Polymer - borate hybrids films - theoretical and experimental determination of the structure

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Abstract: Transparent organic-inorganic hybrid films with composition (wt%) PVA(54,5): PEG(40): B₂O₃(5,5) is obtained by the sol-gel process and solution casting method at ambient temperature. Two different precursors of boron aqua solutions of boric acid (H₃BO₃) and ethanol solution of trimethyl borate (CH₃O)₃В) are used for the preparation of hybrid solutions. The effect of starting boron solution type on the structure of obtained materials are studied by infrared spectroscopy (IR). It was found that degree of cross-linking and type of bonding in the hybrid structure are depended on by the functionality of borate units. From experimental and calculated spectral data it can be concluded that the best cross-linked hybrid structure is obtained from the aqua solution of H₃BO₃ at pH 10, with a predominant amount of polyborate ions involved in the B-O-C ester complexes. By combined experimental and computational study, a probable mechanism of boron-containing organic-inorganic network are proposed.

Keywords: organic-inorganic hybrid films, sol-gel process, spectral data

1 Introduction

In the recent years, there is an increasing interest to produce polymeric and hybrid hydrogel materials with improved properties by blending existing polymers and cross-linking agents. The main reason for intensive research in this area is the new and different properties of these materials, which the traditional composites and conventional materials do not have [1-5]. For reasons of environmental problems, it is significant to develop biodegradable polymeric materials by modification of the traditional and non-degradable polymers. Available commercial biodegradable polymers are mainly limited to aliphatic polyesters, polyethers, for example, PEG, polyvinyl alcohol, and native polysaccharides [6]. Polymeric hydrogel networks based on PVA/PEG and hybrid are broadly studied because they have many realised and potential applications, especially in the field of biomaterials such as contact lenses, real-time immunoassay, tissue engineering matrices, drug delivery systems, acid-resistant biomembrane [1-9].

PEG one of the most widely used polymers possessing properties such hydrophilicity, a solubility in water and organic solvents, non-toxicity, and absence of antigenicity and immunogenicity, which allow using for many biomedical and cosmetic applications [1, 2, 5, 8-10]. Poly(vinyl alcohol) (PVA) is a water-soluble polymer, employed in practical applications due to its excellent chemical resistance, processing facilities, non-toxicity, biodegradability, physicochemical properties, and most importantly good film forming by solution casting [1-5, 9-13]. Addition of these it is immiscible or partially miscible with most polymers, even with acrylic polymers. The presence of a second polymer, or/ and crosslinking nanostructure can perform a significant change in the structure and properties of the PVA-hydrogel.

Boric acid B(OH)₃ is a weak Lewis acid and in aqua and have been widely investigated, diluted solutions B(OH)₄ and B(OH)₃ species are presented simultaneously. At boron concentration...
higher than about 0.025M and pH 7-10, due to the shifting of acid-base equilibrium various polyborate anions are formed [14]. It is known crosslink effectiveness of borate ions so that H$_3$BO$_3$ is relatively well dissolved in polyvalent alcohols PVA, PEG, polysaccharides to form organic-inorganic hydrogels [11-13, 15-16]. This present paper preparation of PVA/PEG/Boron hybrid films, morphological and structural study by SEM and FTIR. In this work, we use a combined approach including computational modelling and the interpretation of experimental vibration spectra to determine a probable mechanism of crosslinking for obtained boron containing hybrid network.

2 Experimental and Theoretical calculations

Transparent polymer-borate hybrid films of mass ratio PVA/PEG/B$_2$O$_3$ = 10/7/1 are obtained by the sol-gel process, and solution casting method at an ambient temperature referred to in our previous papers [17-19]. The following analytical grade reagents are used: polyvinyl alcohol 72000 (PVA)-98 % hydrolyzed, polyethylene glycol 400 (PEG), trimethyl borate (CH$_3$O)$_3$B from Sigma-Aldrich Chemie, Germany and boric acid (H$_3$BO$_3$), ammonia solution 25% (NH$_3$H$_2$O) from the Laboratory of High Purity Substances, University of Sofia. Stock solutions of 4 wt. % PVA and four wt. % H$_3$BO$_3$ are prepared in double distilled water, while four wt. % (CH$_3$O)$_3$B 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 PEG and boron contained solutions, after that the mixture is added to the PVA of stirring constantly. The hybrid solutions are cast onto glass plate and are dried at ambient temperature for one week, after that the films are peeled off. The thickness of the obtained self-standing hybrid films is in the range 24-48 µm. The surface morphology is observed by SEM (JEOL JSM 5510). IR spectra of the precursors and films are recorded a Bruker Tensor 27 spectrometer.

Ground-state fully optimized geometries; analytical vibrational frequencies were obtained using Density Functional Theory (DFT). Calculated IR spectra are presented and discussed without scaling. The calculations were run by using the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional coupled with 6–31g(d) basis set. All calculations were performed with Gaussian 09 package.

2.1 Results and discussion

In Figure 1(a) is presented the SEM image of the hybrid film, obtained by boric acid solution without adjustment of pH (pH=5). It is shown relatively homogeneous microporous surface structure, with larger single surface pores and free of crystallities. The surface of the film obtained by boric acid solution at pH=10 is roughened, containing randomly distributed structural aggregates (Fig. 1(b)).

**Figure 1.** SEM images of PVA/PEG/Boron hybrid films prepared from an aqueous solution of H$_3$BO$_3$ at (a) pH=5 and (b) pH=10.

FTIR spectroscopy is used to study characteristic bands of organic and borate compounds, in starting solutions and structural changes observed after mixing in obtained hybrid films. Figure 2 shows IR spectra of polymer compounds and absorption bands of following frequencies are assigned to: 3700-3100 cm$^{-1}$ (v$_s$H-OH, v$_s$C-OH, hydrogen bonds), 2960-2850 cm$^{-1}$ (v$_s$CH$_3$), 2300-1900 cm$^{-1}$ (δ vibration of hydrogen bonds), 1650 cm$^{-1}$ (bending mode of H$_2$O), 1460 cm$^{-1}$ (O–H and δCH$_3$), 1380 cm$^{-1}$ (δasCH$_3$), 950 cm$^{-1}$ (γC-OH). The bands of regions 1330-1220 cm$^{-1}$ (δC-
OH) and 1065-1020 cm\(^{-1}\) (\(\nu\)C-OH) can be attributed to primary alcohol (PEG), while 1370-1260 cm\(^{-1}\) (\(\delta\)C-OH) and 1120-1080 cm\(^{-1}\) (\(\nu\)C-OH) from secondary alcohol (PVA). The absorption bands at 1200-970 cm\(^{-1}\) are related to C-O while 1100-1000 cm\(^{-1}\) to C-O-C stretching vibrations of esters [1, 2, 10-13, 20-24]. The boron exists in the crystals, glasses and aqueous solutions as a BO\(_3\) and BO\(_4\) groups and their rearrangement lead to the formation of super structural units such as metaborate, pentaborate, triborate and diborate. The bands at 1500-1200 cm\(^{-1}\) are related to (vB-O of BO\(_3\)), 1200-850 cm\(^{-1}\) to (vB-O of BO\(_4\)) and 800-600 cm\(^{-1}\) (bending vibrations for various borate segments) [25-27]. The IR spectra of an aqueous solution of H\(_3\)BO\(_3\) are presented in Figure 3.

![Figure 2](image2.png)  ![Figure 3](image3.png)

**Figure 2.** IR spectra of 4% aqueous solutions of PVA, and PEG\(_{400}\).  **Figure 3.** IR spectra of 4% aqueous solution of H\(_3\)BO\(_3\) at pH=10 and pH=5.

The characteristic frequencies for BO\(_3\) can be assigned to: ortoborates (BO\(_3^3\)\(^-\)), metaborates (BO\(_2^4\)\(^-\)), pyroborates (B\(_2\)O\(_4^6\)\(^+\)) (1440-1430 cm\(^{-1}\), 1330-1220 cm\(^{-1}\), 690-660 cm\(^{-1}\)), pentaborates (B\(_5\)O\(_8^6\)\(^-\)) (1430 cm\(^{-1}\), 1320 cm\(^{-1}\), 1220 cm\(^{-1}\), 1090 cm\(^{-1}\), 690 cm\(^{-1}\)) and triborates (B\(_3\)O\(_5^5\)\(^-\)) 1430 cm\(^{-1}\), 1320 cm\(^{-1}\), 1020 cm\(^{-1}\), 915 cm\(^{-1}\), 690 cm\(^{-1}\)).

![Figure 4](image4.png)  ![Figure 5](image5.png)

**Figure 4.** IR spectra of PVA-PEG-B\(_2\)O\(_3\) hybrid films prepared with an aqueous solution of H\(_3\)BO\(_3\) at pH=10 and pH=5.  **Figure 5.** IR spectra of PVA-PEG-B\(_2\)O\(_3\) hybrid films prepared with an ethanol solution of (CH\(_3\))\(_3\)B at pH=10 and pH=5.
After changing of pH to 10, the band of 1220 cm\(^{-1}\) is disappeared and shifted to higher wave number frequency 1500-1200 cm\(^{-1}\). This displacement is due to the partial transformation of BO\(_3\) to BO\(_4\), a result in the spectra occur new bands 1160-1080 cm\(^{-1}\) concerning BO\(_4\) probably of tetraborate (B\(_2\)O\(_4^2-\)) (1445 cm\(^{-1}\), 1330 cm\(^{-1}\), 1160-1080 cm\(^{-1}\) и 670 cm\(^{-1}\)) [25-29]. The spectra of the hybrid films are presented in Figures 4-5.

The absorption bands of initial polymers with that of hybrid films obtained by different boron precursors are compared in Table 1.

**Table 1.** Infrared vibrational frequencies of PVA, PEG and hybrid PVA-PEG-B\(_2\)O\(_3\) films obtained by different boron precursors and pH.

| Experimental IR spectra (Frequencies - (\(\text{cm}^{-1}\)) | PEG | PVA | Hybrid PVA-PEG-B\(_2\)O\(_3\) films | An aqueous solution of H\(_2\)BO\(_3\) | An ethanol solution of (B(OCH\(_3\))\(_2\)) |
|---|---|---|---|---|---|
| | | | pH=5 | pH=10 | pH=5 | pH=10 |
| 3400 | 3407 | 3370 | 3370 | 3370 | 3385 |
| 2877 | * | 2908 | 2908 | 2910 | 2910 |
| 1950 | 2100 | * | * | 1955 | 1950 |
| * | * | 1725 | 1725 | 1730 | 1730 |
| 1640 | 1640 | 1655 | 1655 | 1655 | 1655 |
| * | * | 1570 | * | * |
| 1460 | 1427 | 1425 | 1425 | 1430 | 1425 |
| 1346 | * | 1335 | 1330 | 1335 | 1335 |
| 1297 | * | 1290 | * | 1295 | 1290 |
| 1246 | * | 1245 | 1245 | 1250 | 1250 |
| 1100 | 1100 | 1105 | 1095 | 1110 | 1110 |
| 940 | * | 940 | 920 | 940 | 940 |
| 886 | * | 845 | 840 | 845 | 845 |
| 836 | 815 | * | * | * | * |
| * | 775 | * | * | * | * |
| * | 690 | 665 | 660 | 665 | 665 |
| 511 | 500 | 590 | 610 | 605 | 605 |

The main changes in the spectra are associated with characteristic frequencies of OH groups on PEG and H\(_2\)BO\(_3\). Hydrogen-bonded and ester type cross-linking between inorganic and organic compound is observed. In Figure 4 can be seen that absorption bands of the hybrid film obtained on the aqueous solution of H\(_2\)BO\(_3\) are shifted in compared those of PEG. The displaced of absorption bands 2908 cm\(^{-1}\) (vs CH\(_2\)), 1655 cm\(^{-1}\) (bending mode of H\(_2\)O), (1105 cm\(^{-1}\) C-O-C of esters) and 590 cm\(^{-1}\) (bending of OH) to higher frequencies is a result of hydrogen-bonded interaction between O and H atoms from the polymers, boron species and aqueous molecules. The absence of bands in region 2280 cm\(^{-1}\) and 1870 cm\(^{-1}\) concerning BO\(_4\) of the polymer films is disappeared and shifted to higher frequency 1725 cm\(^{-1}\) to the framework vibrations of C-H and ester bonds with BO\(_4\) (1200-850 cm\(^{-1}\)). The polymer-borate esters bonds may expect in an interval 1400-1000 cm\(^{-1}\), where are occurred absorptions bands of C-OH, C-O-C, BO\(_3\) and BO\(_4\) groups. Characteristic frequency of B-O-C bonds in the literature occurs at 1030 cm\(^{-1}\) [11-13]. The changes observed in the IR spectrum of the film obtained from an aqua solution of H\(_2\)BO\(_3\) at pH=10 are related to higher BO\(_4\)/BO\(_3\) ratio. The bands concerning BO\(_3\) and BO\(_4\) structural groups are more shifted to lower frequencies accordingly (1095 cm\(^{-1}\), 920 cm\(^{-1}\), 840 cm\(^{-1}\)) and (660 cm\(^{-1}\), 610 cm\(^{-1}\)). Furthermore simultaneously increase of intensities of bands 1100 cm\(^{-1}\) and decrease in region 1425-1250 cm\(^{-1}\) are observed. The IR
spectra of films obtained from ethanol solution of \((\text{CH}_3\text{O})_3\text{B}\) are similar, resulting in hydrolysis rate (Figure 5). If the synthesis is approved without pH adjustment (pH=5) in the precursor solutions almost no hydrated boron ester and the structure is based on hydrogen bonding network and minimal quantity BO\(_4\)-complexes.

Figure 6. Probable PEG-borate structures taking part in the PVA/PEG/Boron hybrid network prepared with an aqueous solution of \(\text{H}_3\text{BO}_3\) at pH=5 (A) and pH=10 (B). Correlations of the experimental vs. calculated IR frequencies (cm\(^{-1}\)).
On the base of spectral results and above analyses in Figure 6 are supposed following polymer-borate structures taking part in the hybrid network and computer simulated IR spectra are made. Experimental absorption bands concerning PEG-borate complexes are in a good correlation with the simulated IR spectra. Therefore, we suppose that PVA-PEG-B₂O₃ network is based on initial crosslink between the borate units and PEG to the formation of PEG-borate esters followed by hydrogen bonding them with long chains of PVA.

2.2 Conclusions

Transparent PVA/PEG/Boron hybrid films are obtained by solution casting method. Surface morphology of hybrid films analysed by SEM is revealed homogeneous, microporous surface, with larger single surface pores and free of crystallites. Results of the FTIR analysis showed that borate species existing in the precursors are depended on pH that determines the BO₃/BO₃ ratio, a cross-linking, final morphology and a structure of a hybrid network. The best cross-linked hybrid structure is obtained from an aqueous solution of H₃BO₃ at pH=10, with the major amount of polyborate ions. A probable mechanism based on the formation of a hybrid network involving PEG-borate ester complexes entanglement through the hydrogen bonds of PVA is supposed.

Acknowledgments

Authors are grateful to the Operational programme "Science and Education for Smart Growth", project BG05M2OP001-2.009-0028.
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