

Influence of UV Irradiation for Biopolymer and It's Composite

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Abstract— *The purpose of this research is to study the mechanical strengths and physical changes of the biopolymer (BP) and biopolymer composite (BPC) after exposed to UV irradiation. Virgin vegetables oil (VO) and Waste vegetables oil (WO) has been treated with chemical process and mixed with Methylene Diphenyl Diisocyanate (MDI) to produces BP. BPC samples were doped with 2.5, 5, 7.5 and 10 % metal oxide, Titanium Dioxide (TiO₂). These samples were exposed using UV weatherometer at 0, 250, 500, 750, 1000, 2000, and 3000 hours. The effects of UV light on the mechanical properties of BP and BPC were determined by tensile test. The colour changes of BP and BPC were observed after expose to UV light.*

Keywords— Biopolymer composite; virgin vegetables oil; waste vegetables oil; titanium dioxide, UV light; tensile strength

I. INTRODUCTION

In recent years, increasing interest in the development of more environment friendly polymer products such as plastics is observed. This trend has been spurred not only by the realization that the supply of fossil resources is inherently finite, but also by a growing concern for environmental issues, such as volatile organic solvent emissions and recycling or waste disposal problems at the end of a resin's economic lifetime. Furthermore, developments in organic chemistry and fundamental knowledge on the physics and chemistry of paints and coatings enabled some problems encountered before in vegetable oil based products to be solved. This resulted in the development of coatings formulations with much improved performances that are based on renewable resources [1].

Palm oil is one of the most widely used plant oils in the world, which is grown in mass plantation in tropical countries. The competitive environment of the industry provides the drive needed to develop plastic materials that utilize less expensive material. Palm oil differs from its major competitors (soybean, sunflower seed, and rapeseed oil) in that it is obtained from a perennial tree crop and drought impacts are less severe in comparison to oilseed crops. Palm oil which contains significant amount of saturated bonds that presumably contribute to the non drying property of the resin synthesized.

The non-drying alkyds have made tremendous improvement in quality of nitrocellulose lacquers. Preparation of the alkyd resin from non-drying palm oil may expand the application of the oil in various areas as environment-friendly materials, because of its abundance and renewability. There is no study reported on the synthesis of alkyd resin based on palm oil so far. However, the use of petroleum based monomers in the manufacture of polymers is expected to decline in the coming years because of spiraling prices and the high rate of depletion of the stocks. This has inspired the technologists all over the world to investigate renewable natural materials as an alternate source of monomers for the polymer industry as substitute for the petroleum-based monomers to manufacture polymers [2].

The evaluation of the resistance to weathering of materials can be done by direct weathering outdoors, but for most purposes it is more practical in economical and time consumption terms to assess material performance by exposed to artificial light sources that accelerate the degradation. Degradation of polymeric materials by exposure to solar radiation or light is referred to as photo-oxidation. It is a free radical process, progressing even at low temperatures by the combine action of light and oxygen. Thermal oxidation is always superimposed on photo-oxidation [3].

Under the action of sunlight, polymer materials undergo a series of oxidative reactions that lead to chemical degradation, with consequences like brittleness, loss of brightness, colour change, opacity and formation of surface cracks. Besides the reduction in molecular weight, a number of changes take place in the molecules during photodegradation with the formation of chemical groups like carbonyl, carboxylic acids and hydroperoxides [4].

Products like fibres and films tend to deteriorate under UV exposure to UV light, resulting mainly in fragility and loss of transparency. The degradation and stabilization of some types of polymer, like polyethelene were extensively investigated throughout the years and hence the degradation mechanisms and their controlling factors are reasonably well established [5]. The common polymers normally photo degrade are fairly well known, but various aspects of the mechanisms involve remain

uncleared. It is important to take into account very significant influence of compounding additives in modifying the chemical pathways, which are pigments, extenders, photo stabilizers and thermal stabilizers [6].

II. METHODOLOGY

A. Materials

Biomonomer from virgin vegetable oil (VO) and waste vegetable oil (WO) was used as received from E1, Sustainable Polymer Engineering Group. Biomonomer of VO and WO was mixed with MDI as cross linking agent to form virgin oil polymer (VOP) and waste oil polymer (WOP) [7].

B. Preparation of BP and BPC

The mixture was stirred together using mechanical stirrer for about 60 minutes at 50 °C resulting viscous compound. The compound was then cast into a container and spread to uniform thickness. The VOP and WOP was leave to cure at ambient temperature for at least 6 hours, as to ensure complete removal of solvent traces. Once dry, the film was stripped from the plate. Micrometer was used to measure the thickness of the sample at particular point ranging from 110 µm to 250 µm according to MS 133-C5:2010 Paint and Varnishes- Part C5: Determination of Film Thickness (Second Revision) (ISO 2808: 2007, IDT), the dry-film thickness was measured using micrometer. The above steps were repeated to fabricate BPC doped with different percentage of TiO₂ as shown in Table 1. The sample of BP based on VOP and WOP while BPC was namely according to TiO₂ percentage as VOP_{2.5}, VOP₅, VOP_{7.5}, and VOP₁₀; WOP_{2.5}, WOP₅, WOP_{7.5}, and WOP₁₀ respectively [8].

C. UV irradiation of BP and BPC

The BP and BPC thin film samples were placed on a rack with a rack holder in the UV weatherometer chamber at 50 °C with different exposure time at 250, 500, 750, 1000, 2000 and 3000 hours. The UV accelerated weathering test was conducted according to ASTM D 4587-Standard practice for fluorescent UV-condensation exposures of paint and related coatings. The UV Weatherometer used UV irradiation was carried out using an array of UV fluorescent lamps emitting light in the region from 280 to 320 nm with a tail extending to 400 nm.

TABLE I. BP and BPC of VOP and WOP doped with different percentage of TiO₂

Sample name	Percent of fillers (%)	Mass of monomer (g)	Mass of MDI (g)	Mass of TiO ₂ (g)
VOP	-	30	15	-
VOP _{2.5}	2.5	30	15	0.75
VOP ₅	5.0	30	15	1.50
VOP _{7.5}	7.5	30	15	2.25
VOP ₁₀	10	30	15	3.00
WOP	-	30	15	-
WOP _{2.5}	2.5	30	15	0.75
WOP ₅	5.0	30	15	1.50

WOP _{7.5}	7.5	30	15	2.25
WOP ₁₀	10	30	15	3.00

D. Tensile test of BP and BPC thin film

Tensile strength for BP and BPC of VOP and WOP were measured by Universal Testing Machine (LLOYD Instruments LR30K) as in Figure 3.9, with load range; 20N, cross head speed; 500 mm min⁻¹, gauge length; 100 mm and efficiency within ±1%. All specimens were tested at room temperature. A minimum of five samples was analyzed in order to obtain average result. Original length and area of the gauge sample was measured using vernier calipers. The sample was mounted between two jaws of the tester. The average tensile strength for the films was calculated and the results were compared with unexposed bio polymer thin films samples. Stress tests for each material were according to ASTM D882. ASTM D882 which is the standard test method for tensile properties of thin plastic sheeting is very similar to the common ASTM D638 test whereby plastic material is pulled until in breaks in order to measure elongation, tensile modulus, tensile yield strength, and tensile strength at break. However, it is designed specifically for thin sheeting and film less than 1 mm (0.04") thick where the BP and BPC films samples thickness were 0.11-0.25 mm.

III. RESULTS AND DISCUSSION

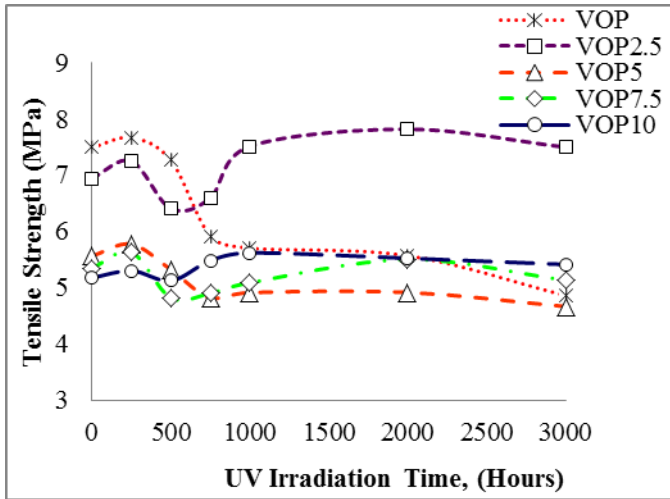
A. Tensile strength of BP and BPC

Define abbreviations and acronyms the first time they are used in the text, even after they have been defined in the abstract. Abbreviations such as IEEE, SI, MKS, CGS, sc, dc, and rms do not have to be defined. Do not use abbreviations in the title or heads unless they are unavoidable.

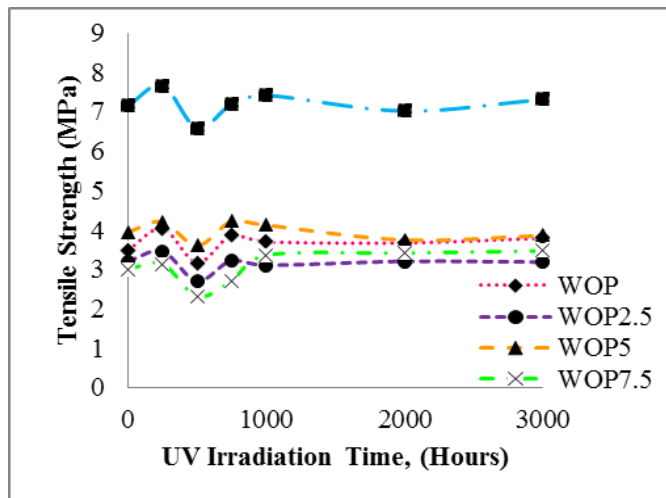
After BP and BPC thin film were exposed to UV light for several hours, the samples were mechanically test using UTM tensile test according to ASTM D882. Five samples were tested to get the average value of each BP and BPC at 250, 500, 750, 1000, 2000 and 3000 hours exposed to UV light. The mechanical properties of BP and BPC were study according to the tensile strengths and maximum elongation.

Fig. 1. present the tensile strength (MPa) as a function of UV irradiation time to UV (hours) of BP and BPC of VOP and WOP. The tensile strength for all unexposed BPC of VOP and WOP is lower than after UV irradiation at 250 hours. Evidently, at 500 hours UV irradiation, the tensile strength for BP and BPC were decreases. Meanwhile tensile strength of BP and BPC of VOP increases after 750 hours of UV exposure and remains increasing in systematic way after 1000 hours until 2000 hours. The tensile strength slightly decreases at 3000 hours. Meanwhile tensile strength of BP and BPC of WOP increases at 750 hours of UV exposure. The tensile strength remains stable after 1000 hours until 3000 hours. The decrement of the tensile strength at 500 hours exposure for BP and BPC show the crosslinking interaction of TiO₂ in the polymeric structure is at the initial stage. Results show tensilized films of VOP_{2.5} tend to have higher tensile strength at 2000 hours UV irradiation while 3000 hours for sample VOP₅ has lowest tensile strength of 7.818 MPa and 4.668 MPa

respectively. Meanwhile, the results show tensilized films of WOP₁₀ tend to have higher tensile strength at 250 hours UV irradiation while WOP_{7.5} has lowest tensile strength at 500 hours of 7.668 MPa and 2.358 MPa respectively.



(a)



(b)

Fig. 1. Graph of tensile strength (MPa) against UV irradiation time for BP and BPC of (a) VOP and (b) WOP

This is due to the UV degradation, which causes a breakdown of chemical bonds, resulting in embitterment and also increased cross linking and chain scission, which lead to shrinking and crack. Thus neat BPF shows rapid loss of tensile strength but the addition of TiO₂ can improve its performance. This result is in good agreement with result obtained by Salem [9]; Saleh and Shnean [10]. Mechanical properties of BP and BPC can be strongly influenced by photo-oxidation upon UV weathering exposure. The ductility disappears and the strength and strain at rupture strongly decrease at 500 hours and stable until 3000 hours UV exposure. The active participant of OH group with isocyanate was lead to failure.

B. Physical observation of BP and BPC

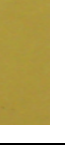
The BPC after exposed to UV light for several hours were observed to study the appearance of the thin film. Table 2 and Table 3 show visual observation of BP and BPC of VOP and WOP after UV irradiation in the UV accelerated weatherometer according to UV irradiation time. After exposure to UV light for certain period of time, it is clear that colour of of BP and BPC of VOP and WOP changes from pale yellow to dark colour while for the VOP and WOP doped with 10 % TiO₂, the colours does not change dramatically.

Table 2: Visual observation of BP and BPC of VOP after exposed in the UV Accelerated Weatherometer according to UV irradiation time

Table 3: Visual observation of BP and BPC of VOP after exposed in the UV Accelerated Weatherometer according to UV irradiation time.

Time exposed to UV (Hour)	WOP ₀	WOP _{2.5}	WOP ₅	WOP _{7.5}	WOP ₁₀
0					
250					
500					
750					
1000					
2000					
3000					

BP and BPC were turn to yellow after exposed to UV light from 250 hours to 3000 hours. Sample thin film for BP of VOP and WOP has turned a red-brown colour due to the well-established formation of quinone products produced from the photolysis of the biopolymer. Sample thin films for BPC were slowly reduce the colour change due to increasing the TiO₂ in

Time exposed to UV (Hour)	VOP ₀	VOP _{2.5}	VOP ₅	VOP _{7.5}	VOP ₁₀
0					
250					
500					
750					
1000					
2000					
3000					

the BPC. Fortunately, the yellowing decrease with the increasing of the % TiO₂ added to the both biopolymer. Therefore, a basically linear increase in yellowness is observed with the time of exposure for BP and BPC of VOP and WOP exposed to UV light. This is consistent reported by Davis and Sims [11]. Additionally, most organic polymers undergo chemical modification upon irradiation with UV light because their impurities or additives possess chromophoric groups, and the early stages of photo initiation must involve the absorption of photons by chromophoric groups or impurities [12].

IV. CONCLUSIONS

This paper presents experimental results of the influence of UV irradiation on mechanical strengths and physical observation of biopolymer composite. This study is a new process, particle-bonding technology, to produce biopolymer composites from agricultural commodities. In this technology, matrix-polymer complexes are formed by the interaction of micrometer-scale matrix material with particulate filler. This spontaneous process make use of the unique characteristic behavior of biomonomer adsorb to the surface of hydrophilic particles when the toluene content of solvent mixture increases. After that, van der Waals force between matrix-polymer complex particles induces the formation of even larger agglomerates. Removal of solvents from agglomerates yields the final product. Biopolymer thin film composites thus formed shows a broad range of strengths depending on the hardness of the starting raw material used as a matrix material. Incorporation of TiO₂ turns the composite into a semi-conductive polymer composite. It is also shown that TiO₂ can be used as low-cost substitute for UV stabilizer, colourant and plasticizer.

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