Effect of 1,4-Napthaquinone (NQ) and benzophenone (BPH)on the photodegradation and biodegradation of methyl cellulose film

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Abstract:

The induced photodegradation of methyl cellulose (MC) films in air was investigated in the absence and presence of aromatic carbonyl compounds(photosenssitizers): 1,4-naphthaquinone (NQ) and benzophenone (BPH) by accelerated weathering tester. The addition of (0.01 wt %) of low molecular weight aromatic carbonyl compounds to cellulose derivatives films(25µm in thickness) enhanced the photodegradation of the polymer films.The photodegradation rate was measured by the increase in carbonyl absorbance.

Decreases in solution viscosity and reduction of molecular weight were also observed in the irradiated samples. Changes in the number-average chain scission, the degree of deterioration and in the quantum yield of chain scission values are also observed, and it was concluded that branching or cross-linking has occurred for cellulose derivative with NQ and BPH. Findings from all analytical techniques indicated that the 1,4-naphthaquinone (NQ) photosensitizer enhance the photodegradation of methyl cellulose more than benzophenone (BPH).

The effect of the photosensitizer concentration, (ranging from 0.01 to 0.1 %), on the rate of photodegradation was also monitored for MC films. The rates are increased with increasing the photosensitizer concentration.

The effect of film thickness is also studied at fixed sensitizer concentration (0.05%), and results show that the rate of cellulose derivative photodegradation decreases with increasing film thickness.

The rate constants of the photodegradation of the photosensitizers deduced in cellulose derivatives films, [at concentration of (0.1%)by weight and thickness (25µm)].

Biodegradation of irradiated cellulose derivatives films was conclusively established with bacteria type *Pseudomonas aeuroginosa Rb-19* isolated from crude oil. The amount of bacteria growth on MC after 30 days was lower, while there was no growth observed in MC with BPH

Key words: 1,4-Napthaquinone, benzophenone, biodegradation

Introduction

Structural diversity and functional versatility of polysaccharides such as methylcellulose polymer and others are described in Dimitriu book[(1)], while photodegradation details for these polymers are given in the literature[(2-6)].

Cellulose ethers such as methylcellulose undergo photo-rheological change when exposed to ultraviolet (UV) radiation[(2-6)]. A major cause of such change is the main chain scission as a result, the molar mass

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and, therefore, the molecular dimensions of the polymer conformational state, also, change.

During UV-irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack of bacteria in natural environment[7].

biodegradable polymers have currently attracted high interest as ideal carriers in drug delivery and tissue engineering applications. In situ forming devices based on these materials will synergistically provide the advantages of the customary prefabricated devices as well as ease of administration[8]. In the present work , we describe the effects of Naphthaquinone (NQ), benzophenone (BPH) as photosensitizers on the degradation of methyl cellulose and study of its biodegradation.

Martial and Methods:

a- Film Preparations

1% of (MC)polymer solutions in acetone is used to prepare (25μm)polymer films which is measured by a micrometer type,(2610 a Germany)with and without various concentrations of (BPH , NQ) photosensitizors, The films were prepared by casting and evaporation techniques at room temperature for 12 hr., To remove the possible solvent residue, the film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on a special holder for irradiation (which is made from aluminum plate (0.6 mm) in thickness supplied from (Q-panel) company).

b- Irradiation Experiments

The accelerated weather-o- meter, Q.U.V. tester,(Q-panel company , U.S.A),was used for irradiation of polymer films. The accelerated weathering tester contains stainless steel plate with two cavities in the front and rear sides. Each side contains four lamps, type (U.V.B.313) located horizontally, giving spectrum range of wavelength between 290 to 360 nm and the maximum intensity is located at the wavelength 313 nm .The polymer film holders are fixed vertically and parallel to the lamps ,so that the UV radiation is vertically incident on the polymeric samples . The irradiated sample holders were changed in positions from time to time to ensure that all samples received the same intensity of light.

During the irradiation process, the degree of photodegradation of polymer films was monitored by taking different exposure times.

c- Determination of Viscosity Average Molecular Weight (M_v) Using Viscometry method

The viscosity property was used to determinate the molecular weight of the polymers using Mark -Houwink relation [9]

$$[\eta] = K\left(\overline{M}_v\right)^{\alpha} \quad \ldots(1)$$

where,

$[\eta]$ = intrinsic viscosity

K and α: are constants for a given polymer at a given temperature in a given solvent.

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer .Solutions were made by dissolving the polymer in a solvent (g/100mL) and the flow times of polymer solution (t)and pure solvent ($t_\circ$),were measured respectively.

d- Ultraviolet Visible Spectrophotometry (U.V)

The absorption spectra was recorded using the ultraviolet visible spectrophotometer type (Hitachi U-2000), in the wavelength range between 200 to 800 nm.

e- Infrared Spectrophotometry (IR)

The (IR) spectra were recorded using Pye Unicam,SP3-100spectrophotometer. In this work the band index method was used ,by comparing IR absorption peaks at the specified position with reference peak e.g. measurements changed in hydroxyl peak in relation to the reference band at 2950 cm^{-1},which refers to the C-H aliphatic ,and changed in carbonyl peak in relation to the reference band at 1430cm^{-1} which refers to the CH_2 bending in cellulose derivatives.

Results and discussion

The photodegradation of (MC),which has specifically been studied, is used as a thickening agent and emulsifier in cosmetics, pharmaceuticals and clarity in various industrial fields [1].

The UV-visible spectrum of irradiated MC film (25µm in thickness) at different time intervals shows the decrease in absorbance in the region (200-300)nm which due to the scission of main chain bonds in MC polymer. The spectra changes during photolysis of MC films (25µm in thickness) with 0.1% of NQ and BPH photosensitizers are shows the decrease in absorption in the region at wavelength below 300 nm which attributed to photodissociation of the photosensitizers with macromolecular chain breaking.

The IR spectrum of MC film (control) (25µm in thickness)shown small changes in carbonyl group located at 1730cm^{-1} after 200 hr of irradiation time. The photoactivity of MC film(control)(25 µm in thickness) and with 0.1% of BPH and NQ photosensitizers is followed by the growth of carbonyl group only which is expressed in term carbonyl index (I_{CO}) where calculated and tabulated with irradiation time in table (1).

It has been observed that the carbonyl index increase greatly with irradiation time for MC films with BPH and NQ photosensitizers compared to MC film (control).

Accordingly, these photosensitizers are considered as photoinducers for MC films degradation.

Table (1) Calculated values of carbonyl index (I_{CO}) with irradiation time for MC film (25 µm in thickness) containing 0.1 wt% of photosensitizers.

photosensitizersconcentration	Irradiation time					
	0	22	72	144	200	360
MC(control)	0	0	0	0	0.093	0.1
MC+NQ	0	1.181	1.59	2.039	2.53	2.611
MC+ Bph	0	0.253	0.5004	1.639	1.72	1.813

The photosensitizers can be degrade the MC polymer via the generation of free radical. The produced radicals from irradiated photosensitizers can abstract hydrogen from the methyl group of the MC polymer to resulting the photodissociation.

These results are agreetment with PMMA-CO-CMA film photodegradation by BPH reported by Yoshikatsu and co-workers[10].

Also these results show that NQ act as better inducer for MC photodegradation compared to BPH, as the rate of carbonyl index formation is higher than that for similarly exposed MC (control) or MC with BPH . The above result is similar to results of photodegradation of poly styrene [11] and cellulose[12].

Effect of Film Thickness

The rate of photodegradation of MC films was studied in different thickness (25, 75 and150 µm) with fixed concentration (0.05 %) of BPH photosensitizer .

The calculated values and relationships between carbonyl index and irradiation time are tabulated in table (2).

It can be observed from the results in the abovementioned table and figure that carbonyl index (Ico) decrease with

increasing film thickness, which is attributed to a longer residential time for the oxygen to diffuse within the thicker MC layers.

Table(2) :Calculated values of carbonyl index (I_{CO})with irradiation time for MC with different thickness containing 0.05wt% of BPH.

Thickness µm	Irradiation time				
	0	22	72	144	200
25	0	1.181	1.363	1.437	1.513
75	0	0.411	0.64	.887	1.509
150	0	0.38	0.5	0.866	1.2125

Effect of Photosensitizer Concentration

In the present work, the photodegradation of MC films (25 µm in thickness)was also examined with different photosensitizer concentration.

Tables (3) and (4) show the calculated values of carbonyl index (I_{CO}) with different irradiation times using different concentration of BPH and NQ photosensitizers , ranging from 0.00 % (MC control) to 0.1 % (wt/wt %).

It can be observed from the below tables, that the carbonyl index increase with increasing photosensitizer concentration, the rates of carbonyl index(I_{CO}) formation are higher than those of the similarly exposed MC (control), confirming that these photosensitizers are accelerators for MC degradation.

One might suggest that oxidative degradation of MC is greatly enhanced in the presence high concentration of photosensitizers as seen in cellulose acetate. The difference in reactivity of the photosensitizers is also noticed from the differences in the rates of carbonyl index formation .BPH shows the lowest reactivity in degradation of MC polymer compared to NQ.

Table (3) :Calculated values of carbonyl index (I_{CO}) with irradiation time for MC film (25µm in thickness) containing different concentration of NQ photosensitizer.

sensitizer concentration	Irradiation time					
	0	22	72	144	200	360
MC(control)	0	0	0	0	0.093	0.1
0.01%	0	0.54	0.919	1.528	1.54	1.632
0.05%	0	0.205	1.38	1.508	1.587	1.668
0.1%	0	1.181	1.59	2.039	2.53	2.611

Table (4) :Calculated values of carbonyl index (Ico) with irradiation time for MC (25µm in thickness) containing different concentration of BPH photosensitizer.

sensitizer concentration	**Irradiation time**					
	0	**22**	**72**	**144**	**200**	**360**
MC(control)	0	0	0	0	0.093	0.1
0.01%	0	0.2935	0.6219	1.0486	1.1	1.156
0.05%	0	0.118	1.363	1.437	1.513	1.592
0.1%	0	0.253	0.5004	1.639	1.72	1.813

Molecular Weight Changes During Photolysis

In the present work ,the application of Mark-Houwink-Sakurada[97] (equation 1) in degradation of MC films was examined. The degradation was followed by the determination of the change in molecular weight by measuring the intrinsic viscosity.

Viscosity measurements for MC films(control) (25 µm in thickness)and with 0.1 wt% of BPH and NQ photosensitizers were carried out before and after irradiation time , in distilled water solvent at 25°C .The MC films with BPH and NQ photosensitizers are not dissolved in distilled water after 20 hr irradiation, therefore it is assumed that crosslinking or branching occurs during photolysis course.

The problem of photocrosslinking of polymers is very important effected on account of the wide applications in commercial processes. Photo polymers are macromolecules which can become crosslinked polymers by the formation of interchange bonds under the influence of light.

Tsuda[13] has suggested that the energy from an excited triplet state of the sensitizer can be transferred to the triplet state of the polymer group which then undergoes crosslinking reaction as in equation (10).

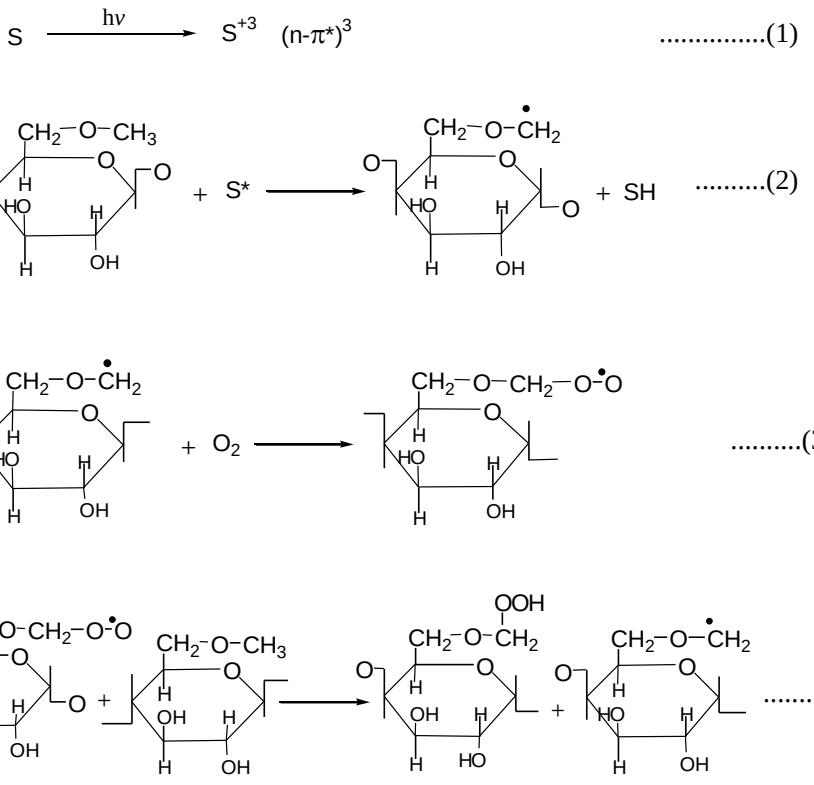
These results are in an agreement with a previous study[137,138] which indicated that benzophenone and its derivatives cause extensive crosslinking of polyethylene. The change in molecular weight M_v of MC film (control) with irradiation time is shown in table (5) .

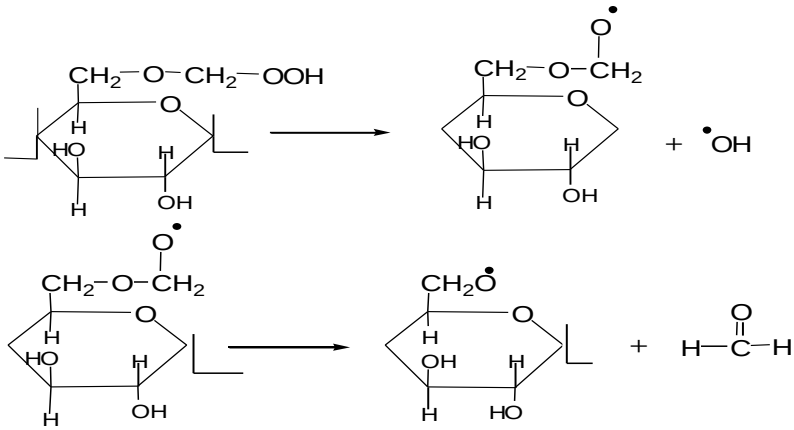
The degree of deterioration (α) and the average number of chain scissions(S) are also calculated in table (5) where they are increased with irradiation time which indicating to random breaking of bonds in the MC polymer chain. The quantum yield of the chain scission (Φ_{cs}) calculated for MC film is equal to(1.38×10^{-3}).

Table(5) :The variation of α ,S ,P_t , dM_V/dt ,$(M_V)^2$ and M_V with irradiation time for MC films (control) (25 μm in thickness) .

Time(hr)	M_v	$(M_v)^2 \times 10^5$	d M_v/dt	P_t	1/ P_t	α	S
0	11174	1248		57.597	0.01736		
22	8203	672	135.045	42.285	0.0236	0.0063	0.3622
144	7409	548	26.146	38.191	0.0262	0.0088	0.508
192	7296	532	20.198	37.608	0.0266	0.00923	0.5316
288	7000	490	14.493	36.082	0.0277	0.01035	0.5964

Therefore the suggesting mechanism for photodegradation of MC by photosensitizers is that:

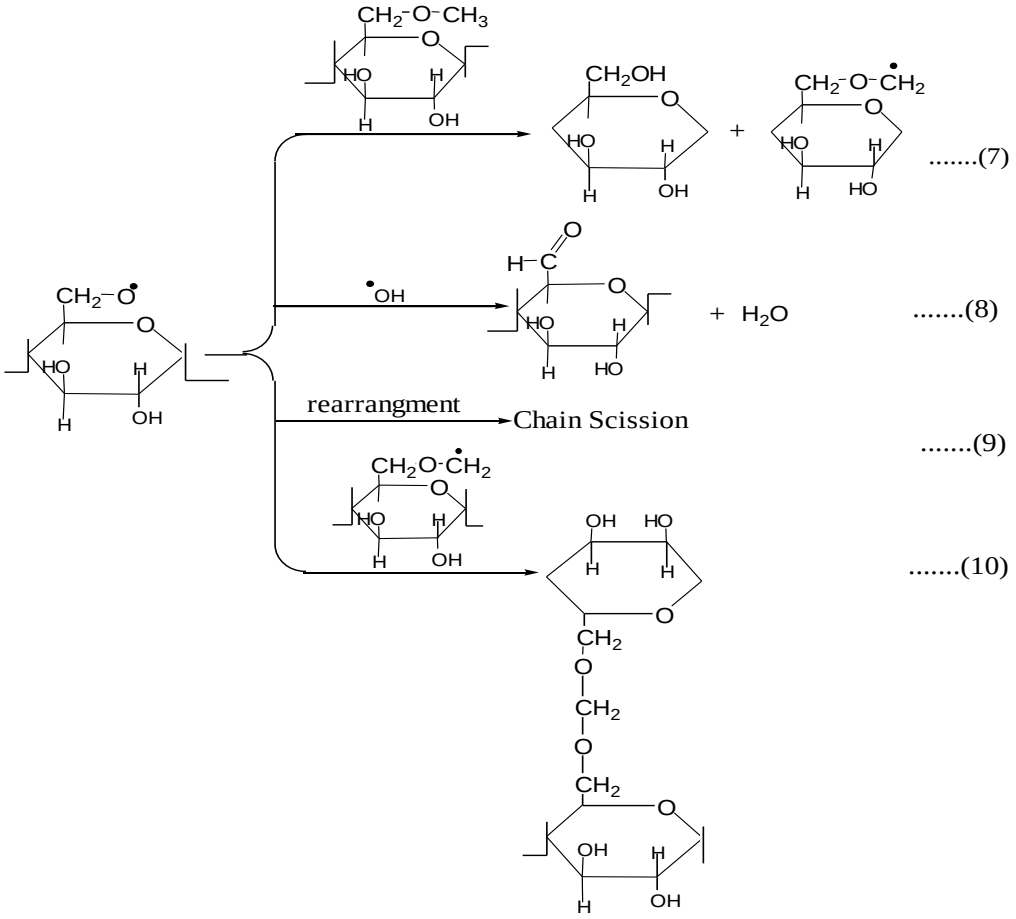




.....(5)

.....(6)

S = Photosensitizers (BPH, NQ)
SH= BPH–H or NQ–H



.....(7)

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Biodegradation of Cellulose Derivatives

The bacteria, *Pseudomonas aeuroginosa RB-19* ,which is used in this work, was isolated from crude oil as utilizing of aliphatic and aromatic hydrocarbons(such as phenol and n-hexane).

In order to ensure that the bacteria isolated were indeed capable of growing with irradiation polymers as the sole available carbon source. Series of experiments was carried out in which the growth with polymer was compared to that in control [mineral medium(MM) free of carbon source

].The Growth of bacteria (*Pseudomonas aeuroginosa RB-19*) on cellulose derivatives after photolysis is 10-20%

Our results support the conclusion that these bacteria were indeed capable of a significant amount of growth when the only carbon source present was the polymer. Color changes from colorless solution to green solution indicating microbial growth.

The biodegradation are followed by percentage weight loss of polymer through biodegradation , where the polymer precipitated by mixture of ethanol and water from bacteria solution and dried under vacuum .

% loss weight = weight of polymer before biodegradation - weight of polymer after biodegradation

The % loss weight for cellulose diacetate is 34% , In general, during UV-irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack of bacteria in natural environment. It is also well known that the efficient main chain scission in irradiated polymers causes their mechanical deterioration and breaking on to small pieces. Thus, the access of oxygen and microorganisms is facilitated to the bulk of such destroyed products. In this way polymers become biodegradable.

The biodegradation of cellulose ethers has been studied and it is known that MC has low degraded because the microorganism attacks the unsubstituted residues of the polymers, the ether linkages to the cellulose backbone are considered resistant to microbial attack. The crosslink which occurred during photodegradation of MC with 0.1 wt% BPH prevent the biodegradation of MC along (30) days.

Conclusion

It has been found that photooxidative degradation of methyl cellulose (MC) are more efficient in the presence of these photosensitizer ,and 1,4-Naphtaquinone ,Benzophenone are higher action , especially in sample contained (0.1wt%) . The rates of degradation in cellulose derivatives films are inversely related to film thickness. Increasing film thickness can limit oxygen diffusion; therefore reduce the degradation rate of the polymer films.

Calculation based on the viscosity average molecular weight (M_v) clearly indicates an overall decrease in molecular weight during irradiation. From the calculated values of the degree of deterioration (α) and the number average chain scission(S), it is concluded that the type of degradation is random.

Methyl cellulose are biodegradable polymers and can be expected to be degraded in natural environmental systems .The rate of biodegradation cellulosic polymers to readily participate in natures carbon cycle. This work, however , show that cellulose acetate has potentially degradable in the environment .

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تأثير 1،4- نفثاكوينون و بنزوكوينون والتكسر الضوئي والحيوي لفلم مثيل سليلوز

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الخلاصة

تضمن هذا البحث دراسة التجزئة الضوئية المحتثة لافلام المثيل السليلوز في الهواء بوجود وعدم وجود بعض مركبات الكاربونيل الاروماتية (متحسسات ضوئية) التالية:
[1,4-Napthaquinone (NQ) and benzophenone (BPH)]
وقد تم التشعيع بواسطة جهاز التعجيل الحاوي على مصابيح فلورسنت لدراسة عملية التجزئة الضوئية هذه . ان اضافة (0.1wt%) من مركبات الكاربونيل الاروماتية الى افلام مشتق السيليلوز بسمك (25 مايكروميتر) يزيد التجزئة الضوئية للبوليمر . تم قياس التجزئة الضوئية بواسطة الزيادة في امتصاص الكاربونيل. كما تم ملاحظة النقصان في اللزوجة والوزن الجزيئي من خلال متابعة التغير في المعدل العددي لقطع السلسلة ودرجة التجزئة وفي قيم منتوج الكم لعملية قطع السلسلة. وقد وجدنا بان التفرع والتشابك العرضي يحصل في مشتق السيليلوز مع (NQ ,BPH) .اظهرت نتائج التحليل ان 1,4-Napthaquinone (NQ) تزيد التجزئة الضوئية لمشتق السيليلوز اسرع من benzophenone (BPH) . كذلك تم دراسة تاثيرتركيز المضافات في المدى(% 0.1-0.01) على سرعة التجزئة الضوئية, وقد اظهرت النتائج ان سرعة التجزئة الضوئية تزداد بزيادة تركيز المضاف . و تم كذلك دراسة تاثير سمك الرقائق البوليمرية عند تركيزثابت من المضاف(0.05%) وقد اظهرت النتائج ان التجزئة الضوئية تقل مع زيادة سمك الرقائق البوليمرية. إضافة الى ذلك تم اجراء تجارب على التجزئة الحيوية لمشتقات السليلوزالمشعة باستخدام بكتريا *Pseudomonas aeuroginosa RB-19* معزولة من النفط حيث وجد ان نمو البكتيريا على المثيل سليلوز بعد 30 يوم يكون قليل , كما لم يلاحظ نمو أي بكتيري على المثيل سيليلوز الحاوي على مضاف (BPH) .