

Study the Photodegradation of Hydroxypropyl Cellulose in Presence and Absence of Benzophenone and Eosine Dye

Zainab Naeif Majeed¹, Hamid Hashim Mohammed^{2*}, and Safana Ahmed Farhan¹

1. Al-Mustansiriya University, College of Science, unit of research polymer
P.O. Box 46136, Al-Mustansiriya University, Baghdad, Iraq

2. Al-Mustansiriya University, College of Science, Department of Chemistry
P.O. Box 46136, Al-Mustansiriya University, Baghdad, Iraq
Corresponding author. E-mail : hammed_sugar@yahoo.com

Abstract

The induced photodegradation of poly hydroxypropyl cellulose films in air was investigated (for 350 hrs.) in presence and absence of benzophenone and eosine dye (photosensitizer) by accelerated weathering tester.

The addition of (0.1wt %) of benzophenone and eosine dye to poly hydroxypropyl cellulose films (25 μ m in thickness) enhanced the photodegradation of the polymer films. The photodegradation rate was followed by increase in carbonyl absorbance of polymers using infrared (I.R.) and UV-visible spectra respectively and viscosity.

It is concluded from this work that eosine dye enhances degradation of polymer more than benzophenone. According to the spectra results, the induced photodegradation mechanisms of polymer films were suggested under the experimental conditions employed using UV-radiation at $\lambda = 313$ nm, light intensity 3.49×10^{-5} einsteins.dm⁻³.S⁻¹ at temperature 45 °C.

Key words: photodegradation, hydroxypropyl cellulose

Introduction

Hydroxypropyl cellulose (HPC) is non-ionic, it is less reactive to active ingredients compared with ionic excipients. This excellent compatibility is the main reason for HPC being the first choice of Japanese pharmaceutical companies. For example, aspirin tablets with HPC were stable under high temperature whereas ionic ingredients showed whiskers of salicylic acid formed by hydrolysis (See picture below). Vitamin C tablets formulated with HPC showed no interaction compared with tablets using ionic disintegrants⁽¹⁾.

Photodegradation of polymers is generally accepted as the main factor that limits their use in outdoor applications. It is caused by the ultraviolet (UV) component of solar radiation and is a serious problem in the sunniest climates. Photo-oxidation creates free radicals that start a chain reaction that can progress quite rapidly, causing rapid deterioration of mechanical properties. The chemical and physical mechanisms of degradation and their effects on engineering properties and morphological changes (such as secondary crystallization) are discussed. Photostabilizers that can produce spectacular improvements in polymer lifetime under UV exposure are discussed. Testing for photodegradability is dealt with. It usually involves accelerated laboratory conditioning and this is difficult to calibrate against natural conditions to produce lifetime prediction. Photodegradation products are often prodegradants placing restrictions on the recyclability, which is also discussed⁽²⁾.

The ageing of plastics, polymers and resins leads to several possibilities. Several oxidation products are formed. Free radicals, produced by formation of peroxides, lead to depolymerization, crosslinking, chain termination to polymer leading to chain branching and reversal to monomers in specific cases. Completely new small molecules those were not present at the time of polymerization are formed contributing to volatile organics over the useful life of the product and beyond it. When we have a look at the literature on the subject of photodegradation of polymers the polymer chemist dealing with bulk polymers seem to have worried about it far more than the paint and coatings chemist. The reasons are mainly environmental. The used plastic products are posing a great threat to the environment and efforts have been made to deliberately accelerate the process of photo-degradation of polymers in ordinary sunlight⁽³⁾.

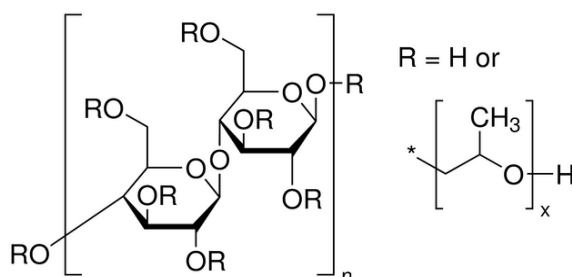
The degradation of polymer materials on outdoor exposure can often be attributed to photochemical reactions arising from absorption of UV-radiation by polymeric chromophores, impurities like ketone groups, and hydroperoxide groups present on the polymer backbone. Ketones and hydroperoxide groups are more likely to be formed by air oxidation on moulding and synthesis of the polymer. The aim of this work is studying and comparing the photodegradation of poly hydroxypropyl cellulose in presence and absence of benzophenone and eosine dye as photosensitizers.

Experimental

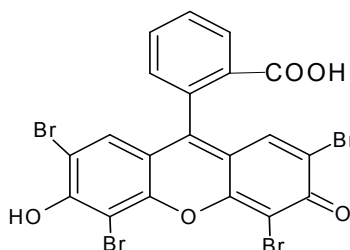
The following materials were used

a- Laboratory poly hydroxypropyl cellulose powder (B.D.H. Ltd A.R. Grade , purity 99%) was used at the test

sample .



b- Laboratory eosine dye powder (B.D.H. Ltd A.R.Grade , purity 99%) was used at the test sample .



c- Benzophenone (B.D.H. Ltd A.R.Grade , purity 99%).

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.

Infrared spectrophotometry (IR)

A Pye-Unicam SP₃-100 infrared spectrophotometer was used to record the IR spectra between (600-4000) cm^{-1} .

Film preparations

0.1% solution of eosine dye or benzophenone was added to 1% solution of poly hydroxypropyl cellulose in distilled water. A thickness of about 25 μ m was measured by a micrometer type, (2610 , Germany) , poly hydroxypropyl cellulose films with and without dye and benzophenone 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 .

Irradiation

The accelerated weather-o- meter, Q.U.V. tester, (Q-panel company , U.S.A), was used for irradiation of poly hydroxy propyl cellulose films. The films were positioned (25 μ m) apart from the UV.lamps (eight fluorescent lamps give essentially monochromatic light at $\lambda=313$ nm) . Temperature of the tester chamber is nearly constant at 45 °C

Analysis

The photodegradation of the polymer film was followed by I.R and UV-visible spectrophotometer. The absorption spectra (for I.R method) of the film samples were recorded in the wave number ranged from 600 to 4000 cm^{-1} . Carbonyl index were calculated by comparison of the I.R absorption peak at 1725 cm^{-1} for (C=O) group with reference peak at 1457 cm^{-1} for (-CH₂) group for poly hydroxypropyl cellulose.

The ultraviolet-visible spectrophotometer was used to measure the change in the U.V-Visible spectrum during irradiation.

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⁽⁴⁾

$$[\eta] = K (\overline{M}_v)^\alpha \dots\dots\dots(1)$$

where,

[η] = 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 (t₀),were measured respectively.

Results and discussion

The photodegradation of polymer films has been studied. The UV.-visible spectra of poly hydroxypropyl cellulose films (control) irradiated with different time intervals . After 350 hrs. of irradiation, the absorbance is decrease ,the rate of decrease is relatively much greater than in the wavelength region of ($\lambda= 230-325$)nm. The decrease in absorbance is due to the scission of main chain bonds in polymer.

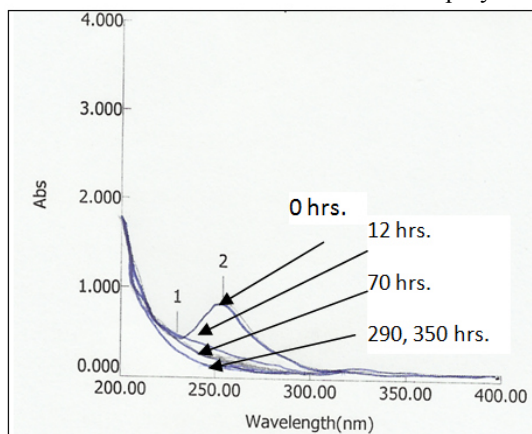


Figure (1) : UV. -visible spectral change of hydroxy propyl cellulose film without photosensitizer (25 μ m in thickness)

In the present work, the photodegradation of polymer films was studied using (BPH and dye) photosensitizers .The spectral changes during photolysis of polymer films with 0.1 %w/v of photosensitizers (BPH and dye) are shown in figures (2) and (3) for poly hydroxypropyl cellulose with BPH and dye respectively.

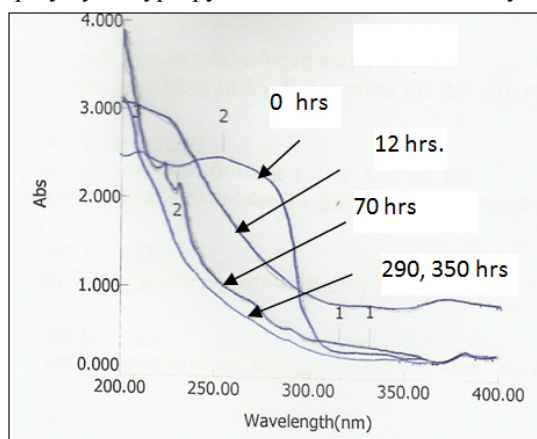


Figure (2) : UV. -visible spectral change of hydroxypropyl cellulose film with BPH photosensitizer (25 μ m in thickness)

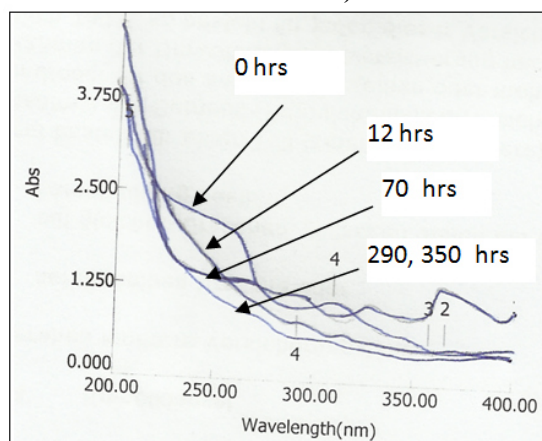


Figure (3) : UV. -visible spectral change of hydroxypropyl cellulose film with dye photosensitizer (25 μ m in thickness)

From the results obtained in these figures ,one can be observed that the absorbance of the polymer with dye and

BPH in the wavelength 230-325 nm range decrease with irradiation time because the dissociation of photosensitizers (dye and BPH).

When the polymer film (control) samples, irradiated with wavelength ($\lambda=313$ nm), the FTIR shows the high growth of carbonyl groups absorbance in the wave number 1725 cm^{-1} , and this band intensity increases exponentially with irradiation time. which is expressed in term carbonyl index (I_{CO}).

The relationship between the carbonyl index (I_{CO}) with irradiation time is showed in figures (4).

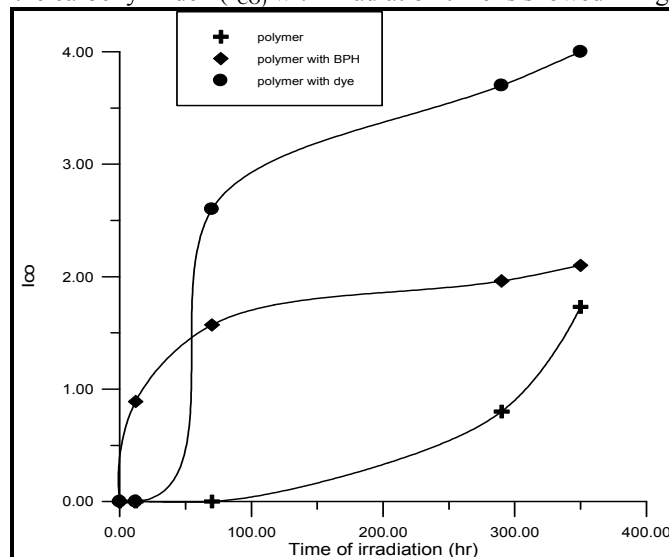
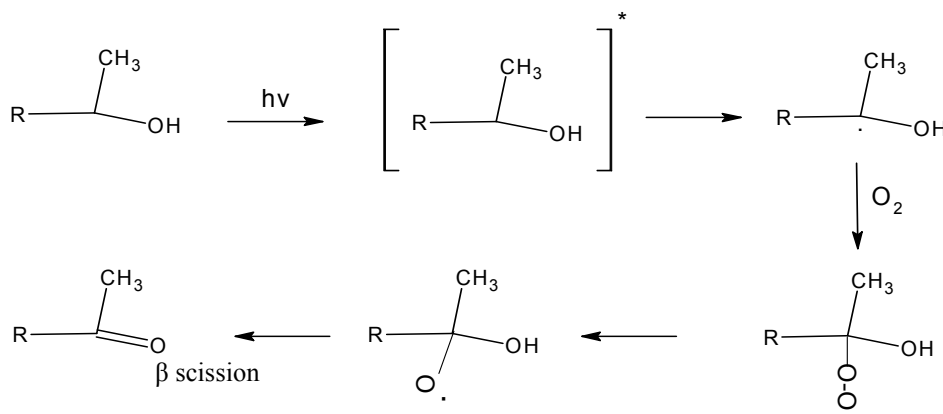


Figure (4) :The relationship between carbonyl index and irradiation time for poly hydroxypropyl cellulose films with and without (0.1% w/w) of photosensitizers

It has been observed that the carbonyl index greatly increases with irradiation time for poly hydroxypropyl cellulose film with dye and BPH photosensitizers. The degradation of polymers and formation of carbonyl groups are similar to general mechanism in literatures^(5,6).



R = hydroxypropyl cellulose

Scheme (1) : Reaction scheme for the photodegradation of poly hydroxypropyl cellulose in the presence of O₂

So these photosensitizers (i.e dye and BPH) are all considered as photodegradation inducers for poly hydroxypropyl cellulose, as the growth of carbonyl index with these photosensitizers is higher than polymer without photosensitizers. Also results show that (dye) act as better-inducer of polymer photodegradation compared to other photosensitizer (BPH), this is because the increased in carbonyl index (I_{CO}) are higher than that for polymer(control) or with photosensitizers BPH, these results are in agreement with literatures⁽⁷⁻¹¹⁾.

Molecular Weight Change During Photolysis

To provide another indication of degradation, viscosity measurement was made on solutions of poly hydroxypropyl cellulose films to determine changes in molecular weight. After irradiation time in air with alight intensity of 3.49×10^{-5} einsteins.dm⁻³ S⁻¹, part of the poly hydroxypropyl cellulose films with dye and BPH

photosensitizers was not dissolved in water solvent due to the crosslinking or branching, while poly hydroxypropyl cellulose films (control) dissolved in water solvent. Table (1) show the variation of α , S , P_t , $d\overline{M}_v/dt$, $(\overline{M}_v)^2$ and \overline{M}_v with irradiation time for poly hydroxypropyl cellulose films 25 μ m in thickness containing 0.1 Wt % photosensitizers.

Table (1): The variation of α , S , P_t , $d\overline{M}_v/dt$, $(\overline{M}_v)^2$ and \overline{M}_v with irradiation time for films 25 μ m in thickness containing 0.1 Wt % photosensitizers.

Polymer	Irradiation time (hr)	\overline{M}_v (g/ml)	$(\overline{M}_v)^2 \cdot 10^4$ (g/ml)	$d\overline{M}_v/dt$	P_t	$1/P_t$	α	S
poly hydroxypropyl cellulose	0	1003.05	6761	0	4.28	0.23	0	0
	72	749.69	5041	3.51	3.20	0.31	0.07	0.32
	96	476.54	3615	5.48	2.03	0.49	0.25	1.09
	156	435.15	1521	3.64	1.85	0.53	0.30	1.29
	228	201.54	544	3.51	0.86	1.16	0.92	3.96

Table (1) show a rapid decrease in \overline{M}_v initially which then slow down, for the poly hydroxypropyl cellulose films (control) suggesting that the initial rapid in \overline{M}_v is due to scission of bonds at various weak links which distributed along the polymer chain. The photodegradation process becomes slower and the bonds scission may be random⁽¹²⁾. Figure (5) show the changes in the molecular weight of poly hydroxypropyl cellulose films without photosensitizers.

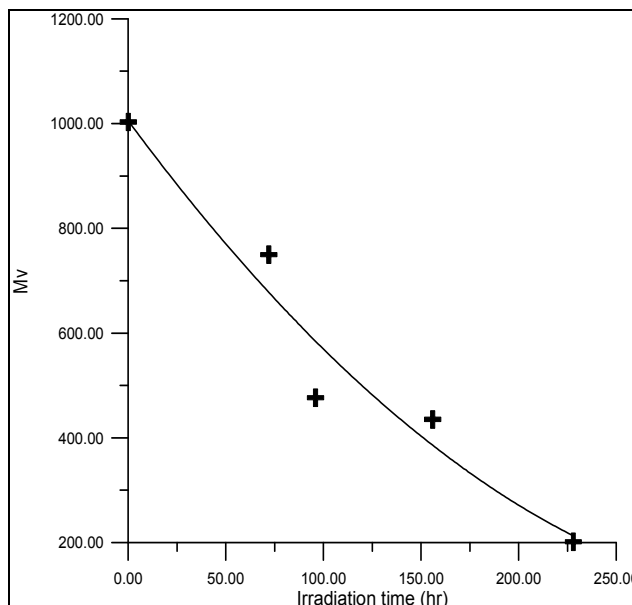


Figure (5) : Changes in the viscosity average molecular weight during irradiation of poly hydroxypropyl cellulose without photosensitizers

In general, for random scission in the absence of concurrent crosslinking, the degree of polymerization changing with time according to the following equation:

$$\alpha = kt = \frac{1}{P_{n,0}} - \frac{1}{P_{n,t}} \quad \dots\dots\dots(1)$$

Where, α is the degree of deterioration, $P_{n,0}$ and $P_{n,t}$ are degrees of polymerization at zero and (t) time. As shown in figure (6), the plot of data is linear. This confirms that the degradation is taking place by random scission of bonds.

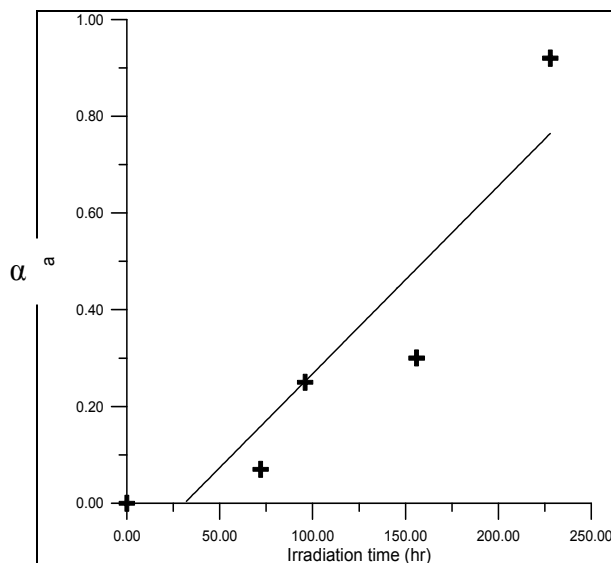


Figure (6) : Changes in the degree of deterioration during irradiation of poly hydroxypropyl cellulose without photosensitizers

More detailed analysis of the data was used to calculate a scission rate (S) using the relation:

$$S = \alpha P_{n,o} \quad \dots\dots\dots(2)$$

Where, S is the number average chain scission or average number cut per single chain, P_{n,o} is the number average degree of polymerization at zero time. The plot of (S) versus exposure time is shown in figure (7). The plots are also linear, confirming that crosslinking does not occur.

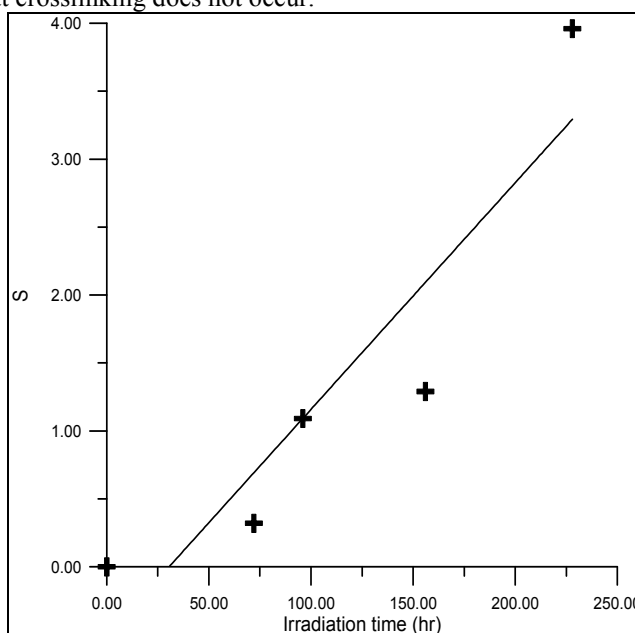


Figure (7) : Changes in the number-average chain scission poly hydroxypropyl cellulose without photosensitizers

Figure (8) : Change in the reciprocal value of number –average degree of polymerization during irradiation of poly hydroxypropyl cellulose without photosensitizers

Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH⁻ ion generating OH• free radical. The dye is now being bleached by this free radical.

The participation of OH• radical was confirmed by using scavenger, which almost stops the bleaching reaction. Colour change from yellow to colourless is irreversible and degradation rate of the dye follows the pseudo-first order kinetics⁽¹³⁾.

Infrared spectroscopy and x-ray analysis of HPC subjected to ultrasonic treatments remained unchanged, suggesting that there were no chemical or structural (e.g., degree of order) changes on irradiation. The decreases in molecular weights on irradiation arise due to random chain scission whereas similar decreases in Huggins coefficients can be attributed to physical changes (decrease in molecular weight or branching) in the degraded HPC samples⁽¹⁴⁾.

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 by 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.

Conclusions

It can be concluded that addition of small amount (0.1% w/v) of low-molecular compounds such dye and BPH effectively influences the photoprocesses in polymer. It has been found that photo-oxidative degradation of polymer is more efficient in the presence of these sensitizers and dye action is strongest as inducer for poly hydroxypropyl cellulose and BPH is less for poly hydroxypropyl cellulose. Calculation based on the viscosity average molecular weight (M_v) clearly indicates an overall decrease in molecular weight during irradiation. At longer exposure periods, degradation of poly hydroxypropyl cellulose, continue but are reduced at lower rate. It is likely that random polymer chain scission occurs at the early stages of exposure. 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.

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