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Photochemical stability of collagen/poly(ethylene oxide) blends

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Abstract

The photochemical stability of the blends of collagen and poly(ethylene oxide) PEO has been studied by Fourier transform infrared spectroscopy (FTIR), UV–vis spectroscopy and viscosimetry. Surface properties before and after UV irradiation were observed using an optical microscope.

Collagen and PEO were immiscible in diluted solution and only small interactions between the two components in the solid state were observed. New materials based on the blending of collagen and PEO that we obtained have a different photochemical stability than those of single components. In general, collagen/PEO blends are less stable under UV irradiation than pure collagen. The influence of PEO on the photochemical stability of collagen depends on the concentration of this polymer in the blend. Microscopic photographs show that the surface characteristics of thin films of collagen/PEO blends are not drastically altered after UV irradiation.

Keywords: Collagen; Poly(ethylene oxide); UV irradiation; Biomaterials; Blends

1. Introduction

In the last two decades polymeric biomaterials based on blends of collagen and synthetic polymers have been investigated for a wide range of applications (hydrogels, films, and sponges) [1–4].

Collagen is the most abundant biopolymer in animals where it provides the principal structural and mechanical support [5]. The main amino acids in collagen are: glycine, proline, hydroxyproline and alanine. The ordered triple helical structure of collagen is stabilized by both intrachain hydrogen bonds and by structural water molecules [6–10]. Collagen is readily available, non-toxic and has the fibril architecture inherent in natural tissues. This fact emphasises that collagen provides an excellent basis for biomaterials, such as arterial prostheses and artificial skin [11,12].

Poly(ethylene oxide) (PEO) is a water soluble polymer; an aqueous solution of low concentration is very tacky and sticky. Poly(ethylene oxide) can be used as a long fibre dispersing agent in the manufacture of paper and adhesives, as a friction reduction, flocculating or thickening agent, as lubricants and has a variety of further applications. PEO in water is an important component of so-called ‘smart gels’, which may in future be an application in manufacturing exotic foods, cosmetics, medicines, sensors, and other technological applications.

Both poly(ethylene oxide) and collagen are very important polymers and their blends can be of significant practical application [13]. PEO is a simple chain polymer with etheric linkages while collagen is a biopolymer (protein) with peptide bonds and side groups. These peptide bonds and side groups can be a source of hydrogen bonding and hence of assistance in the formation of polymer blends [14,15]. The miscibility of PEO with other synthetic polymers and the properties of the blends have been studied previously [16–18]. However, the miscibility of PEO with collagen has not been studied.

As the miscibility and structure of collagen/PEO blends have not been studied previously, there is a lack of information about the stability of such blends during UV irradiation. In case of polymer blends, the microstructure depends on

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miscibility or immiscibility of components, their crystallinity and dispersion degree of one component in the matrix of the other. Moreover, segment interpenetration and interphase adhesion are also important factors affecting the photochemical reactions.

It is well known that UV irradiation is a good method of sterilization of biomedical materials [19,20]. The treatment with UV light represents a simple and inexpensive procedure, which is quite effective. However, it is necessary to test polymers and new biomaterials for their susceptibility to changes in their properties generated by exposure to UV irradiation.

The aim of this work was to study the photochemical stability of binary blends made up of collagen and poly(ethylene oxide) PEO.

2. Materials and methods

2.1. Sample preparation

Collagen was obtained in our laboratory from tail tendons of young albino rats. PEO was obtained from Fluka (MW about 100,000). Polymeric blends were prepared by mixing of suitable volumes of collagen and PEO aqueous solution and the final weight ratio was 3:1, 1:1, 1:3. Polymer films were obtained by casting solution onto glass plate or CaF_2 specrophotometric windows. After solvent evaporation, the samples were dried in vacuum at room temperature.

2.2. Illumination of the sample

The samples, in the form of the solutions and films of pure collagen, PEO and collagen/PEO blends were irradiated in air at room temperature using a mercury lamp, Phillips TUV-30, which emits light mainly at 254 nm wavelength. The intensity of radiation was 0.263 J/cm^{2}min. The intensity of the incident light was measured using an IL 1400 A Radiometer (International Light, USA). Irradiation experiments were carried out in a quartz cuvette at a distance of 3 cm from the light source. All measurements were performed in the same conditions of temperature and humidity to avoid any influence on the physico-chemical properties of collagen films.

2.3. UV–vis spectroscopy

The UV–vis absorption spectra of the collagen solution, before and immediately after UV irradiation were recorded with a Shimadzu spectrophotometer (Model UV-1601PC). Data were collected and plotted using UVPC program and computer data station supplied by the manufacturer.

2.4. Viscosity measurements

The relative viscosity of collagen solution was measured at 20 °C using a quartz Ubbelohde viscometer.

2.5. FTIR measurements

The IR spectra were obtained using a Mattson Genesis II spectrophotometer. The FTIR spectra of collagen/PEO blends before and after UV irradiation were compared with FTIR spectra of collagen and PEO. All spectra were recorded at the resolution 4 cm^{-1} and 16 times scanning.

2.6. Microscopy observations

The optical microscopy in polarized light (Motic DMB1-223) was used for studying the morphology of samples.

3. Results and discussion

3.1. Miscibility

An important aspect of the properties of a blend is the miscibility of its components. Miscibility in polymer blends is assigned to specific interactions between polymeric components, which usually give rise to a negative free energy of mixing inspite of the high molecular weight of polymers. The most common interactions in the blends are: hydrogen bonding, ionic and dipole interactions, π-electrons and charge-transfer complexes. Most polymer blends are immiscible with each other due to the absence of specific interactions. In the first stage of this work, the miscibility of collagen and PEO blend has been studied. The viscosity measurements data obtained by methods published in [21] show that collagen and PEO are immiscible in diluted solution (data not shown). However, from the mixture, it was possible to prepare films which can have a potential for future applications. FTIR spectra revealed some minor interactions between collagen and PEO in a solid state (thin film). The position of amide bands of collagen in blends were slightly different than that for pure collagen (Tables 1–3). Solutions and thin films of single

Table 1
Amide bands position in collagen before and after 2, 4, 8 h of UV irradiation

Amide band	Time of irradiation (h)			
	0	2	4	8
A	3324	3314	3320	3315
B	3072	3067	3070	3067
I	1657	1657	1657	1657
II	1553	1551	1551	1551

Table 2
Amide bands position in collagen/PEO blend (1:1) before and after 2, 4, 8 h of UV irradiation

Band (cm^{-1})	0 h	2 h	4 h	8 h
A 3300	3330	3328	3330	3328
B 3080	3073	3072	3073	3073
I 1650	1661	1661	1661	1661
II 1556	1540	1550	1550	1548
$-CH_2$ 2950	2882	2883	2883	2883

Table 3
Amide bands position in collagen/PEO blend (3:1) before and after 2, 4, 8 h of UV irradiation

Band (cm^{-1})	0 h	2 h	4 h	8 h
A 3300	3329	3328	3329	3326
B 3080	3075	3072	3075	3075
I 1650	1661	1661	1661	1661
II 1556	1553	1550	1551	1550
$-CH_2$ 2950	2945	2945	2945	2945
CH_2 1460	1467	1467	1467	1467

components and their blends were irradiated with UV light ($\lambda = 254$ nm).

3.2. UV–vis spectroscopy

The UV–vis spectra of collagen before and after UV irradiation are shown in Fig. 1. The absorption spectra of a solution of acid soluble type I rat tail tendon collagen in acetic acid reveal absorption in the 250–280 nm region with maximum at 275 nm. The UV–vis spectra, which characterize the collagen solution were significantly altered after UV irradiation (Fig. 1, curves 2 and 3); irradiation of the collagen solution at a wavelength of 254 nm leads to a minor increase in overall absorption, most notably between 240 and 300 nm. After irradiation, the peak at 275 nm is less pronounced, becoming more shoulder-like with increasing irradiation time. This may be due to increasing turbidity in the irradiated solution, since the UV irradiation causes the changes in conformation of the collagen molecule (helix-coil transition). The increased presence of a coil structure and the progressive loss of the helical character of collagen bring about an overall increase in the scattering level of the sample. After 1 h of UV irradiation, the maximum of absorption/scattering is not further altered.

The absorption spectra of PEO are shown in Fig. 2. UV–vis spectroscopy revealed that pure PEO does not absorb above 220 nm. After UV irradiation, the absorption spectrum was altered much more in comparison with UV–vis spectra of UV-irradiated collagen. The absorption of irradiated samples was smaller than that of the control samples. The absorbance at 275 nm before and after UV irradiation have been compared in Fig. 3. The values of absorbance at 275 nm have been chosen for comparison of alterations by UV irradiation of collagen, PEO and collagen/PEO blends. The absorption spectra of PEO before UV irradiation do not show clear, characteristic peak in the UV–vis region. It was pointed out previously that even pure non-irradiated PEO contains small amount of chromophores, probably abnormal groups formed during polymerization. It is well known that such groups are responsible for the initiation of photodegradation of polymers, which do not absorb UV light. After lengthy UV irradiation, the new chromophores are generated that absorb at approximately 280 nm. Previous studies showed that formation of new chromophores resulted from polymer photo-oxidation [22,23].

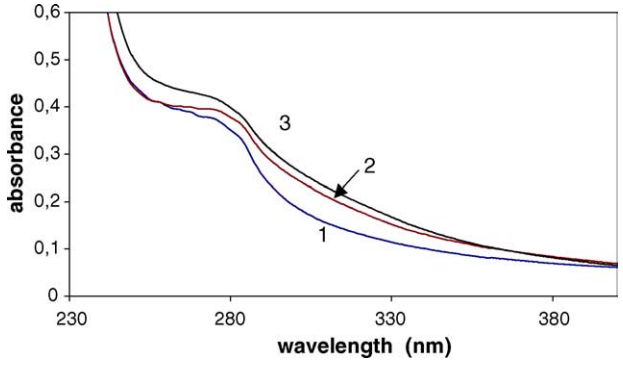

Fig. 1. UV–vis spectra of collagen before (1) and after 30 min (2) and 120 min (3) of UV irradiation.

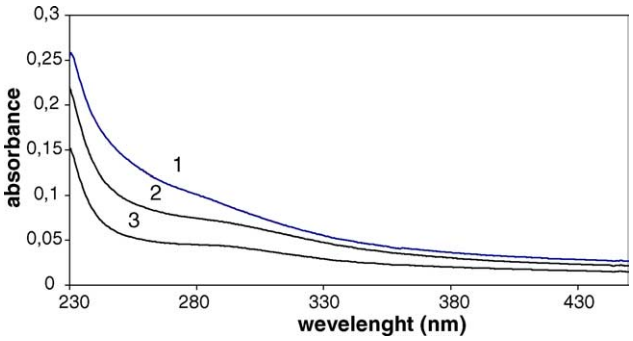

Fig. 2. UV–vis spectra of PEO before (1) and after 30 min (2) and 120 min (3) of UV irradiation.

For collagen/PEO blends (ratio 3:1), there is only a small increase in the absorbance of the sample; smaller than that of pure collagen (Fig. 3, curve 3). The difference between absorption/scattering after 1 and 2 h irradiation is smaller than in pure collagen for the blends with compositions 1:1 as well (Fig. 3, curve 4). As the content of PEO increases in the sample, and the content of collagen decreases, the absorbance at 275 nm after UV irradiation decreases also. For collagen/PEO

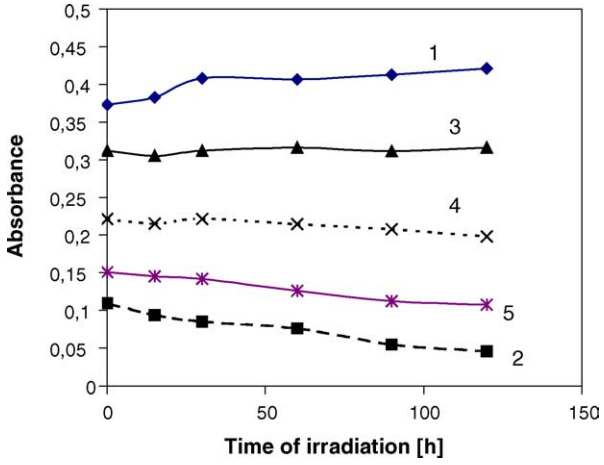

Fig. 3. The absorbance at 275 nm vs. UV-irradiation time for collagen (1), PEO (2), collagen/PEO 3:1 (3), collagen/PEO 1:1 (4), and collagen/PEO 1:3 (5).

blends (ratio 1:3), the absorption at 275 nm decreases after UV irradiation (Fig. 3, curve 5).

This observation suggests that PEO alters both the photochemical stability of collagen and the processes, which lead to the increase in absorption, i.e. photodegradation (with scission of bonds in the main chains) or phototransformation (with changes in the conformation of collagen molecules). Moreover, the decrease in absorption for collagen/PEO blends (ratio 1:3) with UV-irradiation time is due to the alteration of PEO [23–26]. The UV–vis spectra of collagen/PEO blends may suggest that after blending collagen with PEO, the conformation of collagen molecules in solution has been changed. For collagen in solution, an effect of increasing turbidity in irradiated sample was observed (helix-coil transition). In collagen/PEO, after UV irradiation, the maximum of absorption/scattering is not altered.

3.3. Viscosity measurements

The relative viscosity of collagen, PEO and collagen/PEO blend (ratio 3:1, 1:1, and 1:3) before and after UV irradiation is presented in Fig. 4. For the non-irradiated collagen/PEO blends, the experimental relative viscosity is similar to one predicted from theoretical calculation. This fact points to the immiscibility of collagen and PEO in solution.

After UV irradiation, the relative viscosity of collagen changes faster than relative viscosity of PEO. It is evident that in solution, PEO is more stable under short UV exposure than collagen (Fig. 4, curve 2). Changes of viscosity in PEO after UV irradiation are caused by degradation [22–26], whereas in collagen mainly by conformational transformation (helix–coil transition) [27–29]. The relative viscosity of collagen decreases rapidly after UV irradiation and after 3 h reaches the lowest value 1.1 without any changes with further irradiation.

The viscosity data showed that after UV irradiation of the collagen/PEO blends (ratio 3:1), the plateau is reached earlier than that for pure collagen (Fig. 4, curve 3). For pure collagen, the lowest value of viscosity was reached after 3 h of UV irradiation, whereas for collagen/PEO blends, it was reached after 1.5 h of UV irradiation. When the blend contains 50% of collagen and 50% of PEO the relative viscosity is 1.2 after 2 h of UV light (Fig. 4, curve 4), whereas for pure collagen, such low viscosity is obtained after 3 h of UV light. For the collagen/PEO blend (ratio 1:3), the relative viscosity is 1.1 after 1 h of UV irradiation (Fig. 4, curve 5). These results suggest that the blend of collagen/PEO is less stable under UV than collagen, but in the blends with PEO content more than 50% the viscosity before UV irradiation is similar to viscosity of the 2 h irradiated collagen solution. The viscosity results may suggest again that collagen/PEO blends in solution are less photochemically stable than collagen alone. Moreover, the viscosity measurements of collagen/PEO blends before irradiation may suggest that after blending of collagen with PEO, the conformation of collagen molecules in solution have been changed. For collagen in solution, the viscosity was very high (helix conformation) and after blending it decreased (helix-coil transition). In collagen/PEO, after UV irradiation, the viscosity was altered less, as some alteration had been already caused by blending with PEO.

3.4. FTIR spectroscopy

FTIR spectra of collagen, PEO, and collagen/PEO blends show that the positions of amide bands are at the same wavenumbers for all the blends and only slightly different than for pure collagen film (the example of FTIR spectra is shown in Fig. 5, data are listed in Tables 1–3). It suggests only small interaction between collagen and PEO in solid state and immiscibility of these two polymers. It seems that hydrogen bonds formation between collagen molecules competes with the formation of hydrogen bonds between molecules of PEO and collagen.

The positions of amide bands A and B after UV irradiation in blend are nearly unchanged (Tables 2–3), whereas for collagen, the shift of amide A and amide B bands was observed (Table 1). The amide I band at around 1655 cm^{-1} (C=O stretching) in FTIR spectra of collagen is sensitive to the secondary structure of collagen [30,31]. A slight shift of the position of bands suggests conformational changes in the collagen molecule.

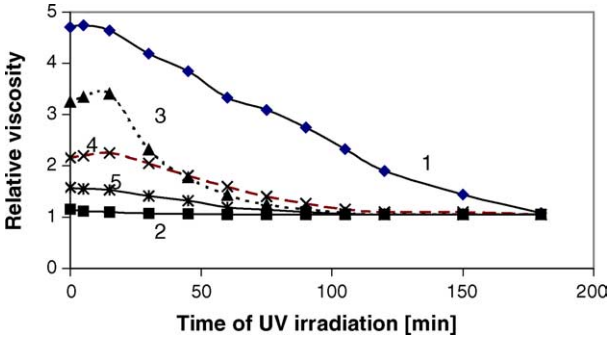

Fig. 4. The influence of UV irradiation on relative viscosity of collagen (1), PEO (2), collagen/PEO blends 3:1 (3), collagen/PEO 1:1 (4), and collagen/PEO 1:3 (5).

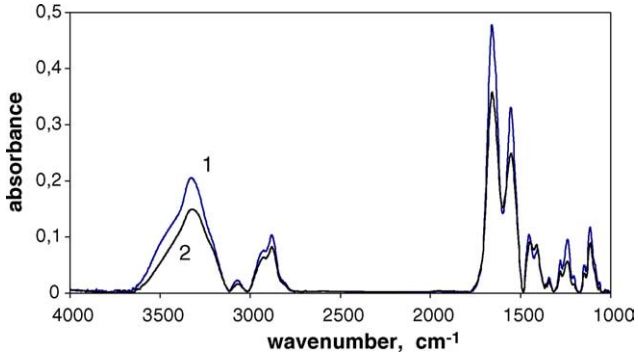

Fig. 5. FTIR spectra of collagen/PEO blend (3:1) before (1) and after 8 h (2) of UV irradiation.

Table 4
The area of amide bands and CH_2 bands (integral absorbance) in collagen before and after 2, 4, 8 h of UV irradiation

Band in FTIR spectra	Time of irradiation (h)			
	0	2	4	8
A	63	54	47	46
B	1.5	1	1	1
I	34	31	25	25
II	15	13	11	11
$-CH_2$	2.5	2.5	2	2

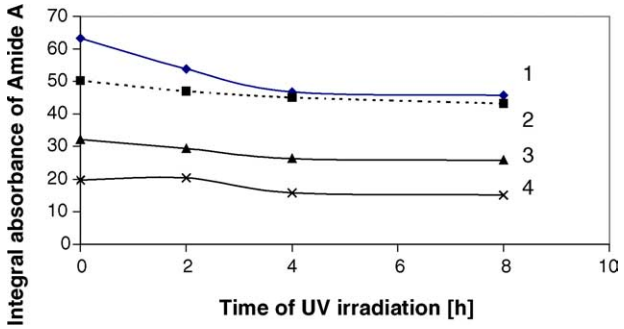

Fig. 6. The influence of UV irradiation on integral absorbance of amide A band of collagen (1), collagen/PEO blends 3:1 (2), collagen/PEO 1:1 (3), and collagen/PEO 1:3 (4).

Integral absorbance of amide bands A, B, I and II in collagen decrease after UV irradiation (Table 4). Integral absorbance for PEO peaks is nearly unchanged after UV irradiation (data not shown). For collagen/PEO blends, the changes of integral absorbance of amide bands (A and II) are similar to those for pure collagen (Figs. 6 and 7). The area of amide I band could not be compared because photo-oxidation of PEO gives the peak at the same wavenumber (after 8 h of UV irradiation, FTIR absorption spectra showed the formation of carbonyl bands in PEO samples: small peak at 1720 cm^{-1}).

FTIR results have shown that for collagen/PEO films, a greater length of irradiation time is required to bring about changes to the characteristics of the blends compared to blends in solution.

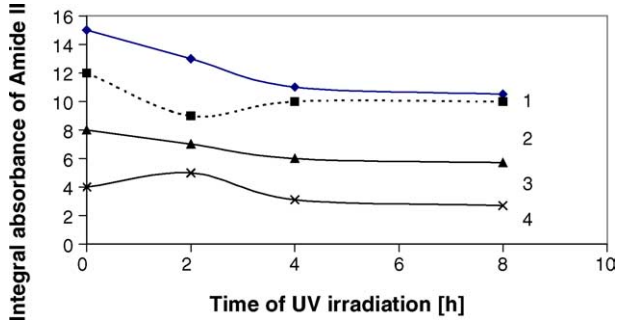

Fig. 7. The influence of UV irradiation on integral absorbance of amide II band of collagen (1), collagen/PEO blends 3:1 (2), collagen/PEO 1:1 (3), and collagen/PEO 1:3 (4).

3.5. Microscopy

Structural alterations on the surface of collagen/PEO films induced by UV irradiation have been observed using microscope. The microphotographs of non-irradiated and irradiated collagen/PEO films are shown in Fig. 8. The photograph of non-irradiated films shows the immiscibility of collagen and PEO. UV irradiation does not cause significant changes in collagen/PEO film surface.

3.6. Discussion: mechanisms of photodegradation

It is generally known that tyrosine and phenylalanine are sensitive chromophores, which absorb light below 300 nm and may initiate the photodegradation of collagen chains [29]. In PEO, the primary photochemical reaction is breaking of macrochains (chain scission arises at the weak chemical bond). Structural defects (hydroperoxides, carbonyls, tail-to-tail structures, etc.) are responsible for the initiation of photochemical reactions in PEO, but the energy of UV radiation is also enough to cause the random breaking of PEO chains [22]. Macroradicals, formed in the primary process, interact easily with atmospheric oxygen and various products of oxidation may be produced. Active radicals again initiate polymer destruction and also the destruction of the second polymer in the blend.

On the basis of studies on the viscosity of diluted solutions, UV–vis spectroscopy and FTIR spectra we can comment on the photodegradation of collagen/PEO blends. A decrease in integral absorbance in the FTIR range is related to scission of collagen and PEO chains into smaller fragments. This is confirmed by the measurements of viscosity of diluted collagen/PEO solutions. Collagen and PEO radicals formed during UV exposure may interact with each other and alter the properties of collagen/PEO blends. Very active radicals and macroradicals derived from irradiated polymers can interact with macromolecules and produce new radicals and macroradicals. Those macroradicals may form a crosslinking structure and branching one, which deteriorate the overall properties of polymers. In the presence of O_2, photo-oxidation of macroradicals contributes to the formation of polar groups. The presence of these groups changes the surface properties of polymer films.

More pronounced changes after UV irradiation were observed using viscosity measurement for solutions than FTIR spectroscopy for thin films. This observation points out that all photoreactions observed in collagen, PEO and collagen/PEO blends are faster in solution than those in films. In the solid state, the samples are much less homogenous, can contain crystalline phases, which are more photoresistant than the amorphous phases. The access of radicals and macroradicals to macromolecules in the solid state is limited and usually all photoreactions occur only in the thin surface layer. Both collagen and PEO possess a helical conformation. In solution, both the polymers possess random coil fragments separated by helical segments. In

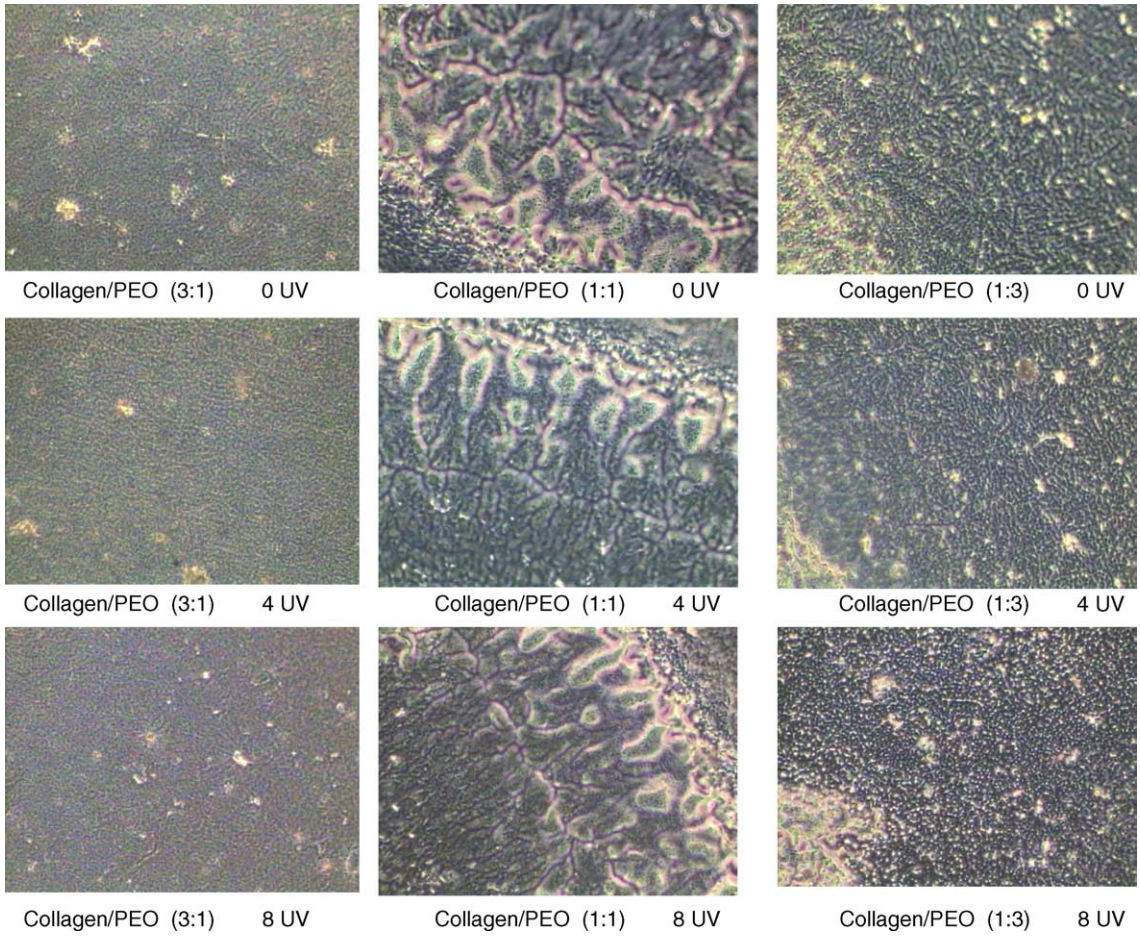

Fig. 8. Microscope images of collagen/PEO blends before and after UV irradiation.

diluted solutions, the interactions between macromolecules are weaker because they are separated from each other by many solvent molecules. Moreover, in solution, oxygen can penetrate more easily and thus photodegradation is facilitated. Photo-oxidative degradation of polymers in solution is more homogenous process than that in solid state. In solid state, photodegradation occurs mainly at the surface layer. For PEO, this effect was discussed in [22]. It was found that the degree of crystallinity in UV-irradiated PEO samples increases because of the fast decay of the amorphous phase.

4. Conclusions

The blending of collagen with PEO may give the possibility of producing new materials for potential biomedical applications. Collagen and PEO are immiscible, but from the mixture, we could prepare films in which some interactions occur between the synthetic and biological component in solid state. In diluted solution where the molecules are well separated, there is no interaction leading to miscibility. However, in the film, where two different molecules are close together in homogenous mixture some interaction appears. The new materials thus obtained have different photochemical stability than those made up of single components. In general, collagen/PEO blends are less stable under UV irradiation than pure collagen. The influence of PEO on the photochemical stability of collagen depends on the concentration of this polymer in the blend. For collagen/PEO films, a greater length of irradiation time is required to bring about changes to the characteristics of the blends compared to blends in solution. Microscopic photographs showed that the surface characteristics of collagen and collagen/PEO blends in film form are not drastically altered after UV irradiation.

Acknowledgments

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