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Investigation of Renewable Polymer Composite from Waste Oil Endurance to UV Irradiation Exposure by using FTIR and UV-Vis

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ABSTRACT

Waste vegetable from palm oil are most abundant biological sources and important raw materials for production of renewable polymer foam (RF) because of their versatility with high possibility to modify the chemical structure of triglycerides and it derivatives. In this study, waste vegetable oil was synthesized and crosslink with polymethane polyphenyl isocyanate, distilled water and titanium dioxide (TiO_2) as filler to produce RF and its composites (RFC) by manual casting method. The physical property of RF and RFC were measured endurance to UV irradiation exposure for a period of 1000 hours by FTIR and UV-Vis. The RF shows an increase of yellowing due to formation of highly coloured quinone on photo-oxidation of the MDI-based polymer on UV irradiation exposure. The quinone oxidations products have been identified by combining FTIR measurement and UV-Visible spectroscopy, for example an absorption at 1510 cm^{-1} in the FTIR spectrum

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is due to formation of quinone structure that also absorb strongly at the range of 490 nm to 570 nm in UV-Visible spectrum. The increasing of TiO_2 *content in RF and RFC shows significant increases of absorbance peak and wavelength after UV irradiation exposure. As the loading of* TiO_2 *increased (up to 10 % of monomer weight), the* RFC_{10} *shows highest photostability at 10 % of* TiO_2 *loading. Hence,* RFC_{10} *has shown no significant or abrupt changes to the functional groups after UV irradiation exposure, allowing it to have a considerably good UV stabilizer to generate better UV protection.*

Keywords: *Renewable polymer, Waste vegetable oil, UV irradiation, FTIR, UV-Vis*

Introduction

Weathering or more specifically photo-oxidation of polymers refers to the chemical and physical changes that occur when radiation is absorbed by a polymer. Weathering is a degradation process and as such is temperature dependent leads to occur more rapidly at higher temperatures [1]. Polymer was degrading under the influence of sunlight [2]. Almost all synthetic polymer require stabilization against the adverse effects; with the development of synthetic resin, it became necessary to find ways and means to prevent or at least reduce, the damage caused by the environment parameters such as light, air and heat. This is why the photostability of polymer is an important consideration for applications.

Photostability can be achieved through the addition of special chemicals, light stabilizers or UV stabilizer, that have to modify to the nature of the resin and the specific application considered. The most important method for photostabilization are screening or absorbing UV radiation by stabilizing agents and use of antioxidants, which react with the polymer radicals, stopping the degradation process by forming inactive product [3].

UV absorber were the first protection agent used for polymer. The protection mechanism of UV absorbers is to absorb harmful UV light and quickly transform it into harmless. The reaction mechanism depends on the agents but common to all, the reaction flow is cyclic. Titanium dioxide (TiO_2) also act as UV absorber and commonly used to improve the UV protection of coatings and polymer. TiO_2 also act as an oxidation catalyst [4].

Furthermore, irradiation of polyurethanes polymer with UV light leads to many possible changes in their structure. The changes are formation of quinoid structure (yellowing of polyurethane sample) as refer to Figure 1.

The changes also occurs of homolytic scission of bonds in the urethane groups on further irradiation leading to the formation of free radicals. Recombination and formation of new structures such as amino, azo and carbodiimide. Addition of oxygen to the free radical yields hydroperoxide (•$OOCH_2$), whose decomposition leads to the carbonyl-containing structures. Destruction of material during the formation of new structures, which causes further darkening of the irradiated samples. Formation of gaseous products such as CO and CO_2. Also small amounts of formaldehyde and H_2O can be formed.

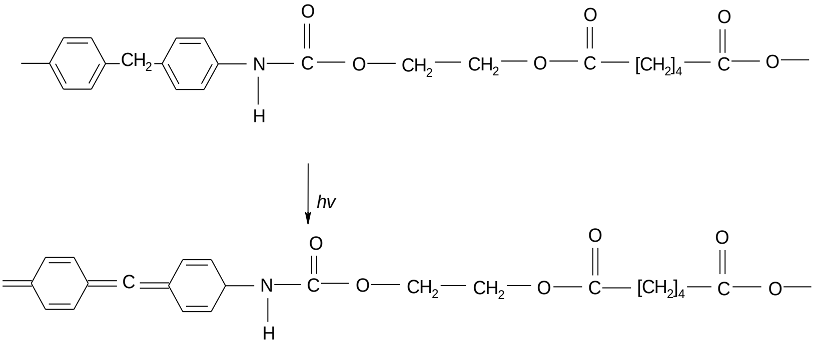

Figure 1: Formation of quinoid structure [5]

Methodology

Materials

Renewable monomer from waste vegetable oil, Polymethane Polyphenyl Isocyanate (Modified Polymeric-MDI) (viscosity at 25°C = 120 – 160cps, specific gravity at 25°C = 1.18 – 1.20g/ml, NCO Content, % wt = 26.3 – 27.3) and distilled water.

Sample Preparations

Renewable monomer based on waste vegetable oil from Small Medium Entrepreneur (SME's) was prepared by using in-house catalyst preparation to generate the epoxides from unsaturated fatty compound which comprises the acid-catalyst ring opening of the epoxides to form polyols [6,7]. The renewable monomer is mixed with Modified Polymeric-MDI was prepared by simple open casting method to produce the renewable polymer foam. The mixture was poured into open mould and allowed to rise freely and the renewable polymer foam was removed from the mold after 12 hours. The samples were exposed to the UV light in UV Lamp Test Chamber Model HD-703 (Haida International Equipment Co., LTD) at different exposure time at 250 hours, 500 hours, 750 hours and 1000 hours at 40°C. The UV exposure of the samples 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.

Fourier Transform infrared spectrometry (FTIR)

The functional groups of renewable polymer samples were tested by Perkin–Elmer (UK) Spectrum spectrometer at 32 scans with resolution of 4 cm^{-1} at the wavelength regions of 4000 – 650 cm^{-1}.

Ultraviolet Visible light (UV-Vis)

The renewable polymer samples were tested by UV Visible light and measured in the wavelength range of 200-900 n according to ASTM E275-08. UV Visible light was used to characterize the absorption of renewable polymer samples in visible light by using UNICO SQ-3802 model spectrophotometer.

Results

FTIR of renewable polymer

The overlay spectra of RF and RFC as referred to Figure 2 shows that all curves exhibit similar absorption peaks of CH asymmetrical stretching vibration peaks at region 3000-2850 cm^{-1}. A strong absorption band characteristic of the N-H group was found in 3400-3250 cm^{-1} region. Constant noticeable spectral changes were seen in the alkyl region around 2960-2849 cm^{-1} due to the C–H stretch of RF and RFC samples. Thus, the change in the absorption band at 2918 cm^{-1} was taken as an example of the relative measure of methylene group loss. The rutile particles provide the same degree of protection as the UV absorber combinations by reducing the rate of the absorbance at 2918 cm^{-1}. Meanwhile, all results shows the absorption intensity decreased after UV irradiation exposure at 1000 hours.

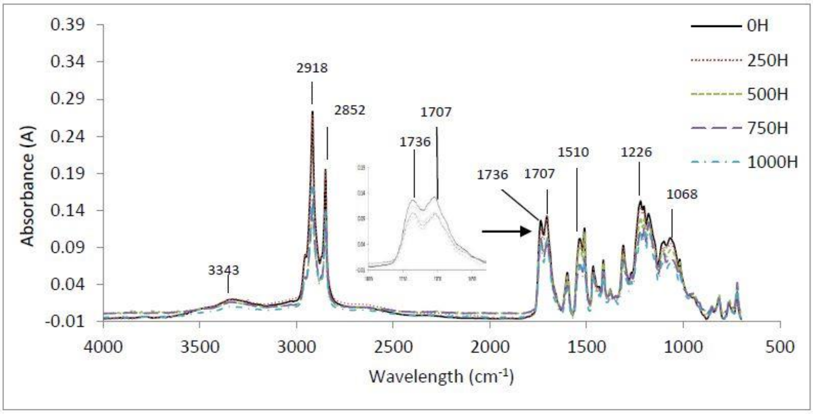

Figure 2 : FTIR overlay spectra of renewable polymer composite (RFC_{10}) after UV irradiation exposure

The absorption peak of the C-H band at 2923-2850 cm^{-1} reduced as the UV irradiation exposure time increased. The hard segment corresponding to urethane band at 2918 cm^{-1} is symmetric stretching of $–CH_2$ and 2852 cm^{-1} asymmetric stretching of CH_3 shows strong and sharp peak. These peaks attributed of the polyether. The peak observed was weak absorption band after UV irradiation exposure based on the decreasing of intensity absorption band of RF and RFC samples. Meanwhile, the increase of OH (bonded) peak at 3340 cm^{-1} of exposed renewable polymer can be correlated to the formation of carboxylic acid byproduct. While the decrease of 2918 cm^{-1} and 2852 cm^{-1} peak intensity is due to C-H bond cleavage from methylene (CH) group. In the region below 2000 cm^{-1} the spectrum exhibit two main bands assigned to C=O and N-H. Meanwhile, the duplet sharp peak of RFC_{10} was observed at 1736 cm-1 and 1707 cm-1 respectively, corresponded to C=O as shown in Figure 2.

Irradiation of polymer with UV light leads to many possible changes in their structure such as formation of quinoid structure (yellowing of polyurethane sample) at absorption peak at ranges 1650 cm^{-1} to 1500 cm^{-1} [8]. After UV irradiation exposure, the N-H and O-H bands broaden remarkably with increasing of UV irradiation exposure time, which may reflect hydroperoxide formation. This suggests the generation of new carbonyl species which includes the formation of quinine amides structure (yellow) and the decline of bands at 1538 cm^{-1}.

UV-Vis of renewable polymer

Figure 3 and Figure 4 shows the maximum wavelength versus UV irradiation exposure and absorbance peak versus of RF and RFC, respectively. The maximum absorbance increased and the maximum wavelength shifted to the higher wavelength with the increasing of UV irradiation exposure time. The range of maximum wavelength of RF and RFC is around 490-570 nm.

In theoretical, the shorter wavelength give the higher absorption energy in the polymer. Thus, RF shows less absorption energy as compared to RFC. It indicates that photo-oxidation leads to chain breaking of C=O and formation of free radicals. Furthermore, increasing of absorption peak was considered as evident of the quinone structure formation of renewable polymer. These spectral changes suggest that the aromatic structure were oxidized in the central methylene group leading to highly conjugated quinone product [9].

RFC absorbed more light at longer wavelength as compared to RF and leads to more yellowing (darker) colour after UV irradiation exposure time. Light from 400 to 500 nm corresponds to the blue region of the visible spectrum, thus when absorbance increases in this region, the green and red colours become dominant. As a result, the sample appeared yellowish due to the combination of green and red colours, and the actual sample indeed have a slightly yellowish tinge due to the UV irradiation exposure.

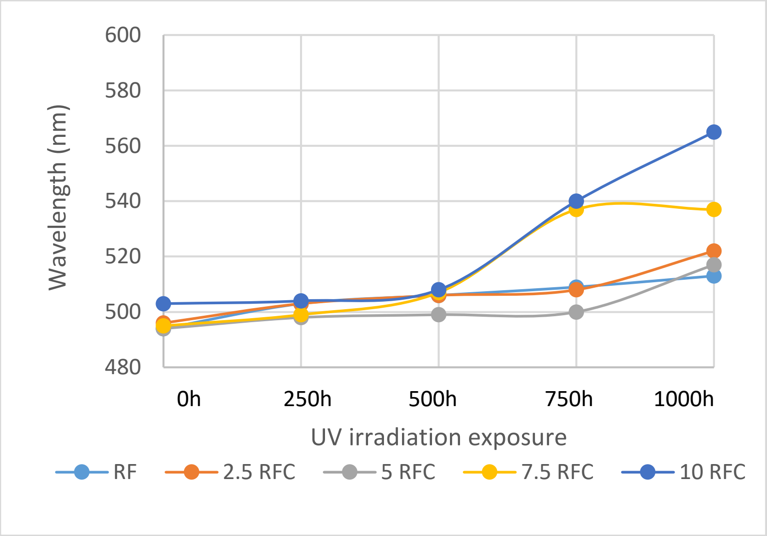

Figure 3: Wavelength at maximum peak of RF and RFC with UV irradiation exposure

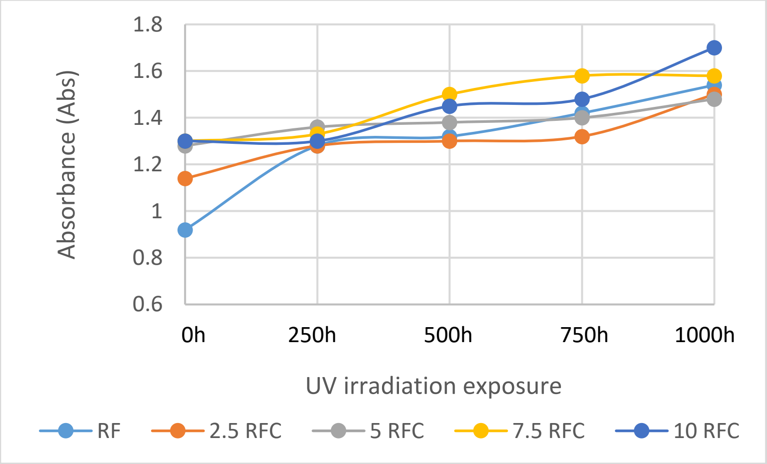

Figure 4: Maximum absorbance peak of RF and RFC with UV irradiation exposure

The peak of absorption increased due to the increasing of UV absorption of TiO_2 filler loading. It was reported that peak of absorption was found to increase with time of UV irradiation exposure [10]. The maximum absorbance peak of RF and RFC is the range of 0.8-1.7. Meanwhile, the intensity absorption peak of RF and RFC is around 1.5 and similar with previous research [11]. This is due to RFC surface which were less yellowish as compared to RF.

TiO_2 performed absorbing in UV light at the wavelength 230-400 nm [10].The result shows the absorbing peak of RFC with TiO_2 loading started at broad peak at 300 nm of UVA by the renewable polymer doped with TiO_2, shifts towards at the maximum peak at the range 500 nm and remains stagnant after 700 nm. This is due to the fact that TiO_2 shows a light response at 300-400 nm in polymer which can be attributed the electron transition from the valence to the conduction band [12].

The absorption peak of renewable polymer composite is generally depending upon the ratio of TiO_2 loading in polymer. Increasing of TiO_2 content in the renewable polymer typically increases the absorbance peak and wavelength in the polymer. Hence, 10 % of TiO_2 filler loading of RFC gives the highest absorbance peak. According to SEDAC (1998) proved that when the TiO_2 polymer composite is exposure on the UVA, it is desirable to increase the absorption peak and it tends to increase the surface energy of the polymer, which turn can result in better functional from damage on degradation under exposure to UVA radiation [13]. It is suggested that, the renewable polymer composite gives the maximum energy absorbing peak at RFC_{10} in which TiO_2 act as a good UV stabilizer to generate better UV protection.

Conclusion

This study intendent to contribute understanding of RF with TiO_2 filler loading in demonstrating the photo stability upon UV irradiation exposure at 1000 hours. The RF shows an increase of yellowing due to formation of highly coloured quinone on photo-oxidation of the MDI-based polymer on UV irradiation exposure. The quinone oxidation product have been identified by combining FTIR measurement and UV-Visible spectroscopy, for example an absorption at 1510 cm^{-1} in the FTIR spectrum is due to formation of quinone structure that also absorbs strongly at the range of 490 nm to 570 nm in UV-Visible spectrum.

In the present of UV irradiation exposure (<400 nm), moisture and air, the TiO_2 will produce hydroperoxide at that region. RFC has peak radiation wavelength of 380 nm, which is below than 400 nm and the maximum of peak observed at range of 490-600 nm. Thus in this region, the

TiO_2 acted as UV stabilizer in which retardation the production of hydrogen peroxide.

Acknowledgment

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