Sargassum siliquosum *J. Agardh extract as potential material for synthesis of bioplastic film*

Jia-Yee Lim, Siew-Ling Hii, Swee-Yong Chee & Ching-Lee Wong

Journal of Applied Phycology

ISSN 0921-8971
Volume 30
Number 6

J Appl Phycol (2019) 30:3285-3297
DOI 10.1007/s10811-018-1603-2

Springer

Journal of Applied Phycology (2018) 30:3285–3297
https://doi.org/10.1007/s10811-018-1603-2

8TH ASIAN PACIFIC PHYCOLOGICAL FORUM

Sargassum siliquosum J. Agardh extract as potential material for synthesis of bioplastic film

Jia-Yee Lim[1] · Siew-Ling Hii[2] · Swee-Yong Chee[3] · Ching-Lee Wong[1]

Received: 26 January 2018 / Revised and accepted: 8 August 2018 / Published online: 17 August 2018

Abstract

In this study, alginate extracted from the brown alga *Sargassum siliquosum* J. Agardh was used as raw material for the synthesis of bioplastic film. Two-level full factorial design (FFD) and augmented central composite design (CCD) were employed in analysing the effects of following parameter toward the physical properties of the film produced: alginate loading, addition of sago starch and sorbitol as well as the concentration of calcium chloride ($CaCl_2$) used during treatment process. Statistical analysis of results indicated that bioplastic film could be produced from *S. siliquosum* by using a mixture containing 2 g of extracted alginate powder and 15% *w*/*w* of sorbitol followed by the treatment with 75% *w*/*w* of $CaCl_2$. Model validation proved that the percentage error was below 3.21% in general, indicating the proficiency of the models in predicting an optimised film with the following properties: tensile strength of 33.90 MPa, elongation at break of 3.58%, water vapour permeability of 2.63×10^{-10} g Pa^{-1} s^{-1} m^{-1} and water solubility of 33.73%.

Keywords Alginate · Bioplastic film · Two-level full factorial design · Augmented central composite design · Optimisation

Introduction

Conventional plastic is one of the most utilised materials in the world with annual global plastic production that surpassed 311 million tonnes in year 2014 (Plastics Europe 2015). However, the production of conventional plastics is still largely dependent on fossil fuels that are depleting at an alarming rate. The large production and application of conventional plastic potentially create plastic waste problem and inevitably leads to pollution and environmental issues (Gade et al. 2013; Ellen MacArthur Foundation 2016) with 95% of the plastic packaging material value lost after a short first use cycle. Thus, bioplastic film is introduced as an alternative in view of its bio-based and biodegradable properties.

Alginate is a phycocolloid that can be extracted from brown seaweed as a starting material for the bioplastic film. It is a linear binary copolymer that consists of two 1,4-linked uronic acids which are α-L-guluronic acid and β-D-mannuronic acid (Draget and Taylor 2011). Alginate can be extracted from different species of brown seaweeds, and in this study, it was extracted from *Sargassum siliquosum* J. Agardh collected from the coastline of Port Dickson, Malaysia. Alginate is preferentially extracted in their sodium form using sodium carbonate, with optional formaldehyde pretreatment prior to the extraction process (Pegg 2012). However, comparison of yield and molecular weight of alginate extracted from *Sargassum* species in Malaysia in the presence of formaldehyde have not been studied.

One of the important characteristics of alginate is the formation of water-insoluble gels in the presence of multivalent cations such as calcium ions (Ca^{2+}). The water-insoluble property is attributed to the strong cross-linking interaction between the C=O groups of guluronic acid with Ca^{2+}, resulting in a three-dimensional gel-like conformation which is known as the "egg box" structure (Sellimi et al. 2015). In addition, film produced by immersion treatment

✉ Ching-Lee Wong
chinglee.wong@taylors.edu.my

[1] School of Biosciences, Faculty of Health and Medical Sciences, Taylor's University Lakeside Campus, No. 1, Jalan Taylor's, 47500 Subang Jaya, Selangor, Malaysia

[2] Department of Food Technology, School of Engineering and Technology, University College of Technology Sarawak, 868 Persiaran Brooke, 96000 Sibu, Sarawak, Malaysia

[3] Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

was with improved properties compared to the direct addition of Ca^{2+} into the polymer blend (Rhim 2004; Fazilah et al. 2011; Crossingham et al. 2014).

To date, there are quite a number of studies focused on the application of alginate in the production of bioplastic (Blanco-Pascual et al. 2014) with the incorporation of a secondary biopolymer (Wang et al. 2010a; Fazilah et al. 2011; Azeredo et al. 2012b; Benavides et al. 2012; Galus and Lenart 2013). There are also studies evaluating the effect of different concentrations of plasticiser (Talja et al. 2007; Jost et al. 2014) and $CaCl_2$ immersion treatment (Rhim 2004; Fazilah et al. 2011). However, limited research has been performed on the relationship between each of the process parameters, namely alginate (primary polymer), sago starch (secondary polymer), sorbitol (plasticiser) and $CaCl_2$ treatment (chemical modification) affecting the production of bioplastic film toward a series of physical properties (tensile strength, percentage of elongation at break, water vapour permeability and percentage of water solubility) of the synthesised bioplastic films. Such relationships among the factors can be effectively identified by statistical design of experiment (DoE) with the benefits of reduction in time, effort and materials. The use of statistical DoE focused on discovering the significant factors, and then to propose the optimised process solution once the relationships among different factors were established (Barka et al. 2014).

In the present study, preliminary screening on the effect of the formaldehyde pretreatment on the physicochemical properties of alginate from *S. siliquosum* was investigated. Subsequently, a two-level full factorial design (FFD) and augmented central composite design (CCD) were employed to determine the effect of four factors: alginate loading, sago starch loading, sorbitol concentration and $CaCl_2$ treatment concentration, toward the properties of bioplastic film produced (tensile strength, percentage of elongation at break, water vapour permeability and percentage of water solubility).

Materials and methods

Seaweed collection

Samples of *Sargassum siliquosum* were collected from Teluk Kemang, Port Dickson, west coast of Peninsular Malaysia (2° 26′ 23.02″ N, 101° 51′ 25.2″ E) on September 2015, April 2016, March 2017 and July 2017. The seaweed samples collected were washed, air dried and milled into a size not larger than 1 mm^2.

Alginate extraction

The extraction of alginate from *S. siliquosum* was performed with or without the addition of formaldehyde. In the method without formaldehyde pretreatment, extraction of alginate was done according to the method of Chee et al. (2011) with minor modification. Seaweed sample (20 g) was soaked in 1% *w*/*v* calcium chloride ($CaCl_2$) for 18 h. Following this, the seaweed was rinsed with distilled water prior to the reaction with 5% *v*/*v* hydrochloric acid (HCl) for 1 h. The seaweed sample was rinsed again with distilled water, stored in 3% *w*/*v* sodium carbonate (Na_2CO_3) for 1 h, before 250 mL of distilled water was incorporated for further reaction (15 h). The alginate extract was subsequently separated from the insoluble seaweed residue by centrifugation at 16,000×*g*, precipitated with absolute ethanol and dried cryogenically. While for the extraction with formaldehyde pretreatment, the seaweed sample was treated similarly with an additional pretreatment of 5% *v*/*v* formaldehyde for 1 h before the reaction with HCl.

Characterisation of extracted alginate

FTIR spectroscopy FTIR spectra of the extracted alginate were acquired with FTIR spectroscope (Perkin-Elmer, Spectrum 100) through KBr pellet technique. Spectral scanning was taken between the wavenumber of 4000 and 650 cm^{-1}. Commercial sodium alginate (Sigma Aldrich) was used as standard.

Alginate yield Percentage of yield of the extracted alginate was calculated with Eq. 1.

$$\text{Yield of alginate} = \frac{\text{Weight of alginate}}{\text{Weight of dry seaweed}} \times 100 \qquad (1)$$

Intrinsic viscosity and molecular weight Measurements for intrinsic viscosity of the alginate sample was performed following the method of Torres et al. (2007) and Chee et al. (2011) with minor modification. Alginate solution (0.15% *w*/*v*) was added into the Ubbelohde glass viscometer (Cannon, size 1) and immersed in a water bath at 25 °C. The alginate solution was pumped to the upper indicator line of the viscometer and left to flow under the influence of gravity. Flow time of the alginate solution was denoted as t, while flow time of ultrapure water recorded was denoted as t_o. The starting alginate solution was subsequently diluted for at least eight times. Intrinsic viscosity $[\eta]$ is obtained as the intercept of the regression lines from graphs of reduced viscosity, η_{red} and inherent viscosity, η_{inh} against the concentration c of the alginate solution. Molecular weight of the alginate sample was calculated through intrinsic viscosity $[\eta]$ using Mark-Houwink-Sakurada equation (Eq. 2), with k value of 0.023 and a value of 0.984, to empirically relate the intrinsic viscosity with the average of molecular weight (Eq. 3) (Clementi et al. 1998; Torres et al. 2007).

$$[\eta] = kM_i{}^{a} \quad (2)$$

$$[\eta] = 0.023\ M_w{}^{0.984} \quad (3)$$

Statistical analysis Statistical analysis for yield and molecular weight of the extracted alginate were performed with SPSS (Version 16.0; SPSS Inc.) by using one-way ANOVA coupled with Tukey's post-hoc test.

Statistical design of experiment

Two-level full factorial design A four-factor, two-level full factorial design (FFD) was carried out in this study to evaluate the effects of four factors, namely alginate loading (X_1), sago starch loading (X_2), sorbitol concentration (X_3), and $CaCl_2$ treatment concentration (X_4) on four responses, namely tensile strength (Y_1), percentage of elongation at break (Y_2), water vapour permeability (Y_3) and percentage of water solubility (Y_4). By using this design, each of the factors was examined on their low (− 1) and high (+ 1) level as shown in Table 1, with three additional centre point experiments at their respective mean (0) level. Each of the generated formulations were tested in three independent experiments ($n = 3$). The overall experimental design and analysis were completed using Design-Expert 9.0.4.1 (Stat-East, Inc). The experimental data were fitted to fourth-order models (Eq.4) to express the responses as a function of the different factors.

$$\begin{aligned} Y &= b_o + \sum_{i=1}^{4} b_i X_i + \sum_{i<j} \sum_{j=2}^{4} b_{ij} X_i X_j \\ &\quad + \sum_{i<j} \sum_{j<k} \sum_{k=3}^{4} b_{ijk} X_i X_j X_k \\ &\quad + b_{1234} X_1 X_2 X_3 X_4 + \\ &\quad \sum_{i=1}^{4} b_{ii} X_i{}^2 + \sum_{i=1} \sum_{j=1 \neq i}^{4} b_{iij} X_i{}^2 X_j + \varepsilon \end{aligned} \quad (4)$$

The last two terms before ε in the model equation were accounted for additional quadratic functions if the model was found to have significant curvature, while the last term (ε) was the residual from the fitted model. Regression analysis and analysis of variance (ANOVA) were also performed, along with the test of statistical significance at a confidence level of 95% ($p < 0.05$). Main and interaction effects were illustrated by effect plots, which showed variations on factors of interest while keeping other factors constant at their respective mean level.

Synthesis and characterisation of bioplastic film

Preparation and casting of film Alginate powder with the corresponding amount of sorbitol (Table 2) was dissolved in distilled water (150 mL) at room temperature followed by incubation in water bath (60 °C) for complete dissolution (Wong 2011). The gelatinisation of sago starch in 50 mL of distilled water was then carried out in water bath at 90 °C. Different amount of alginate powder, sago starch and sorbitol were adjusted according to the statistical experimental design. Then, the polymer solutions of alginate and sago starch were mixed together and hold at a process temperature of 50 °C with constant agitation for 90 min. The solution was casted on an acrylic container (300 × 200 mm), which was subsequently air dried for 24 h to obtain the cast film.

Calcium chloride immersion treatment The cast films were treated for 1 min with various concentrations of $CaCl_2$ with reference to the statistical experimental design (Fazilah et al. 2011). Sorbitol (5% *w/w* of the dry weight of cast film) was added to improve the flexibility of the film. Films were then dried at ambient conditions prior to characterisation.

Mechanical properties Tensile strength and percentage of elongation at break of the cast bioplastic films were tested by a microtester with a 2 kN load cell. Prior to the testing, bioplastic films were conditioned at 52% relative humidity (RH) at 25 °C for 48 h. Films were cut to a dimension of 20 mm × 90 mm following the method of Benavides et al. (2012) while the thickness of the films were measured with a digital micrometre. Testing was done according to ASTM D882 (ASTM International 2012) and the method of Benavides et al. (2012). Initial grip separation was 50 mm and the test speed was set at 12.5 mm min^{-1}.

Water vapour permeability Water vapour permeability (WVP) of the films was acquired in accordance with Mungo (2003) and ASTM E96 (ASTM International 2010). A portion of the film (permeation area = 3850 mm^2) was cut, conditioned, mounted on an aluminium cup filled with silica gel, and was placed in a desiccator with distilled water. Weight was measured every hour for 7 h continuously after steady state was reached (Blanco-Pascual et al. 2014). WVP for each individual film was calculated by Eqs. 5 and 6, where w was weight gained (g), t was time gained (s), A was permeation area (m^2),

Table 1 Different levels of factors used in the experimental design

Code	Factors	Low level (− 1)	Mean (0)	High level (+ 1)
X_1	Alginate loading (g)	2	3	4
X_2	Sago starch loading (% w/w)	0	25	50
X_3	Sorbitol concentration (% w/w)	15	30	45
X_4	$CaCl_2$ treatment concentration (% w/w)	0.0	37.5	75.0

Table 2 Design matrix of two-level FFD and augmented CCD

Group	Factors[a]			
	X_1	X_2	X_3	X_4
1	− 1 (2)	− 1 (0)	− 1 (15)	− 1 (0)
2	+ 1 (4)	− 1 (0)	− 1 (15)	− 1 (0)
3	− 1 (2)	+ 1 (50)	− 1 (15)	− 1 (0)
4	+ 1 (4)	+1 (50)	−1 (15)	− 1 (0)
5	− 1 (2)	− 1 (0)	+ 1 (45)	− 1 (0)
6	+ 1 (4)	− 1 (0)	+ 1 (45)	− 1 (0)
7	− 1 (2)	+ 1 (50)	+ 1 (45)	− 1 (0)
8	+ 1 (4)	+ 1 (50)	+ 1 (45)	− 1 (0)
9	− 1 (2)	− 1 (0)	− 1 (15)	+ 1 (75)
10	+ 1 (4)	− 1 (0)	− 1 (15)	+ 1 (75)
11	− 1 (2)	+ 1 (50)	− 1 (15)	+ 1 (75)
12	+ 1 (4)	+ 1 (50)	− 1 (15)	+ 1 (75)
13	− 1 (2)	− 1 (0)	+ 1 (45)	+ 1 (75)
14	+ 1 (4)	− 1 (0)	+ 1 (45)	+ 1 (75)
15	− 1 (2)	+ 1 (50)	+ 1 (45)	+ 1 (75)
16	+ 1 (4)	+ 1 (50)	+ 1 (45)	+ 1 (75)
17	0 (3)	0 (25)	0 (30)	0 (37.5)
18	0 (3)	0 (25)	0 (30)	0 (37.5)
19	0 (3)	0 (25)	0 (30)	0 (37.5)
20	− 1 (2)	0 (25)	0 (30)	0 (37.5)
21	+ 1 (4)	0 (25)	0 (30)	0 (37.5)
22	0 (3)	− 1 (0)	0 (30)	0 (37.5)
23	0 (3)	+ 1 (50)	0 (30)	0 (37.5)
24	0 (3)	0 (25)	− 1 (15)	0 (37.5)
25	0 (3)	0 (25)	+ 1 (45)	0 (37.5)
26	0 (3)	0 (25)	0 (30)	− 1 (0)
27	0 (3)	0 (25)	0 (30)	+ 1 (75)
28	0 (3)	0 (25)	0 (30)	0 (37.5)

[a] Factors: X_1, alginate loading (g); X_2, sago starch loading (% w/w alginate); X_3, sorbitol concentration (% w/w total macromolecule); X_4, $CaCl_2$ treatment concentration (% w/w alginate). The uncoded values were presented in brackets

x was film thickness (m), ΔP was the atmospheric vapour pressure between desiccant and distilled water, P was the saturated vapour pressure of water at the test temperature (Pa), R_1 was the %RH of the environment inside desiccator and R_2 was the %RH of the environment inside aluminium cup.

$$\mathrm{WVP} = \frac{w}{t}\left(\frac{1}{\mathrm{A}}\right)\frac{x}{\Delta P} \tag{5}$$

$$\Delta P = P\,(R_1\text{-}R_2) \tag{6}$$

Percentage of water solubility Film was cut to a dimension of 40 mm × 40 mm and placed in a desiccator for 7 days prior to the solubility testing (Fazilah et al. 2011). The initial dry weight of the film was recorded and the film was then submerged in 50 mL distilled water at 25 °C. After 24 h, the insoluble fragments were first collected through filtration by filter paper, dried in an oven at 105 °C for 24 h and weighed to obtain the final dry weight. Percentage of water solubility (%WS) was calculated by Eq. 7.

$$\%\mathrm{WS} = \frac{\text{initial dry weight-final dry weight}}{\text{initial dry weight}} \times 100 \tag{7}$$

Optimisation and validation

Response surface methodology Additional experiments were required for models with experimental data that were not fitting well, i.e. with insignificant model and a highly significant lack of fit. This was done with the response surface methodology technique, particularly augmented central composite design (CCD) where additional formulations around the centre points of the design matrix on the basis of experimental data from two-level FFD was generated and performed. By this, curvature that was captured but was failed to be explained by the two-level FFD can be described.

Validation of model Following the regression analysis and ANOVA, model equations were generated to use in prediction and optimisation of various bioplastic film characteristics. Since this is a multi-response optimisation, all the responses were taken into consideration simultaneously. Derringer's desirability function was used to calculate the desirability of the targeted combination (Yuan et al. 2015). Additional experimental runs were carried out subsequently to validate the optimisation solution.

Results

Characterisation of sodium alginate extract

The extracted sodium alginate from *S. siliquosum* was characterised based on its physical appearance, FTIR spectra, percentage of yield and molecular weight. The freshly precipitated alginates were gelatinous and soft but strong in texture. After air drying for 24 h, the samples were subjected to freeze drying as there was still moisture retained in the sample. Sodium alginate extracted from *S. siliquosum* with 5% *v/v* formaldehyde appeared in lighter colour (light brown) as compared to those extracted without formaldehyde pretreatment (dark brown in colour). FTIR was carried out for both of the extracted alginate samples and the standard alginate. The FTIR results showed that the IR spectra for both of the extracted alginate samples were comparable to that of the standard alginate. The visible peaks for the extracted samples corresponded to the wavenumbers of alginate in literature. The yield of alginate extracted, 33.75 ± 1.21% *w/w*, was significantly higher (p

< 0.05) with protocol without formaldehyde pretreatment in comparison to the mixture pre-treated with formaldehyde (26.91 ± 1.59% *w*/*w*). The intrinsic viscosities of the extracted alginate samples were measured and were used for the calculations of molecular weight. There was no significant difference ($p > 0.05$) found in molecular weight for alginate extracted with ($M_w = 15.32 \pm 0.56 \times 10^5$ g mol^{-1}; $[\eta] = 31.34 \pm 1.13$ dL g^{-1}) or without formaldehyde ($M_w = 16.56 \pm 0.50 \times 10^5$ g mol^{-1}; $[\eta] = 33.83 \pm 1.01$ dL g^{-1}) for *S. siliquosum*. The inherent viscosities of alginate extracted from *S. siliquosum* with or without formaldehyde pretreatment ranged from 14.12 to 18.15 dL g^{-1} and 14.32 to 18.66 dL g^{-1}, respectively.

Statistical model development

Bioplastic films were cast according to the design matrix as shown in Table 2. There were a total of four responses which equivalent to the four properties of the synthesised film, namely, tensile strength (response 1), percentage of elongation at break (response 2), water vapour permeability (response 3) and percentage of water solubility (response 4). In order to perform ANOVA on the generated two-level full factorial models, assumptions of normality, homoscedasticity, linearity, as well as model adequacy were first checked.

All the models developed in this study achieved normality (Hii et al. 2014). The models developed were achieving homoscedasticity for all the models as seen in the plot of residuals versus the predicted response values, where the variances for all the residuals were free from the effect of the size of the predicted response values and scattered randomly within a horizontal band (Smith 2005). Factorial designs assume only linear relationships. Therefore, experimental data with significant curvature might lead to misleading interpretation of the model. The linearity was verified by the insignificant *p* value ($p > 0.05$) of curvature through the ANOVA testing on the results from centre point runs, which in this case achieved by the model of response 1, 2 and 3 ($p = 0.5705$, 0.4786 and 0.0675, respectively), but not response 4 ($p < 0.0001$, data not shown). Model adequacy was then tested on the respective models based on the significant model *p* value and the insignificant lack of fit *p* value. It was followed by performing the model analysis for model terms using ANOVA to assess the effect of each of the model terms toward the responses.

Response 1: tensile strength ANOVA between the four factors toward tensile strength were presented in Table 3. The model *p* value of < 0.0001 and its lack of fit *p* value of 0.5705 indicated that the model is valid for further analysis. The adjusted

Table 3 ANOVA analysis of response 1 (tensile strength)

Source	SS[a]	*df*[b]	MS[c]	*F* value	*p* value[d] (prob >*F*)
Model	1.92	15	0.13	37.87	< 0.0001
X_1	0.044	1	0.044	13.15	0.0009
X_2	0.002	1	0.002	0.60	0.4429
X_3	0.93	1	0.93	276.50	< 0.0001
X_4	0.27	1	0.27	78.84	< 0.0001
X_1X_2	0.003	1	0.003	0.92	0.3435
X_1X_3	0.072	1	0.072	21.36	< 0.0001
X_1X_4	0.00004	1	0.00004	0.01	0.9136
X_2X_3	0.071	1	0.071	21.11	< 0.0001
X_2X_4	0.36	1	0.036	106.18	< 0.0001
X_3X_4	0.0006	1	0.0006	0.19	0.6672
$X_1X_2X_3$	0.023	1	0.023	6.95	0.0124
$X_1X_2X_4$	0.048	1	0.048	14.28	0.0006
$X_1X_3X_4$	0.007	1	0.007	2.06	0.1605
$X_2X_3X_4$	0.036	1	0.036	10.73	0.0024
$X_1X_2X_3X_4$	0.051	1	0.051	15.15	0.0004
Residual	0.12	35	0.003		
Lack of fit/curvature	0.001	1	0.001	0.33	0.5705
Pure error	0.12	34	0.003		
Total	2.04	50			

[a] Sum of squares

[b] Degree of freedom

[c] Mean square

[d] Significant if $p < 0.05$; adjusted $R^2 = 0.9171$; predicted $R^2 = 0.8710$; percentage of coefficient of variation = 4.85%; adequate precision = 21.72

coefficient of determination (adj-R^2) and the predicted coefficient of determination (pred-R^2) were 0.9171 and 0.8710, respectively. The percentage of coefficient of variation (CV) was 4.85% while the adequate precision was 21.72.

A model equation was generated to express the mathematical relationship between different factors on tensile strength in coded terms. The original model equation of response 1 was transformed into a logarithmic scale (Eq. 8) in order to meet the normality and homoscedasticity assumptions. This model equation can be used to identify the significance of the factors and their effects, as indicated by the magnitude of the coefficients.

$$\begin{aligned} log_{10}Y_1 = {} & 1.197 + 0.030X_1 + 0.007X_2 - 0.139X_3 \\ & + 0.074X_4 + 0.008X_1X_2 + 0.039X_1X_3 \\ & + 0.001X_1X_4 - 0.039X_2X_3 - 0.086X_2X_4 \\ & + 0.004X_3X_4 - 0.022X_1X_2X_3 + 0.032X_1X_2X_4 \\ & + 0.012X_1X_3X_4 - 0.027X_2X_3X_4 - 0.033X_1X_2X_3X_4 \end{aligned} \quad (8)$$

Each of the factors was further examined for their effects toward the response. All model terms with p value less than 0.05 were deemed as significant. Among the significant terms, those with larger F value and sum of squares while having smaller p value will have a greater impact on the final response. As shown in Table 3, ten model terms were considered as significant factors. Further comparison between the individual sum of square to total sum of squares revealed that the negative effect of sorbitol (X_3) on tensile strength was the most critical with an overall 45.85% contribution. The effect of sorbitol on tensile strength is illustrated in Fig. 1. An increase from low to high level of sorbitol brought a decrease of 10.37 MPa in the tensile strength of the film.

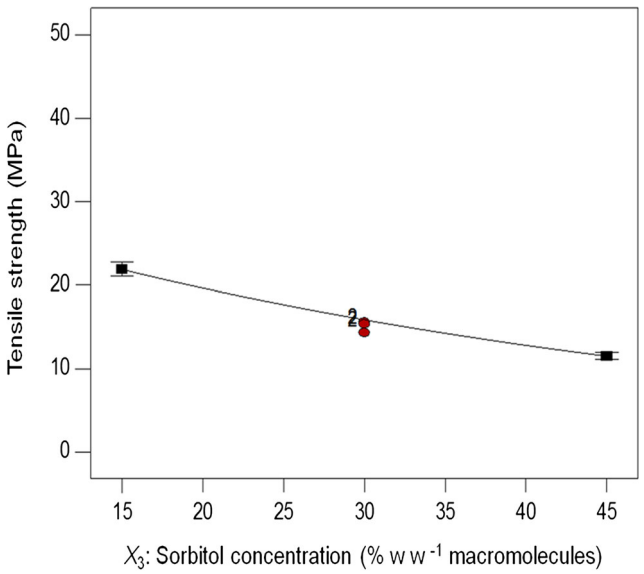

Fig. 1 Effect of sorbitol concentration (X_3) on response 1 (tensile strength)

Response 2: percentage of elongation at break Similar to response 1 (tensile strength), the relationship of the factors on the percentage of elongation at break was assessed using ANOVA (Table 4). The experimental data fitted the model well with the p value of the regression model lesser than 0.05 ($p < 0.0001$) and the p value of lack of fit was well above 0.05 ($p = 0.4786$). The obtained experimental data were used to develop a mathematical equation where the transformation of square root scale was involved, which can then describe the association of factors to the percentage of elongation at break of the film in coded terms (Eq. 9).

$$\begin{aligned} \sqrt{Y_2} = {} & 4.110 + 0.380X_1 + 0.141X_2 \\ & + 1.125X_3 - 0.566X_4 - 0.065X_1X_2 - 0.073X_1X_3 \\ & - 0.027X_1X_4 + 0.529X_2X_3 + 0.212X_2X_4 - 0.371X_3X_4 \\ & + 0.148X_1X_2X_3 + 0.003X_1X_2X_4 \\ & - 0.227X_1X_3X_4 + 0.145X_2X_3X_4 + 0.425X_1X_2X_3X_4 \end{aligned} \quad (9)$$

Similar to tensile strength, sorbitol (X_3) was most critically affecting the percentage of elongation at break (48.57% contribution), but in this case, it has portrayed a positive effect (Fig. 2). The percentage of elongation at break increased from 9.06 to 27.57% when the concentration of sorbitol increased from 15 to 45% *w/w*.

Response 3: water vapour permeability The amount of significant terms was lesser (only seven) for the model of response 3 (Table 5). Therefore, model reduction can be performed. The original equation was transformed (inverse square root) in order to meet the assumptions of normality and homoscedasticity (Eq. 10). By inspecting their individual sum of squares, alginate loading (X_1) was revealed to be significantly affecting the response with its positive effect and an overall percentage of contribution of 71.76%. It can be seen from the effect curve (Fig. 3) that the water vapour permeability was increased with a higher alginate loading, particularly with an increment of 2.00×10^{-10} g Pa^{-1} s^{-1} m^{-1} when the amount of alginate in the blend increased from 2 to 4 g.

$$\begin{aligned} \frac{1}{\sqrt{Y_3}} = {} & 51175.06 - 6422.70X_1 - 1468.31X_2 - 1296.81X_3 \\ & + 309.80X_4 + 501.99X_1X_2 + 1468.82X_1X_3 \\ & + 364.51X_2X_3 + 527.45X_2X_4 + 911.45X_3X_4 \\ & - 1580.19X_1X_2X_3 - 1537.10X_2X_3X_4 \end{aligned} \quad (10)$$

Response 4: percentage of water solubility The experimental data acquired by two-level full factorial design was first analysed by ANOVA but the model possessed a significant lack of fit ($p < 0.0001$; data not shown). Consequently, the two-level FFD for this response was altered into an augmented central composite design (CCD) to explain the curvature that occurred in the experimental data. The model is highly significant ($p < 0.0001$) with an insignificant lack of fit ($p = 0.9355$) (Table 6),

Table 4 ANOVA analysis of response 2 (percentage of elongation at break)

Source	SS[a]	*df*[b]	MS[c]	*F* value	*p* value[d] (prob > *F*)
Model	119.88	15	7.99	52.94	< 0.0001
X_1	6.94	1	6.94	45.95	< 0.0001
X_2	0.96	1	0.96	6.35	0.0164
X_3	60.79	1	60.79	402.65	< 0.0001
X_4	15.35	1	15.35	101.67	< 0.0001
X_1X_2	0.20	1	0.20	1.33	0.2563
X_1X_3	0.26	1	0.26	1.70	0.2011
X_1X_4	0.034	1	0.034	0.23	0.6375
X_2X_3	13.42	1	13.42	88.88	< 0.0001
X_2X_4	2.16	1	2.16	14.28	0.0006
X_3X_4	6.59	1	6.59	43.67	< 0.0001
$X_1X_2X_3$	1.05	1	1.05	6.95	0.0124
$X_1X_2X_4$	3.29×10^{-4}	1	3.29×10^{-4}	2.18×10^{-3}	0.9630
$X_1X_3X_4$	2.48	1	2.48	16.40	0.0003
$X_2X_3X_4$	1.01	1	1.01	6.67	0.0142
$X_1X_2X_3X_4$	8.65	1	8.65	57.31	< 0.0001
Residual:	5.28	35	0.15		
Lack of fit/curvature	0.079	1	0.079	0.51	0.4786
Pure error	5.21	34	0.15		
Total	125.17	50			

[a] Sum of squares

[b] Degree of freedom

[c] Mean square

[d] Significant if $p < 0.05$; adjusted $R^2 = 0.9397$; predicted $R^2 = 0.9079$; percentage of coefficient of variation = 9.45%; adequate precision: 22.70

indicating that the experimental data can be explained well after the alteration made on the statistical design. The mathematical relationships of this model in coded model terms are presented as (Eq. 11).

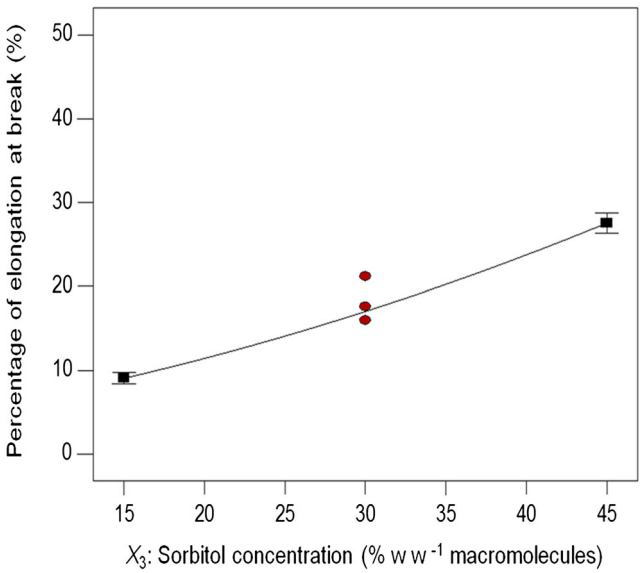

Fig. 2 Effect of sorbitol concentration (X_3) on response 2 (percentage of elongation at break)

$$\begin{aligned} Y_4 = {} & 89.11 + 7.99X_1 - 2.07X_2 - 0.76X_3 - 0.47X_4 \\ & - 4.62X_1X_2 - 5.05X_1X_3 + 2.63X_1X_4 + 2.13X_2X_3 \\ & + 7.94X_2X_4 - 2.36X_3X_4 - 5.72{X_1}^2 - 12.84{X_2}^2 \\ & + 6.20{X_4}^2 + 3.78X_1X_2X_3 - 4.11X_1X_2X_4 \\ & - 5.42X_1X_3X_4 + 0.34X_2X_3X_4 - 10.21{X_2}^2X_4 \\ & - 6.47X_1{X_2}^2 + 4.42X_1X_2X_3X_4 \end{aligned} \quad (11)$$

The 3-D response surface contour plot is shown in Fig. 4. It was noted that when the film was not treated with $CaCl_2$ and without the supplementation of sago starch, the percentage of water solubility was relatively high (~99%). The percentage of water solubility gradually reduced when the concentration of sago starch increased to 50% *w/w*. Conversely, the percentage of water solubility was at its lowest when the concentration of $CaCl_2$ was at high level (75% *w/w*) and no sago starch was incorporated in the formulation. Moreover, when sago starch present in high level (50% *w/w*) in the formulation, the percentage of water solubility was in a similar range (~80%) regardless of the concentration of the $CaCl_2$ treatment.

Validation experiments

The four models developed using the statistical designs were utilised to perform a multi-response optimisation.

Table 5 ANOVA analysis of response 3 (water vapour permeability)

Source	SS[a] ($\times 10^8$)	*df*[b]	MS[c] ($\times 10^8$)	*F* value	*p* value[d] (prob > *F*)
Model	25.77	11	2.34	50.29	< 0.0001
X_1	19.80	1	19.80	425.00	< 0.0001
X_2	1.04	1	1.04	22.21	< 0.0001
X_3	0.81	1	0.81	17.33	0.0002
X_4	0.05	1	0.05	0.99	0.3262
X_1X_2	0.12	1	0.12	2.60	0.1152
X_1X_3	1.04	1	1.04	22.23	< 0.0001
X_2X_3	0.06	1	0.06	1.37	0.2491
X_2X_4	0.13	1	0.13	2.87	0.0984
X_3X_4	0.40	1	0.40	8.56	0.0057
$X_1X_2X_3$	1.20	1	1.05	25.73	< 0.0001
$X_2X_3X_4$	1.13	1	1.13	24.34	< 0.0001
Residual:	1.82	39	0.05		
Lack of fit	0.20	5	0.04	0.85	0.5255
Pure error	1.62	34	0.05		
Total	27.59	50			

[a] Sum of squares

[b] Degree of freedom

[c] Mean square

[d] Significant if $p < 0.05$; adjusted $R^2 = 0.9156$; predicted $R^2 = 0.8873$; percentage of coefficient of variation = 4.22%; adequate precision: 24.15

An optimisation strategy called Derringer's desirability function was used to determine the combinations of factors that will produce bioplastic films with "most desired" responses. Validation of the predicted responses was done concurrently in triplicates, where the desirability value of 0.8853 was found for the suggested solution by the software. The comparison between the predicted and actual experimental values is tabulated in Table 7.

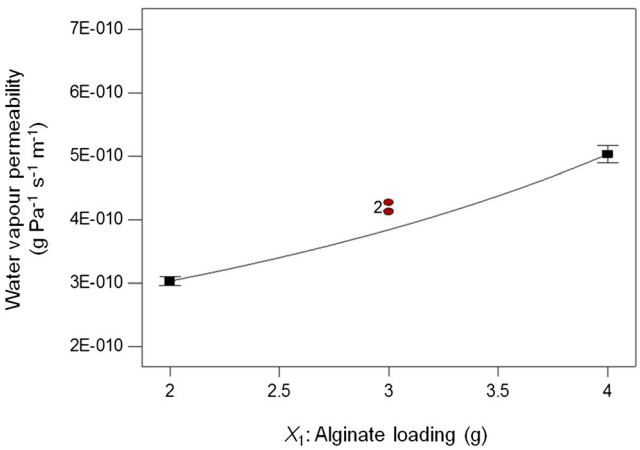

Fig. 3 Effect of alginate loading (X_1) on response 3 (water vapour permeability)

Table 6 ANOVA analysis of response 4 (percentage of water solubility)

Source	SS[a]	*df*[b]	MS[c]	*F* value	*p* value[d] (prob > *F*)
Model	17,341.93	20	867.10	96.67	< 0.0001
X_1	127.70	1	127.70	14.24	0.0005
X_2	215.16	1	215.16	23.99	< 0.0001
X_3	28.57	1	28.57	3.19	0.0821
X_4	0.44	1	0.44	0.05	0.8254
X_1X_2	1026.57	1	1026.57	114.45	< 0.0001
X_1X_3	1222.41	1	1222.41	136.29	< 0.0001
X_1X_4	332.19	1	332.19	37.04	< 0.0001
X_2X_3	218.33	1	218.33	24.34	< 0.0001
X_2X_4	3026.69	1	3026.69	337.45	< 0.0001
X_3X_4	266.64	1	266.64	29.73	< 0.0001
X_1^2	93.63	1	93.63	10.44	0.0025
X_2^2	472.14	1	472.14	52.64	< 0.0001
X_4^2	110.03	1	110.03	12.27	0.0012
$X_1X_2X_3$	685.29	1	685.29	76.40	< 0.0001
$X_1X_2X_4$	809.76	1	809.76	90.28	< 0.0001
$X_1X_3X_4$	1410.66	1	1410.66	157.28	< 0.0001
$X_2X_3X_4$	5.62	1	5.62	0.63	0.4332
$X_1X_2^2$	80.40	1	80.40	8.96	0.0048
$X_2^2X_4$	200.21	1	200.21	22.32	< 0.0001
$X_1X_2X_3X_4$	938.60	1	938.60	104.64	< 0.0001
Residual	349.80	39	8.97		
Lack of fit	7.90	4	1.98	0.20	0.9355
Pure error	341.90	35	9.77		
Total	17,691.74	59			

[a] Sum of squares

[b] Degree of freedom

[c] Mean square

[d] Significant if $p < 0.05$; adjusted $R^2 = 0.9701$; predicted $R^2 = 0.9530$; percentage of coefficient of variation = 3.80%; adequate precision: 36.69

Discussion

Extraction and characterisation of the extracted alginate The brown seaweed *S. siliquosum* was chosen in this study due to a relatively higher yield of alginate (38.9% under ambient condition) as compared to other *Sargassum* species (Chee et al. 2011). The dark brown colouration that was reflected in the final alginate samples was due to the leaching of soluble phenolic compounds that were found in brown seaweed into the sodium alginate crude extract (Haug 1964). The observed lighter brown colour in sample treated with formaldehyde was contributed by the reaction of formaldehyde as a fixative (Thavarajah et al. 2012). The addition of formaldehyde polymerises the phenolic compounds in the plant matrix which in turn lowers its solubility and retains it in the matrices, thus minimises the release of phenolic content into the final alginate samples (Fertah 2017).

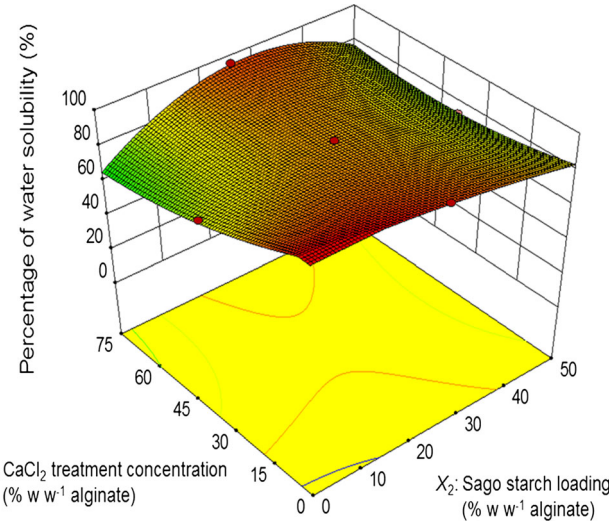

Fig. 4 Response surface plot of interaction effect between sago starch loading and $CaCl_2$ treatment concentration (X_2X_4)

The percentage of yield recorded in this study was in the acceptable range of industry standard alginate yield of 13 to 38% (Bertagnolli et al. 2014). However, the additional formaldehyde pretreatment step caused the higher loss of seaweed biomass due to the transfer process between chemical treatments. The higher percentage of yield of the extracted alginate without formaldehyde pretreatment may be partly due to the phenolic compounds which leached into the crude alginate extract in view of the darker brown colour of the final product.

Alginate has the ability to form viscous solution when dissolved in water. The contribution of solute (alginate) to the viscosity of a solution is known as the intrinsic viscosity (da Costa et al. 2017). The solution of a polymer with higher molecular weight possessed higher intrinsic viscosity because of its larger hydrodynamic volume, as well as the higher intermolecular forces between polymer and solvent molecules (Ghosh and Karmakar 2014). In the present study, the molecular weights of all the alginate samples were in the magnitude of 10^6 g mol^{-1} and this is higher than those reported in other studies; as summarised by Torres et al. (2007) which were normally in the magnitude of 10^5 g mol^{-1}. The application of freeze-drying as the drying method in this study helped to preserve the molecular integrity of the extracted alginate since alginate is known to degrade significantly under high temperature, particularly above 60 °C (Hernández-Carmona et al. 2002).

Table 7 Averaged experimental data and their respective percentage error based on predicted responses

Responses[a]	Predicted[b]	Experimental[c]	Error (%)
Y_1	34.59	33.90	2.00
Y_2	3.47	3.58	3.21
Y_3	2.64	2.63	0.49
Y_4	34.24	33.73	1.49

[a] Responses for optimised film: Y_1, tensile strength (MPa); Y_2, percentage of elongation (%); Y_3, water vapour permeability ($\times 10^{-10}$ g Pa^{-1} s^{-1} m^{-1}); Y_4, percentage of water solubility (%)

[b] Predicted responses by the model

[c] Averaged experimental data based on the calculated optimised solution

Bioplastic synthesis and statistical model development

Alginate and sago starch were two of the polymers applied in the synthesis of bioplastic film in this study. The range of alginate loading used in this study was from 2 to 4 g (1 to 2% *w*/*v* distilled water), corresponded to the usual concentration used in production of bioplastic film (Wang et al. 2010a; Benavides et al. 2012; Blanco-Pascual et al. 2014; Crossingham et al. 2014; Liu et al. 2017). Sago starch was then incorporated in the polymer blend owing to its good compatibility with alginate (Siddaramaiah et al. 2008; Weerapoprasit and Prachayawarakorn 2016), and the high production of sago starch in the world at 25,000 kg ha^{-1} year^{-1} (Yamamoto 2015) which render lower stable price of sago starch in the international market (FAO 2013).

Two-level FFD was used as the main statistical design in this study owing to its efficiency in evaluating two or more factors simultaneously, with the ability to detect interaction effects (Mutuk and Mesci 2014). This design also permits the study of all possible combinations of the factor values, eliminating the confounding problem as shown in other design such as Plackett-Burman design or fractional factorial design (Cavazzuti 2013). The addition of centre point in the design was to detect any curvature presented in the model. In cases of curvature p value was found to be significant, additional quadratic terms would be applied (Seyed Shahabadi and Reyhani 2014). This was shown in response 4 (percentage of water solubility), where the initial linear equation from two-level FFD was not sufficient in explaining the experimental data and the significant curvature.

A model is deemed to be well-fitted to the experimental data if and only if its model p value is significant ($p < 0.05$) while the lack of fit is insignificant ($p > 0.05$) (Yuan et al. 2015). The experimental data obtained for response 1 to response 3 can be explained adequately with two-level FFD based on the model and lack of fit p values. As for response 4, additional quadratic terms were needed due to the significant curvature and lack of fit ($p < 0.05$) in the data. Therefore, augmented CCD was performed. The interesting part about augmented CCD was that the data obtained in two-level full factorial design can be readily incorporated with the addition of a small number of extra runs (the star points) to estimate the probable curvature, where the experimenter does not require to build a response surface methodology (RSM) design from scratch (Rashvand et al. 2016). ANOVA was then done on the model terms if all the assumptions of normality and

homoscedasticity were proved. As a result, the data for response 1, 2 and 3 were further transformed with the assistance of Box-Cox transformation into other scales (response 1: base 10 log; response 2: square root; response 3: inverse square root) (Osborne 2010).

Some model descriptors were then examined in order to assess the quality of the fitted model. As stated in the "Results" section, the model of response 1 (tensile strength) has an adj-R^2 of 0.9171 and pred-R^2 of 0.8710. This implied that the goodness of fit of the generated model was 91.71% on the overall experimental data, and that 87.10% of the future data can be predicted by this model (Hii et al. 2014). All the other models (response 2, 3 and 4) were having adj-R^2 and pred-R^2 higher than 0.8710 (Tables 4, 5 and 6), indicating that their goodness of fit and prediction power were higher than 87.10%. This showed that the generated models were strong in response prediction. CV of response 1 was 4.85%, which was the percentage of ratio of standard deviation to mean of the overall model (Karunanithy and Muthukumarappanm 2011). In general, the CV should be 10% or lower (Linko et al. 1984). The CV achieved by all the models in this study were generally lower than 9.45%, which suggested that the models under this study are reliable (Hii et al. 2014). The adequate precision achieved by all the models were higher than 21.72. Adequate precision is the measure of signal to noise ratio, where a larger ratio signified a better prediction (preferably more than 4), for the permission to navigate the design space (Karunanithy and Muthukumarappanm 2011).

Results from response 1 (tensile strength) and response 2 (percentage of elongation at break) suggested that the main effect of sorbitol concentration plays a major role in affecting the bioplastic film's mechanical properties (negative effect on tensile strength and positive effect on percentage of elongation at break), on account of the close relationship of the two responses in inversely manner, although not necessarily (Rhim 2004; Olivas and Barbosa-Canovas 2008). Sorbitol is a type of plasticiser from the polyol family which is compatible and easily incorporated to the alginate and sago starch matrix (Zhang and Han 2006). The hydroxyl (-OH) groups presented in the structure of sorbitol were capable of forming hydrogen bonds with water molecules, thus more water molecules tend to be incorporated into the film matrix (Mali et al. 2005). Since water is a natural plasticiser, it produces a plasticising effect which could help in improving the mobility of the polymer chain, and thus lowers the tensile strength while improving the elongation of the film, complementing the similar findings in this study (Karbowiak et al. 2006; Suppakul et al. 2013; Gao et al. 2017).

Film water vapour permeability was recorded as the amount of water vapour that was able to pass through a film in a given time, based on the film's thickness and the partial pressure of the water vapour. Alginate loading was far more significant on the water vapour permeability compared to other model terms with its 71.76% contribution, which might be attributed to the hydrophilic nature of alginate molecules. Alginate comprises of quite a number of hydroxyl and carboxyl group along its polymeric chain (Pawar and Edgar 2012; Ibrahim et al. 2015). These functional groups help in promoting the permeability of the film and rendered it ineffective as moisture barrier (Rangel-Marrón et al. 2013).

The percentage of water solubility of the film was recorded as response 4 in this study. A closer look at the 3-D response surface contour plot (Fig. 4) suggests that the effect of $CaCl_2$ treatment was highly significant when sago starch was absent from the formulation. When there was no $CaCl_2$ treatment, the film dissolved completely in water. This might be contributed by the highly hydrophilic nature of pure sodium alginate film without Ca^{2+} cross-linking (Rhim 2004; Fazilah et al. 2011). The increase in $CaCl_2$ treatment concentration from 0 to 75% (w/w) reduced the percentage of water solubility by at least 30%, most probably with the assistance of cross-linking of the alginate polymeric chain without the interference from sago starch. In the case where high level of sago starch loading was used, there was decrement in the percentage of water solubility when the film was treated with high level of $CaCl_2$, but not as much as when pure alginate film was treated. This was most probably attributable to the interaction of sago starch with alginate, in which the hydroxyl groups of sago starch compete with the Ca^{2+} ions in reacting with the carboxyl groups of alginate (Siddaramaiah et al. 2008; Wang et al. 2010b; López et al. 2015). Therefore, the use of $CaCl_2$ treatment solution improved the film's integrity in water, but in a much lower efficiency. As for film's percentage of water solubility in the condition where no $CaCl_2$ treatment involved, the increase in sago starch concentration did improve the film's resistance to water. This was most likely because of the lower solubility of sago starch in water compared to alginate (Fazilah et al. 2011; Poeloengasih and Anggraeni 2014). Studies have been done on several combinations of alginate with secondary biopolymers, for instance cashew tree gum (Azeredo et al. 2012a), pectin (Galus and Lenart 2013) and lignin (Aadil et al. 2016).

Optimisation and validation experiments Derringer's desirability function was used in this study to perform a multi-response optimisation. Multi-response optimisation is more advanced compared to single-response optimisation because the output responses are to be optimised simultaneously (Alshaibani et al. 2014; Seyed Shahabadi and Reyhani 2014; Yuan et al. 2015). There are some techniques that can be used to perform such optimisation, but desirability function is one of the most frequently applied strategies (Raissi and Farsani 2009). Desirability function was used to determine the combinations of factors that will produce final products with "most desired" responses. This function can combine the effect of multiple responses into a single

response which goes by the term of "desirability function" (d_i) and the value will always be in between 0 to 1, with 1 being the most desired and 0 otherwise (Seyed Shahabadi and Reyhani 2014). This function has the ability in assisting the experimenter to select best conditions that can yield the desired responses (Yuan et al. 2015) and multi-response optimisation works in such a way that an experimental region and targets of optimisation must be first defined for the software to search for combinations that fulfilled all the preset criteria. Then, d_i will be assigned to each of the possible combinations. In this study, the boundaries of the experimental region to search for the optimised solution were set to be the lower and upper range of the factors.

The goal of optimisation in this study was to search for a combination that can serve as an alternative to conventional plastic bags, with high desirability. Mechanical properties were considered to be one of the most important parameters for plastic films (Harunsyah et al. 2017). In this study, the optimisation target for the tensile strength (response 1) was set to maximum with minimum level of elongation at break (response 2) in the hope of increasing the resistance of tension force since plastic bag was designed to contain and transport goods (Rayne 2008). On the other hand, water barrier properties, i.e. water vapour permeability (response 3) and percentage of water solubility (response 4) were both set at the minimum target of optimisation, with the purposes to maintain the film's integrity when in contact with water, and to protect the goods from water vapour.

The desirability function achieved by this solution was 0.8853, which implied that 88.53% of the set target can be fulfilled. Further validation of the optimised combination revealed that the percentage error for the responses was generally not greater than 3.21%. This suggested that optimisation of the bioplastic film was completed, and that the developed four models of tensile strength, percentage of elongation at break, water vapour permeability and percentage of water solubility were able to explain and predict responses accurately based on the factors. The comparison of all the properties implied that the values acquired with the synthesised film in this study was comparable to other alginate-based films reported (Blanco-Pascual et al. 2014; Fazilah et al. 2011).

In conclusion, native alginate extracted from *S. siliquosum* without formaldehyde pretreatment was found to be the most suitable candidate for the synthesis of bioplastic film based on its yield and molecular weight. This paper also demonstrated the development of statistical models by two-level FFD and augmented CCD. Significant effects of different factors on the final properties of the synthesised bioplastic film were successfully determined. Assumption of normality and homoscedasticity were achieved by each of the models, while linearity of the data in response 1, 2 and 3 were verified with insignificant p value of the curvature. Augmented CCD was applied in addition to the two-level FFD on response 4 to accommodate the significant p value of the curvature in the data. Model adequacy of the developed model were within the acceptable range, with the overall model p value < 0.05 and lack of fit p value > 0.05. Optimisation analysis revealed that a bioplastic film with good tensile strength (33.90 MPa), low percentage of elongation at break (3.58%), minimised level of water vapour permeability (2.63×10^{-10} g Pa^{-1} s^{-1} m^{-1}) as well as percentage of water solubility (33.73%) could be produced by using the statistical model generated from the study. Validation experiments indicated that the percentage errors between predicted and experimental values were generally below 3.21%. To the best of our knowledge, the present study could be considered as the first multi-response statistical model developed for the synthesis process of bioplastic film from *S. siliquosum* extract.

Acknowledgements The authors would like to acknowledge the following: Ministry of Education Malaysia (ERGS/1/2013/TK04/TAYLORS/02/01), Taylor's University (TU), Universiti Tunku Abdul Rahman (UTAR) and University College of Technology Sarawak (UCTS/RESEARCH/4/2016/05) for funding and technical support.

References

Aadil KR, Prajapati D, Jha H (2016) Improvement of physcio-chemical and functional properties of alginate film by *Acacia* lignin. Food Packag Shelf Life 10:25–33

Alshaibani AM, Yaakob Z, Alsobaai AM, Sahri M (2014) Optimization of Pd-B/γ-Al_2O_3 catalyst preparation for palm oil hydrogenation by response surface methodology (RSM). Braz J Chem Eng 31:69–78

ASTM International (2010) Standard test methods for water vapor transmission of materials. ASTM International, West Conshohocken

ASTM International (2012) Standard test method for tensile properties of thin plastic sheeting. ASTM International, West Conshohocken

Azeredo HMC, Magalhães US, Oliveira SA, Rebeiro HL, Brito ES, de Moura MR (2012a) Tensile and water vapour properties of calcium-crosslinked alginate-cashew tree gum films. Int J Food Sci Technol 47:710–715

Azeredo HMC, Miranda KWE, Rosa MF, Nascimento DM, de Moura MR (2012b) Edible films from alginate-acerola puree reinforced with cellulose whiskers. LWT-Food Sci Technol 46:294–297

Barka N, Abdennouri M, Boussaoud A, Galadi A, Baâlala M, Sahibed-Dine A, Nohair K, Sadiq M (2014) Full factorial experimental design applied to oxalic acid photocatalytic degradation in TiO_2 aqueous suspension. Arab J Chem 7:752–757

Benavides S, Villalobos-Carvajal R, Reyes JE (2012) Physical, mechanical and antibacterial properties of alginate film: effect of the crosslinking degree and oregano essential oil concentration. J Food Eng 110:232–239

Bertagnolli C, da Silva MGC, Guibal E (2014) Chromium biosorption using the residue of alginate extraction from *Sargassum filipendula*. Chem Eng J 237:362–371

Blanco-Pascual N, Montero MP, Gómez-Guillén MC (2014) Antioxidant film development from unrefined extracts of brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum*. Food Hydrocoll 37:100–110

Cavazzuti M (2013) Design of experiments. In: Cavazzuti M (ed) Optimization method: from theory to design scientific and technological aspects in mechanics n. Springer, Heidelberg, pp 13–42

Chee SY, Wong PK, Wong CL (2011) Extraction and characterisation of alginate from brown seaweeds (Fucales, Phaeophyceae) collected from Port Dickson, Peninsular Malaysia. J Appl Phycol 23:191–196

Clementi F, Mancini M, Moresi M (1998) Rheology of alginate from *Azotobacter vinelandii* in aqueous dispersions. J Food Eng 36: 51–62

Crossingham YJ, Kerr PG, Kennedy RA (2014) Comparison of selected physico-chemical properties of calcium alginate films prepared by two different methods. Int J Pharm 473:259–269

da Costa MPM, Delpech MC, de Mello Ferreira IL, de Macedo Cruz MT, Castanharo JA, Cruz MD (2017) Evaluation of single-point equations to determine intrinsic viscosity of sodium alginate and chitosan with high deacetylation degree. Polym Test 63:427–433

Draget KI, Taylor C (2011) Chemical, physical and biological properties of alginates and their biomedical implications. Food Hydrocoll 25: 251–256

Ellen MacArthur Foundation (2016) The new plastics economy: rethinking the future of plastics

FAO (2013) Expert consultation on the establishment of a sago network for Asia and the Pacific. Roundtable report, Bangkok

Fazilah A, Maizura M, Abd Karim A, Bhupinder K, Rajeev B, Uthumporn U, Chew SH (2011) Physical and mechanical properties of sago starch—alginate films incorporated with calcium chloride. Int Food Res J 18:1027–1033

Fertah M (2017) Isolation and characterization of alginate from seaweed. In: Venkatesan J, Anil S, Kim S-K (eds) Seaweed polysaccharide: isolation, biological and biomedical application. Elsevier, Amsterdam, pp 11–26

Gade R, Tulasi M, Bhai V (2013) Seaweeds: a novel biomaterial. Int J Pharm Pharm Sci 5:40–44

Galus S, Lenart A (2013) Development and characterization of composite edible films based on sodium alginate and pectin. J Food Eng 115: 459–465

Gao C, Pollet E, Avérous L (2017) Properties of glycerol-plasticized alginate films obtained by thermo-mechanical mixing. Food Hydrocoll 63:414–420

Ghosh P, Karmakar G (2014) Solvent free microwave assisted synthesis of poly myristyl acrylate—characterization and evaluation as additives for lubricating oil. Pet Sci Technol 32:1465–1472

Harunsyah, Yunus M, Fauzan R (2017) Mechanical properties of bioplastics cassava starch film with zinc oxide nanofiller as reinforcement. IOP Conf Ser Mater Sci Eng 210:1–8

Haug A (1964) Composition and properties of alginates. Norwegian Institute of Seaweed Resources, Trondheim

Hernández-Carmona G, Mchugh DJ, Arvizu-Higuera DL, Rodríguez-Montesinos YE (2002) Pilot plant scale extraction of alginates from *Macrocystis pyrifera* 4. Conversion of alginic acid to sodium alginate, drying and milling. J Appl Phycol 14:445–451

Hii SL, Lip KF, Loh YT, Wong CL (2014) Statistical optimization of fermentable sugar extraction from the Malaysian brown alga *Sargassum binderi*. J Appl Phycol 27:2089–2098

Ibrahim NA, El-Bisi MK, Ibrahim HM, Hashem MM, Fahmy HM (2015) Triclosan-loaded alginate films for topical medical applications. Int J Adv Res 3:547–554

Jost V, Kobsik K, Schmid M, Noller K (2014) Influence of plasticiser on the barrier, mechanical and grease resistance properties of alginate cast films. Carbohydr Polym 110:309–319

Karbowiak T, Hervet H, Leger L, Champion D, Debeaufort F, Voiley A (2006) Effect of plasticizers (water and glycerol) on the diffusion of a small molecule in iota-carrageenan biopolymer films for edible coating application. Biomacromolecules 7:2011–2019

Karunanithy C, Muthukumarappanm K (2011) Optimization of switchgrass and extruder parameters for enzymatic hydrolysis using response surface methodology. Ind Crop Prod 33:188–199

Linko P, Mattson C, Linko YY (1984) Production of fat bread by continuous extrusion cooking from high alpha-amylase. J Cereal Sci 2:43–51

Liu S, Li Y, Li L (2017) Enhanced stability and mechanical strength of sodium alginate composite films. Carbohydr Polym 160:62–70

López OV, Ninago MD, Lencina MMS, García MA, Andreucetti NA, Ciolino AE, Villar MA (2015) Thermoplastic starch plasticized with alginate-glycerol mixtures: melt-processing evaluation and film properties. Carbohydr Polym 126:83–90

Mali S, Sakanaka LS, Yamashita F, Grossmann MVE (2005) Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. Carbohydr Polym 60:283–289

Mungo T (2003) Water vapour transmission through weather resistive barrier. Masters dissertation, Concordia University, Quebec, Canada

Mutuk T, Mesci B (2014) Analysis of mechanical properties of cement containing boron waste and rice husk ash using full factorial design. J Clean Prod 69:128–132

Olivas GI, Barbosa-Canovas GV (2008) Alginate-calcium films: water vapor permeability and mechanical properties as affected by plasticizer and relative humidity. LWT-Food Sci Technol 41:359–366

Osborne JW (2010) Improving your data transformations: applying the box-cox transformation. Pract Assess Res Eval 15:1–9

Pawar SN, Edgar KJ (2012) Alginate derivatization: a review of chemistry, properties and applications. Biomaterials 33:3279–3305

Pegg AM (2012) The application of natural hydrocolloids to foods and beverages. In: Baines D, Seal R (eds) Natural food additives, ingredients and flavourings. Elsevier Science, Amsterdam, pp 175–196

Plastics Europe (2015) Plastics—the facts 2015. http://www.plasticseurope.org/documents/document/20151216062602-plastics_the_facts_2015_final_30pages_14122015.pdf. Accessed 28 May 2016

Poeloengasih CD, Anggraeni FD (2014) Exploring the characteristics of sago starch films for pharmaceutical application. Starch 66:1103–1108

Raissi S, Farsani R-E (2009) Statistical process optimization through multi-response surface methodology. World Acad Sci Eng Technol 3:247–251

Rangel-Marrón M, Montalvo-Paquini C, Palou E, López-Malo A (2013) Optimization of the moisture content, thickness, water solubility and water vapor permeability of sodium alginate edible films. In: Moller JAD, Kibler MR, Hefferlin R (eds) Recent advances in chemical engineering, biochemistry and computational chemistry. WSEAS Press, Paris, pp 72–78

Rashvand M, Vosough M, Kargosha K (2016) Preparation of magnetic nanographene sorbent for extraction and quantification of targeted PPCPs in environmental water samples. RSC Adv 6:75609–75617

Rayne S (2008) The need for reducing plastic shopping bag use and disposal in Africa. Afr J Environ Sci Technol 3:7–9

Rhim J-W (2004) Physical and mechanical properties of water resistant sodium alginate films. LWT-Food Sci Technol 37:323–330

Sellimi S, Younes I, Ayed HB, Maalej H, Montero V, Rinaudo M, Dahia M, Mechichi T, Hajji M, Nasri M (2015) Structural, physicochemical and antioxidant properties of sodium alginate isolated from a Tunisian brown seaweed. Int J Biol Macromol 72:1358–1367

Seyed Shahabadi SM, Reyhani A (2014) Optimization of operating conditions in ultrafiltration process for produced water treatment via the full factorial design methodology. Sep Purif Technol 132:50–61

Siddaramaiah, Swamy TMM, Ramaraj B, Lee JH (2008) Sodium alginate and its blends with starch: thermal and morphological properties. J Appl Polym Sci 109:4075–4081

Smith WF (2005) Model evaluation. In: Experimental Design for Formulation. Society for Industrial and Applied Mathematics, Philadelphia, pp 183–204

Suppakul P, Chalernsook B, Ratisuthawat B, Prapasitthi S, Munchukangwan N (2013) Empirical modeling of moisture sorption characteristics and mechanical and barrier properties of cassava

flour film and their relation to plasticizing-antiplasticizing effects. LWT-Food Sci Technol 50:290–297

Talja RA, Helén H, Roos YH, Jouppila K (2007) Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. Carbohydr Polym 67:288–295

Thavarajah R, Mudimbaimannar VK, Elizabeth J, Rao UK, Ranganathan K (2012) Chemical and physical basics of routine formaldehyde fixation. J Oral Maxillofac Pathol 16:400–405

Torres MR, Sousa APA, Silva Filho EAT, Melo DF, Feitosa JPA, de Paula RCM, Lima MGS (2007) Extraction and physicochemical characterization of *Sargassum vulgare* alginate from Brazil. Carbohydr Res 342:2067–2074

Wang L, Auty MAE, Kerry JP (2010a) Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. J Food Eng 96:199–207

Wang Q, Hu X, Du Y, Kennedy JF (2010b) Alginate/starch blend fibers and their properties for drug controlled release. Carbohydr Polym 82:842–847

Weerapoprasit C, Prachayawarakorn J (2016) Properties of biodegradable thermoplastic cassava starch/sodium alginate composites prepared from injection molding. Polym Compos 37:3365–3372

Wong PK (2011) Preparation and characterisation of polymeric biocomposites using plant-based materials. Masters dissertation, Universiti Tunku Abdul Rahman, Kuala Lumpur, Malaysia

Yamamoto Y (2015) Starch productivity. In: The Society of Sago Palm Studies (ed) The sago palm: the food and environmental challenges of the 21st century. Kyoto University Press, Kyoto, pp 230–231

Yuan J, Huang J, Wu G, Tong J, Xie G, Duan J, Qin M (2015) Multiple responses optimization of ultrasonic-assisted extraction by response surface methodology (RSM) for rapid analysis of bioactive compounds in the flower head of *Chrysanthemum morifolium* Ramat. Ind Crop Prod 74:192–199

Zhang Y, Han J (2006) Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. J Food Sci 71:109–118