CHARACTERIZATION OF HYDROPHOBIC UV-CURABLE ACRYLATED COATING FROM PALM OIL BASED URETHANE ACRYLATE (POBUA) FOR WOOD COATING APPLICATION

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ABSTRACT

Acrylated hydrophobic coating was prepared from palm oil-based urethane acrylate (POBUA) by using the UV-curing technique. The purpose of the study was to investigate wetting properties and the application of this UV-curable palm oil resins for wood coating. Five different sample formulations were prepared that used silica as the roughness agent, PFOA as the modifier and IC-500 as the photoinitiator. Surface contact angle and IR spectroscopy were characterized for each sample. IR spectroscopy confirmed the presence of POBUA resins in all samples. Nine hydrophobic coatings are obtained, and the highest water contact angle value acquired is 116.29° which can be considered as a good hydrophobicity value for a wood coating application.

ABSTRAK

Salutan hidrofobik berakrilat telah disediakan daripada akrilat uretana berasaskan minyak sawit (POBUA) dengan menggunakan teknik pematangan UV. Tujuan kajian ini ialah untuk mengkaji sifat kebasahan dan aplikasinya terhadap resin minyak sawit dapat matang UV untuk salutan perkayuan. Lima sampel formulasi telah disediakan menggunakan silika sebagai agen pengasaran, PFOA sebagai bahan penyesuai dan IC-500 sebagai pemulafoto. Sudut sentuh permukaan dan spektroskopi IR dicirikan untuk setiap sampel. Spektroskopi IR mengesahkan kehadiran resin POBUA dalam semua sampel. Sembilan salutan hidrofobik didapati dan nilai sudut sentuh tertinggi yang diperoleh ialah 116.29° yang boleh disimpulkan sebagai nilai hidrofobia yang tinggi bagi aplikasi salutan perkayuan.

Keywords: acrylated hydrophobic coating, pobua, palm oil resin, uv-curable palm oil resin

INTRODUCTION

For the last few decades, bio-based polymers and resins have seen growing demands in industrial applications because of their potential reduced cost and environmental effect. When compared to traditional petroleum-based polymers, such polymers have numerous advantages and massive benefits towards green environment. Presently, Malaysia is known as the second largest producer and exporter of palm oil in the world after Indonesia. Global palm oil production increases tremendously in the past decades, almost doubling every 10 years (Khatun et al., 2017). Due to palm oil industry developing rapidly in Malaysia, it is taken as the subject for research and invention process.

Palm oil and its derivatives such as palm olein and stearin, have unsaturation levels that are half or less than half of that of soybean oil. As a result, it has never been considered as a suitable raw material for the production of resins. Nevertheless, it was interested in knowing the application of palm oil or its derivatives compared to linseed oil, soybean oil, and other oils. Materials from the palm oil products can be modified into radiation curable oligomers or resins, namely acrylated oils. Ibrahim et al. reported that the epoxidation of palm oil products produced compounds such as epoxidized palm oil products (EPOP) that can be used as a plasticizer and plastic stabilizer (Ibrahim et al., 1987). Acrylated palm oil is produced using the acrylation method, in which acrylic acid is inserted into the oxirane group of the EPOP. This method is similar to that used to produce epoxy acrylate (Husin et al., 1990). Palm oil-based urethane acrylate (POBUA) can then be synthesized from the epoxidized palm olein acrylate (EPOLA) by isocyanation process. The potential application of POBUA is as a UV-curable palm oil resins for coating. UV–radiation curable coating is an environmentally friendly method that avoids or minimizes the emission of volatile organic compounds and harmful air pollutants. It is a fast-drying process that turns a reactive liquid chemical system into a non-tacky solid crosslinked at room temperature by using UV light to produce polymerization (Mehnert et al., 1998). This form of coating requires three components which are polymerizable resin, a photoinitiator, and a UV radiation source (Rosli et al., 2003). Since most radiation curable resins on the market today are derived from non-renewable, petroleum-based synthetic resins, there is an urgent need for developing new radiation curable resins based on renewable resources for wood coating, printing ink, and pressure sensitive adhesive applications.

In this study, the characteristics and wetting properties of UV-curable palm oil-based urethane acrylate (POBUA) as a wood coating were investigated and discussed. The application of palm oil coatings in the current market is also evaluated. The goal for starting this study is to gain a better understanding of the explored system, which will be valuable for researchers working on developing this coating for technologically promising applications requiring hydrophobic property.

MATERIALS AND METHOD

Materials

The chemicals used in this study were palm oil-based urethane acrylate, POBUA (Nuklear Malaysia), 1H, 1H, 2H, 2H-Perfluorodecyl acrylate, PFOA namely, silica, (Sigma), Irgacure-500, IC-500 and acetone. All chemicals were used as received.

Preparation of resins formulations

The formulations of the resins involve four main materials which are POBUA as the oligomer, PFOA as the modifier or monomer, silica as the roughness agent and IC-500 as the photoinitiator. All formulations have a fixed weight of POBUA which is 15g and photoinitiator was 5% of the total weight of POBUA. Meanwhile the compositions of PFOA and silica were varied as shown in Table 1. The materials are mixed together by stirring the mixture at 200-250 revolutions per minute (rpm) using the mechanical stirrer until all the mixture are fully miscible. Then, the resins are left overnight at room temperature.

Table 1: Composition of SiO2 and PFOA for the preparation of UV-curable film at fixed dose of POBUA and IC-184

Sample	POBUA content (g)	PFOA content %	Silica content (%)	IC-500 content (%)
A	15	-	-	5
B	15	0.25	-	5
C	15	1.0	-	5
D	15	1.0	0.1	5
E	15	1.0	0.5	5

Coating and UV-curing process

Figure 1 shows the coating and UV-curing process of the sample. Acetone was used to clean the substrate and bar coater before the coating process. All formulation samples were coated on a 7.4 x 6.4 cm wood substrate using a bar coater into a 250 µm thickness of film. The films were then exposed to UV radiation using IST UV radiation machine. The UV conveyor's speed was set at 10m/min for each pass and the current was at 7.5 Ampere. Each sample was passed for 2 times to be cured and the characteristics for each cured sample were analyzed.

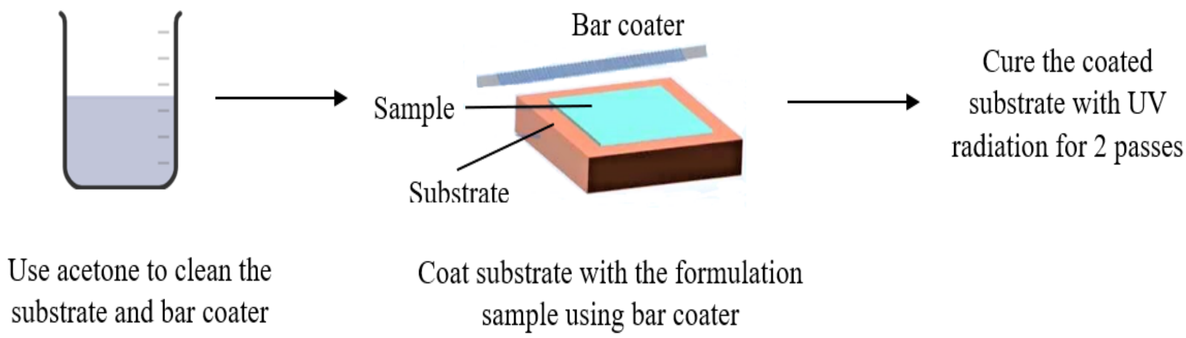

Figure 1: Coating and UV-curing of the sample

Characterization

The properties of all cured films were studied from several tests. The thermogravimetric analysis (TGA) records the weight fluctuation, which the weight loss during heating as a function of temperature. Optical contact angle tests were performed on coating samples via Attention Theta Lite Optical Tensiometer (Biolin Scientific, TL 100) by sessile drop method. Fourier transform infrared (FTIR) spectra to determine the chemical bonds and molecular structure of cured samples. Meanwhile the gel contents test was done using Soxhlet method with acetone as the solvent. In each case a small mesh packet containing the sample was suspended vertically in the Soxhlet extractor such that it is lower than the siphon arm level. The solvent is then boiled for 20 hours. The films then were dried in a vacuum oven at 60°C and finally reweighed the films. The gel content was calculated as follow:

$$\text{Gel content, \%} = \frac{\text{Mass of sample after extraction, g}}{\text{Mass of sample before extraction, g}} \times 100$$

RESULTS AND DISCUSSION

Water Contact Angle Studies

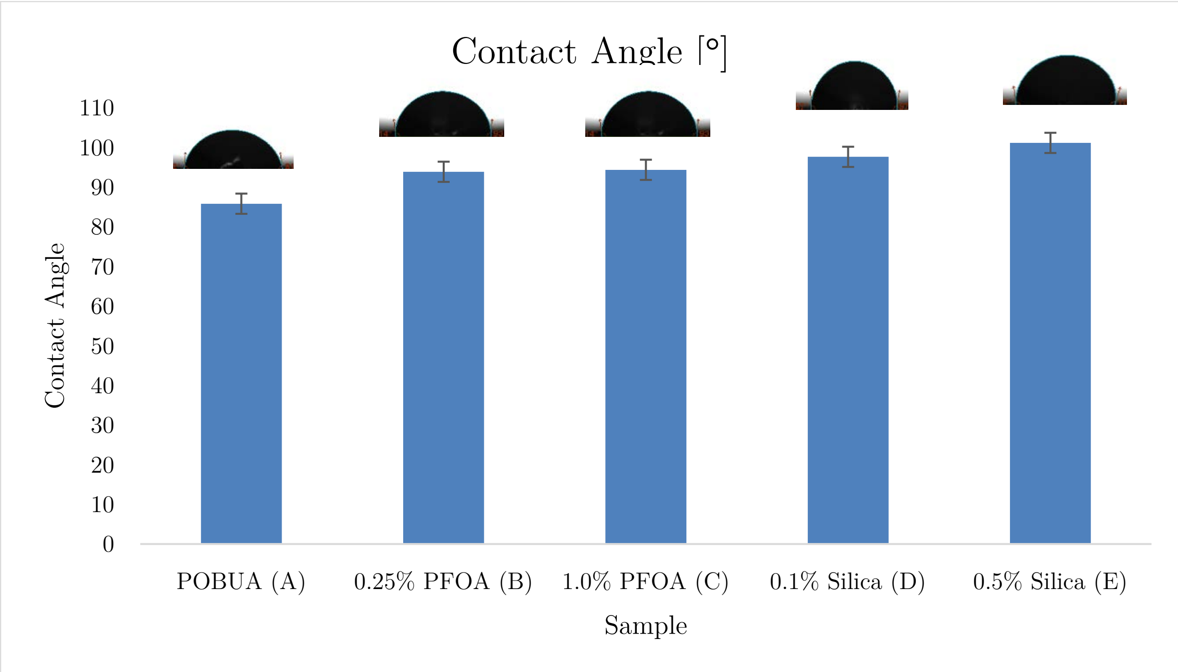

Figure 2: Contact angle for different POBUA formulations

Figure 2 shows the optical contact angle for the wood substrates that have been coated and cured with different POBUA formulations. From the figure, it can be summarized POBUA formulation showed the lowest hydrophobicity at 85.8º and it is due to the unavailability of any modifier and roughness agent (Harun et al., 2018). When POBUA was introduced with the 0.25% PFOA modifier, the coating exhibited hydrophobic properties with water contact angle obtained was 93.9º. When the modifier was increased up to 1.0%, the water contact angle slight increased at 94.4º. The formulations then were introduced with roughness agent which was silica and the amount of silica improved the hydrophobicity with water contact angle obtained for 0.1% Silica was 97.64º and for 0.5% Silica 101.1º respectively. In summary, an optimum composition for each component in the formulation is needed to obtain a higher value of surface hydrophobicity. For example, if the amount of silica is increased, the amount of PFOA also need to be increased to compensate each other and then good hydrophobicity will be obtained and in turn improve the wood coating formulation.

FTIR

FTIR analysis results in an absorption spectrum which provides information about the chemical bonds and molecular structure of a material. The chemical composition of different hydrophobic coatings coated on wood was studied by FTIR spectroscopy using ATR technique in transmission mode. The functional groups of POBUA, silica and PFOA were determined by FTIR spectroscopy and results are shown in Figure 3. The FTIR spectra of POBUA shows clearly strong band of CH_3 and CH_2 stretching at 2923 cm^{-1} and 2853 cm^{-1} respectively. C=O (carboxylic group) at 1727 cm^{-1}. Absorption band at 1636 cm^{-1}, 1409 cm^{-1} and 809 cm^{-1} ascribed to C=C stretching, scissoring and out-of-plane bending of the C=C of the vinyl moieties of the acrylate groups. Si-O-Si symmetric vibration mode is noticed at 1060 cm^{-1} and 1068 cm^{-1} for 0.5% Silica in POBUA-SiO_2, meanwhile C-F stretching shows at 1000 cm^{-1} for the addition of 1% PFOA. The conversion of double bond that occurred within palm oil acrylate coating during the polymerization reaction under UV radiation was observed. The disappearance of the reactive C=C bond upon cured was detected at 1660-1600 cm^{-1} and 809 cm^{-1}. Before UV radiation, the FTIR spectrum showed unsaturation C=C bond peak at 1636 cm^{-1}, 1409 cm^{-1} and 809 cm^{-1}. Due to the consumption of C=C of POBUA vinyl group in the curing reaction, no more traces for their IR bands detected after being cured (Saharudin et al., 2018).

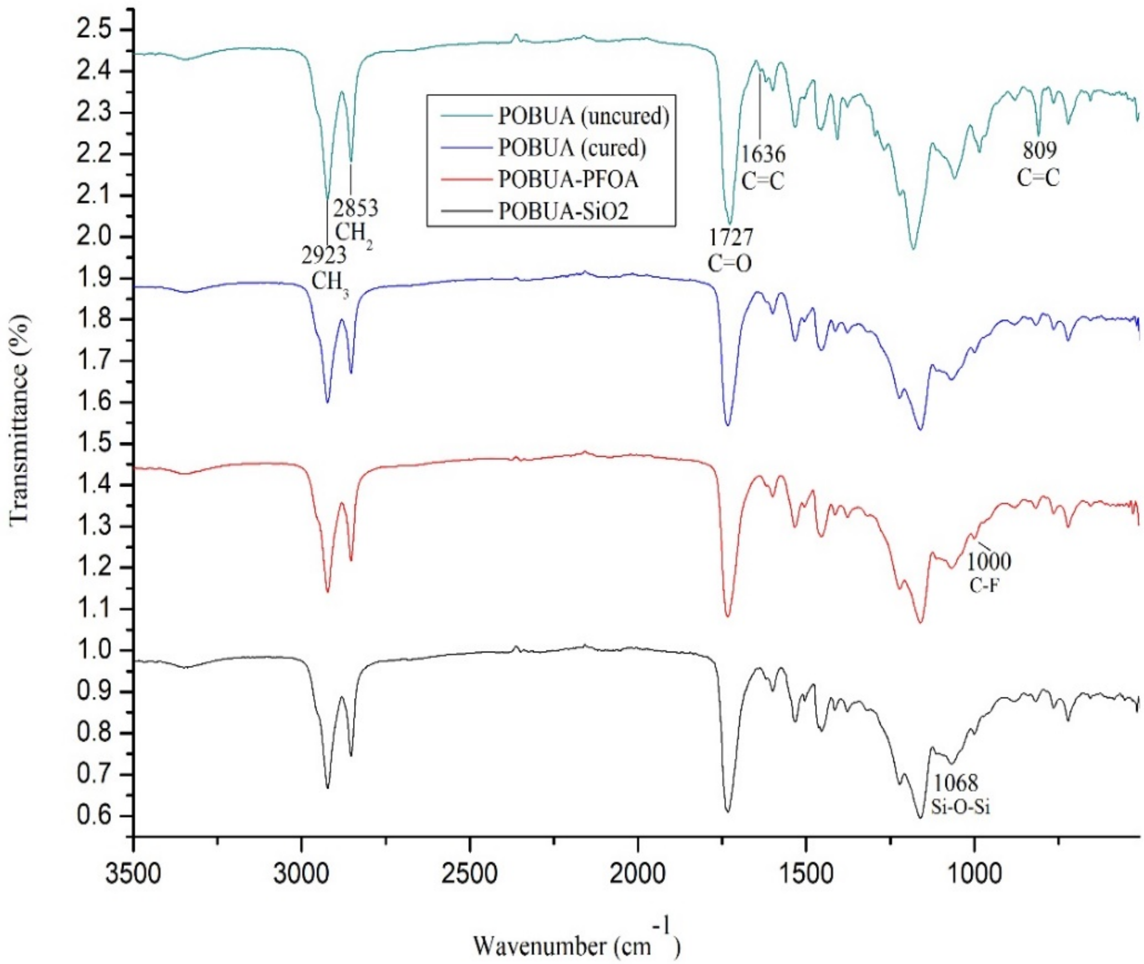

Figure 3: IR spectra of different acrylated POBUA formulations

Degree of Crosslinking

Gel content allows the measurement of swell ratio which a measure of the degree of cross-linking in the gel phase. The film was extracted with acetone solvent to determine the crosslinked portion which the insoluble fraction that produced from the film. Table 2 tabulated the gel content percentage of UV-cured film for all compositions. The gel content of all UV-cured films increases with the increasing amount of silica and PFOA. Furthermore, the crosslinking percentage of palm oil-based cured coating for all compositions was greater than 90%. This indicated that POBUA and the modifiers was compatible to each other (Nik Salleh et al., 2019).

Table 2. Gel content for different composition of hydrophobic coating surfaces at different passes of UV exposure

Samples	**Gel Content (%)**		
	3	6	10
POBUA	93.83	94.90	96.97
0.25% PFOA	94.83	98.55	99.10
1.0% PFOA	91.73	93.90	97.14
0.1% Silica	96.83	98.33	99.67
0.5% Silica	93.10	94.52	97.01

Thermogravimetric analysis (TGA)

Thermal properties of the POBUA coating films were evaluated by TGA. Figure 4 shows TGA thermograms of the POBUA coating surfaces. The thermograms for all surface coating exhibits a same degradation temperature (Salih et al., 2015). TGA thermograms reveal that the decomposition of palm oil-based acrylate coating was two-stage degradation. The first stage occurred at the temperature range at 150°C, and can be attributed to the loss of the volatile compounds or the photoinitiator; The total weight loss at this stage (at the end of the stage at 208°C) was found to be around 4% of the total weight for POBUA with silica and PFOA while POBUA with silica and POBUA with PFOA film lost around 5% of its total weight. The onset temperature of this stage in POBUA films was 50°C. The major decomposition of the polymer films occurred in the second stage, which was attributed to the decomposition of the organic polymer chains. The onset temperature for this stage was 260°C for all surface coating. From 260 °C to 450 °C, the weight loss was dramatic decrease at ~85% and was attributed to the decomposition of the cured POBUA; the rest was the SiO_2 component and carbon.

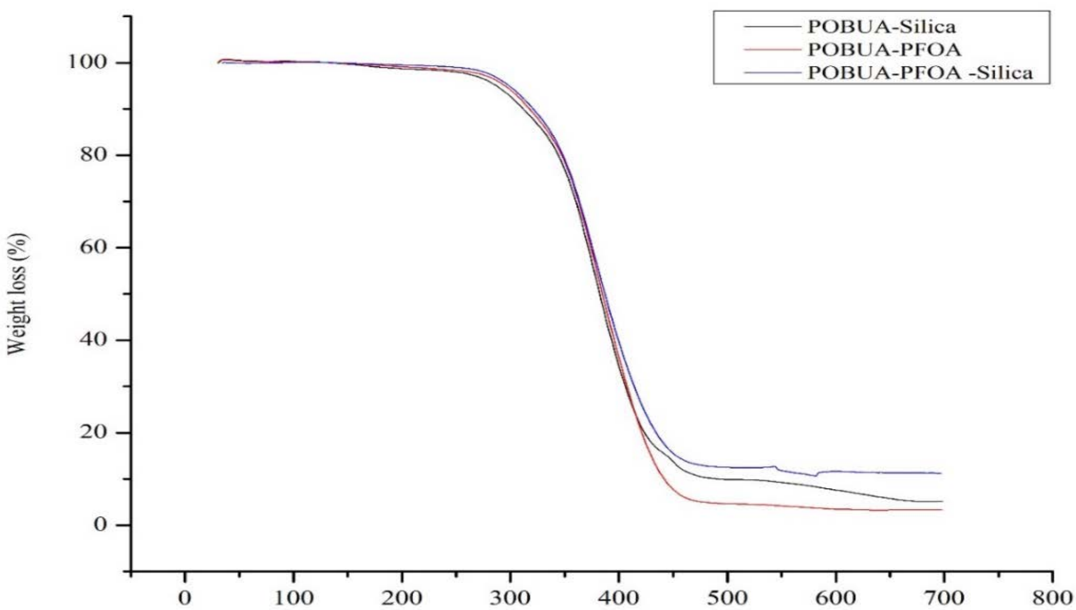

Figure 4: TGA thermograms of the POBUA coating formulations

CONCLUSIONS

POBUA formulations with different compositions of SiO_2 and PFOA were successfully prepared along with the same composition of IC-500 in all samples. These formulations were successfully cured onto the wood substrate to obtain a coating using the UV-curing technique. Water Contact Angle test was conducted to identify the surface wetting properties of the cured POBUA samples. The samples containing silica showed the highest water contact angle indicates the significant contribution of roughness agent in repelling water from being contacted with the coated surface. Based on the film properties, the palm oil acrylate coating was successfully cured as the peak for C=C disappeared after being cured. The results of gel content showed the percentage of cross-linking within the palm oil acrylate and the modifiers was more than 90%. These results proved the polymerization and crosslinking of the POBUA resins during the curing process. In conclusion, a hydrophobic acrylated coating from POBUA was successfully obtained by using the UV-radiation technique. From the analysis conducted, the POBUA resins can be a potential hydrophobic coating for wood applications in the industry.

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