significantly increased the wettability of the superhydrophobic surface until the point where the hysteresis and condensation effects were amplified.

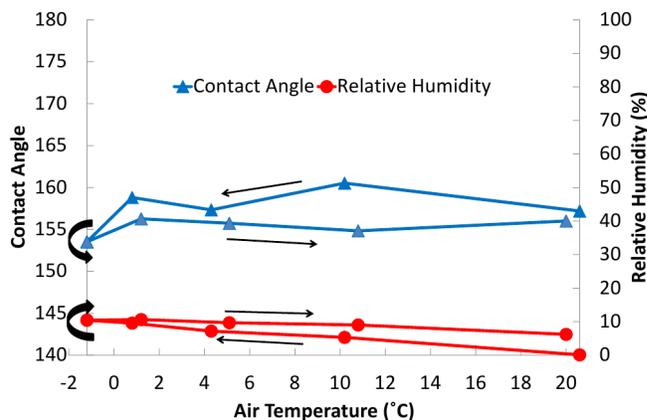


Figure 5: Water contact angle measurements for a complete temperature cycle at low humidity

4 CONCLUSIONS

The study of humidity and humidity hysteresis effects on the superhydrophobicity of polyurethane/organo-clay nanocomposites throughout a full temperature cycle ranging from 20°C to -2°C was conducted. Results indicate that at high humidities (RH>85%), a reduction in temperature slightly decreases the contact angle of the nanocomposite surface. In addition, results show that contact and averaged sliding angle measurements at the end of the temperature cycle diverge from the measurements taken at the beginning of the cycle. This suggests the presence of contact and averaged sliding angle path dependency as well as humidity hysteresis effects in the performance of the coating. These effects were still slightly detected in low humidity tests (RH<10%) but its impact was discovered to be less significant as compared to the high humidity experiments. In addition, results obtained from the first half of the temperature cycle for low and high humidity tests show a decrease in contact angle measurement as relative humidity was reduced. This was believed to be partially due to a minor degradation in nanocomposite surface structure.

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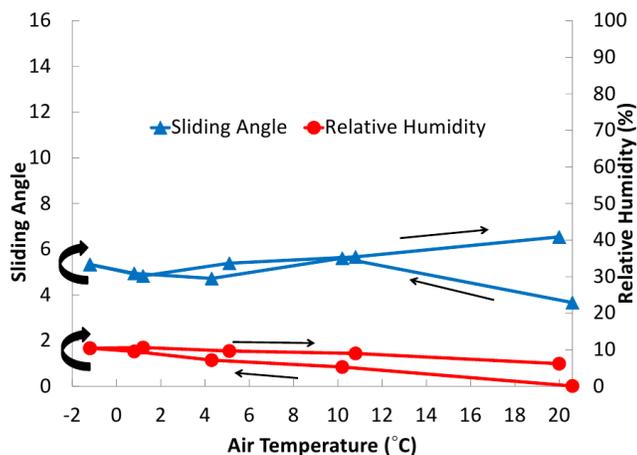


Figure 6: Sliding angle measurements for a complete temperature cycle at low humidity

The humidity hysteresis and path dependency effect were further investigated in Figure 7. The contact angle measurements at both high and low humidity conditions at 20°C, 5°C and -2°C taken from the first half of the temperature cycle tests were plotted with experimental data from Yin *et.al.* [8]. It can be observed that the contact angle of the surface across all temperatures decreases when relative humidity was lowered. Since the same nanocomposite surface was used for both the high and low humidity tests, the reduced contact angle in the low humidity tests was believed to be a result of minor degradation in nanocomposite surface structure. However, the path dependency effect of the contact angles through different temperatures and humidities may also play a role.

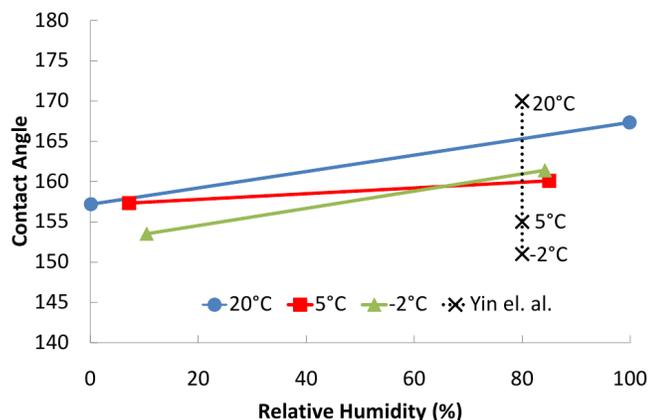


Figure 7: Water contact angle measurements at high and low humidity conditions taken from measurements from the first half of the temperature cycle tests