International Journal of Biological Macromolecules 76 (2015) 138–145

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Alternative plasticizers for the production of thermo-compressed agar films

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ARTICLE INFO

Article history:
Received 2 January 2015
Received in revised form 10 February 2015
Accepted 20 February 2015
Available online 26 February 2015

Keywords:
Agar
Urea
Choline chloride
Mechanical properties
Response surface methodology
Central composite rotatable design

ABSTRACT

Agar films were produced by thermo-compression using choline chloride (ChCl) as a plasticizer with urea. The three solid components were mixed together with the salt and urea (minor components) added to agar (main component) according to a fixed mass ratio of, respectively, 1.16:1:5. A central composite rotatable design (CCRD) with three parameters, 2^3, was used to evaluate the effects of temperature (X_1; °C), time (X_2; min) and applied load (X_3; kN) of heat-pressing on the maximum tensile strength (*TS*) of the films (*Y*; MPa). Mixtures of urea and agar prepared at a mass ratio of 1:5 did not form homogeneous films suggesting the important plasticizing role of the salt. Heat-pressing the mixtures at more draconian conditions led to much darker and opaque films, with better mechanical resistance (higher values of *TS*). The most resistant film (~15 MPa) was obtained at 140 °C, 20 min and 176 kN. Selected films, including the optimal, showed similar water sorption profiles and close values of water vapor permeability (~2.5–3.7 × 10^{-9} g m^{-1} s^{-1} Pa^{-1}). The fracture behavior and mechanical properties of the films were greatly affected by additional water plasticization when the films were stored at different conditions of relative humidity.

1. Introduction

Current trends of the bio-plastic sector include cost-effective polyolefins from bio-based origin with similar performances to their synthetic equivalents [1,2]. Good examples of these materials used to manufacture numerous commodity goods are polyethylene and/or polypropylene, polymerized from monomers resultant from biorefinery processes [1]. As their synthetic equivalents, these bio-polyolefins are not biodegradable.

Bio-plastics made from natural polymers directly separated or extracted from living biomass (e.g. cellulose, starch, seaweed polysaccharides) do not show competitive performances and/or prices with bio-polyolefins [3]. However, they can biodegrade under appropriate conditions, be easily processed and have shown good properties to be used as bio-plastics [4–7]. Moreover, some of these materials do not compete with food nor imply land cultivation of raw materials. This is the case for instance of bio-plastics made from seaweed and/or seaweed polysaccharides [8–10].

Agar is a polysaccharide extracted from selected marine red seaweeds [11]. Like other gelling gums, agar is mainly used as gelling, thickening or stabilizing agent in a wide range of applications in areas such as food, biotechnological, biomedical and pharmaceutical [5,12]. Several researchers have also tested with success the ability of agar to form films [10,13–23].

In recent decades, polymer specialists have been challenged to find new and sustainable solutions that can make bio-plastics more cost-attractive and performance-competitive with conventional plastics. One possible strategy to improve the properties of bio-plastics is the use of additives such as plasticizers. Plasticizers can improve the polymer's processability and deformability, reduce brittleness and in some cases, lower the cost of the plastic material. Ideally, these small compounds should also be non-toxic, biodegradable, non-volatile and be well incorporated in the polymer matrix [24]. Glycerol has been one of the most used plasticizers to improve the properties of agar films [10,13,16,18–23,25].

Very recently, our group has explored deep eutectic solvents (DES), based on the quaternary ammonium salt (2-hydroxyethyl)trimethylammonium chloride (choline chloride, ChCl), to fabricate thermo-compressed agar films [26]. The low cost, biodegradability and non-toxicity of ChCl make it a very attractive compound to explore [27]. In this early study, the DES was the main

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http://dx.doi.org/10.1016/j.ijbiomac.2015.02.030
0141-8130/

component of the film, acting as solvent and plasticizer, and agar was the minor component (2–6 wt%). The films showed improved mechanical properties (high elongations, $E \sim 15.4$–39%, without significant losses in the tensile strength, $TS \sim 24$–42 MPa; [26]) when compared to agar films made by traditional casting methods and using water as solvent. However, the proposed method to obtain the films was laborious and had some drawbacks, namely the need for solvent removal with ethanol washings [26]. In a different approach, Abbott et al. used ChCl as a plasticizing agent with urea to fabricate thermoplastic starch (TPS) [28]. The authors found that the salt acted as a bridge between the urea and the sugar units in TPS, helping to break the intramolecular hydrogen bonds.

In the present study, we describe a greener and less laborious method for the production of agar films by thermo-compression using alternative plasticizers. Following Abbott's approach, ChCl was used as a plasticizing agent with urea (minor components) to fabricate agar films where the polymer was the main component. A central composite rotatable design (CCRD) with three parameters, 2^3, was used to evaluate the effects of temperature (X_1; °C), time (X_2; min) and applied load (X_3; kN) of heat-pressing, on the tensile strength (TS) of agar films (Y; MPa). The obtained films were characterized in terms of their color and opacity while selected samples were further investigated by scanning electron microscopy (SEM) and characterized in terms of their water sorption behavior and water vapor permeability (WVP). Finally, the stress–strain profiles were recorded after storing the films at different conditions of relative humidity to observe their fracture behavior upon water plasticization.

2. Materials and methods

2.1. Chemicals

The urea (>99%: CH_4N_2O), choline chloride (> 98%: $C_5H_{14}ClNO$) and commercial agar (A-7002, St. Louis, MO, $(C_{12}H_{18}O_9)_n$) used in the experiments were purchased from Sigma–Aldrich Co.

2.2. Mixture preparation

ChCl (70 °C) and agar (40 °C under vacuum) were dried overnight prior to use. The appropriate amounts of agar, salt and urea were then weighed and mixed thoroughly with a pestle and mortar for 20 min. Each time, the salt and urea were added to agar according to respectively, the following mass ratio, 1.16:1:5. Finally, the mixture was left to rest in an oven at 70 °C for 20 min before being thermo-compressed at the desired conditions.

2.3. Thermo-compression

1.5 g of mixture, prepared as described in Section 2.2, was compacted between two stainless steel plates covered with aluminum foils and thermo-compressed in a hydraulic press (Carver, model 3856CE, Carver Inc., IN, USA) at various conditions of temperature, time and applied load. The hot polymer film was left to cool down between plates (typically ~ 20 min) before being separated from the aluminum foils.

2.4. Optimization strategy

Response surface methodology (RSM) was used to obtain the process parameters that led to agar films with maximum mechanical resistance. This statistical tool can be particularly useful in the study of complex processes where several parameters (independent variables) affect the response (dependent variable). RSM reduces the number of experiments needed to evaluate the influence of multiple variables and their interactions in the measured response [29].

In our study, a central composite rotatable design (CCRD) with three factors, 2^3, was used to evaluate the effects of temperature (X_1; °C), time (X_2; min) and applied load (X_3; kN) of heat-pressing, on the tensile strength (TS) of the films (Y; MPa; dependent variable). The CCRD is able to explore factor levels outside the ranges defined for the factorial design [29]. The independent variables (i.e. X_1, X_2, X_3) as well as their experimental domains were chosen according to preliminary tests. The composition of each mixture used to fabricate the films was kept constant. The percentage of urea was fixed at 20 wt% per dried agar amount and the ChCl was added accordingly, to obtain a final ChCl:urea:agar mass ratio of 1.16:1:5. This decision was based on the observed difficulty in obtaining homogeneous films when using lower/higher contents of plasticizer (10, 30 and 40 wt% urea per dried agar amount) and also due to the need of ensuring that the salt and urea in each film were at the same eutectic proportion than the one used to fabricate the DES in our previous study [26].

The CCRD requires five levels of each factor and a total of 20 runs to estimate the model coefficients: 8 points of a factorial design at levels $\alpha = \pm 1.000$, 6 star points at a distance $\alpha = \pm 1.682$ from the center and 6 replicates of the center point (runs 15–20 in Table 1). The 6 replicates at center point allowed estimating the experimental error and checking the fit. The results in the initial set of experiments (runs 1–8 in Table 1) were fitted to a first order model and its adequacy was checked. Here, the lack of fit was significant ($p < 0.05$), probably due to a quadratic effect and so, additional runs were performed to improve the model adjustment (runs 9–14 in Table 1). Finally, the experimental data of the 20 runs were approximated to a second order model [29],

$$Y_i = b_0 + \sum_i b_i X_i + \sum_{ij} b_{ij} X_i X_j + \sum_i b_{ii} x_i^2 + \varepsilon \quad (1)$$

where Y_i is the experimental response, X_i are the studied factors, b_0 is the average response, b_i are the average effects of the different factors, b_{ij} are the average effects of second interaction factors, b_{ii} are the quadratic components and ε is the experimental error. The lack of fit in the second order model is desired to be not significant and, if it persists, steepest ascent method should be used [29].

The adequacy of the model was checked by multifactor analysis of variance (ANOVA) which included the Fisher's test and its associated probability $p > F$ (significant if p-value < 0.05 for a 95% confidence level), the determination of the quadratic correlation coefficient (R^2) and the lack-of-fit (non-significant if p-value < 0.05 for a 95% confidence level). The significances of each regression coefficient and effects were determined by the Student's t-test and the associated probabilities ($p < 0.05$). The second order model was represented as 3D surface plots where two factors were varied and one fixed at its 0 level value, to map the obtained response in terms of the variation of the process parameters. The optimal conditions of thermo-compression were obtained by inspection of the plotted surfaces and based on ANOVA. All experiments were performed in randomized order to minimize bias effect. The statistical analyses were made using the *Statistica 8.0* software (StatSoft, Tulsa, OK, USA).

2.5. Film properties

2.5.1. Thickness measurement

The thickness of the films was measured using a thickness measuring device (Absolute Digimatic Indicator, model ID-F150, Mitutoyo Co., Japan) with a resolution of 1 μm. At least, five measurements were performed in each case.