

## BIOPOLYMER-BASED THERMOPLASTIC MIXTURE FOR PRODUCING SOLID BIODEGRADABLE SHAPED BODIES AND IT'S PHOTO DEGRADATION STABILITY

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### ABSTRACT

In recent years, biopolymers with controllable lifetimes have become increasingly important for many applications in the areas of agriculture, biomedical implants and drug release, forestry, wild life conservation and waste management. Natural oils are considered to be the most important class of renewable sources. They can be obtained from naturally occurring plants, such as sunflower, cotton, linseed and palm oil. In Malaysia, palm oil is therefore an inexpensive and commodity material. Biopolymer produced from palm oil (Bio-VOP) is a naturally occurring biodegradable polymer and readily available from agriculture. For packaging use however, Bio-VOP is not thermoplastic and its granular form is unsuitable for most uses in the plastics industry, mainly due to processing difficulties during extrusion or injection moulding. For this reason, research workers have developed several methods to render Bio-VOP appropriate for industrial uses. In particular, injections moulding processes, graft copolymerisation, and preparation of blends with thermoplastic polymers have been studied as means to produced solid biodegradable shaped bodies. HDPE was chosen as commercial thermoplastic materials and adding with 10% Bio-VOP to produced solid biodegradable shaped bodies. By adding 10% Bio-VOP to the HDPE was successfully produced HD-VOP as biodegradable shaped bodies. HD-VOP which is exposed to 12 minutes upon UV light shows the highest strength of the materials that is 17.6 MPa. The morphological structure of HD-VOP shows dwi structure surface which is of brittle and ductile surface and also single surface that is brittle surface.

**Keywords:** Biopolymer, Copolymerization, Injection moulding, Biodegradable polymer.

### INTRODUCTION

In recent years, eco-friendly biodegradable polymers and plastics have gained increasing attention because of growing recognition worldwide of the need to reduce global environmental pollution (Kim, 2006). One alternative is renewable polymers made from plants. Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes. Biodegradable plastics and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for

sustainable, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock.

Vegetable oils are becoming extremely important as renewable resources for the preparation of polyols required for the polyurethane industry. Polyols from natural oils, such as soybean, castor, and palm oils are increasingly being viewed by industry as a viable alternative to hydrocarbon based feedstocks. These oils are annually renewable, and are cost-competitive as well as environment friendly. According to a market summary published by the United Soybean Board in February 2000, vegetable oil-based polyurethanes are best suited to three markets namely: polyurethane foams, polyurethane binders and agricultural films (Sharma & Kundu, 2008).

The development of synthetic polymers using monomers from natural resources provides a new direction to develop biodegradable polymers from renewable resources. One of the examples in this regard is PLA, because it is made from agricultural products and is readily biodegradable (Yu et al., 2006).

One of the main disadvantages of biodegradable polymers obtained from renewable sources is their dominant hydrophilic character, fast degradation rate and, in some cases, unsatisfactory mechanical properties, particularly under wet environments. In principle, the properties of natural polymers can be significantly improved by blending with synthetic polymers. Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend. In the 1970s and 1980s, numerous blends of starch with various polyolefins were developed. However, these blends were not biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost (Yu et al., 2006). In this research, thermoplastic polymer blends with renewable polymer from palm oil was discussed. An analysis of the mechanical properties and UV degradation was discussed in detail in a later section.

Normally all plastics products are manufactured using extrusion, injection molding, or extrusion blowing. The processing of polymers using heat and high shear into useful end products introduces impurities and reaction products that make them susceptible to photodegradation. Because of these complications, the extrapolation of research findings on UV-induced degradation of pure polymer resins to compounded and processed products of the same polymer, is often unreliable. Photo degradation data generated on the actual polymer formulations used in practice, processed in the conventional manner are the most useful for assessment of damage (Shammary, 2011).

Polymer photo-degradation and stabilization is an extensive field of study. It is well established that photo-oxidation reactions play an important role in the degradation process of the UV-irradiated polymeric materials, and the controlling mechanisms were studied by some authors (Salem, 2001).

The polymers, used in the building and construction industry, undergo photolytic and photo-oxidative reactions during exposure to solar UV radiation. Microcracking and embrittlement of polymeric substrates are the most serious effects of photodegradation, these effects are often accompanied by extensive deterioration in the mechanical properties of the materials, such as tensile strength, impact strength and elongation, all of which are important parameters in the performance of a building product. It is therefore the prediction of the effect of UV radiation on plastics by natural weathering exposure, particularly where product development is concerned (Shammar, 2011).

## METHODOLOGY

### Materials

Injection grade HDPE (HI1600) was supplied by Titan Petchem (M) Sdn. Bhd, having density of 0.94 to 0.965 g/cm<sup>3</sup> and the melting point of HDPE is >120°.

The origin bio-polymer (Bio-VOP), Vesawit Palm oil was used as original palm oil. The monomer conversion begins with the catalyst preparation to generate the epoxies from the unsaturated fatty compound, and second reaction is the acid-catalyst ring opening of the epoxies to form polyols or bio monomer (M. Rus, 2008, 2009, 2010). The bio-monomer mixed with cross linking agent; 4, 4'-Methylene Diphenyl Diisocyanate (MDI) and Toluene as the solvent. The proportion ratio is 1:0.5 of bio-monomer and MDI respectively. The mixture was stirred at 50°C for 15 minutes until the mixture become high viscous known as Bio-VOP and added to the HDPE in the Brabender Plastograph® EC machine.

For the preparation of polymer matrix materials was started by mixing the HDPE with 10% bio-polymer (wt/wt ratio) by using Brabender Plastograph® EC machine from Germany at 130°C and 25 rpm speed rate for 20 minutes. This polymer/biopolymer compound named as HD-VOP.

### Injection Moulding

The compounding materials were then fed to injection moulding machine (Nissei Horizontal Screw Type Injection Moulding NP7 Real Mini from Japan). The mold was designed according to ISO 527 (5A) standards to produce specimens for tensile tests. Barrel temperature set points of nozzle zone, front zone, middle zone, rear 1 zone, rear 2 zone and feed zone were 150°C, 145°C, 140°C, 135°C, 130°C and 70°C respectively.

### Tensile Test

The tensile test sample was prepared according to ISO 527 (5A). The testing was consists of five samples for each different time exposure and Universal Tensile Machine AG-I, Shimadzu, 10 kN types with 5 mm/min crosshead speed was used.

### UV Weathering Test Chamber

35 dumbbell shape samples produced from injection moulding was exposed to the UV light in UV Lamp Test Chamber Model HD-703 (Haida International Equipment Co., LTD) at different exposure time at 50° C. Different UV exposure time was conducted for each group of 5 sample to calculate the average value of mechanical testing. The sample were identified as A, B, C, D, E, F, G, and H for unexposed sample and exposed to 3 minutes, 6 minutes, 9 minutes, 12 minutes, 15 minutes, 18 minutes, and 21 minutes respectively. The UV- irradiation of the dumbbell sample was carried out using an array of UV fluorescent lamp emitting light in the region from 280 to 320 nm with a tail extending to 400 nm.

### Scanning Electron Microscopy (SEM)

The morphological study based on the fracture surface of HD-VOP was examined using a SEM (JSM-6380LA Analytical Scanning Electron Microscope manufactured by JEOL Company Japan). The samples were cut into 1cm x 1cm x 1cm and was ultrathin coated with gold to produce electrically conductive specimens by JFC-1600 Auto Coater manufactured (JEOL Company Japan). The gold deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Samples were examined after coated with ultrathin platinum, at 10kV voltage supplied by the SEM.

## DISCUSSIONS

Referring to Figure 1, sample E was exposed in 12 minutes to UV light shows the highest mechanical property of tensile strength of 17.6 MPa while sample B exposed to 3 minutes of UV light shows the lowest mechanical property that is 17.2 MPa. According to Figure 1, the strength of UV irradiated samples shows slight decrease of about 3 minutes and then increases up to exposure times of about 15 minutes then decrease again of about 21 minutes. The initial decrease in strength with exposure time may be due to occurrence of chain scission processes as a result of the photo-oxidation. However, the increase in strength with exposure time may be due to crosslink reaction of the polymer chains as a result of exposure to ultraviolet radiation (Salem, 200; Shammar, 2011).

The young's modulus of sample A of unexposed to UV irradiation gives the highest result of 1.23 MPa while sample B gives the lowest result of 1.07 MPa. The young's modulus exhibited small changes. However, these changes are not significant since all results fall within the same statistical range of newly manufactured material. Young's modulus is a measure of the stiffness of an elastic material and is a quantity used to characterize materials. Sample B shows the lowest result for both strength and young's modulus due to cross-linking of the material upon the photo degradation of UV irradiation.

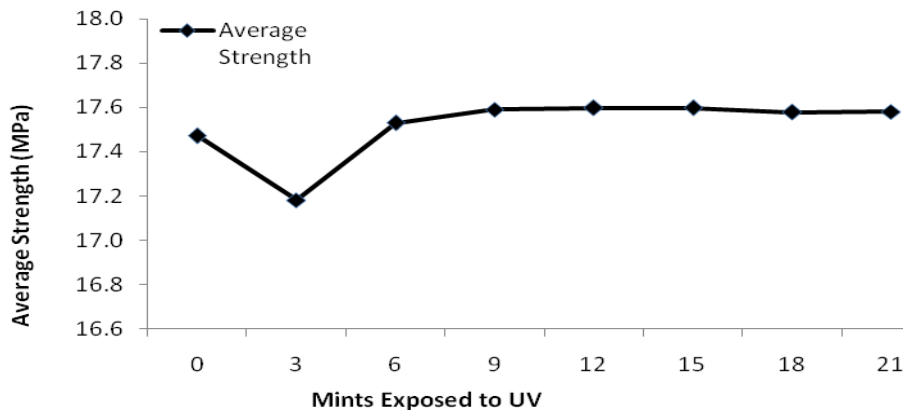


Figure 1. Average tensile strength of the HD-VOP sample

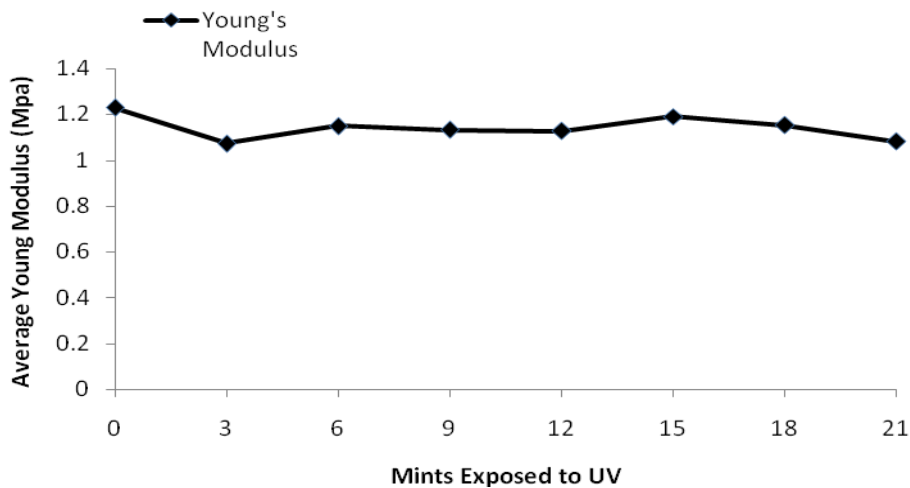
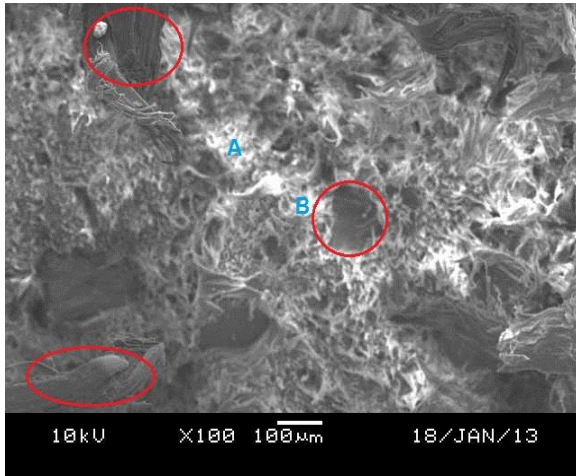


Figure 2. Young's Modulus of the HD-VOP sample

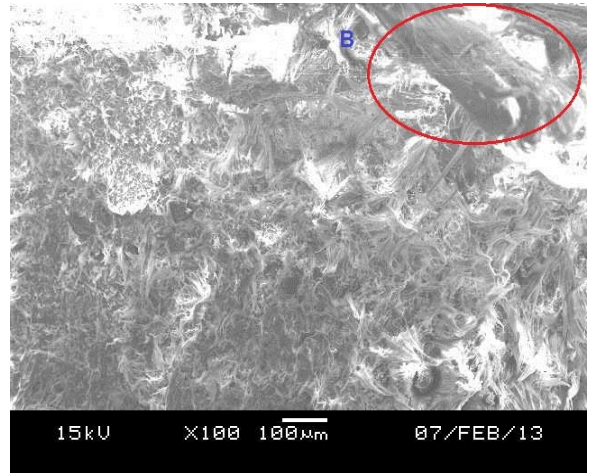
Referring to Figure 3 (a) (b) and (c), the fracture surface of sample A, B and C has two characteristic as shows in part A and part B. From Figure 3, part A can be classified as a brittle fracture while for B is ductile fracture. SEM result for sample A, B and C shows the structure in part A have interconnected and twisted fibrils with large interfibrillar separation. Meanwhile, part B shows ductile fracture with numerous spherical 'dimples' resulting from uniaxial tensile failure. Each dimple is one half of a microvoid that formed and separated during the fracture process. It's also appears fibrous or dull and it have very rough surface compared to the matrix. As looking at the fracture surface of these samples, it's undergo a moderate amount of necking. The fracture process normally occurs in several stages. First, after necking begins, small cavities, or microvoids, form in the interior of the cross section. Next, as deformation continues, these microvoids enlarge, come together, and coalesce to form an elliptical crack, which has its long axis perpendicular to the stress direction. The crack continues to grow in a direction parallel to its major axis by this microvoid coalescence process. Finally, fracture ensues by the rapid propagation of a crack around the outer perimeter of the neck, by shear deformation at an angle of about  $45^\circ$  with the tensile axis which is the angle at which the shear stress is at maximum. Sometimes a fracture having this characteristic surface contour is termed a *cup and-cone fracture* because one of the mating surfaces is in the form of a cup, the other like a cone (Ahmad and Mahanwar, 2010).

For the sample D, E and F shows uneven fracture surface which is no void and dimples appear that cause higher in tensile strength. For sample G and H, there are numerous spherical 'dimples' resulting from uniaxial tensile failure that causes reduced in strength. The sample was exposed longer to UV light which makes these samples more brittle and the behaviour of the cracks propagation will be changed according to the weakness point in specimens.

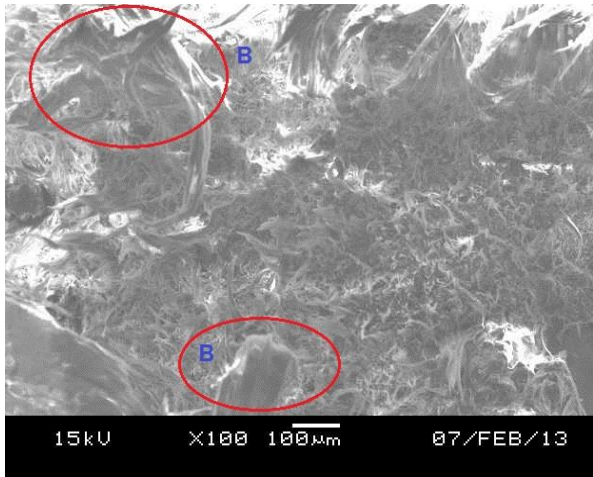
a)



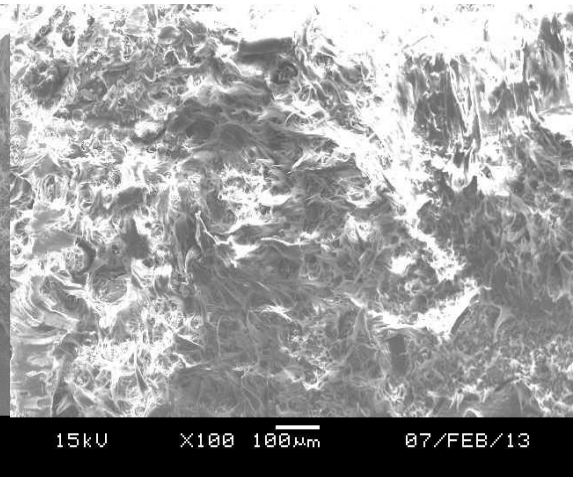
b)



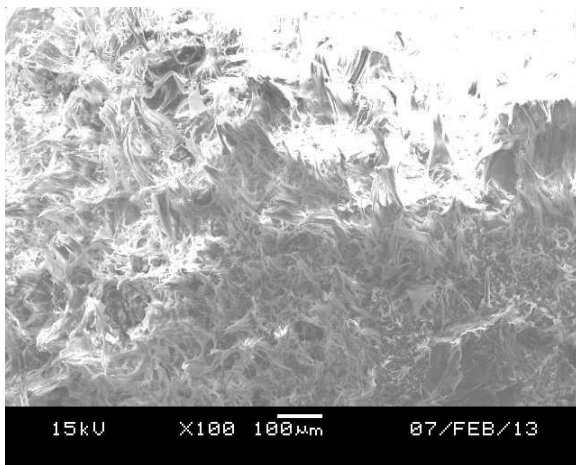
c)



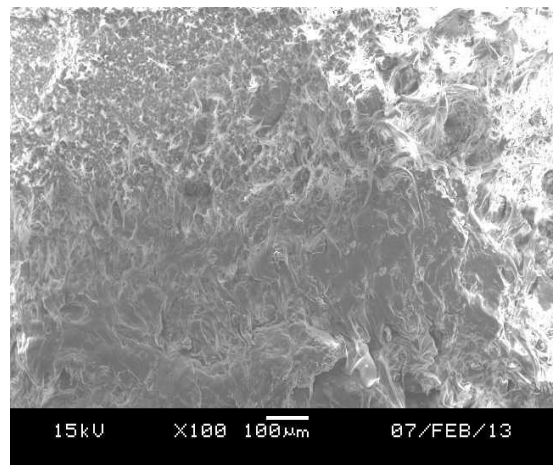
d)



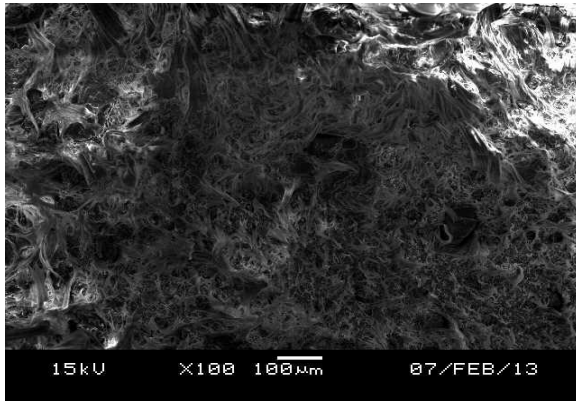
e)



f)



g)



h)

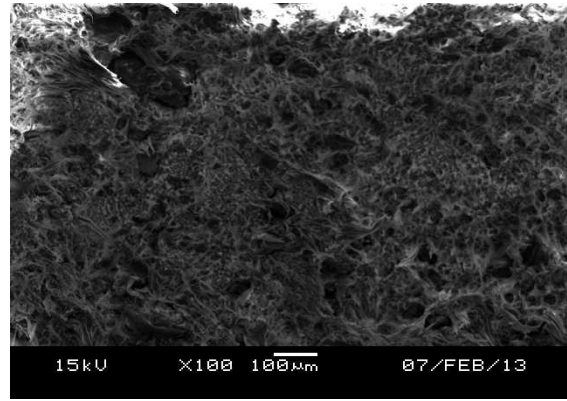


Figure 3. SEM morphology of fracture surface cross-section for HD-VOP

### CONCLUSIONS

As the conclusion, by adding 10% Bio-VOP to the HDPE was successfully produced HD-VOP by injection moulding process which is when exposed to UV light, the highest strength of the materials is 17.6 MPa. The morphological structure of HD-VOP dwi structure surface which is of brittle and ductile surface and also single surface that is brittle surface.

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