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Graft copolymerization of acrylic acid to cassava starch—Evaluation of the influences of process parameters by an experimental design method

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ABSTRACT

The graft copolymerization of cassava starch with acrylic acid was investigated using a free radical initiator system (Fe^{2+}/H_2O_2 redox system) in water. A comprehensive understanding of the important variables and their interaction has been obtained by applying an experimental design method. In this approach, two ('high' and 'low') values of selected variables are considered. Important result parameters are add-on and the grafting efficiency. Out of eight reaction variables, it was found that only temperature, starch concentration and the starch to monomer ratio have a pronounced influence on these response parameters. Moderate reaction temperature (40 °C) and high starch concentration (10%) give relatively good results of add-on and grafting efficiency. A low starch to monomer ratio favors add-on but decreases grafting efficiency. These findings can be used to optimize the production of cassava starch–acrylate copolymers and to gain insight in the process–product property interactions, for various applications.

1. Introduction

The utilization of natural resources like starch and cellulose as a substitute for fossil resources derived materials is growing rapidly. To meet the product properties of many end-products, starch and cellulose modifications are inevitable. A well-established chemical modification of these polymers is graft copolymerization. For example, Stannett, Fanta, Daone, and Chatterjee (2002, chap. IX) reported that grafting cellulose (cotton) with acrylic acid, led to an increase in water absorbency of native cellulose from 4 cm^3/g to 26 cm^3/g. Similarly, by grafting cornstarch with acrylic acid (Hebeish, El-Rafie, Higazy, & Ramadan, 1992) the starch performed better when used as sizing agent in cotton weaving. Especially its removal after the printing process was improved, from ca. 20% for native starch to ca. 80% for the grafted starch.

Various articles on the grafting of vinyl monomers (like acrylic acid, acrylamide, acrylonitrile and also derivatives of acrylic acid, methyl acrylate, methyl methacrylate) onto natural starch have been published. More specifically, grafting of acrylic acid onto starch offers the prospect of replacing many current applications of polyacrylic acid, by more biodegradable products based on renewable raw materials. Examples are the use as a superabsorbent polymer (Athawale and Lele, 1998, 2000; Doane et al., 2004; Kiatkamjornwong, Chomsaksul, Sonsuk, 2000; Sangsirimongkolying, Damronglerd, Kiatkamjornwong, 1999; Thornton et al., 2004), as platforms for controlled drug delivery (Geresh et al., 2002), as an additive in paper and textile manufacturing (Hebeish et al., 1992; Mostofa, 1995), and as thickeners for printing cotton fabric (Bayazeed, Elzairy, & Hebeish, 1989). More recently, Willett (2009) reviewed research on starch grafting with the main focus on water-insoluble monomers.

In this paper, we report on the use of cassava starch for the synthesis of starch–acrylic acid graft copolymers. Cassava starch is abundantly available in tropical regions. In 2008 Indonesia produced over 21 million ton of cassava roots (30% of the total production in Asia) (FAO, 2008). The contribution of Asia to the total world cassava production was ca 33% at that time (FAO, 2010). A gelatinized solution of cassava starch has a low and uniform viscosity and this property facilitates processing considerably compared to other gelatinized starches.

The overall reaction scheme of the most likely reactions between starch and acrylic acid is given as structural formulas in Fig. 1. This scheme is based on a reactivity study of the oxidation of model compounds for starch and cellulose by metal ions (Mn(III), Ce(IV) and V(V) (Doba, Rodehed, & Rånby, 1984). It appeared that both the C1–C2 (end groups) and C2–C3 are predominant sites for the initiation of graft copolymerization. Most commonly, graft polymerization is brought about by free radical addition

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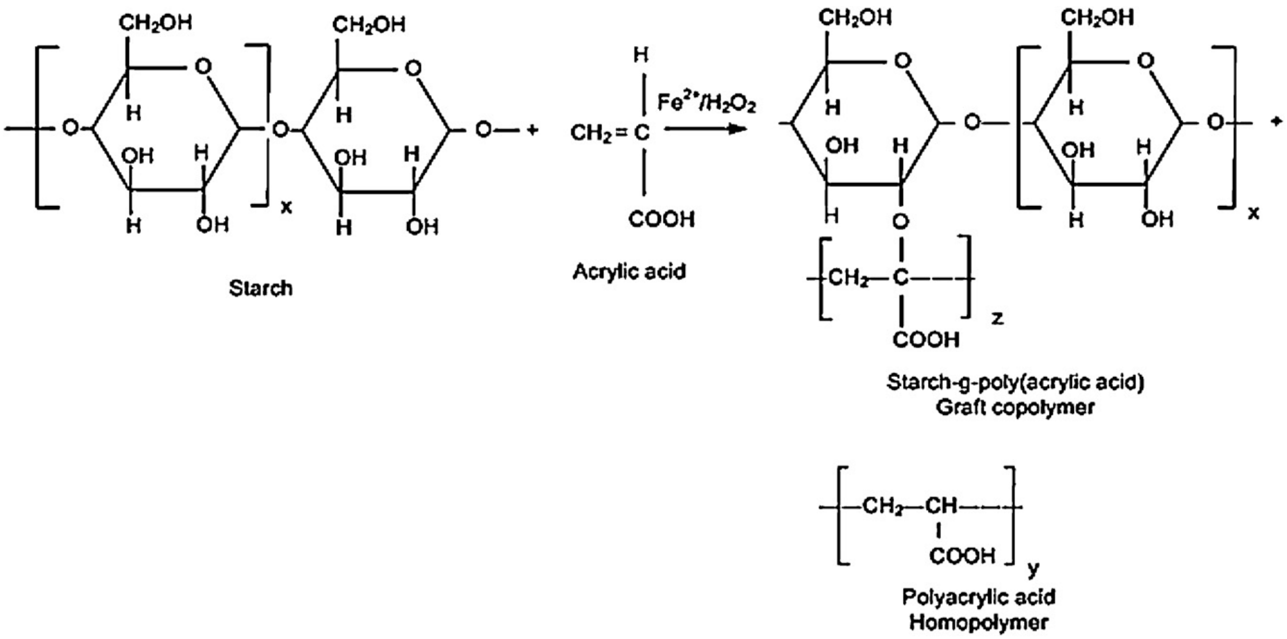


Fig. 1. Possible structures of (grafted) starch and homopolymer.

polymerization. The sequence of the steps with Fenton's reagent as an initiator is shown in Fig. 2. The first step is the formation of hydroxyl radicals by reaction of Fe^{2+} with hydrogen peroxide. A hydroxyl radical reacts with starch to form a starch radical. The subsequent reaction with acrylic acid results in the formation of polyacrylic acid grafts on the starch backbone. However, the OH radical not only reacts with starch but may also serve as an initiator for acrylic acid homopolymerization. Clearly, reaction conditions have to be chosen in such a way as to promote grafting onto the starch and to reduce the formation of homopolymer. This means that the grafting efficiency and the add-on should both be maximized. The reaction is typically performed in water as the solvent. Acrylic acid is completely soluble in water, so the reaction system with gelatinized starch can be considered homogeneous. We chose to use Fe^{2+}/H_2O_2 as the initiator like in Fanta, Burr, Doane, and Russell (1971). Other initiators have also been reported, like $K_2S_2O_8$ (Hebeish, Bayazeed, El-Alfy, & Khalil, 1988; Khalil, Mostafa, & Hebeish, 1993) or Ce^{4+} (Fanta et al., 1971). The choice for Fenton's initiator is based on previous work in our laboratory.

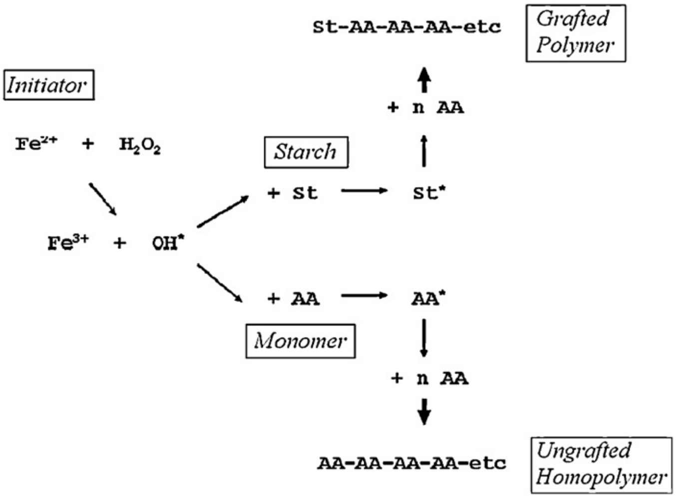


Fig. 2. Reaction scheme for the grafting copolymerization of starch with acrylic acid.

Even though a large number of reports on graft copolymerization has been published (Aravindakshan & Kumar, 2002; Athawale & Lele, 1998, 2000; Athawale & Rathi, 1999; Bayazeed et al., 1989; Brockway, 1964; Burr, Fanta, Doane, Russell, 1976; Doane et al., 2004; El-Rafie, Zahran, El Tahlawy, & Hebeish, 1995; Fakhru'l-Razi, Qudsieh, Wan Yunus, & Ahmad, 2001; Fanta et al., 1971; Fanta, Burr, Russell, & Rist, 1970; Fares, El-faqeeh, & Osman, 2003; Geresh et al., 2002; Goñi, Gurruchaga, Valero, & Guzman, 1983; Hebeish et al., 1992; Khalil, Mostafa, & Hebeish, 1990; Khalil et al., 1993; Kiatkamjornwong et al., 2000; Liu, Cheng, Wu, & Ma, 1993; Lutfor, Sidik, Haron, Rahman, & Ahmad, 2003; Mehrota & Rånby, 1978; Mostofa, 1995; Park, Song, & Song, 1999; Sangramsingh, Patra, Singh, & Patra, 2004; Sangsirimongkolying et al., 1999; Shukla & Atalye, 1994; Trimnell, Fanta, & Salch, 1996; Trimnell & Stout, 1980; Vázquez, Goñi, Gurruchaga, Valero, & Guzmán, 1989; Vera-Pacheco, Vázquez-Torres, & Canché-Escamilla, 1993; Wang & Liu, 2006; Zahran, Williams, & Stannett, 1980), there is not a comprehensive understanding of the grafting process yet. Also, there are only a limited number of papers published on the grafting of acrylic monomers onto cassava starch (Aravindakshan & Kumar, 2002; Kiatkamjornwong et al., 2000; Sangsirimongkolying et al., 1999). Therefore we use literature information on the grafting of other vinyl monomers as well in this introductory overview. Concluding, from this literature it appears that the important variables are: the state of the starch (either gelatinized or granular), the starch to monomer ratio, the initiator concentration, the reaction temperature and the reaction time.

There are conflicting experimental data on the effect of starch gelatinization pretreatment. Most of these data show that the use of gelatinized starch instead of native starch improves the add-on and graft selectivity. Only in the work of Fanta et al. (1971), acrylonitrile, methyl methacrylate and acrylamide show better graft polymerization results with granular starch compared to gelatinized starch. Still, for acrylic acid the results seem independent of starch granule swelling. Meanwhile, Rånby and Rodehed (1981) found that in the graft copolymerization of acrylonitrile onto starch, either granular or gelatinized, gave the same add-on (50%). With gelatinized starch however, longer grafts at lower graft frequency were found. Gelatinization of thermally treated starch mixed with sodium hydroxide (NaOH) also gave a good result on grafting acrylic acid onto hydrolyzed starch as reported by Hebeish, Zahran, El-Rafie, & El-Tahlawy (1996). This work indicates that homopolymer formation is largely suppressed with increasing NaOH addition. In this work we chose to use the starch in the gelatinized state but the method of gelatinization, either by adding NaOH or thermally, is considered as a reaction variable.

Most of the researchers report on the influence of the absolute concentration of monomer used in the graft copolymerization reaction (Athawale & Lele, 1998; Fakhru'l-Razi et al., 2001; Fanta et al., 1971; Fares et al., 2003; Hebeish et al., 1992; Khalil et al., 1990; Mostofa, 1995; Park et al., 1999; Sangramsingh et al., 2004; Shukla & Atalye, 1994; Vázquez et al., 1989; Vera-Pacheco et al., 1993). We think however that the ratio of starch to monomer is a more important factor than the absolute concentrations. Most of the literature data show that higher amounts of monomer give the highest add-on. Different initiator concentrations and other reaction conditions gave different add-on values however. This example already shows that it is very difficult to use the classic approach of observing the optimum value of one variable while keeping all other variables constant.

The concentration of initiator was usually in the range $3–11 \times 10^{-3}$ mol/L. Some researchers report that high add-on is achieved by using a low initiator concentration, like Athawale and Lele (1998), Vera-Pacheco et al. (1993) and Park et al. (1999). Contradictive to this, Vázquez et al. (1989) report a high add-on by using a high initiator concentration.

Research activities on the graft polymerization of acrylic acid to starch so far have not taken into account the complication that arises from the many possible interactions among process variables. A complete study of all of the parameters and their interactions however would increase the number of experimental runs beyond practical limitations. The experimental design method provides for a way out of this dilemma. By applying this method in the underlying work, most of the possible variations of the reaction conditions and their interactions could be included in a limited number of experiments.

2. Experimental

2.1. Materials

The native cassava starch used in this study has an ash content of 0.07%. It was produced by PT. Sungai Budi, Lampung and was kindly supplied by PT. AVEBE Indonesia, Cikampek, Indonesia. Acrylic acid (glacial, 99.5%, stabilized with 200 ± 20 ppm monomethyl ether of hydroquinone, MEHQ) was kindly supplied by BASF PETRONAS Chemicals, Sdn. Bhd., Malaysia and was used without further purification. FAS (ferrous ammonium sulfate), H_2O_2 (hydrogen peroxide) 30% and acetone were reagent grade chemicals and were used as received.

2.2. The experimental set up for the grafting reactions

The grafting reaction of acrylic acid with cassava starch was performed in a 1 L isothermal batch reactor, equipped with an overhead stirrer and a six-bladed turbine impeller. The reactor was surrounded by a water jacket, allowing control of the reaction temperature. The pre-determined amount of cassava starch was loaded to the reactor and suspended in distilled water to a slurry concentration of either 5% or 10% granular starch in a 500 g mixture. The contents were stirred under a N_2 atmosphere throughout the reaction. For the runs using NaOH, this component was added simultaneously with the starch. The slurry was heated to 70 °C and kept at this temperature for a period of 25 min to facilitate homogeneous gelatinization. After that, the gelatinized starch was cooled to 40 °C or heated up to 80 °C, depending on the chosen reaction temperature of the specific run. Subsequently the appropriate amount of acrylic acid was added at once. Then the first initiator component FAS was added and after 5 min the second component, H_2O_2. At the moment the peroxide is entered into the system, radical creation starts and subsequently the polymerization reactions. After the desired reaction time, the reaction was ceased by adding 2 mL of 0.1 M hydroquinone dissolved in water and the contents were stirred for another 10 min before opening the reactor. The conditions for each individual experiment are listed in Table 1.

Table 1
The selected levels for the various factors.

Variable	Units	Low	High
A: NaOH	% (wt/wt. starch)	0	5
B: [Starch]	% wt	5	10
C: St: AA	mol AGU/mol	0.5	2.0
D: [FAS]	mol/L	3×10^{-3}	10×10^{-3}
E: FAS:H_2O_2	mol/mol	0.1	1.1
F: Temperature	°C	40	80
G: Time	min	30	180
H: Stirring Speed	rpm	200	400

2.3. Analytical procedures

After the reaction was stopped, the contents of the reactor form a viscous mixture of grafted starch, homopolymer, unreacted monomer, and initiator. For the analysis and the determination of the grafting result parameters, a new method had to be developed (Marsman, Witono, Noordergraaf, Heeres, & Janssen, 2009) which will be reported in full detail in forthcoming publications. Since the details are not accessible yet, a brief description of the analytical procedure is also provided here. A representative sample from the reactor fluid was taken and subjected to this procedure. To separate the grafted starch from the other components, a washing procedure with a suitable solvent was developed. The testing of various solvents-precipitants led to the selection of acetone for this purpose. Acetone is capable of precipitating starch with grafted PAA while keeping homopolymer and unreacted monomer in the solution. In the procedure as it was developed, a sample of 20 g from the reaction product was washed with 80 mL of acetone—for several times—until no AA or polyacrylic acid (PAA) could be detected in the supernatant (see below). To remove initiator residue as well, in the second washing cycle 20% water was added to the washing fluid. The precipitate was separated from the supernatant about centrifugation (5000 rpm) and subsequently dried in a vacuum oven. The amount of grafted PAA onto the starch was determined using a ^1H NMR technique. The supernatant fluids from the washing cycles contain both unreacted monomer and homopolymer. These components were analyzed by HPLC using a Zorbax PSM 60 column.

2.4. The design of experimental method

To obtain an integrated understanding about the influence of all process variables on important reaction parameters, all the possible variations of process variables should be tested experimentally. By applying an experimental design method (also known as design of experiment—DOE) (Aravindakshan & Kumar, 2002; Arayapranee, Prasassarakich, & Rempel, 2006; Wang & Liu, 2006) the number of experiments can be minimized. A 2-level fractional factorial with 8 independent variables/factors was selected (Montgomery, 1991). With this design approach only the effect of the main factors and two factors interactions have been observed. Interactions of higher order were not included. The number of experiments was 32, all of them carried out in duplicate. The design was divided into 4 blocks. A blocking system was conducted to eliminate expectable variations such as small differences in the raw materials (starch). In each block starch from the same batch was used. The eight selected process variables were: the gelatinization method, starch concentration, the starch to monomer ratio, FAS concentration, the ratio of FAS to H_2O_2, reaction temperature, reaction time and stirring speed. For each of variables a low and a high value were selected based on literature data and previous experience in our group. These values are listed in Table 1.

The usual parameters to characterize results of chemical reactions (conversion, yield and selectivity) are not commonly used in the literature on starch grafting. In order to be able to compare our results to data from other authors we prefer to use those common grafting parameters (Athawale & Rathi, 1999; Fanta et al., 1971; Park et al., 1999; Trimnell & Stout, 1980; Vera-Pacheco et al., 1993). Their relation to more usual chemical engineering parameters is discussed accordingly. The following parameters will be used to monitor the responses of the system:

(A) Grafting Efficiency (GE):

$$\mathrm{GE} = \frac{\mathrm{wt.\ of\ gPAA}}{\mathrm{wt.\ of\ gPAA} + \mathrm{wt.\ of\ HP}} \times 100\% \qquad (1)$$

In this equation, wt. of gPAA is the amount of polyacrylic acid grafted onto starch and 'wt. of HP' is the mass of polyacrylic acid homopolymer. Graft efficiency expresses the selectivity of the main reaction with respect to the most important byproduct homopolymer.

(B) Degree of grafting copolymerization or add-on:

$$\text{add-on} = \frac{\mathrm{wt.\ \ of\ \ gPAA}}{\mathrm{wt.\ \ of\ \ St\text{-}g\text{-}PAA}} \times 100\% \qquad (2)$$

where St-g-PAA is the copolymer of starch grafted with acrylic acid The parameter add-on represents the yield of the desired product. It is common to define it as the fraction (%) of the total of the desired product.

(C) Grafting Ratio (GR):

The Grafting Ratio is grafted polymer with respect to the original amount of starch. Since GR and add-on are closely connected it is better to use only one of these result yardsticks. We chose the parameter "add-on".

(D) Monomer conversion:

$$\mathrm{conversion} = \frac{\mathrm{wt.\ of\ gPAA} + \mathrm{wt.\ of\ HP}}{\mathrm{wt.\ of\ AA_{charged}}} \qquad (3)$$

where $AA_{charged}$ means the amount of monomer charged into the system. Starch conversion is not an item since the chance that one of the long starch chains does not get at least one graft attachment is very low.

The gPAA (grafted polyacrylic acid) data are obtained from the NMR analysis as discussed above. However, the NMR spectra refer to the molar ratio of gPAA to starch (AGU). By assuming that the starch is not degraded during the polymerization reaction, the absolute amount of gPAA in the copolymer can be determined. The amount of homopolymer formed (HP) and unreacted monomer were quantitatively determined from the HPLC spectra by using calibration samples.

The effect of the process variables on each response was analyzed statistically using Analysis of Variance (ANOVA). The sampling distribution was assumed to show a normal distribution. The standard factorial model is given in Eq. (4):

$$y = \beta_0 + \sum_{i=1}^{8}\beta_i x_i + \sum_{j=1}^{7}\sum_{k=j+1}^{8}\beta_{jk}x_{jk}x_k \qquad (4)$$

where y = the observed response, β_n = the regression coefficient associated with the factor (a reaction variable) in the model, which is obtained by statistical analysis of the data, and x_n = the factor in the model. To confirm the assumptions of normality and constant variance, the observed versus the predicted values were plotted on parity plots. For evaluating the significance of effects, the *F*-test was applied. The sum of squares due to error (SS_E) was calculated using Eq. (5):

$$SS_E = SS_T - SS_A - SS_B - \ldots - SS_{AB} - SS_{BC} - \ldots \qquad (5)$$

The total sum of squares (SS_{total}) has been calculated using Eq. (6a):

$$SS_T = \sum_{i=1}^{a}\sum_{j=1}^{b}\cdots\sum_{p=1}^{n} y^2 - \frac{\left(\sum_{i=1}^{a}\sum_{j=1}^{b}\cdots\sum_{p=1}^{n} y_{ijp}\right)^2}{n} \qquad (6a)$$

where a and b are the number of A and B factors respectively and n is the number of experiments.

The sum of squares for any main effect (SS_A, $SS_B \cdots SS_H$) was calculated using Eq. (6b):

$$SS_A = \sum_{i=1}^{a}\frac{\left(\sum_{j=1}^{b}\cdots\sum_{p=1}^{n} y_{ijp}\right)^2}{bn} - \frac{\left(\sum_{i=1}^{a}\sum_{j=1}^{b}\cdots\sum_{p=1}^{n} y_{ijp}\right)^2}{n} \qquad (6b)$$

The respective sum of squares for the interaction effects (SS_{AB}, SS_{AC} $\cdots$) is calculated using Eq. (6c):

$$SS_{interaction} = \sum_{i=1}^{a}\sum_{j=1}^{b}\frac{\left(\sum_{p=1}^{n} y_{ijp}\right)^2}{n} - \frac{\left(\sum_{i=1}^{a}\sum_{j=1}^{b}\cdots\sum_{p=1}^{n} y_{ijp}\right)^2}{n} - SS_A - SS_B - \cdots \qquad (6c)$$

Since the 2-level interaction was selected in this experimental design, the mean square (MS) for the main effect and the interaction effect was equal to the sum of squares (SS). Using the analysis of variance (the *F*-test), the significance of the effect of the main factors (the reaction variables) and the interaction of two factors could be determined. The calculations used Eqs. (5), (6a)–(6c). The *F*-value could be calculated as the ratio of the mean squares of the treatments ($MS_{treatments}$) to the mean squares of the error (MS_{error}). If the variance from the observed response (*F*-value) on a certain parameter was less than $F(1, 14)$ at the 95% confidence interval, it could be concluded that the effect of the specific parameter was not significant. The data processing and the calculations were conducted using Design Expert 6.0.6 software.

3. Results and discussion

3.1. Experimental results

A compilation of the experiments and responses can be seen in Table 2. Run 17–32 are the duplicates of runs 1–16 and all duplicates showed an error margin of less than 5%. The add-on, GE and monomer conversion were found in the range 0–17%; 0–44% and 89–100% respectively. Compared to other research on grafting reactions of acrylic acid to starch, the add-on value is relatively high. For example, Trimnell and Stout (1980) reported maximum values of 11.2% for cornstarch whereas Fanta et al. (1971) reported a maximum value of 12.2%. However, for these studies different reaction conditions and initiator systems were used. The other grafting result parameters were not explicitly reported or were based on other definitions. For instance, the GE in these studies represents the ratio of total reacted monomer with respect to the monomer

Table 2
Overview of the results–responses from variation of the selected factors.

Run	Gelatiniz'n method	[Starch], %wt	St: AA, molAGU/mol	[In. I][a], (10^{-3}) mol/kg	[In.I:In.II][b], mol/mol	Temp., °C	Time, min	Stirring Sp., rpm	Add-on[c], %	GE[d], %	Monomer conversion[e], %
1	–	10	2.0	10	0.1	40	30	400	6.8	33.6	98.5
2	–	5	2.0	3	1.1	40	180	400	4.1	19.2	88.8
3	–	5	0.5	10	0.1	80	180	400	0	0	99.3
4	+NaOH	10	2.0	3	1.1	40	30	200	0.7	3.3	93.9
5	+NaOH	5	0.5	3	1.1	80	180	200	2.7	3.1	96.3
6	+NaOH	5	2.0	10	0.1	40	180	200	4.9	22.9	97.8
7	+NaOH	10	0.5	10	0.1	80	30	200	7.0	8.6	99.4
8	–	10	0.5	3	1.1	80	30	400	0.7	0.8	93.4
9	–	10	0.5	10	1.1	40	180	200	17.3	25.5	99.0
10	+NaOH	10	0.5	3	0.1	40	180	400	7.1	8.8	98.5
11	–	5	2.0	10	1.1	80	30	200	2.0	9.0	97.5
12	+NaOH	5	2.0	3	0.1	80	30	400	2.4	10.9	96.4
13	–	10	2.0	3	0.1	80	180	200	8.1	40.9	99.1
14	+NaOH	5	0.5	10	1.1	40	30	400	9.7	12.4	99.0
15	–	5	0.5	3	0.1	40	30	200	5.9	7.1	99.5
16	+NaOH	10	2.0	10	1.1	80	180	400	4.0	18.8	97.0
17	+NaOH	5	0.5	3	1.1	80	180	200	3.2	3.7	97.4
18	+NaOH	5	2.0	10	0.1	40	180	200	5.3	25.3	97.1
19	–	10	0.5	3	1.1	80	30	400	1.1	1.2	95.7
20	+NaOH	10	0.5	10	0.1	80	30	200	8.7	11.0	98.9
21	+NaOH	10	2.0	3	1.1	40	30	200	2.9	13.3	98.2
22	–	5	2.0	3	1.1	40	180	400	3.7	17.0	100
23	–	5	0.5	10	0.1	80	180	400	0	0	99.1
24	–	10	2.0	10	0.1	40	30	400	6.5	31.7	97.9
25	–	5	0.5	3	0.1	40	30	200	3.4	5.8	99.6
26	–	10	0.5	10	1.1	40	180	200	17.3	25.6	97.9
27	+NaOH	10	2.0	10	1.1	80	180	400	1.5	6.7	96.3
28	+NaOH	5	2.0	3	0.1	80	30	400	1.3	5.9	97.8
29	–	5	2.0	10	1.1	80	30	200	2.4	9.3	96.0
30	–	10	2.0	3	0.1	80	180	200	8.6	44.1	98.2
31	+NaOH	5	0.5	10	1.1	40	30	400	11.2	14.8	99.6
32	+NaOH	10	0.5	3	0.1	40	180	400	10.0	12.9	99.6

[a] In.I (initiator I) = ferrous ammonium sulfate (FAS/Fe^{2+}).
[b] In.II (initiator II) = hydrogen peroxide (H_2O_2).
[c] Calculated by Eq. (1).
[d] Calculated by Eq. (2).
[e] Calculated by Eq. (3).

charged, different from our definition (Eq. (2)). Such differences make it a little difficult to compare literature data with our results.

3.2. Model analysis

The effects of the various process variables on the important reaction result parameters were modeled using the statistical approach discussed in Section 2.4. Monomer conversion was always very high, close to 100%, so it is impossible in fact to predict which variables gave a significant effect to that response. The modeling results for each response are provided in the following paragraph.

3.2.1. Add-on

The relevant factors affecting the add-on value are the starch concentration, starch to acrylic acid ratio, initiator (FAS) concentration and reaction temperature. The other factors have no significant effect. The add-on value is increased by performing the reaction at high starch concentrations, low temperature, and a low starch to monomer ratio and a high FAS intake. The best fit to the experimental data is given by:

$$\text{Add-on} = 2.9 + 1.1 \times [\text{Starch}] - 1.7 \times (\text{St}: \text{AA}) + 310.5 \times [\text{Initiator I}] - 0.1 \times \text{Temp} \tag{7}$$

A parity plot (Fig. 3) shows that the agreement between the model and the experiments is satisfactory.

3.2.2. Grafting efficiency (GE)

Only three factors have a significant effect on the GE: the concentration of starch, the starch to acrylic acid ratio and the temperature. The GE is best described by the following model equation:

$$\text{GE} = -7.4 + 3.4 \times [\text{Starch}] - 7.1 \times (\text{St}: \text{AA}) - 0.2 \times \text{Temp} \tag{8}$$

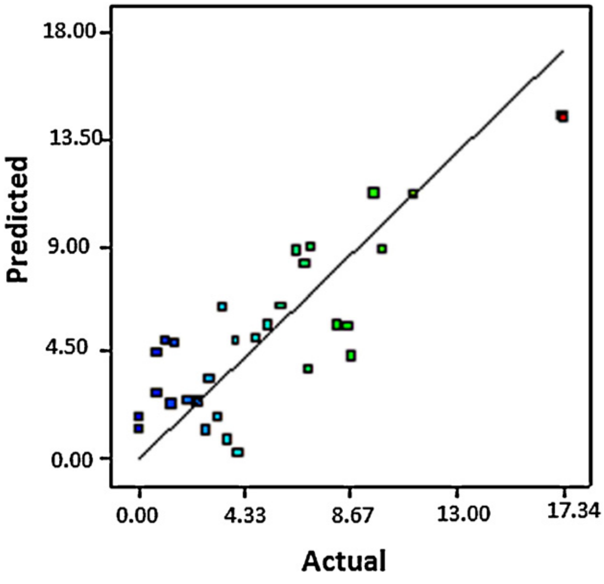
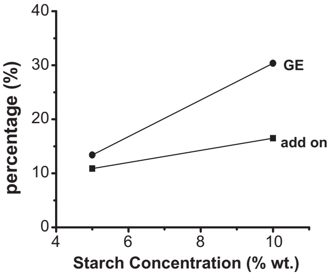
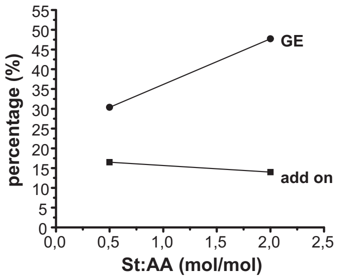


Fig. 3. Parity plot showing the modeled and experimental add-on values.



[Starch: AA=0.5; FAS conc. =3x10^{-3}mol/mol AGU; FAS:H_2O_2=1.1 mol/mol; T=40^{0}C; t=180min.; 200 rpm]

Fig. 4. Add on and GE as a function of the starch concentration.



[Starch conc. =10%; FAS conc. =3x10^{-3}mol/mol AGU; FAS: H_2O_2=1.1 mol/mol; T=40^{0}C; t=180min.; 200 rpm]

Fig. 5. Add on and GE as a function of the ratio of starch to monomer.

Thus, a high starch concentration, a high starch to monomer ratio and a low temperature have a positive effect on the GE. A parity plot for this response also confirms that the agreement between model and observed data is satisfactory.

3.3. Determination of the optimal reaction conditions

Reaction conditions can be optimized with several targets, like the maximal yield of the reaction, the selectivity toward the main product, the desired product properties and of course, economic considerations. In chemical reactions including grafting copolymerization, the selectivity is usually the most importance response that has to be optimized. In this study, it is represented by grafting efficiency (GE). At high GE, the desired product is generated while side product (homopolymer) formation is suppressed. But, if we focus on the product properties related with their application, the amount of grafted polymer, the yield as represented by add-on is the most importance response. In this work, the optimum conditions within the selected ranges of the reaction variables have been determined with respect to both add-on and GE.

3.3.1. Effect of the starch concentration

In this work, the values of add-on and GE obtain at 10% starch concentration are higher than at 5%, where more homopolymer is formed (see Fig. 4). If starch concentration is low, apparently the kinetic probability of a starch molecule to be attacked by initiator is too low as well, in competition with the monomer. The add-on value that is obtained at 10% starch concentration is also dependent on the other parameters, but could be up to 17.3%. It may still be possible to increase add-on further, when starch concentration would be increased beyond 10%. This could however not be tested in the equipment used, because too high viscosity would arise from polymerization at (much) higher starch concentrations. Then, the homogeneity of the mixture will become very uncertain.

It is not really possible to compare these results to literature data, since in most research papers the authors work with a fixed concentration of starch. The concentrations of either granular or gelatinized starch (wheat, potato, sago, cassava, corn) reported for all kind of grafting copolymerization were mostly in the range 1–5% (Athawale & Lele, 1998; Brockway, 1964; Burr et al., 1976; Fanta et al., 1970; Fares et al., 2003; Khalil et al., 1990; Kiatkamjornwong et al., 2000; Liu et al., 1993; Lutfor et al., 2003; Mehrota & Rånby, 1978; Park et al., 1999; Sangramsingh et al., 2004; Vázquez et al., 1989). Some authors used a higher concentration of starch (≥10%), but the add-on result was also not satisfactory. E.g., Fanta et al. (1971) and Trimnell and Stout (1980) found lower values of add-on of acrylic acid (12.2% and 11.2% respectively) than our result (17.3%) at a starch concentration of ca. 10%. This difference just illustrates the importance of studying the combined effect of other parameters as well, like monomer concentration, reaction temperature, etc.

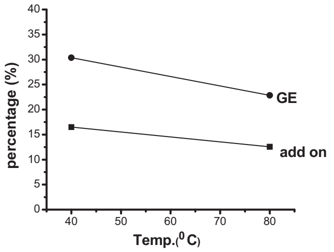
3.3.2. Effect of the mol ratio of starch to monomer

As already explained, the ratio of starch with respect to monomer is not commonly considered as a reaction variable in many reports. In many grafting studies, the monomer concentration is used as a variable instead. In this work however, the starch to monomer ratio (with fixed starch intake) was found to be a very important variable since it has a significant effect on the add-on and on the GE. Fig. 5 shows that add-on values are higher at low starch to monomer ratio compared to the high ratio, whereas graft efficiency shows an opposite trend. A high add-on value (17%) is obtained at the low level of the starch to monomer ratio (0.5 mol AGU/mol AA) while high GE (44%) is found at the high level (2 mol AGU/mol AA). At the low ratio, the amount of the acrylic acid in the system is larger than the amount of starch, so the chance of acrylic acid to collide with other molecules (initiator) and react is larger as well. Activation of the monomer molecules then both enhances grafting and homopolymerization. This result creates a dilemma: by increasing the amount of monomer, the add-on would increase but as a consequence the amount of homopolymer formed increases too.

In literature reports on graft polymerization, regardless whether the starch to monomer ratio (Hebeish et al., 1992; Liu et al., 1993; Lutfor et al., 2003) or the absolute amounts of the reactants (Athawale & Lele, 1998; Brockway, 1964; El-Rafie et al., 1995; Fakhru'l-Razi et al., 2001; Fares et al., 2003; Hebeish et al., 1992; Mehrota & Rånby, 1978; Mostofa, 1995; Park et al., 1999; Sangramsingh et al., 2004; Trimnell et al., 1996; Vázquez et al., 1989) were considered, there was always an optimum ratio or an optimum specific amount of monomer found. Beyond the optimum, the values of add-on are either stable or decrease gradually. For example, Lutfor et al. (2003) and Kiatkamjornwong et al. (2000) found that the highest value of the percentage of grafting (∼add-on) was achieved at a starch-to-monomer (acrylonitrile—AN and acrylic acid/acrylamide—AA/AM, respectively) ratio of 1:4. At an even lower starch to monomer ratio than 0.5, the high amount of homopolymer formed will be more difficult to separate from the grafted system, probably due to physical entanglement of high molecular weight polymer chains. Then, the percentage add-on cannot be measured with sufficient accuracy. So, we did not explore beyond that the ratio of 0.5.

3.3.3. Effect of the initiator concentration

The low and high levels of FAS used in this experiment are shown in Table 1. The results show that the larger amount of FAS only slightly improves the add-on and has no effect on GE. From these results it can be interpreted that the minimal amount of Fe^{2+} needed to induce the grafting copolymerization was already obtained at the low level. Excess use of Fe^{2+} did not increase grafting but only induced a stronger yellow-brownish color of the mixture due to oxidation of Fe^{2+} into the much less soluble Fe^{3+}. The statistical calculations from this study also confirm that variation



[Starch conc. =10%; starch: AA=0.5; FAS conc. =32x10^{-3}mol/mol AGU; FAS: H_2O_2=1.1 mol/mol; t=180min.; 200 rpm]

Fig. 6. Add on and GE as a function of the grafting temperature.

of the initiator concentration has almost no effect on the grafting result parameters. Although the concentration of Fe^{2+} at high level gave no clearly better results compared to the low level, for further experiments we prefer to use the higher concentration. Then there are just more radicals that can start the polymerization reactions. The ratio of Fe^{2+} to H_2O_2, or initiators I and II, also showed no significant effect on the reaction results add-on and GE. Still, we prefer to use 10 times excess of H_2O_2 also since it enhances radical production. The validity of this choice was later confirmed by experiments on starch breakdown by the initiator, as will be reported later.

3.3.4. *Effect of the reaction temperature*

In Fig. 6 it can be seen that the percentages of add-on and grafting efficiency decreased with an increase of the reaction temperature: 40 °C gave a higher grafting yield compared to the reaction carried out at 80 °C. Considering GE, the temperature level of 40 °C also showed the best result. Apparently, at higher temperature more homopolymer is formed. This finding is in agreement with the grafting of acrylic acid onto cornstarch in aqueous isopropanol solution by Park et al. (1999). It is contradictory however to the results of Vázquez et al. (1989) and Sangramsingh et al. (2004). In both articles it was stated that there was no graft polymerization found below 60 °C with methacrylic acid monomer and Fe^{2+}/H_2O_2 and CAN as initiator, respectively. El-Rafie et al. (1995) found almost total monomer conversion al low temperature (30 °C) in the grafting of maize starch with AA, using potassium bromate ($KBrO_3$) and thiourea dioxide as initiators. However, it looks like there was more homopolymer formed at 30 °C compared to the reaction at higher temperatures. This would be contradictory to our results. Hebeish et al. (1992) and Khalil et al. (1990) with $KMnO_4$ as the initiator and Lutfor et al. (2003) with ceric ammonium nitrate (CAN) reported that 50 °C was the optimum temperature for grafting copolymerization. Above that temperature, grafting decreased. The most apparent conclusion that can be made is that the optimal temperature for the grafting reaction is very dependent on the initiation system.

3.3.5. *Effect of reaction time*

A reaction time of 3 h appears to be more effective than the shorter period (30 min). Like many other polymerizations, grafting copolymerization exhibits a fast initial rate which slows down with time. When mixing is slower than the rate of the reaction, inhomogeneity can occur in the system. At a longer reaction time, this effect is probably leveled out so a more homogeneous product can be obtained. Khalil et al. (1993) have reported that the reaction time needed depends on the type of monomer used. Acrylic acid appears to have the lowest reactivity hence needs a longer reaction time. Acrylonitrile needs a reaction time of 60–90 min (Khalil et al., 1990, 1993; Lutfor et al., 2003). These and other articles report reaction times for AA of 120–240 min. (Athawale & Lele, 1998; Park et al., 1999). These values show resemblance to our results.

3.3.6. *Effect of the method of gelatinization*

When the starch is gelatinized, the hydrogen bonds between starch molecules are broken which greatly increases the accessibility of the individual Anhydroglucose Units (AGU) for reactants. Gelatinization can be brought about by adding NaOH to a suspension of starch granules, or just thermally by heating the suspension beyond the gelatinization temperature for a certain period (25 min in this work). From the evaluation of the DOE-results is appears that the use of NaOH for starch gelatinization gives a much lesser result compared to thermal gelatinization, at all conditions.

3.3.7. *Effect of the rate of stirring*

It was found that the rate of stirring during reaction is not a significant factor because it does not influence the grafting result parameters much. Since in our work the starch is pregelatinized, there are no mass transfer limitations inside particles (starch granules). Our result shows some disagreement with Hebeish et al. (1992). They found the large influence of the rate of stirring in the range of 200–400 rpm, on the total conversion of graft copolymerization of acrylic acid onto corn and rice starch. These authors however did not report other graft parameter results so the comparison cannot be completed.

4. Conclusions

By using a design of experiment 2-level fractional factorial, the effect of eight reaction variables in the grafting of acrylic acid onto cassava starch could be screened. Temperature, starch concentration and the starch to monomer ratio were found the most significant variables, i.e. showing the largest effect on the results of the grafting reaction. Within the range of variations in this study, the best values for temperature and starch concentration are 40 °C and 10% respectively. The optimum ratio of starch with respect to acrylic acid should be investigated further to find a trade-off value between the desired output values of the result parameters add-on and GE. The best results were always obtained when gelatinization was done thermally, without the addition of NaOH. From the range selected, the higher level of FAS concentration (0.01 mol/L) slightly influenced add-on but not GE. However, the tested variations in the ratio of FAS to H_2O_2, the reaction time and the speed of stirring did not have a very significant influence on the results. Monomer conversion was always near 100% at all conditions chosen.

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