# Effects of UV Exposure on Poly (hydroxy urethane) -Poly (vinyl alcohol) (PHU-PVA) Blends for Polymer Membranes

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*The effects of UV exposure on physico-chemical properties of polymer membranes were studied in this paper. The membranes having different surface energy, resilience and initial modulus of elasticity were obtained from a series of blends of poly (hydroxy-urethane) and poly (vinyl alcohol). UV treatments in air, at room temperature, decrease the water contact angles as a result of higher surface energies of the polymer membranes. Some important modifications appear in ATR-FTIR spectra. The mechanical properties of the untreated polymer films are better than of the UV treated samples. Short-term UV irradiations lead to a photo stabilization effect of polymer surface. Bulk chemical changes are induced through photo oxidation and photo degradation processes for long-term UV irradiation.*

*Keywords: UV treatment, photo oxidation, photo degradation, photo stabilization resilience*

New materials with improved physico-chemical properties have been obtained by alloying poly (vinyl alcohol) (PVA) with poly (hydroxy-urethane) (PHU) in order to use them for biomedical applications [1-4]. Polymer selection for a specific application depends on theme physico-chemical properties which determine its biocompatibility. The common polymers generally do not possess proper surfaces as required for biomedical applications. In this case a surface treatment may be necessary. Surface treatments are important due to the possibility to change surface properties without changing the bulk material properties [5].

Treatments using UV radiation are widely used since long for substrate surface modification. The UV radiation initiates photophysical and photochemical processes in polymers but its influence is restricted to a thin surface layer [6].

Studies made until now show that the effects of UV radiation on the mixture of PVA and polyurethanes are strongly wavelength dependent [7] but also with exposure time. Short-term UV irradiation induced reversible changes of molecular mobility and stereo regularity of the films based on polyvinyl alcohol [8, 9]. Long-term UV-irradiation induced chemical effects due to the cleavage of chemical bonds and formation of active species [10]. The presence of oxygen in the environment during irradiation may cause rapid polymer degradation. This takes place when UV radiation interacts with atmospheric oxygen and creates small quantities of ozone resulting in redox reactions at the surface and in the polymer bulk [11]. The UV radiation also modified the roughness of polymer films [1].

A new polymer blend merging the properties of both polymers by mixing PVA and PHU was obtained and analyzed in our previous work [4]. The aim of this study is to analyze the modification of the physico-chemical properties of these polymers by the UV treatment in air.

## Experimental part

The PVA-PHU alloy was obtained using PVA Mn= 65 000-87 000 molecular weight, 20% solution in distilled and deionized water (Loba Feinchemie AG- Austria) and PHU synthesized through a well known method [12]. The PHU was obtained from "P. Poni" Institute of Macromolecular Chemistry Iasi as a gift sample. The mixture was stirred for 2 h at room temperature and a viscous and transparent solution of PHU was obtained. The formed polymer was precipitated in alcohol and then dried for 24 h at a low pressure (1-2 torr).

The PHU and PVA chemical structures are given in figures 1.a and b.

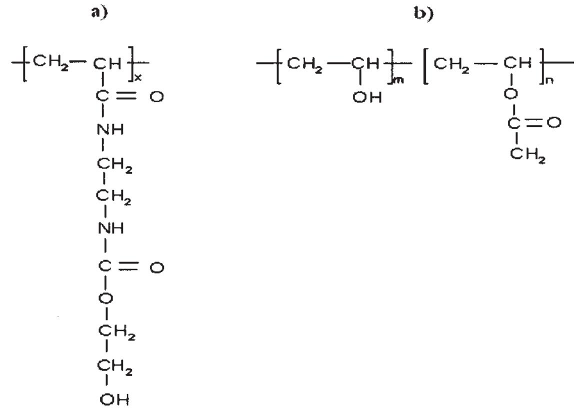

Fig. 1. a) PHU chemical structure; b) PVA chemical structure

Four PHU-PVA blends were obtained by mixing PVA and PHU in different rations (table 1).

**Table 1**
PHU-PVA blends with different concentration of PVA

| Sample | PHU content (%) | PVA content (%) |
|---|---|---|
| S I | 16 | 84 |
| S II | 25 | 75 |
| S III | 32 | 68 |
| S IV | 70 | 30 |

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**Table 2**
BANDS ASSIGNMENT OF THE UNTREATED PHU-PVA BLENDS

| Wave number (cm$^{-1}$) | **Intensity** | L-large; I-intense; VI- very intense; S-shoulder, W- weak. |
|---|---|---|
| 3300 | L<br>I | $\nu_{(OH)}$<br>$\nu_{(NH)}$ urethane associated through H bonds |
| 2940<br>2908<br>2850 | VI<br>I<br>S | $\nu_{(CH2)}$ asym<br>$\nu_{(CH2)}$ sym<br>$\nu_{(CH3)}$ |
| 1731<br>1712 | VI<br>I | $\nu_{(C=O)}$ in ester<br>$\nu_{(C=O)}$ in urethane Amide I |
| 1556 | I | ($\nu_{C\text{-}N} + \delta_{N\text{-}H}$) Amide II |
| 1260 | VI | $\nu_{(C\text{-}N)}$ and $\delta_{(N\text{-}H)}$ asym Amide III |
| 1085<br>1010 | VI<br>I | $\nu_{(C\text{-}C\text{-}O)}$ asym,<br>$\nu_{(C\text{-}O\text{-}C)}$ aliphatic |
| 800 | W | $\nu_{(N\text{-}O)}$ , $\nu_{(OH)}$ sccisoring |

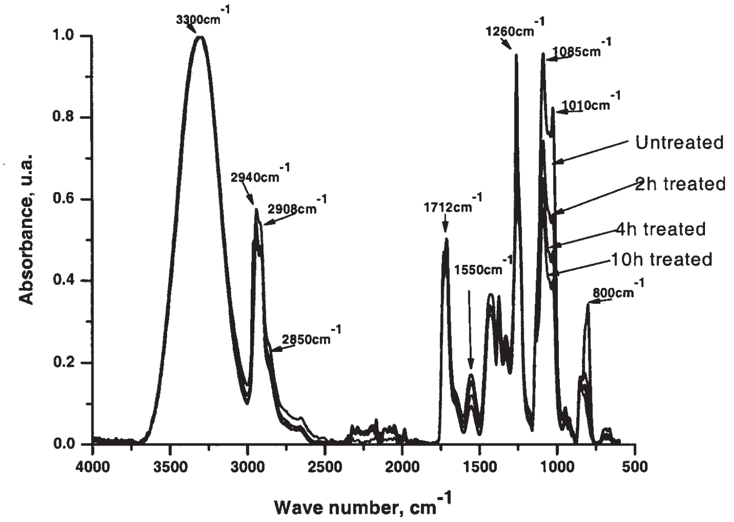

Fig. 2. ATR-FTIR spectra for untreated, 2, 4 and 10 h UV treatment of the 25% PHU sample

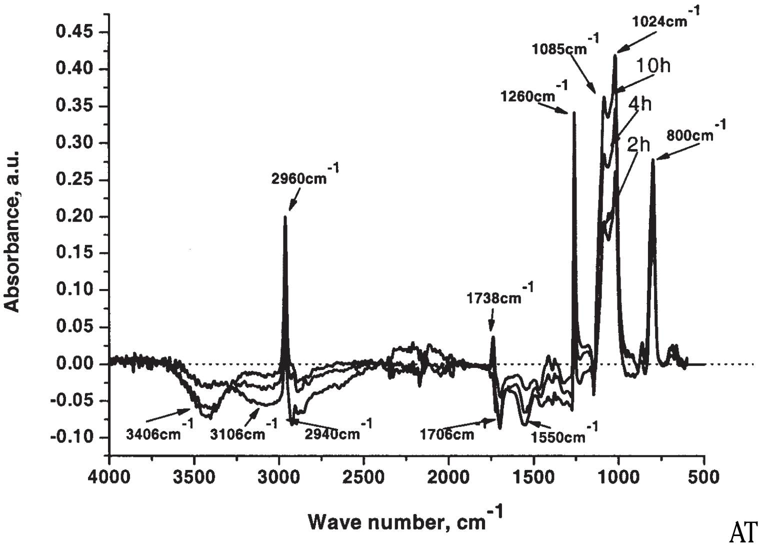

Fig. 3. ATR-FTIR subtracted spectra for 2, 4 and 10 h UV treatment of the 25% PHU sample

The mixed solution was outgased for 8-12 min at 10 – 15 Torr. Then it was cast on a glass plate (220x240mm$^2$) by means of a Doctor Blade with a slit of 0.6 mm. The films were dried at low pressure (1-2 torr), for 48 h.

The UV irradiation of the films was carried out by means of a middle-pressure mercury lamp, HQE-40 type, having a polychrome emission spectrum, for 2, 4 and 10 h at a distance of 20cm in the presence of air, at room temperature.

ATR-FTIR analysis was performed using a Bruker Vertex 70 type spectrometer (Germany), with a diamond ATR device Model. The sample surface was scanned at room temperature. Software for spectral processing was added.

UV-VIS spectra of the solutions in water, at 20°C, 5% concentration, were recorded on a 6505 UV/VIS Spectrophotometer (Selected Science Ltd. England).

The contact angles of the samples were evaluated with KSV CAM 101 (Instruments Ltd., U.S.), using the sessile drop technique with water. The static tension tests were

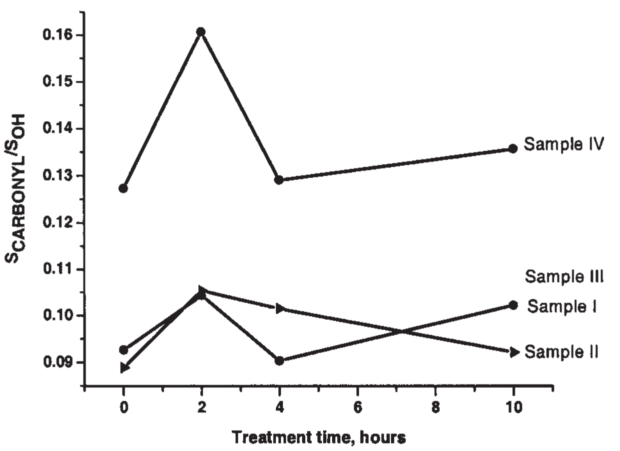

Fig. 4. Ratio R(C) of the studied samples vs. exposure time

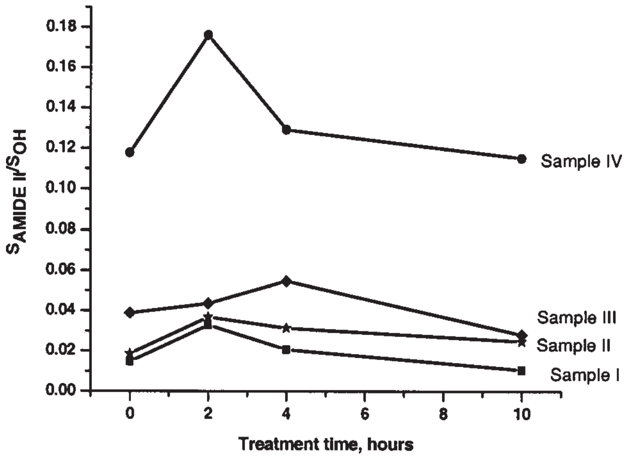

Fig. 5. The ratio R(A) of the studied samples vs. exposure time

**Table 3**

CONTACT ANGLES FOR THE UNTREATED AND TREATED SAMPLES VS. UV EXPOSURE TIME

| Sample, PHU concentrations (%) | Contact angle (degree) UNTREATED | Contact angle (degree) 2h TREATED | Contact angle (degree) 4h TREATED | Contact angle (degree) 10h TREATED |
|---|---|---|---|---|
| S I (16%) | 92 | 88 | 84 | 81 |
| S II (25%) | 96 | 89 | 86 | 82 |
| S III (32%) | 97 | 86 | 83 | 76 |
| S IV (70%) | 94 | 88 | 75 | 71 |

carried out by means of a TIRA-TEST 2161 apparatus (Maschinenbau GmbH Ravenstein, Germany), at a crosshead speed of 16, 8 mm/min.

## Results and discussions

The ATR-FTIR spectra of the mixture were similar. Table 2 summarizes the most representative IR bands for the untreated PHU-PVA mixtures.

The UV-VIS spectra of the untreated samples reveal that the samples absorb in the range of 200-300nm. The ATR-FTIR spectra of the samples recorded after UV irradiation reveal chemical modification in the polymer surface structure. As an example figure 2 shows the ATR spectra of the untreated and different time UV treated polymer. The spectrum differences of 2, 4 and 10 h UV treated samples are given in figure 3. The difference spectra were obtained by normalizing the spectra at 3300 cm $^{-1}$ band and subtracting the spectrum of the treated sample from that of untreated sample. Concomitantly, the negative bands in the difference spectra indicate the new functional groups appearance and the positive bands reveal the lost groups at the observed surface.

The difference spectra reveal the following chemical changes occur: gain of OH (3500 cm$^{-1}$ band), NH (3400 cm$^{-1}$ band), COOH (3106 cm$^{-1}$ band) [13], $CH_3$ (2940 cm$^{-1}$ band) and urethane (1550 cm$^{-1}$ band); loss of $CH_2$ (2960 cm$^{-1}$ band), Amide III (1260 cm$^{-1}$ band), C-C-O (1085 cm$^{-1}$ band), C-O-C (1024 cm$^{-1}$ band) and N-O (800 cm$^{-1}$ band) [14]. The lost of carbonyl groups may be noticed at 1738 cm$^{-1}$ band for 4 and10 h UV treatment and the appearance of new vibration at 1706 cm$^{-1}$ band . The modifications of the absorption signal in the spectral range (1740-1690 cm$^{-1}$ band) may prove the formation of ketones, esters and/or carboxylic acid functionalities after the oxidative processes [15]. Lost of the associated carbonyl and gain of the unassociated carbonyl due to absorption of UV light may occur, proving the above mentioned chemical changes.

The increase of the absorbance at 3424 cm$^{-1}$ could be due to the hydroxyl groups formed by the molecular oxygen able to extract hydrogen atoms from the polymer chains [15]. The appearance of hydroxyl group IR-band in the range (3500-3400) cm$^{-1}$and the disappearance of $CH_2$ IR band (2960 cm$^{-1}$) could be explained by the oxidation of $CH_2$ groups and formation of carboxylic (-COOH) and aldehydic (–HC=O) groups [15, 16]. The appearance of NH, $CH_3$ bands and the disappearance of C-N-C (1260 cm$^{-1}$ band), C-O-C (1024 cm$^{-1}$ band) and C-C-O (1085 cm$^{-1}$ band) could be explained by the cleavage of the polymeric chain.

Photo oxidative and photo degradative processes may occur after 4 h of UV treatment. The change induced in the (3600-3300) cm$^{-1}$ range, is an indicator for the presence of photo degradative reactions [17] that occurred in the PHU-PVA samples. The formation of the oxidized groups was favored by the presence of atmospheric oxygen during the UV treatments. These processes are more visible at 4 and 10 h than at 2 h UV treatment time.

Atomic oxygen could react with the gaseous species, such as molecular oxygen and ozone. Insertion of reaction into C–H bonds to form hydroxyl groups or into C–C bonds to form ether groups are possible when atomic oxygen reacts with the polymer chains. Further oxidation of hydroxyl and ether groups may occur increasing the treatment time [15]. The intramolecular condensation processes (by formation of ether bonds) or another photo oxidative processes which are specifically to PVA are not excluded [11, 16].

The changes of the carbonyl and Amide II groups absorption signals were analyzed in order to evaluate the photo degradation rate. The ratio of the carbonyl peak area against the hydroxyl peak area of the studied samples (R(C) = $A_{carbonyl}$ / $A_{hydroxyl}$) was evaluated, after the spectra were normalized at the most intense absorbance value of the 3300 cm $^{-1}$ band. The obtained results are given in figure 3.

Figure 3 reflects the increase of the carbonyl absorption signals reported to hydroxyl absorption signals for the same studied sample especially in the first 2 h of UV exposure. The number of carbonyl group at the surface is increasing for 2 h UV irradiation reported to the untreated sample. A slight effect of photo stabilization [17] of the PHU-PVA surface matrix can be noted. A decrease of the calculated ratio R(C) can be observed at 4 and 10 h UV treatment comparing to 2 h UV treatment. These denote the presence of photo oxidation processes.

In figure 4 is presented the variation of the ratio of the Amide II peak area against the hydroxyl peak area of the studied samples, $R(A) = A_{AmideII} / A_{hydroxyl}$) versus UV exposure time.

A small increase of the Amide II IR signals reported to hydroxyl IR signals for the same studied sample in the first 2 h of UV exposure was observed. This phenomenon is more pronounced especially for the sample with 70% PHU. A decrease of the ratio R(A) can be noted at 4 and 10 h UV irradiation suggesting an increase of the photo degradation rate.

The normalized R(A) values for different time treatment to R(A) values of untreated sample (fig. 6) reveal an increase of photo degradation rate with PVA content.

The small changes induced in the Amide II IR band (1574 $cm^{-1}$) may suggest that the urethanic groups are more resistant to the UV radiations [16] than the ester groups.

Changes in the surface chemical configuration, photo stabilization of the PHU-PVA matrix and polar groups appearance, through photo oxidative and photo degradative processes are also demonstrated by the modification of the water contact angles during the UV treatment (table 3). The water contact angles decrease for all the samples after UV treatment, probably due to the oxidative processes taking place at the polymer-air interface. The variation of water contact angles depends on the number of hydrophilic groups at the surface of polymeric network.

Strong oxidizing species, such as ozone, and excited water molecules can be formed when UV radiation interacts with atmospheric oxygen and other compounds from air. Ozone absorbs UV radiation and dissociates into molecular oxygen and atomic oxygen. Ozone can also generate peroxy radicals, unstable species that decompose to form hydro-peroxide, carbonyl and carboxyl functionalities [15] when it comes in contact with the polymer surface. The water contact angle is decreasing. Concomitantly, the surface free energy becomes minimal for this medium, through conformational changes of the functional groups [1]. For example, the untreated sample with 25% PHU has a water contact angle 96°. The water contact angle decreases to 89° for 2 h UV treated sample (table 3).After 4 h UV treatment it became 86° and after 10 h the contact angle was 82°. The decrease of the water contact angle is due to the increase of hydroxyl groups content as it results from the ATR-FTIR spectra.

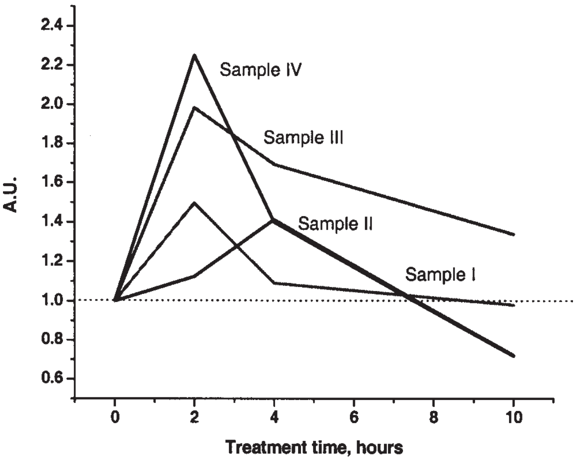

Fig. 6.The normalized R(A) values for different time treatment

The changes induced in the chemical structure of PHU-PVA blends are succeeded by changes in the mechanical properties like resilience, stiffness and modulus of elasticity, probably due to the reactive species which could penetrate the polymer network and split the macromolecular chains by redox reactions (table 4).

**Table 4**
STIFFNESS, ELASTICITY MODULUS AND RESILIENCE FUNCTION UV EXPOSURE TIME.

| Sample (%) | Treatment time | SI (16%) | S II (25%) | S III (32%) | S IV (70%) |
|---|---|---|---|---|---|
| **Stiffness (MPa)** | 0h | 0.98 | 1.23 | 0.88 | 0.27 |
| | 2h | 0.88 | 1.11 | 0.79 | 0.24 |
| | 4h | 0.70 | 1.12 | 0.69 | 0.09 |
| | 10h | 0.56 | 1.02 | 0.66 | 0.05 |
| **Modulus of elasticity (MPa)** | 0h | 2886 | 3459 | 2840 | 884 |
| | 2h | 3063 | 3470 | 3200 | 884 |
| | 4h | 2389 | 4099 | 2454 | 300 |
| | 10h | 1109 | 4122 | 1046 | 138 |
| **Resilience (MPa)** | 0h | 0.50 | 0.64 | 0.50 | 0.14 |
| | 2h | 0.58 | 0.65 | 0.50 | 0.14 |
| | 4h | 0.39 | 0.70 | 0.30 | 0.07 |
| | 10h | 0.02 | 0.51 | 0.008 | 0.002 |

The mechanical tests of materials were the simple static tension test in which a specimen of material cut in epruvet with original length about 40 mm is subjected to an axial tensile load. In this test, measurements are made of the load, F from 0.1 to 2.5 N, and corresponding change in gage length, L. If the original cross-sectional area is $A_o$ and the original length is $L_o$, then the stress (S) and strain (ε) are respectively defined by [18]:

$$S = \frac{F}{A_o} \tag{1}$$

$$\varepsilon = \frac{L}{L_o} \tag{2}$$

With the values of stress and strain known for various values of the tensile load the stress-strain curves for the 70% PHU untreated and UV treated samples are presented in figure 7. The stress-strain curves have two domains. The first domain (OA), corresponding to the elastic deformation is linear, the second domain (AB)

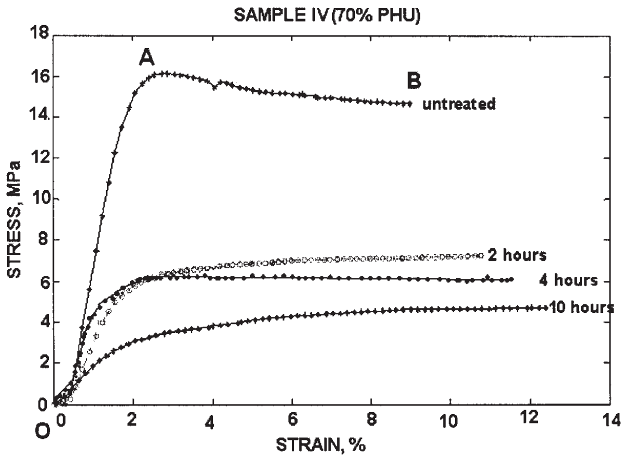

Fig. 7.Stress- strain curves vs. UV exposure time for the 70% PHU sample

corresponding to the plastic deformation finishes with the breaking of the samples. In this way the elongation at break can be defined. The calculated area under the stress-strain curve, for the same elongation, represents the stiffness. The resilience value is given by the area calculated under linear domain of the stress-strain curve. The resilience represents the mechanical work stored during the elastic deformation. The slope of the linear domain is proportional with the elasticity modulus [18].

The values for the stiffness, resilience and modulus of elasticity decreased with the treatment time. For example, the stiffness of untreated sample with 70% PHU is 0. 27 MPa and decreases from 65 % to 0.05 MPa, after 10 h UV treatment. The resilience decreased from 0.14 MPa to 0.002 MPa during the UV exposure. An increase in the elongation at break with the UV treatment time increasing was also observed.

## Conclusions

New materials with improved physico-chemical properties have been obtained by mixing PVA with PHU in order to use them for biomedical applications. The way in which the physico-chemical properties of these new membranes from PHU-PVA blends are modified by the UV treatment, in the presence of air was analyzed in this study.

Important modifications in the ATR-FTIR spectra of the UV irradiated samples depending on the exposure time were evidenced. A slight effect of photo stabilization of the PHU-PVA surface matrix was noted in the first 2 h UV treatment for all studied samples. Photo oxidative and photo degradative processes were noticed for long time exposure. The presence of oxygen favored the formation of the oxidized groups during UV treatment times. This process is more visible at 10 h than at 4 and 2 h UV irradiation time. The water contact angles decrease for all the samples after UV treatment.

The photo oxidative and photo degradative processes chemical changes in the polymer network, revealed by changes in its physico-mechanical properties. The changes become more evident when the exposure time increased.

It was noticed that the urethane groups are more resistant to UV radiations than the ester groups. The mixtures with less concentration of PVA are more stabile to the UV treatment than the mixture with big concentration of PVA.

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