Fabrication and Characterization of Superhydrophobic Plasticized Polyvinyl Chloride Filled with Stearic Acid Coated Calcium Carbonate

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Abstract. Superhydrophobic surfaces are favourable for coating applications to protect various substrates from aggressive environments. In this work, the superhydrophobic coating materials was successfully prepared from plasticized polyvinyl chloride (pPVC) filled with stearic acid coated calcium carbonate particles (CaCO₃) by a simple approach. The thermal, surface properties and wettability of the materials were studied. Combination of microstructured surface roughness and low surface energy increases the superhydrophobicity of the pPVC surfaces. The results indicated that the increase in c-GCC fillers magnified the degree of roughness with the highest contact angle achieved at 167 ± 3°.

1. Introduction

The discovery of self-cleaning effect of the lotus leaves made by Barthlott and Neinhuis have inspired academics and industrial researchers in developing superhydrophobic surfaces[1]. The astonishing property of the lotus leaves was reported to be a result of the hierarchical surface topography composed of micro- and nano-structures with optimized geometry and the unique chemical composition of the epicuticular waxes[2]. A surface is said to be superhydrophobic when the water beads up with a contact angle of greater than 150°[3]. So far, there has been numerous attempts made to mimic the lotus leaf’s multiscale topographic surfaces to achieve superhydrophobicity. However, multistep fabrication process, complicated surface treatments and the use of expensive materials in the formulation have limits their applications for a large scale production[4]. Furthermore, most of the fabricated superhydrophobic surfaces appeared to have low mechanical durability as they can be easily damaged by routine use, resulting in a decline of their superhydrophobicity[5]. The micro- and nano-particles filling was reported to be a promising method that would enhance their mechanical stability and durability[5].

Polyvinyl chloride (PVC), an intrinsically hydrophobic material, is one of the most widely used thermoplastics materials in various applications. The pPVC for instance, can be produced in the form of a suspension, known as plastisols, suitable for the production of foams, films, sheets, rotational casting and coatings. However, the addition of plasticizer in pPVC compound could actually reduce the water
contact angle below than 90° hence decreasing its hydrophobicity\[^6\]. The increase in hydrophobicity of pPVC compounds would therefore extend the long-term protection against corrosion, mechanical wear and fouling resistant \[^5\]. In this research, we aim to fabricate the superhydrophobic pPVC by inexpensive ground calcium carbonate (GCC) particles filling. The presence of multiscale coated ground calcium carbonate (c-GCC) fillers would magnified the degree of surface roughness with the increase in water contact angle. The effects of coated c-GCC fillers on the thermal and surface properties of pPVC were evaluated. The surface morphology, topography and wettability of the samples were compared using field emission scanning electron microscopy (FESEM), atomic force Microscopy (AFM), and water contact angle measurement.

2. Experimental study

2.1 Materials

Emulsion grade PVC resin, EH250, with a K-value of 73, was kindly supplied by Kaneka Paste Polymers Sdn. Bhd. The c-GCC (C18H36O2) having an average particle size, \(d_{50}\) of 2.81 ± 0.3 µm was supplied by Omya Malaysia Sdn. Bhd. Diisononyl phthalate (DINP) plasticizer with a molecular weight of 418.62 g/mol and zinc oxide (ZnO) stabilizer were both purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

2.2 Preparation of pPVC coating materials

The pPVC compounds as listed in Table 1, were pre-mixed using IKA mechanical stirrer with controlled stirring speed and a total mixing time of 15 minutes. Mixing was consequently completed using a high-shear homogenizer (Wiggen Hauser D-500) with a 10 000 rpm speed for 5 minutes. The pastes were aged for 2 weeks in a closed chamber at room temperature and were re-mixed for 5 minutes to reduce sedimentation prior to molding. The pastes were subsequently deaerated and poured into a metal mold of 1 mm thick, and heated in the oven at 190 °C for 12 minutes. All samples were stored for 48 hours to allow complete reformation of crystalline crosslinks in the PVC resin and were further rubbed with 500 grit sandpaper for 20 minutes, for surface analysis.

Table 1. Compositions of pPVC based coating materials.

| Sample Codes | C0 | C1 | C2 | C3 | C4 | C5 |
|--------------|----|----|----|----|----|----|
| Components (phr) | PVC | DINP | ZnO | c-GCC |
|                | 100 | 100 | 100 | 100 | 100 | 100 |
|                | 85  | 85  | 85  | 85  | 85  | 85  |
|                | 2   | 2   | 2   | 2   | 2   | 2   |
|                | -   | 10  | 30  | 50  | 70  | 100 |

2.3 Characterization

The effect c-GCC fillers on the thermal degradation of pPVC based coatings was quantified using a Mettler Toledo Thermogravimetric Analyzer (TGA) in a nitrogen atmosphere. The heating rate was set at 10 °C min\(^{-1}\) with heating range of between 30 °C and 900 °C. The surface morphological analysis of the samples that was sputter-coated with gold in vacuum conditions, conducted in top-view using the Field Emission Scanning Electron Microscope (FESEM, model Zeiss Supra 35VP) at an accelerating voltage of 10kV. Wettability of the samples were determined according to ASTM D7334 using the
Attension Theta Optical Tensiometer by KSV instruments. The measurement was conducted at an ambient temperature with approximately 5 µl of water droplet. The contact angles were obtained as an average values recorded after 10 s and the contact angle for each specimen was calculated from the average of five drops. The three-dimensional (3D) topography and surface roughness of the samples’ surface were evaluated using the tapping mode of the SPA300HV Nanonavi Atomic Force Microscope (AFM). A minimum of five different locations were scanned for each sample, and the average roughness (Ra) value was calculated.

3. Results and Discussion

3.1 Thermal stability

PVC easily degraded at elevated processing temperature, giving off hydrochloric acid (HCl) from the polymer backbone that successively accelerates the degradation process[7]. It was proven that the addition of inorganic fillers such as CaCO₃ increases the thermal stability of PVC by scavenging the released HCl gas and further avoid its self-accelerating effect[8]. The thermal degradation of PVC based coating materials occurs through two main stages, as shown in Figure 1. The first stage (seen at 200-300 °C) can be linked to weight loss, which can be caused from the generation of HCl gas from the thermal decomposition of PVC, or from the release of carbon dioxide (CO₂) and water (H₂O) when CaCO₃ reacted with HCl, which is known as dehydrochlorination.

![Figure 1. TGA curves of pPVC based coating materials filled with various filler loadings.](image)

Weight loss that occurs at higher than 400 °C during the second stage of degradation can be attributed to the formation of H₂O and CO₂ when the dehydrochlorinated residues were thermally decomposed. Thermal degradation had significantly shifted to a higher temperature from 190 °C, up to more than 200 °C with increasing CaCO₃ filler loadings. The presence of higher GCC filler loadings can absorb more HCl gas compared to unfilled C0 samples. CaCO₃ micro particles also inhibited the fusion and entanglement of PVC molecules in the polymer compounds[9]. The increased in thermal stability of the coatings also evidence by the increased in char formation at 900 °C with increasing filler loadings. This condition suggests that only inorganic fillers were left in the samples at that temperature.
3.2 Observation of surface morphology

The change in morphology of the prepared coatings due to the increase in filler loadings is depicted in Figure 2. The characterization were made only on un-abraded samples to observe filler distribution throughout the samples’ surfaces. Unfilled pPVC coating labelled as C0 sample exhibit smooth surfaces. It is clearly seen that c-GCC fillers progressively increases the roughness of pPVC based coatings. The coated fillers are also evenly distributed in the pPVC matrix without any agglomeration in all filled samples. It was reported that pPVC is slightly hydrophilic\cite{10} and the introduction of surface roughness is therefore beneficial to enhance its hydrophobicity as depicted by Wenzel’s law\cite{3}. Addition of less than 50 phr c-GCC fillers (C1 – C3 samples) was unsatisfactory to increase the surface roughness of the coatings. Maximizing the filler loading up to 100 phr shows a significant modifications in the surface properties.

![Figure 2](image)

**Figure 2.** FESEM micrograph of un-abraded pPVC coating surfaces at 500× magnification.

3.3 Wettability

Hydrophobic property of the prepared coatings were studied by measuring water contact angles on both un-abraded and abraded surfaces. Wettability of the pPVC coating materials prepared in this research are tabulated in Figure 3. The water droplet that was placed on un-abraded, unfilled pPVC (C0) sample have shown to be partially wets the surface and shows contact angle of 77 ± 2°. The increase in filler loadings which slightly introduced roughness to the surfaces have steadily increased the hydrophobicity of up to only 106 ± 2°.

Although the use of c-GCC particles reduces the surface energy of the materials, it is however insufficient to increase wettability of the coatings. Hence, roughness of the surfaces were further enhanced with the help of sandpaper abrasion. For that reason, the contact angle of unfilled sample dramatically increases to 120 ± 5°. Superhydrophobic coating materials having water contact angle greater that 150° was achieved with the presence of 50 phr c-GCC fillers. The effect of abrasion along with the presence of high filler loadings further increases contact angle up to a maximum value of 167 ± 3° for C5 sample.
Figure 3. Water contact angle of un-abraded and abraded coating surface samples as a function of filler loading.

3.4 Surface roughness

The effect of surface roughness to wettability of the prepared coating materials were further witnessed using AFM with 100 × 100 µm². The 3D surface topography was presented in Figure 4 and the Rₐ was further charted in Figure 5. Abraded filled sample shows greater surface roughness compared to un-abraded coating surfaces as previously observed with FESEM.

As expected, the Rₐ of the surface was increased when the filler loadings were increased. There was also a remarkable increase in Rₐ due to the effect of sandpaper abrasion. Coating materials filled with 100 phr c-GCC fillers had resulted in the highest Rₐ in both un-abraded and abraded samples as they
introduced higher micro scale roughness to the surfaces. Accordingly the water droplet pins on roughness and the valleys are not penetrated due to the presence of air pockets entrapped between the roughness’s\textsuperscript{[11]}. The entrapped air is necessary to intensify the hydrophobicity of the solid surfaces\textsuperscript{[12]}.

![Figure 5. \(R_a\) of un-abraded and abraded coating surface samples as a function of filler loading.](image)

4. Conclusion
In this study, we have fabricated superhydrophobic pPVC based coating materials from a versatile and simple method. The addition of c-GCC fillers in the prepared coating materials have steadily increased the thermal stability. The increase in fillers along with the effect of surface abrasion increases water CA to 167 ± 3°. The increase in filler loading had introduced higher surface roughness, as presented by AFM, with the introduction of higher amount of air pockets, which had decreased the adhesion of the water droplets to the surface.

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