Industrial Crops and Products xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Graft copolymerization of polyDADMAC to cassava starch: Evaluation of process variables via central composite design

M.A.A. Razali, H. Ismail, A. Ariffin*

School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:
Received 30 May 2014
Received in revised form
22 September 2014
Accepted 4 October 2014
Available online xxx

Keywords:
Grafting
Response surface methodology
Polydiallyldimethylammonium chloride
Cassava starch

ABSTRACT

Grafting of polydiallyldimethylammonium chloride (polyDADMAC) to cassava starch was prepared using potassium persulfate (KPS) as a free radical initiator. Response surface methodology (RSM) comprising a three-level and four-variable central composite designs were implemented for variable evaluation and optimization. These variables include the mole ratio of diallyldimethylammonium chloride (DADMAC) to starch (anhydroglucose unit (AGU)), reaction temperature (°C), initiator concentration (mol/L), and reaction time (*t*). Grafting percentage was considered as a response from the variable interaction. The optimum condition derived were 1.96 [mole ratio of DADMAC to starch (AGU)], 40 °C (reaction temperature) 0.09 mol/L (initiator concentration) and 4.99 h (reaction time). The actual experimental yield was 21.98% at optimum conditions, which is close to the maximum predicted value of 22.80%.

1. Introduction

Recently, the effort in developing carbohydrate polymer that can create effective functional groups for potential end use has been actively studied. One of these developments involves cassava starch (Jyothi et al., 2011). Cassava starch has received great attention due to its low cost, naturally abundant, renewability and biocompatibility. In fact, its roots contain a very low quantity of protein and lipid thus gives the processing of cassava tubers for starch extraction is relatively simple and high purity (Nair and Jyothi, 2014).

A well-established and effective method for modifying and tailoring new and desired properties of cassava starch is graft copolymerization. Jyothi and Carvalho (2013) had defined a graft copolymerization as free radical reactions with initiators create free radical sites on the glucan backbone and serve as micro-initiators. This reaction occurred in the presence of synthetic monomers to yield polymer grafts of high molecular weight (Jyothi and Carvalho, 2013). Many potential applications for these grafted cassava starches have been discovered; for example, as superabsorbent (Kiatkamjornwong et al., 2000, 2002; Lanthong et al., 2006; Parvathy and Jyothi, 2012) and flocculants (Jiraprasertkul et al., 2006; Nair and Jyothi, 2014).

For application as flocculants, the cassava starch frequently grafted with synthetic water soluble polymer. Most of them are based on acrylamide. However, researchers start to explored and utilized others water soluble polymer in grafted with starch such as polyDADMAC. The advantage of this polymer is high-charge-density cationic polymer and extensively been used in the treatment of particle suspension (Razali et al., 2011). There are few studies utilizing polyDADMAC but most of them are co-polymerized with polyarcrylamide before grafted onto the starch (Lu et al., 2004; Li et al., 2011; Lv et al., 2012). To date, there is yet to be published the grafting of PolyDADMAC alone with cassava starch. The grafting process is quite challenging because the monomer itself has a cationic charge.

In this study, the capacity of polyDADMAC to be grafted onto cassava starch was investigated using four variables, including the mole ratio of DADMAC and AGU in cassava starch, reaction temperature, initiator concentration and reaction time. Central composite design (CCD), which is a type of response surface methodology (RSM) was preferred in reducing the time taken to optimize the cassava starch-grafted polyDADMAC. This approach of using a mathematical relationship can describe the response of interest in terms of independent variables aside from building a quadratic response surface. Hence this work aimed to optimize all variables in

* Corresponding author. Tel.: +60 4 5946176; fax: +60 4 5941011.
E-mail address: srazlan@usm.my (A. Ariffin).

http://dx.doi.org/10.1016/j.indcrop.2014.10.010
0926-6690/

Table 1
Grafting variables and their coded levels for central composite design.

Variable (factors)	Code	Units	Coded variables level		
			−1	0	−1
Mole ratio of DADMAC to starch (AGU)	X_1	None	0.50	1.25	2.00
Reaction temperature	X_2	°C	40	50	60
Initiator concentration	X_3	mol/L	0.03	0.06	0.09
Reaction time	X_4	h	3	4	5

obtaining the maximum grafting percentage of polyDADMAC onto cassava starch.

2. Materials and methods

2.1. Materials

The native cassava starch was obtained from Thai Better Foods Co., Thailand. The monomer used was DADMAC in 65 wt% aqueous solutions and was supplied by Sigma Aldrich Sdn. Bhd. The radical initiator used was potassium persulfate (KPS), which was supplied by Merck Sdn Bhd. Acetone and ethanol from J.T. Baker were used as solvents. Meanwhile deionized water was chosen as a medium for cassava starch and KPS solution preparation. All reagents were used without further purification.

2.2. Design experimental method

In this study, the grafted samples were prepared via the radical initiation method, where the variables studied were the mole ratio of DADMAC to starch (AGU) (x_1), reaction temperature (x_2), initiator concentration (x_3), and reaction time (x_4). All variables and their respective ranges were chosen based on literature and preliminary studies (Table 1). Four variables require 30 runs (calculated based on Eq. (1)) which consist of 16 factorial points, 8 axial points and 6 replicates at the center points.

$$N = 2^n + 2n + N_c = 16 + 8 + 6 = 30 \quad (1)$$

where N is the total experiment required.

The α-value for this design was fixed at 1 (face-centered), and the response for this experiment was the grafting percentage (y). The response was used to develop an empirical model that correlated with the response to the four grafting process variables using a second-degree polynomial as shown in this equation:

$$Y = b_o + \sum_{i=1}^{n} b_i X_i + \left[\sum_{i=1}^{n} b_{ii} X_{ii} \right] + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (2)$$

where Y is the predicted response, b_o is a constant coefficient, b_i is a linear coefficient, b_{ij} is an interaction coefficient, b_{ii} is the quadratic equation, and X_i and X_j are the coded values of the grafting reaction variables.

2.3. Experimental set up for grafting reactions

The grafting reaction of DADMAC with cassava starch was performed in a 4 L Atlas Potassium Jacketed laboratory batch reactor (Syrris), which was equipped with a Heidoplh overhead stirrer and a glass-lined three-blade retreat impeller. The reactor was surrounded by an oil jacket to control the reaction temperature. A total of 25 g of cassava starch was loaded to the reactor and was then suspended in 450 mL of deionized water. The contents were heated at 90 °C and stirred (250 rpm) in an N_2 atmosphere for 1 h to facilitate homogenous gelatinization. The homogenous gelatinization was confirmed by color changes from milky into transparent. The gelatinized starch was then cooled to 40 °C. The pre-determined monomer was poured into the reactor and the reaction mixture was heated back to a pre-determined temperature with stirring in an N_2 atmosphere. An aqueous solution of KPS was prepared in 50 mL of deionized water. The aqueous solution was slowly charged into the reactor via an Atlas syringe pump at a speed of 0.5 mL/min. Stirring and heating were stop at a desired reaction time, and the reaction mixture was cooled to room temperature before opening the reactor. After cooling, the samples solutions were precipitated with access of acetone, filtered and dry at temperature 80 °C.

2.4. Purification of graft sample by solvent extraction method

Homopolymer of polyDADMAC was removed from the samples via solvent extraction by using ethanol at 90 °C for 6 h. The remaining grafted product was dried in oven at 65 °C for 12 h. The dried products were then pulverized. The grafting percentage of this synthesized cassava starch-grafted polyDADMAC was evaluated as:

$$\%\text{ of grafting} = \frac{\text{wt. of grafted polymer} - \text{wt. of cassava strach}}{\text{wt. of cassava strach}} \times 100 \quad (3)$$

2.5. Characterization

2.5.1. FTIR spectroscopy

Fourier transformation (FT) InfraRed (IR) analysis was carried out using a Spectrum 2000 FT-IR Spectrometer (Perkin Elmer, CT, USA) in the range of 400–4000 cm^{-1}. The IR spectra for grafted starch and native starch were recorded on a diamond plate.

2.5.2. X-ray diffraction analysis

The XRD pattern of the sample was recorded using an X-ray diffractometer (Bruker D8 Advance, Germany). The instrument was operated with CuKα monochromatic radiation (λ = 1.5406 Å), and the data were collected at a range of 0° to 90°.

2.5.3. Scanning electron microscopy

The surface morphologies of the native starch and the grafted copolymers were examined using a Cambridge scanning electron microscope (FESEM, ZEISS – Supra 35 VP) operating at 5 kV. The samples were coated with gold films prior to imaging.

2.6. Model fitting and statistical analysis

The experimental data were analyzed using the statistical software Design Expert version 8.0.7.1 (STAT-EASE Inc., Minneapolis, USA). An optimum condition of grafting percentage was performed based on three main steps which were analysis of Variance (ANOVA), a regression analysis and plotting of RSM.

3. Results and discussion

3.1. Characterization of cassava starch grafted polyDADMAC

Native starch and grafted samples with different percentages of grafting, which include R11 (1.76%), R25 (14.84%), and OPT (21.98%), were characterized and discussed in details in this section.

3.1.1. FTIR

Confirmation of the prepared grafting samples was conducted via FTIR. The FTIR spectra of cassava starch, R11, R25, and OPT are shown in Fig. 1.