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Study of Poly(vinyl alcohol)/Cyclodextrin Materials Obtained by Different Techniques

Silvia F. C. Patachia* and Catalin Croitoru

"Transilvania" University of Brasov, Department of Product Design, Environment and Mechatronics, Brasov 500036, Romania

Materials based on poly(vinyl alcohol) [PVA] and cyclodextrins [CDs] have been obtained by components mixing in aqueous solution and then, by applying two different techniques of PVA crosslinking: chemical crosslinking with glutaraldehyde in gaseous phase and physical crosslinking (repeated freezing-thawing cycles), aiming the obtaining of materials with different properties and potential applications. Three cyclodextrin derivatives such as beta-cyclodextrin, methyl beta-cyclodextrin and hydroxypropyl beta-cyclodextrin have been used. The obtained materials have been characterized from different points of view: compositional stability at their contact with water (CDs release), materials water sensitivity (swelling capacity), thermal stability and molecular interaction (FTIR absorption).

KEYWORDS: *Poly(vinyl alcohol), Cyclodextrins, Crosslinking, Cryogels.*

INTRODUCTION

Cyclodextrins [CDs] are water-soluble oligosaccharides that possess the remarkable ability to form inclusion complexes with a wide variety of organic compounds. This fitting effect has been successfully exploited by designing polymer-CD materials for the encapsulation of drugs, as well as separation of positional isomers and enantiomers by techniques such as HPLC and capillary electrophoresis.[1–9]

Poly(vinyl alcohol) [PVA] seems to be one of the most efficient polymer matrixes for CDs, owing to its ability to form freestanding films and its hydrophilic character due to the presence of hydroxyl groups.[10] In these materials CDs have been either trapped in PVA or covalently linked to the chain.

Different techniques of PVA-CD-s materials obtaining influence their properties, and as consequence their applications.

GA is reported as being the most commonly used crosslinker for PVA. Nevertheless GA is a toxic compound and thus it is necessary to avoid the existence of unreacted traces in the polymeric matrix.

In this work PVA-CD materials have been obtained by components mixing in aqueous solution and then, by using two types of PVA crosslinking methods: chemical crosslinking with gaseous glutaraldehyde [GA] (method I)[11–13] and physical crosslinking (freezing-thawing cycles) (method II).[14–19]

The crosslinking process with glutaraldehyde in gaseous phase using the method reported in the reference literature[20] leads to minimizing the unreacted crosslinker amount in the polymer matrix, avoiding excess crosslinker sorption into the material. The method of crosslinking with GA in gaseous phase hasn't been applied on PVA-CD systems up to this extent.

Physical crosslinking using freezing-thawing cycles is the most common and ecologically used method of obtaining PVA biomaterials with applications in medicine and pharmacy.[21–24]

Three CD derivatives: β-cyclodextrin [BCD], methyl beta-cyclodextrin [MBCD] and hydroxypropyl beta-cyclodextrin [HPBCD] have been used.

The obtained materials have been characterized from compositional stability point of view, when they are in contact with water. CD-s release from the PVA matrix has been monitored. The influence of the obtaining technique and of the CD's type on total CD's released amount and their release kinetic have been evidenced.

Water sensitivity of the obtained materials has been tested. Swelling studies on all materials (obtained by both crosslinking methods) have been done, in order to

*Author to whom correspondence should be addressed.
Email: st.patachia@unitbv.ro
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determine if the PVA-CDs interaction modifies the swelling capacity of the PVA.

Thermo-reversibility of the PVA-CD-s materials obtained by the two above-mentioned techniques has been checked by determining the dissolving temperature of the gels at their immersion in water, as a function of temperature. Influence of the CD's type on the PVA crosslinking process is discussed.

Thermal stability of the materials obtained by technique I has been checked by determining their films transparency as a function of temperature.

All the monitored properties have been discussed taking into account the interaction between PVA-CD and GA. The obtained PVA-CD materials have been also characterized by FTIR spectroscopy in order to determine the nature of PVA-CD interaction.

EXPERIMENTAL DETAILS

Materials

PVA 120-98 (1200 polymerization degree and 98% hydrolysis degree) was purchased from Chemical Enterprises Risnov, Romania. Glutaraldehyde (GA) of 45% wt concentration was purchased from "Reactivul" S.A. Bucharest. Sulphuric acid 0.1 N was of reagent grade. BCD, MBCD, HPBCD were purchased from Sigma-Aldrich, and were of reagent grade. All reagents have been used without further purification.

Sample Preparation Methods

PVA/CD Mixture Solution Preparation

PVA solution has been prepared by dissolving the polymer powder in Milli-Q water, under magnetic stirring at room temperature, followed by heating at 85 °C for 4 h. The solid content of the obtained solution was 11%.

To certain amounts of this solution (10 mL), CD has been added respecting the 25 $(\%)_{wt}$ amount of CD in composition, reported to the dry polymer amount.

In the PVA-CD mixture to be crosslinked by method I, sulphuric acid 0.1 N was added as catalyst (0.1 mL of solution per mL of aqueous polymer solution-CD mixture).

PVA/CD Materials Obtaining

The materials designed by method I have been prepared by casting PVA/CD-s aqueous solutions with sulphuric acid in composition (amounts mentioned in Section PVA/CD Mixture Solution Preparation) and solvent evaporation at room temperature for 24 h.

The PVA-CD films obtained as mentioned above have been introduced into the crosslinking installation and placed over a recipient that contained a determined volume of 45% GA solution. The installation has been connected to a vacuum pump, as the films to be in contact with GA vapours for 3 hours.

The materials designed by method II (PVA-CD cryogels) have been prepared by introducing a specific volume of PVA/CD mixture in aqueous solution in a PVC cylindrical recipient and submitting it to freezing at −19 °C for 12 hours, followed by thawing at room temperature (22 °C) for 12 hours. The above mentioned freezing-thawing procedure was repeated four times.

Blank samples, without cyclodextrins, have been crosslinked following the same procedures.

Materials Characterization

Determination of the CD Release at Their Immersion in Water

Pre-weighted samples have been immersed in a determined volume of distilled water at room temperature. Based on the optical activity of CDs, their release from the PVA matrix has been monitored by analysing the solution resulted after PVA/CDs materials immersion in distilled water with a Carl-Zeiss POLAMAT A polarimeter (at 546 nm). After each polarimetric measurement, performed at determined time intervals the materials have been immersed in a fresh volume of distilled water, in order to maintain the concentration gradient between the solution and the material constant.

The CD release rate from the materials has been determined with two significant digits as the slope of the linearly plotted CD release kinetic (until equilibrium reaching).

Swelling Study of PVA/CD Hydrogel

The samples have been soaked in distilled water at room temperature. At different time intervals, each sample was taken out, wiped with filter paper and weighted until a constant mass was obtained. The degree of swelling (SD) was determined from Eq. (1)

$$SD = \frac{(m_t + m_{CD\ rel})}{m_d} \cdot 100 \quad (1)$$

Where m_t is the mass of the swollen sample in water at time "t" (the same as for the polarimetric analysis), m_d the mass of the dried material and $m_{CD\ rel}$ is the total amount of cyclodextrins released from the polymer matrix until time "t" (determined as mentioned in Determination of the CD Release at Their Immersion in Water).

The swelling rate from the materials has been determined with two significant digits as the slope of the linearly plotted SD kinetic (until equilibrium reaching).

Dissolving Temperature of the Obtained Materials

Pieces of materials of equal mass have been immersed in a wide-diameter testing tube filled with 5 mL of distilled water and heated slowly over a water bath, until they started to dissolve. The temperature at which the PVA/CD materials started to dissolve has been determined by using a digital thermometer.

Study of PVA/CD Hydrogels Transparency

The modification in transparency of the PVA/CD films (materials obtained by method I) with temperature increase (from 30 to 80 °C) has been determined. The films have been cut in rectangular pieces with 1.2 × 2.5 cm dimensions and have been introduced in the drying stove at a certain temperature from the interval mentioned above for 10 minutes.

Then the film pieces have been taken out of the drying stove, cooled in a desiccator to room temperature and their absorbance has been measured using a Perkin-Elmer Lambda 25 spectrophotometer at 700 nm.

Fourier Transform Infrared Spectroscopy Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the PVA-CD interactions. PVA/CD films were obtained as 1–2 mm thick films and the cryogels were cut in 3–4 mm slices and analyzed by FTIR using Reflectance Mode.

FTIR spectra were obtained in the range of wave number from 4000 to 600 cm^{-1} during 4 scans, with 4 cm^{-1} resolution (BXII spectrometer, Perkin-Elmer, USA).

The materials have been conditioned before submitting to FTIR analysis by keeping them for 24 hours in a chamber with constant 54% relative humidity.

RESULTS AND DISCUSSION

By applying the above-mentioned techniques of PVA-CD-s materials obtaining, different properties have been obtained.

Films obtained by technique I are transparent, evidencing a high compatibility between PVA and CD-s while the membranes obtained by technique II are white, opaque, heterogeneous and porous.

CD release at their immersion in water is different in function of obtaining technique but also in function of the type of CD used.

From Figures 1 and 2 it could be seen that while from the chemically crosslinked PVA, the CD-s have been released after 20 minutes, reaching an equilibrium state, their release from cryogel is delayed, reaching the balanced state after 50 minutes.

Also it could be noted that while technique I leads to materials with approximately the same release profile for all the CD-s, technique II leads to higher CD's type sensitive release.

The most compositional stable material is PVA/BCD obtained by technique II. In this case no BCD release has been noted.

It could be noted that the amount of CD-s released from the PVA matrix crosslinked by technique I is higher by comparing with that released from materials obtained by technique II. This could be explained both by the higher crosslinking degree of the PVA matrix obtained

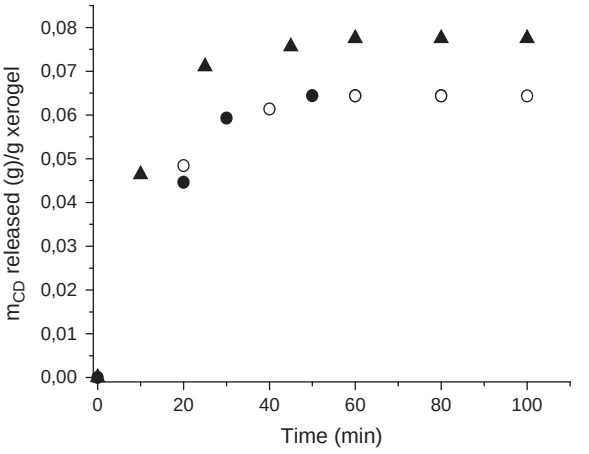

Figure 1. **CDs release kinetic profile from the PVA/CD materials obtained by method I ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD.**

by repeated cycles of freezing and thawing comparatively to PVA crosslinking with GA in gaseous phase, but also by PVA-GA-CD-s interaction. As it was reported by Constantin and co-workers[26] a competition between OH groups from PVA and CD-s against GA could occur. CD-s could consume a part of GA giving water-soluble oligomers that are released from the matrix.[26]

In case of PVA cryogel matrix, very high interaction between the PVA and BCD occurs, completely avoiding the BCD release. HPBCD could interact also with the matrix by hydrogen bondings between OH from PVA and HPBCD, respectively, leading to a low release. The higher amount released has been noted for MBCD, due to the lower interaction of this CD having no OH groups with PVA.

The release rate of the CD-s from the polymeric matrix suggests also a stronger crosslinked and more dense structure for the materials obtained by technique II (Table I). The interaction between CD-s and PVA matrix is also

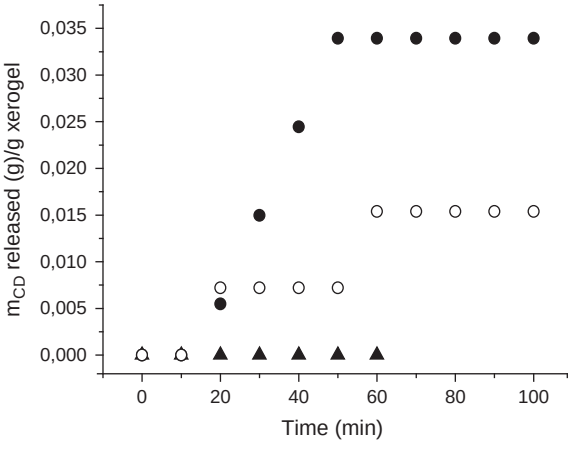

Figure 2. **CDs release kinetic profile from the PVA/CD materials obtained by method II ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD.**

Table I. Release rate of the CD from PVA/CD materials.

	Release rate (g CD/min) · 10^3		
Material type	PVA/BCD	PVA/MBCD	PVA/HPBCD
Crosslinked by TI	2.84	2.43	2.33
Crosslinked by TII	0.00	0.78	0.68

important: higher interaction between PVA cryogel and BCD leads to a very stable material; the interaction decrease leads to increase of the release rate.

The CD-s release rate from hydrogels obtained by technique I decreases also with the increase of the molecular mass of the CD (BCD > MBCD > HPBCD). The same dependence has been noted in case of cryogels for MBCD and HPBCD respectively.

The interaction between the PVA and CD-s could be evidenced also by calculating the percent of the CD released from the matrix reported to the initial CD amount embedded in the polymeric matrix (Figs. 3 and 4).

From Figures 3 and 4 it could be seen that higher percents of released CD-s from the embedded CD-s in the PVA chemically crosslinked matrix has been obtained (55–70%) by comparison with those released from PVA cryogel matrix (maximum 32%). In this way higher interaction between PVA cryogel and embedded CD-s is confirmed by lower percent release in comparison with PVA/GA matrix.

The lower level of crosslinking obtained by technique I could be also confirmed by monitoring the swelling degree of both types of materials (Figs. 5 and 6).

From Figures 5 and 6 the following aspects could be noted:

• The swelling degree of materials obtained by technique I is higher than those of materials obtained by technique II.

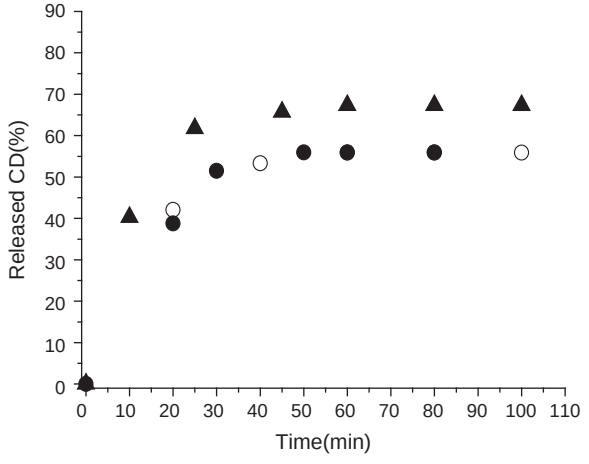

Figure 3. CDs release kinetic profile from the PVA/CD materials obtained by method I ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD.

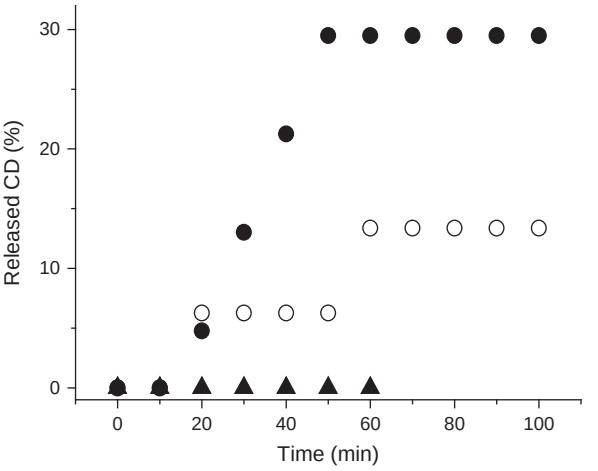

Figure 4. CDs release kinetic profile from the PVA/CD materials obtained by method II ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD.

• The presence of CD-s in the PVA matrix obtained by technique I, increases the materials sensitivity to the water, by comparing to unfilled PVA.

• The CD-s presence in the PVA cryogel matrix decreases the water sensitivity of the materials.

• Even the PVA cryogel seems to be more crosslinked than PVA treated by technique I, water absorption values for the last one are lower then those for the cryogel.

• Both crosslinked matrices evidenced lower water absorption by comparing with un-crosslinked PVA.

• Materials obtained by technique I attained the swelling equilibrium faster (after aprox. 10 minutes) by comparing with materials obtained by technique II, where the swelling equilibrium is reached after approximately 50 minutes. Starting from this time, the equilibrium SD starts to decrease, which may indicate the dissolution of the sample and/or elimination of crosslinking catalyst from the matrix or some non-crosslinked PVA macromolecules.

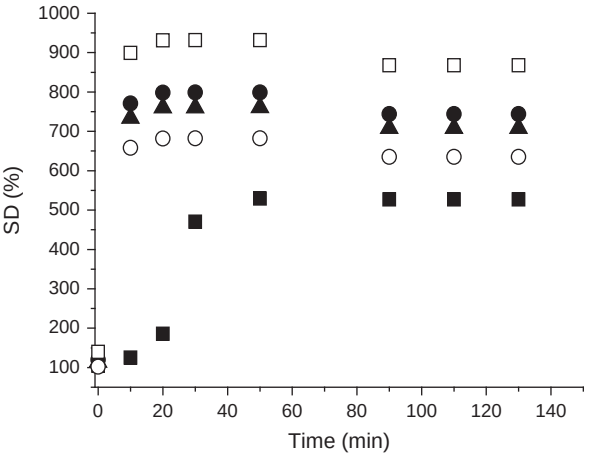

Figure 5. Swelling degree of the PVA/CD materials obtained by method I ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD; ■: PVA; □: non-crosslinked PVA.

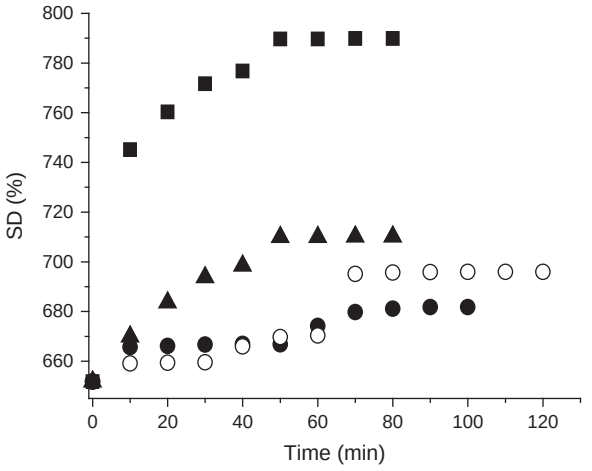

Figure 6. **Swelling degree of the PVA/CD materials obtained by method II ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD; ■: PVA.**

This aspect is not present in the materials crosslinked by method II, which seem to be more stable.

We mention that the calculus of SD from the material took into account the amount of CDs released from the polymeric matrix, as indicated by Eq. (1), in order to compare the apparent swelling degree of the composites obtained by both techniques.

Although the swelling degree of materials obtained by the two used techniques are very close (maximum 10% differences in SD), there are high differences in swelling rate (Table II).

From Table II it could be noted that very low swelling rates have been obtained for materials prepared by technique II, due to their higher crosslinking and denser structure.

Also, it could be seen that the CD-s lowers the swelling degree of the materials, with the decreasing of the –OH groups from their molecules, in the case of materials obtained by technique II.

Aiming to evidence the differences between the materials obtained by chemical and by physical crosslinking, concerning their stability in heated water, the thermo-reversibility of the materials has been checked. Surprisingly, both types of materials are thermo-reversible. This means that the treatment of PVA/CD-s films with GA in gaseous phase did not lead to a real chemically crosslinked

Table II. **Swelling rate of PVA/CD materials.**

	Swelling rate (min^{-1})			
Material type	PVA	PVA/BCD	PVA/MBCD	PVA/HPBCD
Noncrosslinked	81.33	–	–	–
Crosslinked by TI	12.43	63.53	61.95	57.27
Crosslinked by TII	2.84	1.18	0.37	0.61

Table III. **Dissolving temperature of the materials.**

	Dissolving temperature (°C)			
Composite type	PVA	PVA/BCD	PVA/MBCD	PVA/HPBCD
Noncrosslinked	68.20	–	–	–
Crosslinked by TI	73.5	54.00	62.30	61.60
Crosslinked by TII	63.25	66.35	65.50	66.00

structure, but to a PVA functionalizing by semi-acetal bonds formation.

Table III evidences the temperatures at which the materials turn to solution.

From Table III it could be seen that PVA cryogel is more sensitive to the temperature, by comparing to PVA noncrosslinked film, turning to solution at 63.25 °C. The treatment with GA increases the thermal stability of the PVA in water but do not avoid completely its dissolution. In case of materials obtained by technique I, the CD-s presence decreases their thermal stability, the most pronounced effect being that of BCD. This behaviour is in agreement with the GA-BCD hydrophilic oligomers formation and the high composite swelling degree discussed before. In case of materials obtained by technique II, CD-s presence increases their thermal stability.

Heat stability of materials obtained by technique I has been checked also in solid state.

Initially transparent films have been submitted for a determined time interval to increasing temperatures (between 30 °C and 80 °C) in an oven. After heat treatment the films transparency has been checked by UV-VIS spectroscopy.

The obtained results have been plotted in Figure 7.

As it can be seen in Figure 7, the transparency of the PVA/BCD composite decreased significantly at 75 °C, indicating the possible formation of a complex between BCD and GA, insoluble in PVA matrix.

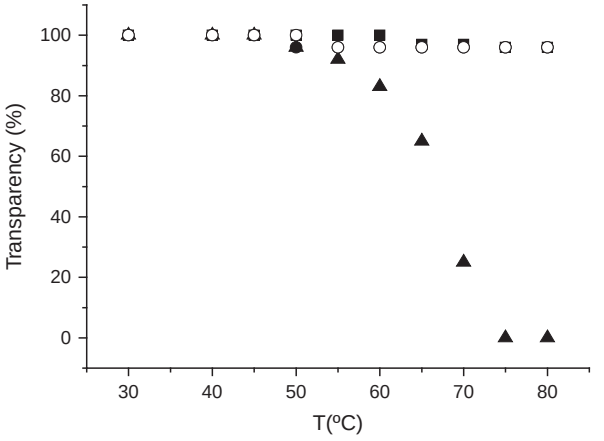

Figure 7. **Transparency of the PVA/CD materials obtained by method I ▲: PVA/BCD; ●: PVA/MBCD; ○: PVA/HPBCD; ■: PVA.**

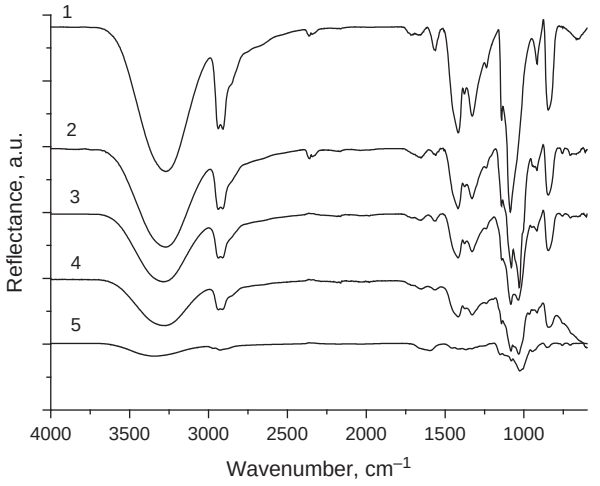

Figure 8. FTIR spectra of materials obtained by method I and CD: 1: PVA; 2-PVA/BCD, 3-PVA/HPBCD, 4-PVA/MBCD, 5-CD.

The variation in transparency of the PVA, PVA/MBCD, and PVA/HPBCD is not significant, which shows that in the case of these materials the complex with GA is not formed.

FTIR spectra have been recorded for the materials obtained by the two applied techniques (Figs. 8, 9). All major bands related to hydroxyl groups were observed. The large bands observed between 3550 and 3200 cm^{-1} are linked to the O–H stretching from the intermolecular and intramolecular hydrogen bonds.[26]

Regarding the FTIR spectra of the cyclodextrins, the main bands centered at 3370 cm^{-1}, 2920 cm^{-1}, 1157 cm^{-1} and 1029 cm^{-1} correspond to the symmetric and antisymmetric stretching of ν[OH], alkyl $\nu[CH_n]_{n=1,...,3}$, ν[C–C] and bending vibration of ν[O–H] respectively.[17, 26]

Related to the materials obtained by method I, the vibrational band observed between 2840 and 3000 cm^{-1} refers to the stretching C–H from alkyl groups.

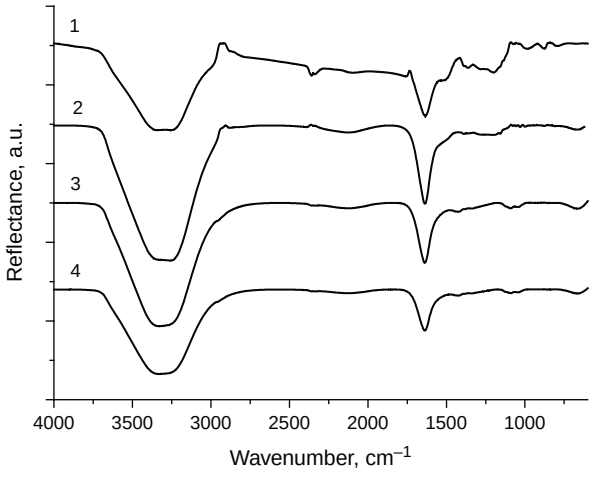

Figure 9. FTIR spectra of materials obtained by method II: 1: PVA; 2-PVA/BCD, 3-PVA/HPBCD, 4-PVA/MBCD.

The reaction of the PVA with the GA results in a reduction of the intensity of the O–H bands (in Fig. 8) from the PVA, indicating a possible formation of acetal bridges.

FTIR spectra obtained for materials prepared by technique II, analyzed in swollen state, seems to have a simpler structure due to the more intense absorption at O–H characteristic wave number and consequently diminishing the other absorption bands.

As shown in Figures 8 and 9, there seem to be no new peaks that appeared in the spectra of the sample containing CD's compared with the unfilled crosslinked PVA sample which indicates that CD's and PVA did not form covalent bonds and the CD was merely physically blended into the polymer matrix.

The –OH band centred at 3350 cm^{-1} related to intermolecular and intramolecular hydrogen bonds broadens significantly which indicates a strong interaction between BCD and the polymeric matrix.

CONCLUSIONS

PVA 120-98/CD-s materials have been prepared by using two methods of crosslinking: with glutaraldehyde in gaseous phase and by repeated freezing-thawing cycles.

The obtained materials have been characterized concerning their compositional stability in contact with water (CD-s release), sensitivity to water (swelling degree), thermo-reversibility, heat resistance in solid state (transparency maintaining). FTIR spectroscopy has been used to explain their behaviour through PVA/CD-s/GA interaction.

Materials obtained by technique II are more stable concerning their compositional stability when they are in contact with water. No BCD release has been noted. Release of MBCD and HPBD, respectively is very slow and up to 14 and 32%, respectively, from the initial embedded CD-s amount.

CD-s decrease water absorption of PVA cryogel while their presence in materials obtained by technique II increases their water sorption comparatively to chemically crosslinked PVA.

All types of composite materials obtained are thermoreversible, indicating an apparent chemically crosslinking occurrence. Semi-acetal bonding formation is responsible for PVA properties changing.

By heating PVA/CD-s materials obtained by technique I, changes in their transparency occurred. PVA/BCD film became turbid due to the complex BCD/GA formation.

This information concerning PVA/CD-s materials behaviour as a function of preparation technique is important because it offers a tool for tailored materials obtaining.

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