Adhesion Strength and Superhydrophobicity in Polyurethane/Organoclay Nanocomposites

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ABSTRACT

Adhesion strength is critical for realistic application of superhydrophobic coatings, which have the potential for dramatic performance improvements such as drag reduction for marine vehicles and fluid power systems, anti-fouling and anti-icing on aircraft and wind turbines, and stain-resistant coatings. In the current study, substrate adhesion was investigated experimentally for superhydrophobic coatings fabricated from polyurethane modified with waterborne perfluoroalkyl methacrylic copolymer and a montmorillonite clay nanofiller. The superhydrophobic coatings were obtained by spray casting precursor solutions onto aluminum surfaces. Upon thermosetting, initial static water contact angles exceeding 160° and contact angle hysteresis values below 8° were measured, yielding anti-wetting and self-cleaning characteristics. This performance could be completely retained under 1750 N/m adhesion strength testing, with significant resistance as high as 3850 N/m.

Keywords: nanocomposite, coating, adhesion, nanoparticle, polyurethane

1 INTRODUCTION

Polyurethane coatings are used on many different materials and in a wide variety of applications due to their high durability and adaptable chemical composition. Such adaptability has allowed researchers to synthesize many different types of polyurethane coatings from a long list of macrodiols, diisocyanates and chain extenders [1]. Moisture cured polyurethanes (MCPUs) are one such type. They contain isocyanate-terminated polyurethane prepolymer, which can cure with atmospheric moisture to produce highly crosslinked networks by a reaction of an excess amount of methylene diphenyl diisocyanate with a polyol. This causes a small amount of left over isocyanate monomer to react with moisture on substrate surfaces and complete the cure [2]. The highly crosslinked networks of MCPU coatings have many potential advantages including superior hardness, strength, stiffness and flexibility. The surface moisture that completes the chemical reaction also allows these materials to adhere well to moist substrates and form strong chemical bonds by infiltrating surface pores and asperities where water is present. Furthermore, the probability of a weak boundary layer caused by water trapped under the coating is greatly reduced since moisture is consumed in the process.

Although there are a number of reports on the fabrication of superhydrophobic coatings with a polyurethane component [3-7], the authors are not aware of any publications which have examined and optimized its influence with regard to adhesion strength and anti-wetting performance. In fact, adhesion strength is typically not even discussed in studies on superhydrophobicity [8-11] since the vast majority of synthetic superhydrophobic coatings are extremely fragile. Only recently have some researchers started to consider substrate adhesion characteristics when creating superhydrophobic nanocomposite coatings [12-15]. Similarly, investigation into the mechanical durability of superhydrophobic surfaces in general is only now beginning [16].

The objective of the current study is to experimentally investigate substrate adhesion for superhydrophobic coatings fabricated from MCPU modified with waterborne perfluoroalkyl methacrylic copolymer (PMC) and a fatty amine/amino-silane surface modified montmorillonite clay nanofiller (organoclay). An organoclay-based nanocomposite coating is of interest in that it can be highly desirable as it incorporates an environmentally and biologically friendly material, which may not be true for other nanofiller materials used for superhydrophobic surfaces, e.g. carbon nanotubes [17].

2 EXPERIMENT

2.1 Nanocomposite Fabrication

Precursor solutions were first created, followed by for spray casting and then thermosetting to produce the final nanocomposite coatings. Alcohols are common solvents for epoxy and polyurethane formulations. A recent study [18] found that alcohols can have a strong tendency to adsorb on layered silicate surfaces rendering the surfaces functional for many applications including polymer reinforcement [19]. Thus, as-received organoclay was first dispersed in ethyl alcohol at room temperature and then PMC was added slowly to the solution and blended with vortex mixing. Separately, the MCPU was also dispersed in ethyl alcohol.

The MCPU was a one-component liquid formula comprising 25% diphenylmethane-diisocyanate and 75% polyurethane pre-polymer (hexanedioic acid, polymer with 1,6-hexanediol and 1,1-methylenebis 4-isocyanatobenzene). Its viscosity was measured to be ~4200mPas at 25°C. 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 min until the mixture was in a homogenous and stable state.

The ethyl alcohol solvent concentration can also be tailored to suit the spray applicator if necessary in order to obtain a "dry" spray coating and counteract the coffee stain effect [20]. 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 and then heat cured at 100ºC overnight. The above steps were used to prepare superhydrophobic nanocomposite coatings, which were ethyl alcohol solution-processable composites of dimethyl dialkyl C14-C18 amine functionalized montmorillonite clay particles (Nanoclay, Nanocor Inc., USA), waterborne perfluoroalkyl methacrylic copolymer (30% wt polymer, 70% wt water; Dupont), and MCPU.

2.2 Performance Characterization

To assess the wettability performance of the cured nanocomposite surface, the apparent contact angle and hysteresis of 10 mL droplets were measured. A goniometer (model CAM 200, KSV Instruments) was used to measure the static contact angle, and a high-speed digital camera (Motion Pro X, Red Lake) was used for dynamic advancing and receding contact angle measurements. A scanning electron microscope (SEM) was also used to characterize the surface morphology and composition (JEOL 6700F). Finally, 90° tape test measurements were made with an Instron 3300 tensile tester at a rate of 2 mm/s, details of which are described in [21].

3 RESULTS & DISCUSSION

3.1 Wettability Performance

Concentrations of MCPU, PMC, and organoclay nanofiller to create superhydrophobic performance were determined by measuring static contact angle and hysteresis in relation to component weight percentage. It has been well established in the literature that superhydrophobic surfaces are characterized by static water contact angles above 150° and contact angle hysteresis values below 10°. This combination leads to small droplets that remain nearly spherical on the surface, causing them to roll and bounce freely so as to be both non-wetting and self-cleaning. As in previous studies, suitable structure for superhydrophobicity can be achieved with a relatively low nanofiller concentration, after which anti-wetting performance can degrade for higher weight ratios [22]. A similar approach is utilized in the current work as shown in Figure 1. It can be observed that contact angle performance plateaus at 11% organoclay weight concentration. A further examination of the data sets for different MCPU/PMC weight ratios in the figure reveals that introducing MCPU to the polymer matrix does not significantly reduce the contact angle until the weight ratio exceeds unity. It was further confirmed that superhydrophobic performance was maintained at an MCPU/PMC weight ratio of unity with an average contact angle hysteresis value well below 10° throughout the surface area. It is also noted that a composite deprived of the low surface energy PMC component exhibited an average contact angle hysteresis much greater than 10° as well as a contact angle well below 150°, evidence of the importance of the fluorinated component with respect to anti-wetting.

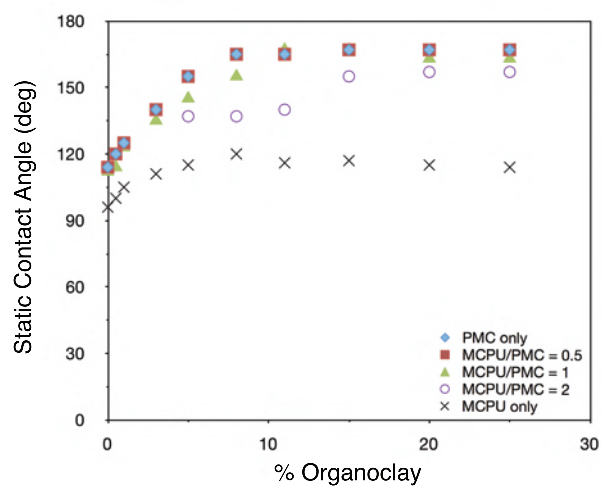

Figure 1: Dependence of apparent static water contact angle on the organoclay concentration as well as MCPU/PMC weight ratio.

3.2 Adhesion

MCPU was introduced as the main component in the composite to improve adhesion strength. After determining the maximum MCPU concentration without compromising anti-wetting performance, adhesion strength was investigated and the MCPU/PMC weight ratio was additionally varied. Twelve 1750 N/m tape tests for select MCPU/PMC weight ratios were carried out on a nanocomposite coating with 11% organoclay weight concentration, i.e. sufficient organoclay to reach the start of the contact angle plateau from Figure 1. The results are plotted in Figure 2. A negative slope can be observed for both a two-component coating composed of PMC binder and organoclay nanofiller as well as for a three-component coating composed of 0.5 MCPU/PMC ratio and nanofiller. This negative trend is evidence of the observation that the coating was peeling off the substrate during testing, leading to an anti-wetting performance degradation. However, MCPU/PMC of 1.0 or higher (including pure MCPU) yielded a near zero slope in Figure 2, which indicates that tape testing had a minimal effect on coating adhesion and wettability. The resulting average contact angle exceeding 160° over the span of tape testing for the 1.0 MCPU/PMC ratio composite suggests that this ratio is near optimal for the given components. It was also confirmed that superhydrophobic performance was indeed maintained at this weight ratio and is suboptimal at other weight ratios tested with respect to contact angle hysteresis. Accordingly, a 1.0 MCPU/PMC ratio with 11% organoclay weight concentration was used throughout the remainder of the study for further analysis.

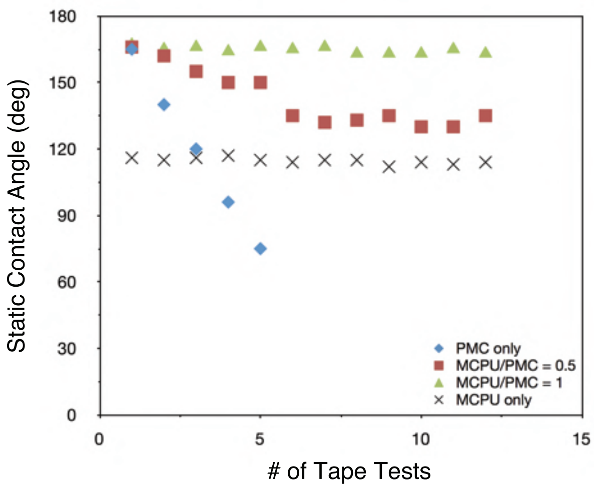

Figure 2: For a nanocomposite coating with 11% organoclay weight concentration: dependence of apparent static water contact angle over twelve 1750 N/m tape tests for select MCPU/PMC weight ratios.

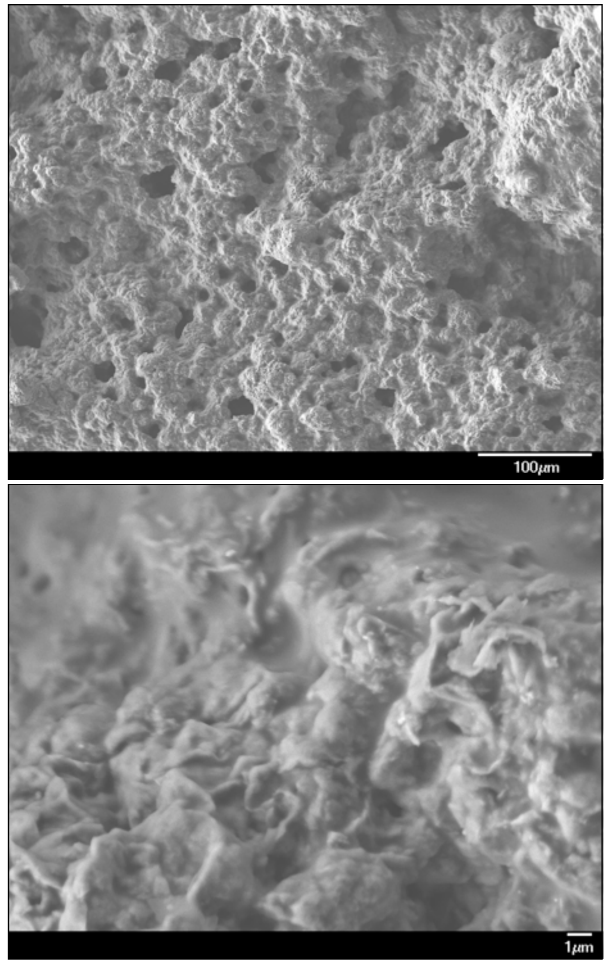

Figure 3: SEM images of the hierarchical morphology of the MCPU/PMC/organoclay nanocomposite.

3.3 Surface Characterization

Detailed SEM observations indicated that the assembly process of the organoclay along the coating surface during polyurethane crosslinking resulted in the formation of hierarchical surface roughness features as shown in Figure 3. The nanocomposite surface morphology shows a remarkable resemblance to self-cleaning superhydrophobic lotus leaf topology shown throughout the literature [9]. Higher magnification SEM images of these surfaces clearly indicate the existence of self-similar micron-sized bumps with unique sub-micron-sized surface roughness from the organoclay nanoparticles. Furthermore, after tape testing, SEM imaging revealed that the surface structure remained essentially unchanged. There was no discernible average morphological difference on the sample for each tape strength tested. Additional SEM analysis of the tapes tested on this MCPU/PMC/organoclay nanocomposite did not reveal an observable amount of coating material that may have been removed from the surface during testing.

3.4 High Adhesion Testing

Higher adhesion strength tape tests up to 3850 N/m were also conducted as shown in Figure 4. A superhydrophobic state was undoubtedly maintained up to 820 N/m over the span of the experiment; however, the data sets for tapes with an adhesion strength of 2100 N/m and 3850 N/m resulted in a slightly negative slope in the figure. After the twelfth tape test, the contact angle degraded from above 160° to within a few degrees of 150° and the contact angle hysteresis increased slightly above 10°. Thus, even though it was observed that these tapes with the highest adhesion strength did not peel off a noticeable portion of the coating, the surface was disturbed enough to slightly degrade anti-wetting performance down to the superhydrophobic threshold. Since it was determined with SEM analysis that the surface morphology was not appreciably altered during tape tests, it is hypothesized that the surface chemistry was slightly altered by the stronger tapes over repeated contact and trace amounts of hydrophilic tape material were deposited on the surface.

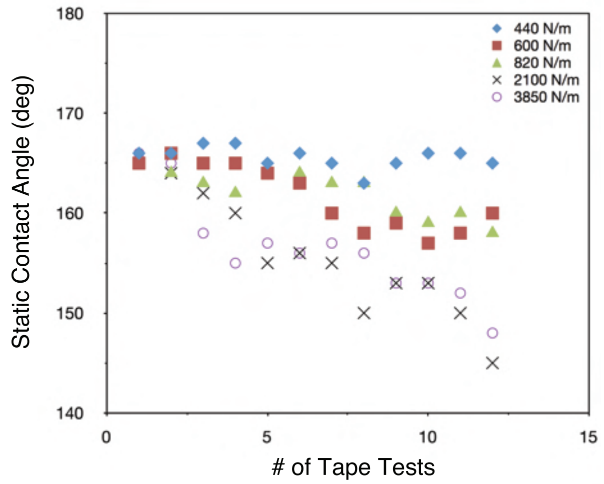

Figure 4: For a nanocomposite coating with 11% organoclay weight concentration and 1:1 MCPU/PMC weight ratio: dependence of apparent static water contact angle over twelve tape tests for select adhesion strengths.

4 CONCLUSIONS

Substrate adhesion was investigated experimentally for superhydrophobic coatings fabricated from polyurethane modified with waterborne perfluoroalkyl methacrylic copolymer and a montmorillonite clay nanofiller. An initial static water contact angle of 167° and an average contact angle hysteresis of 4° were measured on the optimized MCPU-modified coatings, yielding anti-wetting and self-cleaning characteristics. A nanocomposite formulation of 11% organoclay weight concentration and a 1:1 weight ratio of MCPU and PMC was found to result in strong adhesion to the aluminum substrate without a significant degradation of anti-wetting performance. Higher weight ratios of MCPU were observed to reduce anti-wetting performance *before* and *after* tape testing, where as higher weight ratios of PMC were observed to reduce anti-wetting performance *after* tape testing. High contact angles above 160° and low contact angle hysteresis below 10° could be completely retained under 1750 N/m adhesion strength tape testing. Significant resistance was also observed as high as 3850 N/m, which is higher than any reported superhydrophobic coating to the author's knowledge. Furthermore, 3850 N/m tape testing did not noticeably alter the coating surface morphology or remove an observable portion of the coating.

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