Studying the photodegradation of ethylcellulose and methylcellulose in the presence and absence of benzophenone (BPh)

Hammed Hashem
Mohamed

Al-Mustansiriya
University,College of
Science, Department of
chemistry.

الخلاصة

تضمن هذا البحث دراسة التجزئة الضوئية المحتثة لافلام الاثيل سليلوز والمثيل سليلوز في

الهواء بوجود وعدم وجود المتحسس الضوئي (البنزوفينون) benzophenone (BPh) وقد تم

التشعيع بوساطة جهاز المعجل الحاوي على مصابيح فلورسنت لدراسة عملية التجزئة الضوئية

هذه. ان اضافة (0,2wt%) من البنزوفينون الى افلام مشتقة السليلوز بسمك (25

مايكروميتر) يزيد التجزئة الضوئية للاثيل سليلوز و الذي يتجزأ اسرع من المثيل سليلوز. تم

قياس التجزئة الضوئية بوساطة الزيادة في امتصاص مجموعة الكاربونيل وثابت سرعة التجزئة

الضوئية (k_d) للبنزوفينون (BPh) في البوليمر بإستخدام أطياف الاشعة تحت الحمراء و الاشعة

فوق البنفسجية و المرئية. ومن النتائج الحركية والطيفية تم اقتراح ميكانيكية لعملية التجزئة

لمشتقات السيليلوز وباستخدام ضوء بطول موجي 313 نانوميتر وشدة امتصاص مقدارها

3.49*10^{-5} einsteins.dm^{-3}.S^{-1} و بدرجة حرارة 45 م°.

ABSTRACT

The induced photodegradation of ethylcellulose (EC) and methylcellulose (MC) films in air was investigated in the presence and absence of benzophenone (BPh) (photosensitizer) by accelerated weathering tester. The addition of (0.2wt %) of benzophenone (BPh) to cellulose derivatives films (25µm in thickness) enhanced the photodegradation of the ethylcellulose (EC) more than methylcellulose (MC) films.The photodegradation rate was followed by increase in carbonyl absorbance of polymers and decomposition rate constant (k_d) of benzophenone in polymers using I.R and U.V-Vis. spectra respectively.

According to the kinetic data and spectra results, the induced photodegradation mechanisms of cellulose derivatives films were suggested under the experimental conditions employed using u.v.-radiation at $\lambda = 313$ nm , light intensity $3.49*10^{-5}$ einsteins.dm^{-3}.S^{-1} at temperature 45 ^{o}C.

1- Introduction

Polymer degradation is of increasing importance in the production and use of implantable and other medical devices[1]. In recent years, there is a growing awareness caused by fast increase of pollution by plastics. Recycling and incineration of plastic waste have many, serious limitations, thus, the production of new materials with enhanced degradation – plastic friendly for environment – seems to be solution of this problem. Accelerated decay of macromolecules can be achieved during their exposure to UV light[2]. New environmental regulations, societal concens, and a growing environmental awareness throughout the world have triggered the search for new products and processes that are compatible with the environment[3]. Degradation of polymeric materials occurs in a wide variety of environments and service conditions, and

very often limits the service lifetime. It occurs as the result of environment-dependent chemical or physical attack, often caused by a combination of degradation agents, and may involve several chemical and mechanical mechanisms[4]. The induced photodegradation of cellulose triacetate (CTA),cellulosediacetate (CDA) , cellulosemonoacetate (CMA) and methylcellulose (MC) films in air, were investigated in the absence and presence of aromatic carbonyl compounds (photosensitizers): 1,4-naphthaquinone (NQ), benzophenone (BPh) , dibenzoylperoxide (DBP) and acetophenone (APh) by accelerated weathering tester[5].

The aim of this work is studying and compared the photodegradation of some of ether derivatives for cellulose in presence and absence of benzophenone as photosensitizer.

2- Experimental

2-1 Material used

a- Laboratory ethylcellulose and methylcellulose powder (B.D.H. Ltd A.R.Grade , purity 99%) was used at the test sample .

b- Benzophenone (BPh)[6]

Laboratory benzophenone (B.D.H. Ltd A.R.Grade) was recrystallized from methanol, then dried in air at room temperature.

2-2 Ultraviolet visible spectrophotometry (U.V):

The absorption spectra was recorded using the ultraviolet visible spectrophotometer using the Hitachi U-2000 and Cary 100 conc. to record the absorption spectra in the wavelength range between (200-600)nm.

2-3 Infrared spectrophotometry (IR)

A Pye-Unicam SP_3-100 infrared spectrophotometer was used to record the IR spectra between (600-4000) cm^{-1}.

2-4 Film preparations

0.2% solution of BPh (in acetone or distilled water) was added to 1% solution of ethylcellulose in acetone and methylcellulose in distilled water in suitable ratio .A thikness of about 25µm was measured by a micrometer type, (2610 , Germany) , ethylcellulose and methylcellulose films with and without BPh were obtained by casting of solutions into horizontal glass plate . After solvent evaporation , samples were dried in vacuum for 24 hrs. this was found to be adequate to completely remove of solvent from films .

2-5 Irradiation

The accelerated weather-o- meter, Q.U.V. tester, (Q-panel company , U.S.A), was used for irradiation of ethylcellulose and methylcellulose films. The films were positioned (25µm) apart from the u.v.lamps (eight fluorescent lamps give essentially monochromatic light at $\lambda=313$ nm) . Temperature of the tester chamber is nearly constant at 45 ℃

2-6 Analysis

The photodegradation of the polymer film was followed by I.R and U.V-Vis. spectrophotometer. The absorption spectra (for I.R method) of the film samples were recorded in the wavenumber ranged from 600 to $4000\,cm^{-1}$. Carbonyl index were calculated by comparison of the I.R absorption peak at 1730 cm^{-1} and 1740 cm^{-1} for (C=O) group with reference peak at 1450cm^{-1} for (-CH$_2$) group for ethylcellulose and methylcellulose. The ultraviolet-visible spectrophotometer was used to measure the change in the U.V-Visible spectrum during irradiation and this was used in calculating the rate of photodecomposition of the BPh by monitoring the increase in absorbance at $\lambda=367$ nm with irradiation time .

3- Results and Discussion

3-1 Photoactivity of Photosensitizers in Methylcellulose(MC) and ethylcellulose (EC) Films.

Hydrocarbon polymer degrade by a free radical chain reaction involving oxygen of the atmosphere. The primary products are hydroperoxides and the latter either thermolyse or photolyse with chain scission and the production of biodegradable low molar mass oxidation products such as carboxylic acids, alcohols and ketones[7]. The UV-visible spectrum of irradiated MC film (25µm in thickness) at different time intervals is shown in figure (1). The decrease in absorbance in the region (200-300)nm due to the scission of main chain bonds in MC polymer.
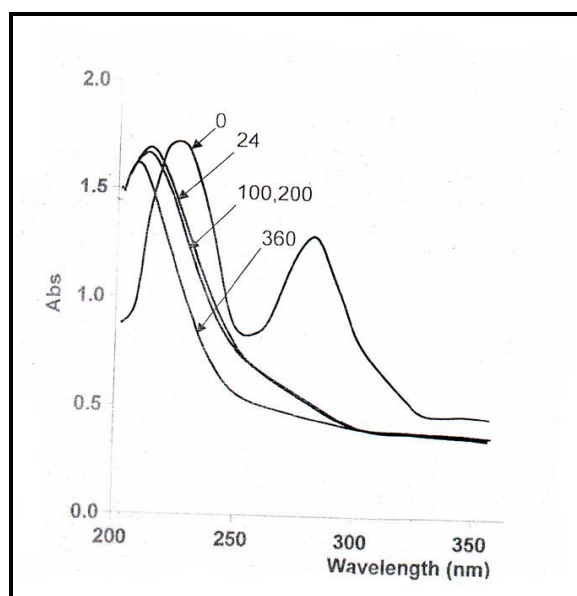

Figure (1): U.V. –visible spectral change of MC film (control) (25 µm in thickness). Number on the spectra are the irradiation times in hours

The spectral changes during photolysis of MC films (25µm in thickness) with 0.2% of BPh photosensitizers are shown in figures (2) , where the decrease in absorption in the region at wavelength below 300 nm was attributed to photodissociation of the photosensitizers with macromolecular chain breaking
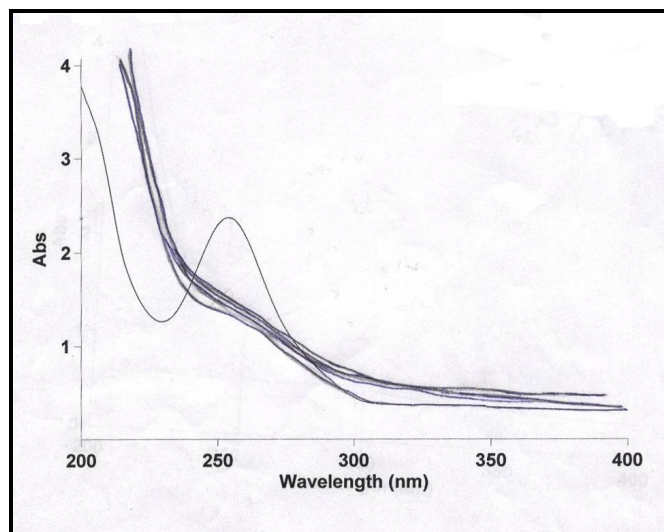
Figure (2): U.V. –visible spectral change of MC film with BPh photosensitizer (25 µm in thickness). Number on the spectra are the irradiation times in hours

The spectral changes during photolysis of EC film (control) (25µm in thickness) is shown in figures (3) ,where the increase in absorption in the region at wave length (280-350)nm with irradiation time. The small peaks at longer wave lengths might be attributed to the formation of the
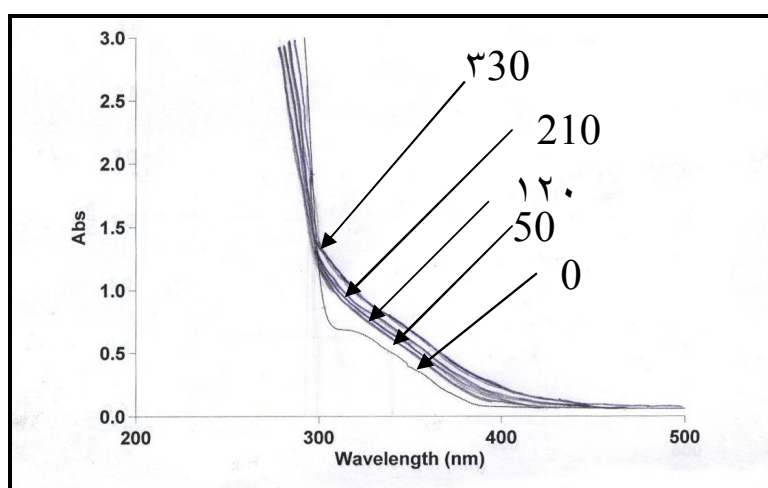

Figure (4): U.V. –visible spectral change of EC film with BPh (25 µm in thickness). Number on the spectra are the irradiation times in hours

Figure (5) and (6) show the variation of ln $(A_\infty - A_t)$ and ln $(A_t - A_\infty)$ of ethylcellulose and methylcellulose films respectively with benzophenone

(BPh)   with irradiation time at λ=313 nm at wave length (λ = 339 nm) , (λ = 254 nm) respectively . A straight line is obtained which indicates primarily a first order reaction and the decomposition rate constant (k_d) for polymers was calculated from the slope value .The photodecomposition rate constant (k_d) was calculated and it has been found the (k_d) of ethylcellulose films with benzophenone (BPh) (k_d = 0.01147 min^{-1}) is higher than (k_d) for methylcellulose films with benzophenone (BPH) (k_d =0.00069 min^{-1}) .It is concluded that the photodegradation rate for ethylcellulose is higher than methylcellulose, this could be attributed to formation secondary free radical in ethylcellulose which is more stable than primary free radical in methylcellulose through photodegradation processes (see scheme 1) .
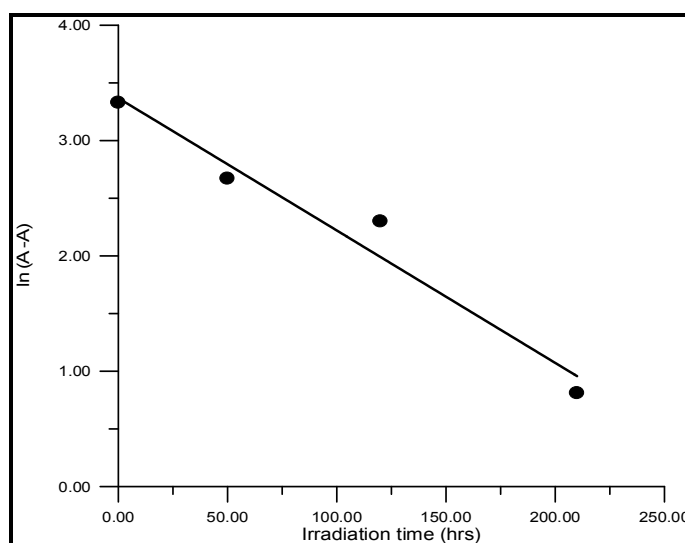

Figure (5) : Variation of natural logarithm of (A_∞ - A_t) with irradiation time for ethylcellulose film with BPh
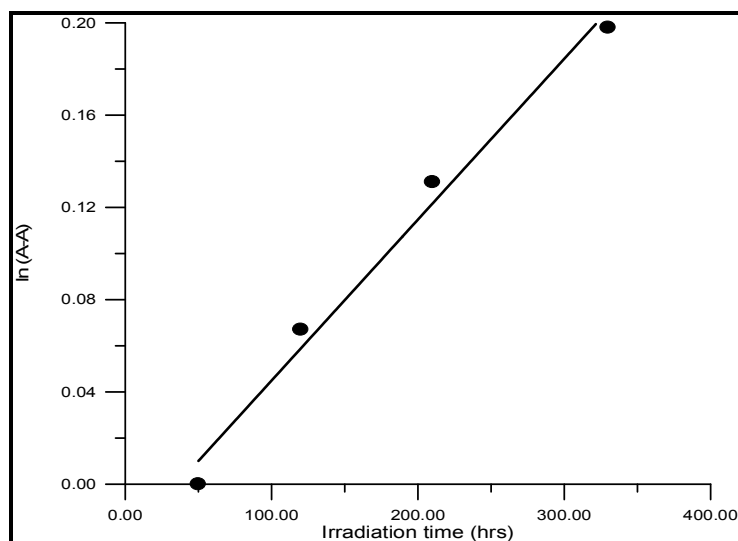
Figure (6) : Variation of natural logarithm of (A_t-A_∞) with irradiation time for methylcellulose film with BPh

The IR spectrum in figure (7) of EC films (control) (25µm in thickness) shown small changes in carbonyl group located at 1730 cm^{-1} for EC after irradiation time .
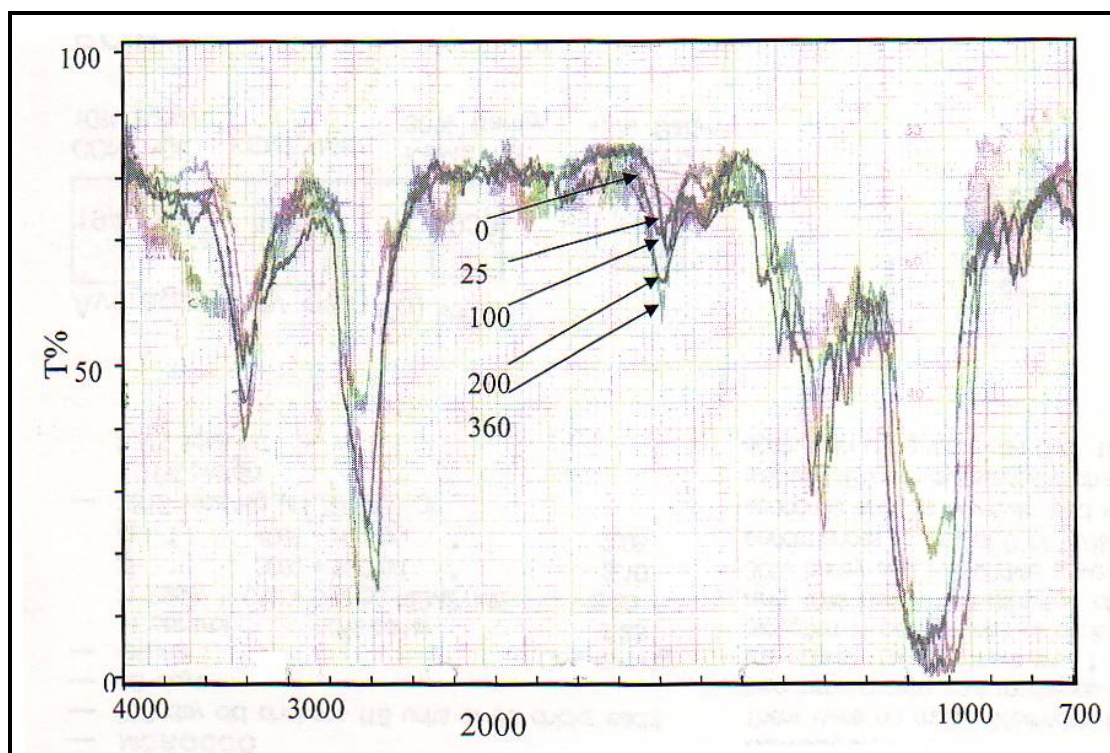

Figure (7): Change in IR spectrum of EC (control) (25 µm in thickness).Numbers on the spectra are the irradiation times in hours
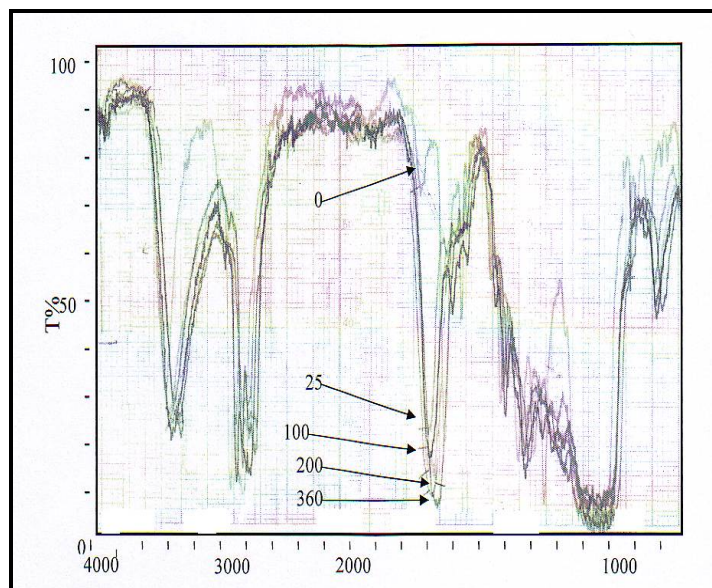
Figure (8): Change in IR spectrum of EC with BPh (25 μm in thickness).Numbers on the spectra are the irradiation times in hours

It has been observed that the carbonyl group in figures (8) increases greatly with irradiation time for EC films with BPh photosensitizers compared to EC films (control). Accordingly, this photosensitizer is considered as photoinducer for MC and EC films degradation.Table (1) show the calculated values of the carbonyl index (I_{CO}) with different irradiation time for MC and EC in the absence and presence benzophenone (BPh) photosensitizers

Table (1): The calculated values of the carbonyl index (I_{CO}) with different irradiation time for MC and EC in the absence and presence benzophenone (BPh) photosensitizers

Comp.	Irradiation time (hrs)				
	0	**25**	**100**	**200**	**360**
EC (control)	0.60	1.03	1.12	1.20	1.93
EC (with BPh)	0.34	2.36	3.60	4.60	5.96
MC (control)	0	0	0	0.09	0.10
MC (with BPh)	0	0.28	0.76	0.91	0.95

The photoactivity of MC and EC films (control)(25 μm in thickness) and with 0.2% of BPh photosensitizers is followed by the growth of carbonyl group only, which is expressed in term as carbonyl index (I_{CO}), where figures (9) , (10) and (11) shows the relationship between carbonyl index and irradiation time for MC and EC films (25 μm in thickness) with and without (0.2 wt %) of BPh photosensitizers , and also compared between EC and MC films in presence (0.2 wt %) of BPh photosensitizer. It has been observed that the carbonyl index increases greatly with irradiation time for EC, MC films with BPh photosensitizers compared to EC and MC films (control) , also the carbonyl index increases with irradiation time for EC films compared with MC films in presence BPh photosensitizers. It can be concluded that photo-oxidative degradation of EC and MC is more efficient in the presence of BPh as photosensitizer, and EC was degraded higher than MC .
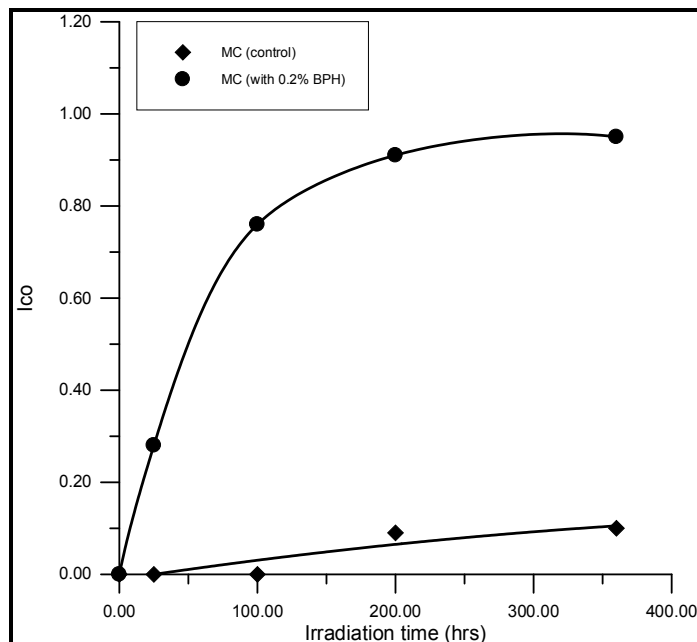

Figure (9): The relationship between carbonyl index and irradiation time for MC films(25 μm in thickness) with and without (0.2 wt %) of photosensitizers

Figure (10): The relationship between carbonyl index and irradiation time for EC films(25 µm in thickness) with and without (0.2 wt %) of photosensitizers
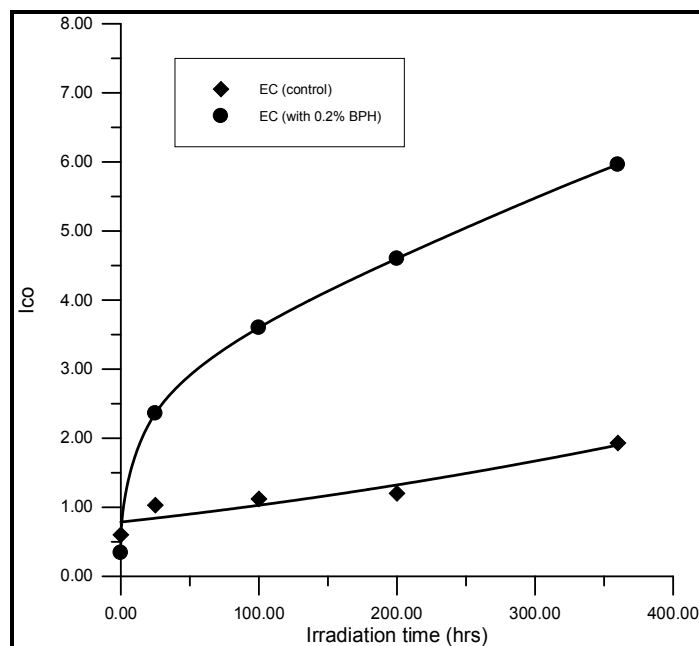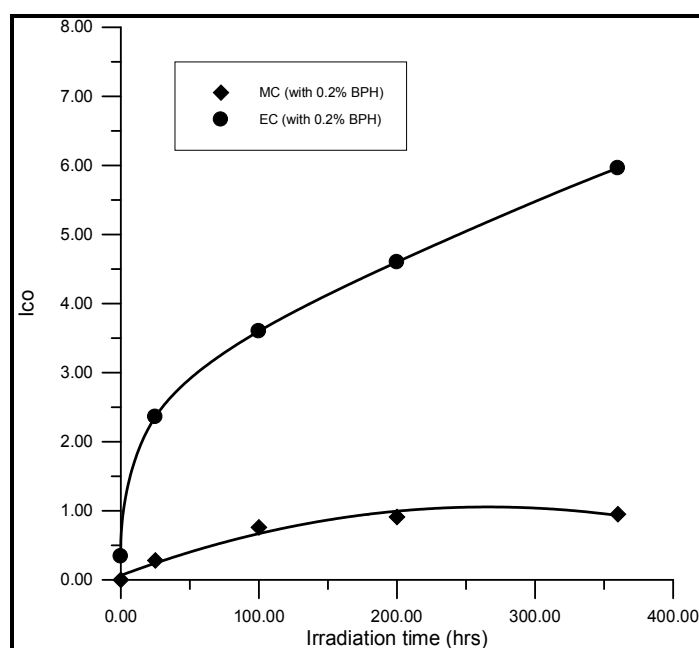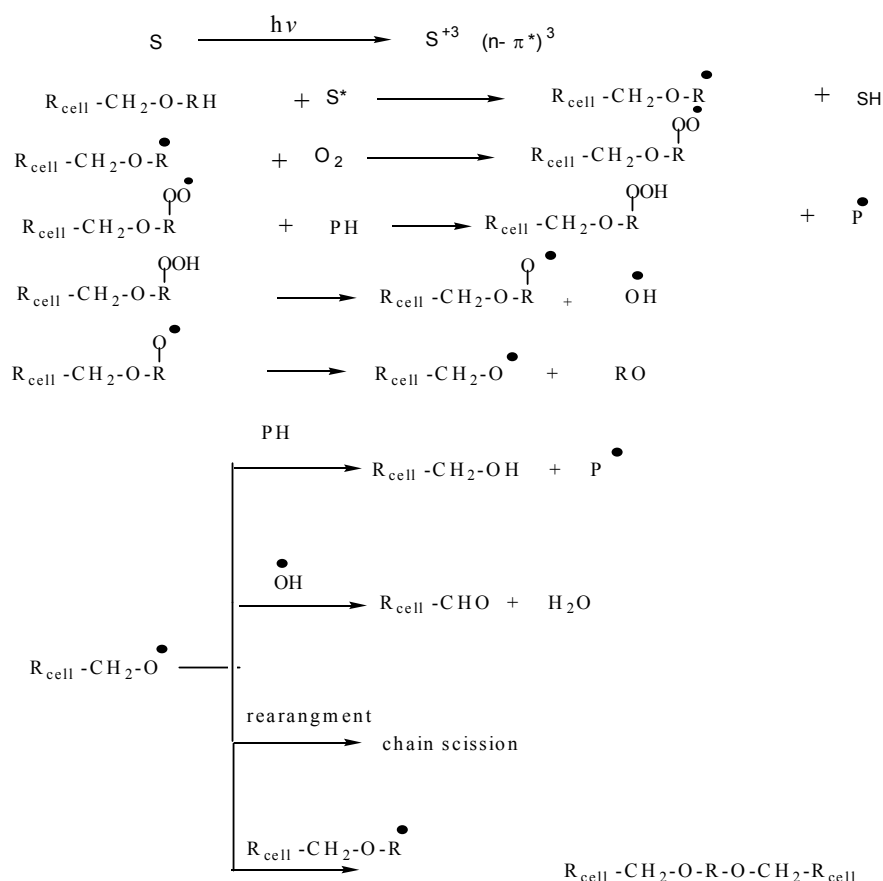

Figure (11): The relationship between carbonyl index and irradiation time for EC films and MC films (25 µm in thickness) with (0.2 wt %) of photosensitizers

The photosensitizers initiated the degradation of the MC and EC polymers via the generation of free radical, as in photodegradation of cellulose acetate derivatives with the same photosensitizers. The

produced radicals from irradiated photosensitizers can abstract hydrogen from the methyl group of the MC and EC polymers .

The rate of carbonyl index formation is higher than that for similarly exposed EC (control) or EC with BPh compared with MC . The above results are similar to results of photodegradation of poly methyl metha acrylate – co – cellulose monoacetate film by BPh[8] , photodegradation of poly styrene [9] and methylcellulose [5].

Therefore the following mechanism for photodegradation of MC and EC by photosensitizers might be suggested[5] (scheme 1):

$$S \xrightarrow{h\nu} S^{+3} \quad (n\text{-}\pi^*)^3$$

$$R_{cell}\text{-}CH_2\text{-}O\text{-}RH + S^* \longrightarrow R_{cell}\text{-}CH_2\text{-}O\text{-}\overset{\bullet}{R} + SH$$

$$R_{cell}\text{-}CH_2\text{-}O\text{-}\overset{\bullet}{R} + O_2 \longrightarrow R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{OO^\bullet}{|}$$

$$R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{OO^\bullet}{|} + PH \longrightarrow R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{OOH}{|} + \overset{\bullet}{P}$$

$$R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{OOH}{|} \longrightarrow R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{O^\bullet}{|} + \overset{\bullet}{O}H$$

$$R_{cell}\text{-}CH_2\text{-}O\text{-}R\overset{O^\bullet}{|} \longrightarrow R_{cell}\text{-}CH_2\text{-}\overset{\bullet}{O} + RO$$

$$R_{cell}\text{-}CH_2\text{-}\overset{\bullet}{O} \begin{cases} \xrightarrow{PH} R_{cell}\text{-}CH_2\text{-}OH + \overset{\bullet}{P} \\ \xrightarrow{\overset{\bullet}{O}H} R_{cell}\text{-}CHO + H_2O \\ \xrightarrow{rearangment} chain\ scission \\ \xrightarrow{R_{cell}\text{-}CH_2\text{-}O\text{-}\overset{\bullet}{R}} R_{cell}\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}CH_2\text{-}R_{cell} \end{cases}$$

Where : S = Photosensitizers (BPH),SH = BPH – H ,R_{cell} = cellulose molecule

PH = ethyl or methylcellulose,RH = -CH_3 or - CH_2-CH_3

R- = - CH_2 or - CH-CH_3

Scheme (1) : Mechanism for photodegradation of MC and EC   by photosensitizers

Conclusion

The results presented in this work have shown that the effect of UV radiation on the photodegradation of ether cellulose derivatives. It has been found that photo-oxidative degradation of ether cellulose derivatives was more efficient in the presence of benzophenone and the ethylcellulose was degraded higher than methylcellulose.

References

1. C. M. Vaz., R.L.Reis and A.M. Cunha, "*Degradation model os starch-EVOH + HA composites", Mat. Res. Innovat,* <u>4</u>,375-380,(2001)

2. H.Kaczmarek , A.Kaminska , J.Kowalonek and A.Szalla , "*Accelerated Degradation of polymer", Mol. Cryst. and Liq. Cryst.*, <u>354</u>,421-425, (2000)

3. N.Ramani, "*Rationale, Drivers and Standards for Biodegradable Plastics", J. of Center of Applied and Scientific Research* , University of Qatar, p. 21, (2001) .

4. D.Feldman, "Polymer weathering: photo-oxidation", J. of Polymer and Environment, Vol. 10, No. 4 , 163 (2002) .

5. Z.N. Mageed, *PhD .Thesis," Induced Photodegradation of Some Cellulose Derivatives*" AL-Mustansiriah Univerisity ,(2006) .

6. W.L.F.Armarego and D.D.Perrin," *Purification of Laboratory Chemicals", Fourth Edition*,pp.95,(1998)

7. G.Scott, , *ICS- INDO Report. "Environmental Degradable Plastics".* 20-24 March, (2000).

8. ITO.Yoshikatsu, Y.Aoki, T.Matsuura, N. Kawatsuki and M.Uetsuki, *J.Appl.Polym.Sci.*,<u>42</u>,409-415,(1991)

H.Kaczmarek , A.Kaminska , M. Swiatek, and S.Sanyal, "*Photoinitiation degradation of polystyrene in the presence of low-molecular organic compounds", European Polymer Journal* ,<u>36 </u>, 1167 (2000)