

Water-soluble polyamidhydroxyurethane swelling behaviour

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In this paper, swelling/dehydration in distilled water and physiological Ringer solution of films network with less water of polyamidhydroxyurethane hydrogel was investigated. The kinetics of desorption process is different to that of sorption one. The swelling capacity in physiological Ringer solution is smaller than a half of that in distilled water. Water swelling increases the molecules volume and the interstitial volume between molecules that stress the network bounds and reduce the chains mobility. The network behaviour depends on relative humidity that determines the type of water bound process; the network of polyamidhydroxyurethane hydrogel changes from a ordered structure to a amorphous one by a series of intermediate stages.

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1. Introduction

Polymers which mimic biological behaviour by using the same types of fundamental molecular interactions, have been designed to used in a number of novel applications such as smart and/or controlled drug delivery, controlled cell patterning etc. [1]. It was determined that the less water content matrix of neutral non-biodegradable hydrogels, such as poly(hydroxyethyl methacrylate), poly(vinyl alcohol), poly(N-vinyl pyrrolidone), and poly(ethylene-co-vinyl acetate) experience good properties for artificial hard/soft tissue artificial implants [2,3].

The biological evaluation of medical devices is currently governed by the set of standards developed by the International Organization for Standardization (ISO) and known as ISO 10993 [4].

ISO 10993-1 states that in the selection of materials to be used in device manufacture, the first consideration is referred to the materials characterization, which includes structural, toxicological, physical, electrical, morphological, and mechanical properties. Additionally, the following should be considered for their relevance to the biological evaluation: chemistry of material, additives, process contaminants and residues, leachable substances, degradation products, other components and their interactions in the final product.

For materials that will contact body tissues, extraction activity (swelling/dehydration) in both polar and nonpolar environments is relevant.

Melnig et al. [5] have shown that poly(lactateurethane) exhibits characteristics more suitable for biomedical applications than (polyesterurethane) materials, due to incorporation of a soft lactate segment.

In a previous paper [6], we reported the synthesis and preparation conditions of less water in films of poly(amidhydroxyurethane) (PAmHU) non-biodegradable hydrogel. In the presence of water PamHU becomes a non-biodegradable hydrogel with a high water capability of

sorption, exhibiting rubbery behaviour and good biocompatibility. Structural investigations demonstrated that the network structure is one consisting of three phases: a water phase of low PamHU concentration, an amorphous phase, and a crystalline phase that restrict some of the motion degree of the amorphous domains. In the network PamHU molecule is packed as a ball and the molecules are interconnected between them by inter-molecular bonds in the bidentate or three-dimensional hydrogen bonding.

Prepared with less content of water and suitable mixing components, this becomes a promising biomaterial for artificial soft tissue biomedical applications.

Our purpose is to analyze the biocompatibility behaviour of polyamidhydroxyurethane (PamHU) films for artificial soft tissue applications. PamHU is soluble in aqueous solution [6], and a few minutes of storage in water or physiological solution will induce considerable swelling of the films. In Ringer solution the rate of swelling is minimized. The sorption/desorption kinetic mechanisms are different. Swelling characterization provided insight into the effect of water solvent on the elastic properties at the molecular level.

2. Experimental

The PamHU synthesis and films preparation have been presented in the Refs. [6,7]. The resulted films were translucent, gummy, elastically and very sticky.

Swelling/dehydration measurements were performed gravimetrically at 37 °C, on two set of 10 disc film samples with 10 mm diameter (thickness 0.11 mm) in distilled water and Ringer solution respectively. The sorption of water was determined by immersing the membrane in deionized water and was characterized by the swelling parameter, $G(wt)$, named equilibrium content, that can be calculated from the water mass uptake, $M_{\infty} = M_{eq} - M_d$, of the membrane at equilibrium and the mass of dry polymer M_d [8]:

$$G(wt) = \frac{M_{eq} - M_d}{M_d} = \frac{W_{eq} - W_d}{W_d} \quad (1)$$

Water content was determined by weighting with a Mettler H51 balance (accuracy $d = 0.01$ mg). The wet films' weight, $W(t)$, at different immersion times, t , was measured after extracting the samples from water bath and the superficial water content was discarded by instantaneous immersing in pure ethanol and cold air dried for a few seconds.

The momentary water content was computed with equivalent formula:

$$G(wt, t) = \frac{W(t) - W_d}{W_d} \quad (2)$$

As swelling reaches equilibrium, $W(t)$ approaches the saturated swelling weight, W_{eq} . The dry polymer weight, W_d , was determined after 48 hours drying in a vacuum oven in the presence of P_2O_5 . The dehydration (drying) process was performed in air at $37^\circ C$ for a longer time than these of hydrated process. In order to obtain information about the changes in microphase structure during the swelling process, the samples were statically hydrated in a controlled relative humidity (r.h.) chamber with saturated salt solution for 48 hours. Seven saturated salt solutions were used to maintain specified r.h. in closed chambers (see Table 1). The experiment starts with in vacuum drying in the presence of P_2O_5 for 48 hours, followed by an X-ray diffraction analysis of the films microphase. For each saturated salt solutions hierarchically vapour partial pressure increased, the same samples were introduced in controlled r.h. chamber in the presence of saturated salt solutions for the same time (48 hours), followed by X-ray analysis. The microphase structure was investigated by X-ray diffraction (XRD) performed on a DURON-2 diffractometer, employing nickel-filtered Co radiation (1.78890 \AA) at 25 kV operational voltage. The r.h. was controlled with a TCM radio-controlled weather station.

3. Results

In Fig. 1 are presented the representative experimental dependences of momentary water content of PAmHU films subjected to swelling/dehydration processes performed in distilled water and physiological Ringer solution respectively. The diffractograms from Fig. 2 were performed in order to obtain information about the r.h. – microphase films structure relationships. In Table 1 are presented also the characteristics of main peaks of PAmHU hydrated films diffractograms from Fig. 2, obtained after hydration in r.h. chambers in the presence of corresponding saturated salt solution.

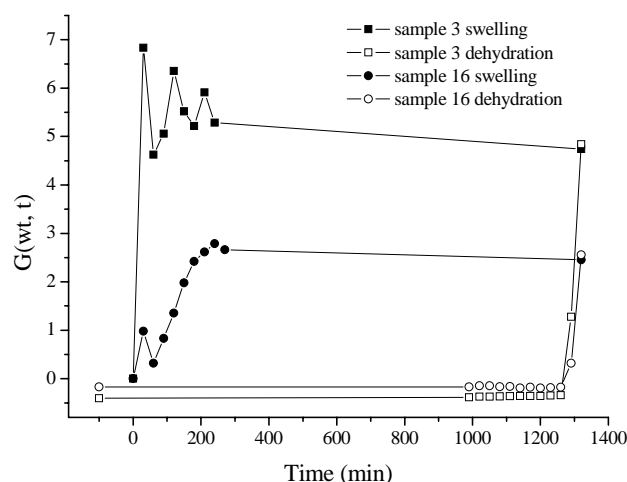


Fig. 1. Momentary water content vs. time for PAmHU films subjected to swelling/dehydration processes performed in distilled water and Ringer solution respectively.

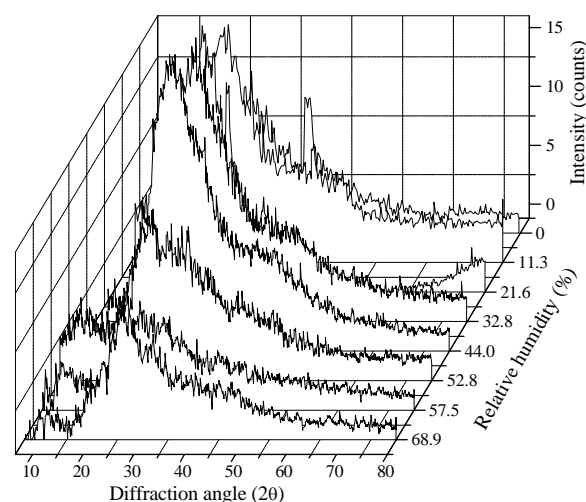


Fig. 2. X-ray diffractograms of PAHU hydrated films.

4. Discussion

Thermodynamically, when a rubbery polymer swells a good solvent, elastic interactions and mixing entropy are favoured (Fig. 3). At equilibrium:

$$\Delta G_{mix} = -\Delta G_{elastic} \quad (3)$$

with:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

Table 1. Relative humidity given by saturated salt solutions and corresponding significant diffractograms peaks characteristics of water content of PAmHU films (θ - diffraction angle; d - diffraction plane; I - relative intensity).

Salt solution	r.h. (%)	2 θ (degree)	D (nm)	I (counts)
P ₂ O ₅ (powder)	0	26.19	3.94	10.33
		38.32	2.72	9.29
LiCl	11.3	24.73	4.17	17.90
		30.39	3.41	12.48
		42.52	2.46	7.76
		47.85	2.16	5.94
		64.35	1.67	2.64
CH ₃ COOK	21.6	19.88	5.18	20.07
		21.66	4.76	18.25
		24.73	4.17	14.49
		32.01	3.24	5.65
		34.11	3.04	3.77
MgCl ₂	32.8	26.27	3.93	21.47
		31.39	3.30	14.63
		40.62	2.57	7.47
		45.56	2.31	6.40
		66.73	1.62	1.69
K ₂ CO ₃	44	24.97	4.13	23.41
		31.44	3.30	19.72
		42.03	2.49	7.64
		45.99	2.28	7.02
		50.48	2.09	4.90
Mg(NO ₃) ₂	52.8	10.50	9.77	4.45
		24.08	4.28	12.16
		27.96	3.70	10.52
		32.01	3.24	10.44
		35.40	2.94	7.69
		41.71	2.51	5.35
		48.98	2.15	4.04
		54.98	1.93	2.27
NaBr	57.5	10.50	9.77	2.36
		25.87	3.99	7.26
		28.12	3.68	6.30
		30.55	3.39	6.15
		33.47	3.10	4.71
		42.03	2.49	3.39
		45.92	2.29	2.53
		66.29	1.63	1.00
KI	68.9	9.57	10.72	0.73
		11.18	9.18	1.05
		13.19	7.78	0.73
		17.17	5.99	0.92
		19.42	5.30	2.89
		22.28	4.62	5.13
		24.05	4.29	7.21
		26.06	3.96	9.42
		27.47	3.76	8.48
		30.69	3.37	6.31
		31.89	3.25	6.72
		34.31	3.03	5.01
		36.93	2.82	4.11
		38.94	2.68	3.79
		40.55	2.58	3.66
42.96	2.44	3.12		
44.77	2.34	3.43		
47.38	2.22	3.12		

48.60	2.17	2.85
55.23	1.92	1.27
60.46	1.77	0.82
66.90	1.62	0.69
68.91	1.58	0.87

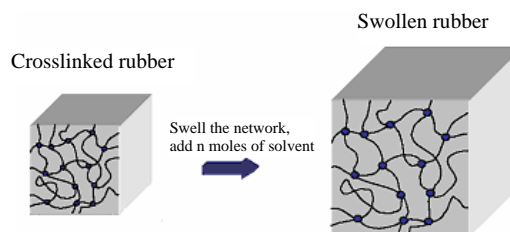


Fig. 3. Swelling mechanism. Interactions due to elastic energy and mixing energy are equal at equilibrium.

Considering $\Delta H_{mix} = \Delta H_{elastic} < 0$ as exothermic processes, at equilibrium the entropy of elastic deformation network, $\Delta S_{elastic}$, exerts reactive generalized force to oppose swelling generalized forces, characterized by entropy of solvent-polymer phases mixing, ΔS_{mix} .

Generally, the microstructures of polymers water friendly (pwf), depends on the interactions between water and the polymer molecules. Consequently, water content has a great influence on the physico-chemical properties of the polymer films such as short term effects: strength, flexibility, permeability and dimensional changes, and the long term effects causing "aging" or chemical modifications of the original material.

In principle, according to its state, a definite amount of water is necessary for the molecular stability of the polymer structure [9]:

- water bound by high-energy sorption centres (0-10 % r.h.). This water sits at charged residues and inside the secondary polymer structure and plays a major role in its stabilization through intramolecular hydrogen bonds;
- structural water (10-40 % r.h.). This is the water directly bound on the hydrophilic sites in the polymer.

Excess of bound water favour the monomolecular layer to transforms into a polymolecular layer (40-90 % r.h.). Near saturation free water exists; this role for water is demonstrable in the region above 90 % r.h.

The tensile properties of pwf are a function of moisture content. Water sorption is also intimately involved in dimensional changes and swelling of the material. In addition to chain-breaking of a macromolecule by hydrolysis resulting in a decrease in molecular weight, another mode of pwf degradation can occur through pseudo-denaturation process.

In a previous paper [6], it has been showed that PAmHU molecules are cross-linked and form a network structure within the molecule are packed as a ball and are interconnected between them by inter-molecular bonds in the bidentate or three-dimensional hydrogen bonding. The network structure is one consisting of three phases: a water phase of low PAmHU concentration, a PAmHU amorphous phase, and a PAmHU crystalline phase that

restrict some of the motion degree of the amorphous domains.

The great capacity of PAmHU swelling is revealed in Fig. 1. Practically, the polymer network swallows 7 times its mass maximum quantity of water in the first 30 min (first stage), followed by the variation in momentary water content second stage of about 3 hours. The dehydration process reaches the final stage in 1 hour with kinetics of desorption process different to that of sorption one.

The variation in momentary water content, $G(wt, t)$, from the second stage, is supposed to be done by the changes in equilibrium between interactions due to elastic energy and mixing energy, and probably loses of mass observed by non-closed of cycle swelling/dehydration processes.

The water content as water bond on high-energy sorption centre and structural H-bond water is due more probably to Donnan effect and osmosis. The decreases of swelling capacity in physiological Ringer solution can be the results of diminishing the rate of osmosis due to the higher value of the osmolality solution comparatively with bidistilled water.

The dynamics of the changes at the molecular and meso level vs. hydration can be observed from Fig. 2 and Table 1.

Water swelling increases the molecules volume and the interstitial volume between molecules that stress network bounds and reduce the chains mobility. These are argue by the dynamics of the reflections peaks with a lattice spacing of 4.97 Å and 4.66 Å correspond to the plane formed by C = O H-bonding from acrylamide groups and urethane groups respectively, in the bidentate or three-dimensional hydrogen bonding (Table 1, in grey) [5]. These lattices spacing starts with 4.17 nm in the case of LiCl saturated solution (r.h.=11.3%) considering that in this stage the network has been fixed only water bound on high-energy sorption centres and a small quantity of structural water. In this stage all the physico-chemical properties are unaltered. In the case of CH₃COOK saturated solution (r.h.=21.6%) the peak corresponding to the lattice spacing 4.17 nm diminishes in intensity and the amount of structural water directly bound to the polymer (both inside and outside packed as a ball molecules) increase the volume of molecules and the interstitial volume between molecules. These stress network bounds and the lattices spacing at 5.18 nm and 4.76 nm with corresponding peaks more intense than those corresponding to 4.17 nm highlight the increases in order degree; the membrane looks like consistent and stiffly. At r.h.=32.8% (MgCl₂ saturated solution) a first returning to the initial drayed in P₂O₅ film structure but with an increase in percentage is obtained; the film own a gel aspect. After r.h.=44% the picture peaks in diffractograms behave oscillations in position and intensity. With increasing of r.h. the secondary peaks growth in number and relative intensity. These reveal the decreasing in ordered phase (crystallinity) due to the polymolecular layer that favour the breaking of bidentate or three-dimensional hydrogen bonding and partially rebuilding of them between other partners.

5. Conclusions

In the presence of water, PAmHU becomes a non-biodegradable hydrogel with a high water capability of sorption, exhibiting rubbery behaviour and good biocompatibility.

Extraction activity (swelling/dehydration and loss of mass) in distilled water and physiological Ringer solution of films network with less water of PAmHU hydrogel was investigated.

The PAmHU network swallows 7 times its mass maximum quantity of water in the first 30 min (first stage) followed by the variation in momentary water content second stage of about 3 hours.

The dehydration process reaches the final stage in 1 hour. The kinetics of desorption process is different to that of sorption one. The swelling capacity in physiological Ringer solution is less than a half than in distilled water as results of the higher value of the osmolality solution comparatively with bidistilled water.

The dynamics of the changes at the molecular and meso level vs. hydration was investigated by XRD. Water swelling increases the molecules volume and the interstitial volume between molecules that stress the network bounds and reduce the chains mobility.

The network behaviour depends of r.h. that determines the type of water bound process; the network of PAmHU hydrogel changes from a ordered structure to a amorphous one by a series of intermediate stages. In each stage, the stability is respected as long as the strength of network bounds is higher than collective effects of interstitial water but as more water is swollen the network becomes more stressed and the system pass in a new stable network structure.

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