Digest Journal of Nanomaterials and Biostructures Vol. 6, No 4, October-December 2011, p. 1793-1803

CHARACTERIZATION OF ELECTRON BEAM IRRADIATED COLLAGEN-POLYVINYLPYRROLIDONE (PVP) AND COLLAGEN-DEXTRAN (DEX) BLENDS

M. DUMITRAŞCU[a,*], V. MELTZER[b], E. SIMA[b], M. VÎRGOLICI[c], M. G. ALBU[d], A. FICAI[d], V. MOISE[c], R. MINEA[a], C. VANCEA[a], A. SCĂRIŞOREANU[a], F. SCARLAT[a]

[a] *National Institute for Lasers Plasma and Radiation Physics, 409 Atomiştilor Street, 077125, Măgurele, Romania*

[b] *University of Bucharest, Faculty of Chemistry, 4-12 B-dul Regina Elisabeta, 030018, Bucharest, Romania*

[c] *Horia Hulubei National Institute of Physics and Nuclear Engineering - IFIN-HH, 407 Atomiştilor Street, 077125, Măgurele, Romania*

[d] *Leather and Footwear Research Institute - INCDTP, Collagen Department, 93 Ion Minulescu Street, 031215, Bucharest, Romania*

[e] *Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science, 1-7 Polizu Street, 011061, Bucharest, Romania*

The aim of the present study was to investigate the influence of electron beam (EB) irradiation on some blends of collagen-polyvinylpyrrolidone (PVP) and collagen-dextran (DEX). The blends were prepared by irradiating the mixtures of aqueos solutions of collagen, PVP and DEX by EB irradiation at different doses. After irradiation the obtained hydrogels were processed by freeze-drying. Both types of materials were characterized by FT-IR, FT-Raman, TG/DTG, water uptake and SEM. The intensity of the characteristic bands, in the range 2800-3600 cm^{-1} from FT-IR spectra, varied considerably as function of absorbed radiation dose. Raman spectra revealed the absence of the characteristic peak at 2700 cm^{-1} for irradiated blends at 30 kGy. Thermal stability of irradiated blends had increased with incresing of radiation dose. Water uptake studies were carried out in PBS solution (phosphate buffer saline) at 37°C and pH = 7.4 and the results revealed a decrease of the water uptake with increasing of absorbed radiation dose. The SEM images of investigated blends show a highly ordered porous structure function of blend type, which was less affected by EB irradiation at radiation dose of 30 kGy.

(Received October 28, 2011; accepted November 22, 2011)

Keywords: Polymeric blends; Collagen-PVP; Collagen-DEX; EB irradiation

1. Introduction

Blends of synthetic and natural polymers represent a new class of materials with better mechanical properties and biocompatibility than those of the single components. Recently the mixtures of collagen with synthetic polymers, and also with other natural polymers are becoming more and more interesting for scientists and technologists [1]. Collagen has been investigated for a variety of biomedical and biotechnological applications including drug delivery, wound dressings and as a substrate for tissue engineering [2]. This biopolymer possesses many interesting properties that make it a notable material for biomedical applications. Since collagen alone does not show interesting enough mechanical properties the idea to develop collagen based composite materials by adding a selected synthetic polymer is interesting. Polyvinylpyrrolidone (PVP) is an

*Corresponding author: maria_dumitrascu@yahoo.com

interesting water-soluble synthetic polymer with a broad range of applications. PVP has been used for preparation synthetic plasmas (substitute of blood plasma), for hydrogel production by radiation methods and for creations of hydrophilic gels [3].

Dextran (DEX) is a class of polysaccharides with a linear polymer backbone with mainly 1,6-α-D-glucopyranosidic linkages. It is water soluble and has three hydroxyl groups, one ring oxygen and one bridge oxygen prone to hydrogen bond acceptor [9]. It is obtained from bacterial cultures of *Leuconostoc mesenteroides* [4]. DEX is widey used as plasma expanders, blood substitutes, bone healing promoters, and also for dermal and subcutaneous augumentaion [5]. Collagen and polyvinylpyrrolidone (PVP) are miscible, and they are also well known for their interesting biological properties. The blending of collagen with PVP makes it possible to obtain new materials, in which strong interactions between the synthetic and biological components occur. Studies on influence of UV irradiation on different ratios of collagen and PVP blends were performed by Sionkowska et al., [6], [7], [8]. However, the influence of EB irradiation has not been investigated on collagen-PVP blends. Polymeric blends from dextran (DEX) and other polymer like PVP [9], PEG [10], PAA [5], have been performed, but collagen-DEX blends were found to not be performed yet.

The goal of this study was to determine the influence of EB irradiation on collagen-PVP and collagen-DEX blends, using ATR-FTIR, FT-Raman, thermal analysis, water absorption and SEM techniques.

2. Experimental

2.1. Polymeric materials

Collagen type I extracted from calf hide with average molecular weight of 3×10^5 Da was obtained at the National Research & Development Institute for Textile and Leather, Collagen Department [11]. Polyvinylpyrrolidone (PVP) with average molecular weight of 3.6×10^5 Da was purchased from Sigma-Aldrich. Dextran (DEX) with nominal molecular weight of 5×10^5 Da was purchased from Sigma-Aldrich.

2.2. Preparation of polymeric blends

Polymeric blends were prepared by mixing of suitable weights of collagen with polyvinylpyrrolidone (PVP) and dextran (DEX) aqueous solution to obtain the final weight ratio of 50:50 (w/w). The obtained blends were placed in glass Petri dishes and were irradiated with EB at room temperature and atmospheric pressure. The absorbed radiation doses and dose rate were cheked with ceric-cerrous dosimeter. The final absorbed radiation doses were: 0, 5, 10 and 30 kGy and dose rate of 2 kGy/min. The irradiated blends were freeze-dryed to obtain the sponge materials.

2.2. Methods of measurement

2.2.1. ATR-FTIR spectroscopy

The ATR-FTIR investigations were performed on Perkin Elmer spectrophotometer type Spectrum 100. All spectra were recorded in the 600-4000 cm^{-1} range with a resolution of 4 cm^{-1}, and 40 scans were performed per sample. The recorded spectra were processed using OPUS v. 6.5 software package.

2.2.2. FT-Raman spectroscopy

The FT-Raman instrument used in this study was a VERTEX 70 FT-IR spectrometer coupled to a RAM II FT-Raman module (Bruker Optics, Germany) with the following technical characteristics: Nd:YAG laser source with wavelength of 1064 nm, spectral range of 3600 – 50

cm^{-1}, liquid nitrogen cooled detector. The power laser source for recorded spectra was setup in the 100-500 mW range. Raman spectra of collagen-PVP and collagen-DEX blends before and after irradiation with EB were achived in air at room temperature with 20 scans/sample. All Raman spectra were processed with OPUS v 6.5 software package.

2.2.3. Thermal analysis (TG/DTG)

Simultaneous Thermal Analyzer STA 409 PC Luxx (NETZSCH Geratebau GmbH, Germany) equipped with TG/DSC type K was used to study the thermal stability of pure collagen, PVP, DEX and irradiated collagen-PVP and collagen-DEX blends in order to establish the thermal behaviour of these blends under EB irradiation. All samples were investigated in dynamic atmospheric conditions under static air with a flow rate of 40 mL/min, sample mass about ~10 mg at the heating of 10 K min^{-1}, in the temperature range 25-500°C. The TG/DTG curves were obtained using NETZSCH Proteus Thermal Analysis software. The heating of the sample was performed in an aluminum crucible and an empty crucible was used as reference.

2.2.5. Water absorption

Water absorption studies were carried out by immersing the irradiated samples in a medium with pH = 7.4 (phosphate buffer) at 37±1°C. Swollen samples were then taken out at regular time intervals; the surface water was removed by filter paper and weighed again. The percent water uptake was calculated using the follow equation:

$$\textbf{Water absorption (\%)} = (W\text{-}W_0/W_0)\times 100, \quad (1)$$

Where **W** is weight of the swollen sample and $\mathbf{W_0}$ is the weight of the dried sample. The experiment was carried out until equilibrium was attained.

2.2.6. Scanning electron microscopy

SEM images were recorded on a HITACHI S2600N electron microscope coupled to an EDS detector. Prior to the analysis, all samples were covered with a layer of silver by plasma sputtering.

3. Results and discussion

3.1 ATR-FTIR analysis

Fourier transform infrared (FTIR) spectroscopy has been widely used by many researchers to study the formation of polymeric blends. FTIR spectroscopy provides information regarding intermolecular interaction *via* analysis of FTIR spectra corresponding to stretching or bending vibrations of particular bonds. The positions at which these peaks appear depends on the bond type (force constant and reduced mass). Hydrogen bonding or other secondary interactions between chemical groups on the different polymers usually cause a shift in peak position of the participating functional groups. Hydrogen bonding interactions usually move the stretching frequencies of the participating groups, e.g. O−H towards lower wavenumbers usually with increased intensity and peak broadening. The shift in peak positions will depend on the strength of the interactions [10]. The FTIR spectra of pure collagen, PVP, DEX, collagen-PVP and collagen-DEX blends are shown in Figure 1. FTIR spectrum of the native collagen presents characteristic bands to its specific molecular organization: the amide A (3300-3330 cm^{-1}), amide B (3070-3080 cm^{-1}), as well as amide I (1630 cm^{-1}), amide II and III (1545 and 1237 cm^{-1}) [12]. These bands are related to the peptide linkages of collagen. When comparing the behavior of collagen in native and denatured conformations under exposure to ionizing radiation, the amide I regions is a useful area for assessing of changes in the relative intensity as it is conformation dependent [13]. The amide A and B bands of collagen are associated with NH-stretching. The amide I band is useful for

identification of the secondary structure of proteins. The amide band I may be assigned to the vibrations of amide carbonyl along carbonyl backbone. The amide II band absorption consists of amide N-H bending vibrations and C–N stretching vibrations [14]. The infrared spectrum of PVP is characterized by strong C=O absorbtion peak from amide group of PVP at 1652 cm^{-1}, C–N group appeared at 1287 cm^{-1}, C–H stretching and bending vibrations were observed at 2800-3000 and 1420-1460 cm^{-1}, respectively.

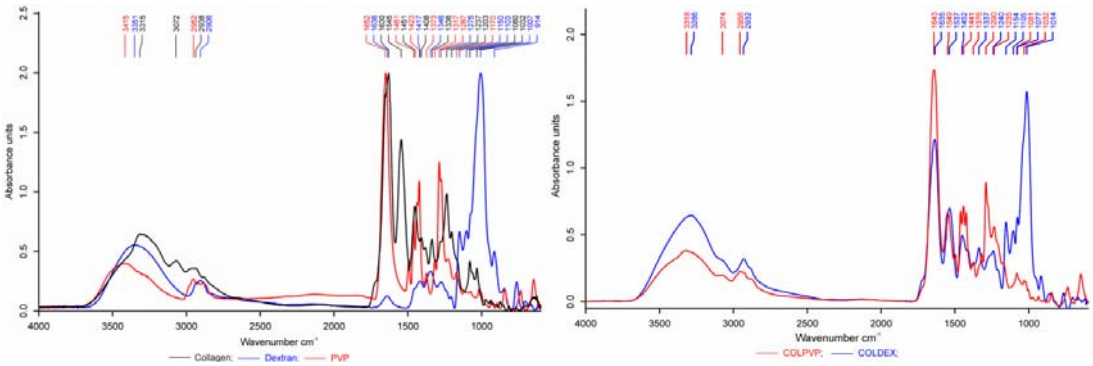

Fig. 1. The FTIR spectra of collagen, PVP, DEX (left) and collagen-PVP and collagen-DEX (right) blends.

In the FT-IR spectrum of DEX the presence of OH groups could be confirmed by the appearance of broad band with a maximum at 3351cm^{-1}, C–H stretching at 2906 cm^{-1}, C–H bending and rocking vibrations at 1450 cm^{-1} and 950 cm^{-1}. The broad band witch starts at 1200 cm^{-1} with a maximum at 1007 cm^{-1} caracterizing asymmetrical –C–O–C– stretching of the ring [9].

The interaction between collagen, PVP and DEX has been confirmed by FTIR spectra of collagen-PVP and collagen-DEX blends (Figure 1). All the major functional groups of collagen, PVP and DEX were present in FTIR spectra of collagen-PVP and collagen-DEX blends. Each blend was individualy analized before and after EB irradiation. The FTIR spectra of irradiated blends are presented in Figure 2. After blending, the position of amide A and B bands in collagen-PVP blend are shifted to higher frequencies. Also, the amide I band position in the blend has shifted from 1630 cm^{-1} to 1643 cm^{-1}. Amide II band in collagen has been shifted after blending with PVP, from 1545 cm^{-1} to 1549 cm^{-1}. A significant shifting is present in the case of amide III band, from 1237 cm^{-1} in collagen to 1290 cm^{-1} in collagen-PVP blend.

After EB irradiation of collagen-PVP blend with doses to 5 kGy up to 30 kGy, the position of amide A (3318 cm^{-1}) band has remained almost unchanged, but the relative intensity has increase considerably with radiation dose, from 0.387 to 0.527. The position of amide B (3074 cm^{-1}) band after irradiation, has also remained unchanged, but has suffered a relative decrease in intensity at radiation dose of 30 kGy. The 2936 cm^{-1} band in collagen, which is related to CH and CH_2 strech, was shifted to higher frequencies after blending with PVP, but after irradiation this band has decrease to 2926 cm^{-1} with radiation dose . The relative intensity of this band has increased considerably with radiation dose. The positions of amide I (1643 cm^{-1}) and amide II (1549 cm^{-1}) bands were shifted towards lower frequencies and the position of amide III (1290 cm^{-1}) band has been unchanged. In Table 1 the position and relative intensity of unirradiated and irradiated blends are summarized. The spectra of collagen-DEX blends samples display characteristic absorption bands of collagen and DEX. On the right side of Figure 2 the FTIR spectra of unirradiated and irradiated collagen-DEX blend can be seen.

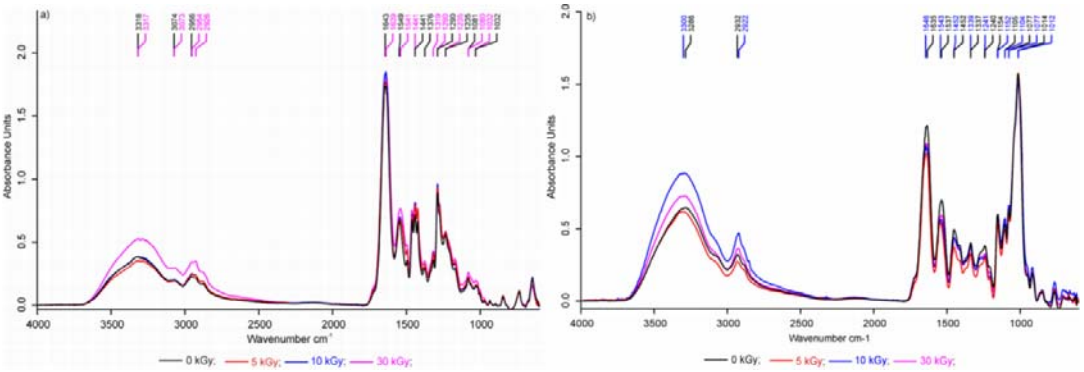

Fig. 2. The FTIR spectra of irradiated collagen-PVP(left) and collagen-DEX (right) blends

Table 1. The position and relative intensity of FTIR bands from collagen-PVP and collagen-DEX blend before and after EB irradiation

Samples	**Wavenumber, [cm^{-1}]**				**Relative Intensity**			
Dose of radiation, [kGy]	**0**	**5**	**10**	**30**	**0**	**5**	**10**	**30**
Collagen-PVP	3318	3318	3318	3317	0.387	0.354	0.387	0.527
	3074	3073	3073	3073	0.020	0.018	0.018	0.015
	2956	2955	2953	2926	0.083	0.093	0.101	0.125
	1643	1642	1638	1638	1.756	1.772	1.858	1.855
	1549	1544	1542	1541	0.352	0.341	0.357	0.360
	1290	1289	1289	1290	0.729	0.743	0.770	0.686
Collagen-DEX	3286	3320	3300	3287	0.649	0.619	0.888	0.729
	2933	2932	2924	2922	0.116	0.110	0.214	0.158
	1635	1639	1646	1641	1.194	1.012	1.068	1.075
	1537	1543	1543	1536	0.435	0.362	0.346	0.368
	1452	1453	1452	1452	0.322	0.288	0.321	0.300
	1014	1013	1012	1013	1.609	1.618	1.517	1.542

In the FTIR spectrum of the collagen-DEX blend, the position of amide A band has shifted from 3315 cm^{-1} to 3286 cm^{-1}. The amide B band present in collagen, canot be identified in collagen-DEX blend. The bands from collagen (2938 cm^{-1}) and DEX (2906 cm^{-1}) which are related to the CH_2 and C−H streching vibrations were shifted to 2933 cm^{-1} in this blend. The amide I (1630 cm^{-1}) band position was shifted towards higher wavenumbers, to 1635 cm^{-1}, while the amide II (1545 cm^{-1}) was shifted towards lower wavenumbers, to 1537 cm^{-1}. The bands from 1452 cm^{-1} and 1014 cm^{-1} are specific of DEX molecule, and describe C−H bending vibrations and asymmetrical –C–O–C– stretching. The absorption band in pure DEX is present at 1007 cm^{-1}, after blending with collagen, it was shifted to 1014 cm^{-1}. After EB irradiation of collagen-DEX blends,

the absorption band from 2933 cm^{-1} shifted with radiation dose to lower wavenumbers and at the radiation dose of 10 kGy, the relative intensity has incresed. The absorption band located at 3286 cm^{-1} (0 kGy) which was shifted to 3320 cm^{-1} after EB irradiation with 5 kGy had the highest relative intensity value of 0.888. This beahviour prouve that EB irradiation of polymeric blends, leads to the formation of hydrogen bonding or other interactions between chemical groups. Thus, we observed after irradiation dose of 30 kGy, for collagen-PVP and collagen-DEX blend a different behaviour related to CH_2 and C−H stretching vibrations. In the case of collagen-PVP blend, the relative intensity increased with radiation dose, while for collagen-DEX blend at 30 kGy it has decresed.

3.2 FT-Raman analysis

The spectral characteristics of the studied irradiated blends were also investigated by FT-Raman spectrosopy. In Figure 3 FT-Raman spectra of collagen-PVP and collagen-DEX blends before and after EB irradiation are presented. The specific Raman shifts of collagen, PVP and DEX are summarized in Table 2.

Table 2. Characterization of FT-Raman bands of collagen, PVP and dextran.

Vibration frequency, [cm^{-1}]	**Vibration of characteristic functional groups**
Collagen	
1600-1700	C=O stretching (Amide I)
1200-1300	N-H in-plane bending and C-N stretching
PVP [15]	
2989, 2954	Asymmetric CH_2 stretch, chain; asymmetric CH_2 stretch, ring
2923 2895, 2860	Symmetric CH_2 stretch, chain; Symmetric CH_2 stretch, ring; C−H stretch
1662	Amide
1494, 1462	C−N, CH_2 scissoring
1380, 1296	C−H bend; CH_2 wagging, C−N stretch
1023, 900, 851, 754	CH_2 twist, C−C, CH_2 rock, C−C ring, C−C chain
Dextran [10]	
2906, 2912 [16]	C−H stretch
1466	CH_2, scissoring
1343, 1272	CH_2, wagging; CH_2, twisting
853, 923 1083, 1133	C−O−C, symmetric stretching; CH_2, rocking; C−C, stretching C–O–C, asymmetric stretching; C–O–C, asymmetric stretching
771	C–C–O, symmetric stretching

It is well known that any interaction, e.g. hydrogen bonding formed between two polymers, will affect the Raman shifts. For the investigations of these interactions, we compared the characteristic Raman shifts of pure collagen, PVP and DEX with collagen-PVP and collagen-DEX blends. As it can been seen, the FT-Raman spectra of blend samples displayed the characteristic absorption bands for all constituents. For unirradiated blends, it was easily seen that the peak maximum specific of C−H and CH_2 stretching bonds were observed at lower wavenumbers than those observed for pure components (Table 2 and Table 3). The absorption band specific to the C=O stretching bond was shifted towards higher wavenumbers.

The bands from 1688 cm^{-1} and 1671 cm^{-1}, respectively were shifted to lower wavenumbers with radiation dose. For both type of blends, the band from 2700 cm^{-1} may be assigned to the O−H intramolecular hydrogen bonding. This band presented no change until radiation dose of 10 kGy, and, for all investigated samples, cannot be detected after radiation dose of 30 kGy. This may be due to the leakage of hydrogen bonds produced by EB irradiation.

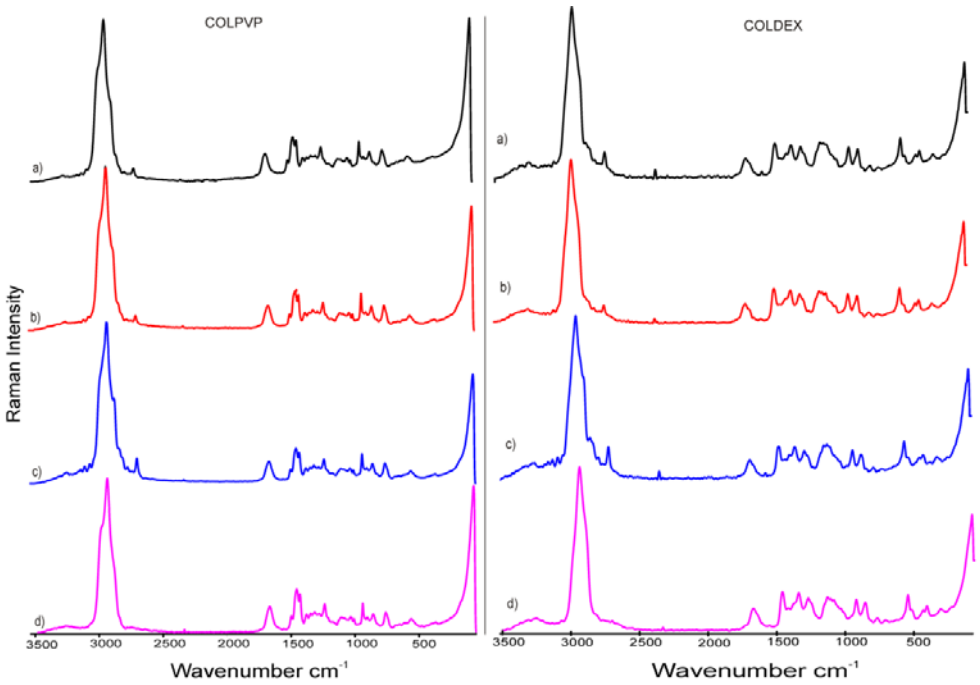

Fig. 3. FT-Raman spectra of collagen-PVP (left) and collagen-DEX (right) blends before and after EB irradiation; a) 0 kGy; b) 5 kGy; c) 10 kGy; d) 30 kGy;

Table 3. Assignments of Raman bands of collagen-PVP and collagen-DEX blends.

Materials	**Vibration frequency, [cm^{-1}]**				**Characteristic vibrations of functional groups**
Radiation dose, [kGy]	**0**	**5**	**10**	**30**	
Collagen-PVP	2933	2933	2936	2937	Asymmetric CH_2 strech (chain and ring)
	2700	2700	2700	-	O−H intramolecular hydrogen bonding
	1688	1664	1667	1667	C=O stretching (Amide)
	1454 1452	1494 1452	1456 1430	1457 1430	CH_2 scissoring, C−N
	1234	1234	1237	1237	N-H in-plane bending and C-N stretching
	936 855 757	936 855 757	939 858 761	940 859 760	C−C ring C−C chain
Collagen-DEX	2938	2939	2938	2938	CH_2 and C−H stretch
	2700	2700	2700	-	O−H intramolecular hydrogen bonding
	1671	1668	1668	1669	C=O stretching (Amide)
	1458	1459	1458	1458	CH_2, scissoring
	1341	1338	1340	1339	CH_2, wagging
	1271	1272	1271	1270	CH_2, twisting
	1129	1130	1129	1130	C–O–C, asymmetric stretching
	920 853	920 853	919 857	920 854	C−O−C, symmetric stretching; CH_2, rocking

3.4. Water absorption

The water absorption (%) of irradiated collagen-PVP and collagen-DEX was measured during immersion in water for 24 h for collagen-PVP, respectively 4 h for collagen-DEX at 37^{o}C.

Figure 4 shows the behavior of irradiated blends with different radiation dose during water absorption process depending on immersion time. After 4 hours the collagen-DEX samples were degraded and they couldn't be weighted; because of this reason different immersion time appears between the two types of blends. The blends water absorption increased with increasing immersion time, but in specific way function of blend type.

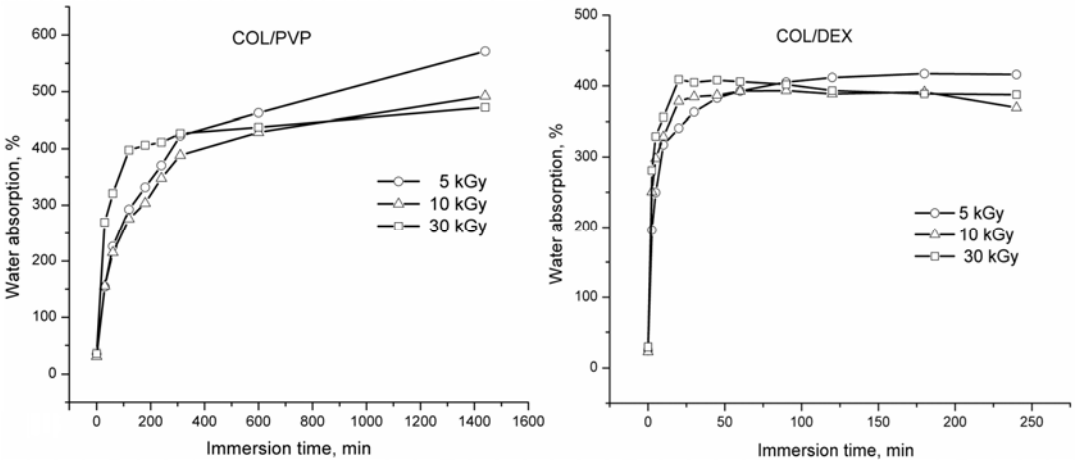

Fig. 4. Water absorption profile of irradiated collagen-PVP (left) and collagen-DEX (right) blends.

For collagen-PVP blends, the water absorption had a rapid evolution up to 4 h and continued to increase even after 24 h, however as it can be observed that the blends reached almost an equilibrium level. In the case of collagen-DEX blends, water absorption increased remarkably in first minutes of immersion, up to 30 minutes, and then water absorption reached the equilibrium level. The maximum absorption at the equilibrium states was in the range 450-500 % for collagen-PVP and 350-450% collagen-DEX blends. Regarding the evolution of water absorption with radiation dose, a decreasing of water absorption power with increasing radiation dose can be seen for both blends. Corresponding decreases of water absorption power is probably due to the increase of inter- and intramolecular crosslinks and/or forming of a new polymeric network with increasing of radiation dose. According with Kim et al., [17], the maximum absorption water at the equilibrium state for some polymeric blends were found to be in the range 400-800%. These values seem to be almost equal with those of some commercial hydrogel dressings.

3.5. Thermal analysis (TG/DTG)

Fig. 5 shows the typical thermal analysis, TG and DTG curves recorded in static air at 10 K min^{-1} for pure collagen, PVP, dextran and collagen-PVP and collagen-DEX. These results are in good agreement with those reported for collagen [18], [19], PVP [20] and dextran [21]. The thermo-oxidation process of collagen, PVP and dextran occurs through two, respectively three main successive processes. The first endothermic process indicated by I, for all samples consists in the loss of physical absorbed water. The next processes (denoted by II and III) might be related to the thermo-oxidation or decomposition process. The TG/DTG curves of unirradiated collagen-PVP and collagen-DEX blends containing 50:50 weight fractions of collagen, PVP, respectively DEX are shown on the right side of Figure 5. It was noticed that collagen-PVP blend exhibited three steps of decompositions profiles, while collagen-DEX blend had presented four decompositions profiles. The typical TG curves obtained in this study for unirradiated collagen-PVP clearly indicated that the first decompositions process starts at approximately 40°C and stops at 220.9°C with a maximum decompositions rate at 106.9°C and a weight loss of 11.87 %. The second decompositions stage has been recorded in the 220.9 – 377.3°C range, with a maximum decomposition rate at 333.2°C and a weight loss of 22.93 %. The third decomposition stage starts at 377.3°C and ends at 497.9°C, with a maximum decomposition rate at 440.0°C and a weight loss

of 42.22%. As can been seen in Figure 5, the collagen-PVP blend is more stable from a thermodynamic point of view in contrast with component materials. The four decomposition steps found for the second blend, collagen-DEX presented in this study are describe as follows: the first stage starts at 40°C and ends at 166.8°C, with a maximum of decomposition at 97.3°C having a weight loss of 8.23 %; the second one begins at 166.8°C and ends at 283.3°C, with a maximum decomposition at 225.9°C and a weight loss of 23.48%; the third process of decompositions starts at 283.3°C and ends at 406°C with a maximum decompositions at 324.2°C and a weight loss of 23.29%; the last stage of decomposition (denoted by IV), starts at 406°C and ends at 513°C with maximum decomposition at 472.4°C and a weight loss of 16.74%. According to our results, the most stable blend performed from collagen, PVP and dextran seems to be collagen-DEX.

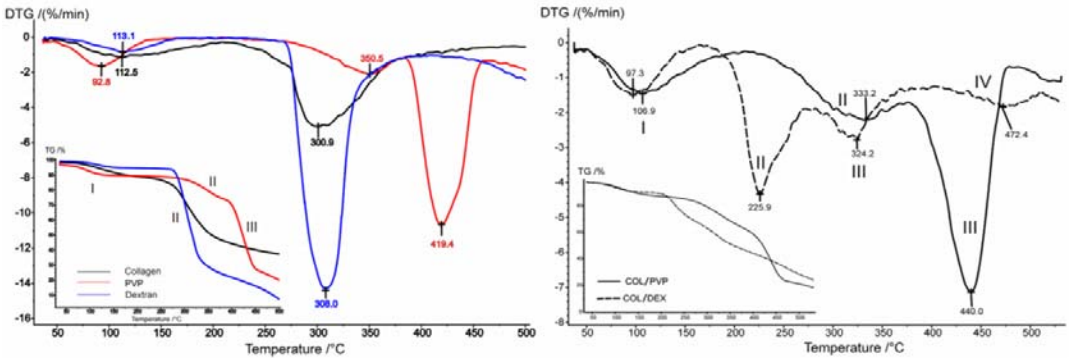

Fig. 5. The TG/DTG curves for pure collagen, PVP, dextran (left), collagen-PVP and collagen-DEX blends (right).

In Table 4 are presented the results obtained from DTG curves recorded for both types of irradiated blends, collagen-PVP and collagen-DEX. It should be noted that, after EB irradiation of collagen-PVP and collagen-DEX blends with doses from 5 kGy up to 30 kGy, the thermal profile of these samples exhibits the same stages.

Table 4. Peak maximum of DTG curves of unirradiated and EB irradiated collagen-PVP and collagen-DEX blends at a heating rate of 10 K min^{-1}

Dose, [kGy]	Collagen-PVP			Collagen-DEX			
	T^{I}_{max}/°C	T^{II}_{max}/°C	T^{III}_{max}/°C	T^{I}_{max}/°C	T^{II}_{max}/°C	T^{III}_{max}/°C	T^{IV}_{max}/°C
0	106.9	333.2	440.0	97.3	225.9	324.2	472.4
5	112.9	304.5	439.5	94.6	223.5	315.2	462.3
10	124.9	318.5	440.2	93.2	222.7	315.7	459.8
30	184.2	301.5	439.4	95.4	225.3	315.1	480.8

As can be seen in Table 4 significant changes related to behavior of collagen-PVP blend under EB irradiation have appeared in the case of the first thermo-oxidative process, where for the sample irradiated with 5 kGy, the maximum peak temperature has been found at 112.9°C; at the 10 kGy the maximum peak temperature was at 113.3°C. With increasing of radiation dose we observed a displacement of the maximum peak temperature at 184.2°C for a radiation dose of 30 kGy. Concerning to collagen-DEX blend, after EB irradiation with radiation dose of 30 kGy, the thermal stability increased up to 480.8°C (Table 4).

3.6. Scanning electron microscopy (SEM)

In order to study the morphology of irradiated collagen-PVP and collagen-DEX blends, scanning electron microscopy was employed. In Figure 6 the SEM images of EB irradiated

collagen-PVP and collagen-DEX are shown. The SEM images of investigated blends show a highly ordered structure function of blend type. In collagen-PVP blends, a structure with well defined, randomly disposed pores can be observed, while in the case of collagen-DEX blends, we cannot assumed the formation of well defined pores, in fact, the formation of some horizontally disposed lamellar structure can be observed. In respect to the action of EB irradiation, up to radiation dose of 30 kGy, the blends structure was not affected.

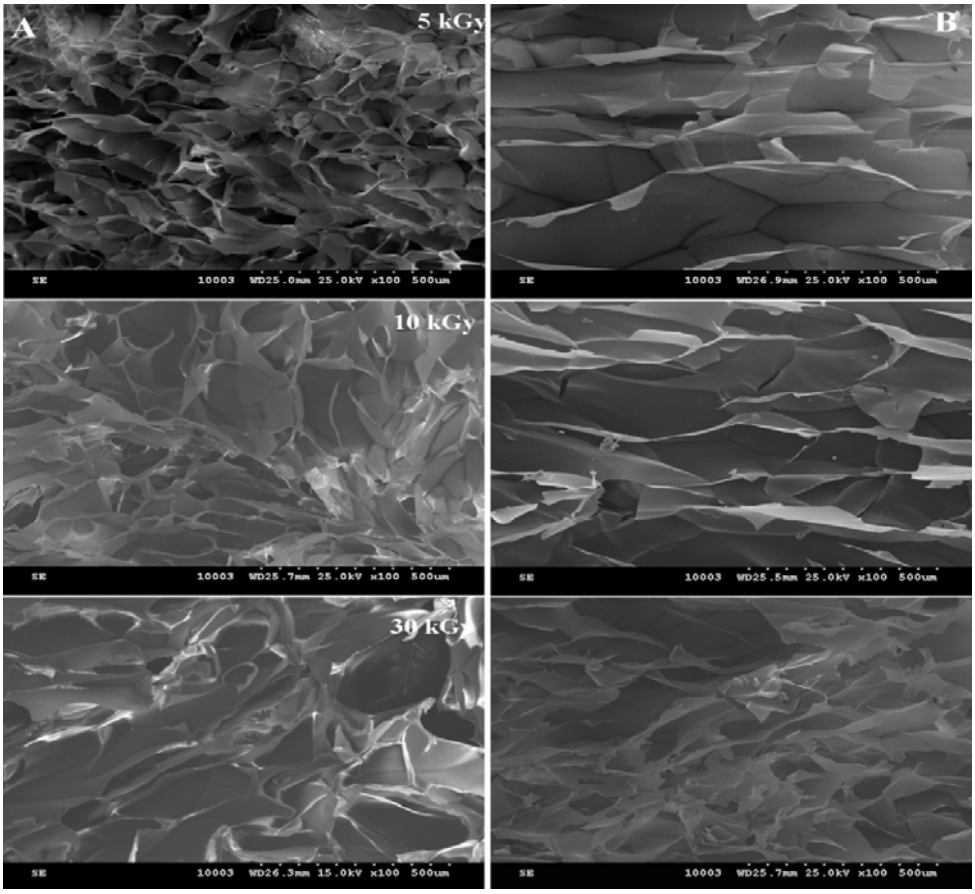

Fig. 6. *SEM images of irradiated collagen-PVP and collagen-DEX blends; A - collagen-PVP; B - collagen-DEX*

4. Conclusions

In the present work, the influence of EB irradiation on collagen-PVP and collagen-DEX blends was investigated using ATR-FTIR, FT-Raman, thermal analysis, water absorption and SEM techniques. The ATR-FTIR, FT-Raman, thermal analysis, water absorption and SEM results clearly pointed out strong interaction between collagen, PVP and DEX. FTIR analysis confirmed that the EB irradiation of polymeric blends, leads to the formation of hydrogen bonding or other interactions between chemical groups. Thus, we observed after irradiation dose of 30 kGy, for collagen-PVP and collagen-DEX blend a different behaviour related to absorption bands of CH_2 and C−H stretching vibrations. In the case of collagen-PVP blend, the relative intensity increased with radiation dose, while for collagen-DEX blend at 30 kGy it has decresed. FT-Raman studies have shown the leakage of hydrogen bonds produced by EB irradiation for the samples irradiated with 30 kGy. Regarding the evolution of water absorption with radiation dose, a decreasing of water absorption power with increasing radiation dose can be seen for both blends. Corresponding decreases of water absorption power is probably due to the increase of inter- and intramolecular crosslinks and/or forming of a new polymeric network with increasing of radiation dose. Thermal

stability of irradiated blends had increased with increasing of radiation dose. The most stable blend performed from collagen, PVP and DEX seems to be collagen-DEX. The SEM images of investigated blends show a highly ordered porous and lamellar structure function of blend type. In respect to the action of EB irradiation, up to radiation dose of 30 kGy, the blends structure was not affected.

Acknowledgements

The authors would like to thanks to the National Authority of Scientific Research (ANCS) for funding of Nucleu Program PN 09 39.

References

[1] A. Sionkowska, European Polymer Journal **39**, 2135 (2003).
[2] J. D. Berglund, M. M. Mohseni, R. M. Nerem, and A. Sambanis, Biomaterials **24**, 1241 (2003).
[3] R. K. Wanchoo and P. K. Sharma, European Polymer Journal **39**, 1481 (2003).
[4] B. H. Kim, D. Kim, Y. S. Jung, H. Kim, and D. L. Cho, Macromolecular Research **11**, 291 (2003).
[5] M. G. Cascone, G. Polacco, L. Lazzeri, and N. Barbani, Journal of Applied Polymer Science **66**, 2089 (1997).
[6] A. Sionkowska, H. Kaczmarek, M. Wisniewski, J. Kowalonek, J. Skopinska, Surface Science **566**, 608 (2004).
[7] A. Sionkowska, M. Wisniewski, H. Kaczmarek, J. Skopinska, P. Chevallier, D. Mantovani, S. Lazare, and V. Tokarev, Applied Surface Science **253**, 1970 (2006).
[8] J. Skopinska-Wisniewska, A. Sionkowska, A. Kaminska, A. Kaznica, R. Jachimiak, T. Drewa, Applied Surface Science **255**, 8286 (2009).
[9] D. Mete, C. Goksel, and A. Guner, Macromolecular Symposia **302**, 257 (2011).
[10] M. Barsbay and A. Guner, Carbohydrate Polymers **69**, 214 (2007).
[11] V. Trandafir, G. Popescu, M. G. Albu, H. Iovu, and M. Georgescu, Bioproduse pe baza de colagen, Ars Docendi, Bucuresti (2007).
[12] B. Madhan, V. Subramanian, J. R. Rao, B. U. Nair, and T. Ramasami, International Journal of Biological Macromolecules **37**, 47 (2005).
[13] J. Fassett, D. Tobolt, and L. K. Hansen, Mol Biol Cell **17**, 345 (2006).
[14] J. H. Muyonga, C. G. B. Cole, and K. G. Duodu, Food Chemistry **85**, 81 (2004).
[15] Y. Borodko, S. E. Habas, M. Koebel, P. D. Yang, H. Frei, and G. A. Somorjai, Journal of Physical Chemistry B **110**, 23052 (2006).
[16] R. G. Zhbankov, S. P. Firsov, E. V. Korolik, P. T. Petrov, M. P. Lapkovski, V. M. Tsarenkov, M. K. Marchewka, and H. Ratajczak, Journal of Molecular Structure **555**, 85 (2000).
[17] H. D. Kim and H. J. Yoo, Journal of Biomedical Materials Research Part B-Applied Biomaterials **85B**, 326 (2008).
[18] P. Budrugeac, L. Miu, V. Bocu, F. J. Wortman, and C. Popescu, Journal of Thermal Analysis and Calorimetry **72**, 1057 (2003).
[19] P. Budrugeac, L. Miu, C. Popescu, and F. J. Wortmann, Journal of Thermal Analysis and Calorimetry **77**, 975 (2004).
[20] M. A. Moharram and M. G. Khafagi, Journal of Applied Polymer Science **102**, 4049 (2006).
[21] D. C. Culita, O. Carp, L. Patron, P. Budrugeac, M. Feder, L. Diamandescu, Journal of Thermal Analysis and Calorimetry **101**, 181 (2010).