The Effects of Biopolymers Composite Based Waste Cooking Oil and Titanium Dioxide Fillers as Superhydrophobic Coatings.

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Abstract. This project presents the effect of biopolymer composite surface coating on TiO2 fillers by analysing the static water contact angle, SEM micrographs, porosity, density and refractive index of biopolymer doped with different loading of TiO2. The different ratio loading of 0.5, 1.0, 1.5, 2.0 and 2.5 (wt/wt%) TiO2 can be used to improve the material properties in practical use for outdoor application especially to enhance the stability of surface coating. It is found that the smooth surfaces with a low ratio loading of TiO2 fillers on biopolymer composite surface coating increases the static water contact angle up to 162.29°. It is interpreted with respect to the nano-features existing on the surface of the water repellent creates a thin superhydrophobic layer. The relationship between porosity and density is indirectly proportional where the higher the loading of TiO2 filler produce the lower porosity up to 0.86% of the surface coating. The movement from shorter to longer of wavelength was observed before and after exposure indicates that there are optimization of absorption of UV-B radiation as the amount of delocalisation.

1. Introduction
The growth in various types of industries and population has resulted in enormous increase in production of various types of waste material all over the world [1]. The creation and disposal of non-decaying of some of these waste materials such as waste cooking oil has been posing difficult problems in developed countries. Used of industrial waste has been widely studied for seeking suitability utilized in surfaces applications [2]. The concept of sustainable development, currently a very hot issue requires that the society as a whole becomes aware of necessity to make the most off all existing resources, trying to minimize creation of residues [3]. Recently, the use of renewable resources has concerned the consideration of researchers due to their potential to substitute petrochemical products [4]. By renewable resources is meant agriculture products mainly from five principal crops such as soybean, palm oil, rapeseed, sunflower and coconut oil can be used to produce polyols from composition of fatty acid esters.
or fatty acids as tabulated in Table 1 [5]. These natural products are already processed by the chemical industry and used in many fields of application especially in the biopolymers production [6].

Some scientists tried to synthesize the epoxy from palm oil but their synthesize resin showed poorer curing properties in radiation curable coating applications due to limited unsaturated in the fatty acid chain of palm oil molecules [7]. Coating protects the underlying membrane from exposure to ultraviolet (UV) light and heat also slowing the concrete aging process. Highly reflective white coatings also significantly reduce the membrane temperature which leads to improve long-term performance of the system. This lower temperatures also reduces the building’s heat load resulting in lower cooling costs for the building [8]. It has been possible to assess the feasibility of using waste cooking oil to produce biopolymer composites and titanium dioxide (TiO$_2$) fillers as superhydrophobic coating. The use of TiO$_2$ in this coating due to TiO$_2$ has nanoscale materials, high refractive index and effective opacifier properties. This alternative is to reduce the pollution and disposal problem. Furthermore, UV illumination of TiO2 leads to the formation of powerful agents with the ability to oxidize and decompose many types of bacteria, organic and inorganic materials.

| Oils/ Fats   | Saturated fatty acids (SFA) | Mono unsaturated fatty acids (MUFA) | Linoleic Acid | Alpha Linoleic Acid | Omega-6: Omega-3 ratio |
|-------------|-----------------------------|------------------------------------|--------------|---------------------|-----------------------|
| Soya bean oil | 15                          | 27                                 | 53           | 5                   | 10.6:1                |
| Olive Oil   | 13                          | 76                                 | 10           | <0.5                | 20:1                  |
| Palm Oil    | 45                          | 44                                 | 10           | <0.5                | 20:1                  |
| Sunflower Oil | 13                         | 27                                 | 60           | <0.5                | 120:1                 |
| Canola Oil  | 4                           | 62                                 | 22           | 10                  | 2.2:1                 |
| Rice bran Oil | 22                         | 41                                 | 35           | 1.5                 | 23:1                  |

Currently, bio-based polyols and polyurethanes still have higher costs than petroleum-based. However, the continuing advances in technologies and the inevitable depletion of the world’s petroleum resources, the future of bio-based polyols and polyurethanes looks very promising and bright.

2. Methodology

2.1 Preparation of monomer
The waste cooking oil was chemically manipulated at laboratory scale using less than 1 liter of waste cooking oil as claimed in Intellectual Property Protection PI 201000633. The monomer based on waste cooking oil and its composite material was prepared by mixing the crosslinking agent. The monomer material comprises of waste cooking oil added with water, orthophosphoric acid, diisocyanate, hydrogen peroxide and TiO$_2$ with the ratio of 0.5 – 2.5 weight by weight. The preparation of waste cooking oil of hydroxylated monomer was divided by two stages, beginning with the preparation of catalyst to generate the epoxides from the unsaturated fatty compounds, while the second stage composed of the acid-catalysed ring opening of the epoxides to form polyols.

2.2 Preparation of bio-polymer
The monomer based on waste cooking oil and its composite material was prepared by mixing the crosslinking agent and different percentages of superhydrophobic powder which were 0.5, 1.0, 1.5, 2.0 and 2.5 % equivalent to weight of monomer. The hand lay up technique was used to coat the concrete surfaces with waste cooking oil bio-polymer doped with superhydrophobicity powder. A natural bristle brush was used to apply coating on concrete surfaces. The first coat was act as the sealer and apply liberally with a brush and any bubbles were wiped off. After the first coat was dried, the superhydrophobicity paint was applied smoothly on the surfaces with a foam brush with a suitable
thickness 0.30 mm is shown in Fig. 1 [9]. All the samples was tested to determine the effects of biopolymer composite based waste cooking oil and titanium dioxide fillers for water droplet test, porosity-density test and refractive index.

Figure 1. Samples of concrete substrate; (a) A: Uncoated surface; (b) B: Surface coated with bio-polymer; (c) C: Surface coated with bio-polymer doped with 0.5% TiO$_2$; (d) D: Surface coated with bio-polymer doped with 1.0% TiO$_2$; (e) E: Surface coated with bio-polymer doped with 1.5% TiO$_2$; (f) F: Surface coated with bio-polymer doped with 2.0% TiO$_2$; (g) G: Surface coated with bio-polymer doped with 2.5% TiO$_2$

3. Results and discussion

3.1 Water droplet test

Superhydrophobic surfaces is a surfaces processing high advancing water contact angle (WCA) and low water contact angle hysteresis has recently attracted significant attention because their unique water-repellent and self-cleaning properties and their potential for practical applications ranging from biotechnology to self-cleaning commodity materials. Water droplet test was measured using Goniometer and the water droplet image was captured by Canon Digital SLR Camera, model no: EOS Rebel XT/350.

Figure 2. SEM micrograph and water droplet test for coated with different percentages of TiO$_2$
As a result, biopolymer from waste cooking oil doped with TiO$_2$ as surface coating were applied on concrete surfaces to create superhydrophobic coatings. Seven types of surface coating was tested by water droplet test to measure the static water contact angle by Canon Digital SLR Camera – EOS Rebel XT/350D and Goniometer. Contact angle measurements are interpreted with respect to the morphology of the porous sustainable polymer composites structure of nano- and micro-features by SEM. According to the Fig.2 and Fig.3 shows the result of static water contact angle for polymer composites with different percentage of TiO$_2$. The higher water contact angle measurements up to 150° were interpreted with respect to nano- and micro- features existing on the surface of the water repellent TiO$_2$ filled polymer composites coating [10]. The smooth coated surfaces of polymer composites with TiO$_2$ as fillers shows the systematic increasing static water contact angle (θst) for uncoated, polymer composites with different percentages of TiO$_2$ which is 0.5, 1.0, 1.5, 2.0 and 2.5 % shows 12.23º, 77.27º, 120.55º, 125.62º, 141.78º, 158.06º and 162.29º, respectively. It is also demonstrated in Figure 6. From static water contact angle measurement revealed that polymer composites with different percentages of TiO$_2$ fillers by only 2.0% loading ratio shows the ability to form superhydrophobicity property.

### 3.2 Porosity-density test

The porosity and density test was measured using Mettler Toledo XS64 according to ASTM D7063-05 standard test method. The average porosity percentage result was calculated the percentage porosity by coating with biopolymer gives higher porosity with 1.49 %, followed by loading ratio of 0.5 %, 1.0 %, 1.5 %, 2.0 % and 2.5 % TiO$_2$ with 1.24 %, 1.01 %, 0.92 %, 0.91 %, 0.86 % respectively. The commercial standard surface coated with biopolymer gives higher porosity than the others types of coating. From the results, it can be concluded that loading higher ratio TiO$_2$ in concrete surface, the lower the porosity percentage in the concrete were evidence. This characteristic is important as most masonry substrates contain moisture at the time the coating is applied. Water vapor permeability is also a factor subsequent to application as it is virtually impossible to completely prevent access of water to masonry walls [12]. Therefore, the porosity of the interface between coated concrete by TiO$_2$ must be lowest than that uncoated surfaces. Average density result was summarized the density for coated with biopolymer doped with 2.5 % TiO$_2$ shows higher density with 1.426 g/cm$^3$, followed by 2.0 %, 1.5 %, 1.0 %, 0.5 % TiO$_2$ and biopolymer with 1.396 g/cm$^3$, 1.312 g/cm$^3$, 1.281 g/cm$^3$, 1.238 g/cm$^3$, 1.162 g/cm$^3$ respectively. However, coated standard lightweight roof tile density is higher when compared with coated surfaces. In this study, a relationship was determined between porosity and density of coated with different percentages of TiO$_2$ and biopolymer. Based on Fig.4, a systematic decrement in density and porosity percentage for coated with TiO$_2$ and biopolymer for all specimens when compared to uncoated and coated commercial standard.
3.3 Refractive Index

The refractive index was determined by using Ultra-Violet/Visible Spectroscopy model HACH DR 5000 according to ASTM E275-01. Based on Fig.5, it shows that as percentages TiO\(_2\) increasing, a systematic increment of refractive index responses were obtained. Refractive index for unexposed polymeric composites with 0.5%, 1.0%, 1.5%, 2.0% and 2.5% TiO\(_2\) is a systematic increment started with refractive index 2.112, 2.134, 2.155, 2.181, 2.209 and 2.329, respectively. Upon exposure, the refractive index were decrease with 0.5%, 1.0%, 1.5%, 2.0% and 2.5% TiO\(_2\) with refractive index 1.9197, 1.944, 1.9581, 1.974, 1.999 and 2.0461, respectively. The refractive index of polymer composites with TiO\(_2\) coatings is generally depending upon the ratio of TiO\(_2\) coating layer.

![Figure 5 Refractive index before and after sunlight exposure for polymer composites with different percentages of TiO\(_2\) (alt text)]
the UV-rays through its high refractive index. Although the erythermal hazard of long-wavelength UV is lower than of short-wavelength UV, the former penetrates deeper into the surface and has an accumulating effect on the surface. Thus, TiO$_2$ is used as a solar UV blocker; certain techniques should be adopted to generate better UV protection [11].

4. Conclusion
Different ratio loading of TiO$_2$ can be used to improve the material properties in practical use for outdoor application especially to enhance the stability of surface coating. The harsh equatorial environmental exposure test at certain period of time was revealed that biopolymer from renewable resources doped with only 2.5% TiO$_2$ shows no evidence of color or surface property changes such as sunburn, crack, dirt, oily deposition and surface roughness. The conditions of the superhydrophobic surfaces turns into a higher water contact angle up to 150° especially after UV irradiation show the great potential of the backside exposure for the formulation sustainable polymeric composites coating of such structures with smooth thin film keeps itself free of dirt and bacteria. The effect of biopolymer composite surface coating on TiO$_2$ fillers was studied by analyzing static WCA and SEM images. This study demonstrates that a water droplet test by static WCA on smooth surfaces was created in the range more than 120°. It is found that at low ratio loading of TiO$_2$ fillers on biopolymer composite surface coating increases the static WCA. The reason for the observed superhydrophobicity is that the present of nanoscale roughness of the coated surfaces started with only 2.0% ratio loading of TiO$_2$ in the polymerization mixture.

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