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# Sustainable Waste Oils Polymer Doped with Titanium Dioxide as Ultraviolet Stabilizer

Anika Zafiah Mohd Rus<sup>1,\*</sup>, Nurul Syamimi Salim<sup>1</sup>, Hanani Abd Wahab<sup>1</sup>, Noraini Marsi<sup>1</sup>, Nik Normunira Mat Hassan<sup>1</sup>, Hendi Saryanto<sup>1,2</sup>, Nurulsaidatulsyida Sulong<sup>1,3</sup>, Nik Alnur Auli Nik Yusuf<sup>1,4</sup>, Muhammad Hafizh Alamsyah<sup>5</sup>, Ita Mariza<sup>5</sup>

- <sup>1</sup> Sustainable Polymer Engineering, Advanced Manufacturing and Materials Center (SPEN-AMMC), Faculty of Mechanical and Manufacturing, Engineering Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia
- <sup>2</sup> Mechanical Engineering Programme, Universitas Muhammadiyah Prof. Dr HAMKA, Jl. Tanah Merdeka No. 6, Pasar Rebo, 13830 Jakarta Timur, DKI Jakarta, Indonesia
- <sup>3</sup> Fakulti Kejuruteraan Mekanikal, Universiti Teknologi MARA (UiTM), Caw. Johor, Kampus Pasir Gudang, Jalan Purnama, 81750 Masai, Johor, Malaysia
- <sup>4</sup> Universiti Malaysia Kelantan, 17600, Jeli, Kelantan, Malaysia
- <sup>5</sup> PT Inoac Polytechno Indonesia Plant, Kawasan Bintang Puspita Dwi Karya, Wanasari, Teluk jambe Barat, Karawang, West Java 41361, Indonesia

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### ABSTRACT

Waste oils for biopolymer conversion process namely as sustainable monomers with biodegradable properties that are prepared in a multi-stage synthesis route from vegetable oils. These sustainable monomers from virgin oil (VO) and waste oil (WO) were mixed with hardener to form virgin oil sustainable polymer (VOP) and waste oil sustainable polymer (WOP). VOP and WOP were left to cure at ambient temperature for at least 6 hours and removed from the mould. The steps were repeated to fabricate sustainable polymer composite (SPC) doped with different percentages of TiO<sub>2</sub>. The samples of biopolymer (BP) are based on VOP and WOP, while biopolymer composites (BPC) were based on TiO<sub>2</sub> percentage. The thickness of the prepared sample is from 110 to 250  $\mu\text{m}$  according to ASTM D1005-95. The study on the thermal stability property of these polymers in oven thermal exposure shows a significant stability of these polymer films which was determined by calculating the carbonyl index (CI) of polymer films. The VOP shows the least stability upon thermal exposure which its molecular chains contain many reactive sites, thus providing more potential for degradation, resulting in lower thermal and bio-stability. Also, it is revealed that polymers are susceptible to photodegradation initiated by heat or UV light during processing or long-term use. Therefore, UV accelerated weathering test was conducted according to ASTM D 4587-Standard practice for fluorescent UV-condensation exposures of paint and related coatings. Furthermore, a tensile test was conducted to determine the strength and ductility of a material. The mechanical properties of polymer thin films were significantly reduced by UV irradiation exposure. As opposed to WOP, VOP gives better results for tensile strength and elongation at break.

\* Corresponding author.

E-mail address: [zafiah@uthm.edu.my](mailto:zafiah@uthm.edu.my)

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## 1. Introduction

Natural oils are regarded as an important class of renewable resources. These renewable resources are vegetable oils derived from naturally occurring plants such as sunflower, cotton, and linseed, which are primarily composed of triglycerides. Soybean, linseed, sunflower, rapeseed, castor, palm, tall, and rapeseed oils are common triglyceride oils used in the synthesis of oil-modified polymers. The double bonds in these vegetable oils are being manipulated, used as reactive sites, and polymerized via epoxidation. According to Yow *et al.*, [1] the epoxidation of these vegetable oils has a significant potential for low-cost, renewable, and sustainable materials for industrial uses. It is also suitable to replace or substitute petroleum-based polymers. Through innovation for new bio-based polymers, it is believed to compete with or even outperform existing petroleum-based materials in terms of cost performance, with the added benefit of being environmentally friendly. As a result of Zhan *et al.*, [2] research into new biobased thermoset polymers is advancing.

Plastics are long-chain polymeric compounds that humans have made. In the early half-century, synthetic polymers began to replace natural materials in practically every domain, and today, plastics are an essential part of our lives. Plastics' stability and longevity have steadily increased over time, and this class of materials is generally considered a metaphor for materials that are resistant to a wide range of environmental impacts. Today's plastics are created from both inorganic and organic basic components, including carbon, silicon, hydrogen, nitrogen, oxygen, and chlorine. The raw materials for plastics are derived from oil, coal, and natural gas. Thus, according to Shah *et al.*, [3] these plastics are resistant to microbial attack, but some evolutions have developed novel enzyme structures that are capable of dissolving synthetic polymers during their brief existence in nature.

In previous research by Sasek *et al.*, [4] the use of biodegradable polymers, specifically in uses with a short product lifespan, such as packaging, would be an environmentally economical option for minimizing solid waste material. Koutny *et al.*, [5] stated that plastics are also applied in huge amounts in agriculture for green house construction or applied directly to the soil surface as mulching films, raising concerns about whether microplastics damage soil quality.

Bioplastics are classified as either biodegradable plastics (derived from fossil materials) or bio-based plastics (manufactured from biomass or renewable resources). Under diverse environmental conditions, with the presence or action of various microbes, polymers harvested or taken from natural resources can be degraded and altered. Polymers have also been classified according to their synthesis technique or source, as follows:

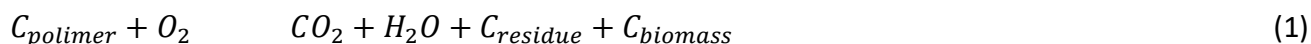
- i. Polymers generated or synthesized directly from plant or animal biomass, such as polysaccharides and proteins.
- ii. Polymers are created using traditional chemical synthesis with sustainable bio-based monomers such as polylactic acid (PLA) as basic ingredients.
- iii. Microorganism-produced polymers such as polyhydroxyalkanoates (PHAs), cellulose, xanthan, and pullulan.

The production of biopolymers from renewable or sustainable natural resources gives added value to the new direction for the development of biodegradable polymers. Plant oils, or vegetable oils, are presently regarded as the most important renewable raw ingredients for the manufacture of bio-based polymer products. According to Narine *et al.*, [6] vegetable oils are triglycerides of fatty acids that can be turned into high-value biochemicals for a range of industries. These chemicals must be functionalized to generate polyols before they can be used as starting ingredients for polyurethane production. Epoxidation and ring-opening reactions with halo acids or alcohols, ozonolysis, and hydration are among the popular methods for functionalizing unsaturated vegetable

oils. They are then polymerized further to form a high-molecular-weight, solid polymer thin film. Cross-linking agents such as methylene-4, 4' diphenyl diisocyanate (MDI), introduced by Rus and Abdullah [7], are used in the curing process.

Polyurethanes (PUs) are well-known resins that are employed in a wide range of commercial and industrial applications. This is due to its high tensile strength, chemical resistance, processability, and mechanical qualities. One of the disadvantages of PU-based materials is their extreme sensitivity to light, specifically under exposure to ultra-violet (UV) light. Polyurethanes made with an aromatic isocyanate will turn yellow on exposure to UV light. The yellowing is caused by an oxidation reaction in the backbone of the polymer. According to Rosu *et al.*, [8] irradiation modifies the physical and chemical characteristics of polymer surfaces and results in rapid color change and degradation.

Biodegradation is a broad field that involves the use of a variety of microorganisms to dissolve chemical bonds. According to Seo *et al.*, [9] this is likewise centered on the bacterial catabolism routes of selected aromatic contaminants in aerobic culture conditions. Biodegradable polymers created from renewable sources (plants and microorganisms) are adequate for land disposal since they depict the complete mineralization of the starting chemical to simpler compounds such as CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub>, and other inorganic compounds, as stated in Mohid *et al.*, [10]. Therefore, microorganisms are responsible for plastic biodegradability by using it as a food source. During aerobic biodegradation, carbon in polymer molecules is converted by microorganisms into biomass, or humus, water, carbon residues, and carbon dioxide gas, as defined in Eq. (1):



From Kijchavengkul *et al.*, [11] and Lucas *et al.*, [12] this activity results in carbon recycling, mineralization (CO<sub>2</sub>, H<sub>2</sub>O, and salts) of organic molecules, and the creation of new biomass. Enzymes from naturally existing microbes (like bacteria and fungi) attack and destroy biodegradable plastics under certain circumstances found in soil and composts. Small bits of macromolecules are digested by bacteria. The byproducts of this metabolic activity are released and become part of natural material cycles. Microorganisms require food (nutrients); hence, the amount of nutrients accessible has a significant effect on the pace of deterioration.

Thermal degradation of polymers is molecular degeneration as a response to heating at elevated or high temperatures. According to Tang *et al.*, [13] previous studies, the elements of the polymer's long chain structure can begin to split and react with one another, altering the polymer's properties. The stability of polyurethanes when exposed to external conditions over time represents one of the most essential qualities in various high-interest applications, as stated by Flandrin *et al.*, [14]. Carbonyl groups then act as photolytic cleavage centers for the polymeric chains. Cleaved chains are most often ended by carboxylic groups, but esters, ketones, alcohols, and double bonds will also be detected.

Hydrolytic breakdown. Hydrolytic bond cleavage occurs in biodegradable polymers, resulting in water soluble breakdown products that can dissolve in an aquatic environment and polymer erosion. Degradation is a biochemical process in this sense, whereas erosion includes physical events like dissolving and diffusion. The most common hydrolytic breakdown reaction is the hydrolysis of PU's ester bond. Hydrolysis can also dissolve urea and urethane bonds, but at a slower rate. Hydrolysis is accelerated by acidic environments.

In general, the degradation rate of polymeric materials is greatly influenced by the nature of the substance and the abrasiveness of the environment to which they are exposed. This study discusses current research on the degradation of biodegradable polymers as well as the use of several methodologies for in vitro degradation analysis.

## 2. Methodology

### 2.1 Materials

Waste vegetable cooking oil was collected from small and medium entrepreneurs (SMEs) nearby and used in the process of synthesizing bio-monomers. The monomer preparations begin with the catalyst used to generate hydroxylated epoxies from unsaturated fatty compounds, followed by the acid ring opening to create hydroxylated polyols or monomers, as taken from previous studies [15-18].

### 2.2 Samples Preparation

Unsaturated waste oil was mixed with water, orthophosphoric acid, and hydrogen peroxide before being heated to 100°C. Then, the bio-monomers were added with cross-linking agents, diphenylmethan-4, 4'-diisocyanate, and 98% (MDI) in a ratio of 1:0.5. A simple casting method into the plastic tray was used to shape bio-polymer thin films of VOP and WOP according to ASTM D1005-95 (average thickness of 110-150 µm; initial weight: 10 mg) [19]. The above steps were repeated to fabricate sustainable polymer composite (SPC) doped with different percentage of TiO<sub>2</sub>. The samples of BP are based on VOP and WOP while BPC was namely according to TiO<sub>2</sub> percentage as VOP<sub>2.5</sub>, VOP<sub>5</sub>, VOP<sub>7.5</sub>, and VOP<sub>10</sub>; WOP<sub>2.5</sub>, WOP<sub>5</sub>, WOP<sub>7.5</sub>, and WOP<sub>10</sub> respectively.

### 2.2 Sample Preparation for Ultra Violet Irradiation Exposure, Tensile Test, Hydrolytic Degradation and Carbonyl Index

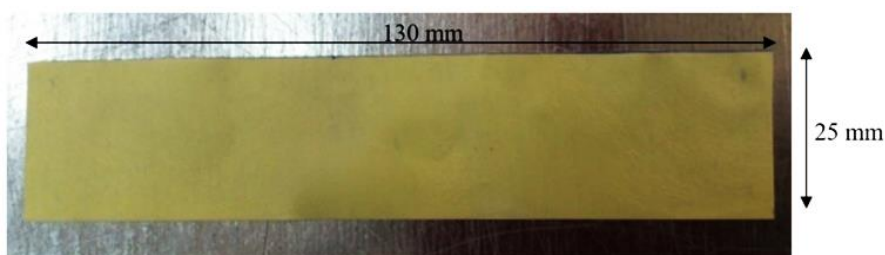
A UV-accelerated weatherometer from Haida International Equipment Ltd. was used to irradiate samples with UV light. The UV-accelerated weathering test was conducted according to ASTM D 4587-Standard Practice for fluorescent UV-condensation exposures of paint and related coatings [20]. The UV Weatherometer used UV irradiation, which 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. The BP and BPC thin film samples were placed on a rack with a rack holder as shown in Figure 1 in the UV weatherometer chamber at 50°C with different exposure times at 250, 500, 750, 1000, 2000, and 3000 hours of UV exposure to examine the changes in mechanical and physical properties.



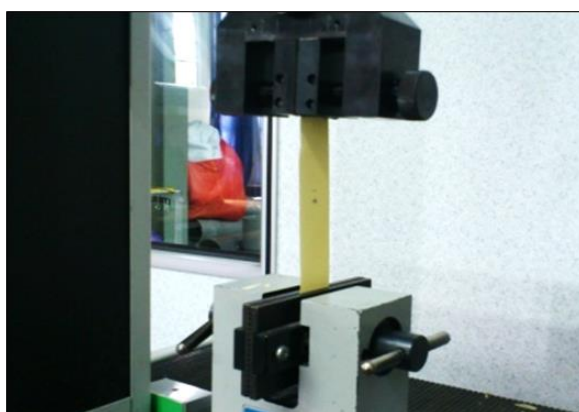
**Fig. 1.** Biopolymer thin film samples on a rack for UV light exposure

Tensile strength, elongation at break, and strain at break were measured by a Universal Testing Machine (LLOYD Instruments LR30K) with a load range of 20N, a cross-head speed of 500 mm min<sup>-1</sup>, a gauge length of 100 mm, and an efficiency of  $\pm 1\%$ . All specimens were tested at room temperature. A minimum of five samples were analyzed to obtain an average result. The original length and area of the gauge sample were measured using vernier calipers. The sample was mounted between two jaws of the tester.

Stress tests for each material were according to ASTM D882 [21], which is the standard test method for tensile properties of thin plastic sheeting and is very similar to the common ASTM D638. The plastic material is pulled until it breaks to measure its elongation, tensile modulus, tensile yield strength, and tensile strength at break. However, it is designed specifically for thin sheeting and films less than 1 mm (0.04") thick, whereas the BP and BPC film sample thicknesses were 0.11-0.25 mm. The ASTM D882 test specimens are rectangular, as shown in Figure 2. Care must be taken to ensure that the film is in line with the direction of pull, as shown in Figure 3. The average tensile strength for the films was calculated, and the results were compared with unexposed polymer thin film samples.



**Fig. 2.** Biopolymer as thin film sample for tensile test



**Fig. 3.** The sample is mounted between two jaws of the tester and in line with the direction of pull

A hydrolytic degradation test was performed by immersing a thin film sample in a basic aqueous solution (distilled water). Each sample was stored in a closed container containing 100 ml of solution. The polymer sample was obtained at 10-day intervals and dried in the oven for 1 hour before being weighed. The pH of the water was also measured. A Perkin-Elmer (UK) Spectrum One FTIR spectrophotometer (in the range of 4000 to 400 cm<sup>-1</sup>, absorbance units) was used to investigate the changes in sample chemistry caused by heat exposure. Thermal deterioration of VOP and WOP thin films was tested for five hours in an oven at 50°C, 100°C, 150°C and 200°C. The carbonyl index (CI) was calculated as the ratio of the peak area between 1680 cm<sup>-1</sup> and 1800 cm<sup>-1</sup> to the peak area

between 2950 and 2850  $\text{cm}^{-1}$  (which is the characteristic vibration of stretching band of CH). The CI at various temperatures is used to determine the variance in deterioration. The presence of the NH group may be seen at 3400  $\text{cm}^{-1}$ , carbonyls between 1800 and 1800  $\text{cm}^{-1}$ , and alkyls between 2930 and 2860  $\text{cm}^{-1}$ . Based on previous study by Rus, for each FTIR spectra, at least two replicates were evaluated, and the average CI values are presented with good repeatability (5%) [17].

### 3. Results and Analysis

#### 3.1 Mechanical Properties of BP and BPC upon UV Irradiation

This The BP and BPC with average thickness of 110-250  $\mu\text{m}$  with standard deviation  $\pm 0.02$  using micrometer according to ASTM D1005-95. The average thickness,  $t_{\text{avg}}$  for VOP and WOP is 0.148 to 0.91 mm and 0.44 to 0.221 mm respectively. Figure 4 shows the plotted graph of average thickness of BP and BPC in the thickness range of thin film between 110-250  $\mu\text{m}$ .

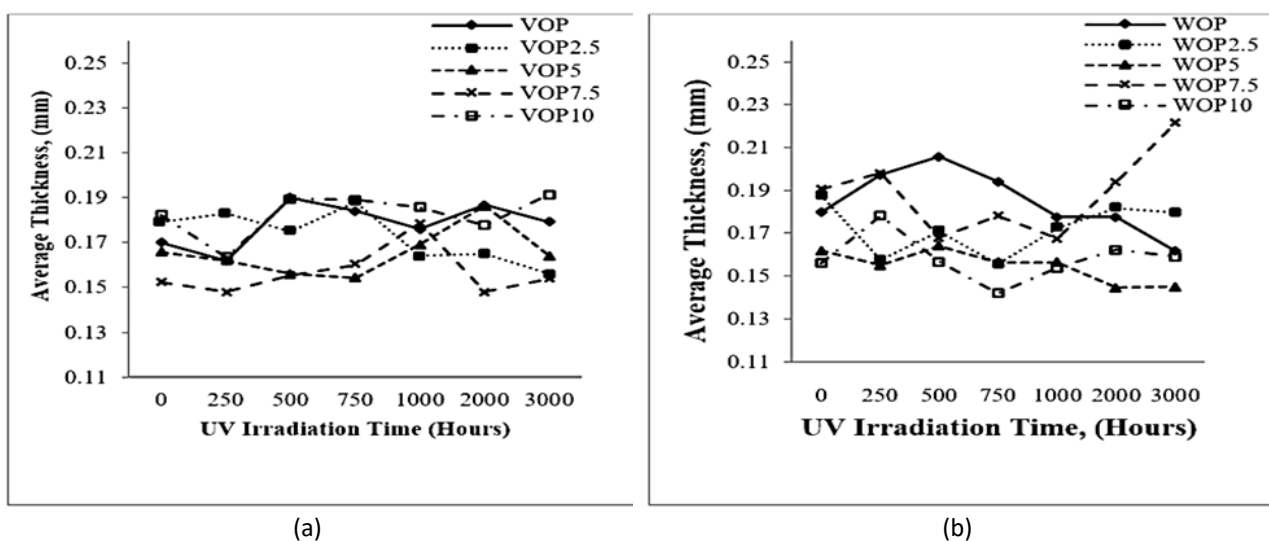


Fig. 4. Average thickness for BP and BPC (a) VOP (b) WOP

Throughout the thickness monitoring of BP and BPC for VOP and WOP, the plotted average thickness is still in the range of 110-250  $\mu\text{m}$  after UV irradiation up to 3000 hours. Therefore, the results of the mechanical test, such as tensile stress and elongation at break, are acceptable. The study by Salem [20] only states that the thickness of commercial LDPE films produced by using co-extrusion machines is approximately 50  $\mu\text{m}$ .

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

Figures 5 and 6 show the tensile strength as a function of UV irradiation time for BP and BPC of VOP and WOP, respectively. The BP of VOP shows a rapid loss in tensile strength from 250 hours to 3000 hours, or about 20%. It is due to UV degradation, which causes a breakdown of chemical bonds, resulting in embitterment due to increased cross-linking and chain scission, which lead to shrinking and cracking. However, the addition of  $\text{TiO}_2$  to the BP can improve the mechanical performance. This result is in good agreement with the results obtained by Salem [22] and Saleh and Shnean [23].

The tensile strength from 0 hours to 250 hours UV irradiated BP and BPC of VOP and WOP is increased. From 250 to 500 hours of UV irradiation, the tensile strengths for BP and BPC of VOP and WOP decreased. Meanwhile, the tensile strength of BP and BPC in VOP and WOP increases from 500 to 750 hours of UV irradiation, except for VOP and VOP5. For VOP, the tensile strength decreased from 500 hours to 3000 hours of UV irradiation. The trend continues to increase systematically after 1000 hours until 2000 hours for BPC of VOP. The tensile strength slightly decreases from 2000 hours to 3000 hours for the BP and BPC of VOP and WOP.

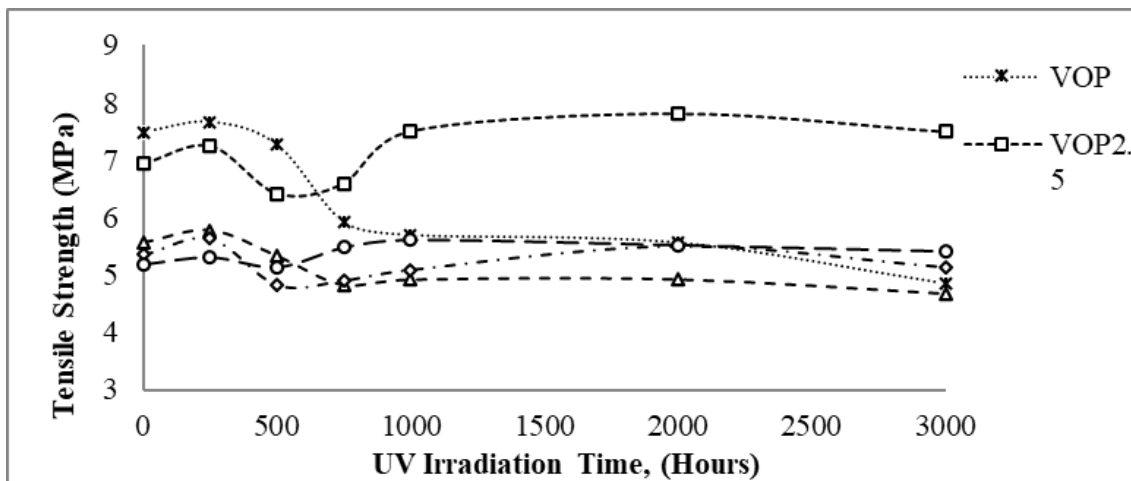


Fig. 5. Tensile strength against UV irradiation time for BP and BPC of VOP

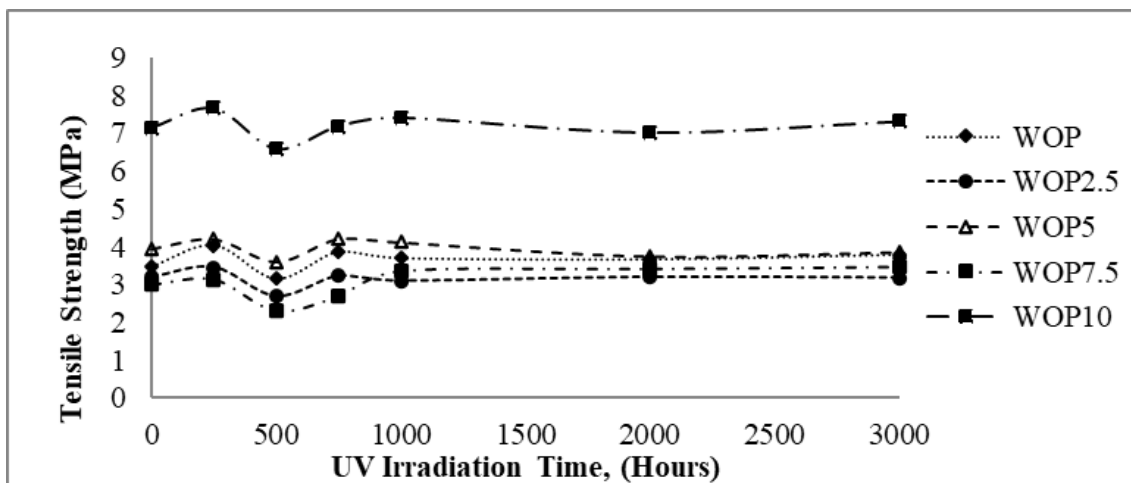


Fig. 6. Tensile strength against UV irradiation time of BP and BPC for WOP

According to the mechanism of photodegradation, the increment from 0 to 250 hours of UV irradiation shows radical initiation of the soft segment. At 250 hours of UV irradiation, the value of the tensile strength of BP and BPC of VOP and WOP was higher than that of the unexposed (0 hour) due to the cross-linking of the soft segment radical. It can be proved by FTIR spectra at  $1202\text{ cm}^{-1}$  becoming more intense after UV irradiation for 250 hours for BPC, which can be assigned to crosslinking of the soft segment.

Meanwhile, the decrement of the tensile strength at 500 hours of UV irradiation is due to the propagation, and the increment of the tensile strength at 750 hours is due to the crosslinking of the soft segment radical at the initial stage in both samples of VOP and WOP thin films. It can be proved by increasing the quantity of hydroxyl groups that can be observed at  $3340\text{ cm}^{-1}$ , which is also broadened by the NH groups. The tensile strength of BP and BPC thin films is significantly stable at

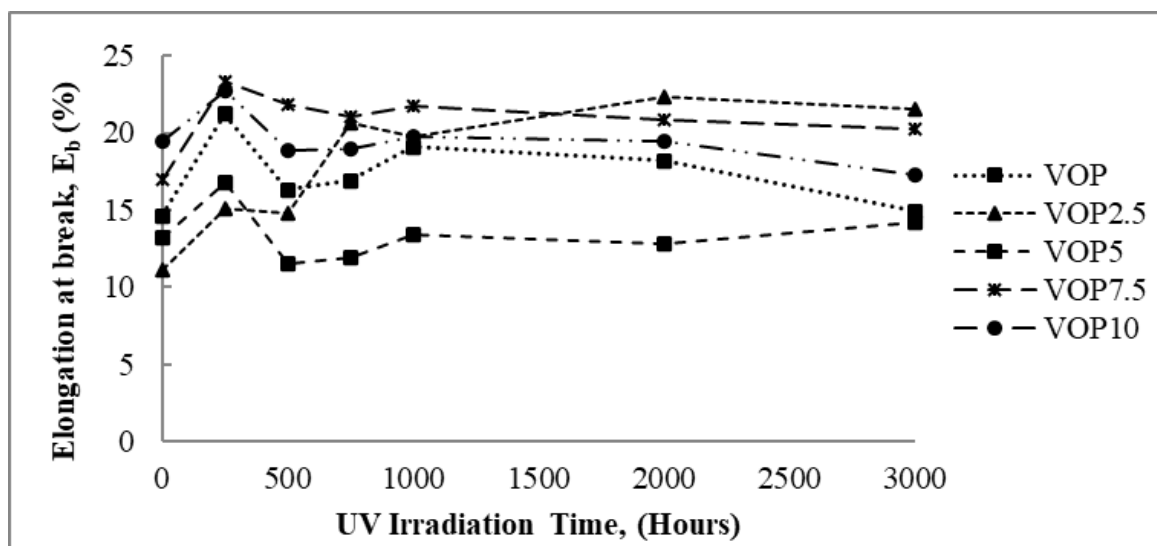
more than 750 hours to 3000 hours of UV exposure. The chain scission of the soft segment radical happened beyond 3000 hours of UV irradiation, and the decreased intensity at  $1700\text{ cm}^{-1}$  peaks was due to the oxidation reaction of C=O in the (NH-CO-O) bond.

From this study, the results for BP and BPC of WOP show tensile films of WOP<sub>10</sub> tend to have a higher tensile strength of 7.67 MPa at 250 hours of UV irradiation. This is the maximum tensile strength before failure, which is indicated by chain scission. WOP<sub>7.5</sub> has the lowest tensile strength at 500 hours, with 2.36 MPa. Meanwhile, results for BP and BPC of VOP show tensile films of VOP<sub>2.5</sub> tend to have higher tensile strength at 2000 hours of UV irradiation, while at 3000 hours, sample VOP<sub>5</sub> has the lowest tensile strengths of 7.82 MPa and 4.67 MPa, respectively. The addition of TiO<sub>2</sub> to the BP of VOP and WOP reduces the tensile strength as compared to pure BP due to agglomeration between BP and TiO<sub>2</sub>, so it could be the starting point for stress concentration and the initiation of cracks, and this will reduce the strength and reflect on the strain of the samples. A further drop in tensile strength was noticed when the samples were exposed to UV.

The 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 remain stable until 3000 hours of UV exposure. The tensile strength of VOP and WOP shows a significant change in UV irradiation. From the data, BP and BPC of VOP give better tensile strength as compared to BP and BPC of WOP.

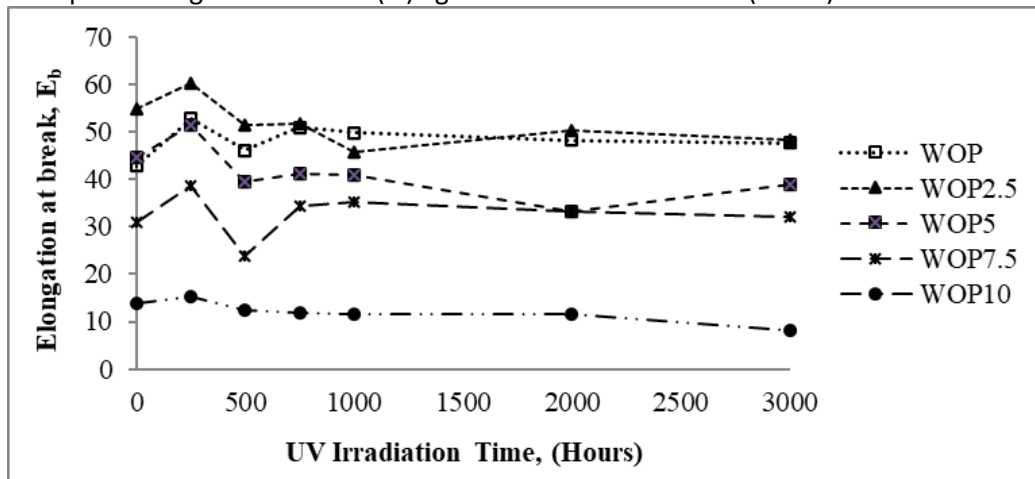
Figure 7 and Figure 8 show elongation at the break against UV irradiation time for BP and BPC of VOP and WOP, respectively. For both BP and BPC, the higher elongations at break were at 250 hours of UV irradiation. This is similar to tensile strength, where 250 is the higher tensile value. While under 500 hours of UV irradiation, the elongations at break decreased. This is due to the mechanical properties of BP and BPC in VOP and WOP, where the tensile strength decreased and the elongation at break also decreased. The highest percentage elongation at break for unexposed and UV exposure for VOP is VOP<sub>7.5</sub>, which is 21% and 26%, respectively. Meanwhile, the highest percentage of elongations at break for unexposed and UV exposure for WOP is WOP<sub>2.5</sub>, which is 64% and 69%, respectively.

This study is similar to that of Fechine *et al.*, [24] where they found that both properties, tensile strength and maximum elongation, showed a significant decrease with UV irradiation time, a typical behavior of a polymer that undergoes chain scission reactions during weathering. Comparing the various types of samples, those containing the UV stabilizer are more stable, confirming the protective action of this additive in the amorphous region for BP and BPC of VOP and WOP.





**Fig. 7.** Graph of elongation at break (%) against UV irradiation time (hours) for BP and BPC of VOP

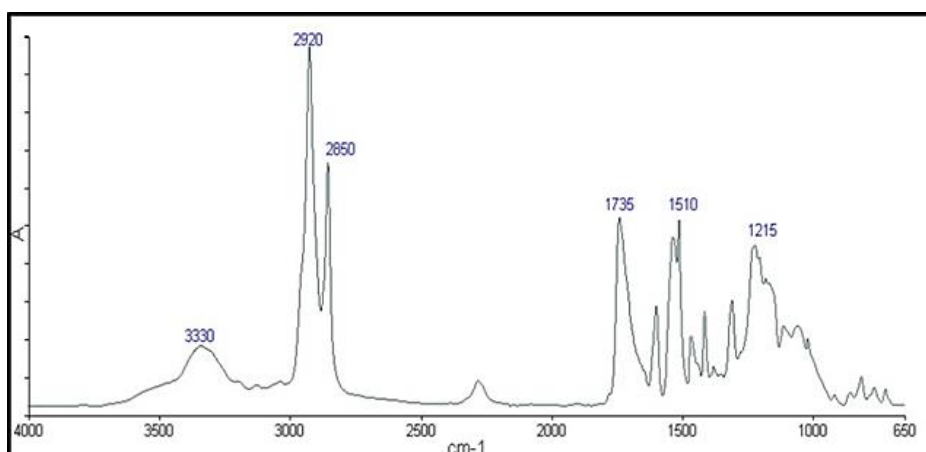


**Fig. 8.** Elongation at break (%) against UV irradiation time (hour) for BP and BPC of WOP

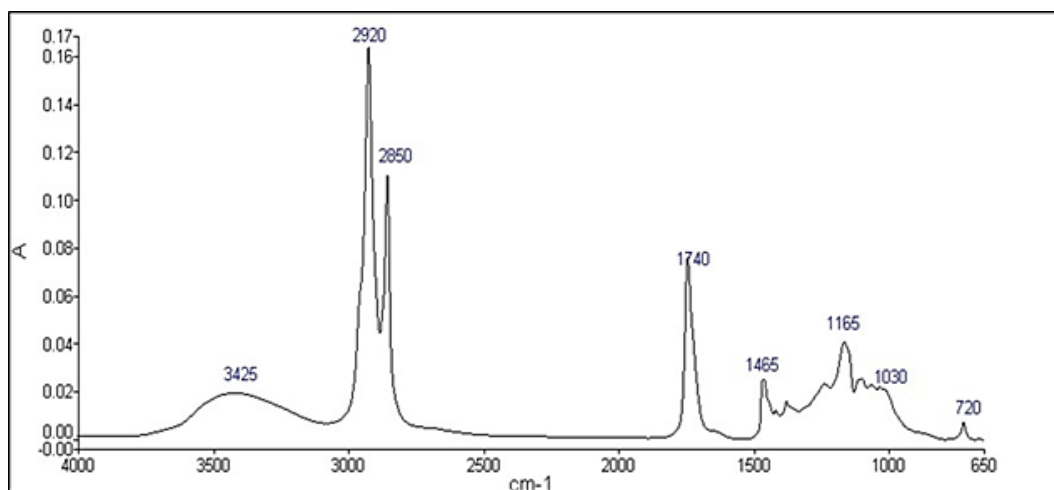
The progressive reduction in mechanical properties is reflected by the inhomogeneity of  $TiO_2$  fillers in the BP of VOP and WOP, which affect the mechanical properties. The reductions in tensile strengths and elongation at break are attributed to the distribution of particles of  $TiO_2$  between the chains of BP, since these particles give more spacing between the fold chains, and the stretch mobility of the main chain will be affected. This will reduce the interaction of the applied stress with these specimens. When these chains are stressed, the aggregation of some of these particles in the local area will decrease the strength of the polymer because these particles will act as weak points. According to Al-Shammary [25] these weak points will accumulate stress around these areas, and the crack will propagate, causing a failure in the polymers.

### 3.2 Infrared Spectroscopic (FT-IR) Study of The Polymer Thin Films

Many naturally occurring fats and oils are glycerol fatty acid esters. The IR spectra of the biomonomers exhibit a high, wide peak at  $3450$  to  $3340\text{ cm}^{-1}$ , confirming the presence of hydrogen-bonded hydroxyl (OH) groups in the produced product (Figure 9). After that, the OH group will react with a cross-linking agent to generate a biopolymer. The NH group frequencies suggested biopolymer production in the FTIR spectra, as seen in the stretching band of the amine (N-H) group, which occurs in the range of  $3500$  to  $3100\text{ cm}^{-1}$ , are taken from previous studies [26,27]. As seen in Figure 10, a strong band at  $1730$  and  $1740\text{ cm}^{-1}$  is ascribed to hydrogen-bonded (NHC=OO) stretching vibrations and is also shown as the carbonyl groups of the ester band (C = O) of WOM.

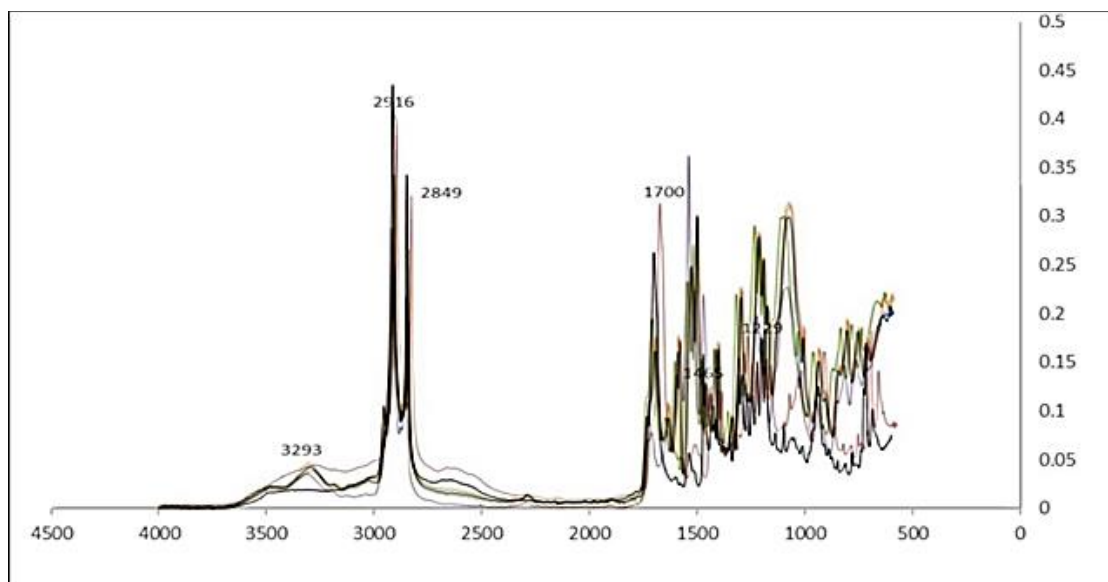


**Fig. 9.** FTIR spectra of Waste Oil Monomer (WOM)

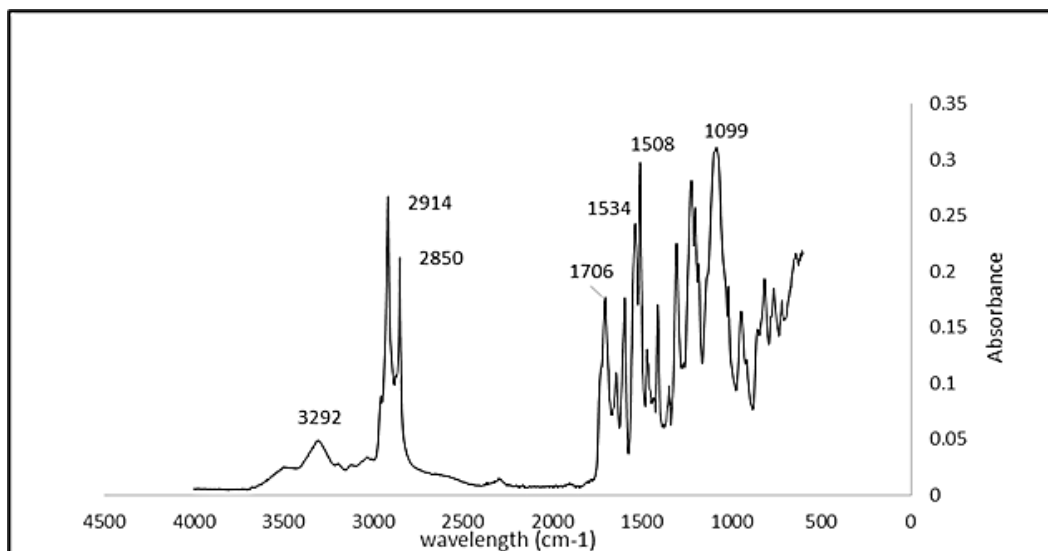


**Fig. 10.** FTIR spectra of Waste Oil Polymer (WOP)

Thin films immersed in water were analyzed by the FT-IR spectroscopic technique, which showed considerable evidence of degradation, as shown in Figure 11. In the absorption spectra of films after 10, 20, 30, 40, and 50 days of immersion, distinct changes are observed when compared to before degradation. First, the absorption band at 2850-2914  $\text{cm}^{-1}$  is contributed by the increased hydrocarbon C-H stretching. This may have happened due to the hydrolysis of the hydrocarbon parts of the polymer chain network. Next is the adsorption band at 1706  $\text{cm}^{-1}$ , which increases from ester carbonyl stretching vibrations and the formation of double bonds because of the breakdown of the polymer chain (Figure 12).



**Fig. 11.** IR Spectra at region 400-600  $\text{cm}^{-1}$  for bio-thin films before and after submerged in water. Thin films not exposed. Thin films exposed at regular times interval (days), -10, -20, -30, -40, and -50

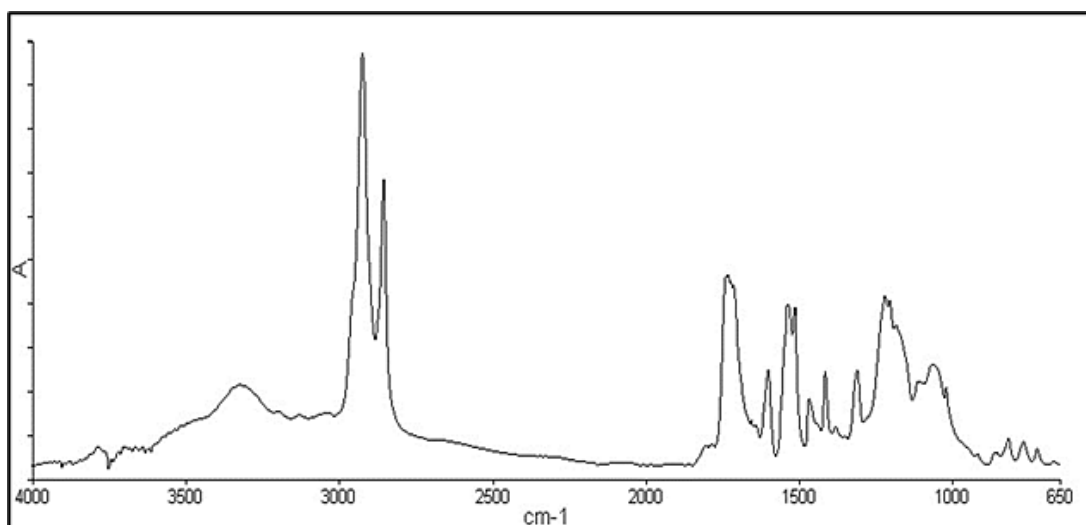


**Fig. 12.** FTIR spectra of bio thin films after 50 days immersion

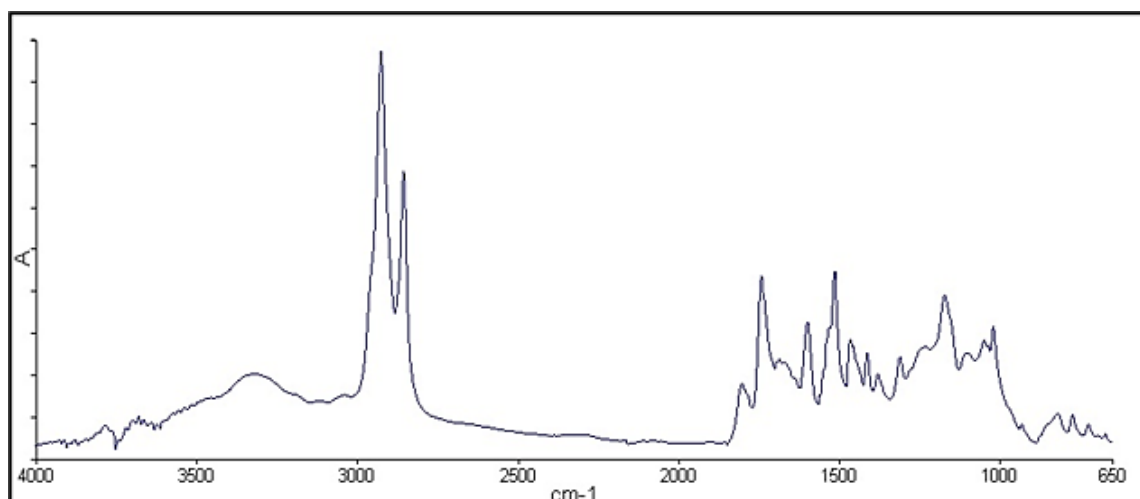
### 3.3. Thermal Degradation as Measured by Carbonyl Index (CI)

The IR spectra of VOP during unheated and heated over thermal exposure at 100°C and 200°C for 5 hours are referred to in Figures 13, 14, and 15. The spectra revealed, as expected, a rise in the carbonyl peak when the heat exposure temperature was increased. According to Yousif and Raghad, this is a well-known phenomenon that is closely related to polyurethane photooxidation [28].

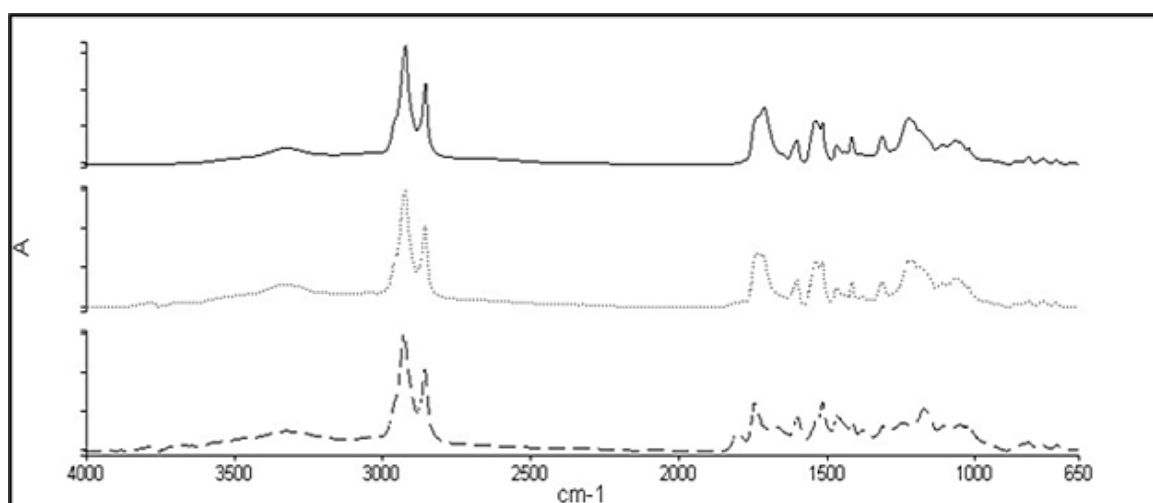
The carbonyl index (CI) computed was employed as a measure of the level of heat deterioration of the polymer thin films over time. The computed CI of polymer thin film thermal exposure indicated that at 100°C and 200°C, VOP has the greatest CI, indicating the least thermal stability (0.542 and 0.596), while WOP has the lowest CI (0.477 and 0.521). Therefore, it is revealed that WOP thin films are more thermally stable at higher temperatures as compared to VOP polymer thin films.



**Fig. 13.** FTIR spectra of VOP of peak carbonyl region of 100°C up to four hours over thermal exposure



**Fig. 14.** FTIR spectra of VOP of 200°C for up to five hours over thermal exposure



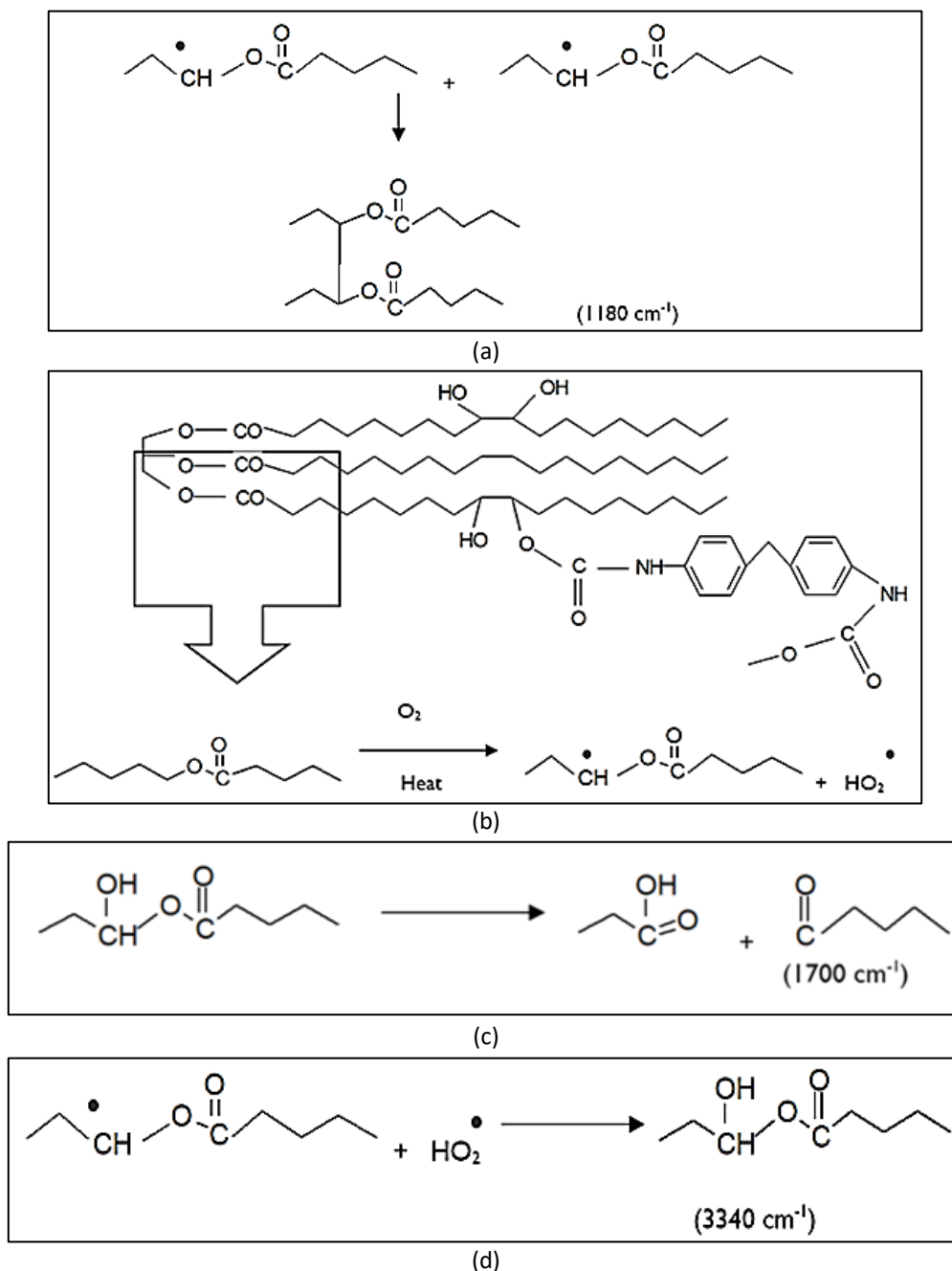
**Fig. 15.** FTIR spectra of VOP of peak carbonyl region up to four hours oven thermal exposure (a) Unheated (b) 100°C (c) 200°C

The vibration of the N-H stretching group is represented by a distinctive band in the FTIR spectra of unheated thin films at 3360 to 3330  $\text{cm}^{-1}$ . The bands at 2950  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  are the CH<sub>2</sub> stretching asymmetric and symmetric groups, respectively. Carbonyl (C=O) stretching vibrations are studied in the vibration band in the carbonyl region (1800 to 1650  $\text{cm}^{-1}$ ). The bands in this area can be attributed to both the hydrogen-bonded carbonyl vibration of polyurea (NH-CO-NH) and the free carbonyl stretching of PU caused by oven temperature exposure.

The loss of urethane structures because of heat exposure is shown by a drop in the intensity of the band corresponding to the stretching vibration of the N-H group (3340 to 3330  $\text{cm}^{-1}$ ). Carbonyl stretching vibration manifests as a complicated absorption band with overlapping bands. The FTIR spectra demonstrate that the prolonged carbonyl signal of the PU sample after 5 hours of heat exposure was deconvoluted into three peaks at 1800  $\text{cm}^{-1}$ , 1740  $\text{cm}^{-1}$ , and 1700  $\text{cm}^{-1}$ , respectively. In a previous study by Rosu *et al.*, [8] the novel band at 1800  $\text{cm}^{-1}$  identifies peroxide compounds formed by PU photooxidation. The action is caused by the creation of various types of carbonyl groups, and it is therefore to reveal the responsible and proposed that this renewable polymer after treatment contributed to the formation of aliphatic esters, as taken from the previous studies [14-18,29].

The peak at 1180  $\text{cm}^{-1}$  becomes more pronounced after five hours of heat exposure at 200 °C, which can be attributed to soft segment crosslinking as shown in Figures 16(a) and 16(b). This

demonstrates that greater crosslinking of the soft segment occurs following exposure. According to previous studies by Shah *et al.*, [3] and Rus [17] this can be due to the stability of the thin films' chain radicals, which increases the radical lifespan and therefore the chance of chain radical combination. The number of hydroxyl groups increases at  $3300\text{ cm}^{-1}$ , with a combined shoulder of NH groups and a widened peak at  $3340\text{ cm}^{-1}$  (Figure 16(c) and 16(d)). In a previous study, Rabek provided a more extensive overview of the mechanisms involved in oxidative breakdown in a polymer film. When a polymer is subjected to heat radiation in the presence of oxygen, a free radical chain process called oxidative degradation develops. Chemical alterations have been attributed to polymer chain scission and cross-linkages [30].

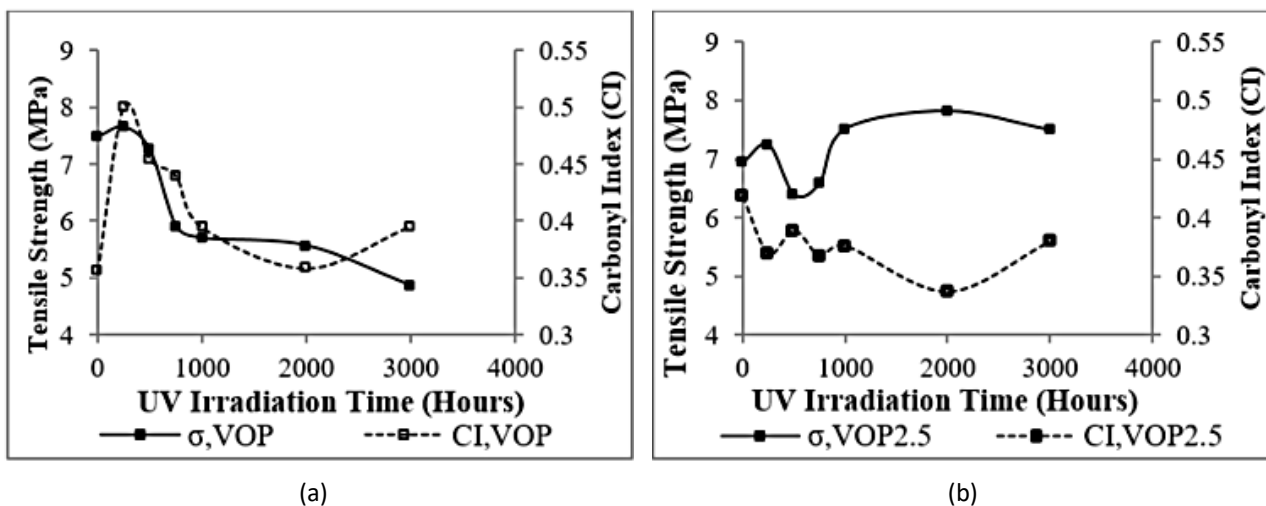


**Fig. 16.** Degradation of thin films after exposed to five hours thermal exposure (a) Radical initiation of soft segment (b) Crosslinking of the soft segment radical (c) Propagation and chain scission of the soft segment radical (d) Chain scission

Further studies on the CI values for UV-irradiated biopolymers were calculated as the ratio of the area of the peak centered in the carbonyl (C=O) region to the area of the peak centered in the alkene (CH) group ( $CI = A_{1702}/A_{2916}$ ). The tensile strength and CI values for BP and BPC of VOP and WOP, as referred to in Figures 17(a) to 17(e), and Figures 18(a) to 18(e), show that an increase in the carbonyl index will decrease the mechanical strengths. The increasing CI of BP and BPC of VOP and WOP thin films after UV irradiation is an indication that oxidation occurred during the exposure. The growth of CI relates to the level of oxygen that has been incorporated into the polymer, and wherever a carbonyl group is introduced, the polymer undergoes chain scission, such as molecular weight reduction and a change in physical and chemical properties. The increase in CI formation for polymers after UV irradiation is proportional to the number of chain scissions that occur in the polymer thin films associated with the scission of the (NHCO-O-).

The increase in the absorption intensity of these bands indicated that the formed products resulted from an extensive chain scission due to UV exposure, followed by oxidation of the formed fragments due to the presence of oxygen during irradiation. Peak positions were changed, which indicates that the photo-degraded products are not the same during the degradation process. From previous studies by Al-Ani and Ramadhan [31], it has been reported that the rate of photooxidative degradation of poly (Florostyrene) caused by polychromic irradiation ( $\lambda \geq 290$  nm) at 55°C in the presence of oxygen is reduced in copolymers containing aromatic systems. In the same way, introducing aromatic rings into aliphatic compounds increases their stability. It was assumed that the aromatic moiety, which is very radiation-resistant, accommodated the extra energy while remaining unaffected.

The carbonyl index (CI) of the BP of VOP and WOP<sub>2.5</sub> revealed higher values at 250 hours and 1000 hours, which are 0.5 and 0.57, respectively. The CI value decreases with increased UV irradiation. The lowest CI is VOP<sub>.5</sub> and WOP<sub>2.5</sub> at 2000 hours and 3000 hours, which are both approximately 0.3.



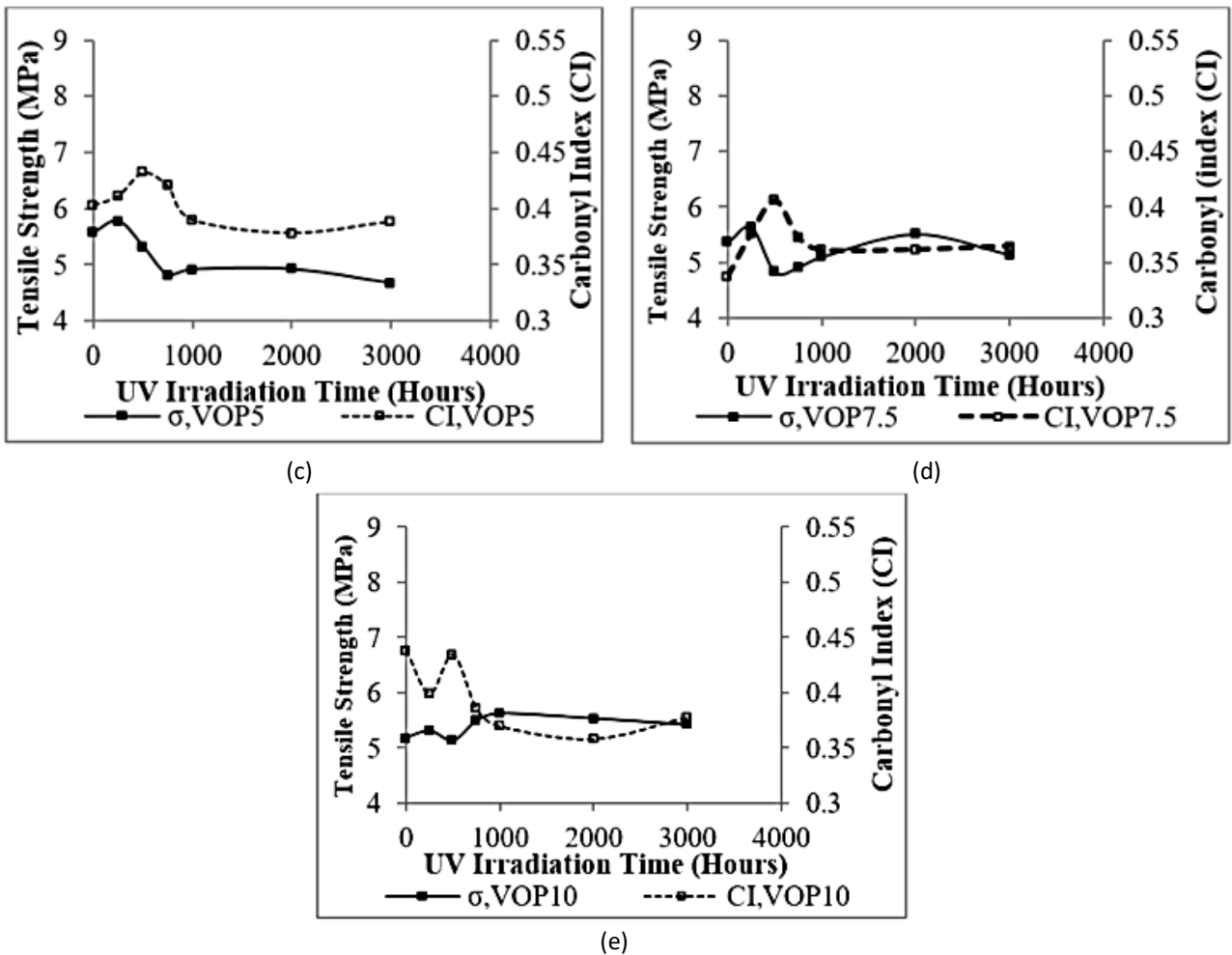
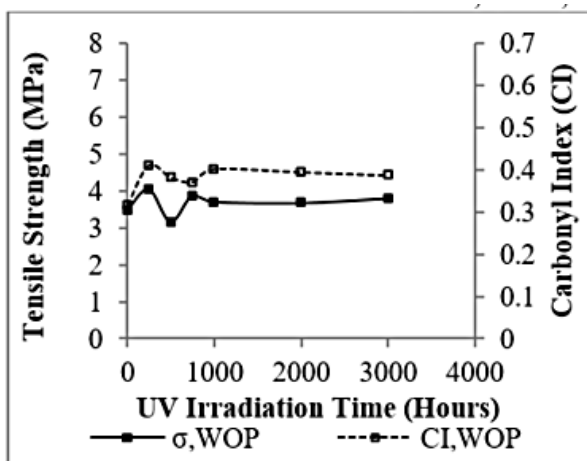
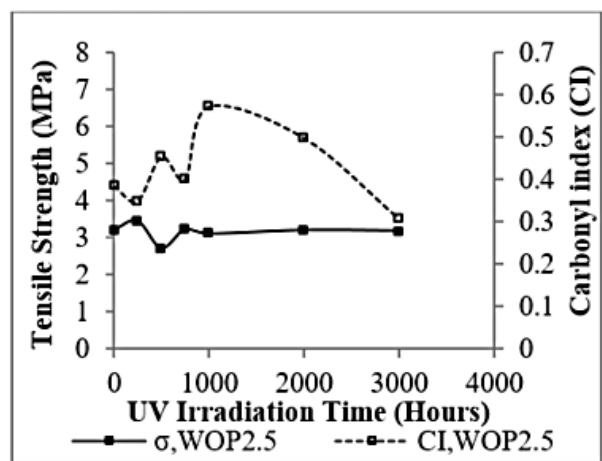


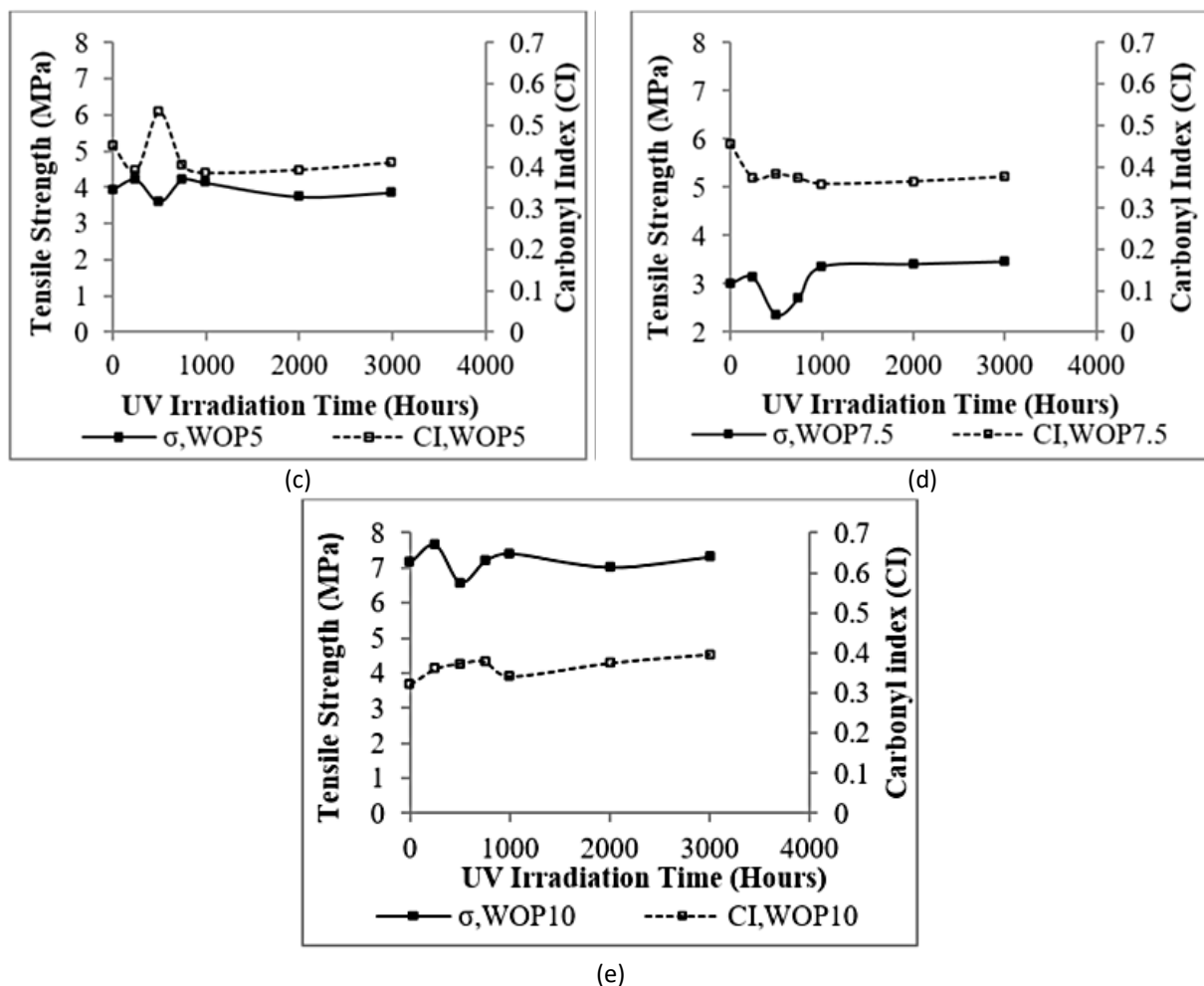
Fig. 17. Carbonyl index (CI) for non-UV irradiated and UV irradiated BP and BPC at 250, 500, 750, 1000, 2000, and 3000 hours (a) VOP (b) VOP<sub>2.5</sub> (c) VOP<sub>5</sub> (d) VOP<sub>7.5</sub> (e) VOP<sub>10</sub>



(a)



(b)



**Fig. 18.** Carbonyl index (CI) for non-UV irradiated and UV irradiated BP and BPC at 250, 500, 750, 1000, 2000, and 3000 hours (a) WOP (b) WOP<sub>2.5</sub> (c) WOP<sub>5</sub> (d) WOP<sub>7.5</sub> (e) WOP<sub>10</sub>

#### 4. Conclusions

Thin films of polymers derived from renewable sources were synthesized to test their stability against bio, thermal, and hydro-induced degradation. The thermal breakdown of the biopolymers reveals that they are least stable at high temperatures up to 200°C. The FTIR spectrum alterations demonstrated that heat breakdown of the thin films altered the chemical structure and mechanical properties of the biopolymers. A higher computed carbonyl index (CI) indicates more polymer chain scission. Visual inspection reveals polymer fading and even describes physical deterioration. The results obtained support the photodegradation mechanism of BP and BPC after UV irradiation proposed in the literature for aromatic polymers from renewable resources, involving the scission of the (-NHCO-O) group and oxidation of the central methylene group with quinone (yellow) formation as a chromophoric reaction product. The highest percentage filler loading in the BPC gives small changes in CI as well as a decrease in the discoloration of the biopolymer. The CI and yellowing decrease with the increasing percentage ratio of TiO<sub>2</sub> loading on VOP and WOP thin films. For future studies on the stability of polymer composite properties, the biopolymer thin film doped with TiO<sub>2</sub> irradiated by UV light is to enhance the degradability and stability of polymer composites applied in the coating industry.



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