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CHARACTERIZATION OF WATER - SOLUBLE POLYAMIDHYDROXYURETHANE FOR BIOLOGICAL APPLICATIONS

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Polyamidhydroxyurethane becomes in the presence of water, a non-biodegradable hydrogel with a high capability of water sorption, exhibiting rubbery behaviour and good biocompatibility. When prepared with less content of water and suitable mixing hydrogel components, this becomes a promising biomaterial for artificial hard/soft tissue in biomedical applications. In this paper, the less-water films of polyamidhydroxyurethane are discussed, and are analysed the nature of inter- and intra- molecular interactions. Using X-ray diffraction, optical microscopy with polarized light, steady-state linear dichroism, infrared and UV-ellipsometry, the network structure of water in film of polyamidhydroxyurethane was determined. Water exhibits a high degree of homogeneity and consists of three phases: a water phase of low polyamidhydroxyurethane concentration, an amorphous phase, and a crystalline phase that restricts the motion of the amorphous domains.

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1. Introduction

Macromolecules containing hydrophilic and hydrophobic groups with strong inter- and intra-molecular associations are known as associating polymers. Water-soluble polymers, by modulating the hydrophilic/hydrophobic balance, have a wide range of applications as thickeners, flocculants, detergents, hydrogels, and surface modification of polymers, waste water treatment, and promising biocompatibility characteristics. Polymers can be made water soluble by making them compatible with the strong polar environment of the aqueous media, e.g., by introducing either charges or strong dipoles on the chains.

The water-soluble polymers undergo interactions with solvent and other high- and low-molecular weight species present in the aqueous solutions. Due to these interactions, macromolecules in solution exhibit, beyond their chemical structure, complex behaviour including changes of the polymer chain conformation, macro- and meso- phase separation, self-association and aggregation, excluded volume, surface activity, or formation of higher-order structures as aggregates, gels, etc. Polymers that associate in solution via physical interactions are often efficient rheology modifiers. In agreement with these experiments, the water solvent was found to affect drastically the elastic properties. There was determined that an increase in time of water elimination resulted in an increase of the tensile force. This led the scientists to use less-water content matrix of neutral non-biodegradable hydrogels, such as poly(hydroxyethyl methacrylate), poly(vinyl alcohol), poly(N-vinyl pyrrolidone), poly(acrylamides), and poly(ethylene-co-vinyl acetate) for artificial hard/soft tissue in biomedical applications [1-3].

In this paper are analyzed the preparation conditions for limiting the presence of water in films of poly(amidhydroxyurethane) (PamHU) non-biodegradable hydrogel and the network structure of the films.

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2. Experimental

PAmHU has been obtained from poly(acrylohydroxyurethane) salt (PAcHU) precursor by condensation of $COO^{-}H_3N^{+}$ to amide group (Fig. 1). PAcHU was obtained by polyaddition reaction of ethylene carbonate (EC) and ethylene diamide (ED), and by neutralization with acrylic acid (AA) in the ratio EC:ED:AA=1:1:1, and firstly was used for improving surface characteristics of synthetic poly(estherurethane) leather [4]. The temperature is an important parameter for the two steps complex kinetic of polymerization process conducting to PAmHU [5]. The average molecular weight number, determined by osmometry, was $\overline{M}_n = 18{,}700$ g/mol. Calibration was performed using mono-disperse standard dextran with $\overline{M}_n = 40{,}000$ g/mol and the cellulose used membrane [6,7].

The resulted PAmHU polymer is crystalline, very tough and soluble in water. The capability of swelling is more than hundreds percents (*vol/vol*) of water, the result being a hydrogel. The viscosity of gel reaches a maximum value at low concentration of polymer in water solution. The gel becomes less viscous at less than 1-2% *w/w* in the presence of ethylic alcohol.

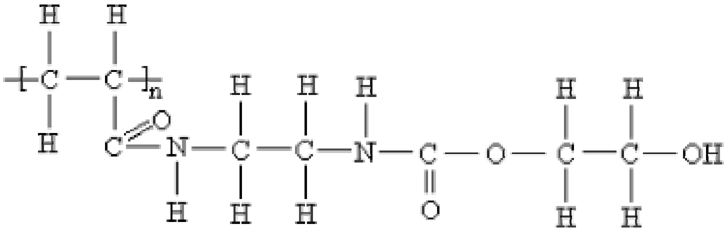


Fig.1. Primary structure of PAmHU.

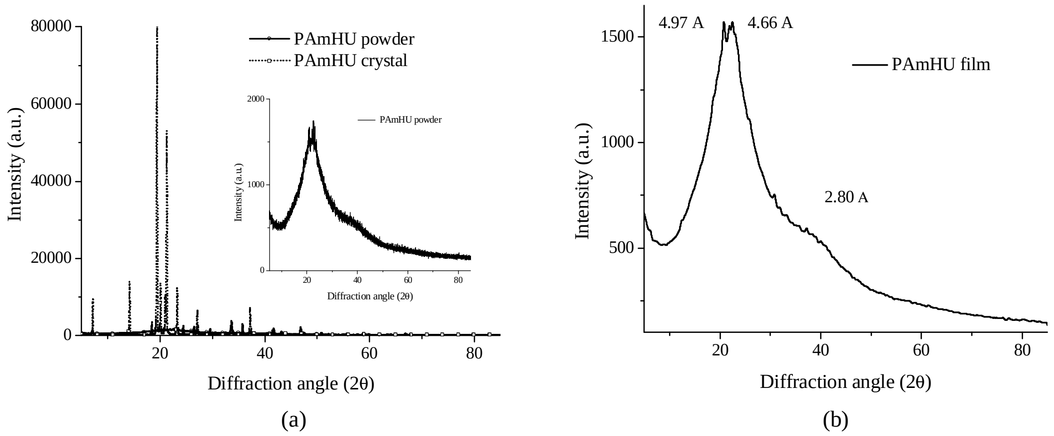
The less water in film PAmHU were prepared by pouring the in water 1% *w/w* PAmHU, 10% *vol/vol* C_2H_5-OH solutions into Teflon mould. Film thickness was controlled by using suitable solution volumes. After casting, the solvent (water) was removed by annealing and air-dried in isothermal conditions into a Gallenkamp Incubator Plus Series at 75 Celsius degree for 24 hours. The resulted films were homogeneous, translucent, gummy, and very elastically.

The crystallite morphology was studied by polarized light optical microscopy (PLOM). The microphase structure was investigated by X-ray diffraction (XRD) performed on a DRON-2 diffractometer, provided with nickel-filtered Co radiation (1.78890 Å) at 25 kV operational voltage. The molecular and supra-molecular structure and organization were investigated by steady-state Linear Dichroism-Infrared (LD-IR) using a BOMEM MB-104 spectrometer with 4 cm^{-1} resolution in the range 4000-500 cm^{-1} and combined UV-ellipsometry scattering techniques (LD-UV) with a SLM 8000 spectrofluorometer, using 2 mm slit widths that involves a spectral bandwidth of 4 nm. The set-up is similar to that used in refractive index ellipsometry [8]. Film samples were placed in spectrofluorometer at the diagonal position of a cuvette chamber. This confers a 45° relative position of excitation monochromator polarizer and of detector polarizer with respect to the normal of the film plane, and 90° between the two polarizers. All the spectra were obtained at room temperature in air. Ordinary and extraordinary polarized states of second order Rayleigh scattering at 790 nm (excitation beam was set at 395 nm maximum absorption band of UV-VIS spectrum) have been recorded.

3. Results

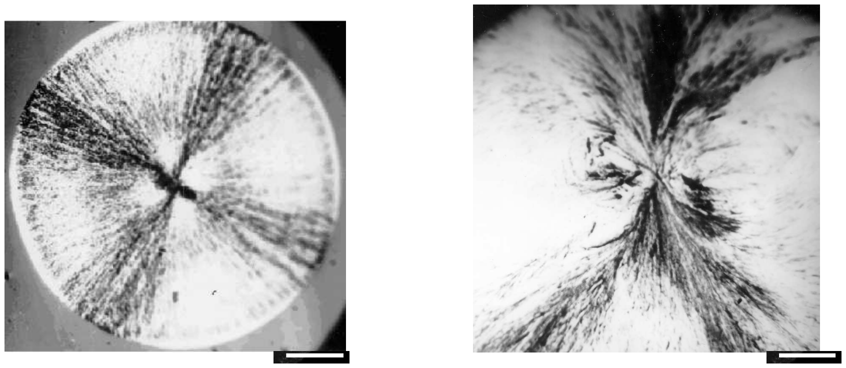
In Fig. 2 are presented the XRD patterns of PAmHU crystal and powder (a) and for less water in film (b). The film prepared in the conditions mentioned above, no significant differences can be revealed between X-ray diffractograms of PAmHU film and powder.

In the isothermal condition at room temperature, crystallization of PAmHU is different from the chosen condition for film preparation. Observations in PLOM show throughout the viewing field a diffuse structure with variations in the *μm*-range. These objects are subsequently filled in statistical manner with small crystallites whose orientations are correlated so that the birefringence of the objects continuously increases. Simultaneously with this peculiar crystallization mode, spherulites are nucleated and grow. The growth is terminated at a certain size, which fact is common to all spherulites.



(a) (b)

Fig.2. X-Ray diffractograms of PAmHU crystal and powder (a) and film (b).



(a) (b)

Fig. 3. PLOM images of spherulites morphology; a) of the final state reached after an isothermal crystallization; b) precursor objects are found everywhere, outside of the spherulites and also as inclusions (white stick mark is 100 μm).

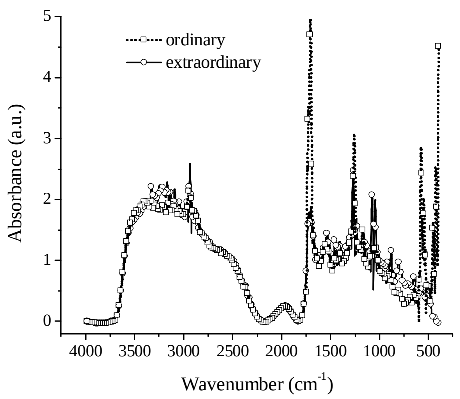


Fig. 4. The ordinary and extraordinary LDIR spectra of PAmHU film.

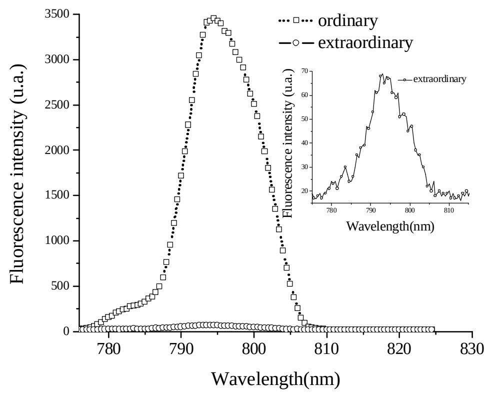


Fig. 5. The ordinary and extraordinary SLDF spectra of PAmHU film.

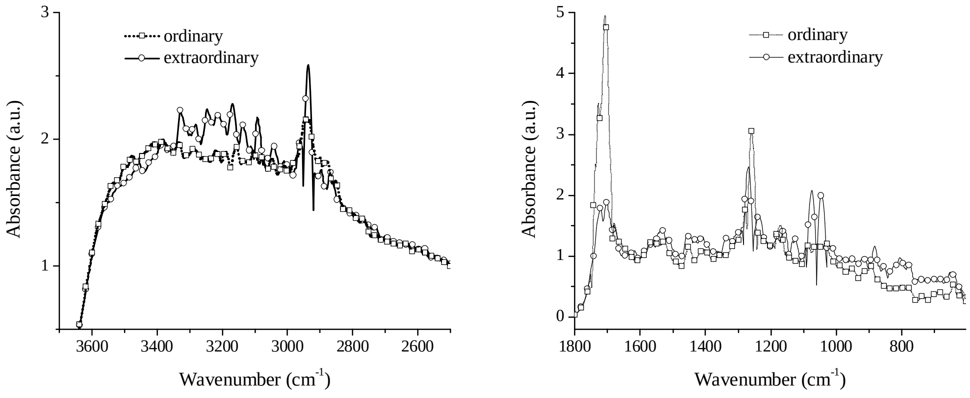
Fig. 3a presents an example of the finally reached structure. One notes that the spherulites fill the sample volume only partially but the precursor objects are found everywhere, outside of the spherulites and also as inclusions (Fig. 3b). The low mesophase organization of obtained films is supported also by the LD-IR (Fig. 4) and LD-UV (Fig. 5) spectra.

While steady-state LD-IR experiments has been used to analyze molecular orientation and micro-phase characterization by monitoring the orientation of different functional groups, using well defined bands from correlation charts, the steady-state LD-UV offer informations about anisotropy characteristics of the weak interactions involved in self-assembling of polymer, using the second order Rayleigh scattering [8].

4. Discussion

Previous rheological, and UV degradation studies of PAmHU in aqua solutions [6, 7], indicate high value of the limiting viscosity number $[\eta]$ at lower concentration, respectively, decrease of the number of chain scissions, the quantum yield of chain scission and the rate of degradation, with decreasing of polymer concentration solution, at the same values of the incident UV irradiation. This behaviour of PAmHU in aqua solution has been explained by the formation of inter- and intra- molecular hydrogen bonds from amide, urethane and hydroxyl groups and by the great affinity of hydrogen bonds formation between the polymer and water molecules [6-7, 9] and represent the starting point for the network analysis of less-water in PAmHU film.

A comparison of ordinary and extraordinary LD-IR spectra of PAmHU film show noticeable differences both in the functional group region, 4000-1500 cm^{-1}, and fingerprint region, 1500-400 cm^{-1}.



(a) (b)

Fig. 6. Details of the domains of interest in the functional region (a) and fingerprint region (b).

In Fig. 6 are shown the detailed domains of both functional and fingerprint regions of interest.

Inspection of the functional group region and correlation chart reveals characteristic bands of N – H and C – N groups of urethane bond, C = O and N – H bands from acrylamide and urethane groups, and O – H from hydroxyl. The fingerprint of PAmHU is done by ether group, C – O – C, both of urethane bond and ethyl groups, amide modes, O – H from hydroxyl and CH_2 from ethyl group.

The regions of strong water absorption are within 3600 – 2800 cm^{-1} and 1750 – 1550 cm^{-1}, representing the stretching and deformation vibration of O – H group in water, respectively (the fundamental stretching vibrations mode of water occur within the 3900–2800 cm^{-1} region and the in-plane bending mode at around 1640 cm^{-1} [10, 11]).

The broad band 3500 – 3200 cm^{-1} specific of O – H vibrations stretching could be due to a small population of water bonded by hydrogen with PAmHU polymer (water – PAmHU hydrogen bond band), probably from the three possible proton acceptors groups: the ether oxygen, the urethane carbonyl oxygen, and the acrylamide carbonyl oxygen.

In the range of stretching vibrations of carbonyl group of the urethane bond, the presence of H bonds shifts to lower frequencies of $C = O \cdots H$ stretching vibration mode, coupled with a marked increase of the intensity of the absorption bands.

Usually, two distinct bands are considered, due to $C = O$ not bonded and $C = O$ ($\cdots N - H$) bonded urethane groups and, respectively, the typical network of intermolecular bonds between the segmented polyurethanes [12-15].

The presence of $C = O$ from acrylamide, increase the number of twins by two, posted on the left side of urethane peaks. From this point of view, the band at 1742.17 cm^{-1} represents vibrations of free $C = O$ and 1726.12 cm^{-1} the vibrations of bonded $C = O$ from acrylamide groups. The high peak at 1706.40 cm^{-1} is due to vibrations of free $C = O$ from urethane groups (hard segment), and the shoulder at 1680.67 cm^{-1} is assigned to carbonyl groups involved in H bonding with the $N - H$ groups of the urethane hard fragments. It is also important the wag mode at 1268.53 cm^{-1} of $C - O - C$ and CH_2 bands from ether and ethyl respectively (soft segment); H-bonded at 1170.93 cm^{-1} (soft segment) and 1073.66 cm^{-1} (hard/soft segment) and not bonded at 1154.88 cm^{-1} (soft segment) and 1047.59 cm^{-1} (hard/soft segment) bands of $C - O - C$ from ether.

Because no molecular anisotropy has been created by pouring the PAmHU solution into the mould, it is supposed that the anisotropy is due to the hydrogen of the water (HW) bonding with the polymer proton acceptor free groups: $C = O$ from acrylamide and urethane and $C - O - C$ from ether, revealed in the ordinary-extraordinary profiles of LD-IR spectra. The percentage HW bonding with “free” proton acceptor groups is also supported by the shifts toward lower frequencies, the increases of intensities of corresponding “free” vibration bands, and the shifts toward high frequencies, 1258.50 cm^{-1}, of the wag modes of $C - O - C$ and CH_2 bands from ether and ethyl soft segment, with increases of water content of PAmHU film.

In order to obtain information about microphase structure of less-water PAmHU film, the second order Rayleigh scattering has been used. As in UV-VIS-IR ellypsometry technique [16] the depolarization ratio:

$$\rho = \left(\frac{\Phi_{ordinary}}{\Phi_{extraordinary}} \right)^{-1}, \qquad (2)$$

defines the degree of symmetry (anisotropy) of molecule as a whole. If the geometry of molecules is spherical and the symmetry of fluorophore dipole moments is high, the polarization of incident beam is maintained after scattering and the depolarization ratio is very small. In contrast, if the molecules exhibit lower symmetry and/or transition fluorophore dipole moments distort the symmetry of scattering potential, a significant depolarization occur. For symmetric scattering potential, the theory predict a depolarization ratio value $\rho < 0.75$. For other cases one gets higher values.

Inspection of LD-UV spectra from Fig. 5 reveals a high symmetry of PAmHU molecules (depolarization ratio less than 0.01), in low water film structure. In other words the PAmHU are packed as a ball and more probably the molecules are interconnected between them by H-bonds.

More information has been obtained from XRD investigations. The reflection at 4.97 Å and 4.66 Å from XRD patterns of PAmHU film (Fig. 2b) could be related to the planar reflection caused by hydrogen bonding of the ether oxygen and the urethane carbonyl oxygen groups in hard segments, while the peak at 2.80 Å should be assigned to the diffraction plane related to the acrylamide carbonyl oxygen H bonding units.

It was proposed by Sung and Bonart, and supported by Cooper, that in poly (urethane)s and poly(urethane-urea)s there exists a “three dimensional hydrogen bonding” that has substantial impact on the mechanical properties of the elastomers [18-20]. The most important consequence of the bidentate or three-dimensional hydrogen bonding in poly(urethane-urea)s, is that such systems, are not readily melt processable and must be spun from solution.

Comparing our results with those of Ishihara [20, 21] and Born and Hespe [22] it can be concluded that the reflections with a lattice spacing of 4.97 Å and 4.66 Å correspond to the plane formed by C = OH-bonding from acrylamide groups and urethane groups, in the bidentate or three-dimensional hydrogen bonding, respectively.

All this investigation suggests that intra-molecular bonds between the urethane groups exists, which fact is typical for segmented polyurethanes [12-14], but a network with a high stability is formed by inter-molecular bonds in the bidentate or three-dimensional hydrogen bonding. This is an argument in favour of a high capacity of swelling. Water swelling increases the volume of molecules and the interstitial volume between molecules that stress the network bonds and reduce the chain mobility. As a consequence the network becomes rigid. As long as the strength of network bonds is higher than the collective effects of interstitial water, more water swelling more stressed becomes network, but the stability is respected. Probably, in solutions the effect of strengthening leads to an increase in viscosity.

6. Conclusions

Less-water films of PAmHU hydrogel were prepared by annealing and air-drying in isothermal conditions.

Structural investigations by XRD, LD-IR and LD-UV demonstrated that the network structure consists of three phases: a water phase of low PAmHU concentration, an amorphous phase, and a crystalline phase that restrict the motion degree of the amorphous domains.

In the network PAmHU the molecule is packed as a ball and the molecules are interconnected by inter-molecular bonds in the bidentate or three-dimensional hydrogen bonding.

The bidentate or three-dimensional hydrogen bonding is achieved by hydrogen bonding of the ether oxygen, the acrylamide carbonyl oxygen and the urethane carbonyl oxygen groups.

This very stable network structure furnishes a strong capacity of swelling.

These results are in good agreement with the rheological behaviour of water - PAmHU solutions.

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