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Some investigations on films of poly(vinyl alcohol) with pendant p-azidobenzoate groups

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Poly(vinyl alcohol) (PVA), due to its many desirable characteristics is preferred for a variety of applications ranging from stabilizing colloids to pharmaceutical, medical and cosmetic field. Polymer-analogue reaction of PVA with functional azides leads to new material characterized by film forming property and photosensitivity. This paper deals with some characteristics of films obtained from poly(vinyl alcohol) with pendant p-azidobenzoic tested as potential membranes. The electric potential in ionic solutions, the behaviour in the presence of water and permeability parameters of films of modified poly(vinyl alcohol) were investigated.

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1. Introduction

Polymer films play an increasing role in a wide range of applications such as packaging, barriers, membranes, sensors, medical implants, coatings. Among the polymers that are able to form films it is notable the presence of the poly(vinyl alcohol) (PVA), the largest volume water-soluble polymer produced today. Its chemical structure, characterized by the presence of polar hydroxyl groups mainly in 1,3-diol structure favour both physical interactions by hydrogen or van der Waals bonds (dipole-ion or dipole-dipole interactions) and chemical transformation by polymer-analogue reaction, complexing or crosslinking of the polymer. It is non-toxic, biocompatible, biodegradable and can cut out ultraviolet and infrared radiation. The incorporation of pendant substituents along the polymer main chain of poly(vinyl alcohol) by esterification is one of the various attempts tested in order to obtain new polymers which may be tailored to the demanding requirements of specific applications. The delivery system based on PVA membrane may be useful for obtaining therapeutic, non-toxic levels of Retrovir in AIDS patients. On the other hand it is well known that aromatic azides have been attracting much attention because of their high reactivity and applications in biomedical field. Azide derivatives inhibit the human immunodeficiency virus (HIV) replication, hepatitis B virus DNA polymerase, the insertion of cytochrome into the thylakoid membrane. [1-10].

Due to high reactivity of azide groups the films of polymer can be used for preparation of crosslinked poly(vinyl alcohol) (PVA) membranes. Using this way we have obtained and characterized new potential biodegradable polymers starting from poly(vinil alcohol) and p-azidobenzoic acid. Since modified poly(vinyl alcohol) films are potential materials in membranes development, the purpose of this research is to study the possibility to prepare membranes by incorporating the aromatic azide groups into the structure of this simple polymer. Some characteristics of films prepared from substituted PVA such as electric potential in ionic solutions, the behaviour in the presence of water and permeability parameters of modified poly(vinyl alcohol) films were investigated in this paper in order to test their characteristics as potential membranes.

2. Experimental

Poly(vinyl alcohol – vinyl p-azidobenzoat), PVAz, having a 50% degree of substitution was obtained by the Schotten-Bauman method using a slight excess of acid chloride. Polymer films were prepared on PET, glass or teflon supports by gravity deposition from solutions containing 10 wt% of polymer. Then, the films were dried in vacuum for 24 h. The thickness of films was taken as an average of ten measurements. Infrared spectra spectra were recorded on a VERTEX 70 FT-IR spectrometer in the reflectance mode. The scanning wave number ranged from 4 000 to 550 cm^{-1} with a scan resolution of 4 cm^{-1}. UV-VIS absorption spectra were acquired on a SPECORD M42 Carl Zeiss Jena spectrophotometer. Before testing, the films were maintained for 10 h in bidistilled water at room temperature in order to fill up the pores. Thus only ions flux is predominantly through membrane. Membrane testing was carried out in a stirred cell. The measurement of membrane potential was carried out using unpolarizable electrodes filled with a filtered solution of 3M KCl. The electrodes were connected to a high impedance amplifier and the voltage was displayed on a storage cathodic oscilloscope. The membrane to be tested is held in place between two cavities of equal size. For measurement of membrane potential (electrical potential difference) across the films of polymer one compartment of the cell is filled with salt solutions containing 100 mEq/L of NaCl, KCl, or $CaCl_2$ and the other is filled with an equal volume of bidistilled water. The process was monitored for 1 h at different time intervals. The permeability parameters were determined by monitoring concentration of Na^+, K^+ and Ca^{2+} by flam-photometric method after dialysis through membrane of 2 cm^2 for 1h. The following characteristics of membranes were determined:

a. gradient of concentration (mEq/L) was determined as difference between initial concentration of ions (C_1) and the concentration of ions from compartment with bidistilled water (C_2).

b. flux of ions through membrane (F) was calculated with following equation taking in account the law of Fick [11-13]:

$$F = (C_1 – C_2)/ t\times S \text{ mEq/L h cm}^2$$

where: t – time, h; S – surface area, cm^2

c. coefficient of permeability (P) was determined by relation:

$$P = FG/S(C_1 – C_2) = [(F:3600) – G]/ S(C_1 – C_2)$$

where: G – thickness of membrane, cm; S – surface area, cm^2; 3600 – time, s

d. capacity of performance (CP), that evidenced the total ionic transport capacity of memebrane was estimated using the equation:

$$CP = P \times S$$

where P- coefficient of permeability, cm $s^{-;}$ S– surface area, cm^2.

3. Results and discussion

The incorporation of p-azidobenzoate units in the structure of poly(vinyl alcohol) was performed into homogeneous medium, namely aqueous solution by the Schotten-Bauman method [14-16]. The polymers obtained were dissolved in dioxane and precipitated in water before depositing on substrates (PET, glass, Teflon). Eight film samples (Mb1-Mb8) were obtained and tested.

The Fourier Transform Infrared (FTIR) spectra for modified polymer films revealed the vibrational changes that occurred due to the effect of the substituent in polymer. The absorption noticed around 3470 cm^{-1} due to the OH stretching vibrations for the absorbed moisture and hydrogen bonded hydroxyl groups presented in the spectrum of PVA decreases in the case of poly(vinyl alcohol–vinyl p-azidobenzoat). The traces of ethanol, entrapped within the PVA matrix in the step of purification may also broaden the peak. Characteristic OH in-plane deformation vibration of OH groups in PVA gives an absorption band in the region of 1420 cm^{-1} which overlaps with the CH deformation vibrations in the same region. The adjacent absorption band at 1326 cm^{-1} is the combined absorptions due to OH and CH bending vibrations. The peak that appears at 920 $cm^{-1}$is associated with C-O symmetric stretch in aliphatic ether and it is due to etherification reactions in some vicinal OH groups during the dissolution of PVA in boiling water.

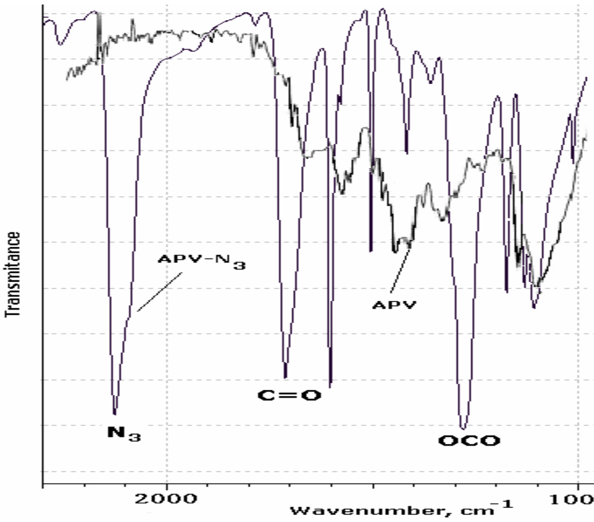

Fig. 1. 1000-2200 cm^{-1}region of the FTIR spectra of APV and APV-N_3 films.

Other characteristic vibration bands are observed at 2940, 2910, 2660, 1446, 1430, 850 and 835 cm^{-1}, attributed to CH_2 units and at 2840, 2660 1326 and 1235 cm^{-1}associated with –CH– units. As expected, the incorporation of p-azidobenzoate groups affects the carbonyl stretching region (1680–1800 cm^{-1}) of the FT-IR spectra. The absorption bands which reflect the presence of functional group, appears at 2125cm^{-1} for N_3 group and at 1712 cm^{-1} for C=O linkage.

Some physical and functional characteristics of polymer films such as: porosity, thickness, aspect of surfaces, permeability and electric potential in ionic solutions were tested in order to appreciate the potential use of these materials as membranes. The samples of interest in this study were obtained from solutions of the polymer purified by different techniques and deposed on PET sheet (Mb1-6), Teflon sheet (Mb7) and glass plate (Mb8) by a cast-evaporating technique. The characteristics obtained in this study will serve to improve the casting technique of polymer film and/or to change the synthesis and purification methods. The best films were those deposed on Teflon and glass plate. The samples films had different thickness, in the range 0.00975-0,0121 cm.

The films deposed were glossy on one side and lustreless on the other. Samples Mb1 and Mb3-5 are fragile and easy to break, but samples Mb2 and Mb6-8 are resistant to handling. The values of electric potential, in the presence of NaCl, KCl and $CaCl_2$ solutions and other charcateristics of the membranes are presented in Table 1 and Table 2, respectively. The intensity of ionic diffusion is generally low for all samples. The potential of diffusion had really low values, higher ones being recorded for samples Mb1, Mb2 and Mb8.

Table 1. Characteristics of membranes.

Sample	Thickness (cm)	Ion	Dialysis sense	Ionic transport mEq/ L×h ×s	Gradient (C_1-C_2) mEq/L	F (flux) mEq/ L×h×cm^2	P (permeability coefficient) (cms^{-1})	CP (performance capacity
Mb1	0,0105	Na^+	L-G	0.780	99.220	0.390	5×10^{-9}	10×10^{-9}
		K^+	L-G	2.810	99.985	1.405	20×10^{-9}	40×10^{-9}
		Ca^{2+}	L-G	0.165	99.900	0.083	1×10^{-9}	2×10^{-9}
		Na^+	G-L	0.960	99.040	0.480	7×10^{-9}	14×10^{-9}
		K^+	G-L	1.069	98.934	0.534	7×10^{-9}	14×10^{-9}
		Ca^{2+}	G-L	0.085	99.915	0.043	6 x 10^{-10}	12.5×10^{-10}
Mb2	0.0116	Na^+	L-G	1.830	98.170	0.915	15×10^{-9}	30×10^{-9}
		K^+	L-G	5.115	94.885	2.557	43×10^{-9}	86×10^{-9}
		Ca^{2+}	L-G	0.975	99.025	0.487	7×10^{-9}	14×10^{-9}
Mb3	0.0107	Na^+	L-G	0.830	99.170	0.415	6×10^{-9}	12×10^{-9}
		K^+	L-G	0.511	99.489	0.255	3×10^{-9}	6×10^{-9}
		Ca^{2+}	L-G	0.115	99.885	0.057	8.5×10^{-10}	17×10^{-10}
Mb4	0.0115	Na^+	L-G	1.960	98.040	0.980	15×10^{-9}	30×10^{-9}
		K^+	L-G	0.793	99.207	0.396	6×10^{-9}	12×10^{-9}
		Ca^{2+}	L-G	6.000	94.000	3.000	5×10^{-9}	10×10^{-9}
		Na^+	G-L	1.830	98.170	0.915	14×10^{-9}	28×10^{-9}
		K^+	G-L	0.563	99.437	0.281	4×10^{-9}	8×10^{-9}
		Ca^{2+}	G-L	2.260	97.740	0.130	2×10^{-9}	4×10^{-9}
Mb5	0.00975	Na^+	L-G	3.830	96.170	1.915	26×10^{-9}	52×10^{-9}
		K^+	L-G	7.672	92.328	3.836	56×10^{-9}	112×10^{-9}
		Ca^{2+}	L-G	5.250	94.750	2.625	37×10^{-9}	75×10^{-9}
Mb6	0.0116	Na^+	L-G	0.090	99.910	0.045	7×10^{-10}	14.5×10^{-10}
		K^+	L-G	0.384	99.616	0.192	3×10^{-9}	6×10^{-9}
		Ca^{2+}	L-G	0.200	99.800	0.100	1×10^{-9}	2×10^{-9}
Mb7	0.0121	Na^+	L-G	1.740	98.260	0.870	22×10^{-9}	44×10^{-9}
		K^+	L-G	5.626	94.374	2.813	77×10^{-9}	154×10^{-9}
		Ca^{2+}	L-G	0.955	99.045	0.477	12×10^{-9}	24×10^{-9}
		Na^+	G-L	2.000	98.000	1.000	26×10^{-9}	52×10^{-9}
		K^+	G-L	5.626	94.374	2.813	77×10^{-9}	154×10^{-9}
		Ca^{2+}	G-L	2.050	97.950	1.025	27×10^{-9}	54×10^{-9}
Mb8	0.0106	Na^+	L-G	1.520	98.480	0.760	11×10^{-9}	22×10^{-9}
		K^+	L-G	0.460	99.540	0.230	3×10^{-9}	6×10^{-9}
		Ca^{2+}	L-G	1.275	98.725	0.637	9×10^{-9}	18×10^{-9}

Table 2. Electric potential difference (± mV) of membranes (L = lustreless site of film, G = glossy side of film).

Solution (mEq/L)	t (min)	Electric potential (± mV)/dyalysis sense										
		Mb 1		Mb2	Mb3	Mb4		Mb5	Mb6	Mb7		Mb8
		L-G	G-L	L-G	L-G	L-G	G-L	L-G	L-G	L-G	G-L	L-G
NaCl 100 mEq/L	5	+1	-1	-4	-2	-4	-2	+2	-2	-1	-1	-2
	10	+2	-3	-5	-5	-6	-3	+1	-5	+7	+3	+3
	20	+3	-5	-8	-10	-7	-6	-5	-13	+12	+5	+10
	30	+3	-8	-10	-15	-10	-8	-7	-16	+15	+16	+15
	40	-1	-12	-10	-14	-13	-15	-10	-23	+18	+22	+19
	50	-2	-14	-8	-13	-18	-20	-12	-24	+23	+25	+22
	60	-5	-15	-7	-12	-25	-22	-14	-25	+28	+27	-
KCl 100 mEq/L	5	+1	-2	-4	-3	-3	-2	-2	-2	-2	+2	-2
	10	+2	-5	-5	-5	-3	-2	-3	-5	-2	+3	+7
	20	+3	-10	-7	-7	-5	-5	-5	-6	+5	+12	+10
	30	+4	-12	-10	-8	-5	-6	-6	-8	+10	+12	+18
	40	+5	-14	-12	-13	-6	-7	-7	-10	+15	+12	+23
	50	+6	-15	-11	-15	-7	-7	-8	-13	+17	+13	+27
	60	+8	-15	-11	-18	-8	-8	-10	-15	+18	+13	-
$CaCl_2$ 100 mEq/L	5	-4	-4	-2	-5	-2	-2	-2	-3	-1	+5	-2
	10	-8	-9	-5	-8	-3	-4	-4	-5	-1	+7	+2
	20	-14	-18	-12	-16	-7	-5	-5	-18	+2	+8	+3
	30	-18	-24	-24	-25	-8	-5	-5	-12	+6	+10	+6
	40	-22	-26	-28	-22	-14	-12	-9	-17	+10	+10	+8
	50	-23	-28	-31	-20	-16	-13	-10	-20	+10	+8	+17
	60	-23	-27	-34	-18	-19	-15	-12	-23	+8	+14	

The diffusion differs depending on ion and membrane type. Thus, the diffusion is more intense for NaCl solution through samples Mb4, Mb6 and Mb 7 while the diffusion of KCl solution is more intense for samples Mb7 and Mb8. The samples Mb1-3 and Mb6 are able to favour the diffusion of $CaCl_2$ solution. The diffusion of the anion (Cl^-) is predominant in comparison with the one of cations because generally negative values of membrane potential were recorded. In the case of the sample Mb8 the diffusion of the cations is more intense than that of the anions. The two sides of samples (glossy and lustreless) are generally symmetric regarding the intensity of the diffusion process in the two senses (G-L and L-G). The values of parameters of permeability as it is expected are higher in the case of Na^+.

The transport of ions through membrane is influenced by ion and membrane type and after 1 h is enough weak (0.085 -7.672 mEq/L×h×s) for all membranes and in the case of all ions. There are not differences between the sides of films. However, the transport of Ca^{2+} is more intense in comparison with the one of other ions excepting the membrane Mb1 and Mb3. The low values of permeability coefficient (10^{-9}-10^{-10}) are correlated with the values of thickness, flux and gradient of concentration. The values of the flux and permeability coefficient corresponding to monovalent ions are higher for all membranes in comparison with the one of Ca^{2+}.

4. Conclusions

The membrane tested present selectivity evidenced by values of electric potential and permeability coefficient. The two sides of samples (glossy and lustreless) did not show important difference of functional membrane parameters as function of dialysis sense (G-L and L-G). The samples, especially Mb1 Mb3 and Mb6 exhibit low intensity of dialysis and low permeability. Based on experimental results one can appreciate that the samples films obtained from poly(vinyl alcohol) bearing p-azidobenzoate units show membrane characteristics but they are of medium level. In this sense it is necessary to enhance the performance of polymer films by modifying some aspects regarding to casting technique and preparation method. It can be also taken into consideration the ability of azide groups to generate azo units and crosslinking the polymer under irradiation with UV light. Thus materials with electro-optical properties could be obtained.

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