An insight into the properties of *Aegle marmelos* pectin–chitosan cross-linked films

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ABSTRACT

Pectin of *Aegle marmelos* (AP) ripe fruits processed in equal proportion with chitosan (CH) formed films that exhibited minimum swelling index and volume index on exposure to buffers of acidic and alkaline pH. Highest contact angle and spreading coefficient coupled with lowest work of adhesion in all buffers for this film suggested availability of limited number of functional groups for interaction with water molecules due to optimum cross-linking between $-NH_3^+$ groups of CH and $-COO^-$ groups of AP. This contention was substantiated by the presence of almost negligible charge on this film. The endothermic transition ΔH characteristic of $-NH_3^+-COO^-$ cross-linking between groups in this film was observed to decrease by only 1% after its sequential exposure to pH 1.2 (3 h) and pH 7.4 (6 h). Furthermore, the absence of pores or erosion in the scanning electron photomicrograph suggested the versatility of this film due to its resistance to acidic and alkaline pH.

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1. Introduction

Films play a multifacet role in food packaging and pharmaceutical products. They are often used for modifying drug release characteristics from pharmaceutical dosage forms. Films are also useful in reducing water vapor and gaseous permeation. The properties of films depend on the type of material used and the process conditions employed which in turn determine their applications. Although, synthetic polymers are good film formers and provide reproducible performance, they lack the benefits of biodegradability and biocompatibility. Natural polysaccharides, on the other hand, are well tolerated due to their non-toxic nature and possess the distinct advantage of being abundantly available, biodegradable, biocompatible and multifunctional due to the presence of different functional groups. It is due to these properties that natural polymers offer vast opportunities to the scientist for cross-linking with other ions/polymers in bid to design new biodegradable materials for specific applications.

Aegle marmelos fruit is a good source of pectin. The ripe fruits (commonly called Bael in Hindi language) are edible and are advocated for use in diarrhea, gastroprotection, ulcerative colitis and diabetes [1]. The pectins present in *A. marmelos* fruit (AP)

contribute to the adhesive property of its aqueous dispersions. However, this abundantly available gum is known to possess moderate film forming property that adversely affects its utilization in food formulation and drug delivery systems. The bael gum contains galactouronic acid indicating the presence of free $-COO^-$ moieties. One option for enhancing its application in food and pharmaceutical industry could be to co-process it with a good film forming polymer. Chitosan (CH) is a well known, widely investigated polysaccharidic polymer carrying positive charge due to presence of $-NH_3^+$ groups. However, both AP and CH are poor film formers and readily dissolve in acidic pH when used alone. These properties of AP and CH limit their applicability in their putative form.

The presence of $-COO^-$ in AP and $-NH_3^+$ groups in CH can be expected to interact to yield a AP–CH composite complex. Interaction between $-COO^-$ or $-HSO_3^-$ groups of chondroitin sulfate [2], sodium citrate [3], sodium alginate [4] with chitosan has been reported. These films have been investigated for rectification of mechanical weakness [5,6], decreasing water solubility [7,8] and improving drug delivery in colo-rectal drug release dosage forms [9], sustained release drug delivery systems [10] and transdermal film formulations [11]. On these lines it is logical to contemplate the interaction of $-COO^-$ groups present in galactouronic acid moieties of AP with $-NH_3^+$ groups present in CH molecules. This interaction can be hypothesized to improve the functional properties of putative AP and CH as well as film forming property of AP.

Hence, the present investigation was aimed at developing a interpolymer association between AP and CH and evaluating the

physico-mechanical and electrical attributes of the films formed by their association.

2. Experimental

2.1. Materials

A. marmelos fruits, fully ripe were collected from local market. AP extracted from ripe fruits was stored in airtight polypropylene jars in desiccated condition. De-ionized (Milli-Q) water was used for all experiments. All other chemicals used were of analytical reagent grade.

2.2. Extraction of AP

AP was extracted by using a modified method reported earlier [12]. In brief, ripe fruits were collected from the *A. marmelos* tree being grown at Punjabi University, Patiala, India campus. Inner ripe mass was washed and extracted with HCl (1 N) solution (Scheme 1). Equal quantities of water and extract were added and boiled for 25 min. The extract was strained through muslin cloth, cooled, mixed with potassium meta-bisulfite, and filtrate was kept overnight for clarification. The supernatant was concentrated, precipitated with alcohol, vacuum dried, and powdered. The pectin was further purified by dialysis and purified AP was freeze dried.
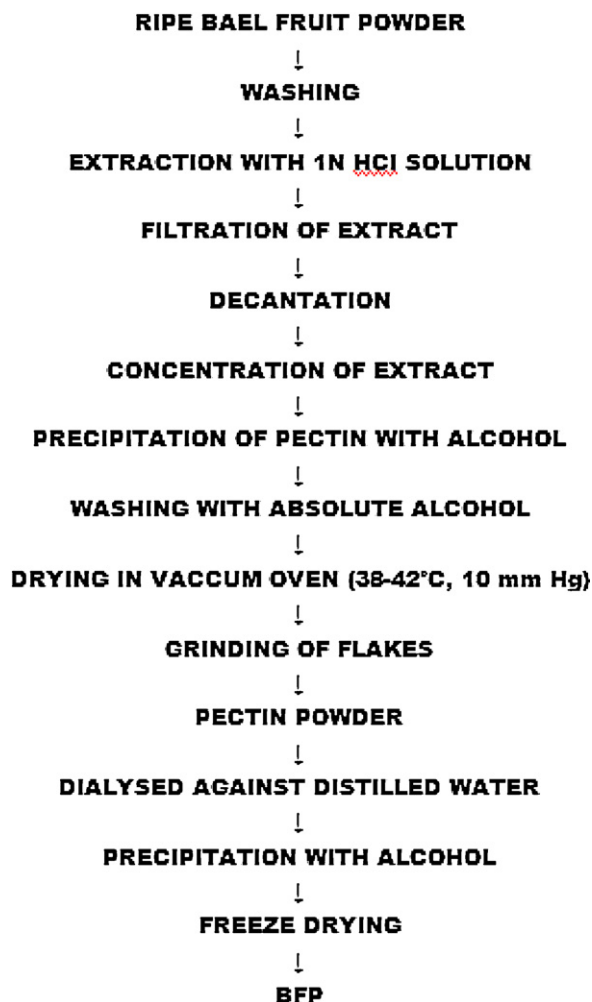
Scheme 1. Brief outline for extracting pectin from ripe fruits of *Aegle marmelos*.

2.3. Preparation of CH–AP solution

The total concentration of polymer was fixed at 2% (w/v). CH was dissolved in 2% (v/v) acetic acid. AP was dissolved separately in water. Ammonium acetate (5 M) solution was prepared in water and equally distributed in AP and CH solutions. The CH solution was then added to AP solution drop wise with continuous stirring to obtain clear CH–AP solution.

2.4. Preparation of CH–AP film

The CH–AP films were prepared by spraying CH–AP solution employing spray gun (5 ml/min) with the help of peristaltic pump using spray gun of 1 mm nozzle (Electrolab, PP20IV, Mumbai, India) on non-sticky surface of rotating drum with hot air blown at 50 °C for solvent evaporation. The dried films were microwaved (85 W, 15 s, 5 cycles) to remove bound water from the films. The films were stored in large size sealed packs till further use.

2.5. Physical characterization of films

2.5.1. Swelling index (SI)
SI [13] of the CH–AP films was determined after exposing the films to buffers of different pH (1.2, 7.4 or 6.8). The swelling index was calculated according to the formula:

$$SI = \frac{W_2 - W_1}{W_1}$$

where W_1 is the initial weight of the film and W_2 is the weight of the swollen film.

2.5.2. Volume of films (V_f)
V_f in the swollen state was obtained by determining its weight in air (W_{air}) and in n-heptane (W_h), a non solvent for the CH:AP films and calculated using the buoyancy principle:

$$V_f = \frac{W_{air} - W_h}{\rho_h}$$

where ρ_h is the density (0.684 g/cm^2) of n-heptane.

2.5.3. Volume index (V_i)
V_i was obtained by determining its volume in air (V_{air}) and in n-heptane (V_h) and calculated using the buoyancy principle:

$$V_i = \frac{V_{air} - V_h}{V_h}$$

2.5.4. Film surface contact angle with buffer pH 1.2, 7.4
Contact angle of the prepared films with buffer pH 1.2, 7.4 or 6.8 was determined by employing digital camera (NIKON, 14.2 MP, 10× zoom, in Mega mode). 200 μl of respective buffer solution was placed gently over the film surface with the help of a micro pipette and the images captured were magnified and printed on A4 paper. The contact angle of the drop was calculated manually. The results reported represent mean of twelve determinations.

2.5.5. Work of adhesion (W_a)
W_a was calculated by using the value of contact angle obtained above:

$$W_a = \gamma_L(\cos\theta + 1)$$

where γ_L is the surface tension of the respective buffer calculated using stalgamometer method.