

Insight into polymer-borate hybrid films - structural approach

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Transparent organic-inorganic hybrid films (mass ratio PVA/PEG/B₂O₃=10/7/1) are obtained by polymer-assisted sol-gel synthesis and solution-casting method at ambient temperature. An aqueous solution of boric acid (H₃BO₃) and ethanol solution of trimethyl borate ((CH₃O)₃B) with pH adjustment are used as sources of cross-linking borate units. Surface morphology and structure of the obtained hybrid films are studied by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). XRD indicated that amorphous structure with poor crystallinity is formed. SEM showed a homogeneous and microporous surface free of crystallites. The results of FTIR spectroscopy revealed that the borate unit types and chemical bonds in the hybrid network are functionally dependent on the type of boron-containing solution and pH. The most crosslinked hybrid structure including a large number of polyborate ions is obtained from an aqueous solution of H₃BO₃ at pH 10. Based on spectral data a probable crosslinking mechanism in the hybrid network consisting of B-O-C bonds of ester complexes and hydrogen bonds is proposed.

Keywords: Organic-inorganic hydrogels; Polymer-borate hybrid films; Poly(ethylene glycol); Poly(vinyl alcohol); Boric acid.

INTRODUCTION

Hydrogels are subject to considerable attention in the past 50 years, due to their excellent promise in a wide range of applications. They also have a degree of flexibility very comparable to natural tissue due to their significant water content. The biocompatibility properties and swelling effects in biological conditions make them an ideal class of materials for biomedical applications, such as drug delivery and tissue engineering. It is essential to develop biodegradable materials by modification of traditional natural or non-degradable polymers about specific environmental problems. Commercially available biodegradable polymers are mainly limited to the natural polysaccharides, aliphatic polyesters, and polyethers, for example, polyethylene glycol (PEG), polyvinyl alcohol (PVA) [1-6].

PVA is a water-soluble polymer, employed in practical applications due to its excellent chemical resistance, biocompatibility, good film-forming capability, non-toxicity, and biodegradability in the presence of suitable microorganisms. The properties of PVA make it particularly interesting for the industrial elaboration of new environmentally friendly biomaterials. PVA-hydrogels obtained in the presence of crosslinking agents (a second polymer, an inorganic species or organically modified nanostructures) produce materials with a significant change in structure and

properties [3-13].

PEG possesses properties such as high hydrophilicity, solubility in water and organic solvents, biocompatibility and absence of immunogenicity, antigenicity, toxicity. (PEG)-based hydrogels are applied as optically transparent photoactive substrates, solid polymer electrolytes, biomedical and cosmetic materials with tunable properties. Polymer blends and organic-inorganic hydrogels based on PVA/PEG are extensively studied for material packaging, anti-microbial films, contact lenses, real-time immunoassays, tissue engineering matrices, acid-resistant biomembranes and drug delivery systems [1-5, 10-14].

H₃BO₃ is a weak Lewis acid possessing antibacterial properties, and in dilute aqueous solutions, B(OH)₄⁻ and B(OH)₃ species are existing simultaneously. At a concentration higher than 0.025M and pH between 7 and ten a shifting of acid-base equilibrium occurs, and various stable polyborate anions are formed [15]. The crosslinking efficiency of borate ions is well known, as well as the formation of diol complexes so that H₃BO₃ relatively well dissolves in polyvalent alcohols and polysaccharides to obtain organic-inorganic hydrogels with biomedical applications [16-21].

The purpose of this study is the preparation of PVA/PEG/Borate hybrid films by different boron-containing solutions and respective pH adjustment, as well as their structural-morphological characterization by XRD, FTIR and SEM. A

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probable crosslinking mechanism of the polymer-borate hybrid network based on infrared spectral data is proposed.

EXPERIMENTAL

Transparent self-standing hybrid films with mass ratio PVA/PEG/B₂O₃= 10/7/1 are obtained by the sol-gel process and solution casting method at an ambient temperature as referred in our previous studies [22-24]. The following analytical grade reagents are used: polyvinyl alcohol 72000 (PVA)-98% hydrolyzed, polyethylene glycol 400 (PEG), trimethyl borate (CH₃O)₃B, boric acid (H₃BO₃), ammonia solution 25% (NH₃.H₂O). Stock solutions of 4wt. % PVA and 4wt. % H₃BO₃ are prepared in double distilled water, while 4wt. % (CH₃O)₃B in ethanol. The pH value is adjusted of 5 to 10 by ammonia solution (absent of alkali ions). The hydrogels are made by initially mixing and homogenization of relevant amounts of PEG and boron containing solutions, after that PEG-borate mixture is added to the PVA by constant stirring. PVA-PEG-borates viscous solutions are cast onto glass plates, dried at ambient temperature for one week, after that the dried films are peeled off. The surface morphology is observed by SEM (JEOL JSM 5510). XRD is carried out on Siemens D500 diffractometer. FTIR spectra of starting materials and obtained hydrogel films are recorded a Bruker Tensor 27 instrument.

RESULTS AND DISCUSSION

The SEM micrographs of hybrid films prepared of the boric acid solution are presented in Figure 1.

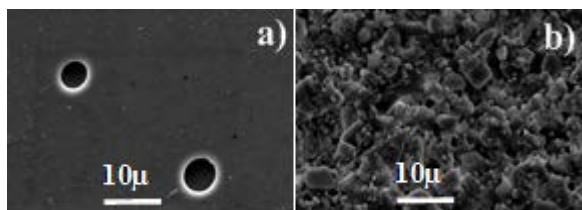


Fig. 1. SEM images of PVA/PEG/Borate hybrid films prepared from an aqueous solution of H₃BO₃ at (a) pH 5 and (b) pH 10.

The surface morphology of the hybrid film, obtained from boric acid solution without adjustment of pH (pH=5) is shown as a relatively homogeneous microporous surface structure with large single surface pores and free of crystallites (Fig.1a). The absence of microstructure in the SEM picture also indicates the amorphous as well as homogeneous nature of the samples. The surface of the film obtained by a boric acid solution with pH correction (pH=10) is different. The micrograph

shows the presence of roughness and randomly distributed structural aggregates (Fig.1b).

The structure of PVA/PEG/borate hybrid film is studied by XRD. The X-ray diffraction pattern of the sample obtained by boric acid solution without adjustment of pH (pH=5) is represented in Figure 2.

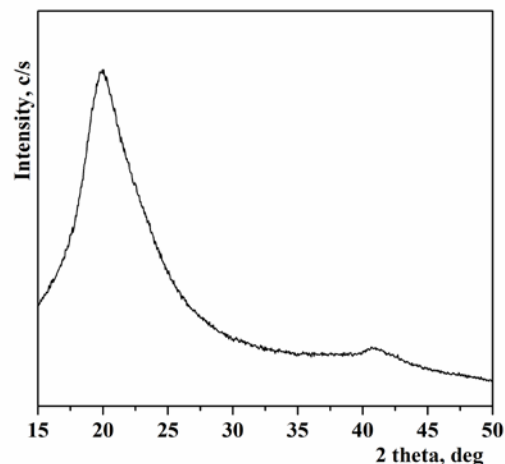


Fig. 2. XRD pattern of PVA/PEG/Borate hybrid film prepared from an aqueous solution of H₃BO₃.

The diffractogram contains an amorphous halo at 19.7 deg2θ (relatively broad peak) and a diffused peak at 40.9 deg2θ, originating from the semi-crystalline nature of PVA. There are no reflections indicating crystallization of boric acid. XRD confirmed the homogeneous and amorphous structure of the hybrid film-observed by SEM.

The structural changes caused by cross-linking of polymers and hydrated borate species derived from different solutions at different pH values are studied by FTIR spectroscopy. IR spectra of the starting polymer compounds and aqueous solutions of boric acid (pH 10 and pH 5) are presented in Figures 3 and 4, respectively.

The following vibrational modes are assigned to the chemical bonds in polymer compounds (Fig. 3): 3700-3100 cm⁻¹ (ν_sH-OH, ν_sC-OH, hydrogen bonds), 2850-2960 cm⁻¹ (ν_sCH₂), 2300-1900 cm⁻¹ (δ hydrogen bonds), 1650 cm⁻¹ (bending of H₂O), 1460 cm⁻¹ (O-H and δCH₂), 1380 cm⁻¹ (δ_{as}CH₃), 950 cm⁻¹ (γC-OH), 780-850 cm⁻¹ (bending vibrations of CH₂). Absorption bands in the regions 1330-1220 cm⁻¹ (δC-OH) and 1065-1020 cm⁻¹ (νC-OH) can be attributed to the primary alcohol (PEG), while these the in intervals 1370-1260 cm⁻¹ (δC-OH) and 1120-1080 cm⁻¹ to (νC-OH) from the secondary alcohol (PVA). Absorption bands in the region 1200-970 cm⁻¹ are related to C-O bonds, while these in the area of 1100-1000 cm⁻¹ are related to C-O-C stretching vibrations of esters [1, 2, 10-24].

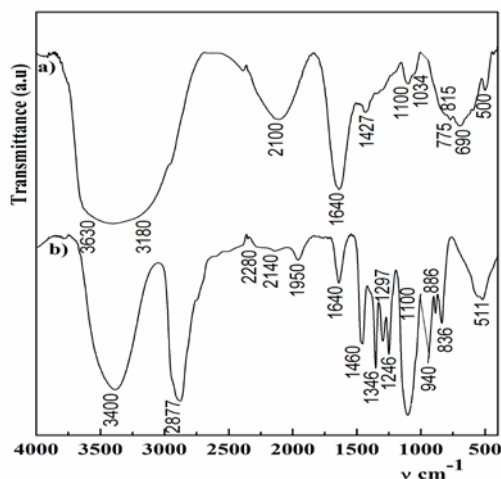


Fig. 3. FTIR spectra of (a) 4% aqueous solutions of PVA, (b) PEG₄₀₀.

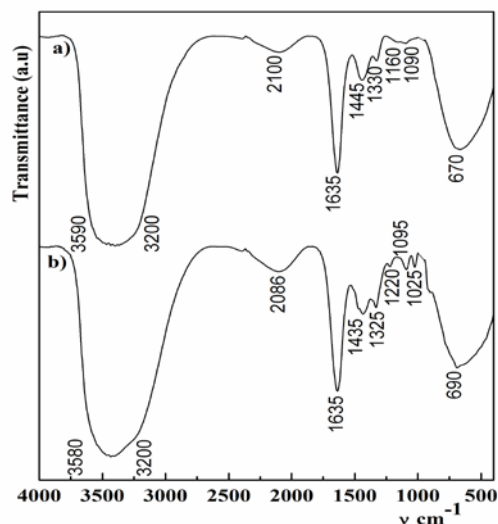


Fig. 4. FTIR spectra of 4 % aqueous solution of H₃BO₃ at (a) pH 10, (b) pH 5.

The main structural units under which boron exists in crystals, glasses and aqueous solutions are BO₃ and BO₄ groups and their rearrangement leads to superstructural species such as pentaborate, triborate, diborate, a.g. The B-O bonds frequency regions are 1500-1200 cm⁻¹ (νB-O of BO₃), 1200-850 cm⁻¹ (νB-O of BO₄) and 800-600 cm⁻¹ (bending vibrations for various borate segments). The bands in the intervals 1440-1430 cm⁻¹, 1330-1220 cm⁻¹, 690-660 cm⁻¹ are related only to BO₃ units of orthoborates (BO₃³⁻), metaborates (BO₂⁻), pyroborates (B₂O₅⁴⁻) (Fig. 4). The vibrational frequencies at 1430 cm⁻¹, 1320 cm⁻¹, 1220 cm⁻¹, 1090 cm⁻¹, 690 cm⁻¹ are assigned to pentaborates (B₅O₈⁻) and these at 1430 cm⁻¹, 1320 cm⁻¹, 1020 cm⁻¹, 915 cm⁻¹, 690 cm⁻¹ - to triborates (B₃O₅⁻) [22-28]. The spectrum changes when pH of an aqueous solution of boric acid is adjusted to pH 10 (Fig 4a). The main differences affect the band at 1220 cm⁻¹,

which is shifted to higher wavenumber-frequency of 1500-1200 cm⁻¹. At the same time, new bands appear in the region 1160-1080 cm⁻¹ related to BO₄ groups, probably tetraborates and diborates (B₄O₇²⁻: 1445 cm⁻¹, 1330 cm⁻¹, 1160-1080 cm⁻¹, 670 cm⁻¹). These effects are explained by partial transformation of BO₃ to BO₄ and are reported in [25-28].

FTIR spectra of hybrid films prepared from aqueous solutions of H₃BO₃ and ethanol solutions of (CH₃O)₃B (pH 10 and pH 5) are presented in Figures 5 and 6, respectively.

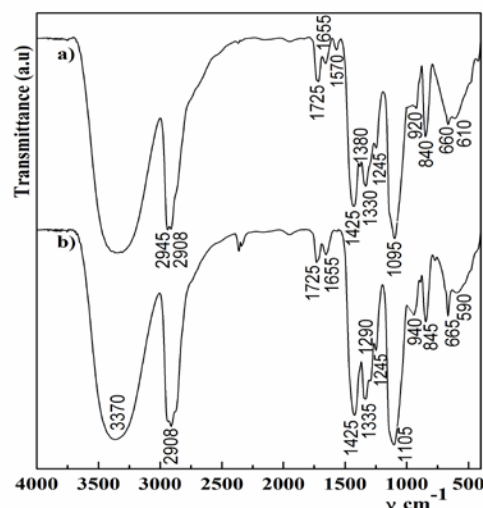


Fig. 5. FTIR spectra of hybrid films prepared with an aqueous solution of H₃BO₃ at (a) pH 10, (b) pH 5.

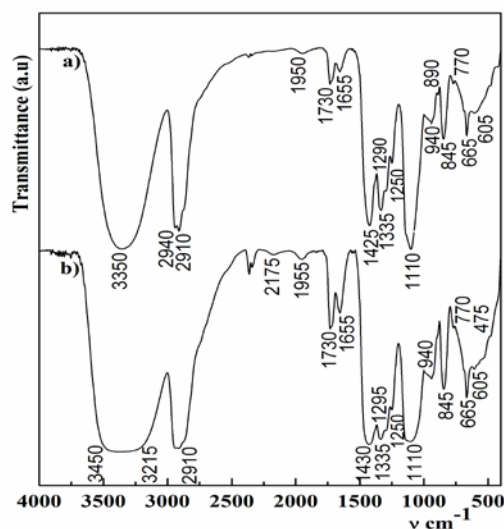


Fig. 6. FTIR spectra of hybrid films prepared with an ethanol solution of (CH₃O)₃B at (a) pH 10, (b) pH 5.

The comparison of FTIR spectra of the polymer-borate films and these of initial compounds indicates that the main changes are associated with characteristic frequencies concerning OH groups of PEG and H₃BO₃. The characteristic bands of the hybrid film obtained from an aqueous solution of

H_3BO_3 are shifted compared with the original vibrations of PEG.

Two types of crosslinking interactions between inorganic and organic components are observed - hydrogen bonding and ester type. It can be seen that absorption modes 2908 cm^{-1} (νsCH_2), 1655 cm^{-1} (bending vibration of H_2O), and 590 cm^{-1} (bending vibration of OH^-) are displaced to higher wavenumbers compared to PEG and PVA (Fig. 5). The same tendency is observed with absorption bands at 1105 cm^{-1} (C-O-C or C-O-B of esters) and 845 cm^{-1} (rocking mode of CH_2), overlapping with the region of BO_4 groups ($1200\text{--}850\text{ cm}^{-1}$). Furthermore, the absence of absorption bands in the region $2280\text{--}1950\text{ cm}^{-1}$ and frequency was shifting from 3400 cm^{-1} to 3370 cm^{-1} is due to the appearance of intermolecular hydrogen bonds. Hydrogen bonding interaction between the polymers and different boron species in solutions as well as water molecules is taking place. Replacement of intramolecular hydrogen bonds (present in all precursors) with intermolecular (involved in all hybrid films) is reported in [23, 24]. The opposite tendency is observed for absorption bands at 1425 cm^{-1} , 1335 cm^{-1} , 1290 cm^{-1} (C-OH of PEG), being shifted to lower wave number frequencies. In this interval are also included the specific modes concerning BO_3 groups ($1500\text{--}1200\text{ cm}^{-1}$). Based on these effects the formation of PEG-borate ester complexes including BO_3 and BO_4 groups is assumed. Polymer-borate ester bonds (B-O-C) are expected to be in the absorption interval $1400\text{--}1000\text{ cm}^{-1}$ concerning C-OH, C-O-C, and B-O (from BO_3 and BO_4 units) chemical bonds. The characteristic frequency of B-O-C bonds is noted at 1030 cm^{-1} and is reported in [16-18]. The FTIR spectrum of a hybrid film prepared from aqueous solutions of H_3BO_3 at pH 10 shows differences expressed by the higher BO_4/BO_3 ratio (Fig. 5a). The absorption bands assigned to B-O bonds in BO_4 groups are shifted to lower wave number frequencies (1095 cm^{-1} , 920 cm^{-1} , 840 cm^{-1}), and their intensities are increased. Moreover, the intensity of bands near to 1100 cm^{-1} (BO_4 groups) increases simultaneously with the decrease in those in the region $1425\text{--}1250\text{ cm}^{-1}$ (BO_3 groups). This is indirect evidence that the organic-inorganic borate films obtained from aqueous solutions of H_3BO_3 at pH 10 contain more PEG- BO_4 crosslinked structures.

FTIR spectra of films obtained from an ethanol solution of $(\text{CH}_3\text{O})_3\text{B}$ at pH 10 are similar to those of films prepared with aqueous solutions of H_3BO_3 without pH correction (Fig. 6a). This fact is explained with the low degree of hydrolysis of

$(\text{CH}_3\text{O})_3\text{B}$ in ethanol, i.e. negligible amounts of hydrated borate ions, respectively crosslinked PEG- BO_4 containing structures exist. When the synthesis is carried with an ethanol solution of trimethyl borate without pH adjustment, there is almost no hydrolysis (in a solution lacking hydrated borate ions) and the network is represented mainly by hydrogen bonding. The films are completely soluble in contrast to these obtained by aqueous solutions of H_3BO_3 that swell [23].

Taking into account the spectral data, the following crosslinked PEG-borate structures involved in the construction of the hybrid network are proposed (Fig. 7). It is suggested that PVA-PEG-Borate network is based on initially crosslinked PEG-borate ester complexes entanglement through hydrogen bonds to long PVA chains.

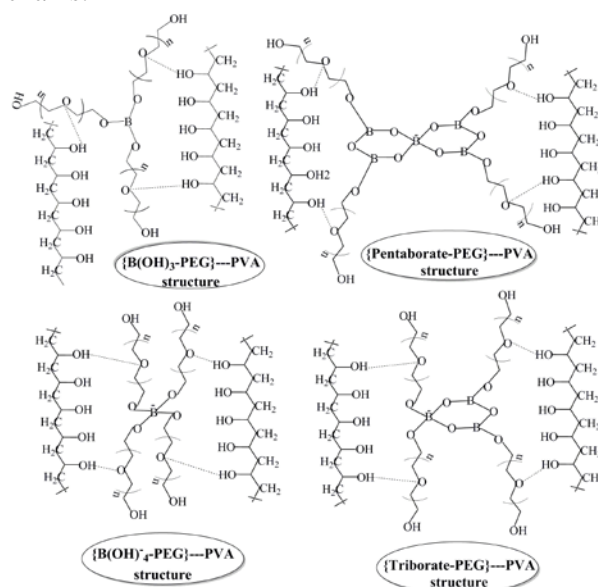


Fig. 7. A possible mechanism for the formation of PVA/PEG/Borate hybrid network based on cross-linked PEG-borate structures.

CONCLUSIONS

Transparent PVA/PEG/Borate hybrid films are prepared under different conditions by polymer-assisted sol-gel process and solution casting method.

The amorphous, homogeneous and microporous nature of the hybrid materials was confirmed by SEM and XRD analyses.

By FTIR spectroscopy it was found that the types of borate units and chemical bonds in the hybrid network are functionally dependent on the type of boron-containing solution and pH. The BO_4/BO_3 ratios, type of crosslinking, final structure and morphology of hybrid network are depending on experimental conditions. The best crosslinking hybrid structures with a predominant amount of

polyborate ions are obtained from an aqueous solution of H_3BO_3 at pH 10.

Based on FTIR data a probable mechanism of the formation of a hybrid network involving PEG-borate ester complexes linked through the hydrogen bonds of PVA chains is supposed.

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ПОГЛЕД КЪМ ХИБРИДНИ ПОЛИМЕР-БОРАТНИ ФИЛМИ – СТРУКТУРЕН ПОДХОД

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(Резюме)

Прозрачни органично-неорганични филми (масово съотношение PVA/PEG/ $B_2O_3=10/7/1$) са получени чрез полимерно асистиран зол-гелен синтез и формоване из разтвор при стайна температура. Воден разтвор на борна киселина (H_3BO_3) и етанолов разтвор на триметилборат ($(CH_3O)_3B$) с определено рН са използвани като източници на омрежващи боратни единици. Повърхностната морфология и структурата на получените хибридни филми са изучени с помощта на сканираща електронна микроскопия (SEM), Fourier трансформираща инфрачервена спектроскопия (FTIR) и рентгенова дифракция (XRD). XRD сочи че се образува аморфна структура със слаба кристалинност. SEM показва хомогенна микропореста повърхност, свободна от кристалини. Резултатите от FTIR спектроскопията показват, че видовете боратни единици и химичните връзки в хибридната мрежа са функционално зависими от вида на бор-съдържащия разтвор и рН. Най-силно омрежената хибридна структура, включваща голям брой полиборатни йони, се получава от воден разтвор на борна киселина при рН 10. Въз основа на спектралните данни е предложен вероятен механизъм на омрежването в хибридната мрежа, състояща се от В-О-С връзки на естерни комплекси и водородни връзки.