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# Rheological Behavior of Reaction Mixtures during the Graft Copolymerization of Cassava Starch with Acrylic Acid

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**Literature data on the rheological behavior of a reaction mixture during the graft copolymerization of acrylic acid onto gelatinized starch are scarce. Yet, such information is important for process design. In this work, continuous torque recording was found to be a suitable method to monitor the apparent viscosity. Reactions were performed in a bench scale reactor at ambient conditions with the monomer to starch ratio as the main variable. Apparent viscosity of the reaction mixture increased rapidly, which could be fitted with good accuracy with a first order exponential growth model. The maximum viscosity of 18 Pa·s was seen at the intermediate monomer to starch ratio of 1.0, a phenomenon that is in accordance with literature data. Starch thixotropy is influenced by the grafting of poly-acrylic acid, until it has almost disappeared at the highest monomer to starch molar ratio of 2.0. POLYM. ENG. SCI., 57:1285–1292, 2017. © 2017 Society of Plastics Engineers**

## INTRODUCTION

To improve the economic potential of cassava starch, a commodity in tropical countries like Indonesia, a non-food industrial application needs to be developed [1, 2]. Chemical modification of starch is necessary to adapt the properties of the biopolymer towards applications like water absorbents, flocculants or thickening agents. Graft copolymerization of starch with water soluble monomers like acrylic acid is a suitable method to bring about the desired properties [2–5]. In the homogeneous reaction system, the formation of (some) homopolymer is all but inevitable while separation is difficult and perhaps detrimental for process economics [4, 6]. Therefore, it is interesting to look for an application where this separation is not needed, like use of the complete (dried) product as a thickening agent. The rheological behavior in solution is an important property of such materials. Especially in the case of application as thickening agents, the stability of gels is of high relevance [7].

However, knowledge of the rheological properties of starch and the development of the viscosity during the graft polymerization reaction is not just interesting because of product properties, it is as important for the design of both the reactor and the process-set up, especially when processing in the gelatinized

state is opted. Processing starch as a gel is not common in the traditional starch modification reactors used in industry, due to the high viscosity that comes along with the gelatinized state. In several recent research articles, it was demonstrated, however, that starch modification reactions perform better, in terms of reaction rate and selectivity, when starch is first brought into the gelatinized state [4, 8–11]. High viscosity requires strong and perhaps purpose-designed pumping and stirring systems. Still, cassava starch is considered a good candidate for testing of a process in the gel phase since it gelatinizes more easily and at a lower total viscosity than starches from many other sources [1].

The rheological properties of gelatinized starch are unique for a specific type of starch. They are influenced by its structure, the presence of other components in the system, the shear rate that is applied and also by storage time [12–14], but most of all by chemical modification of the starch molecules. Abu-Jdayil et al. [15] observed that in the presence of glucose, a dispersed starch system changes its behavior over time from Bingham to thixotropic, but in the absence of glucose, it changes from Bingham to shear thinning. Dewar and Malcolm [16] showed that this rheological behavior was dependent both on the shear rate and the starch concentration. The presence and relative concentrations of salts, acids, and oxidizing agents also have an effect on the peak viscosity of gelatinized cassava starch, according to Jyothi et al. [17].

Many more studies on the viscosity of natural starches [14, 18–20], starch blends [17–22], modified starches [18, 20, 23], and starch-based products in aqueous gels [24, 25] have been published. In several recent papers, the apparent viscosity and other rheological properties of flocculants based on grafted starches was reported. Either acrylamide [26] or mixtures of acrylamide with co-monomers were applied [27, 28]. Xu et al. [29] report that the gel of a waxy starch grafted with poly- $\gamma$ -glutamic acid exhibits viscoelastic solid behavior while the original control sample of waxy starch showed viscoelastic liquid behavior. After all, these reported properties are those of the final products. Still, there is no information in literature on the development of viscosity during graft copolymerization reactions.

The viscosity of the components involved in the reaction as such cannot be used to predict the viscosity during the reaction, or the rheological properties of the product after the polymerization reactions. Offline measurement is also difficult since the highly viscous systems make the taking of representative samples from the reaction mixture virtually impossible or unreliable at least. For inline measurement of the development of the true viscosity of the reaction mixture there are simply no suitable instruments [30]. Therefore, in our opinion, the best possible approach to this situation is to use a combined stirrer-torque meter. Whereas the torque is proportional to the viscosity in

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Several topics included in this paper were presented orally by dr.ir. I.W. Noordergraaf at the 8th European Conference on Chemical Engineering, Berlin, FRGermany, September 2011.

A large part of the experimental material in this article was included in the PhD-Thesis of dr.ir. J. Witono-Retti, defended September 21, 2012. More measurements and most calculations, especially those for the Rheokinetics, were made more recently by dr.ir. I.W. Noordergraaf.

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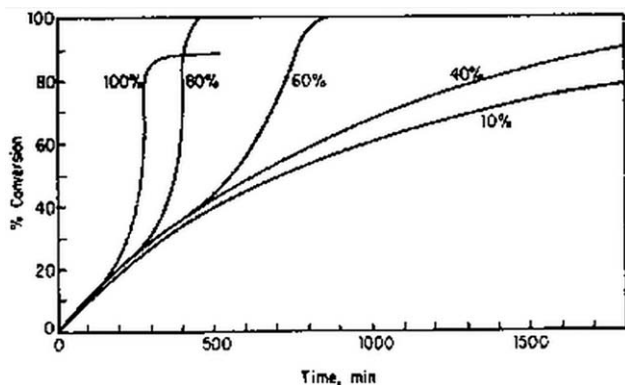


FIG. 1. The conversion rate of methylmethacrylate homopolymer at different monomer concentrations (from Schulz and Harborth, *Die Makromol. Chem.*, 1947, Vol. 1, p. 106, © Publisher name, reproduced by permission).

Newtonian fluids, the relation between torque and viscosity in the non-Newtonian fluids involving gelatinized starch is not straight forward, however. In fact, the property entitled as “viscosity” is only really well defined in Newtonian fluids and the resistance to flow in non-Newtonian fluids is more usually designated as the “apparent viscosity” [31] and is also dependent on the shear distribution in the measurement device. However, by testing the same material both in the reactor with the torque meter and in a well-defined rheometer, an estimation-calibration of the relation between torque and apparent viscosity may be possible. If so, from recording torque during the polymerization reaction, an indication of the relative development of viscosity during the reaction can be obtained as it has not yet been found in the (open) literature. This is an important novelty in this work.

Since polymerization by definition results in the formation of high molecular weight chains and thus increased viscosity, the rheological behavior of the mixture is likely to have an important effect on the kinetic behavior of the reaction. Many researchers have detected a deviation from the classical mechanism of bulk free radical polymerization. At a high density of polymer formation, that is, at high initial monomer concentration, viscosity develops rapidly. In this situation, the chains of already formed polymer with radical activity have a lower chance to meet and terminate while the smaller monomer molecules are much less restricted in diffusion movements. So, propagation is favored over termination which results in a higher overall polymerization rate and longer polymer molecules than it could be expected from straight forward kinetics of free radical bulk polymerization. This effect, causing auto-acceleration of the polymerization reactions, was first reported by Norrish and Brookman [32] on poly-methyl methacrylate (PMMA) polymerizations. It was described later by Trommsdorff et al. [33] who observed and reported in great detail on this almost explosive auto-acceleration, in the polymerization of a.o. methyl methacrylate. This phenomenon is now well known as the Trommsdorff effect, or gel effect. It was also observed and explained theoretically by many other research workers [34–36] and also in our laboratory by Jongbloed [37] and Cioffi [38] with various acrylate monomers. In Fig. 1, showing results from work of Schulz and Harborth [36], it can be seen that the reaction reaches its final level of conversion

much earlier at higher monomer concentrations. According to that previous work [37, 38], such is caused by the Trommsdorff effect and can be considered a good indication that it has occurred.

For this study, we carried out graft copolymerization in a batch reactor at constant temperature and stirring speed. Noordergraaf et al. [39] concluded that the monomer-to-starch ratio was the variable with the greatest influence on the grafting results. In this work, this parameter was varied over the range  $M:S = 0.5, 1.0, 1.5,$  and  $2.0$ . The apparent viscosity during the reaction was monitored continuously by the integrated stirrer-torque meter, applying the viscosity-torque relation that was separately derived from experiments in the calibrated rheometer. To evaluate whether torque registration can also be used to obtain information on the reaction kinetics, torque profiles were fitted with a kinetic formula derived from the model we developed previously [2, 40]. Since the reaction mixture without homopolymer separation can be regarded as a basis for a product (thickening agent—viscosifier), the profiles of the apparent viscosity over time are also relevant for product properties like the occurrence of thixotropic behavior.

## EXPERIMENTAL

### Materials

Cassava starch with 99.93% purity was kindly supplied by Avebe, Indonesia. Acrylic acid (glacial, 99.5%) was donated by BASF-PETRONAS, Chemicals, Sdn. Bhd., Malaysia). FAS (Ferrous Ammonium Sulfate) and  $H_2O_2$  were reagent-grade chemicals. The reactions were carried out in milli-Q water prepared at our lab. All other reactants were used as received. For the curve fitting calculations in Rheokinetics section, Origin 8.1 software was used.

### Reaction System and Conditions

All graft copolymerization runs were carried out in a stainless steel batch reactor of 500 mL content, fitted with a water jacket to control reaction temperature as depicted in Fig. 2. Pregelatinized cassava starch was graft copolymerized with acrylic acid using Fenton’s reagents as the initiating system [4]. A set of reaction conditions was derived from previous work: thermal gelatinization ( $70^\circ\text{C}$ , 25 min),  $40^\circ\text{C}$  reaction temperature, 7.5% starch concentration and stirring at 300 rpm. The concentration of the initiator components was  $[\text{Fe}^{2+}]$  0.01 mole/L and  $[\text{H}_2\text{O}_2]$  0.1 mole/L. The molar ratio of acrylic acid monomer to starch (M/S) was used as a reaction variable, over the range 0.5–2. Reactions were run for up to 2 h under nitrogen atmosphere. The complete procedure is described in detail in Torque profiles during reactions section. The chemistry of the grafting system has been reported before [2].

### Torque Measurement

For the measurement of torque during the reaction, a Heidolph overhead stirrer RZR 2102 Control was used. It is shown also in Fig. 2. In the batch reactor, the shear rate was controlled by maintaining a constant stirring speed of 300 rpm. The increase of torque (shear stress) is automatically compensated by the instrument and the torque value is recorded. The interface

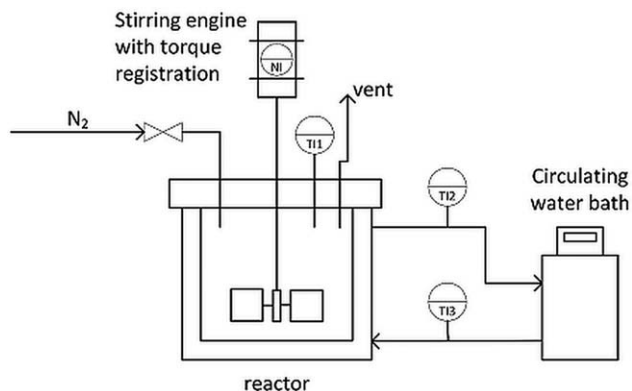


FIG. 2. Scheme of the batch reactor with the combined stirrer-torque meter.

of this system was connected to a computer using Lab view software to store the relevant data.

#### Calibration Measurements with a Rheometer

For the calibration of the apparent viscosity in the reactor, a standard viscosimetry test was run in a TA Instruments AR-1000 N rheometer with a cone and plate geometry. The diameter of the aluminum cone was 40 mm, the cone angle 2°, and the truncation gap 52 μm. To compare as good as possible with the reactor experimental conditions, a constant 5 s<sup>-1</sup> (300 rpm) shear rate was applied also in the rheometer. Cassava starch at 7.5% concentration in water was gelatinized in the polymerization reactor according to the standard procedure and the viscosimetry was run shortly thereafter in the rheometer, at 40°C for 1 h. There, the samples were tested in a closed system to prevent evaporation during the measurements.

## RESULTS AND DISCUSSION

### Torque versus Viscosity Measurements and Starch Thixotropy

At first, it must be found out whether torque recording has a quantitative correlation with the apparent viscosity in the

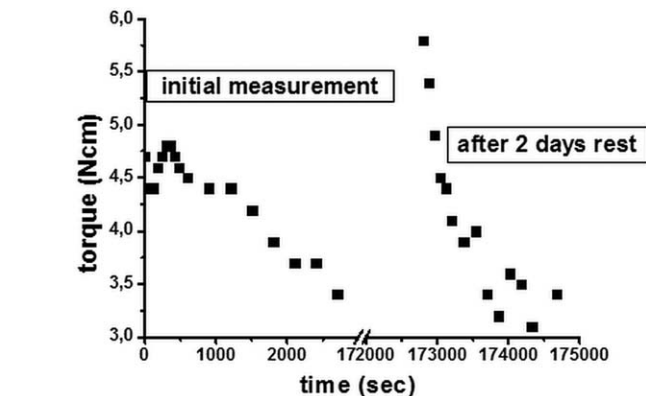
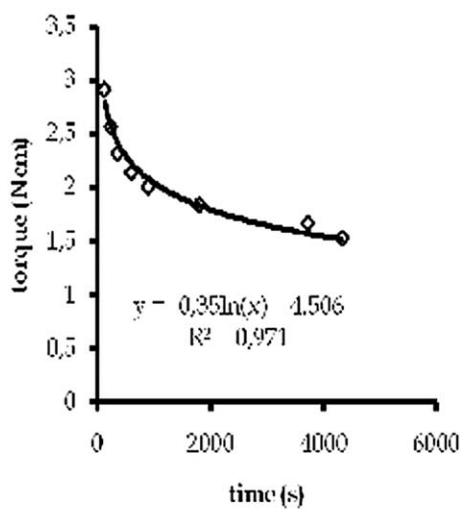


FIG. 4. Torque data of the gelatinized starch with the same shear stress applied over two periods intermitted by restoration time.

reactor. In literature some correlations between torque and the real (apparent) viscosity of non-Newtonian fluids can be found but these are only qualitative trends [1]. Standard models for torque versus viscosity are not valid for fluids with strong non-Newtonian flow properties like gelatinized starch and the polymer products from the grafting reaction [41]. Therefore, the correlation between torque and the apparent viscosity has to be estimated from experimental data.

In Fig. 3, the result of torque recorded in the reactor by just stirring 7.5% pregelatinized starch at 40°C for about 1 h (3a) is compared to the result of the same procedure in the real viscosimeter (3b). They exhibit a very similar shape. Therefore, we are confident that an experimental relation for the development of viscosity and the progress of the reaction expressed as torque (Eq. 1) can be obtained by combining the results from both figures.

$$\tau \text{ (N} \cdot \text{cm)} = 1.6 \mu \text{ (Pa} \cdot \text{s)} - 11.6 \quad (1)$$

where  $\tau$  represents torque and  $\mu$  represents the apparent viscosity.

The graphs are also a good example of a system showing thixotropic behavior. This property is characterized by a decrease of torque (and viscosity) under mechanical stress over

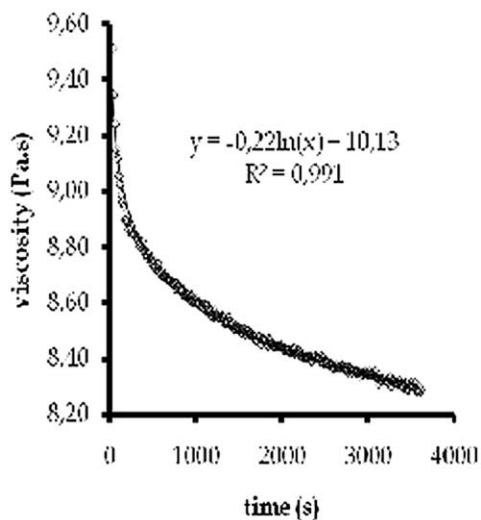


FIG. 3. The relation between torque in the reactor and the apparent viscosity in a calibrated viscosimeter.

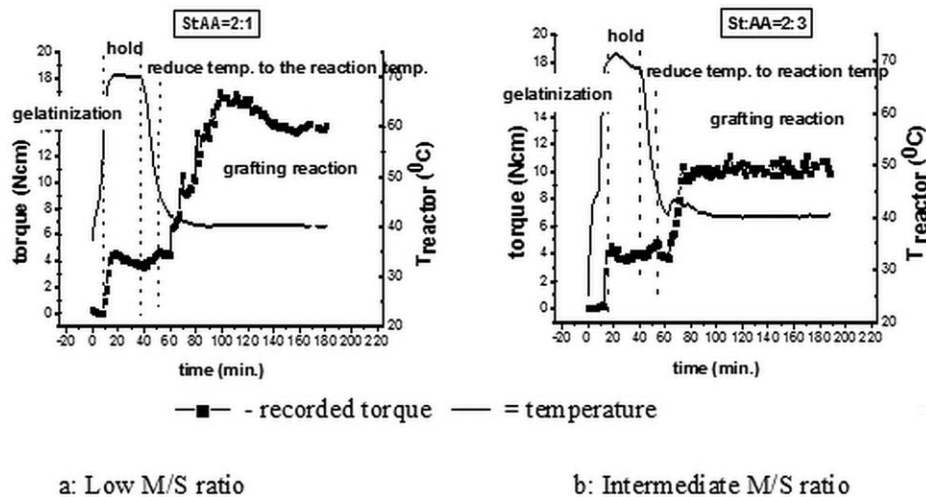


FIG. 5. Torque profiles along the whole of the reaction time including the preceding gelatinization procedure.

time. But, thixotropy is a reversible effect, probably by a certain rearrangement of the starch molecules to cope with the mechanical stress. When the solution is left at rest, the Brownian movement should eventually restore viscosity to, or close to, its original value. If viscosity stays lower after sufficient time, irreversible chain degradation may have occurred. To test whether there is real thixotropic behavior, the gelatinized starch was left at rest for two days and started stirring again. This could not be tested at the original reaction temperature of 40°C, however, since the time needed to warm up the gelled mass again (>20 min) interfered with the effects we wanted to observe. Therefore, we did this entire test at room temperature (20°C). The result is shown in Fig. 4. A clear restoration of viscosity after two days at rest is observed. The apparent viscosity seems even higher than the value after gelatinization but that starch mixture was already stirred for over 45 min, the time needed for gelatinization and subsequent cooling to 20°C. We can consider this observed viscosity restoration as a proof of real thixotropy. A further test after 7 more days could not be done since after that long time at rest, the starch paste was dishomogenized by syneresis effects. It only proves that cassava starch pastes as such do not have long-term stability.

#### Torque Profiles during Reactions

Two torque profiles during the gelatinization and subsequent reaction steps are plotted in Fig. 5 to illustrate the characteristic rheological response of the system. The system temperature is also shown, although this is a variable, not a result. In Fig. 5a, there is a relatively low monomer-to-starch ratio and at this condition, the thixotropic behavior of starch is still a dominant effect. The reaction procedure is preceded by thermal gelatinization of the cassava starch slurry at 70°C for 25 min. The increase of torque (viscosity) by gelatinization is clearly seen in the second part of the curves. The torque value obtained after gelatinization shows good reproducibility, it is always around 3 N·cm at 7.5% starch. Using Eq. 1, this can be converted to an apparent viscosity of  $\approx 9$  Pa·s. Then the mixture is cooled to the intended reaction temperature of 40°C. During the

gelatinization phase, a slight decrease is already seen in the torque reading probably due to thixotropic effects, which are apparently not completely compensated by the increase of the viscosity by cooling.

When the mixture is at the desired temperature, the graft polymerization reaction was started by adding monomer and initiator subsequently. The addition of the second part of the redox initiator, the hydrogen peroxide, is counted as  $t = 0$  for the start of the reaction. The polymerization process causes a rapid increase of the viscosity as shown by the torque profile, reaching a maximum after some time. Both the maximum value observed as the time when it occurs vary, due to several effects. Logically, the polymerization rate increases at higher monomer concentration, and with more polymer formed since there are more and perhaps longer molecules that cause viscosity. There is however also the effect of starch thixotropy which appears most clearly at the lower level of monomer addition (Fig. 5a). The values of the maximum torque found at different monomer additions relative to starch are shown in Table 1.

It is perhaps surprising that the maximum torque value is found when the ratio of starch to monomer is equal to 1, since at the higher level of monomer dosage there must be more polymer and probably longer chains of both grafted PAA and homopolymer in the system. However, a similar result was found by Biswas et al. [42], with blends of 5% starch with polyacrylic acid in water. The highest viscosity occurred when the ratio of starch to polyacrylic acid is 1 (mole AGU/mole AA). Their explanation is that apparently the same amount of active

TABLE 1. The maximum torque measured during reaction, at different levels of monomer addition and at constant starch concentration.

Ratio monomer to starch (mol/mol)	Maximal value of torque (N·cm)
0.5	15.8
1.0	17.5
1.5	10.5
2.0	8.6

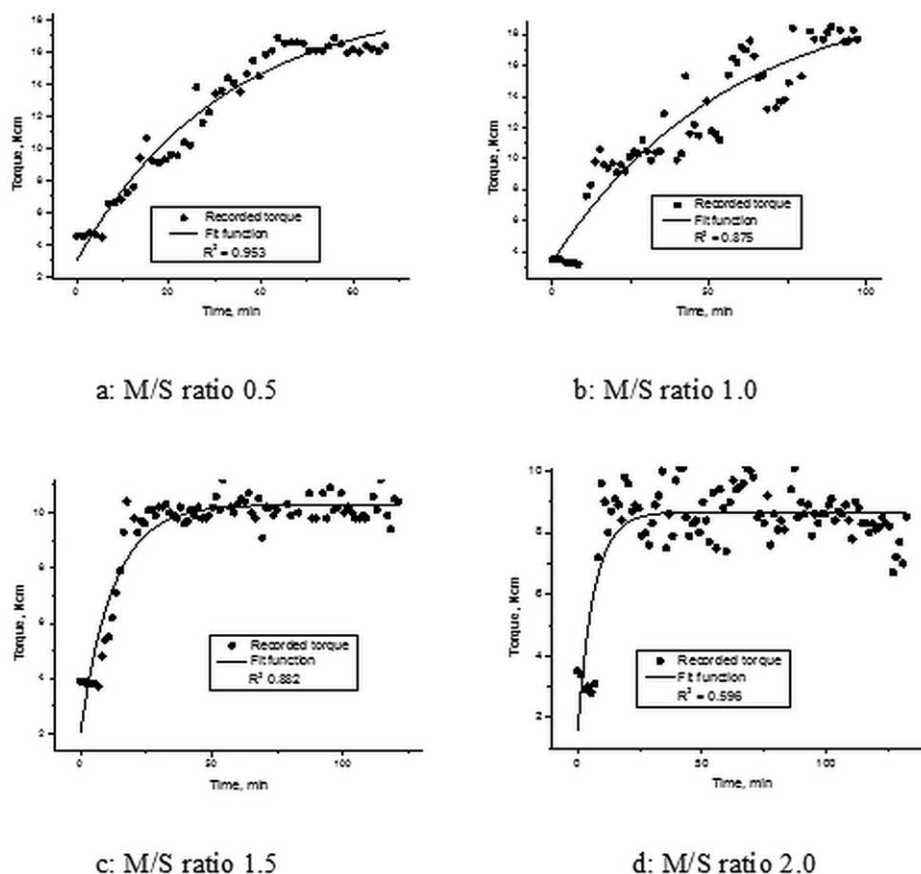


FIG. 6. Curvefitting on the experimental data of torque development with a 1st order kinetic model.

functional groups from monomer and starch construct a stable gel. A more detailed explanation for the observed maximum in viscosity/torque is given by Crisp at al. [43]. These authors state that increased hydrogen bonding between polyacrylic acid chains as well as with starch chains results in a more stable but also a more compact gel, resulting in a lower overall viscosity.

#### Rheokinetics

The development of a kinetic model for the grafting reaction of acrylic acid onto cassava starch, including a term for graft selectivity, was reported before [2, 40]. It was demonstrated that the reaction rate is pseudo-first order for the graft copolymer, and shows 1.5th order dependence for homopolymer formation, both with respect to monomer concentration. However, from recent experiments and from literature data [31, 44] applied to the relevant reaction conditions, it could be expected that the contribution of homopolymer formation to the overall increment of viscosity would be relatively low. Therefore, it was assumed that the viscosity build-up is mainly caused by the graft copolymerization which follows first-order kinetics. To test this assumption, a first-order exponential growth model from standard curve fitting software was applied to the viscosity profiles along the reaction time. The results of curve fitting with this model are presented in Fig. 6a–d, for the four values of the monomer to starch ratio.

The general form of the viscosity growth function is

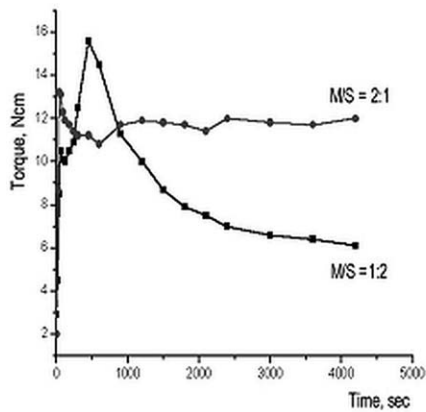
$$Y = Y_0 - Y_1 \cdot \exp(-k_v \cdot t) \quad (2)$$

where  $Y$  = torque,  $Y_1$  and  $Y_2$  are fit constants,  $k_v$  is a first-order kinetic constant and  $t$  is time (in minutes). The calculated fit parameters are shown in Table 2, together with  $R^2$  values.

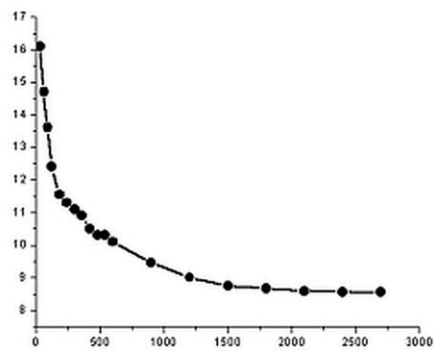
The values of the  $Y_0$ , more or less a maximal torque that can be reached in the model show the same trend as the experimentally observed values in Table 1. More importantly, as it can be seen in Fig. 6, torque profiles during the grafting reaction at different ratios of starch to the monomer can be fitted well with the first-order exponential growth function. In all cases, the start value is approximately 3 N·cm. At the lowest level of monomer to starch, a thixotropic effect was still observed, as already shown in Fig. 5a. This interferes with the increase of the apparent viscosity by graft polymerization at longer reaction times. For this case, the curve fitting calculation was limited to the increasing part of the torque profile, up to ca. 50 min. For the other conditions, fitting was performed over the full range of

TABLE 2. Calculated fit parameters.

Molar ratio AA/St	$Y_0$	$Y_1$	$k_v$	$R^2$
0.5	19.2	16.2	31.6	0.95
1	20.9	17.5	55.9	0.88
1.5	10.3	8.2	12.4	0.88
2	8.7	7.1	6.5	0.60



a: Reaction product  
with grafted starch



b: Physical mixture of  
gelatinized starch and PAA  
corresponding to M/S = 2:1

FIG. 7. The effect of M/S ratio on gel stability of the reaction product as compared to a physical mixture.

the reaction time of up to ca. 120 min. The  $k_p$ -values as calculated from the best fit can be regarded as kinetic constants, but not in the absolute sense (numerical values) since the relation between torque/viscosity and the degree of polymerization is complex as discussed in the foregoing sections. The fits are reasonably good as  $R^2$  values are around 0.9 in most cases. Only at the highest M/S ratio applied in our work, M/S = 2.0, the  $R^2$  value is clearly below 0.9 which indicates a deviation from first-order kinetics.

In Fig. 6d, we see that the torque value increases very fast at the beginning of the reaction and is relatively constant already after a short period of time. This profile is similar to what was seen in the graphs of Schultz and Harborth [36], who observed a Trommsdorff effect in the polymerization of methyl methacrylate at the higher concentration of monomer (Fig. 1). Then polymerization rate is higher than can be expected from the kinetic equation, which is reflected in the poorer fit result. At these conditions, there is relatively much monomer in the system. This high concentration in combination with the high reactivity of the acrylic acid radical [2, 40] is indeed the most logical condition for the gel effect to happen. As already explained, at a high polymerization rate, the strong increase in viscosity hampers terminations, resulting in an even faster overall reaction rate. But, since the monomer will be consumed more rapidly then, the total reaction time is shorter. At conditions with a high shear rate, a Trommsdorff effect can be significantly reduced or sometimes even eliminated [38]. It is not likely at the current conditions since these observations were made in an extruder reactor with a higher magnitude of the shear rate than it can be obtained in a stirred tank. But an extruder type of reactor may be a good option for continuous production studies in the future.

Concluding, apart from the conditions that may cause a gel-effect to occur, the increase of viscosity follows a first-order function. Although the constants of the fit function cannot be related to kinetic constants in the quantitative sense, the first-order growth shown by the torque fit functions does confirm the

results from the development of the kinetic model [2, 44]. This is a new finding which has not yet appeared in any publication on starch grafting yet. It can be of use in further work like scaling-up or for a real process design, although such tests are still in the future.

#### *The Effect of the M/S Ratio on Thixotropy of the Resulting Gel*

Important properties of products used as thickening agents are the stability of the viscous solution under mechanical force, or the reaction upon such. In an application like paint, a rapid decrease and restoration of viscosity may be interesting because it makes the product more easy to brush out and then to stick after application of the coating. For many applications of thickening agents, however, a stable paste viscosity is important [31]. Gelatinized cassava starch clearly shows thixotropic behavior as was concluded from Fig. 4. Now, it is interesting to see the effect of increasing dosage of monomer on the stability of the gel, a mixture of grafted starch and ungrafted homopolymer, during and after the reaction. In Fig.7a, the extremes of the range tested are shown. In both cases, there is a rapid rise of viscosity, although at the higher monomer concentration it is faster. At M/S = 0.5, the effect of starch thixotropy is still dominant in the gel formed after the reaction. However, at a M/S ratio of 2.0, thixotropy appears to have diminished or perhaps even disappeared. This cannot be attributed to the influence of just more polyacrylic acid (homopolymer) in the system since a viscometer analysis of a physical mixture of PAA and gelatinized cassava starch, at a ratio corresponding to M/S = 2.0, still shows the dominant effect of starch thixotropy: Fig. 7b. Apparently, the grafting reaction has changed the structure of the starch based product in such a way that the copolymer chains can no longer move in a way that decreases viscosity under the force of stirring. Since this effect, the leveling out of thixotropic properties, can be adapted to a large extent by varying the dosage of monomer, it may become an option to tailor a gel

product to a certain degree of thixotropy, fitting to the intended application. Clearly, this unexpected but promising finding needs to be investigated, and perhaps can be developed, further.

A diminishing effect of graft copolymerization on starch thixotropy was also found by Singh et al. [45]. In their work, a solution of pure starch shows a decrease of viscosity while a solution of starch grafted with acrylamide shows a much more stable viscosity, even after 72 h of stirring. These authors did not report about variation of the monomer to starch ratio but this result corresponds to our findings.

## CONCLUSIONS

Torque registration has been found a useful tool to observe the rheology of reaction mixtures with starch during graft copolymerization with acrylic acid. From experiments in a calibrated viscometer, an empirical correlation between torque and the apparent viscosity could be made. Gelatinized cassava starch shows thixotropic behavior, which was confirmed by a restoration of the apparent viscosity after a period of rest.

During the graft copolymerization reaction, the apparent viscosity of the reaction mixture increases rapidly. These profiles could be fitted with good accuracy with a simple first-order exponential growth model. In the development of a kinetic model for graft copolymerization, a similar first-order function was found, although logically with different numerical values of the rate constants. Only in the case of the highest monomer to starch ratio applied in this work, a Trommsdorff effect was observed causing deviations from the simple first order model.

The maximum (apparent) viscosity does not appear at the highest acrylic acid dosage but at a molar ratio of polyacrylic acid to anhydroglucose units of ca. 1:1. However, within the experimental region considered, the highest stability against mechanical stress is seen with the grafted copolymer in a reaction mixture that also contains ungrafted homopolymer, at a monomer to starch ratio of 2:1.

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