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Photodegradation Mechanism of Biopolymer Blended with High Density Polyethylene (HDPE)

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ABSTRACT

Synthetic polymer such as polyethylene is used widely in industry, agricultures and daily life owing to its relatively low price and good mechanical and processing properties. These synthetic polymers are, however, often not environmentally friendly because they typically do not undergo the process of biodegradation and, of course, are dependent on a limited petroleum resource. Therefore, concerns on environmental problems caused using of non-degradable petrochemical polymers have caused an increasing interest in degradable polymers especially biopolymers from crop plants. Biopolymers have much potential and several advantages, but they possess some drawbacks as well. Despite increasing production capacity, they are still quite expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectation of converters or users. This concept has led to the development blending of biopolymer and High-Density Polyethylene (HDPE). In this study, 5, 10, 15, 20, 25 and 30% of Biopolymer (BP) was blended with HDPE known as BBP₅, BBP₁₀, BBP₁₅, BBP₂₀, BBP₂₅ and BBP₃₀ were prepared by melt-mixing process by using Brabender Plastograph® EC machine. BBP₅, BBP₁₀, BBP₁₅, BBP₂₀, BBP₂₅ and BBP₃₀ then were exposed in UV weatherometer by using UV Lamp Test Chamber Model HD-703 at different UV exposure, which is 250h, 500h, 750h, 1000h, 2000h, and 3000h. Physical properties and photodegradation mechanism development of BBP₅, BBP₁₀, BBP₁₅, BBP₂₀, BBP₂₅ and BBP₃₀ were examined by means of Fourier Transform Infrared (FTIR) at different UV exposure. The photodegradation mechanism of BBP₅, BBP₁₀, BBP₁₅, BBP₂₀, BBP₂₅ and BBP₃₀ shows relationship with the Norrish type I and Norrish type II reaction as indicated the possibilities of blended polymer degradation process was occurred.

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1. Introduction

Polymers have taken on a vital role as materials in modern applications in almost every sector of manufacturing, including aerospace, automotive, marine, infrastructure, medical devices, consumer products, and sports equipment due to their tunable properties, easy processability, high strength, resistance to chemical and physical degradation, and low cost. According to [1], approximately 140 million tons of synthetic polymers are produced worldwide every year while according to [2], from [3], these synthetic polymers have an annual production of 359 million tons in 2018 throughout the world. However, since polymers are extremely stable, their degradation cycles in the biosphere are limited. In the Western Europe alone, it is estimated that 7.4% of municipal solid wastes are plastic, which are classified as 65% polyethylene/polypropylene, 15% polystyrene, 10% PVC, 5% polyethylene terephthalate and remaining others. Environmental pollution by synthetic polymers, such as waste plastics and water-soluble synthetic polymers in wastewater has been recognized as a major problem [1].

Meanwhile, vegetable oils one of the common resources to produced natural product. It's also one of the most important classes of bio-resources for producing polymeric materials. Soybean, linseed, castor, sunflower, rape seed, and palm oils are some examples of plant oils. Plant oils usually extracted from plant oils while animal oils come from animal fats. Natural oils, which can be derived from both plant and animal sources, are abundant in most parts of the world, making them an ideal alternative to chemical feedstocks [4]. According to [5], in the chemical industry, vegetable oils have a wide range of applications such as soaps, drying agents, coatings, hydraulic fluids, lubricants, monomers (e.g., polyols and dimer acids), and polymers. While, according to [6], plant oils are renewable raw materials for a wide variety of industrial products, including coatings, inks, plasticizers, lubricants, and paints. Furthermore, soybean oil, for example, has been used extensively in the food processing industry such as in salad dressings, sandwich spreads, margarine, and mayonnaise and in non-food applications like crayons, paints, and soy candles. Meanwhile, according to [7], edible plant oil has been heavily used in cooking and also being utilized in the cosmetics and health industry. Biopolymers have much potential and several advantages, but they possess some drawbacks as well. Despite increasing production capacity, they are still quite expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectation of converters or users. Although natural polymers are available in large quantities and are also cheap, their properties are even farther from those of commodity plastics. Consequently, biopolymers must be often modified to meet the expectations of the market [8].

Therefore, polymer blending is an attractive method for producing new polymer materials; moreover, the properties of polymer blends can be controlled by adjusting their composition ratios. Numerous attempts have been made to enhance the properties of bio-based polymers by polymer blending [9]. The goal of blending might be the improvement or tailoring of properties to a certain application, or as it is often described, maximization of the performance of a material. However, the specific, primary motivation of blending could be much more diverse. Some example advantages of blending such as cost reduction, the improvement of mechanical properties generally, and impact resistance particularly or the decrease of sensitivity to water are all common aims [8]. This concept has led to the development of biopolymer and HDPE blends.

One of the possibilities of blended polymer degradation could be exposed to ultraviolet (UV) light. The morphology and the physical properties of the polymer changes when subjected to UV radiations from the sun, which cause the photodegradation of the polymer because of the chain scission or chemical cross-linking.

2. Methodology

2.1 High Density Polyethylene (HDPE)

HDPE (HI1600) injection moulding grade with a density of 0.94 to 0.965 g / cm³ and the HDPE melting point is 120 ° was supplied by Titan Petchem (M) Sdn. Bhd.

2.2 Bio-Monomer (BM)

VeSawit Palm oil was used as the original palm oil to produce the Biopolymer (BP). The conversion of the monomer starts with the catalyst preparation to generate the epoxies from the unsaturated fatty compound, and the second reaction is the opening of the acid catalyst ring of the epoxies to form polyols or bio-monomer (BM) [10-19].

2.3 Blended Biopolymer (BBP)

Bio-monomer (BM) generated from palm oils has been mixed with cross linking agent that is MDI as the composition ratio is 1: 0.5 and Toluene was used as the solvent. The mixture was mechanically stirred for 10 minutes at 50°C until the mixture become highly viscous compound. The compound was poured into the BrabenderPlastograph® EC machine at 130°C and 25 rpm with 30g of HDPE was already poured in the machine 10 minutes before. The blended biopolymer produced were crushed by using crusher (Plastic Granulator SLM 50FY) to produce smaller particle and ready for injection moulding process. This blended biopolymer with HDPE named as BBP₅, BBP₁₀, BBP₁₅, BBP₂₀, BBP₂₅ and BBP₃₀ as referred to different loading of biopolymer with 5, 10, 15, 20, 25 and 30 % (wt /wt biopolymer).

2.4 Injection Moulding

To produced dogbone tensile sample, BBP with different ratio were then fed to injection moulding machine (Nissei Horizontal Screw Type Injection Moulding NP7 Real Mini from Japan). The mould was designed according to ISO 527 (5A). Barrel temperature set points from nozzle zone which is 170°C, 170°C for front zone, 165°C for middle zone, 160°C for rear 1 zone, 155°C for rear 2 zone and 70°C for feed zone.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was conducted using Perkin–Elmer (UK) Spectrum One FT-IR spectrometer (in the range 4000–400 cm⁻¹, absorbance units) to provide detailed information of the functional groups present at the surface of the samples. Scans were executed at scanning of 32 times at resolution 4 cm⁻¹. The spectra were acquired using the spectrometer of Attenuated Total Reflection (ATR). BBP were placed flat on the crystal plate and clamped down for infrared spectroscopy analysis. Materials generated a spectrum or fingerprint that identified the molecular composition of the materials.

2.6 UV Weathering Test

35 dumbbell shape samples BBP were produced from injection moulding were then exposed to UV irradiation in weatherometer UV Lamp Test Chamber Model HD-703 (Haida International

Equipment Co., LTD) according to ASTM D 4587 at 50° C with predetermined exposure time at 0h, 250h, 500h, 750h,1000h, 2000h and 3000h.

3. Results

3.1 Chemical Reaction of Biopolymer (BP) and Blended Biopolymer (BBP) and FTIR Determination

The high hydroxylated palm oil was successfully converted into solid biopolymer (BP) by mixing with crosslinking agent of 4, 4'-Methylene Diphenyl Diisocyanate (MDI) and toluene as solvent. The chemical reaction is as shown in Figure 1 below

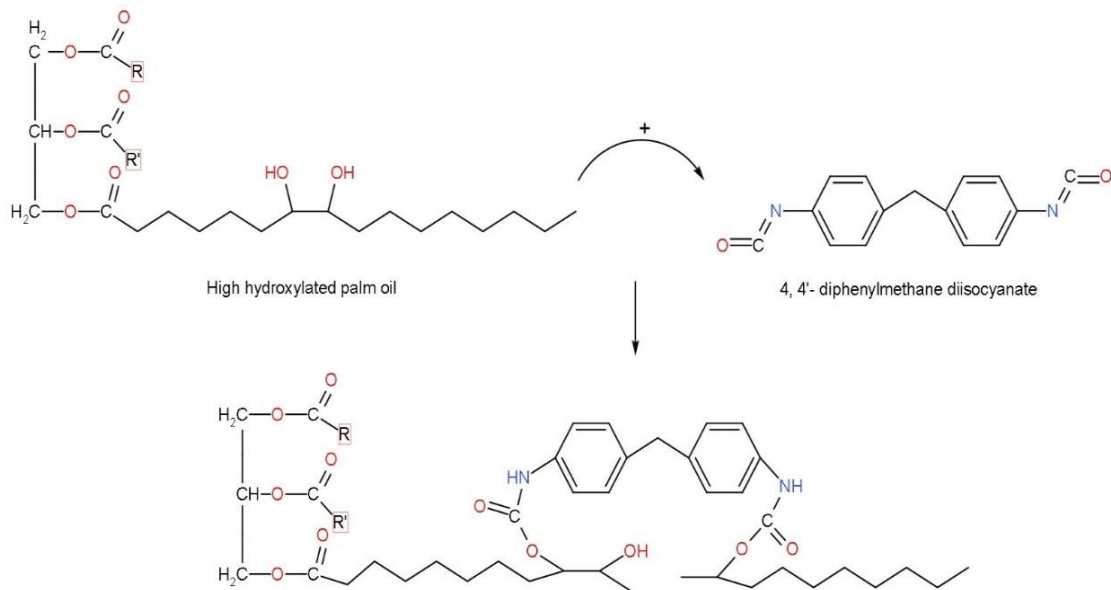


Fig. 1. Preparation of BP with crosslinking agent MDI

BBP was produced by blending HDPE with BP at different ratio (5%, 10%, 15%, 20%, 25% and 30%) by using Brabender Plastograph® EC machine at 130°C and 25 rpm speed rate for 20 minutes. The expected chemical reaction of BBP is as shown below in Figure 2. The successful fabrication reaction of hydroxylated monomer and cross-linker until solidify was postulated using chemical structure of the blending process of BP with HDPE. Nucleophilic reaction of hydroxylated palm oil with 4, 4'-Methylene Diphenyl Diisocyanate (MDI) influence the cross-linking reaction until BP solidification occurred as refer to Figure 1 as the general reactions step. As referring to Figure 2, the blending process between two different polymer HDPE and BP was successfully reacted and expected to give high cross-link structure of BBP blend as refer to Figure 3.

As seen in the carbonyl region (1650–1750 cm⁻¹) in Figure 3, by increasing percentages of BP, the carbonyl stretching band were increased in absorbance intensity value and shifted slightly to a lower wavelength. This is due to the formation of hydrogen bonding between alkenes and carbonyl groups of two polymers. Broad spectra into nearly sharp absorbance intensity at 1698 cm⁻¹ for BBP is assigned to associated carbonyl as a consequence of the hydrogen bonding formed between two different polymers.

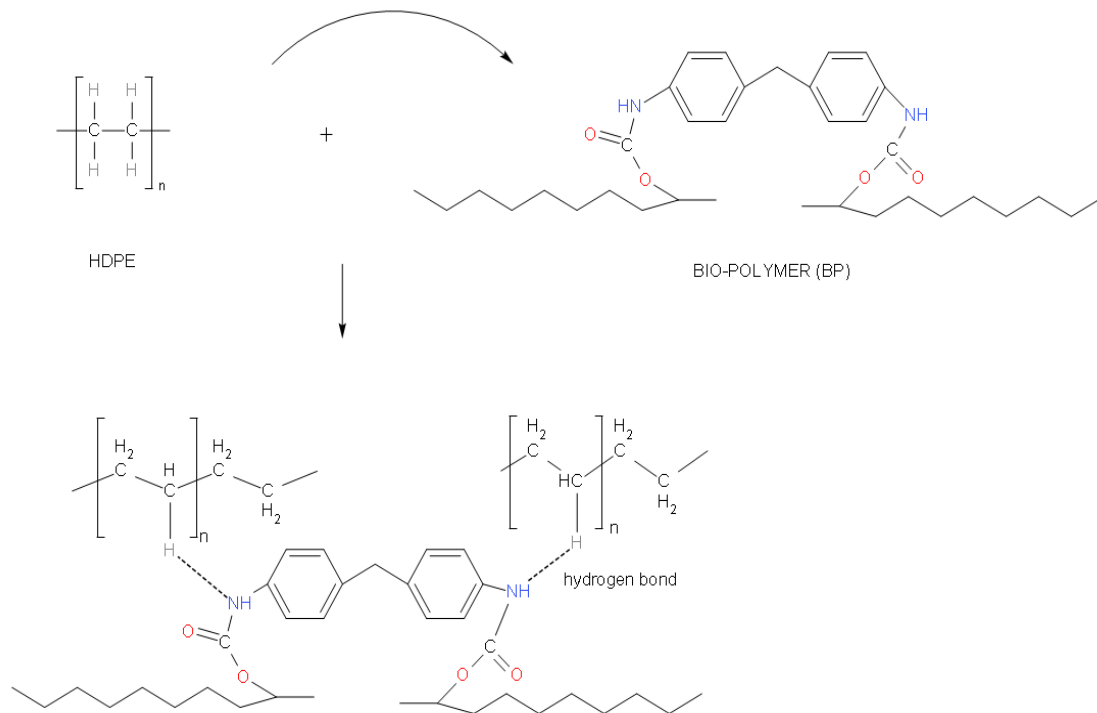


Fig. 2. Expected chemical structure of the BBP

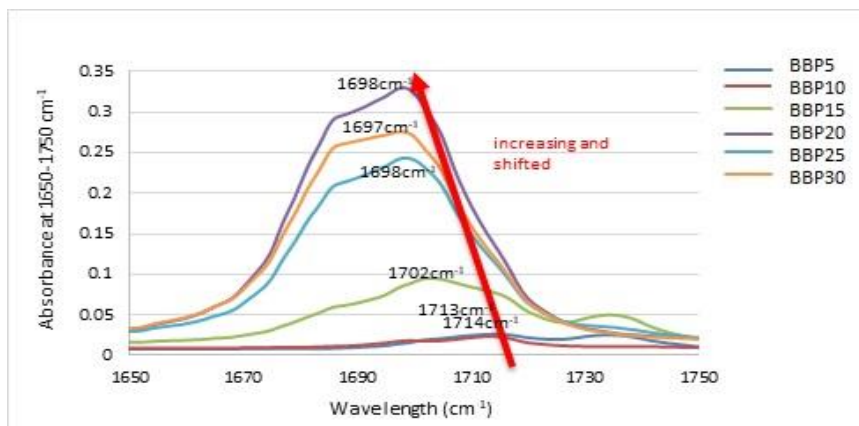


Fig. 3. Absorbance of BBP₅ to BBP₃₀ in carbonyl region at 1650-1750 cm⁻¹

3.1.1 Fourier transform infrared spectroscopy (FTIR) for blending biopolymer (BBP) and its chemical reaction mechanism upon UV irradiation exposure

From Figure 4 to Figure 9, BBP show most of the absorbent peak were highest at the higher UV irradiation exposure especially at carbonyl group (C=O group) and C-H peak. In this degradation process, UV light, heat and oxygen are the main factors that contributed to the degradation process. According to [20], there were two main groups of factors that causing the most polymers degradations, which are chemical factors such as oxygen, chemicals, ozone, polymerization catalysts, etc. Another factor is physical factors such as light, ionizing radiation, heat, mechanical processing, etc. In this study, the main factors of degradation are UV light, heat that produced from the light and also oxygen from the surrounding during exposure process.

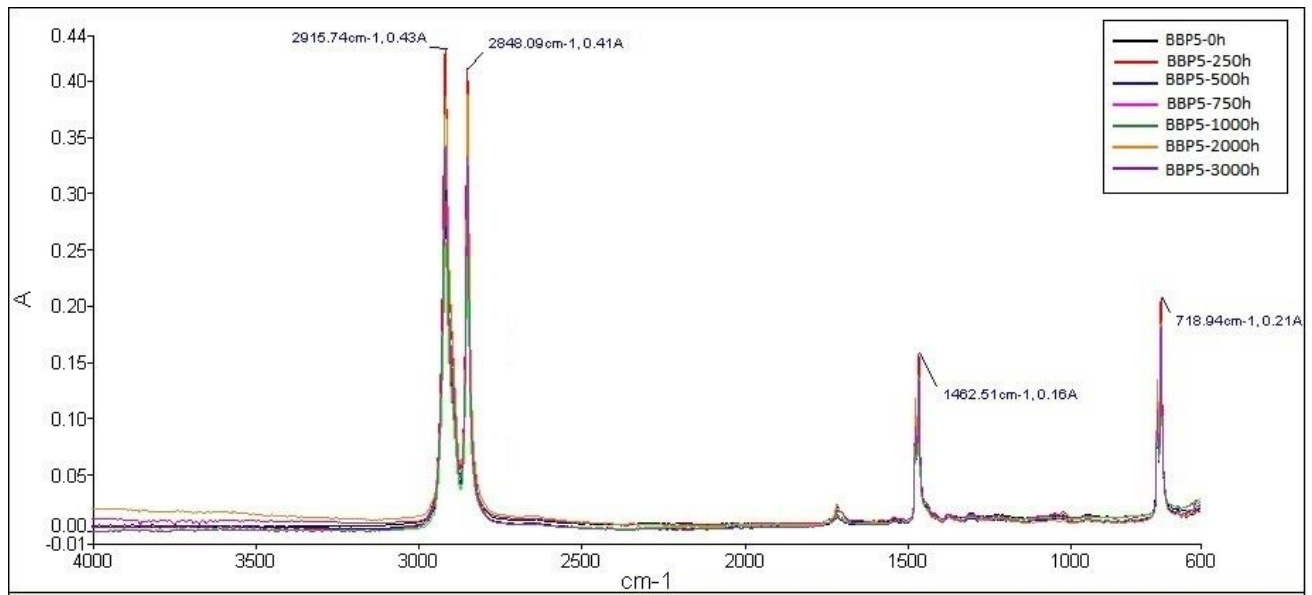


Fig. 4. Overlay of FTIR spectra of BBP_{5-0h}, BBP_{5-250h}, BBP_{5-500h}, BBP_{5-750h}, BBP_{5-1000h}, BBP_{5-2000h}, BBP_{5-3000h}

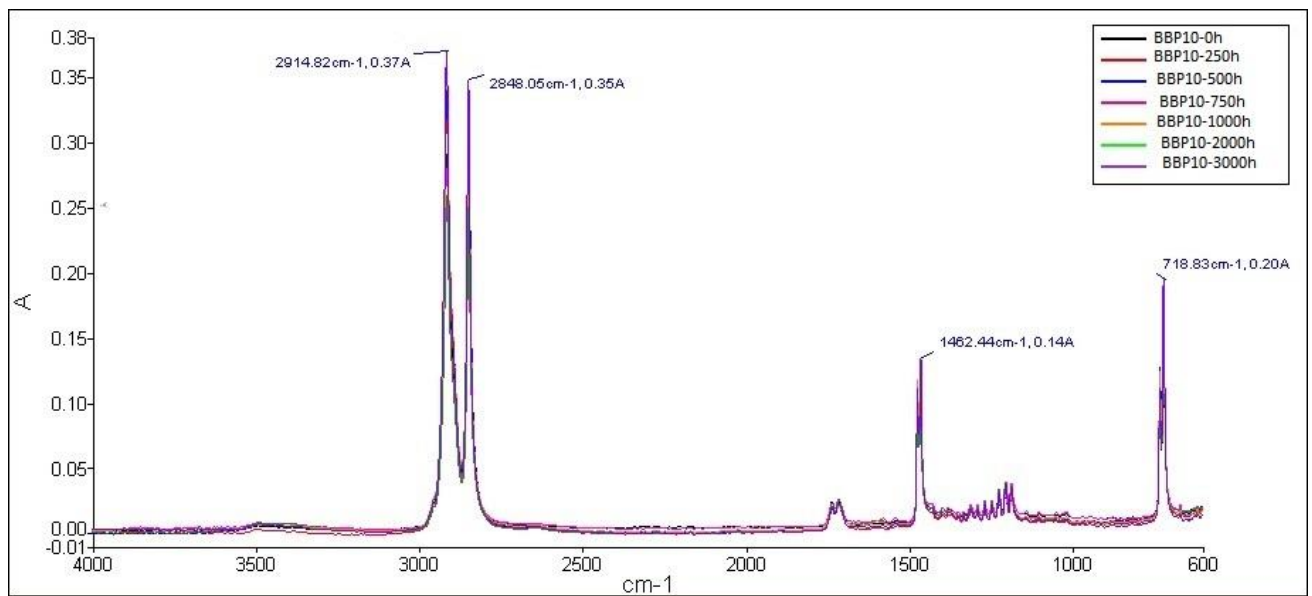


Fig. 5. Overlay of FTIR spectra of BPL_{10-0h}, BPL_{10-250h}, BPL_{10-500h}, BPL_{10-750h}, BPL_{10-1000h}, BPL_{10-2000h}, BPL_{10-3000h}

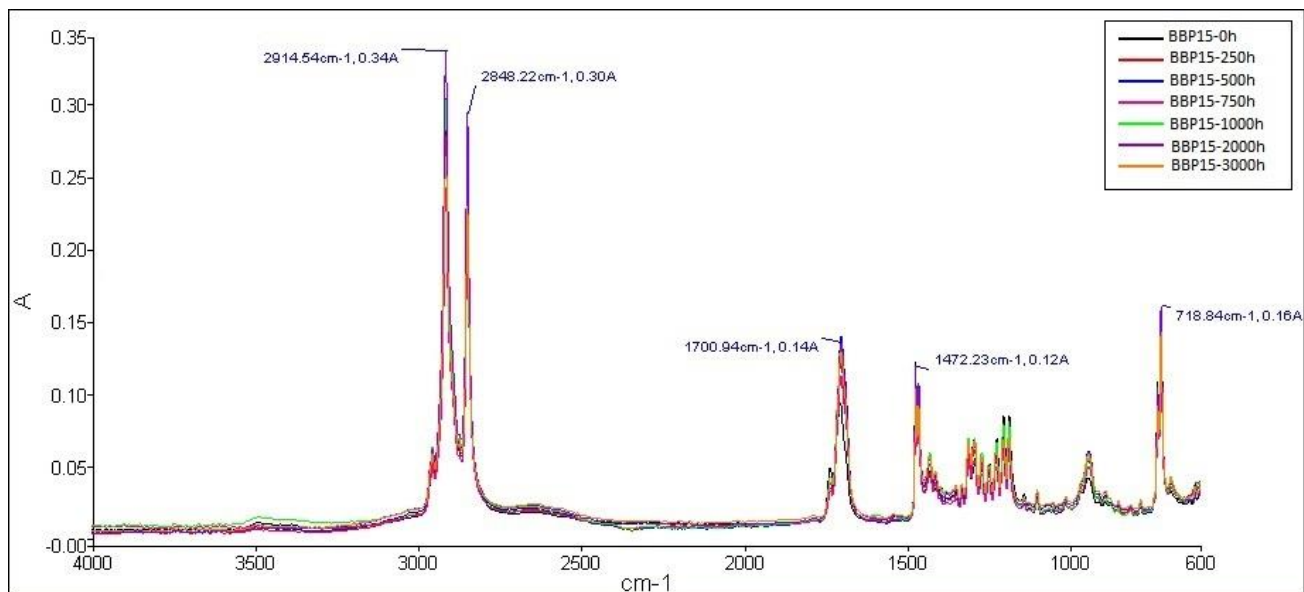


Fig. 6. Overlay of FTIR spectra of BBP_{15-0h}, BBP_{15-250h}, BBP_{15-500h}, BBP_{15-750h}, BBP_{15-1000h}, BBP_{15-2000h}, BBP_{15-3000h}

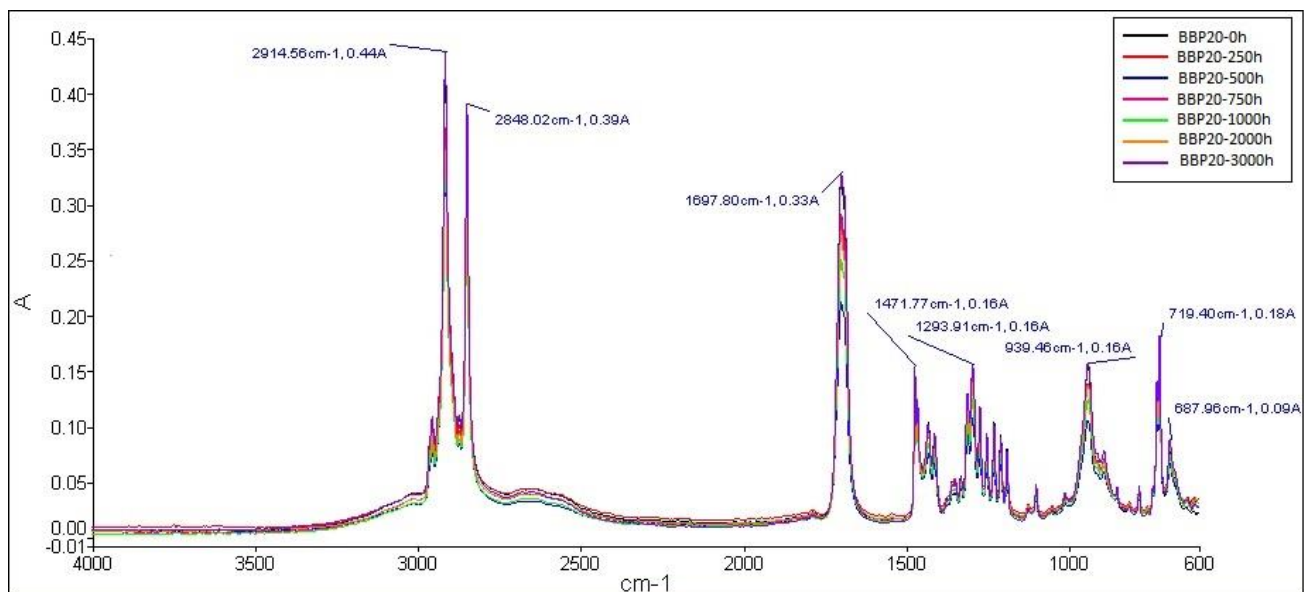


Fig. 7. Overlay of FTIR of BPL_{20-0h}, BPL_{20-250h}, BPL_{20-500h}, BPL_{20-750h}, BPL_{20-1000h}, BPL_{20-2000h}, BPL_{20-3000h}

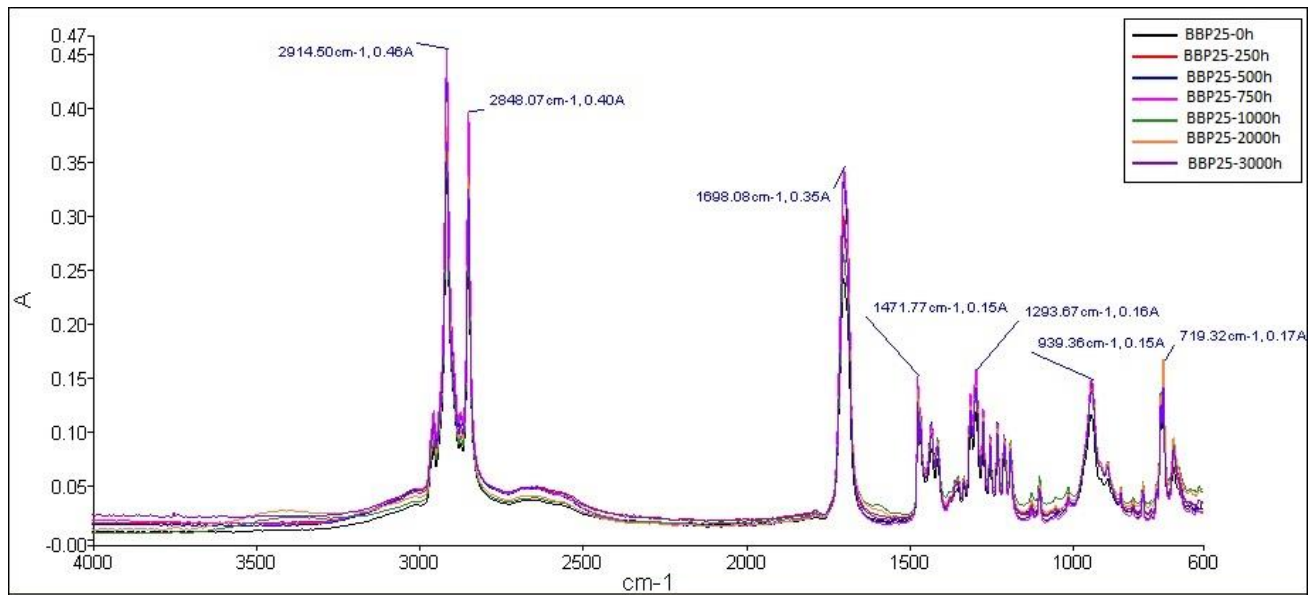


Fig. 8. Overlay of FTIR spectra of BPL_{25-0h}, BPL_{25-250h}, BPL_{25-500h}, BPL_{25-750h}, BPL_{25-1000h}, BPL_{25-2000h}, BPL_{25-3000h}

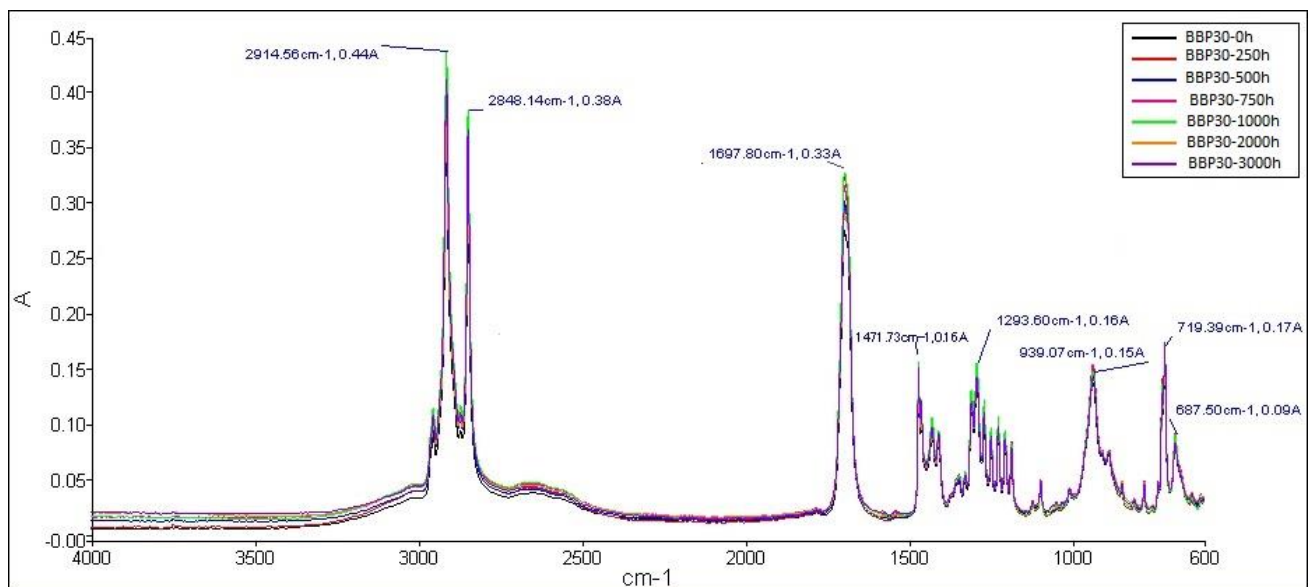


Fig. 9. Overlay of FTIR spectra of BBP_{30-0h}, BBP_{30-250h}, BBP_{30-500h}, BBP_{30-750h}, BBP_{30-1000h}, BBP_{30-2000h}, BBP_{30-3000h}

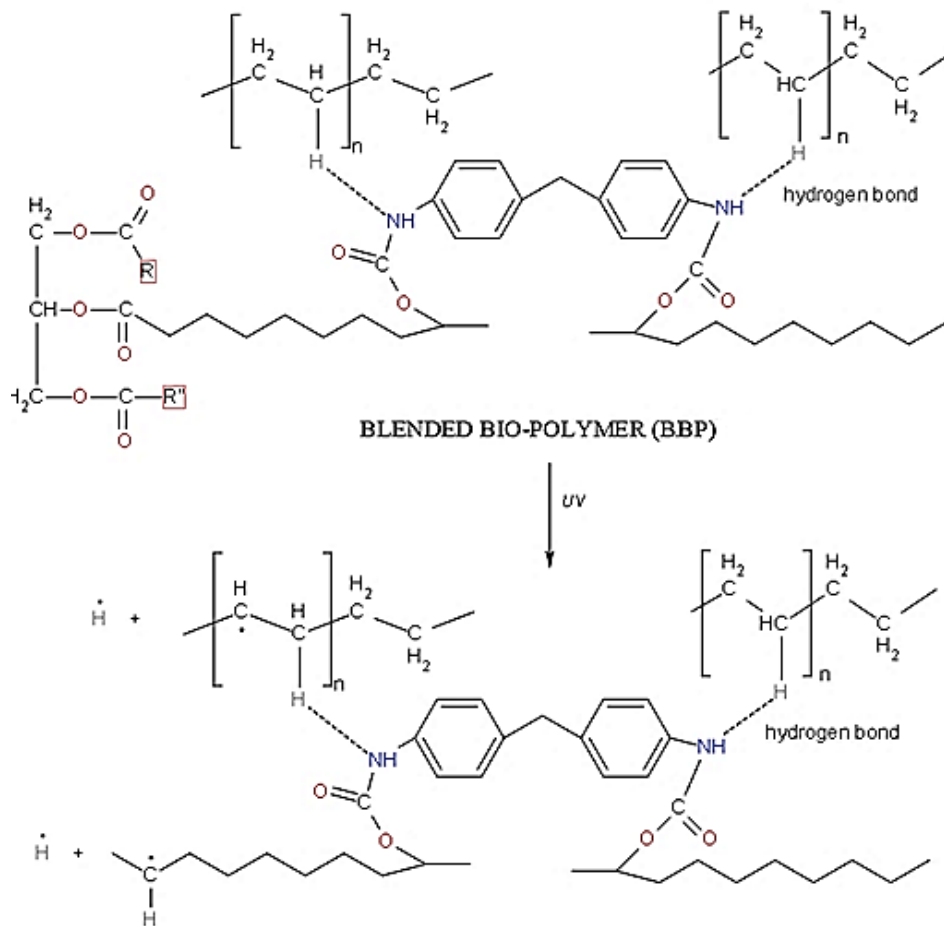
The degradation process starts by releasing a free radical either by energetic photon or by breaking a chemical bond thermally or chemically. This called initiating the process which is repeated several times as long as the light, heat and oxygen is active. Besides, it is also possible for the C-C bonds to be broken due to the energy supplied. In this cases, photo-irradiation and oxygen were supplied to the sample so that photo-oxidation reactions continued.

The highly reactive polymer radical (C*) can react with oxygen resulting in the formation of a peroxy polymer radical (COO*). Two of the hydrogen radicals (H*) can react together resulting in the release of hydrogen gas (H₂). The rate of formation of these peroxy radicals is controlled by the propagation of oxygen into the polymer. The newly formed peroxy radical (COO*) is able to extract hydrogen from the polymer chain to form hydro-peroxide and another polymer radical (C*) as shown

in Figure 10(a) and Figure 10 (b). These hydro-peroxides are unstable and so will decompose to form further radicals from the continued UV radiation [20].

The commonly product associated with oxidation is the production of carbonyl groups (C=O), the formation of which can result in a range of new molecules. The formation of carbonyl groups is also thought to play a key role in the chain scission of the polymer back bone. The formation of a ketone and carboxylic group which is measurable by FTIR spectroscopy with absorption at 1725 cm^{-1} - 1705 cm^{-1} is common as shown at lower percentage blending BP of 5 %, 10% and 15% loading for BBP (Figure 4 to Figure 6).

Another common carbonyl group seen in photo-oxidised is amide group, measurable by FTIR spectroscopy with absorption in $1700\text{--}1640\text{ cm}^{-1}$ when increasing in percentages of BBP (20%, 25%, 30%) as shown in Figure 7 to Figure 9. The formation is thought to typically result in the chain scission of and the polymer chain. This can relate to the Norrish I and Norrish II reaction that occur in soft and hard segment as shown in Figure 10 (c) and Figure 10(d) which is produces ketone, amide group and carboxylic acid as the UV exposed. The carbonyl group (C=O) is located at wave number at 1740 cm^{-1} to 1640 cm^{-1} of weathering is one of the strongest IR absorptions and are a good indication of the formation of degradation products [21].



(a)

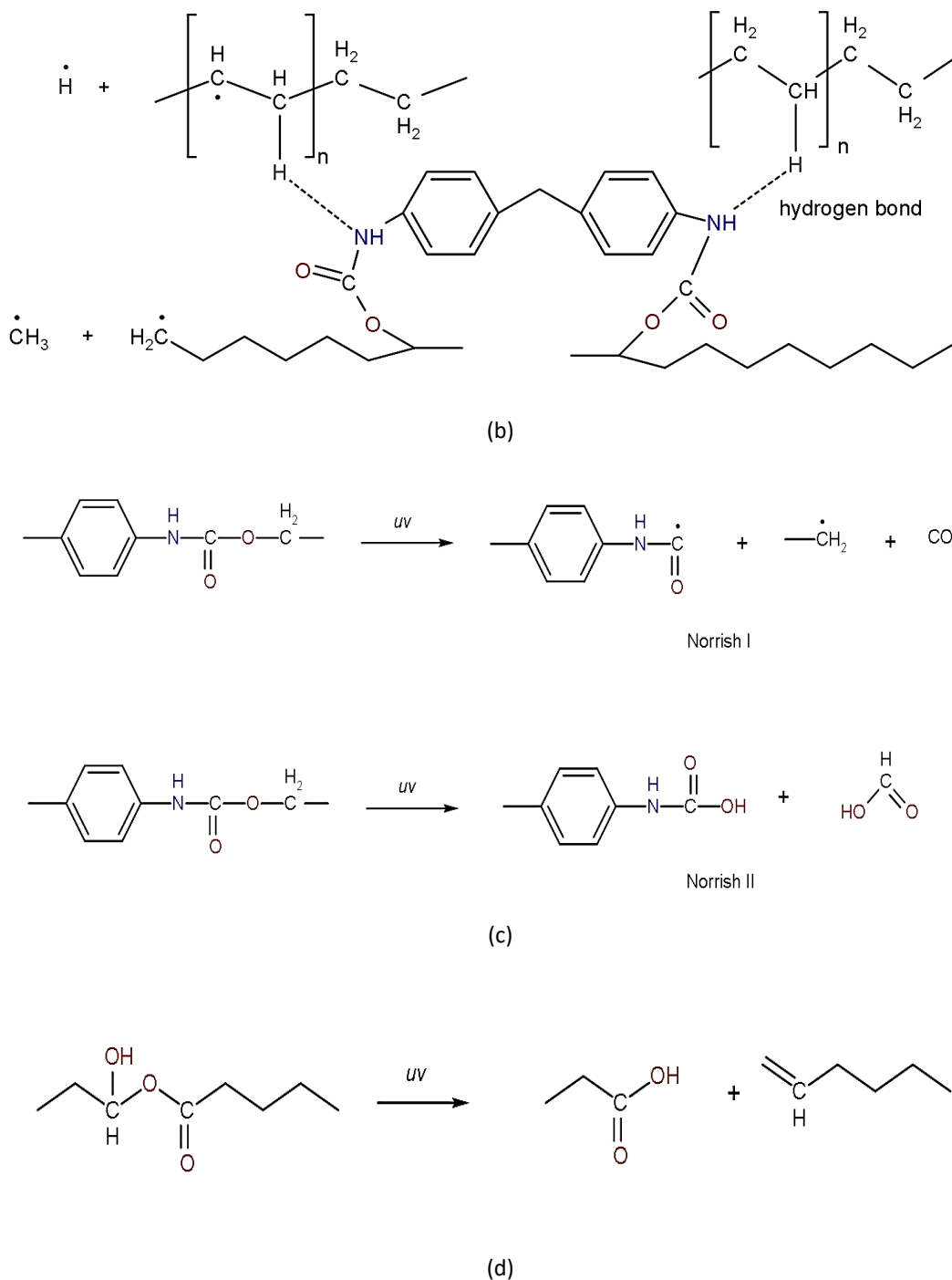


Fig. 10. (a) The hydrogen is separated from the polymer chain leaving hydrogen radical ($\dot{\text{H}}$) and polymer chain radical ($\dot{\text{C}}$) (b) Breaking the C-C bond (c) Norrish I and Norrish II reaction in hard segment (d) Norrish II reaction in soft segment

4. Conclusions

In this research was examine the successfully of blended BP with HDPE and measure photo degradation process upon UV irradiation exposure of blended polymer by different percentage of BP loading and different hour UV irradiation exposure.

For all percentages of BBP show most of the absorbent peak were higher at the higher percentages and higher UV exposure. BBP₅, BBP₁₀, BBP₁₅ show formation of a ketone and carboxylic

acid group while increasing to higher UV exposure of BBP₂₀, BBP₂₅, BBP₃₀, shows formation of another group that is amide group. This can relate to the Norrish I and Norrish II reaction that occur in soft and hard segment which produces ketone, carboxylic acid and amide group when increase in UV exposure and good indication of the degradation process occur.

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