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Synthesis and characterization of hybrid PVA/Al_2O_3 thin film

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ABSTRACT

This paper presents the synthesis and characterization of hybrid PVA/Al_2O_3 thin film at room temperature (RT) and respectively under hydrothermal conditions (HC). The synthesis starts from commercially available Al_2O_3 and 10% PVA solution. When working at RT, regardless of the mixing ratio of PVA and Al_2O_3 (1:4; 1:1 and 4:1 wt) two phases can be identified by SEM due to the high difference between the densities of the two components. When working under HC, the hybrid PVA/Al_2O_3 thin film is homogeneous due to the reactions which occur between PVA and Al_2O_3 as proved by XRD and FTIR.

1. Introduction

Both alumina and polyvinyl alcohol (PVA) are extensively used in medical and non-medical applications due to their remarkable properties. Alumina has an excellent biocompatibility, high corrosion and abrasive resistance being used for over 20 years in orthopedics [1]. Polyvinyl alcohol (PVA) exhibit no toxic activity against the human body, is biodegradable, water soluble and has good physico-mechanical properties; the properties being influenced by polymerization as well as by hydrolysis degree [2].

The preparation of the membrane materials has received much attention in the past few years. Especially glass membranes and ceramic oxide membrane have been of interest. Commercial applications of alumina membranes can nowadays be found in the wine and beer clarification [3–5] and the pharmaceutical industry [6].

Hybrid materials have become one of the most interesting aspects of sol–gel techniques. This is mainly due to the fact that serious draw backs of inorganic sol–gel processing, for example crack formation in coatings, brittleness of sols or high curing and sintering temperatures necessary for complete densification can be overcome. On the other hand, the properties of these materials are in most cases restricted through the presence of organic groupings. For example the temperature stability or the fire resistance is far higher in inorganic materials, but the diffusibility is far higher in hybrids than in inorganic materials due to the free volume caused by organic groupings. On the other hand, due to the inorganic components in the backbone, a variety of properties superior to pure organic polymers is obtained, such as a higher modulus of elasticity or a higher abrasion resistance. Especially the abrasion resistance has been very attractive in the beginnings of the hybrid technologies [6].

New advances in preparation and study of ceramic membranes, such as the use of sol–gel process, template process, chemical vapor deposition, hydrothermal synthesis or modification of membranes, have allowed the preparation of ceramic membranes with narrow pore distributions and with nanometer pore-scale [7].

The purpose of this work is the preparation and characterization of hybrid PVA/Al_2O_3 thin film. The used synthesis method starts from PVA solution and commercial alumina powder. The compatibility of the two phases is assured by the HC which allows covalent bond formation between the alumina and PVA.

2. Experimental

The PVA solution was obtained by dissolving 10 g of PVA (polyvinyl alcohol 18–88, Fluka code 81365, MW = 130,000 g/mol; polymerization degree 2700, hydrolysis degree 86.7–88.7 mol%) in 100 mL solution at 90 °C. When working at RT, the hot PVA solution is cooled down before use.

PVA-Al_2O_3 hybrid materials are obtained starting from a corresponding amount of 10% (wt) PVA solution and Al_2O_3 powder (Sigma-Aldrich code 11028). Two synthesis routes were used: the first one being realized at room temperature (25 °C) while the second, being realized under hydrothermal conditions (~100 °C for 2 h, at a pressure of 1.5 atm). In both cases, three materials with different

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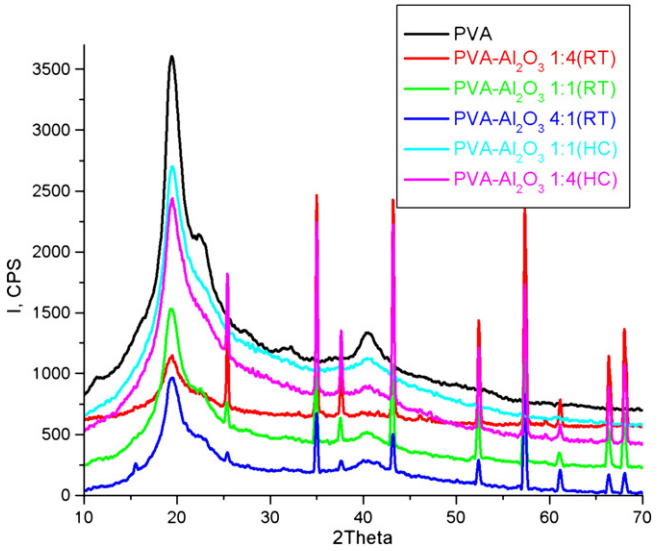

Fig. 1. XRD pattern of pure PVA and PVA-Al_2O_3 hybrid materials obtained at RT and under HC.

compositions were obtained, the weight ratio between the component being 4:1, 1:1 and 1:4. The drying step differs very much because under HC, during the homogenization step almost 90–95% of water is evaporated while in the case of RT synthesis the water is evaporated only in the drying step.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all cases the Cu Kα radiation from a Cu X-ray tube was used. The samples were scanned in the Bragg angle, 2θ range of 10–70° at a scan rate of 2° min^{-1}.

SEM images were obtained by HITACHI S2600N, before analysis all samples were covered with a thin silver layer.

Infrared spectroscopy (IR) measurements were performed using a Vertex 70 instrument (Brucker) with Fourier transformation (FTIR), equipped with an ATR module based on diamond crystal. The spectra were recorded over the wavenumber range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}.

Mechanical testings (tensile strength) were determined on a Walter Bai AG testing machine LFM 50KN.

For cytotoxic effect determination Annexin V-FITC Apoptosis Detection Kit I (BD Bioscience Pharmingen, USA) was used. Briefly, 5×10^5 cells were seeded in 3.5 cm diameter Petri dish and treated with 1 mg/ml compounds for 24 h. The total cells were resuspended in 100 µl of binding buffer and stained with 5 µl Annexin V-FITC and 5 µl propidium iodide for 10 min in dark. At least 10,000 events from each sample were acquired using a Beckman Coulter flow cytometer. The percentage of treatment affected cells was determined by subtracting the percentage of apoptotic/necrotic cells in the untreated population from percentage of apoptotic cells in the treated population.

For cell cycle analysis, diploid cells were treated with 1 mg/ml compound, and maintained for 24 h at 37 °C, 5%CO_2 and humid condition. Thereafter, harvested cells were washed in phosphate saline buffer (PBS) (pH7.5), fixed in 70% cold ethanol and maintained at −20 °C, overnight. Each sample was washed in PBS, treated with 100 µg/ml RNAse A for 15 min and coloured with 10 µg/ml propidium iodide by incubation at 37 °C, 1 h. After staining of cells with propidium iodide the acquisition was done using an Epics Beckman Coulter flow cytometer. Data were analysed using FlowJo 7.2.5 software (Ashland, Oregon, USA) and expressed as fractions of cells in the different cycle phases.

3. Results and discussion

The hybrid materials were obtained by two synthesis routes, the obtained hybrid PVA/Al_2O_3 materials being then compared especially from the point of view of microstructure and compatibility of the two phases.

From the visual point of view, the materials obtained at RT and respectively under HC differ very much to each other. The hybrid materials obtained under HC look very much like polymers, being translucent and flexible (if PVA:Al_2O_3 ratio is 4:1 or 1:1) and homogeneous, white (if PVA:Al_2O_3 ratio is 1:4) while the materials obtained at RT are white, asymmetric (the two sides of the thin films have different roughness) and inflexible–brittle.

3.1. X-ray diffraction

X-ray diffraction is a useful tool to characterize any material with crystalline domains, including polymers, ceramics or composite materials (Fig. 1). The interpretation of these analyses was based on the comparison with the XRD pattern of Al_2O_3 (ASTM 75-1862) and a control PVA material (obtained in the same condition as the composite but containing no alumina powder). Control PVA has limited

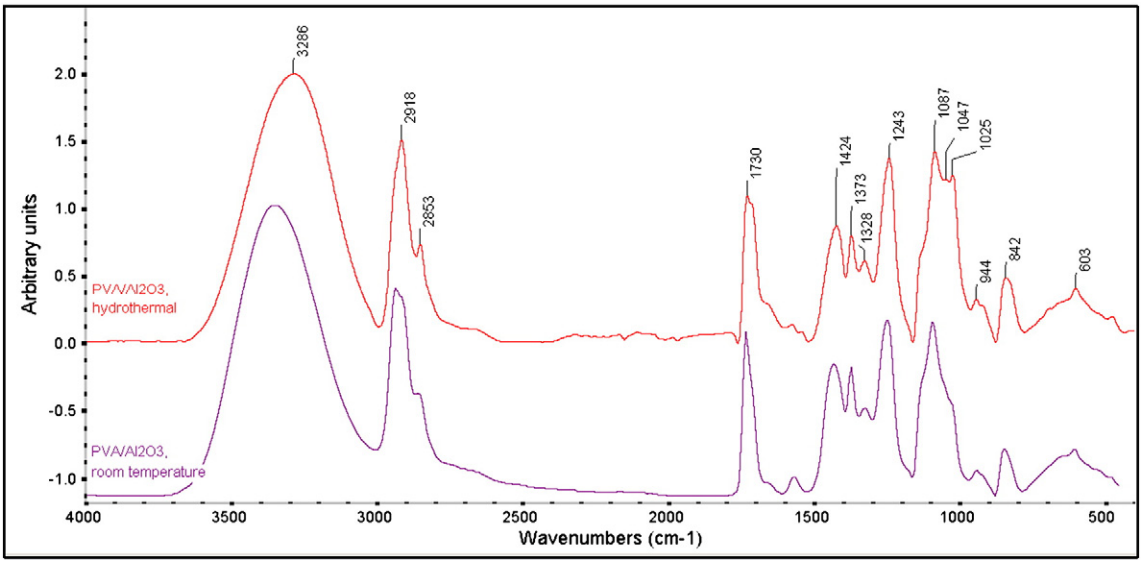

Fig. 2. Infrared spectra of the PVA-Al_2O_3 1:1 hybrid films obtained under the two conditions.