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INFLUENCE OF N_2 AND H_2O ON UV IRRADIATED BIO POLYMER COMPOSITE

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ABSTRACT

This study reports on the effect of UV-light on the FTIR spectra of bio polymer doped with 10 % TiO_2 ($BPF_{1.0}$) in a gas cell full with nitrogen gas (N_2) and a droplet of water (H_2O). The film samples were put in the 10 cm NaCl gas cell with 99.99 % N_2 with H_2O at different exposure time of 40 °C. An unexposed gas cell fill with N_2 and H_2O is used for the purposed of comparison. The chemical structural changes in the UV irradiated gas cell were monitored by Fourier-transform infrared (FTIR) spectroscopy methods. The changes in hydroxyl, (OH) and carbon nitrogen double bond, (C=N) of bio polymer doped with TiO_2 under UV exposures were discussed. OH and C=N intensities decreases of exposed to UV light under N_2 with H_2O in gas cell. The UV-radiation shows FTIR spectrum changes on $BPF_{1.0}$ of exposed to nitrogen gas and water.

Keywords: Bio polymer; Nitrogen (N_2); Water (H_2O); Gas cell; UV light; FTIR spectra.

INTRODUCTION

Nowadays, renewable materials such as plant oils or vegetable oils are oils derived from plant sources. Several arguments can be found to believe in the great potential of plant oils as an alternative resource for the production of polymeric materials (Anika Zafiah, 2008). The necessity of releasing the polymer industry from its dependence on depleting resources represents a major concern, pushing the search for industrially applicable renewable alternatives (Andrew and Allison, 2006).

Titanium dioxide (TiO_2) is a semiconductor and the most important and most widely used inorganic pigments applied in many branches of industry. The effect of TiO_2 on material properties for renewable material was studied (Anika Zafiah, 2009). The most desirable features of TiO_2 from the point of view of thin film as coating applications include the ability of whitening, covering power, brightness, and resistance to environmental factors, chemical neutrality and non-toxicity (Chattopadhyay and Raju, 2007). Different method was identified to make this catalyst more efficient and more applicable, different forms of TiO_2, such as thin and thick film coatings powders, and membranes have been utilized (Arana and Byrne, 2002). Since some years photocatalytically active building materials, e.g., paints, roof tiles, and building materials available on the market contain TiO_2 powder as the photocatalyst (Dillert et al., 2012).

In the past two decades, TiO_2 heterogeneous photocatalyst has been extensively investigated (Fujishima, 2000). TiO_2 meets these criteria and is one of the best semiconductors for photocatalytic reactions. Moreover, by using UV and titanium dioxide thin film coated on a glass or metal surface can to eliminate hazardous indoor air pollutants, for example benzene, toluene and formaldehyde, photocatalytic oxidation (Hager, 2000). However, technical difficulties with coating affect the consistency and quality of the film, leading to variable removal efficiencies and loss of catalyst during the reaction process (Hitchman and Tian, 2002). In general, vinyl polymers are particularly susceptible to thermal degradation, particularly at elevated temperature or during exposure to ultraviolet light (Tham and Willem, 2010).

It should be indicated that irradiated polymeric materials undergo a series of oxidative reactions that lead to photochemical degradation (Zhang et al., 1999; Kaczmarek and Podgorski, 2007; White and Shyichuk, 2007) and with consequences like brittleness, loss of brightness, and color changes. Besides the cross-linking of the polymeric processes, a number of other changes may take place in polymeric chains during photodegradation (Rabek, 1995; Fechine, 2002).

Photocatalytic is a decomposition reaction formed when TiO_2, as a catalyst, absorbs UV radiation from sunlight, that accelerates the oxidation process in the atmosphere and decomposes any air borne toxic organic matters as refer to Figure 1. One approach to reduce the concentration of air pollutants is the light-induced oxidation in the presence of a photocatalytically active material and molecular oxygen (Centers for Disease Control and Prevention, 2008). The similar result was found in the IR spectra of water polyaggregates in a nitrogen cryomatrix (Drobyshev et al., 2007).

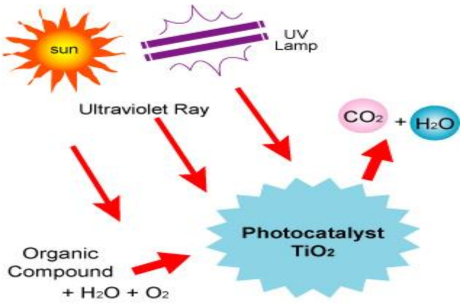


Figure 1: Photocatalytic reaction *(BioEcotech, 2012).*

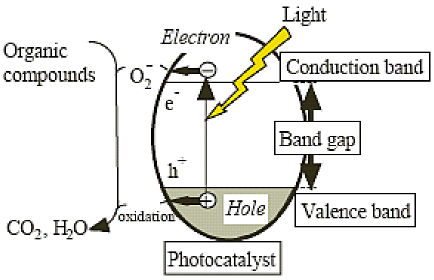


Figure 2: Mechanism of photocatalysis *(TiPE Library, 2008).*

Activation of TiO_2 is achieved through the absorption of a photon (*hv*) with ultra-band energy from UV irradiation source. This results in the promotion of an electron (e−) from the valence band to the conduction band, with the generation of highly reactive positive holes (h+) in the valence band. This stage is referred as the semiconductor's 'photo-excitation' state as referred to Figure 2.

The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is:

$$1240 \text{ (Planck's constant, h) } / 3.2 \text{ ev (band gap energy) } = 388 \text{ nm} \qquad (1)$$

This causes aggressive oxidation of the surface adsorbed toxic organic pollutants and converts them into CO_2 and water:

$$TiO_2 + hv \rightarrow TiO2\,(e_{cb}{}^{-} + hole_{vb}{}^{+}) \qquad (2)$$
$$H_2O \rightarrow OH^{-} + H^{+} \qquad (3)$$

Oxidative reaction

$$hole_{vb} + OH_{ads}{}^{-} \rightarrow \bullet OH \qquad (4)$$
$$\bullet OH + VOCs/Dye + O_2 \rightarrow CO_2 + H_2O \qquad (5)$$

Therefore, this research work concentrate irradiated gas cell to the UV light with bio polymer composite as renewable material. The present paper emphasizes the absorption spectra in the gas cell before and after UV light exposure. As well, it is aimed to determine the functional group of the OH and C=N intensities in the gas cell according to the absorption spectra and the degradation of the $BPF_{1.0}$ after exposed to UV light.

METHODOLOGY

Materials

Bio polymer thin film (BPF) was prepared from renewable resources of waste cooking oil. Waste cooking oil was obtained from Small and Medium Industries (SMIs) and chemically manipulated at laboratory scale using less tan 1L of waste cooking oil (Anika Zafiah, 2010). 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 (Anika Zafiah, 2009).

Preparation of $BPF_{1.0}$

Bio monomer was mixed with Methylene Diphenyl Diisocyanate (MDI) and 10 % TiO_2 (wt by wt ratio of bio monomer) using mechanical stirrer and cast into a container. The $BPF_{1.0}$ was leave to cure at ambient temperature for at least 6 hours, as to ensure complete removal of solvent traces. Micrometer was used to measure the thickness of the sample at particular point ranging from 110 µm to 250 µm.

Irradiation of $BPF_{1.0}$

The film samples of 130 x 25 mm were cut and put in the 10 cm NaCl gas cell with 99.999 % N_2 and one drop of H_2O for different exposure time at 40 °C in the UV accelerated weathering tester (Haida International Equipment Ltd.). The UV-irradiation of the gas cell 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.

Measurements of FTIR spectra

The UV absorption spectra of chemical structural changes for $BPF_{1.0}$ were recorded before and immediately after UV irradiation with a FT-IR Spectrometer according to ASTM D6348 (ASTM International, 2012). The Fourier transform infrared spectroscopy system that was employed in this work was Perkin Elmer spectrometer (Spectrum 100) Universal ATR Sampling Accessory. The working wavenumber range of the spectrometer was from 4000 to 700 cm^{-1}, with a resolution of 32 cm^{-1}.

RESULTS AND DISCUSSION

The effects of UV-light irradiation on the efficiency of photochemical processes in BPF doped with 10 % TiO_2 ($BPF_{1.0}$) were studied by their absorption spectra. The absorption spectra of unexposed and exposed UV light gas cell filled with $BPF_{1.0}$ at different exposure time is shown in Figure 3.

As seen in Figure 3, chemical changes were assessed by FT-IR spectra for photo-irradiated gas cell of $BPF_{1.0}$ (exposed 60 minutes). The changes show typical functional group in the hydroxyl 3800-3000 cm^{-1} and alkenes 1700-1600 regions. The hydroxyl stretching vibration region showed the growth of a broad band between 3700 and 3100 cm^{-1} centered at 3435 cm^{-1}, corresponding to hydroxyl groups associated with carboxylic acids. Aliphatic hydroperoxide, absorbed in the 3300-3500 cm^{-1} region, are also responsible for the formation of this broad band.

Unexposed gas cell of 60 minutes shows the large increases in the absorption intensity at 1640 cm^{-1} indicates that there is an increase in the number of C=N that resulted during chains-scission process. It maybe due to the cross linking on the soft segment of OH group. C=N also gives rise to infrared features. However, the C=N bond is somewhat reactive, and compounds containing it are rare.

The positive feature at 2090 $cm\text{-}^{1}$ can be assigned to the C-N stretching vibration of adsorbed cyanide. The positive character of CN band reflects the surface reaction of cyanide to produce other species. The other species generated at 1640 indicate that it corresponds to a water-nitrogen mixture (Huerta et al., 2000). New bands appeared at 2090 cm^{-1} with very broad absorption due to water in the matrix and the interaction of polymer.

When the sample is exposed to UV light for 60 minutes, the curve was shifted at 2290 cm^{-1} as the nitrogen evaporates and the structural elements “condense” on the substrate. The quotation marks signify that it is difficult to call the deposition of water from the matrix onto the substrate condensation, but it is even more difficult to give a new and precise definition of this process. In any case, the IR spectrum of the substrate after the nitrogen has evaporated can be interpreted in a manner so that water in the solid state is present on the substrate, but it is difficult to compare this solid water with the amorphous and crystalline forms of water. The similar result was found in the IR spectra of water polyaggregates in a nitrogen cryomatrix (Drobyshev et al., 2007).

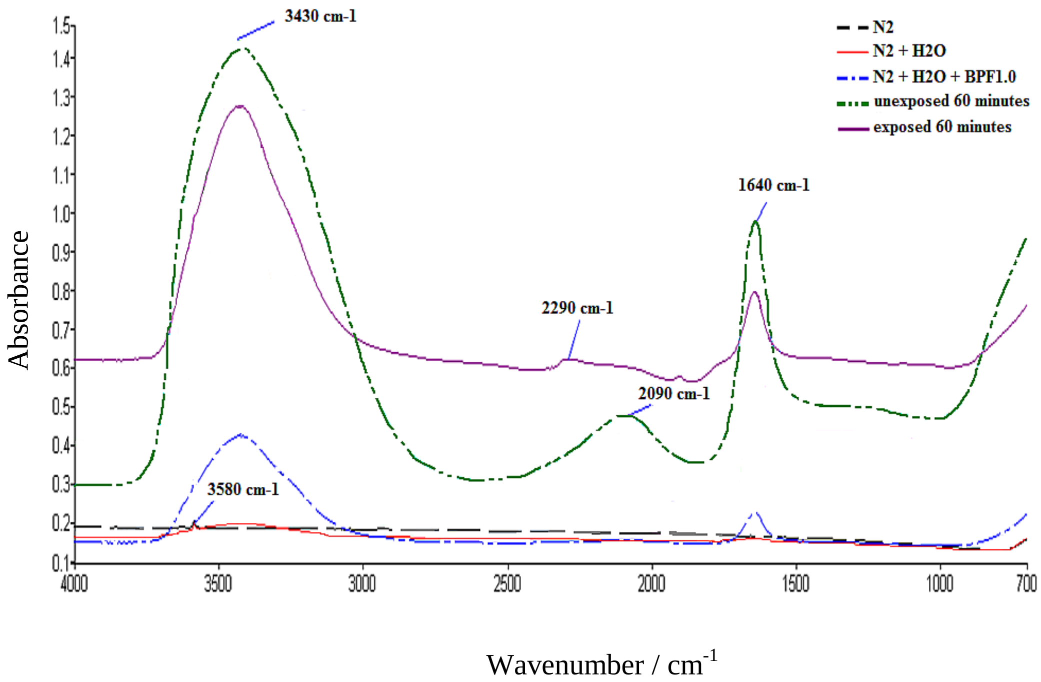


Figure 3: Overlay spectras of FTIR gas cell of $BPF_{1.0}$ of unexposed 60 minutes and exposed to UV light at 60 minutes.

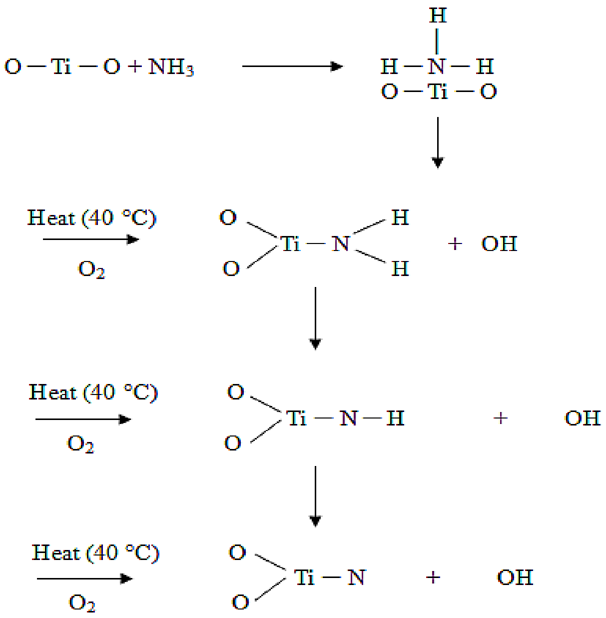


Figure 4: Doping mechanism of nitrogen on titanium dioxide *(Yu et al., 2012).*

In the mechanical process, the high energy could produce the active surface on TiO_2, which would react with nitrogenous substance directly to form chemical adsorb unstable intermediate, and this intermediate could form nitrogen doping in the subsequent thermal treatment. The surface of bio polymer/TiO_2 results the formation of the doped nitrogen may demonstrate chemical adsorption occurring between Ti atom and N atom. Nitrogen atom has unpaired electrons which may be easily adsorbed on Ti. The most probably existing bond in this system is O_2Ti-N-C and this indicated the chemical adsorption occuring between Ti atom and N atom as refer to Figure 4 of the mechanism of nitrogen and titanium dioxide. It has been reported that the nitrogen doped TiO_2 could improve visible light adsorption efficiency with characterization of catalyst (Yu et al., 2012).

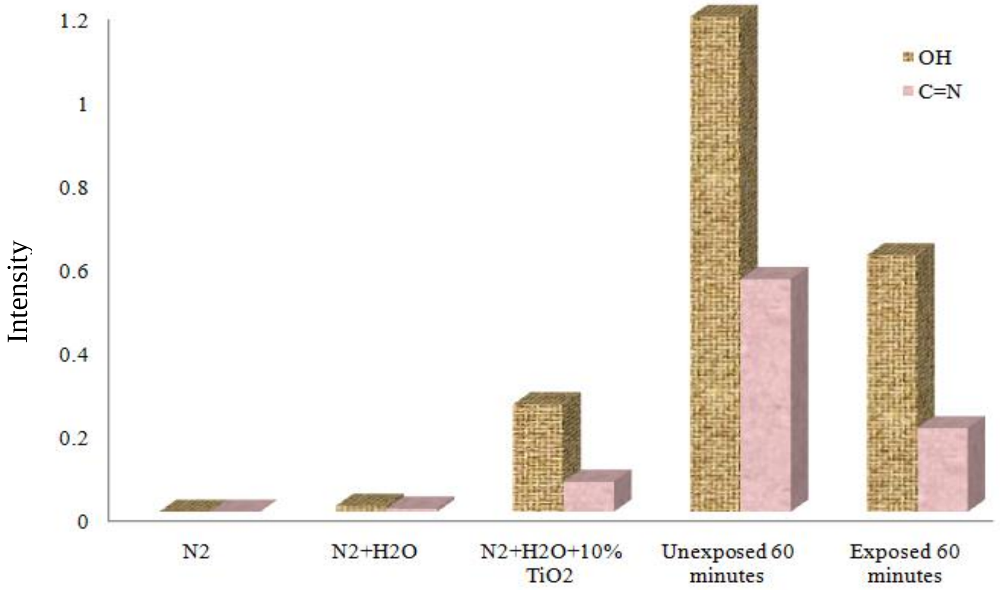


Figure 5: OH and C=N intensity of $BPF_{1.0}$ of exposed at 60 minutes and unexposed to UV light at 60 minutes.

The degradation mechanism shows that the major photo-products resulting from oxidation processes are carbonyl, hydroxyl, hydroperoxide, and conjugated alkenes. In addition to these photo-products, the benzyl radicals generated by UV-irradiation can combine with each others resulting in cross-linking of polymeric chains (Khalid and Afrah, 2010).

Figure 5 shows OH and C=N intensity of $BPF_{1.0}$ for unexposed at 60 minutes and exposed to UV light at 60 minutes. The OH intensities is higher than C=N intensities for unexposed and exposed to UV light. The effect of the irradiation on the absorption spectra of $BPF_{1.0}$ in gas cell resulted in a gradual decrease in the intensity of the absorption spectra with the increase in exposure time. The highest percentage decrease of OH and C=N is 48 % and 64 % respectively.

The infrared spectra of photodegraded $BPF_{1.0}$ after several hours of irradiation are shown in Figure 6. The absorption band of the carbonyl groups near 1705 cm^{-1} was broader with higher intensity on 60 minutes of UV exposure. This type of effect is due to the formation of several types of carbonyl group, and thus suggested that for this renewable polymer for the formation of aliphatic esters was responsible (Anika Zafiah, 2009).

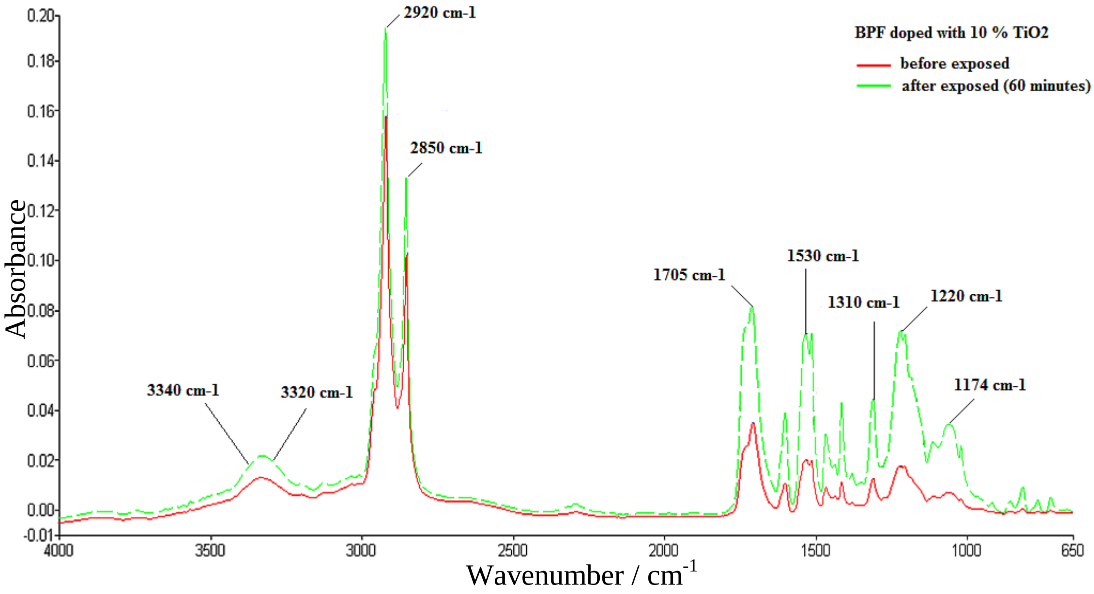
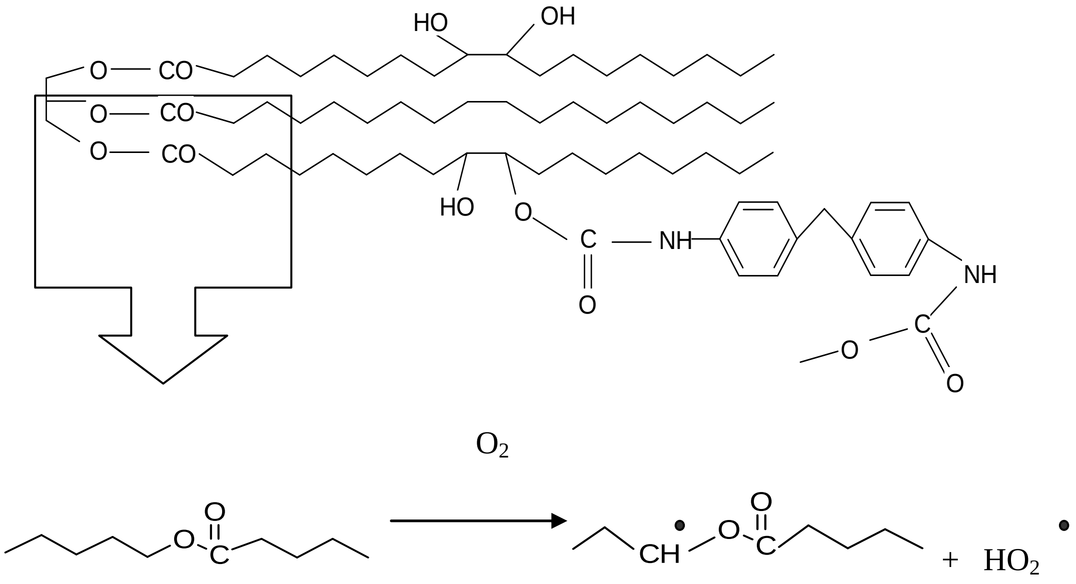
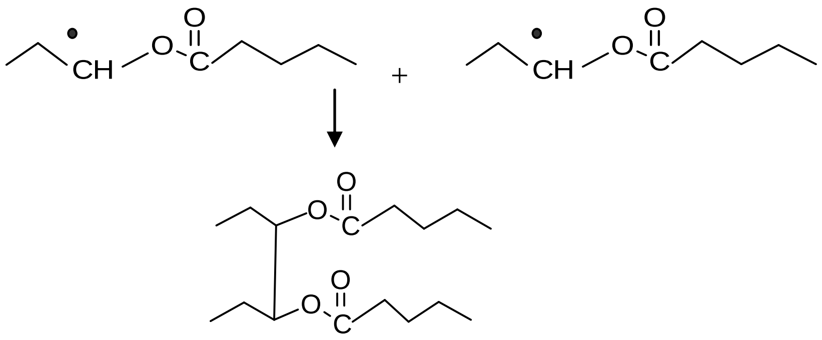


Figure 6: Overlay spectra of FTIR for $BPF_{1.0}$ before and after exposed to UV light at 60 minutes.

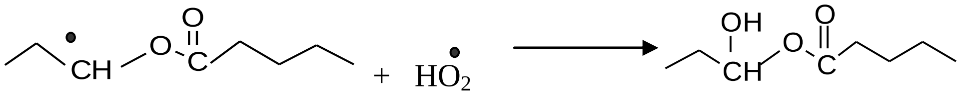


(a) Radical initiation of soft segment



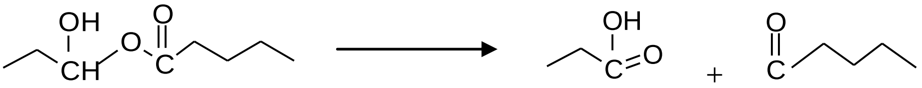
(1174 cm^{-1})

(b) Crosslinking of the soft segment radical



(3340 cm^{-1})

(c) Propagation and chain scission of the soft segment radical



(1705 cm^{-1})

(d) Chain scission

Figure 7: Thermal degradation of $BPF_{1.0}$ after exposed to UV light at 60 minutes *(Anika Zafiah, 2008).*

The prominent peak at 1174 cm^{-1} becomes more intense after UV irradiation for 60 minutes for $BPF_{1.0}$ which can be assigned to crosslinking of the soft segment as shown in Figure 7. This shows that after the UV irradiation the more crosslinking of the soft segment is evidence. This can be attributed to stabilization of the thin films' chain radical, hence increasing the radical lifetime, thereby increasing the probability for combination of chain radicals (Anika Zafiah, 2008). An increase in the quantity of hydroxyl groups can be observed at 3440 cm^{-1}, which is also broadened by the NH groups present in the 3320 cm^{-1}.

A more detailed discussion on the processes involved in the oxidative degradation in a polymer film has been reported (Rabek, 1995). Photo-oxidative degradation is a free radical chain mechanism which occurs when the polymer is exposed to UV-radiation in presence of oxygen. Chemical modifications have been attributed to scission of the polymer chains, and to the cross- linkages.

CONCLUSION

The $BPF_{1.0}$ was prepared in gas cell filled with N_2 and one drop of H_2O. Based on the obtained values of FTIR spectra for the unexposed and exposed $BPF_{1.0}$ the presence of N_2 and H_2O led to significant modification to UV absorption spectra of the exposed sample. Photo-oxidation processes of polymeric chains provoked a marked increase in the absorption and change in the shape of absorption spectra. It was found that the OH and C=N intensities of unexposed gas cell with $BPF_{1.0}$ tend to increase as increasing exposure time while it decreases when exposed to UV light. The absorption spectrum intensitiy for $BPF_{1.0}$ is decrease after exposed to UV light at 60 minutes. This $BPF_{1.0}$ might play an important role as a "green" inexpensive material for the photocatalytic reaction.

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