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Interface design and reinforced features of arrowroot (*Maranta arundinacea*) starch/polyester-based membranes: Preparation, antioxidant activity, and cytocompatibility

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ABSTRACT

The structural, mechanical, antioxidant, and cytocompatibility properties of membranes prepared from the polyhydroxyalkanoate (PHA) and arrowroot (*Maranta arundinacea*) starch powder (ASP) blend (PHA/ASP) were studied. The acrylic acid-grafted PHA (PHA-g-AA) and the coupling agent treated ASP (TASP) were used to enhance the desired characteristics of these membranes. The PHA-g-AA/TASP membranes had better mechanical properties than the PHA/ASP membrane. This effect was attributed to greater compatibility between the grafted PHA and TASP. The water resistance of the PHA-g-AA/TASP membranes was greater than that of the PHA/ASP membranes, and a cytocompatibility evaluation with human foreskin fibroblasts (FBs) indicated that both materials were nontoxic. Moreover, both ASP and TASP enhanced the polyphenol content and antioxidant properties of the membranes. PHA-g-AA/TASP and PHA/ASP membranes had better antioxidant activity than the control group.

1. Introduction

The rhizome of arrowroot (*Maranta arundinacea)* is rich in starch that is effective in disease prevention and a useful biomedical source material [1–3]. Arrowroot starch is mainly produced in Asia, Latin America, and Africa [4], and is multifunctional, non-toxic, biodegradable, blood-compatible, and bioactive [5,6]. Arrowroot starch contains puerarin and is a natural source of polyphenols [7,8]. Arrowroot starch is able to scavenge free radicals and remove reactive oxygen species (ROS). As such, the oxidative stress generated by free radicals is inhibited by arrowroot starch and cells are protected from damage by ROS, preventing the onset of diseases such as diabetes, cardiovascular disease, high blood pressure, and cancer [9–11]. At present, arrowroot starch is used in food (e.g., thickening agent or dietary fiber), textiles, biomass materials (bioethanol), cosmetics (e.g., toilet powder and emulsifier), and drugs (drug carrier) [12–14]. However, because arrowroot starch cannot easily be hot-processed, its applications in industry and biomedical materials are limited. To increase the functionality of arrowroot starch, it is blended with biomedical polymers to make biocomposites, creating a biomaterial with more functional applications.

The main biomedical polymers used in recent years are polylactic acid (PLA), polyvinyl alcohol (PVA), polyhydroxyalkanoate (PHA), and polyethylene glycol (PEG) [15–17]; PHA is the most extensively used material at present. Because PHA can be generated in cytoplasm when microorganisms impel innutritious elements in the presence of an excessive carbon source, it has good biocompatibility, biodegradability, and mechanical properties [18,19]. To extend the application of PHA to biomedical materials and enhance its functionality, the composite is mixed with additives such as starch, keratin, chitosan, and collagen [20–22]. However, blending PHA with additives is likely to enhance its material cladding properties and binding force.

In this study, PHA was used as a substrate and implemented in a grafting modification, wherein arrowroot starch was treated with coupling agent to enhance its mechanical properties. An arrowroot starch composite membrane was produced. The antioxidation activity, polyphenol content, cell viability, and structural identification of the composite membrane were evaluated. Our results demonstrated the enhanced functionality of arrowroot starch/polyester-based membranes for applications in the fields of drugs, food, cosmetics, and biomedical engineering packaging material.

2. Experimental

2.1. Materials

Commercial-grade polyhydroxyalkanoate (PHA) (EM 5400F, Mw: 596,000) was obtained from Shenzhen Ecomann Biotechnology Co., Ltd. (Shenzhen, China). Tetraethoxysilane (TEOS) was obtained from SMS, Merck Chemical Co. (Frankfurt, Germany). Acrylic acid (AA), dicumyl peroxide (DCP), 2,2-diphenyl-1-picrylhydrazyl (DPPH),

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sodium carbonate (anhydrous) (Na_2CO_3), gallic acid monohydrate, Folin–Ciocalteu phenol reagent, and dimethyl sulphoxide (DMSO) were purchased from Sigma–Aldrich Corp. (St. Louis, MO, USA). 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolelium bromide (MTT) was acquired from Promega Corp. (Madison, WI, USA). Fetal bovine serum (FBS) and Dulbecco's modified Eagle's medium (DMEM) were purchased from Gibco-BRL (Gaithersburg, MD, USA). All buffers and other reagents were of the highest-purity commercial grade available. Arrowroot (*Maranta arundinacea*) starch was obtained from Tainan (Taiwan, R.O.C.).

2.2. Modification of the PHA copolymer: grafting reaction of AA onto PHA

As a preliminary test, 180 mL of dichloromethane as a solvent was added to a round-bottomed flask, and a mixture of 6.0 g AA and 1.8 g DCP was added in four equal portions to the molten 54.0 g PHA at 2-min intervals to allow the grafting reaction to take place. The reactions were performed in a nitrogen (N_2) atmosphere at 50 ± 1 °C. Preliminary experiments showed that equilibrium was attained in less than 12 h; therefore, all reactions were allowed to progress for 12 h with stirring at 60 rpm. Samples of 4 g of product were dissolved in 200 mL of refluxing dichloromethane at 60 ± 2 °C, and the solution was filtered through several layers of cheesecloth. The dichloromethane-insoluble product remaining on the cheesecloth was washed with 600 mL of acetone to remove unreacted AA and then dried in a vacuum oven at 70 °C for 24 h. The AA loading of the dichloromethane-soluble polymer was determined by titration and expressed as the grafting percentage [23], which was 5.96 wt%; the loadings of DCP and AA were maintained at 0.3 and 10 wt%, respectively.

2.3. Processing of ASP and TASP

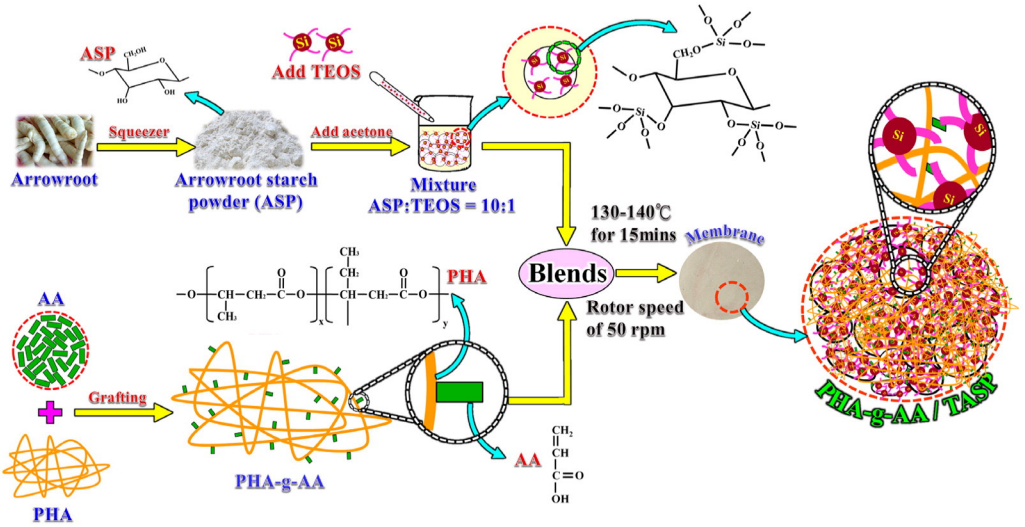
The processing of arrowroot (*Maranta arundinacea*) starch powder (ASP) and coupling agents treated ASP (TASP) was shown in Scheme 1. For the preparation of ASP, the fresh arrowroot was soaked in water to separate foreign soil matter, and the arrowroot was squeezed. The arrowroot starch was dissolved in water by washing. A 60-mesh filter cloth filtration treatment was performed to remove the fiber and other impurities. The arrowroot starch mucilage was kept still for 12 h. The supernatant was then removed and placed in a 105 °C oven for 2 days. The dried arrowroot starch was removed and ground in a grinder to a 300–400 mesh size. For the processing of TASP, a 5-g ASP sample was placed in a beaker and mixed with 0.5 g of silane coupling agent and acetone for 12 h. The bottle neck was sealed with a membrane and kept at room temperature for 12 h. The sample was then washed with acetone. Finally, the sample was dried in an 80 °C oven for 1 day.

2.4. Sample preparation

The ASP or TASP was oven-dried at 80 °C for 2 days prior to composite preparation. The mass ratios of ASP or TASP to PHA or PHA-g-AA were fixed at 10/90, 20/80, 30/70, and 40/60. The composites were prepared in a Plastograph 200-Nm Mixer W50EHT with a blade rotor (Brabender, Dayton, OH, USA). Mixing was performed at 130–140 °C for 15 min at a rotor speed of 50 rpm. Residual AA in the PHA-g-AA reaction mixture was removed *via* acetone extraction prior to the preparation of the PHA-g-AA/TASP. After mixing, the composites were pressed into thin plaques with a 140 °C hot press and placed in a dryer for cooling, after which they were cut into standard sample dimensions for further characterization.

2.5. Measurements

Infrared spectra of the samples were obtained using an FTS-7PC Fourier-transform infrared (FTIR) spectrophotometer (Bio-Rad, Hercules, CA, USA). The spectra show the results obtained at 2-cm^{-1} resolution between 400 and 4000 cm^{-1}, with collection times of ~1 min. X-ray diffraction (XRD) data were recorded using a D/max 3-V X-ray diffractometer (Rigaku, Tokyo, Japan) with a Cu target and Kα radiation at a scanning rate of 2° min^{-1}. The mechanical properties, including the tensile strength and elongation at break, of the dumbbell-shaped samples (according to ASTM-D638) were measured using a mechanical tester (model LR5K; Lloyd Instruments, Bognor Regis, West Sussex, UK) at a crosshead speed of 10 mm min^{-1}. The mechanical properties of five specimens were evaluated to obtain a mean value. Specimens were pulled according to the ASTM D638 standard. After rupture, a membrane section of the fracture plane was removed. The membrane sections were coated with gold, and the fracture surface morphologies were observed using scanning electron microscopy (SEM, Hitachi Microscopy Model S–1400, Tokyo, Japan). Water absorption was evaluated by determining the weight gained by the dried samples after immersion in distilled water for different time periods. The samples were dried in a vacuum oven at 50 ± 2 °C for 12 h, cooled in a desiccator, and then immediately weighed to the nearest 0.001 g; this mass was designated as m_c. The average mass measured at 1-day intervals, designated as m_w,



Scheme 1. Fabrication of composite membranes from acrylic-acid-grafted (AA)-grafted polyhydroxyalkanoate (PHA) (PHA-g-AA) and coupling-agent-treated arrowroot (*Maranta arundinacea*) starch (TASP).