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Phase behaviour of polyvinyl alcohol/β-cyclodextrin blends

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Films of poly(vinyl alcohol) (PVA) containing β-cyclodextrin (β-CD) were obtained by solution casting technique from aqueous solutions of constant concentration. After evaporation of the solvent, all films prepared from PVA/β-CD solutions were found to be transparent. The compatibility of the components in the blends was evaluated by optical microscopy (OM), rheology, Fourier transform infrared spectroscopy (FT-IR), and differential scanning calorimetry (DSC) techniques. Both visual and OM observations showed a good compatibility between PVA and β-CD. The rheologycal behaviour indicates the existence of the specific interactions between components which becomes stronger with the increase of β-CD content. The glass transition temperature (Tg) was found to increase with an increase of the β-CD content in the blends, even at low concentrations of β-CD.

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Keyword: Polyvinyl alcohol, Cyclodextrin, Compatibility, Specific interactions

1. Introduction

Poly(vinyl alcohol) is a highly hydrophilic, water-soluble polymer. Presently, much attention is paid to PVA applications in various biomedical fields, such implants [1], artificial kidney membranes [2], contact lenses [3], cells immobilization [4] and drug delivery systems [5].

Besides its hydrophilic character PVA forms hydrogels with important uses in the controlled release of pharmaceutical components [6, 7]. Hydrogels can be prepared from aqueous PVA solutions using various techniques, such as the photo-cross linking, the freezing-thawing, irradiation and chemical cross-linking methods [8].

In recent years polymers blending has became a method for providing polymeric materials with desirable properties for practical applications. PVA is a good candidate for blends with natural polymeric materials, being highly polar, can be handled in water solutions, and is biodegradable [9]. Miscible PVA blends with cellulose due to the intermolecular hydrogen bonds between hydroxyl groups of the components have been reported [10]. Much attention has been done to the PVA blends with chitosan, due to their good mechanical and chemical properties, with many uses in the biomedical fields [11-13].

PVA in mixture with cyclodextrins, other important polysaccharides widely used in pharmaceutical sciences [14, 15], were also used for biomedical applications. β-cyclodextrin (β-CD) is well known for its ability to form inclusion complexes with several classes of compounds [16-18].

PVA/β-CD complex systems have been reported, the studies especially refer to the effect of adding β-CD to PVA hydrogels on the release of a water-soluble bioactive substances as drugs [7,19,20]. Principally, PVA hydrogels containing β-CD were obtained by chemical cross-linking with glutaraldehyde. PVA/β-CD, as such, not cross-linked, was used to prepare membranes with high selectivity in chromatography and liquid-liquid extraction [21].

Up to now, after our knowledge, very few data were published on the PVA/β-CD compatibility [22]. The aim of this work is to report data regarding the preparation and characterization of PVA/β-CD blends, with the principal goal to establish the compatibility of the components in the blends.

2. Experimental

2.1. Materials

PVA with a number-average molecular weight of 71000 Dalton, a polymeric degree of 1600 and a degree of saponification of 95.8 mg KOH/g was obtained from ROMACRIL S.A. Rasnov (Romania). β-CD with a purity higher than 98%, a molecular weight of 1135 g/mol and a water content comprised between 10 and 15 wt% was purchased from Merck.

2.2. PVA/β-CD blends preparation

PVA dissolved in deionized twice distilled water was magnetically stirred for 8h at 60 ^oC. After removing the insoluble fraction by centrifugation a clear solution of PVA was obtained. β-CD was solved in water at 65^0C for 1h. PVA and β-CD solutions with different concentrations were mixed and stirred at 65 ^oC for 20 min. Films of PVA containing β-CD were obtained by pouring the mixed solutions on Plexiglas plates. The solvent was removed keeping the plates on vacuum at 65^0C. The composition of the obtained PVA/β-CD blends is shown in Table 1.

Table 1. Composition of the studied blends.

Sample	Blends composition (%)	
	PVA	β-CD
1	93	7
2	87	13
3	75	25
4	63	37
5	52	48
6	20	80
7	9.3	90.7

2.3. Characterization

The PVA/β-CD films were analyzed using rheology, Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and optical microscopy (OM).

The rheological study was performed using a RV8 viscometer from UK Ltd. London with eight rotation speeds and temperatures between 20 and 55^0C.

The FT-IR analysis was performed on a Bomem MB 104 apparatus (Canada), on KBr tablets containing a constant mass of 3 mg sample/500 mg KBr.

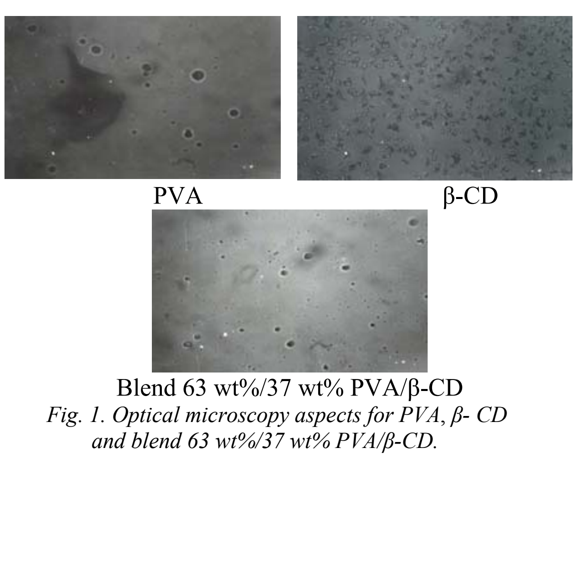
The DSC curves were recorded by means of a DSC-12E Mettler apparatus in dynamic conditions, with a heating, respective cooling rate of 10^0C/min.

The morphology of the studied samples was examinated by means of a MC_1-IOR (Bucharest) microscope equipped with a controlled heating-cooling plate.

3. Results and discussion

PVA/β-CD solutions present a slight opalescent aspect. The phases separation was not observed even after ten weeks. Only the solutions with β-CD content higher than 80 wt% show the presence of a precipitate, which is again dissolved after heating under stirring at 65^0C. All films obtained using PVA/β-CD solutions present a homogeneous aspect (Fig. 1).

These visual and microscopical observations are in favor of a good compatibility between PVA and β-CD.



Blend 63 wt%/37 wt% PVA/β-CD

Fig. 1. Optical microscopy aspects for PVA, β- CD and blend 63 wt%/37 wt% PVA/β-CD.

The rheological behaviour of some PVA/β-CD blends, not included in Table 1, was studied as against the temperature (Fig. 2).

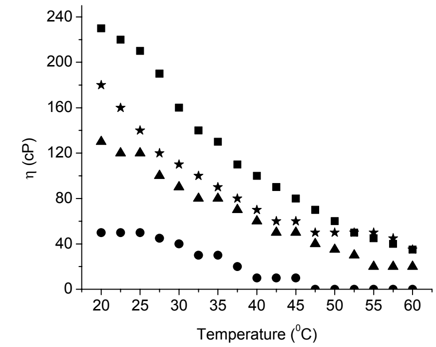


Fig. 2. Variation of the viscosity with temperature and blend composition: (■) PVA; (*) blend 95/5 PVA/β-CD; (▲) blend 90/10 PVA/β-CD; (●) blend 80/20 PVA/β-CD

Incorporation of β-CD in PVA solutions leads to decrease of viscosity, e.g. at 25^0C from 230 cP for PVA up to 50 cP for 80 wt%/20 wt% PVA/β-CD. As it was expected the viscosity decreases with increase of temperature. There is a relative sharp variation in viscosity of PVA at about 32^0C, the same variation being observed for 95 wt%/5 wt% PVA/β-CD at 28-42^0C, between 30 and 50^0C for 90 wt%/10 wt% PVA/β-CD mixture and 40^0C for 80 wt%/20 wt% PVA/β-CD mixture. This behaviour could be explained by a conformational transition of PVA at the mentioned temperatures, which is influenced by the presence of β-CD, which enlarges the transition and shifts it to higher temperatures.

The dependence of the dynamic viscosity on temperature is better evidenced in a logarithmic plot. This shows the existence of a transition temperature (T_{tr}) around 30-35 ^{o}C, which increases with increasing of the β-CD content in the blends (Fig.3). Activation energy of the flow increases with β-CD, at high amount of this. Two values are obtained with important change at transition temperature. These vary between 30 and 58 kJ/mol.

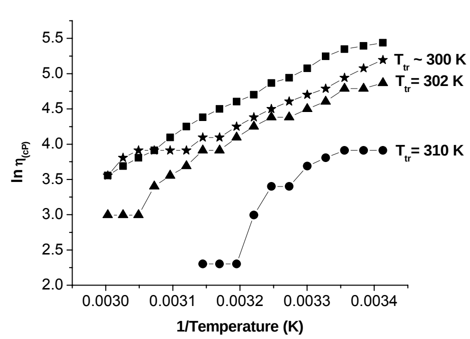
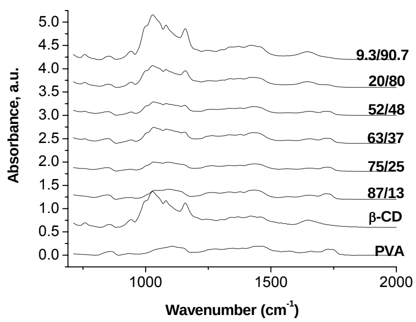


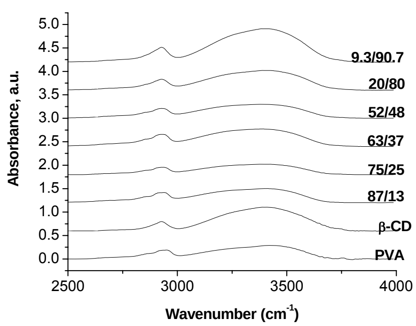
Fig. 3. Logarithmic dependence of the dynamic viscosity versus reciprocal temperature: (■) PVA; (*) blend 95/5 PVA/β-CD; (▲) blend 90/10 PVA/β-CD; (●) blend 80/20 PVA/β-CD.

The rheological behaviour indicates the existence of the specific interactions between components which become stronger increasing β-CD content.

These interactions were proved by FT-IR spectroscopy (Fig. 4, a and b). It can be observed that the intensity of the bands is not directly proportional to the concentration of the components. At the same time, the blends exhibit larger bands as against the components in the region between 3000 and 3500 cm^{-1} (Fig. 4b) and they are shifted to higher wavenumbers with increasing β-CD content. The bands around 1000 cm^{-1} are more complicated (Fig.4a) as compared to the sum of the spectra components. These modifications are proofs for the presence of specific interactions. Moreover the new bonds appeared being both ether and lactone type.



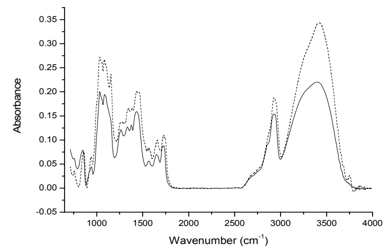
(a)



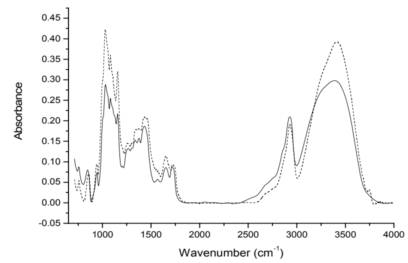
(b)

Fig. 4. FT-IR spectra of the studied samples.

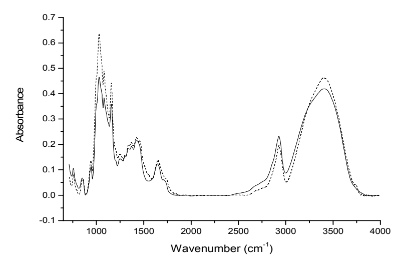
The experimental spectra were compared with those which were evaluated as sum of the spectra of components assuming no interactions between them (Fig. 5, a-c). It can be observed that for some of the analyzed mixtures there is not a perfect concordance between experimental and calculated spectra. The bands in the experimental spectra show lower intensities, are more extended and have more shoulders, especially in 2000-700 cm^{-1} region. This behaviour leads to the conclusion of the presence of some interactions between components.



(a)



(b)



(c)

Fig. 5. Experimental spectra versus calculated spectra (a) – sample 3; (b) – sample 5; (c) – sample 6; (—) experimental absorbance, (...) calculated absorbance.

The DSC curves for the water desorption process (Fig. 6) show that PVA is characterized by a large endotherm, while β-CD presents a very sharp endotherm. The DSC curves for PVA/β-CD blends are specific for each mixture. The temperature at the bottom of the endotherm varies between 92 and 102 ^{o}C, being placed around the temperature of water evaporation and between those of the components. The values for the water desorption heat are shown in Table 2.

Table 2. Water desorption heat for the PVA/β-CD blends

Sample	Water desorption heat (J/g)
PVA	115.54
2	140.72
3	138.9
4	145.2
5	286.9
6	484.28
7	1310.7
β-CD	2998.4

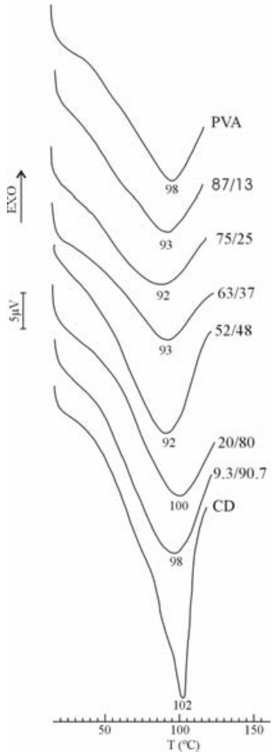


Fig. 6. DSC curves for water desorption process of the studied samples.

The variation of the water desorption heat with β-CD content (Fig. 7) indicate that the water release from β-CD need more energy than PVA and blends and also that these values are not additive.

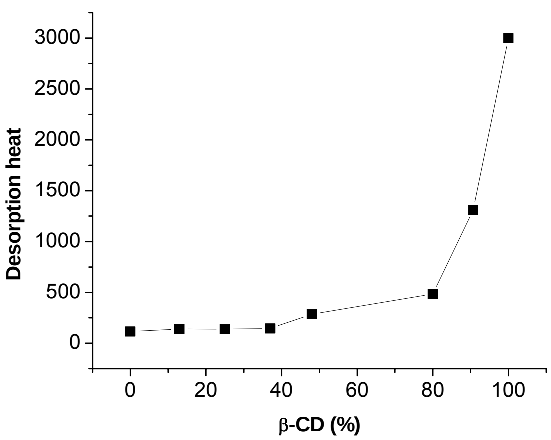
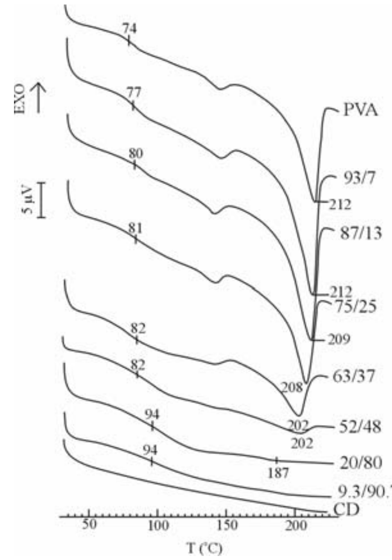
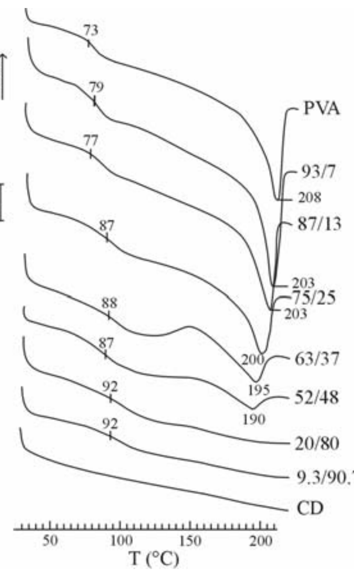


Fig. 7. Variation of the water desorption heat with β-CD content.

Using DSC curves recorded on the first (Fig.8a) and the second (Fig.8b) run both the glass transition (T_g) and melting transition temperatures for PVA and PVA/β-CD blends were evaluated.



(a)



(b)

Fig. 8. DSC curves for the dry samples (a) first run; (b) second run.

It can be noted an increase of the T_g values with increase of the β-CD content in the blends, even at low concentration of β-CD. The increase of T_g values is significantly for 20 wt%/80 wt% PVA/β-CD as well 9.3 wt%/90.7 wt% PVA/β-CD blends, with approximately 20 ^oC.

The miscibility method based on T_g variation was not possible to be applied in this case, because β-CD does not show T_g. Nevertheless, the appreciable increase of T_g values with increase of β-CD content in the blends proves the presence of some important interactions between the components of the blends (Fig. 9).

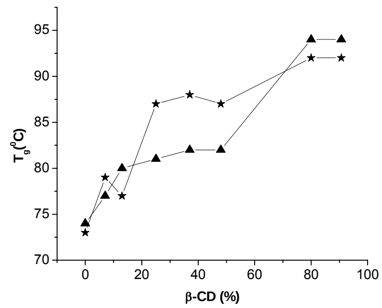


Fig. 9. T_g versus β-CD content: (▲) run1, (*) run 2.

The behaviour of the mixture on melting is also connected to the thermal history of the samples (Fig. 10). Approximately, the same melting temperature (T_m) values are obtained in the both heating cycles, but they are non-reproducible, due to the different ways of PVA crystallization. Thus, in the first run the crystallization occurred from aqueous solution, while in the second run the crystallization was carried out from melting state, so all characteristic temperatures vary with crystallization procedure.

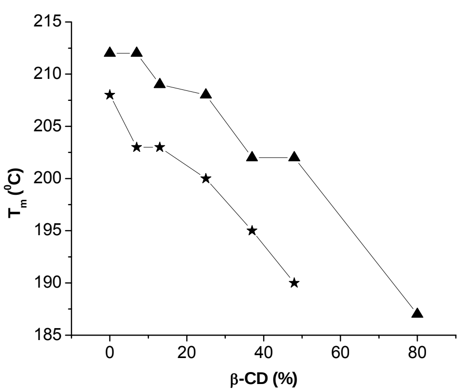


Fig. 10. T_m versus β-CD content: (▲) run1, (*) run 2.

This is evidenced by the differences in the DSC thermograms in both heating cycles. Thus, an additional endothermic peak was remarked around 140^{0}C in the first run (Fig. 8a). In the aqueous medium, the PVA crystallization is favored and this leads to the appearance of some ordered domains of small dimensions, which are distributed in the amorphous matrix and disappear at 140 ^{o}C. In this case a tendency to appear an exothermic peak immediately before the endothermic peak is evident (Fig. 8b).

The area of the melting endotherm decreases with the decrease of PVA content in the blends. For 20 wt% and 9.3 wt% PVA amount incorporated, this process is not present. The temperatures for the minimum of the endotherm and the melting heat (Table 3) decrease in the same way.

Table 3. PVA melting and crystallization heat.

Sample	PVA melting heat (J/g) Run 1	PVA melting heat (J/g) Run 2	PVA crystallization heat (J/g)
PVA	73.15	62.29	69.85
1	76.28	49.50	-
2	80.41	49.77	54.89
3	71.52	56.98	55.87
4	57.31	50.43	47.85
5	25.89	27.09	32.68

β-CD breaks and retards the crystallization of PVA. This is demonstrated by decrease of the exothermic process of crystallization recorded on cooling (Fig.11 and Fig. 12).

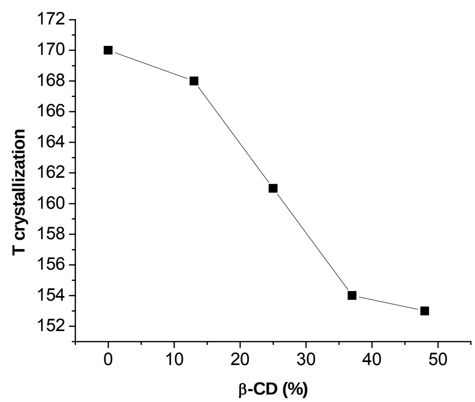


Fig. 12. Crystallization temperature versus β-CD content.

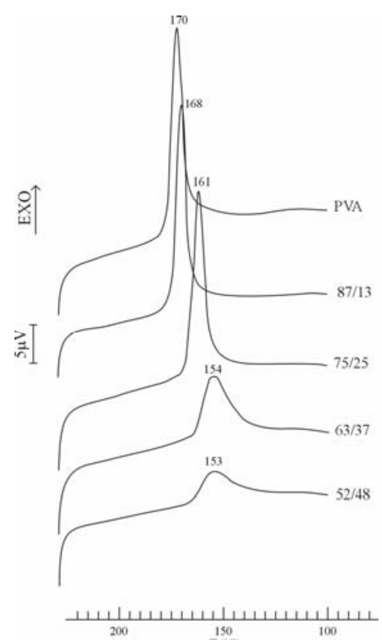


Fig. 11. DSC curves for the PVA crystallization process in some of the studied blends.

4. Conclusions

The compatibility and interaction between PVA and β-CD in PVA/β-CD blends were investigated through DSC, FT-IR, rheology and optical microscopy.

The data obtained show that PVA forms compatible blends with β-CD. The components of PVA/β-CD blends reciprocally influenced and they interact to form homogenous films whose properties can be controlled through the β-CD content and thermal history.

A transition temperature was found at 35^0C. All thermal properties are not additive and depend on the blend composition.

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