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Catalytic composite PVA membranes for acetalisation of phenylacetaldehyde in membrane reactors

T.F. Ceia, A.G. Silva, J.V. Pinto, M.H. Casimiro, A.M. Ramos, J. Vital*

Universidade Nova de Lisboa, Portugal

Abstract

Catalytic composite PVA membranes crosslinked with glutaraldehyde were prepared and used in form of disks in the acetalisation of phenylacetaldehyde and glycerol. Catalytic runs were carried out in batch reactors in order to study the effect of catalyst loading, crosslinking degree and hydrophilic/hydrophobic behavior. It was also preformed catalytic runs in pervaporation assisted catalytic membrane reactor to improve the efficiency of the process. The catalysts were characterized by thickness measurements, contact angles and swelling degree as well as by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Keywords: Biorefinery; hyacinth flavour; acetalisation; PVA membranes

Introduction

Hyacinth flavor is a high value product used in food and cosmetic industry generally synthesized by acetalisation of phenylacetaldehyde with glycerol. Since biodiesel production has been becoming a common practice, the price of glycerol as a byproduct has been declining which apparently makes our synthesis commercial attractive.

Previous approaches suggested reactive distillation to improve reaction conversion by removing the byproduct [1]. However, this technique requires large amounts of toxic solvents such as toluene that takes oversized equipment and shows high energetic costs.

Polymeric catalytic membrane reactors (PCMRs) can offer specific advantages by combining chemical reaction and separation [2-4].

Polymeric catalytic membranes have been prepared, consisting in poly(vinyl alcohol) (PVA) crosslinked with glutaraldehyde and zeolite HUSY dispersed in polymeric matrix. The effects of catalyst loading, polymer crosslinking and hydrophilic/hydrophobic balance in the catalytic behaviour of the prepared membranes, were studied.

Experimental

PVA (Aldrich, ≥99% hydrolysed) was dissolved in water at 80 ºC, during 2 hours. To prepare membranes with different catalyst loading, 20 mL of aqueous 8 wt.% PVA solutions were mixed with 5, 10, 15 and 20 wt. % (zeolite CBV 720, Zeolyst) with magnetic stirring during 20 minutes at room temperature and then it was mixed 2 wt.% glutaraldehyde (Aldrich, aqueous solution, 50 wt.%) for 5 minutes. To prepare membranes with different crosslinking degree, 20 mL of aqueous 8 wt.% PVA solutions were mixed with 10 wt. % (zeolite CBV 720, Zeolyst) with magnetic stirring during 20 minutes at room temperature and then it was mixed 4, 6, 8 and10 wt.% glutaraldehyde (Aldrich, aqueous solution, 50 wt.%) for 5 minutes.

The solutions were transferred for Petri dishes made of polypropylene. The dishes were placed in ultrasonic bath during 30 minutes, at room temperature, in order to spread out the catalyst

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particles over the solution surface while were being deaerated. Crosslinking was accomplished placing the dishes for 72 hours under environmental conditions.

The acetylation treatment of PVA consists in reacting PVA with 1,05, 2,10 and 3,15 mL of acetic anhydride (>99%, Riedel-de Haën), at 110 ºC and atmospheric pressure during 24 hours to prepare membranes with 10, 20 and 30% of acetylation degree, respectively. Finally, acetylated PVA was washed using solid-liquid extractor with acetone as extraction solvent and was dried at 80 ºC during 4 hours. To prepare acetylated membranes, treated PVA were subjected to the same procedure previously described with 10 wt. % of zeolite and 2 wt. % of glutaraldehyde.

The catalysts were characterized by thickness measurements, contact angles and swelling degree as well as by Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Catalytic tests were carried out in batch reactor at 100 ºC and atmospheric pressure with magnetic stirring and equipped with a reflux condenser. Catalytic membranes were cut in form of disks with 0,6 cm of diameter. Reactor was loaded with 12 mL of phenylacetaldehyde and 14 mL of glycerol, being the mass of catalyst different between each run. Samples were taken at regular time periods and analyzed by gas chromatography (GC).

Results and discussion

Table 1 shows the results of swelling degree and angle contact. It can be seen there is a strong affinity between water molecules and PVA chains when compared with glycerol and phenylacetaldehyde swelling values.

For catalyst loading effect, it appears to have a maximum value of water swelling degree on 10 wt% of zeolite, which suggests that the excess of zeolite reduce the mobility of PVA chains and, therefore, the capacity of retain water molecules. In the other hand, the increase of the amount of crosslinking agent shows that the water degree swelling diminishes while there is an increase of the angle contact values.

Table 1 –Results of swelling degree and contact angle of PVA membranes

Study	Code name	Swelling degree			Contact angle (º)
		Water	Glycerol	PhAct	
Catalyst Loading	PVA8C5GU2	255%	23%	11%	55,94
	PVA8C10GU2	280%	45%	23%	54,05
	PVA8C15GU2	229%	55%	29%	66,69
	PVA8C20GU2	211%	83%	31%	55,96
Crosslinked degree	PVA8C10GU4	268%	15%	25%	-
	PVA8C10GU6	218%	15%	18%	52
	PVA8C10GU8	-	43%	15%	56,09
	PVA8C10GU10	215%	31%	18%	57,25
Hyddrofilic/ hydrobobic properties	PVA8C10GU2ACT10	278%	115%	20%	56,36
	PVA8C10GU2ACT20	232%	91%	16%	59,86
	PVA8C10GU2ACT30	228%	104%	20%	61,6

The changes in the PVA chemical structure are shown in Figure 1 and Figure 3 by FTIR spectra, where the typical PVA pattern was recognized: a broad band around 3550-3200 cm^{-1} related to O-H stretching, a band around 3000-2840 cm^{-1} due to C-H asymmetrical and symmetrical stretching and the C-O-C at 1150-1085 cm^{-1} as well as CH_2 and CH_3 at 1461-1417 cm^{-1} [5].

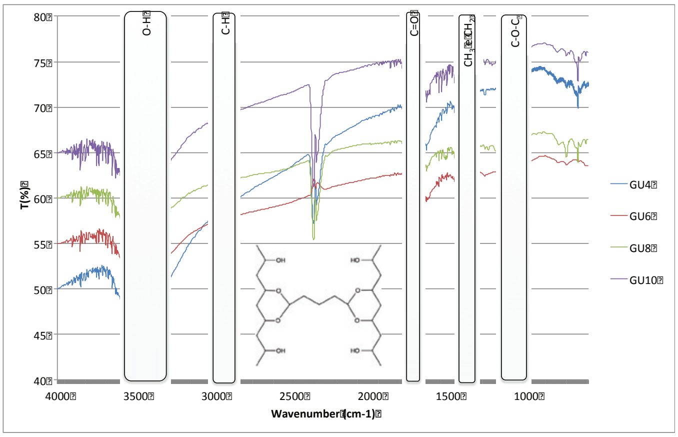

Figure 1 – FTIR spectra of PVA membranes with different crosslinking degrees.

A semiqualitative analysis was performed by absorbance ratio (Figure 2 and Figure 4) to confirm the effectiveness of crosslinking reaction and acetylation treatment. In Figure 2, it can be observed a decreasing of O-H ratio intensity and an increase of C-O ratio intensity with the increase of the amount of glutaraldehyde which supports the thesis that the crosslinking reactions consumes OH groups, replacing them by C-O-C that are characteristic of acetal bridges. It can also be observed an increase of C=O ratio intensity that suggests that an excess of glutaraldehyde can lead to some partial crosslinking reaction, resulting a free aldehyde group corresponded to the branches in the PVA chain.

In Figure 4, it can be observed that there is an increase of C=O ratio intensity, which is representative of acetate group, from fresh PVA to acetylated PVAs. However, among of acetylated PVAs there is no proportional increasing of this band as it was expected.

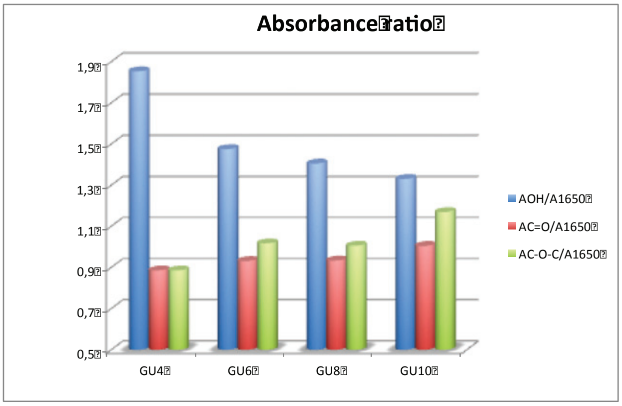

Figure 2 - Absorbance ratio of PVA membranes with different crosslinking degrees.

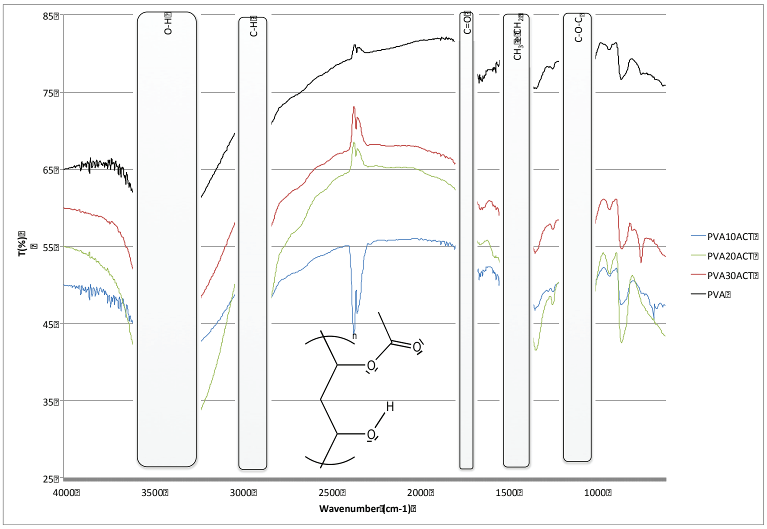

Figure 3 - FTIR spectra of PVA with different acetylation degrees.

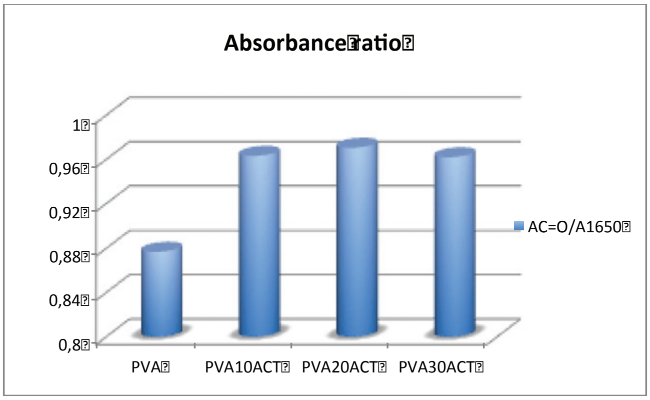

Figure 4 –Absorbance ratio of PVA with different acetylation degrees.

The morphology and topographic of some membranes surface can be observed in Figure 5, Figure 6 and Figure 7 by scanning electron and atomic force microscopies.

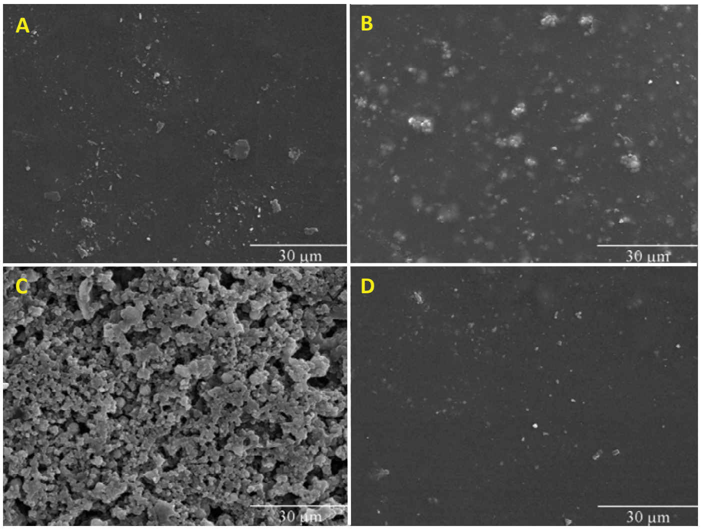

Figure 5-Surface images obtained by SEM of PVA8C5GU2 (A), PVA8C10GU10 (B), PVA8C10GU10 (C) e PVA8C10GU2ACT20 (D).

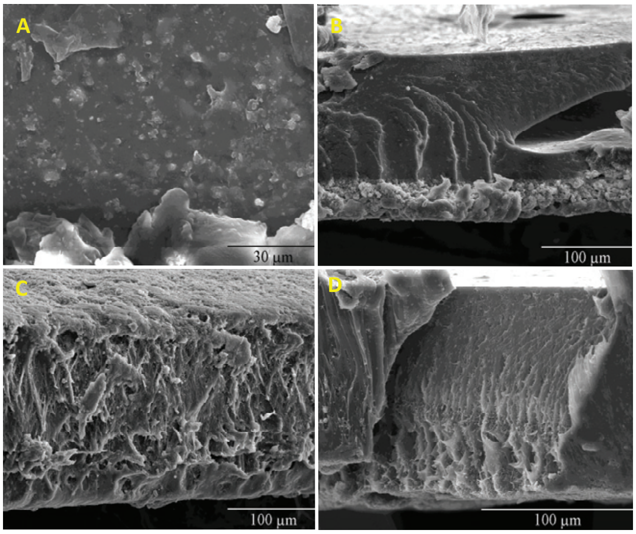

Figure 6 - Section images obtained by SEM of PVA8C5GU2 (A), PVA8C10GU10 (B), PVA8C10GU10 (C) e PVA8C10GU2ACT20 (D).

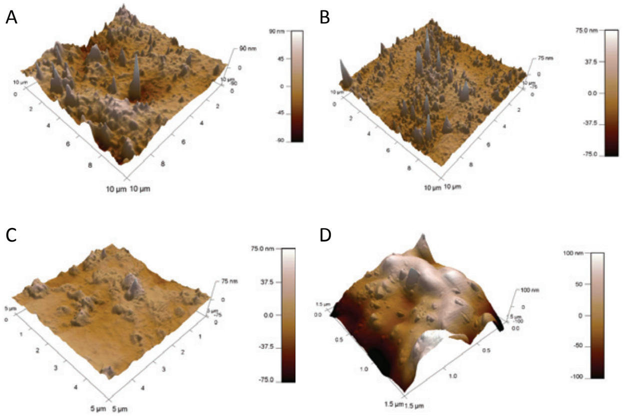

Figure 7 – Profile images of surface membranes obtained by SEM of PVA8C10GU2ACT10 (A), PVA8C10GU2 (B), PVA8C10GU10 (C) e PVA8C5GU2 (D).

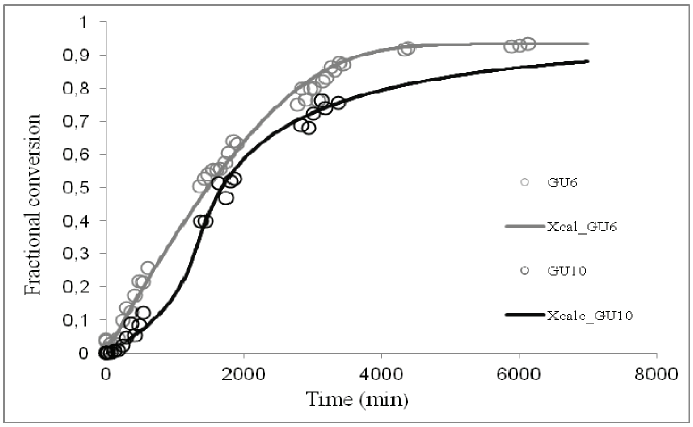

Figure 8 - Kinetic curves of two catalysts with different crosslinking degrees.

Figure 8 shows the effect of crosslinking on the conversion profile of the acetalisation reaction. The pronounced induction period observed with the membrane with 10% of crosslinking degree which is likely to be due to the acetal sorption in the polymer matrix. The fitting of a diffusion-kinetic model assuming fickian transport and dependence of the diffusivity of phenylacetaldehyde on the concentration of the formed acetal supports that hypothesis. The increase of crosslinking leads to the decrease of the calculated initial diffusivity probably due to the increased limitation of membrane swelling.

Conclusions

PVA membranes were successfully crosslinked with glutaraldehyde and have shown good catalytic activity in the acetalisation reaction of phenylacetaldehyde with glycerol.

The increase of catalyst loading seems to improve the membranes' transport properties (not shown). The polymer crosslinkig also strongly affects the membranes' transport properties

Acknowledgments

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