Synthesis and Thermal Stability of Cassava Starch-Grafted Polyacrylamide Hydrogel by Microwave-Assisted Method

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ABSTRACT

Cassava starch-grafted polyacrylamide (CSt-g-PAM) hydrogels were generated by grafting cassava starch as the backbone, acrylamide as the monomer, and potassium peroxodisulfate as the initiator. In this work, we investigated on the effect of monomer concentration and irradiation time on the thermal stability of CSt-g-PAM. Cassava starch, acrylamide, and KPS were added to the distilled water, and microwaves were used to help with grafting. The grafting process was carried out using an irradiation-cooling cycle. The cycle was repeated until a gel was formed for 180 seconds (6 cycles). The gel formed was soaked in acetone until a precipitate formed. The precipitate obtained was dried in an oven at 50°C for 24 hours. The dried precipitated CSt-g-PAM was used in the characterization process. X-ray powder diffraction (XRD) was used to determine the crystalline structure of CSt-g-PAM. The thermogravimetric (TGA) study of CSt-g-PAM revealed its thermal stability. The XRD spectra of CSt-g-PAM revealed that the cassava starch backbone was effectively grafted with polyacrylamide. TGA showed that CSt-g-PAM has much higher thermal stability than native cassava starch. The greatest performance was obtained by preparing CSt-g-PAM with 10 g of acrylamide and 180 s irradiation time, as evidenced by the highest percentage of residual weight in the TGA findings. The contribution of this study is to show the thermal stability features of CSt-g-PAM make it interesting for use in EOR applications.

1. Introduction

Polymer injection in enhanced oil recovery (EOR) technology helps drive remaining oil by improving the viscosity of the displacing fluid. According to field measurements, polymer flooding contributed an additional 20% of oil recovery [1]. Hydrogels are widely used during polymer flooding operations to regulate water output by blocking high-permeability zones in heterogeneous mature reservoirs and subsequently converting the water to low-permeability zones [2]. Grafting modification of natural and synthetic polymers has previously been investigated to improve the characteristics of polymers. Modification by graft copolymerization is an effective and simple technique to enhance functional moieties of natural polymers [3], [4], [5].

Cassava starch is a common resource that may be utilized as a primary material in the synthesis of hydrogels. Natural polymers feature a distinctive helical shape and many active groups, such as hydroxyl, in the molecular chain. It may be complex and quickly absorb water, making it a good material for a polymer flooding agent [3], [6], [7]. Natural polymers are also cost-effective, readily available, biocompatible, and environmentally friendly. However, natural polymers have challenges such as biodegradation and mainly do not possess adequate strength [2], [8]. Natural polymer functionalization with a nonionic monomer such as acrylamide can decrease its biodegradability and improve its solubility in water and thermal stability [3], [9], [10]. Because of the graft of polyacrylamide chains onto the cassava starch backbone, the graft polymer made from natural and synthetic polymers has advantages such as excellent heat stability.

Several earlier investigations have reported on producing graft polymers using a mix of natural and synthetic polymers that increase thermal stability. Previous research investigated the production of graft polymer hydrogels for enhanced oil recovery utilizing polyacrylamide and starch. The thermal stability of polyacrylamide graft starch is greater than that of polyacrylamide hydrogel [2]. Hydrogel from hydroxypropyl guar and hydrolyzed polyacrylamide were synthesized by interpenetrating polymer network technique for an oil recovery application. The hydrogels showed high viscosity stability and thermal stability [11]. Hydrogel from starch and acrylamide was synthesized by aqueous radical polymerization using 1,6-hexanediol diacrylate as crosslinker and ammonium persulfate as initiator. It was prepared for plugging agent application. The hydrogel showed good thermal stability [12]. Polymerization with regular thermal heating was used for all the synthesis outlined above. A previous study has demonstrated that modifying natural and synthetic polymers successfully enhanced the heat resistance of the produced hydrogel.

According to previous literature, a grafting process in this study was conducted using microwave irradiation. The resulting hydrogel, cassava starch-grafted polyacrylamide (CSt-g-PAM) hydrogel, has the potential polymer flooding agent that has never been reported. Microwave irradiation accelerates the synthesis of graft polymers over conventional heating techniques, resulting in uniform grafting with a relatively short time needed for polymer production. The microwave intensity and irradiation exposure period are electronically regulated to control the percentage of grafting [13], [14], [15].

The contribution of this study is to investigate the effect of monomer concentration and irradiation time on the thermal properties of the hydrogel obtained. The crystalline structure of the hydrogel was studied using X-ray powder diffraction (XRD). The essential properties of hydrogel for EOR application can stand in high temperatures reservoirs. The thermal stability of the hydrogel is indicated by thermogravimetric analysis (TGA).

2. Research Methodology

2.1. Materials

The backbone cassava starch (CS) was obtained from a local market in Surakarta, Indonesia. The monomer acrylamide (AM) (>99%) and the initiator potassium peroxydisulfate (KPS) (>99%) were purchased from E. Merck, Germany. Acetone (technical) was supplied from Saba Kimia, Surakarta, Indonesia. All chemicals and reagents are utilized without further processing.

2.2. Synthesis of CSt-g-PAM

As stated in Table 1., CSt-g-PAM was produced by varying the acrylamide concentration and irradiation time. In 50 mL of distilled water, cassava starch, acrylamide, and KPS were added. The solution mixture was placed in a 1000 mL beaker and microwaved (Krisbow 20 L) at 364 W. The solution was irradiated by microwave for 30 seconds until it exceeded the boiling point of <70^{o}C, then cooled by soaking the reaction beaker in cold water. There were different kinds of irradiation time: microwave irradiation - a cooling step, was continued until a gel was formed and a predetermined irradiation period (180 s or 6 cycles). After the microwave-assisted grafting procedure, the gel material was left to stand for 24 hours to complete the grafting reaction process. Excess acetone was absorbed into the reaction beaker's gel material until a precipitate developed, as shown in Fig. 1. The CSt-g-PAM precipitate was dried in a 50^{o}C oven for 24 hours.

Table 1. Various Compositions for Synthesis Of Cassava Starch-Grafted Polyacrylamide Hydrogel

Code	Mass of CS (g)	Mass of AM (g)	Mass of KPS (g)	Irradiation time (s)
CSt-g-PAM A	1	2	0.3	300
CSt-g-PAM B	1	2	0.3	180
CSt-g-PAM C	1	5	0.3	60
CSt-g-PAM D	1	5	0.3	180
CSt-g-PAM E	1	10	0.3	30
CSt-g-PAM F	1	10	0.3	180

Fig. 1. Precipitated formed.

2.3. X-ray powder diffraction (XRD) Characterization

XRD spectra of cassava starch and CSt-g-PAM were obtained to investigate structural differences before and after the grafting procedure. The samples' XRD patterns were acquired using an XRD MD10 minidiffractometer, MTI. Scans were run from 17 to 71°C. The instrument was conducted with CuKα monochromatic radiation (λ= 1.4518°A).

2.4. Thermogravimetric Analysis (TGA) Characterization

Thermal properties of cassava starch and CSt-g-PAM samples were tested using Linseis STA PT1600 (Germany). The temperature was set from 25 to 500°C, and the constant heating rate was 10°C/min).

3. Results and Discussion

3.1. XRD Studies

Fig. 2. shows the XRD spectra of cassava starch and CSt-g-PAM prior to and following the grafting process. From the results, cassava starch revealed two peaks at $2\theta = 18^o$ and $2\theta = 23^o$, as previously reported [16]. Cassava starch typically contains four crystalline peaks around 15°, 17°, 18°, and 23° [17].

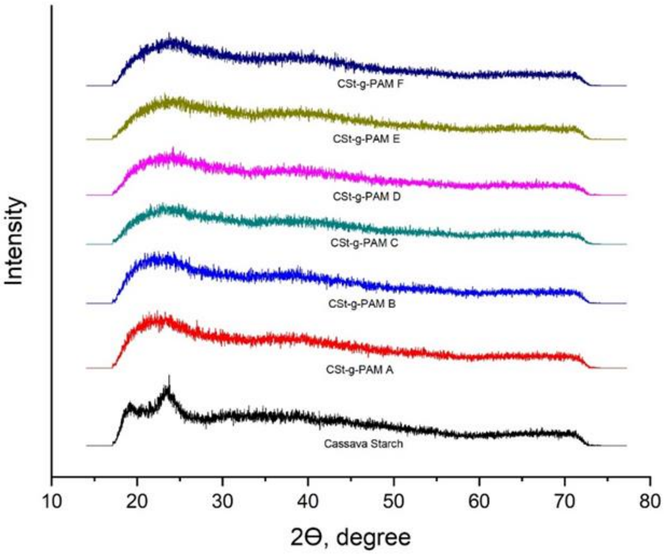

Fig. 2. XRD spectra between cassava starch and CSt-g-PAM

Grafting polyacrylamide chains on the backbone of cassava starch decreased cassava starch crystallinity because grafting polyacrylamide on the cassava starch caused the regular and repeated structure of cassava starch to become irregular so that the design of CSt-g-PAM became amorphous. It was evidenced by the disappearance of the peak at $2\theta = 18^o$, while the intensity at $2\theta = 23^o$ was dramatically lowered in the CSt-g-PAM's XRD structure. The effective grafting of polyacrylamide onto the backbone of cassava starch was established. The disappearance of crystallization peaks suggested that the graft copolymerization procedure disrupted the starch's glucose ring structure and decreased the quantity of the -OH group. To some extent, reducing the -OH group inhibited intramolecular and intermolecular hydrogen bonding [17]. The reduction in crystallinity was caused by adding polyacrylamide chains to the backbone, which is responsible for disrupting the backbone's intermolecular connections [18]. Similar results were reported in the literature [17], [19]. This decrease in crystallinity removed the cassava starch's strong bonds, producing an amorphous CSt-g-PAM.

3.2. TGA Result

Fig. 3. depicts the TGA thermogram of CSt-g-PAM weight residue as a function of temperature. Cassava starch's thermogravimetric characteristics are classified into two categories. At temperatures up to 300ºC, cassava starch lost weight in the first stage, which was related to the degradation of water molecules. The second step involved starch degradation at 300-500°C, which might be related to heat breakdown because the polymer chain weakens, causing significant losing weight [20]. The principal cause of heat degradation of cassava starch molecules is the degradation of the α -1,4iglucoside link between amylose and amylopectin. Furthermore, the α -1,6iglycosidic association can be dissolved, although the α -1,4iglycosidic bond is more easily broken than the α -1,6iglycosidic bond [21].

Four phases of degradation were identified in the CSt-g-PAM samples. The first phase, which occurred at temperatures of up to 100ºC, was related to the evaporation of water. During the second phase, from around 100 to 260ºC, the amide group of polyacrylamide decomposed. The starch chain degraded at temperatures ranging from 260 to 35ºC, and the polymer chain degraded at temperatures ranging from 350 to 500ºC [22].

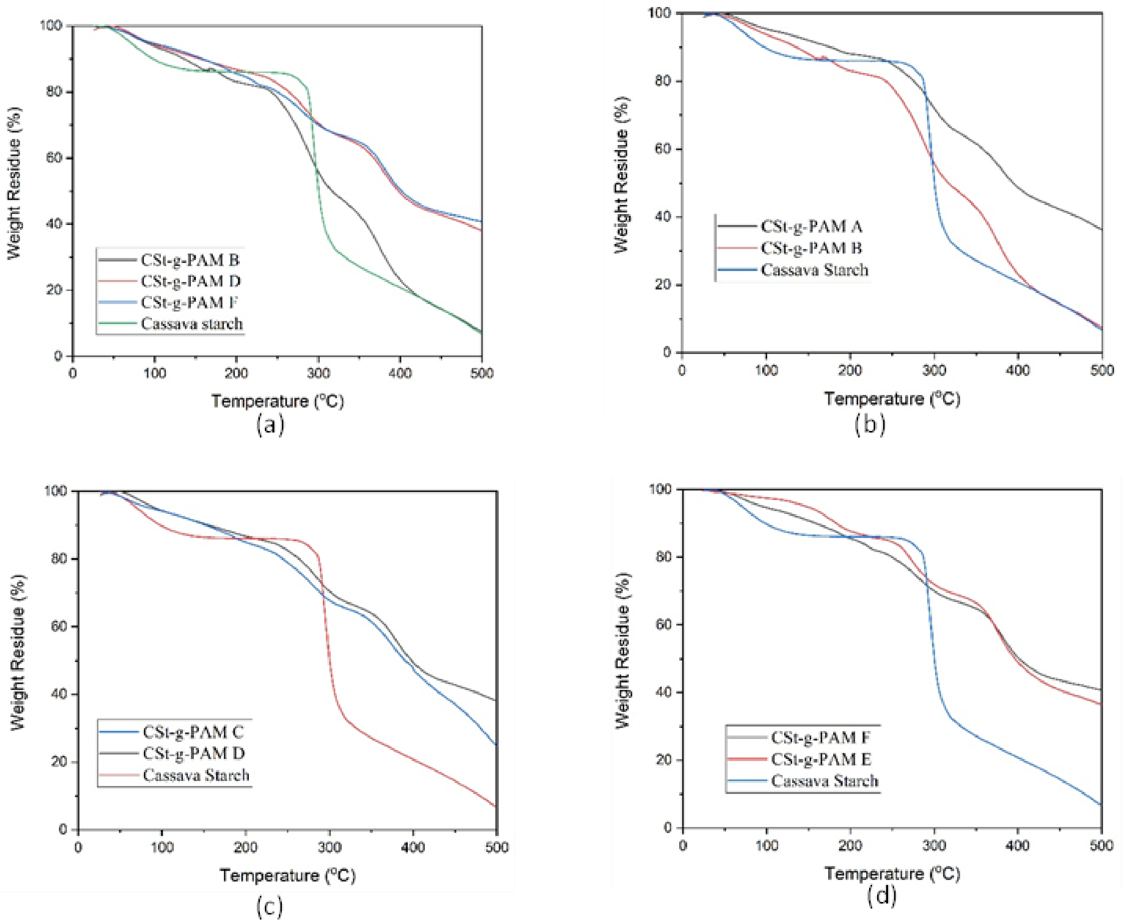

Fig. 3. TGA analysis of cassava starch and CSt-g-PAM (a) effect of acrylamide concentration (b) effect of time irradiation when acrylamide was 2 g (c) effect of time irradiation when acrylamide was 5 g (d) effect of time irradiation when acrylamide was 10 g

The acrylamide concentration and irradiation time affect the thermogravimetric characteristics of the CSt-g-PAM produced. The thermal stability of CSt-g-PAM improved with increased irradiation time and acrylamide concentration. In Fig. 3.(a), CS-g-PAM B, D, and F were irradiated for 180 seconds, and the weight residue improved as the acrylamide increased from 2 to 10 g.

Fig. 3.(b) showed that the weight residue of CSt-g-PAM A and B increased as irradiation time increased from 180 to 300 s. Fig. 3.(c) showed that the weight residue of CSt-g-PAMiC and D increased as irradiation time increased from 60 to 180 s. And Fig. 3.(d) showed that the weight residue of CSt-g-PAM E and F increased as irradiation time increased from 30 to 180 s.

As previously stated, stages 2, 3, and 4 concern polymer degrading side groups, starch chain degradation, and polymer dissolving structure. More polyacrylamide will be grafted onto cassava starch as the acrylamide concentration and interactions between monomers and cassava starch develop. As a consequence, thermal stability has improved [22].

The CSt-g-PAM thermogram revealed a considerable improvement in degradation temperature, which might be attributed to polyacrylamide in the cassava starch backbone. The TGA of CSt-g-PAM at around 500^{o}C indicated that the hydrogel was stable at 25-500^{o}C, representing a significant thermal stability increase over native cassava starch. It was similar to the TGA of chia seed polymer for enhanced oil recovery [23]. Most studies conclude that materials are "thermally stable" if the polymer sample keeps most of its mass at the temperature of interest, generally up to 200^{o}C, which approximates the temperature of an oil reservoir. It came to the conclusion that grafted polymers preserved their original mass across this temperature range, and, as a result, their substance would be thermally stable in high-temperature reservoirs [24]. As a result, the CSt-g-PAM is suitable for use in high-temperature reservoirs.

4. Conclusion

The microwave-assisted procedure and potassium peroxodisulfate (KPS) as the initiator was used to synthesize cassava starch-grafted polyacrylamide (CSt-g-PAM). The existence of XRD spectra indicating that the grafting procedure reduced cassava starch crystallinity suggested that the polyacrylamide chain grafting onto the cassava starch backbone was efficient. The effects of acrylamide monomer and irradiation time on the thermal stability of CSt-g-PAM were examined using thermogravimetric analysis. The thermogravimetric properties of the CSt-g-PAM produced are affected by the concentration of acrylamide utilized and the duration of irradiation. The thermal stability of CSt-g-PAM increased with increasing acrylamide concentration and longer irradiation time. The TGA thermogram of CSt-g-PAM at 500^{o}C indicated that the hydrogel was stable between 25 and 500^{o}C, representing a considerable improvement in thermal stability over native cassava starch. As a result, the CSt-g-PAM is suitable for usage in high-temperature reservoirs.

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