PHOTODEGRADATION OF BIOPOLYMER DOPED WITH TITANIUM DIOXIDE (TiO_2) AS ULTRAVIOLET (UV) STABILIZER

SITI RAHMAH BINTI MOHID

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Universiti Tun Hussein Onn Malaysia

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ABSTRACT

A large amount of waste cooking oil has become an environmental issue around the world. This oil is renewable and biodegradable than the corresponding products made from petroleum sources. The major concern in this study focuses on the resistance of the biopolymer to ultraviolet (UV) light exposure. The virgin oil (VO) and waste oil (WO) was converted into biomonomer. By adding biomonomer with an appropriate amount of 4, 4'-methylene diphenyl diisocyanate (MDI) and solvent, the virgin oil polymer (VOP) and waste oil polymer (WOP) were produced. The biopolymer (BP) were added with low loading metal oxide filler which is 2.5, 5, 7.5 and 10 % of titanium dioxide (TiO_2) to form biopolymer composite (BPC). The resistance to UV light and mechanical properties of BP and BPC were determined after exposure the thin films in UV weatherometer for an extended period of time at 250, 500, 750,1000, 2000 and 3000 hours. The results based on the spectroscopic analysis of UV-Vis and FTIR confirmed the photodegradation processes of BP and BPC of VOP and WOP. The increasing absorbance in UV-Vis spectra indicated the formation of quinone after UV-irradiation of BP and BPC of VOP and WOP. Furthermore, BP thin films shows rapid loss of tensile strength but the increased loading of TiO_2 can improve mechanical performance. Visual inspection based on the colour changes of the thin films showed quinone (yellow) formation of the irradiated films of BP and BPC of VOP and WOP. As a conclusion, the effect of prolonged exposure to UV light, in general promotes photo degradation for BP but BPC gives slower chemical modification. The innovative biopolymer composite were successfully designed and developed by adding the TiO_2 as UV stabilizer to reduce the photo-degradation of the biopolymer.

ABSTRAK

Sejumlah besar sisa minyak masak telah menjadi isu alam sekitar di seluruh dunia. Minyak ini merupakan produk yang boleh diperbaharui dan lebih mudah terbiodegradasi berbanding produk dari sumber petroleum. Tumpuan utama dalam kajian ini fokus kepada rintangan biopolimer terhadap pendedahan cahaya ultraungu (UV). Minyak dara (VO) dan sisa minyak (WO) telah ditukar kepada biomonomer. Dengan menambah biomonomer dengan jumlah yang sesuai 4, 4'-methylene diphenyl diisocyanate (MDI) dan pelarut, polimer minyak dara (VOP) dan polimer sisa minyak (WOP) telah dihasilkan. Biopolimer (BP) telah ditambah dengan pengisi logam oksida yang rendah iaitu 2.5, 5.0, 7.5 dan 10.0 % daripada titanium dioksida (TiO_2) untuk membentuk biopolimer komposit (BPC). Rintangan kepada cahaya UV dan sifat mekanik BP dan BPC telah ditentukan selepas pendedahan filem nipis di dalam alat weatherometer UV untuk tempoh masa yang panjang pada 250, 500, 750, 1000, 2000 dan 3000 jam. Keputusan berdasarkan analisis spektroskopi UV-Vis dan FTIR menunjukkan proses degradasi foto bagi BP dan BPC dari VOP dan WOP. Keserapan meningkat di UV-Vis spektrum menunjukkan pembentukan *quinone* selepas penyinaran-UV bagi BP dan BPC dari VOP dan WOP. Tambahan pula, BP filem nipis menunjukkan kehilangan yang cepat bagi kekuatan tegangan tetapi peningkatan TiO_2 boleh meningkatkan prestasi mekanikal. Pemeriksaan visual berdasarkan perubahan warna daripada filem nipis menunjukkan pembentukan *quinone* (kuning) oleh pancaran sinaran filem BP dan BPC dari VOP dan WOP. Kesimpulannya, kesan pendedahan yang berpanjangan kepada cahaya UV, secara amnya menggalakkan degradasi foto untuk BP tetapi BPC memberikan pengubahsuaian kimia secara perlahan. Komposit biopolimer inovatif telah berjaya direka dan dibangunkan dengan menambah TiO_2 sebagai penstabil UV untuk mengurangkan degradasi foto oleh biopolimer.

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LIST OF SYMBOL AND ABBREVIATIONS

A/Abs	-	Absorbance
ASTM	-	American Society for Testing Materials
ATR	-	Attenuated total reflection
CO_2	-	Carbon dioxide
FTIR	-	Fourier Transform Infrared
H	-	Hours
MDI	-	Methylene diisocyanate
MPa	-	Mega Pascal
TiO_2	-	Titanium dioxide
%	-	Percent
eV	-	1.6×10^{-19} Joule
λ	-	Wavelength
nm	-	Nanometer
µm	-	Micrometer
°C	-	Degree Celsius
BP	-	Biopolymer
BPC	-	Biopolymer composite
CI	-	Carbonyl index
HI	-	Hydroxyl index
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet visible
VO	-	Virgin oil
VOM	-	Virgin oil monomer

VOP	-	Virgin oil polymer
WO	-	Waste oil
WOM	-	Waste oil monomer
WOP	-	Waste oil polymer

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CHAPTER 1

INTRODUCTION

1.1 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 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 (Derksen *et al.*, 1996).

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 (Issam and Cheun, 2009).

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 (Robinson *et al.*, 2011).

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 (Rabek, 1995).

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 polyethylene were extensively investigated throughout the years and hence the degradation mechanisms and their controlling factors are reasonably well established (Fechine *et al.*, 2002). 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 (Al-Shammary, 2011).

Normally polymers such as plastics are susceptible to auto-oxidation initiated by heat or UV-light during processing or long term use. In order to prevent the degradation of polymers, much kind of stabilizers have been developed and are now use widely in many applications. Normally for coloured materials, combination of UV absorbers and light stabilizer are used to achieve a measure of protection and prevent photo-oxidation (Gugumus, 1993). The aim of this study was to investigate the effect of UV stabilizers on the photodegradation of biopolymer composite. Film samples were exposed in the UV weatherometer and tested for mechanical properties and physical changes.

1.2 Background of study

Great interest towards biobased polymer in various applications is due to limited resources of petroleum based polymers and increased environmental concern. The development of novel feedstocks for polyurethanes derived from renewable materials has become important because the use of polyurethane polymers is increasing at a rate of 1 million tonnes a year. The reaction of organic isocyanate with compounds containing OH (hydroxyl) groups is capable of wide application in polymer formation. Thus the urethane linkage, –(NHCOO)- can be produced by reacting compounds containing active hydrogen atoms with isocyanate, where polymer formation can take place if the reagents are di- or polyfunctional.

In this study, virgin and waste monomer was converted into a biopolymer composite with low loading of filler. This filler is widely used as a white pigment because of its brightness, very high refractive index (n = 2.4), cheap and abundance. It is also an effective opacifier in powder form or as a pigment to provide whiteness and opacity to products such as paints, coating, plastics, paper, inks, foods and most toothpaste. Titanium dioxide (TiO_2) is a semiconductor, with a band gap of 3.1 eV for rutile and tends to lose oxygen and become sub-stoichiometric. TiO_2 shows relatively high reactivity and chemical stability under ultraviolet light (λ<387 nm). TiO_2 of photostabilizer is non-toxic and chemically stable (Zaleska, 2008; Anika

Zafiah, 2008). The applications of metal oxide filler as polymer additives included superhydrophobic photocatalysis as self-clean coating and photovoltaic solar cell (Anika Zafiah, 2013).

The primary end-use markets are construction, furniture, packaging and automotive industrial. Automotive interior and under hood parts, electrical connectors and microwaveable containers are examples of applications requiring high temperature resistance.

1.3 Problem statement

Environmental polution and destruction on a global scale have drawn attention to the vital need for totally new, safe and clean chemical technologies and processes, the most important challenge facing chemical scientists for the 21st century. A large amount of waste cooking oil has become an environmental issue around the world. The Energy Information Administration in the United States estimated that some 100 million gallons of waste cooking oil is produced per day in USA, where the average per capita waste cooking oil was reported to be 9 pounds (Radich, 2006). In the European countries, the total waste cooking oil production was approximately 700,000-1,000,000 tons/year (Kulkarni and Dalai, 2006).

Synthetic polymers are produced from petrochemicals that cost very expensive. It also can burden to the environmental because it non-degrade and harming wildlife when they are dispersed in nature. Management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources As large amounts of waste cooking oils are illegally dumped into rivers and landfills, causing environmental pollution, so the use of waste cooking oil to produce biomonomer as biopolymer substitute offers significant advantages because of the reduction in environmental pollution.

The potential of biodegradable polymers has been recognized for a long time since they could be an interesting way to overcome the limitation of the petrochemical resources in the future. The fossil fuel and gas could be partially replaced by green agricultural resources, which would also participate in the reduction of CO_2 emissions (Avareus and Pollet, 2012). Due to concerns over sustainability, environmental issues and raw material costs, the use of renewable resources such as waste cooking oil is very attractive to industries. It is because it most valuable to develop as raw materials for biopolymer composite and offers great choice with biodegradability, clean, safer and it relatively low cost with acceptable mechanical properties and wide range of application such as in coating field.

Such varnishes, lacquers or paints are usually made of highly crosslinked polymers which must exhibit a great resistance to solar radiation, moisture, pollutants and chemicals in order to ensure a long lasting protection. By lowering the mobility of the polymer chains, the network structure reduces the extent of both the production of initiating species (cage effect) and the propagation step, thus making crosslinked polymers more resistant to photo-oxidation. The durability of organic coatings can be further enhanced by the addition of light stabilizers (Decker *et al.*, 1995).

Polymers, such as plastics and coatings, are susceptible to photodegradation initiated by heat or UV-light during processing or long-term use. In order to prevent the photodegradation of polymers, different types of stabilizers have been developed and are now used widely in many applications. With the increasing use of polymers in exterior applications, there seems to be a growing need for excellent UV stabilizers such as TiO_2 to protect polymers from photodegradation (Kikkawa, 1995).

1.4 Importance/significance of the study

Biodegradable polymer composites have been developed from natural oils like epoxidized palm oil that has been used as monomer for production of resins. These vegetable oils have their own particular advantages like they are renewable products derived from natural oils and fats and are more readily biodegradable than the corresponding products made from petroleum sources.

Polymeric materials are commonly used of long-lasting products such as engineering applications, packaging, catering, surgery and hygiene. These polymers bring a significant contribution to a sustainable development in view of the wider range of disposal options with minor environmental impact.

The used of metal oxide as stabilizer with bio polymer in a coating application such as paint is a major concern in this study as the use of TiO_2 give no harm to environment. The stability of the biopolymer composites were tested under UV light using accelerated weathering tester which equivalent to the real outdoor weather condition.

1.5 Objective of the study

The main objectives of this project are:

(i) To prepare biopolymer (BP) and biopolymer composites (BPC) for mechanical properties determination; tensile of unirradiated and UV irradiated for degradation study.

(ii) To study the influence of UV irradiation on physical properties of BP and BPC.

1.6 Scope of the study

In this study, biopolymer (BP) and biopolymer composite (BPC) produced based on monomer of virgin and waste cooking oil. Waste cooking oil was obtained from Small and Medium Industries (SMIs). These BP components were named based on the starting vegetables oil such as virgin oil polymer (VOP) and waste oil polymer (WOP). BPC samples were doped with 2.5, 5, 7.5 and 10 wt. % of Titanium Dioxide (TiO_2). These samples were exposed using UV weatherometer at 250, 500, 750, 1000, 2000, and 3000 hours. The effects of UV light on the properties of BP and BPC were determined by tensile test and visual inspection based on the colour changes of the thin films. Meanwhile, Fourier transforms infrared (FTIR) spectroscopy and UV-Vis spectroscopy were used to provide valuable information of functional groups which can be used to determine the photo degradation of the BP and the influence of TiO_2 on the biopolymer composite. In addition, UV-Vis spectrophotometer was used to obtain the absorption spectra of BP and BPC.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer

Polymer is materials that the molecular structure consists of one or more structural units (monomers) repeated any number of times (Fried, 2008). Homopolymer has only one kind of structural unit which is repeated, while a copolymer has two or more different structural units which are repeated (Oil and Colour Chemists Association Southern Africa, 2011).

A polymer, from the Greek *poly***,** meaning “many”, and *meros* meaning “part” is a long molecule consisting of many small units (monomers) joined end to end. A polymer is analogous to a necklace made from many small beads (monomers). There are many types of polymers including synthetic and natural polymers. Certain polymer, such as proteins, cellulose, and silk, are found in nature which are produced by living organism, known as biopolymers, while many others, including polystyrene, polyethylene, and nylon are produced only by synthetic route (Mc Crum *et al.*, 2003; Wicks *et al.*, 2007).

Another common name for many synthetic polymers is plastic which comes from the Greek word "plastikos", suitable for moulding or shaping. Many objects in daily use from packing, wrapping, and building materials include half of all polymers are synthesized. Other uses include textiles, TV's, CD's, automobiles, and many other

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