



Aminoalcohol functionalized zirconium phosphate as versatile filler for starch-based composite membranes



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ABSTRACT

Microcrystalline zirconium phosphate was exfoliated by treatment with aqueous solutions of α,ω -alkylaminoalcohols and employed for the fabrication of potato starch composite membranes. Glycerol-based and glycerol-free composite membranes, containing 5 wt% of filler, were prepared from gelatinized starch and characterized for their physico-chemical properties. Despite of a partial filler re-aggregation, as revealed by XRD and SEM analysis, all the composites exhibited a significant increase in the Young's modulus with respect to the glycerol-starch membrane, up to 80% and 190% for the glycerol-based and the glycerol-free composites, respectively. For both kinds of membranes the filler delays to a large extent the starch decomposition above about 300 °C. A significant reduction in the water uptake of the composites was also observed with respect to the neat glycerol-based membrane, up to about 70% for the glycerol-free composites.

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1. Introduction

Starch is an agricultural feedstock biopolymer found in a variety of plants. Its granules are actually formed by one branched (amylopectin) and one linear (amylose) polymer. It can be used as a natural filler material in the form of granules which can be incorporated into synthetic plastic matrices as rapidly biodegradable components (Kolybaba et al., 2003), or as biodegradable matrix, for the production of plastic materials. Starch-based plastics often contain glycerol or similar hydrophilic organic molecules, which are used as plasticizers to increase softness and pliability, but reducing, at the same time, mechanical strength and moisture stability (Talja, Helen, Roos, & Jouppila, 2007; Vieira, da Silva, dos Santos, & Beppu, 2011). Several examples in the literature report an improvement of the mechanical stability of plasticized starch films by incorporation of inorganic fillers, among which layered materials such as clays and zirconium phosphates (ZP) and phosphonates (Donnadio, Pica, Taddei, & Vivani, 2012; Pica, Donnadio, & Casciola, 2012). More specifically, recent works demonstrated that high aspect ratio ZP particles allow to improve the mechanical strength and to reduce the water uptake of glycerol-plasticized potato starch films (Pica et al., 2012), while zirconium phosphonate particles, bearing hydroxyalkyl amino phosphonic groups covalently bonded to the inorganic layers, allow to obtain flexible starch

films without using any plasticizing agent and exhibiting superior mechanical and thermal properties with respect to glycerol-starch films (Donnadio et al., 2012). Both these approaches exhibit advantages and drawbacks. On one hand ZP results to be an extremely versatile filler, since it is possible to effectively control the particle morphology, in particular the aspect ratio, by a suitable selection of the starting materials; on the other hand, due to the stiffness of the ZP particles, the use of plasticizing agents, such as glycerol, is generally required for the preparation of starch-based films. Differently, zirconium hydroxyalkyl amino phosphonates turned to be able to act both as reinforcing agent and as plasticizers for the starch matrix, allowing to obtain resistant films with good plastic properties; at the same time, the difficulty to control the morphology of the zirconium phosphonate particles did not allow to obtain a good degree of dispersion of the filler and, then, to reduce its loading within the starch matrix. Taking into account these considerations, it seemed of interest to combine the advantages deriving from the use of an extremely versatile filler, such as ZP, with those arising from the presence of organic species which should be able to interact with both ZP and starch, in order to obtain new glycerol-free starch composites.

In the present work, high aspect ratio ZP particles functionalized with aliphatic α,ω -aminoalcohols ($\text{NH}_2(\text{CH}_2)_n\text{OH}$, $n=3-6$, hereafter indicated as C_n) were used as fillers for a potato starch matrix. Differently from the previous work, in which the aminoalcohol functionalities were covalently anchored to the inorganic layer starting from preformed hydroxyalkyl amino phosphonates, in this case aminoalcohol functionalized ZP was obtained through

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a simpler and more versatile synthetic approach based on the aminoalcohol intercalation into preformed ZP. The aminoalcohol molecules, which are bonded to the ZP layers through ionic interactions involving the $-\text{PO}^-$ and the $-\text{NH}_3^+$ groups, are expected to act both as compatibilizers and as plasticizers for the polymer matrix through the hydroxyl groups which should form hydrogen bonds with the starch-OH groups. In order to investigate the ability of aliphatic aminoalcohols to act also as plasticizers for the starch matrix, glycerol-free starch membranes containing functionalized ZP particles were prepared, together with glycerol-based composites. The samples were characterized by structural, morphological and thermal analysis, mechanical tests and water uptake measurements.

2. Experimental

2.1. Materials

Native potato starch (amylose about 20%, amylopectin about 80%) was kindly supplied by Novamont. Zirconyl propionate ($\text{ZrO}_{1.27}(\text{C}_2\text{H}_5\text{COO})_{1.46}$, MW = 218 Da) was supplied by MEL Chemicals, England. All other reagents were supplied by Aldrich.

2.2. Preparation of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (ZP)

Microcrystalline $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, consisting of platelets with an average planar size of 2–3 μm , was prepared as reported by Capitani, Casciola, Donnadio, and Vivani (2010). 0.88 g of zirconyl propionate was solubilized, under stirring at room temperature, in 35 mL of an aqueous solution of oxalic acid so that the Zr(IV) concentration was 0.1 M and the $\text{H}_2\text{C}_2\text{O}_4/\text{Zr}$ molar ratio was 10. Then 1.43 mL of 14.8 M H_3PO_4 was added so that the $\text{H}_3\text{PO}_4/\text{Zr}$ molar ratio was 6. The resulting solution was heated for 24 h at 80 °C in a closed plastic bottle. The precipitate thus obtained was separated from the solution by centrifugation at 3000 rpm, washed three times with 10^{-3} M HCl, dried overnight at 80 °C, and finally kept in a desiccator over a saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (53% relative humidity, RH).

2.3. Preparation of the colloidal dispersions of ZP and α,ω -alkylaminoalcohols (C_n , $n = 3\text{--}6$)

Four colloidal dispersions of ZP containing the same amounts of C_n were prepared as follows: 0.25 g of microcrystalline ZP was suspended in 16.3 mL of deionised water. Then, 8.6 mL of a 0.1 M solution of C_n was added dropwise and under vigorous stirring to the previous suspension, so that the C_n/Zr molar ratio was 1. Colloidal dispersions of $\text{ZP}\cdot\text{C}_n$ (hereafter $\text{ZP}\cdot\text{C}_n$), were obtained and left under stirring for 24 h. In order to prove that the aminoalcohol molecules are quantitatively taken up by ZP, the pH of both C_n solutions and $\text{ZP}\cdot\text{C}_n$ dispersions was measured. As an example, the pH of the 0.1 M C_3 solution was 10.7, while that of the dispersions obtained after the reaction of ZP with C_3 was 6.5 ± 0.2 and in all cases was in the range 6–7, thus indicating that the fraction of neutral C_n molecules in the solution is negligible.

2.4. Preparation of the composite starch membranes containing $\text{ZP}\cdot\text{C}_n$

Starch films, plasticized with glycerol, containing 5 wt% $\text{ZP}\cdot\text{C}_n$ (hereafter GS/ $\text{ZP}\cdot\text{C}_n$) were prepared as follows. One gram of NS was dispersed in 25 mL of water and heated at 90 °C for 10 min until gelatinization occurred. A weighed amount of the $\text{ZP}\cdot\text{C}_n$ dispersion was added to the starch gelatine and the mixture was left at 90 °C under stirring for 20 min; then a glycerol amount of 0.25 g was added to the previous mixture and left at 90 °C under stirring

for 20 min. The final dispersion was cast on a polystyrene dish and left in an oven at 40 °C overnight.

By using the same kind of procedure a starch/glycerol film (hereafter GS), a glycerol free starch film (S) and glycerol-free composite starch films containing the same amount of $\text{ZP}\cdot\text{C}_n$ per gram of starch were also prepared: these composites will be hereafter indicated as S/ $\text{ZP}\cdot\text{C}_n$. Due to its high rigidity and brittleness, which hampered the film handling, the S sample was used only to compare the structural and thermal properties. All films were 95–105 μm thick.

2.5. Techniques

2.5.1. X-ray diffraction

X-ray diffraction patterns of powders and cast films were collected with a Philips X-Pert powder diffractometer, a PW3020 goniometer equipped with a bent graphite monochromator on the diffracted beam, a PW3011 detector using the Cu-K α radiation source with 2θ step size of 0.030° and step scan of 0.5 s. The LFF ceramic tube operated at 40 kV, 30 mA.

The crystallite size (t), along the c -axis, were determined applying the Scherrer equation, $t = K\lambda/\beta\cos\theta$, in which K was set to 0.9, and $\lambda = 1.5406 \text{ \AA}$. The integral breadths of the (002) peaks, β , were evaluated for all the samples by fitting the peaks with a pseudo-Voigt function, and corrected for the instrumental broadening contribution, that was previously evaluated by the Rietveld refinement of the profile of lanthanum hexaboride, LaB_6 , as external peak profile standard. LaB_6 was provided by The Gem Dugout-Deane K. Smith, 1652 Princeton Drive, State College, PA 16803.

2.5.2. Thermogravimetric analysis

Thermogravimetric determinations were carried out by a NETZSCH STA 449 Jupiter thermal analyser connected to a NETZSCH TASC 414/3 A controller at a heating rate of 10 °C/min, with an air flow of about 30 mL/min. Before measurements, all samples were equilibrated at 33% R.H.

2.5.3. SEM analysis

Scanning electron microscopy (SEM) images were collected by a Zeiss LEO 1525 FE SEM. The composite films were fractured in liquid N_2 . All samples were coated with a thin layer of carbon before SEM observation.

2.5.4. Mechanical tests

Mechanical tests were carried out by a Zwick Roell Z1.0 testing machine, with a 200 N static load cell. Young's modulus (slope of stress-strain curve at low values of strain), tensile strength (maximum force used during measurement) and elongation at break (ratio of elongation to original length of sample at break) were measured on rectangle shaped film stripes, obtained by a cutting machine, length and width of which were 100 mm and 5 mm, respectively. Before testing, samples were equilibrated for 7 days in vacuum desiccators at 33% RH and room temperature (20–23 °C) and the thickness of the film stripe, determined with an uncertainty of $\pm 5 \mu\text{m}$, was in the range 95–105 μm . An initial grip separation of 10.000 ± 0.002 mm and a crosshead speed of 5 mm/min was used. All tests were carried out at room temperature (20–23 °C). Both the uncertainty, deriving from the sample size determination, and the standard deviation, resulting from the analysis of five film stripes for each sample, were considered for statistical analysis. The data were elaborated by the TestXpert V11.0 Master software.

2.5.5. Water vapour uptake

The samples were dehydrated over P_2O_5 before being conditioned in the presence of water vapour. Then, films were equilibrated, at room temperature, at 90% RH for one week. The water uptakes (%w.u.) were calculated from the increase in mass

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