

## Real-time viscosity monitoring during graft copolymerization of gelatinized starch

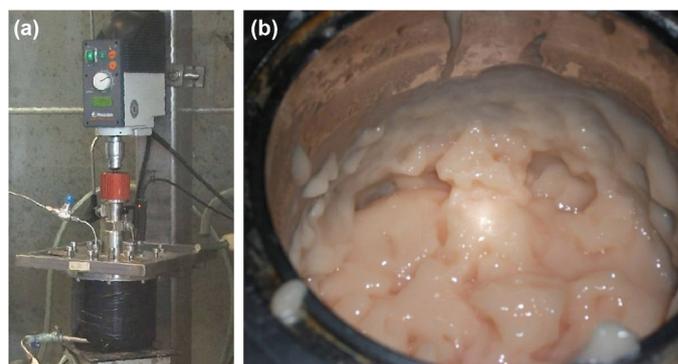
Judy R. Witono, Inge-Willem Noordergraaf, Erik Heeres, and Leon P. B. M. Janssen

*A combined stirrer–torque meter provides a novel and effective way to obtain continuous, in-line measurements of reaction mixtures.*

By using starch (i.e., a biopolymer and a renewable feedstock) rather than traditional plastics to fabricate products, biodegradability can be improved and the need for crude oil can be reduced. Chemical modifications of starch—such as attaching side chains of graft copolymers—are generally required, however, to improve the properties of the material before it can be used in most applications, e.g., as a water absorbent, flocculant, or thickening agent. For example, graft copolymerization of starch with water-soluble monomers (such as acrylic acid) has the potential to replace many traditional petrochemical-based water-soluble polymers.<sup>1–3</sup> To design a suitable reactor system for the production of such starch-based materials, it is thus vitally important to understand the rheological behavior of the reaction mixtures.

The rheological insight required for the design of graft polymerization reactors and processes for starch-based materials, however, is not currently available in the literature.<sup>1,4</sup> Moreover, it is not possible to predict the viscosity of the reaction mixtures from data for the individual components,<sup>4</sup> a suitable device for measuring viscosity directly inside a reactor is unavailable, and offline measurements of highly viscous mixtures are generally hampered by unreliable sampling techniques. Furthermore, although it is uncommon to process starch as a gel in industrial starch-modification reactors because of the associated high viscosities, in several recent studies it has been found that starch modification reactions are improved, in terms of reaction rate and selectivity, when the starch is in a gelatinized state.<sup>1,5–8</sup> A new method for making rheological measurements directly within a reactor during graft polymerization, and when the mixture is in a gelatinized state, is thus urgently required.

To overcome these issues, in this study,<sup>4</sup> we used a combined stirrer–torque meter—see Figure 1(a)—to monitor viscosity variations (these are ‘apparent viscosity’ measurements because viscosity is difficult to



**Figure 1.** Photographs of (a) the graft copolymerization reactor setup, including the combined stirrer–torque meter, and (b) the gelatinized cassava starch mixture after the synthesis reaction was complete.

properly define in non-Newtonian fluids) during polymerization reactions. Specifically, we conducted graft polymerization reactions with acrylic acid monomer and several monomer/starch (M/S) ratios. For the starch in our study, we used cassava starch, which was gelatinized before the monomer was added. We chose this material because it has been employed only rarely in industry to date, e.g., for conversion to bioethanol,<sup>1,9</sup> even though it is an abundant commodity in many tropical countries, and because it can be considered as a model component for other starch graft copolymerizations. In addition, cassava starch has a lower paste viscosity than most other starches, and it is therefore well-suited to testing in the gel phase.

We carried out all our graft copolymerization runs in a 500ml stainless steel batch reactor, within a nitrogen atmosphere and under controlled temperature conditions. We used Fenton’s reagent (i.e., a solution of ferrous iron and hydrogen peroxide) as the initiator for the system. Indeed, with this initiator, the reaction is a free radical addition polymerization.<sup>1,4</sup> The reactions were allowed to run for up to two hours, during which time we used our integrated stirrer–torque meter

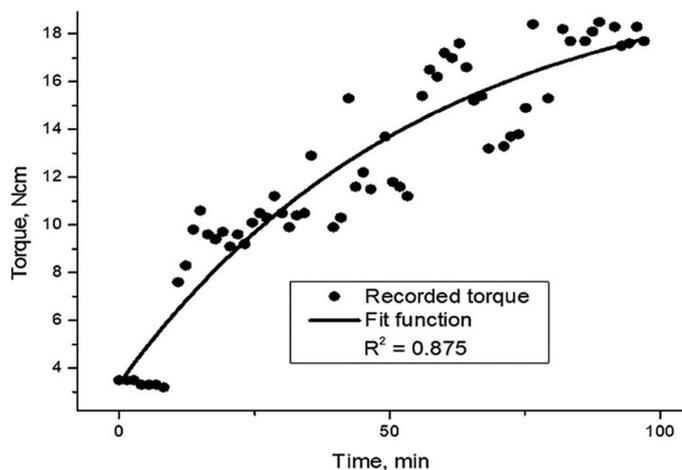
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to obtain continuous and in-line monitoring of the reaction fluid's viscosity. Full details of our experiments are presented elsewhere.<sup>4</sup> A photograph of the gelatinized cassava starch after completion of the graft copolymerization synthesis reaction is shown in Figure 1(b).

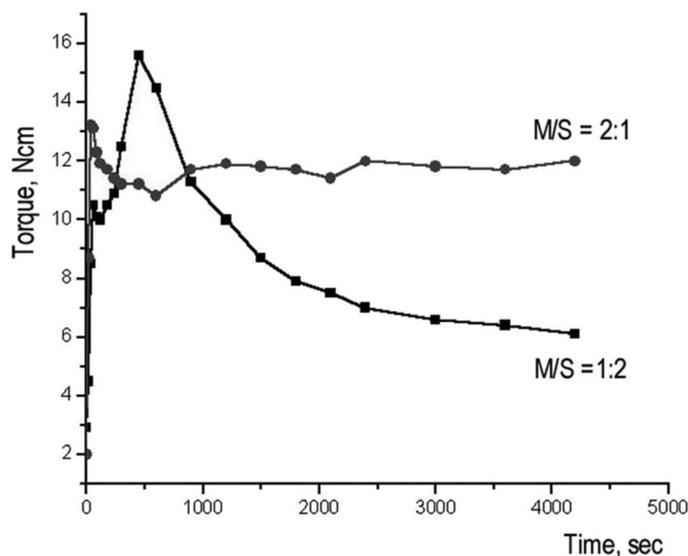
After completing our experimental campaign, we used the Origin 8.1 curve-fitting software to calculate model equations for our experimentally obtained torque profiles, such as the characteristic example shown in Figure 2. We find that all of our torque profiles have relatively similar shapes for the range of M/S ratios (0.5, 1.0, 1.5, and 2.0) we investigated. Furthermore, in all cases, we observe a rapid increase in torque that corresponds to an increase in the apparent viscosity of the reaction mixture. We attribute this effect to the formation of (long) polymer chains that are either graft-attached to the starch or that are unattached, i.e., as homopolymers. We have previously identified a pseudo-first-order dependency of the grafting reaction rate on the monomer concentration.<sup>1,10</sup> In this work, we therefore fitted the torque profiles with first-order rate equations, following the form:

$$Y = Y_0 - Y_1 \cdot \exp(-k_v \cdot t) \quad (1)$$

where Y is torque,  $Y_0$  and  $Y_1$  are fit constants,  $k_v$  is a first-order



**Figure 2.** Experimentally recorded torque profile (dots) for a characteristic reaction, shown as a function of time (in minutes). The first-order fit—according to Equation 1—to the experimental data is also shown (solid line). The agreement between the model and experimental results is relatively good, with a coefficient of determination ( $R^2$ ) of 0.875. These results are for the reaction that included 7.5% gelatinized cassava starch in a water solvent, acrylic acid monomer at a molar monomer/starch (M/S) 1:1 ratio, Fenton's reagent as the initiator (with ferrous iron and hydrogen peroxide at concentrations of 0.01 and 0.1 mol/l, respectively), and that was conducted at a temperature of 40°C and with a stirring speed of 300 revolutions per minute.



**Figure 3.** Torque profiles as a function of time for two reactions, illustrating the diminished thixotropy (reduction of viscosity under shear stress conditions) at higher M/S ratios.

kinetic constant, and  $t$  is time (in minutes). For most of the experimental results, we thus obtained good fits to the data, with a coefficient of determination ( $R^2$ ) of between 0.88 and 0.95. For the highest M/S ratio results, however, there is substantial deviation between the experimental information and our first-order models ( $R^2$  of 0.60). We believe that these poor fits are caused by the 'Trommsdorff' (gel) effect.<sup>11</sup>

Our results also show that the thixotropic behavior (i.e., reduction of viscosity under shear stress conditions, as exhibited by gelatinized starches) of our reaction mixtures varies with increasing M/S ratios (see Figure 3). Moreover, for the M/S of 2.0 reaction, the thixotropy characteristic is completely absent. The lack of thixotropy for this reaction cannot be explained, however, purely by the presence of more polyacrylic acid (homopolymer) in the system because thixotropy is a feature of all physical mixtures of starch and pure polyacrylic acid.<sup>1,4</sup> Instead, we think that our grafting reaction altered the structure of the cassava-based product so that the copolymer chains can no longer move in such a way that decreases the viscosity under the force of stirring.

In summary, we have used a combined stirrer-torque meter in a new method to obtain continuous, in-line viscosity measurements during starch (gelatinized cassava) graft polymerization reactions. Our comparisons of these torque measurements with results from a calibrated rheometer for the same material demonstrate the validity of our approach. In addition, we find that our torque-measurement approach is a good way to monitor the rheokinetic—the interrelation of true

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kinetic behavior and rheological properties of the system—behavior of starch graft polymerizations. We are also able, in most cases, to use a first-order kinetic formula to fit the changes in viscosity of the reaction mixture over time, but not when there is a gel effect (i.e., at very high viscosities). Although our starch mixtures exhibit thixotropic behavior, we find that the addition of grafted chains reduces this characteristic. For our future work, we are planning to test our findings further and to investigate the rheokinetic behavior of starch grafting reaction systems in additional reactors, or in a continuous product setup. We are also currently studying how the grafted chain length affects the rheological, and other, properties of the starch products.

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