Adhesion Strength and Superhydrophobicity of Polyurethane/Organoclay Nanocomposite Coatings

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ABSTRACT: Substrate adhesion was investigated experimentally for superhydrophobic coatings fabricated from polyurethane modified with waterborne perfluoroalkyl methacrylic copolymer and a (fatty amine/amino-silane surface modified) 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 antiwetting and self-cleaning characteristics. Adhesion strength was then characterized with a 90° tape testing method and was analyzed with respect to changes in surface morphology via electron microscopy as well as changes in wettability. The coating remained adhered to the substrate after repeated adhesion testing with 3850 N/m tape (one of the strongest available), showing higher adhesion than any superhydrophobic coating reported to the author's knowledge. Superhydrophobic performance was also shown to be retained even after repeated tape testing. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: E445–E452, 2012

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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 antiwetting performance. In fact, adhesion strength is typically not discussed or even mentioned in studies on superhydrophobicity[8–11] since the vast majority of synthetic superhydrophobic coatings are extremely fragile. However, the degree of adhesion between the superhydrophobic surface and the underlying substrate is a critical enabling factor for many potential applications where system conditions may quickly separate a poorly adhered surface (e.g., marine coatings and wind turbine coatings). 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 this 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

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of interest 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] Recent studies have shown that polyurethane–organoclay nanocomposites can have improved thermal stability and barrier properties compared with pristine polyurethane elastomers.[18] The main reason for the improved performance originates from the nanoscale dispersion of organoclay, and from the strong interactions between exfoliated silicate layers and the polyurethane matrix.[19] Organoclay has also shown strong compatibility with rubber and fluoroacrylic superhydrophobic approaches.[20] It is thus hypothesized that organoclay can be a compatible nanofiller to additionally induce suitable nanoscale structure in a fluoropolymer-MCPU matrix to create a superhydrophobic nanocomposite. Furthermore, because of organoclay's said compatibility with both polyurethane and fluoroacrylics, it should not negatively affect the inherent high substrate adhesion potentially gleaned from the MCPU component in the composite.

EXPERIMENT

Surface fabrication

Precursor solutions were first created, followed by spray casting and then thermosetting to produce the final nanocomposite coatings. Alcohols are common solvents for epoxy and polyurethane formulations. A recent study[21] found that alcohols can have a strong tendency to adsorb on layered silicate surfaces rendering the surfaces functional for many applications including polymer reinforcement.[22] Thus, as-received organoclay (Nanoclay, Nanocor, USA) was first dispersed in ethyl alcohol at room temperature. All dispersions were carried out with vortex mixing (standard heavy duty model, Fisher Scientific) for 5 min unless otherwise specified. Separately, the MCPU was also dispersed in ethyl alcohol. The MCPU was a one-component liquid formula comprising 25% diphenylmethane-diisocyanate and 75% polyurethane prepolymer (hexanedioic acid, polymer with 1,6-hexanediol and 1,1-methylenebis 4-isocyanatobenzene). Its viscosity was measured to be $\sim$ 4200 mPa s at 25°C (OFITE 900, OFI Testing Equipment). This type of polyurethane formula is commonly found in many commercially available adhesives such as Titebond and Gorilla. The alcohol/organoclay suspension was then blended into the MCPU solution and vortex mixed. Finally, the PMC suspension (30 wt % polymer, 70 wt % water; Dupont) was added slowly to the solution and dispersed. The final blend was dispersed until the mixture was in a homogeneous and stable state.

In a typical solution with near optimal component weight ratios (as discussed later in sections Wettability Performance and Adhesion), first 4 g of organoclay and 4.5 g MCPU were separately dispersed in two vials of 10 mL ethyl alcohol. Then each dispersion was blended together, and finally 15 g of the PMC suspension was slowly added and dispersed. The total 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.[23] To create the nanocomposite coatings from this precursor solution, the slurries were spray cast onto 8×8 cm^2 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 $\sim$ 30 cm above the substrate and then heat-cured at 100°C for 24 h.

Performance characterization

To assess the wettability performance of the cured nanocomposite surface, the apparent contact angle and hysteresis of 10 µL droplets were measured. A goniometer (model CAM 200, KSV Instruments) was used to measure the static contact angle ($\pm 5°$ uncertainty), and a high-speed digital camera (Motion Pro X, Red Lake) was used for dynamic advancing and receding contact angle measurements ($\pm 5°$ uncertainty). 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. Tape test measurement results were averaged over five rectangular samples. Six adhesive tapes with different adhesion strengths were procured from 3M, USA. According to the manufacturer specifications, the adhesion strength of the tapes are 440, 600, 820, 1750, 2100, and 3850 N/m reported as adhesion to steel. The tapes are made up of polyester backing material and a proprietary rubber adhesive layer. The tapes were cut into 7 cm pieces and were applied and pressed on each surface by hand ensuring that no large air pockets were trapped between the tape and the surfaces. One end of the tape (about 5 mm in length) was not pressed on the surface so that it could be attached to the grip (a single column system) of the tensile tester. The coatings were clamped to the base of the tester which was equipped with a horizontal translator in accordance with the ASTM F2255, F2256, F2258, and F2458 test standards. The tape experiments were repeated four to five times and at the end of each test the adhesive layer of the removed tapes were inspected via microscopy to see if any debris from the surface was transferred to the adhesive layer. Contact angle and hysteresis

measurements were made on these regions of coatings where the tapes were removed immediately after the peel experiments.

RESULTS AND DISCUSSION

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 antiwetting and self-cleaning.

As in previous work, superhydrophobicity can be achieved with a relatively low nanofiller concentration, after which antiwetting performance can degrade for higher weight ratios.[20] A similar approach is utilized in the current work to determine suitable component weight ratios for antiwetting performance as shown in Figure 1. It can be observed in Figure 1(a) that contact angle performance plateaus at ~ 10% 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. Figure 1(b) confirms that superhydrophobic performance is 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 antiwetting.

These wettability results were not very unexpected based on previous work where the mechanisms for a spray nanocomposite using a low boiling point solvent are explored in more detail.[24] Furthermore, adding components with a much higher surface energy to improve mechanical properties have also been shown in previous work to trivially affect antiwetting performance to a point.[15,25] However, this MCPU/PMC/organoclay blend has created extremely high substrate adhesion properties for a superhydrophobic coating and is explored in the following sections.

Adhesion

MCPU was introduced as the main component in the composite to improve adhesion strength. After determining the maximum MCPU concentration without compromising antiwetting 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 10% organoclay weight concentration, i.e., sufficient organoclay to reach the start of the contact angle plateau from Figure 1(a). The results are plotted in Figure 2. A negative slope can be observed in Figure 2(a) 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 antiwetting performance degradation. However, MCPU/PMC of 1.0 or higher (including pure MCPU) yielded a near zero slope in Figure 2(a), 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. Figure 2(b) confirms
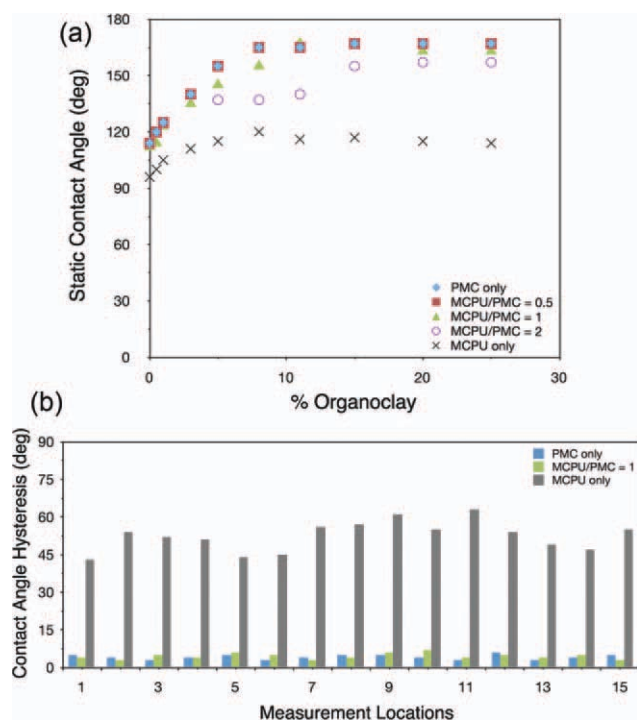

Figure 1 (a) Dependence of apparent static water contact angle on the organoclay concentration as well as MCPU/PMC weight ratio and, (b) dependence of contact angle hysteresis throughout the surface area for select MCPU/PMC weight ratios and an 10% organoclay weight concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
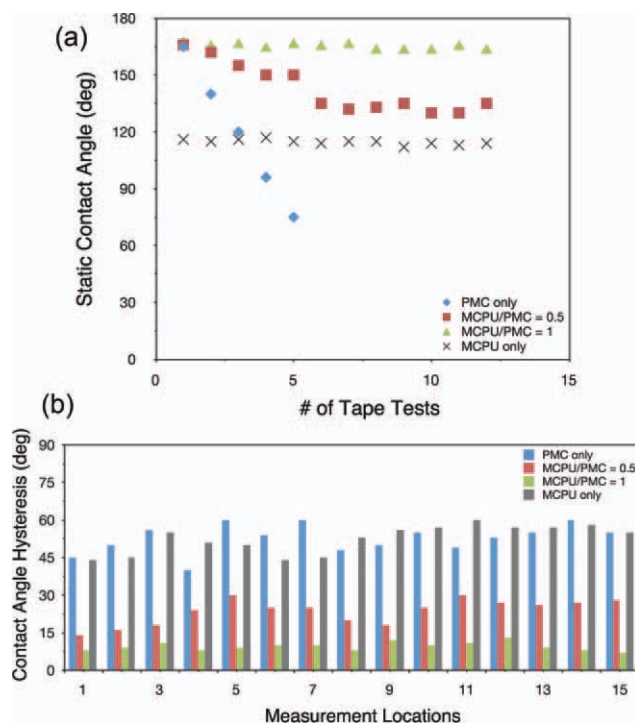
Figure 2 For a nanocomposite coating with 10% organo-clay weight concentration: dependence of (a) apparent static water contact angle over 12 1750 N/m tape tests and (b) contact angle hysteresis after the 12th tape test for select MCPU/PMC weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that superhydrophobic performance is 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 10% organoclay weight concentration was used throughout the remainder of the study for further analysis.

Improved adhesion strength is feasible as a result of the MCPU and PMC curing to form an interpenetrating polymer network (IPN) as shown schematically in Figure 3. Unlike in previous work[15] where the semi-interpenetrated polymer blends could potentially be separated from the constituent polymer network without breaking chemical bonds, here the network cannot be separated without breaking bonds. Additionally, the cross linking mechanism particular to MCPUs strongly depends on the availability of adsorbed moisture on surfaces on which they are applied.[2] Therefore, MCPUs form very strong adhesive forces on metals and ceramics which carry naturally adsorbed moisture on their surfaces. Natural metal oxide layers also exist on metal surfaces under ambient conditions. Thus, the presence of metal hydroxides on the aluminum surface initiates the cross linking mechanism, causing initiation sites for the cross linking reactions of MCPUs via strong hydrogen bonding.[26] Roughening the surfaces may

increase the adhesion strength since more surface area per unit volume becomes available for the initiation of cross linking. However, the aluminum substrates used in this study were not roughened a priori to maintain more consistent substrate surfaces for the varying coating formulations. Finally, because the IPN is entangled in such a way that the two polymer components are linked and cannot be pulled apart (but not chemically bonded), it also exhibited improved cohesion as discussed in the next section.

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 4. The nanocomposite surface morphology of Figure 4(a) 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 as shown in Figure 4(b,c). Furthermore, after tape testing, SEM imaging revealed that the surface structure remained essentially unchanged as shown in the representative images of Figure 5. Figure 5(a) was captured from a sample before tape testing and Figure 5(b) was captured from a sample after the 12th tape test for an adhesion strength of 3850 N/m. Although the images were not captured at the exact same location on the sample, it was clear from careful inspection throughout the surface area that there was no discernible average morphological difference
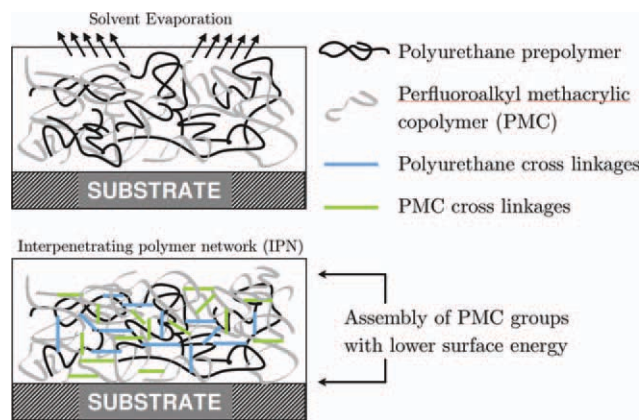

Figure 3 Schematic representation of PMC dispersion within the MCPU network with subsequent solvent evaporation from the coating and polymer crosslinking to form an IPN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
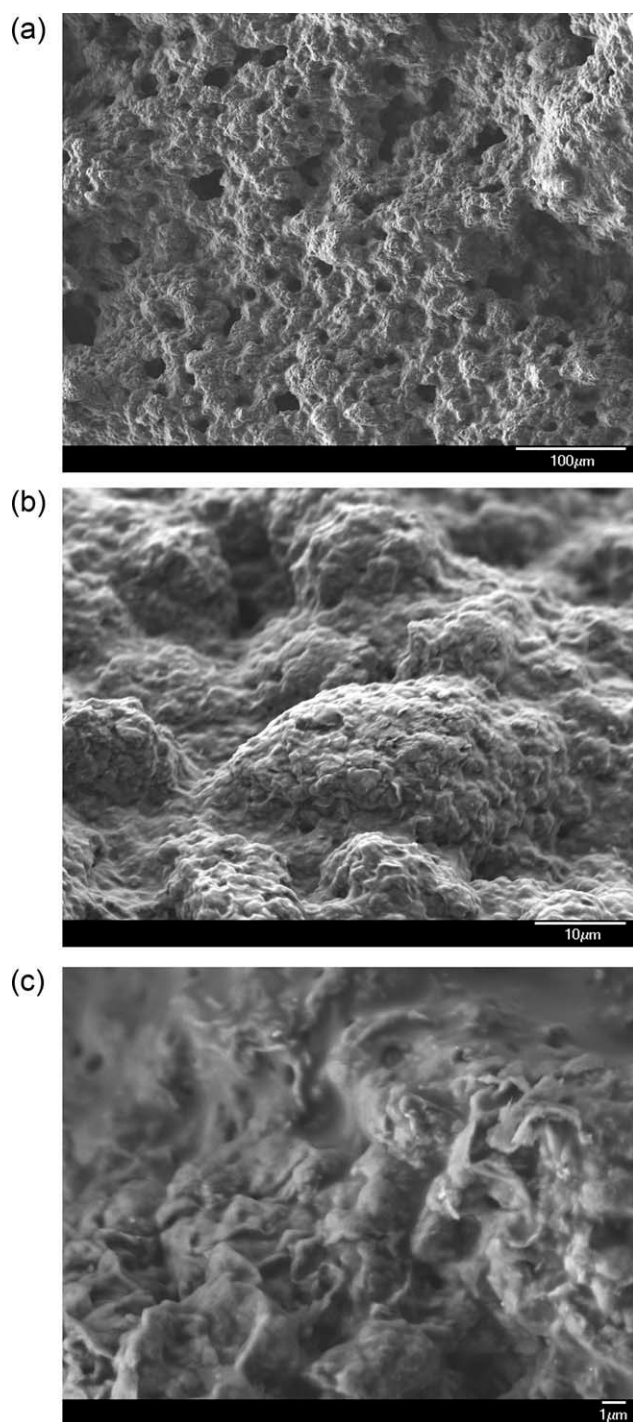
Figure 4 SEM images of (a) surface morphology of the MCPU/PMC/organoclay nanocomposite coating at ×230 magnification, (b) surface structure detail: appearance of self-similar inherently rough micro-bumps at ×1900 magnification, and (c) magnified image of the nanoscale roughness features on the micro-bumps at ×5000 magnification.

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, evidence of improved cohesion compared with previous work where material was removed during similar tape testing.[15]

Further investigation into the composition of the coating was conducted with backscattered electron analysis. Originating from the electron beam, backscattered electrons comprise high-energy electrons that are reflected (i.e., back-scattered) due to elastic scattering interactions with atoms in the sample. Figure 6(a) shows an SEM image formed from backscattered electron detection of the nanocomposite coating with 10% organoclay weight concentration and a 1 : 1 weight ratio of MCPU and PMC. Since heavy elements with a high atomic number backscatter electrons more strongly than light elements with a low atomic number, and thus appear brighter in the image, backscattered electrons can be used to detect contrast between areas with different chemical compositions. It is clear in the figure that the relatively low contrast image with no significant bright areas indicates a coating with a relatively uniform
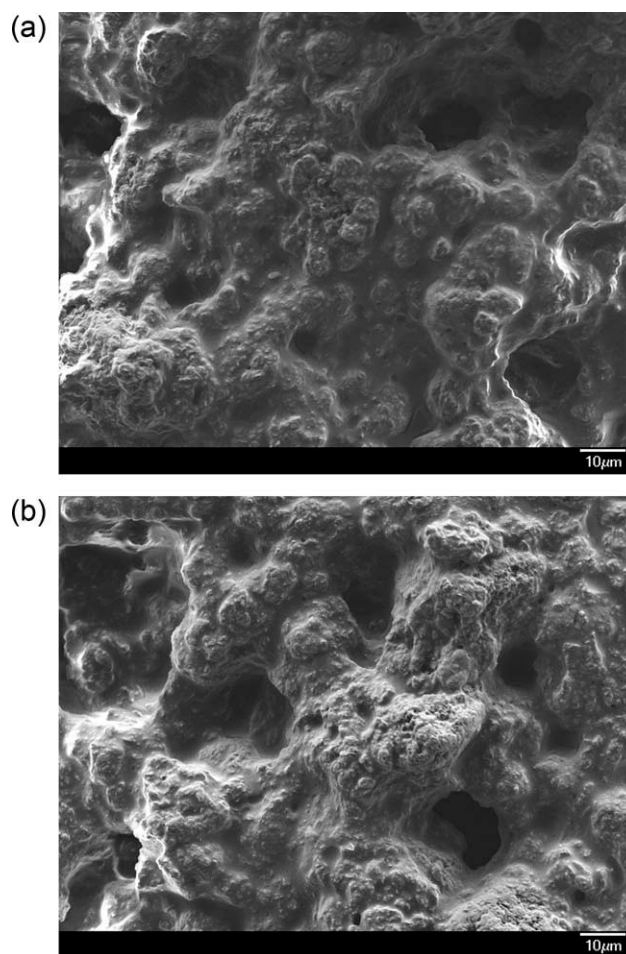

Figure 5 Representative SEM images at ×950 magnification of (a) nanocomposite coating before tape testing and (b) the same nanocomposite coating after 12 tape tests for an adhesion strength of 3850 N/m.
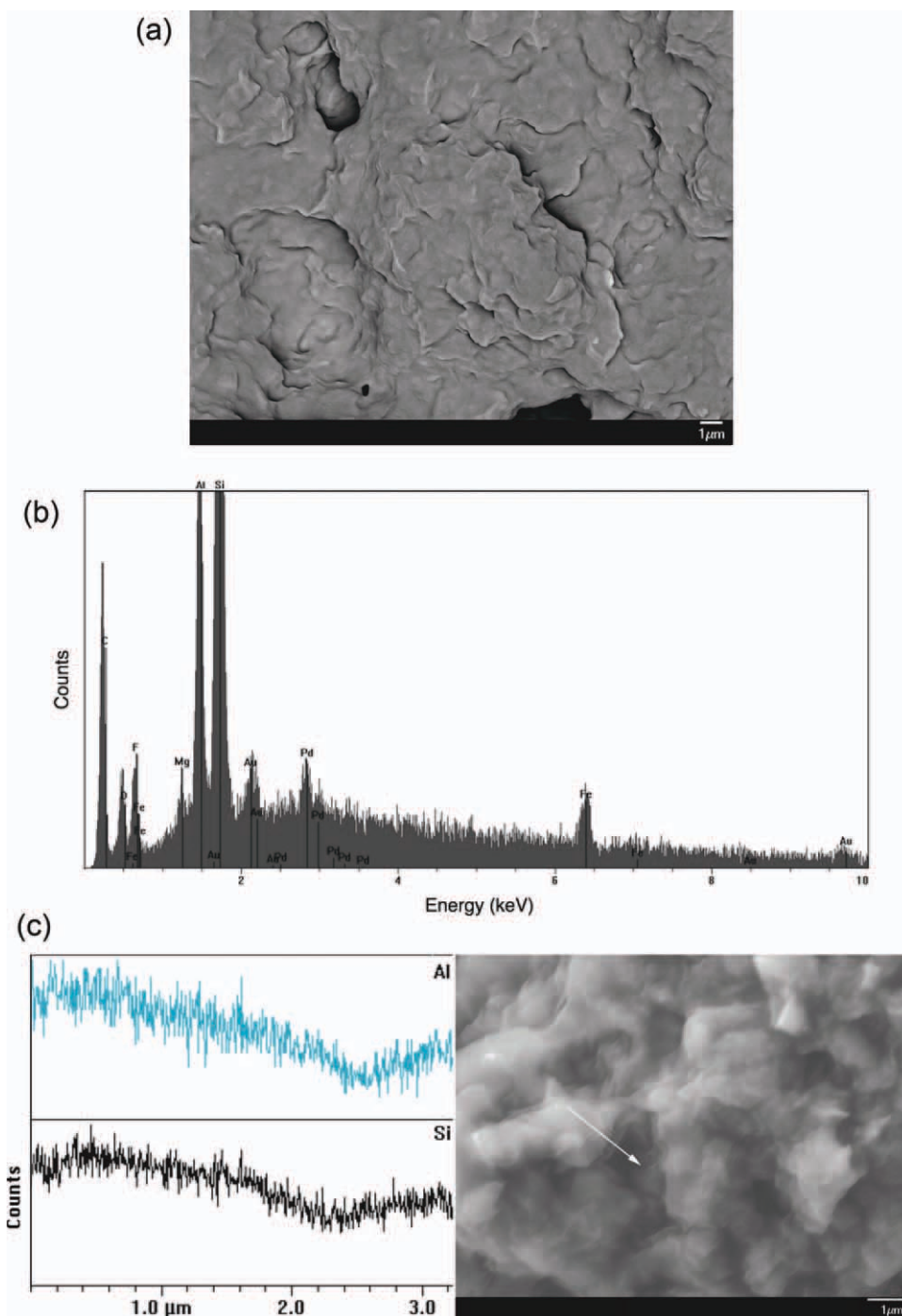
Figure 6 (a) SEM image detecting backscattered electrons of the MCPU/PMC/organoclay nanocomposite coating to show chemical uniformity, (b) energy dispersive spectroscopy plot for the coating, and (c) energy dispersive spectroscopy line scan chemically identifying an organoclay particle at ×9500 magnification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chemical composition. The chemical composition is confirmed with energy dispersive spectroscopy analysis as shown in Figure 6(b). Fluorine, carbon and oxygen from the PMC and MCPU; aluminum, silicon, iron, and magnesium from the organoclay; as well as gold and palladium from the sputter coating (for conduction in the SEM) are all present in the

chemical composition as expected. Figure 6(c) shows a representative energy dispersive spectroscopy line scan chemically identifying an organoclay particle. By detecting aluminum and silicon linearly along 500 points with a scan length of 3.24 μm (6.5 nm between points) for 1000 sec, the line scan distinctly shows presence of these elements on the particle
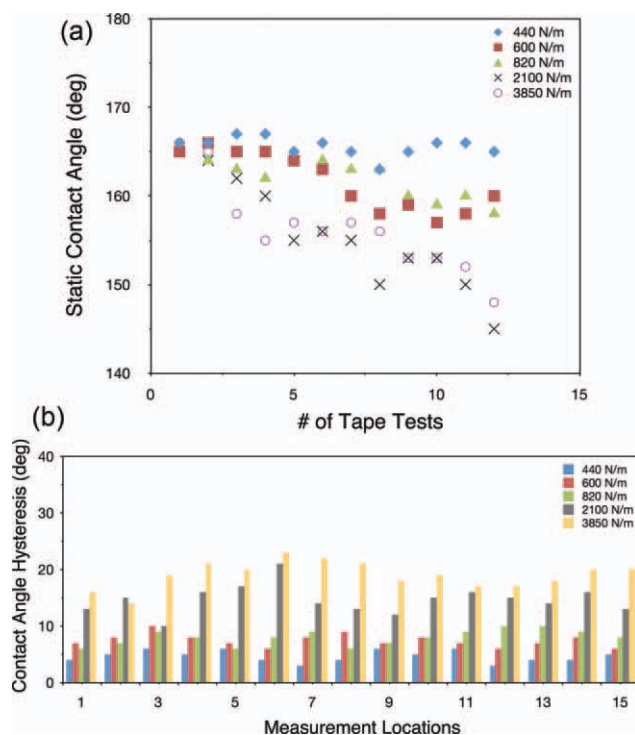
Figure 7 For a nanocomposite coating with 10% organoclay weight concentration and 1 : 1 MCPU/PMC weight ratio: dependence of (a) apparent static water contact angle over 12 tape tests for select adhesion strengths and (b) contact angle hysteresis after the 12th tape test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and then falling off at the edge of the particle, evidence that the organoclay particles are indeed the cause of the micron and submicron surface structure.

High adhesion testing

Higher adhesion strength tape tests up to 3850 N/m were also conducted as shown in Figure 7. A superhydrophobic state was undoubtedly maintained up to 820 N/m over the span of the experiment (Fig. 7) as well as up to 1750 N/m (Fig. 2); 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 Figure 7(a). After the 12th 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 antiwetting 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 probable that the surface chemistry was very slightly altered by the stronger tapes over repeated contact.

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 antiwetting and self-cleaning characteristics. A nanocomposite formulation of 10% 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 antiwetting performance. Higher weight ratios of MCPU were observed to reduce antiwetting performance before and after tape testing, where as higher weight ratios of PMC were observed to reduce antiwetting 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 an order of magnitude higher than previous work,[15] and 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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