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POLYMERIC FILMS PROPERTIES OF POLY (VINYL ALCOHOL) AND POLY (HYDROXY URETHANE) IN DIFFERENT CONCENTRATIONS*

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În această lucrare am analizat proprietățile filmelor polimerice obținute amestecând alcoolul polivinilic (APV) cu diferite concentrații de polihidroxiuretan (PHU). Filmele polimerice obținute în laborator au fost analizate din punct de vedere energetic (măsurători de unghi de contact), morfologic (imagini AFM), spectral (FTIR-ATR) şi mecanic (teste de întindere). Scopul lucrării este identificarea concentrațiilor optime pentru care noul biomaterial obținut din amestecul de PHU cu APV poate fi aplicat în medicină. Ne aşteptăm ca acest nou polimer să imbine atât proprietățile APV-ului cât şi pe cele ale PHU.

In this paper we analyzed the properties of polymeric films obtained by alloying poly (vinyl alcohol) (PVA) and poly (hydroxy urethane) (PHU) in different concentrations. We obtained the polymeric films and we analyzed them energetically (contact angle of water), morphologically (AFM), spectrally (FTIR- ATR) and mechanically (strength tests). The aim of this study is to identify the optimal concentrations for which a new material obtained by mixing PVA and PHU polymers can be used in medical field. We expect that this new polymer will merge the PVA and PHU properties.

Keywords: PVA, PHU, contact angle, hardness, resilience, rughness.

1. Introduction

PVA was prepared by Herman and Haehnel in 1924 for the first time [1] and it founded applications in different domains [2] such as: medicine for substitute the destroyed human tissue [1], as controlled delivery systems for drugs [1], immunological kits, and biosensors. Hydro gel PVA has a much more biocompatibility with human body [3] than PVA films because it is not toxic [4]. Gels are used as contact lenses [5], articulation cartilage replacements,

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hemodialysis membranes, and for obtaining the artificial skin [1]. Another important application of PVA is the tumor embolisis [6].

PVA has a simple chemical structure with pendant hydroxyl groups [7].The monomer unit is vinyl alcohol [1]. PVA is obtained by the vinyl acetate polymerization in alcoholic solutions [1] followed by partial hydrolysis. It is possible that not all acetate groups be substituted by OH radicals [7], consequently polymers with different hydrolysis degree will be obtained [1; 5]. The chemical structure for a 100% hydrolyzed polymer is presented in fig. 1.a Fig. 1.b contains the structure of a partially hydrolyzed polymer.

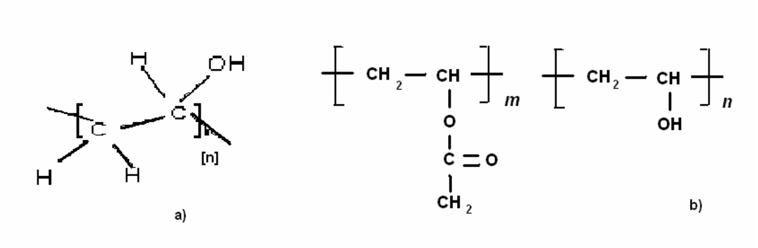


Fig. 1. Chemical structure for: a) 100% hydrolyzed polymer and b) partially hydrolyzed polymer.

The PVA melting temperature is 230 °C for 100% hydrolyzed polymer and 180 – 190 °C for partial hydrolyzed polymer [8]. The PVA density is 1, 26 g/cm^3 for the amorphous phase at 25 °C and for the crystalline phase at the same temperature is 1, 35 g/cm^3 [9].

PHU is a polymer from polyurethane class [10]. This is a principal polymeric class obtained by polymerization of diisocynate, a molecule containing two - NCO groups and two hydroxyl groups [10]. PHU is an elastic polymer characterized by urethane groups, (-O- CO- NH). It is used in electronic and electrical industries for packing fragile objects [11], subaquatic cables, in constructions because they are very good isolators, in medicine for catheters and tubes [12]. These materials are resistant to corrosion and abrasion, they have pores which absorb the humidity of the body and are recommended in hospitals. PHU is also very durable [11].

How we see PVA is a hard and rigid polymer, with good mechanical properties, but it is not elastic, while PHU is an elastic polymer, but less hard. A combination of these two polymers will form a new material which merges both polymers properties.

2. Materials and methods

The polymeric films studied in this paper were obtained by alloying PVA and PHU viscous substances. The PHU concentrations were: 12, 25, 50 and 70 percents. PVA viscous substance was obtain by solving 200 g LOBA PVA in 800 g deionized water at a temperature about 80-90 °C and than the gel was filtrated. PHU was synthesized in our laboratory, and then solved in deionized water.

These two polymers were alloyed in different concentrations, than the mixture was deposed on clean glasses, on level surfaces. Films were let to dry 72 hours at room temperature, and than dried at vacuum for 4 hours. These films were kept in exicator all experimental time.

The films were energetically studied with a goniometric installation, KSV CAM 101, using the sessile drop technique with water. The spectrally analyzes were made by using ATR-FTIR, with VERTEX 70 BRUKER diamond ATR accessory apparatus. The mechanical properties were established by stretching tests using the TIRA TEST 2161 instrument. The films were cut in epruvets with initial lengths about 40 mm and stretched with forces from 0.1 to 2.5 N for the mechanical studies. Morphology of these films was studied with AFM technique at a resolution of 20 μm. The roughness was calculated for each film.

3. Results and discussions

Membranes with different surface energy, resilience and initial elastic module were obtained when different quantities of these two polymers were alloyed.

We found that the water contact angle to PVA membrane was about 70°, while for PVA water-gel it was 112°. This phenomenon is due to the fact that the drying membrane contains a great number of hydrophilic groups (OH) at the surface, while the water-gel membrane with contains a great proportion of hydrophobic groups (CH_2) at the surface.

The water contact angle is about 74-78° for drying PHU membranes, and for gel.

The water contact angles of PVA and PVA with PHU are shown in Table 1. From this table it results that the PHU increases the contact angle.

We observe that the contact angles for these new polymers are bigger than for the pure PVA. This fact could be explained by the presence of the complex branch which is attached to polyethylene chain ($-CONH-CH_2-CH_2-NH-CO-O-CH_2-CH_2-OH$) in PHU. The branch with attached groups –OH contains polar structures: -CONH- and –NH-COO- able to form hydrogen bonds with water molecules. These polar structures can not easily move inside polymer network when it contains water in the gel state and neither when the environmental conditions are modified.

Table 1

Contact angles of water of PVA and PVA with PHU:

Nr.	Sample (% PHU)	Contact angle (degree)
1.	Pure PVA	74
2.	12	89
3.	25	96
4.	50	91
5.	70	94

The obtained ATR spectra are presented in figure 2. It is observed that the most modifications appear in the amide II band, at a wave number 1550 cm^{-1}, amide I, at 1675- 1750 cm^{-1}, amide III band, at 1200-1300 cm^{-1}.

1. The Amide II band, 1550 cm^{-1}, (figure 3) is attributed to stretching vibrations of NH groups; one can observe that the picks intensity increases with increasing of PHU concentration.

2. The Amide I band, 1675-1750 cm^{-1}, (figure 4) is attributed to valence vibrations of carbonyl groups, C=O, one can observe that for sample 3 (50% PHU) and 4 (70% PHU) the picks are shifted at smaller wave number, indicating an increase of C=O bonding when the PHU concentration increases. For samples 1 (12%) and 2 (25%), the number of C=O bonds decreases due to the hydrogen bonds achieved between this group and NH or OH groups of PHU.

3. The Amide III band, 1200-1300 cm^{-1}, (figure 5) corresponds to valence vibrations of O-C-N and N-H bonds.

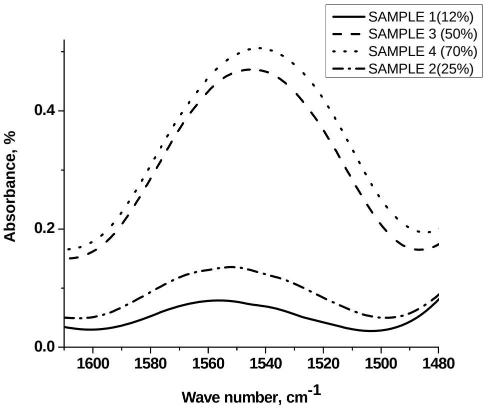


Fig. 3. Amide II band.

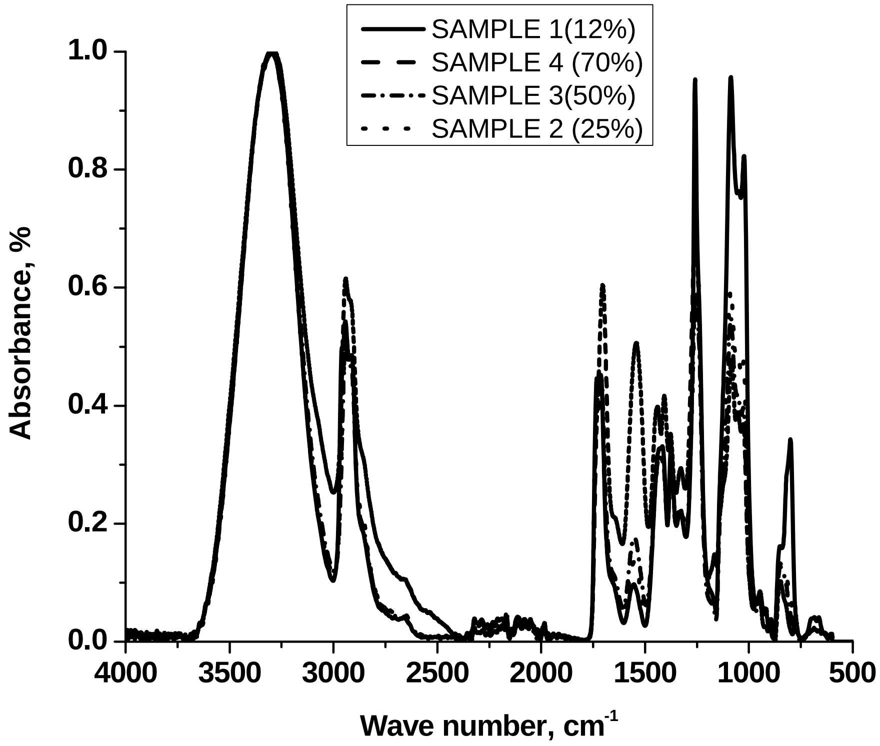


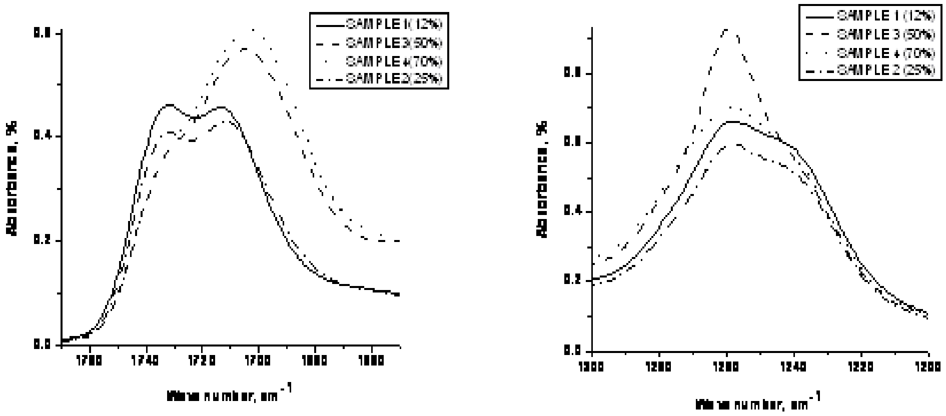
Fig. 2. ATR spectra for PVA with PHU polymers

In table 2 we give the modifications that appeared in ATR spectra for different PHU concentration.

Morphologically, the samples are porous, and the roughness coefficient depends on the PHU concentrations (figure 6).

In table 3 are given the important scales which morphologically characterize the sample: average roughness, Ra, root mean square, Sq, surface skewness, Ssk, coefficient of kurtosis, Ska, and high average, A.

Average roughness, *Ra*, and root mean square, *Sq* are two physical scales describing the roughness degree of the sample. It can be observed from figure 6 and table 3 that the most roughness sample is 6 containing 70 % of PHU and the little roughness sample is 1, containing12% of PHU.



Figs 4 and 5. Amide I and Amide III bands

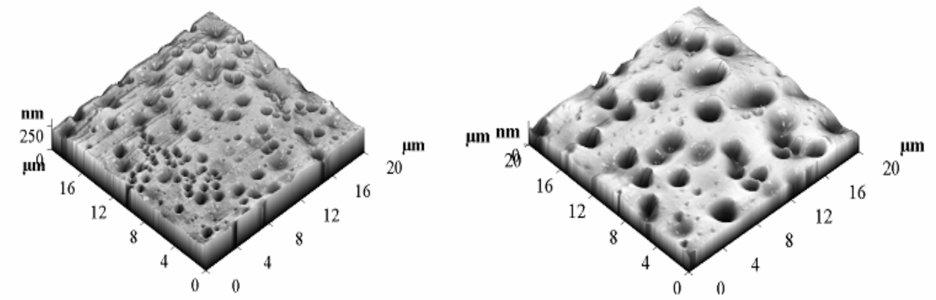
Table 2

Wave number modifications in ATR specters

Nr.	Sample 1 (12%)	Sample 2 (25%)	Sample 3 (50%)	Sample 4 (70%)
1.	3305	3303	3303	3306
2.	2939 2917	2940 2915	2940 2915	2959 2942 2913
3.	1732 1711	1732 1713	1732 1713	1732 1712
4.	1551	1556	1556	1553
5.	1432 1374 1329	1429 1374 1330	1429 1374 1331	1431 1375 1331
6.	1258	1257	1257	1259
7.	1088	1089	1088	1087
	1052	1053	1056	1057
	1025	1026	1025	1024
8.	948	946	946	947
	920	921	921	921
9.	850	850	850	842 800

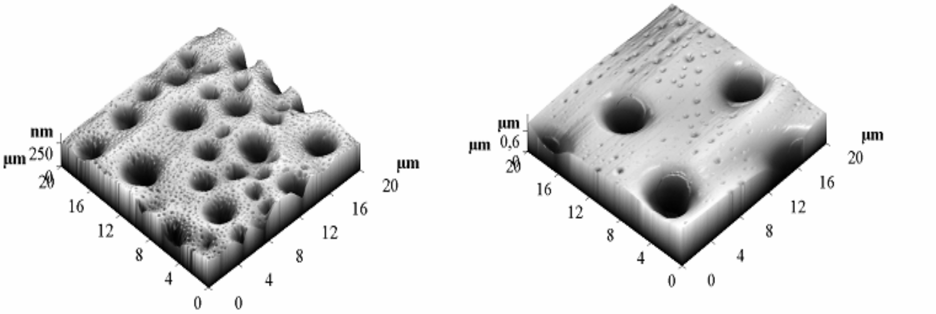
Surface skewness, *Ssk,* is a statistical parameter describing the asymmetry of average high distribution picks in histogram. If Ssk=0, the distribution is symmetrically (Gauss), when Ssk < 0 the surface presents pours, and when Ssk>0 surface presents picks. In our case the values are negative. So the surface present pores, which are very large when Ssk <1.

Coefficient of kurtosis, *Ska* is another statistical parameter. It informs us about the waist of heights picks distribution on surface. If Ska =3 there is a Gaussian distribution, when Ska < 3 picks prevail, and when Ska >3 pores prevail. In our case one single probe with Ska = 2, 31 exists. Pores prevail for the other samples. Picks dimension is proportional to the PHU concentration.



SAMPLE 1 (12%)

SAMPLE 2(25%)



SAMPLE 3 (50%)

SAMPLE 4 (70 %)

Fig. 6. AFM 3D images of the samples

The mechanical properties of the polymeric films are improved by alloying the PHU. In figure 7 the relative elongation versus tensile stress for all samples is represented.

Table 3

Table3. Important scale which characterized the sample morphologically

Sample (%)	Average (nm)	Average roughness, *Ra* (nm)	Root mean square, *Rms* (nm)	Surface skewness, *Ssk*	Coefficient of kurtosis, *Ska*
12 %	225.28	16.00	24.22	-2.42	10.67
25 %	495.77	62.38	85.03	-1.79	3.63
50%	264.69	42.86	57.01	-1.58	2.31
70%	842.07	101.76	162.35	-2.50	6.98

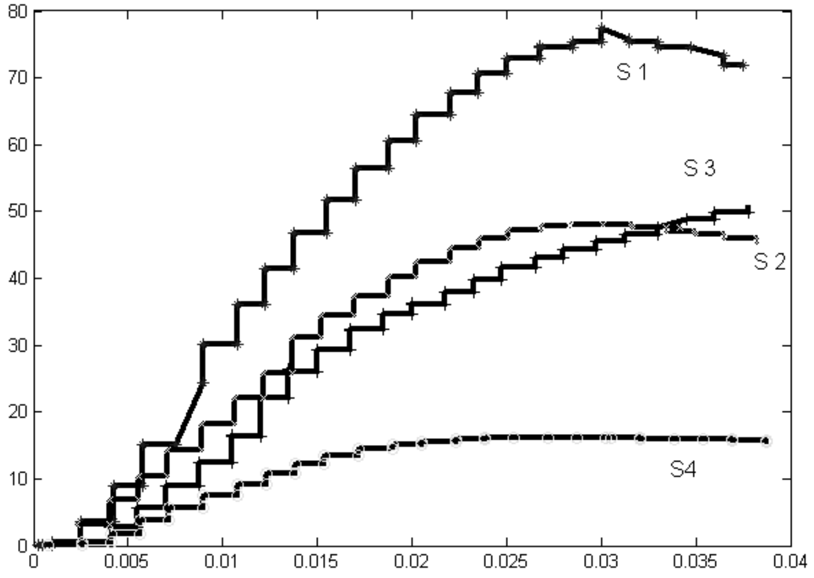


Fig. 7. Relative elongation vs. tensile stress

If we integrate this curve, the results will give us the hardness of the material, (table 4). For linear portion we can calculate the initial modulus, and the resilience of the material, figure 8. Relative elongation versus tensile stress for linear portion is plotted in fig. 8.

Table 4

Hardness, initial modulus and resilience function PHU concentration

Sample (%)	Hardness (MPa)	Initial modulus (MPa)	Resilience (MPa)
12%	1.08	2489	0.12
25%	1.84	4223	0.21
50%	1.23	2117	0.13
70%	0.44	1063	0.07

Both hardness and resilience are calculated for the same elongation. Initial modulus is calculated like linear slope, and resilience is obtained by integrating linear portion for the same elongation.

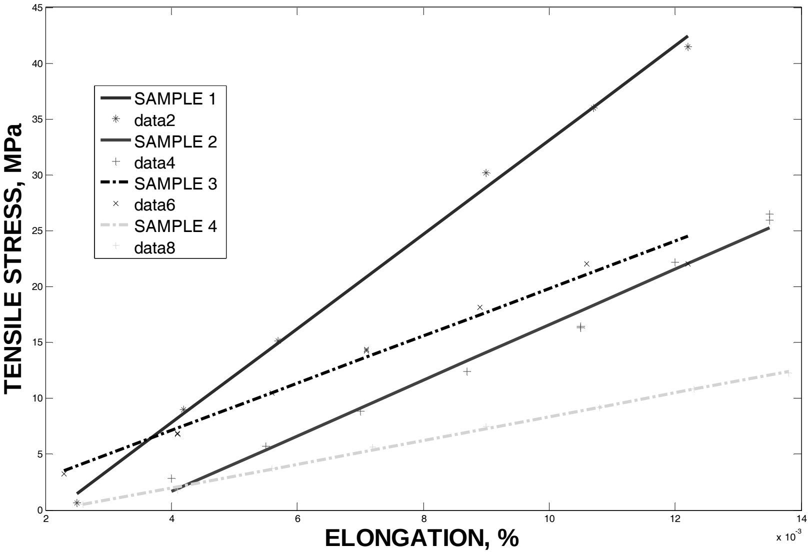


Fig. 8. Relative elongation vs. tensile stress

4. Conclusions

New polymers alloying PVA and PHU in different concentrations were obtained and analyzed (energetically, spectrally, morphologically, and mechanically) in this study.

The non polar functional groups of PHU chains modified hydrophilic properties of PVA films. The water contact angles increased when PHU was added.

ATR spectra indicate the presence of NH groups, and the increase of bonds number of C=O and O-C-N proportionally with the PHU concentrations.

Morphologically it was observed that polymer surfaces are predominantly porous and dimensions of pores are proportionally with the PHU concentration; generally these pores are extremely large. This kind of materials can be used like dressing because of possibility to absorb liquid through their pores.

Mechanical properties are also modified by PHU concentration, decreasing the hardness, resilience and the initial modulus of materials.

Due to these properties we could think about some medical applications of this new material.

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