

# Shear and Extensional Investigations in Solutions of Grafted/Ungrafted Amylopectin and Polyacrylamide

M. STELTER,<sup>1</sup> T. WUNDERLICH,<sup>1</sup> S. K. RATH,<sup>2</sup> G. BRENN,<sup>1</sup> A. L. YARIN,<sup>3</sup> R. P. SINGH,<sup>2</sup> F. DURST<sup>1</sup>

<sup>1</sup> Lehrstuhl für Strömungsmechanik (LSTM), University of Erlangen-Nürnberg, D-91058, Erlangen, Germany

<sup>2</sup> Materials Science Centre, IIT, Kharagpur-721302, India

<sup>3</sup> Faculty of Mechanical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

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**ABSTRACT:** Various polysaccharides, such as starch and its constituent amylopectin, are used as flocculants in industrial effluent treatment. Grafting them with polyacrylamide branches enhances their flocculating and turbulent drag-reducing characteristics drastically. Aqueous solutions of the graft copolymer of amylopectin with polyacrylamide show a shear thinning non-Newtonian behavior. It is also expected that the solutions exhibit extensional effects. When the aqueous solution at 1000 ppm was subjected to a stretching device, the formation of a thread and reduction of the thread diameter with time were observed. The extensional relaxation time was thus estimated and compared with that of polyacrylamide. The measured relaxation time indicates that the performance of the rigid branched amylopectin, when grafted with fewer and longer polyacrylamide branches, is overwhelmed by the grafted polyacrylamide chains and the reduction of rigidity by the grafting process itself. This article reports the details of the investigations that led to these conclusions. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2773–2782, 1999

**Key words:** grafted/ungrafted polymers; aqueous solutions; stretching device; intrinsic viscosity; self-thinning thread; shear rheometry

## INTRODUCTION

Polysaccharides, such as guar gum, xanthan gum, carboxy methyl cellulose, and starch, find several industrial applications.<sup>1</sup> Their efficiency, particularly in turbulent drag-reduction and flocculation, can be increased several fold on purification and grafting with polyacrylamide.<sup>2</sup> High-molecular-weight polyacrylamide, a synthetic linear polymer itself, is an efficient turbulent drag reducer and flocculating agent.<sup>3</sup> However, it suffers from poor mechanical stability, which increases with molecular weight. Polysaccharides, on the other

hand, are poor drag reducers and flocculating agents,<sup>4</sup> and their solutions are susceptible to biodegradation.<sup>5</sup> The limited drag reduction and flocculation effectiveness are also obtained at high concentrations of polysaccharides.<sup>6</sup> Hence, there is a possibility of grafting flexible polyacrylamide chains on robust polysaccharide backbones to develop efficient shear-stable turbulent drag reducers and flocculants effective at low concentrations (<100 ppm) with controlled biodegradation.<sup>7,8</sup> Such novel turbulent drag reducers and flocculants have been developed at the Materials Science Centre, IIT, Kharagpur, India, and well characterized for their end applications.<sup>2,9</sup>

Among various grafted polysaccharides, grafted starch has been found to be the most efficient flocculating agent for various industrial

Correspondence to: G. Brenn.

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effluents.<sup>2,7,8</sup> Starch consists of amylose, a linear low-molecular-weight (10,000 to 60,000) polymer and amylopectin, a branched polymer with high molecular weights up to 50,000-10<sup>6</sup>. Among grafted amylose and amylopectin, the latter exhibits higher flocculation efficiency. Mainly, because of the dangling, flexible polyacrylamide chains grafted on branched amylopectin have easy approachability to contaminant particles in industrial effluents in accordance to Singh's model.<sup>2,7-9</sup>

Various grades of graft copolymers have been recently developed at the Materials Science Centre, IIT, Kharagpur.<sup>7,8,10</sup> The grafted amylopectin (Ap-g-PAM 4) having fewer and longer branches has been found to be the most efficient flocculant. The polyacrylamide chains are grafted onto a polysaccharide backbone by a ring-opening mechanism.<sup>6-10</sup> Hence, flexibility is introduced in the grafted copolymers, both in the backbone and flexible grafted chains. Hence, the investigation of the solutions of grafted and ungrafted amylopectin is rheologically quite interesting. Since extensional and shear deformations also play an important role in both turbulent drag reduction and flocculation,<sup>2,4,11</sup> the solutions of amylopectin, polyacrylamide, and Ap-g-PAM 4 have been investigated extensively by shear rheometry and a novel stretching device<sup>12,13</sup> at LSTM, University of Erlangen-Nürnberg, Germany. The present article reports the details of the investigations and their relevance in various physical phenomena and multiphase flow.

## EXPERIMENTAL

### Materials

Amylopectin (from corn) was purchased from Sigma, USA. Acrylamide (GR) was procured from Merck, Germany. Ceric ammonium nitrate (CAN)

was obtained from Loba Chemie, Bombay, India. Acetone and hydroquinone were supplied by s.d. Fine Chem. Bombay, India. Sodium nitrate was supplied by Merck, India.

### Synthesis

The graft copolymer of amylopectin (Ap-g-PAM) was synthesized by a ceric ion induced redox initiation method.<sup>7,8</sup> The experimental details are described elsewhere.<sup>9,10</sup>

### Viscosity Measurement

The solutions of polyacrylamide, amylopectin, and amylopectin-g-PAM were prepared in deionized water. First the required quantity of the polymers was added slowly to water and stirred by a magnetic stirrer to avoid lumping. Then the temperature of the solution was raised to 80°C with constant stirring until the solution became transparent. The solution was then cooled down. The viscosity measurements of all the solutions of amylopectin and amylopectin-g-PAM were carried out with the help of an Ubbelohde viscometer and a Zimm-Crothers viscometer (M. Krannich, Göttingen, Germany), able to measure the viscosity at almost zero shear rate.<sup>12</sup> For Ubbelohde viscometry, a stock solution of 0.5 g/250 mL was prepared which was further diluted with NaNO<sub>3</sub> solution. Subsequently distilled water was added in such proportion that the required concentration of polymer was obtained in 1M NaNO<sub>3</sub>. The time of flow for a fixed volume of solution was measured at five different concentrations. The intrinsic viscosity was obtained (from the point of intersection) after extrapolation<sup>9,10</sup> of the two plots of the reduced viscosity  $\eta_{red} = \eta_{sp}/C$  versus  $C$  and the inherent viscosity  $\eta_{inh} = \ln(\eta_{rel})/C$  versus  $C$  to zero concentration. Here,  $C$  is the polymer concentration in g/cm<sup>3</sup>. The reduced viscosity was calculated from the relation  $\eta_{red} = \eta_{sp}/C$

**Table I** Details of Synthesis of the Graft Copolymers

No.	Polymer	Polysaccharide (mol AGU) <sup>a</sup>	Acrylamide (mol)	Amount of CAN (mol × 10 <sup>4</sup> )	Conversion (%) <sup>b</sup>	Intrinsic Viscosity <sup>c</sup> [ $\eta$ ] (cm <sup>3</sup> /g)
I	Ap-g-PAM	0.0154	0.14	1.003	84.1	746
II	St-g-PAM	0.0154	0.14	1.003	89.33	686

<sup>a</sup> Calculated on the basis of anhydroglucose units (1 g mol of AGU is equal to 162 g).

<sup>b</sup> Percentage of conversion is calculated from the following relation<sup>9</sup>: conversion = [(weight of graft copolymer - weight of polysaccharide)/amount of acrylamide] × 100.

<sup>c</sup> Intrinsic viscosity was evaluated from 1M NaNO<sub>3</sub> solutions. Intrinsic viscosity was measured with an Ubbelohde viscometer.

**Table II** Intrinsic Viscosities, Measured with a Zimm–Crothers Viscometer, and Extensional Relaxation Times of Various Polymer Solutions at the Concentration  $C = 1000$  ppm

Fluid	Temperature $T$ [°C]	Intrinsic Viscosity $[\eta]$ [cm <sup>3</sup> /g]	Relaxation Time $\Theta$ [ms]
Amylopectin	26	418	—
AP- <i>g</i> -PAM	26	1276	5, 46
Praestol 2500	25	8135	47
Praestol 2540	23	127,000	107
AP 273	26	67,932	36, 6

$= (\eta_{\text{rel}} - 1)/C$ , where  $\eta_{\text{rel}} = \eta/\eta_o = t/t_o$ . In this expression,  $\eta_o$  is the dynamic viscosity of the solvent,  $t$  is the time of flow of the polymer solution, and  $t_o$  is the time of flow of the solvent at the temperature of the measurement.

From the Zimm–Crothers viscometer<sup>14</sup> also, the same procedure was adopted. The synthetic details of the graftcopolymers are given in Table I. In the Zimm–Crothers measurements, the intrinsic viscosity  $[\eta]$  was obtained in deionized water. The results of these intrinsic viscosity measurements are given in Table II. As an example, Figure 1 shows the results for amylopectin-*g*-PAM and amylopectin in detail.

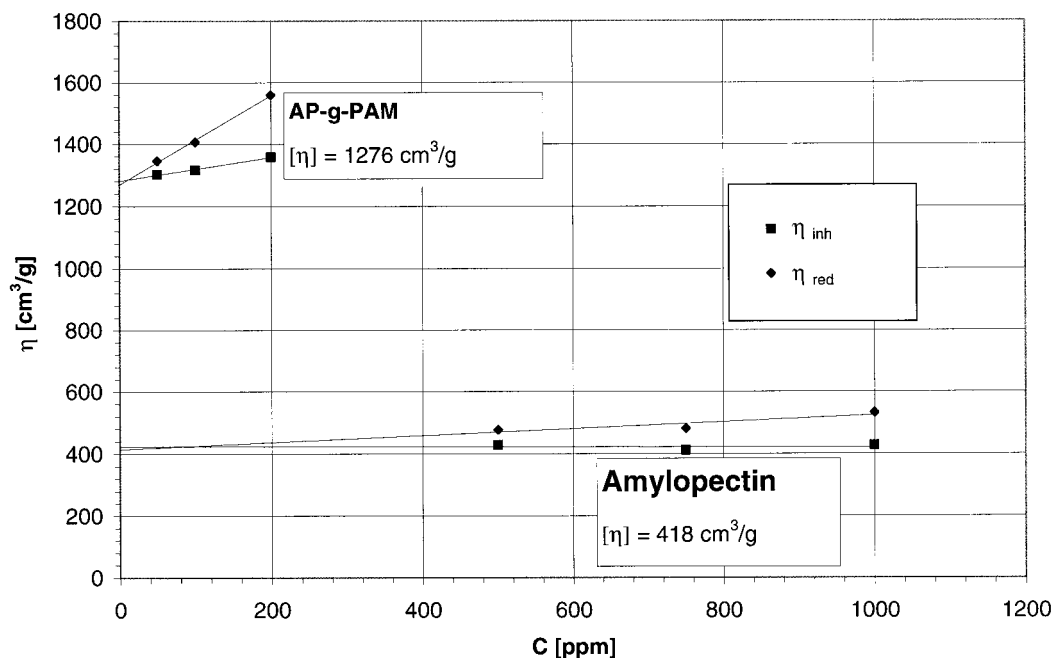
#### Rheological (Shear) Measurements

The rheological measurements at the concentration of 5000 ppm were carried out by a Rheometer

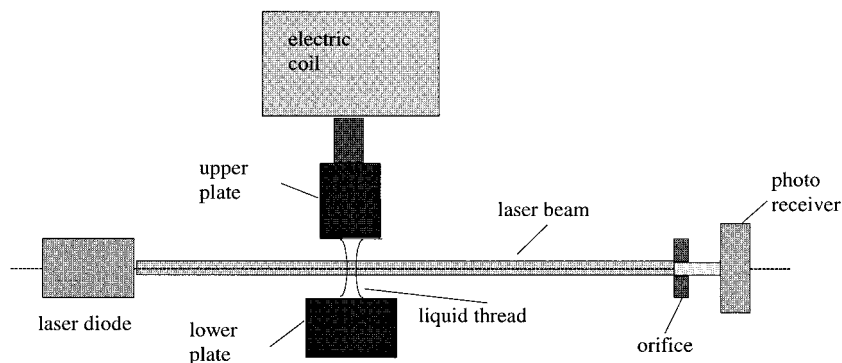
Physica Low Stress LS 100 using a cone plate device (CP 501) and at the concentration of 1000 ppm by a Haake CV 100 using a Couette rotational viscometer ME 46. Some viscosity versus shear rate and dynamic measurements at the concentration of 5000 ppm were carried out using a Physica UDS 200 Universal Dynamic Spectrometer with a cone plate viscometer (MK 24). All viscosity measurements have been carried out at 25°C.

#### Stretching Device

A novel elongational rheometer has been developed<sup>13</sup> for dilute polymer solutions, where a small quantity of liquid is stretched abruptly to form a thread between two plane solid surfaces. The elongational rheometer for dilute solutions is based on the self-thinning of the liquid thread under the action of surface tension. In this device,



**Figure 1** Various characteristics of two of the polymer solutions investigated.



**Figure 2** Schematic diagram of the stretching device.

only a droplet of a liquid is needed to test its rheological behavior.

The stretching device consists of two plates between which a liquid sample in the form of a drop is inserted. With a magnetic coil, the upper plate is quickly pulled up to a fixed position so that a liquid thread of constant length is formed. The formation of the thread takes place very rapidly, that is, with a time scale much shorter than the relaxation time of the thread. Both the formation and relaxation of the thread, therefore, do not depend on the rate of pulling. The decrease of the radius  $a$  of the thread with time  $t$  is described by the following relation<sup>13</sup> (the derivation of which is given in the Appendix):

$$a = a_0 e^{-t/3\theta} \quad (1)$$

where  $a_0$  is the initial radius (at time  $t = 0$ ), and  $\theta$  is the relaxation time.

A laser diode and photo receiver permit the diameter of the thread to be measured as a function of time. The thread crossing the laser beam reduces the light intensity measured by the photo receiver approximately proportional to its diameter. The relationship between the received light intensities and the thread diameter is obtained by means of a calibration procedure. A schematic diagram of the above described device is given in Figure 2.

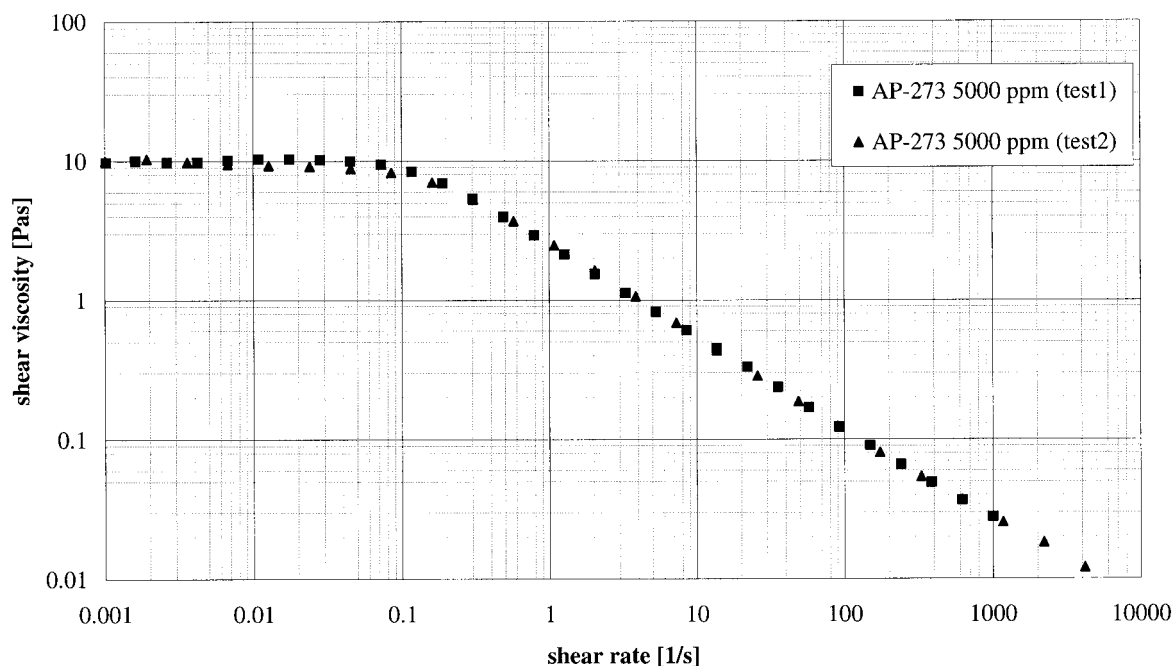
## RESULTS AND DISCUSSION

It was mentioned in the introduction that starch consists of a mixture of two polysaccharides, amylose and amylopectin. Amylose is a linear polymer consisting of a chain of glucose units connected to each other by  $\alpha$  (1  $\rightarrow$  4) links. Depending upon the

source of the starch, the degree of polymerisation of the amylose molecules varies from 250 to 4000 anhydro-glucose units (AGU), corresponding to a molecular weight of approximately 40,000 to 650,000.<sup>1</sup>

The amylopectin fraction of starch is highly branched. The structure consists of short-linear amylose chains with a degree of polymerization ranging from 12 to 50 AGU and an average chain length of about 20 AGU connected to each other by  $\alpha$  (1  $\rightarrow$  6) links. These  $\alpha$  (1  $\rightarrow$  6) linked AGU make up about 4 to 5% of the total amylopectin and are the branch point of the molecule.<sup>1</sup> As for the structure of amylopectin, it is believed that a significant proportion of the branches are separated by no more than a single glucose unit, thus suggesting the presence of regions of dense branching. Based on this premise, French<sup>15</sup> proposed an elongated cluster structure to account for the high viscosity of amylopectin, which would require an asymmetric structure and high crystallinity in the starch granule which would require a high proportion of the branches to run parallel to each other. Amylopectin is a very large molecule, one of the largest natural polymers (weight coverage molecular weight of the order of  $10^7$ – $10^8$ ).

During the grafting reaction, the mechanism of ceric ion involves the formation of a chelate complex,<sup>16</sup> which decomposes to generate two free radical sites on the polysaccharide backbone. In the case of amylopectin, the radical sites are generated both on the backbone and on the branches of amylopectin. These active free radical sites in the presence of acrylic monomers generate graft copolymers. The possibility of homopolymerisation is remote as the monomer concentration is below 2.0M, the limit observed by Owen and Shen.<sup>17</sup> This has also been proved by enzyme



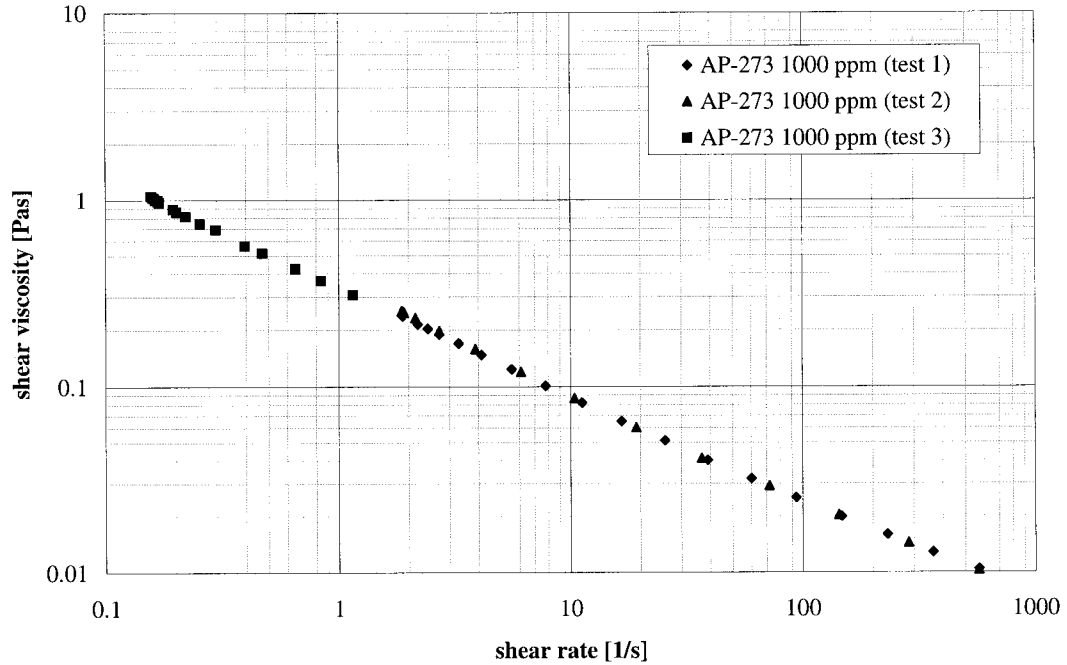
**Figure 3** Dependence of the apparent shear viscosity ( $\eta$ ) on the shear rate ( $\dot{\gamma}$ ) for a 5000 ppm solution of Polyacrylamide (AP-273). The data sets termed “test 1” and “test 2” are repeated measurements at the same conditions, indicating very good repeatability.

hydrolysis of graftcopolymers of amylopectin and polyacrylamide.<sup>18</sup> The graftcopolymer has also been well characterized by elemental analysis, thermal analysis, infrared (IR), nuclear magnetic resonance (NMR), X-ray diffraction, and morphological studies recently.<sup>19</sup> Amylopectin, when grafted by polyacrylamide, performs the best as flocculating agent, particularly for industrial effluents.<sup>9,10,20</sup> This has been attributed to the fact that the dangling polyacrylamide branches on rigid and branched amylopectin have a better approachability to colloid particles in an effluent. Among the graftcopolymers, the one which has fewer but longer grafted polyacrylamide performs the best.<sup>9,10,20</sup> The performance of amylopectin-g-PAM has been the best. As flocculation and drag reduction go hand in hand as far as the material is concerned,<sup>21</sup> it is expected that amylopectin-g-PAM should have a high extensional viscosity.<sup>22</sup> Hence, its solutions have been subjected to shear and extensional investigations in the present study.

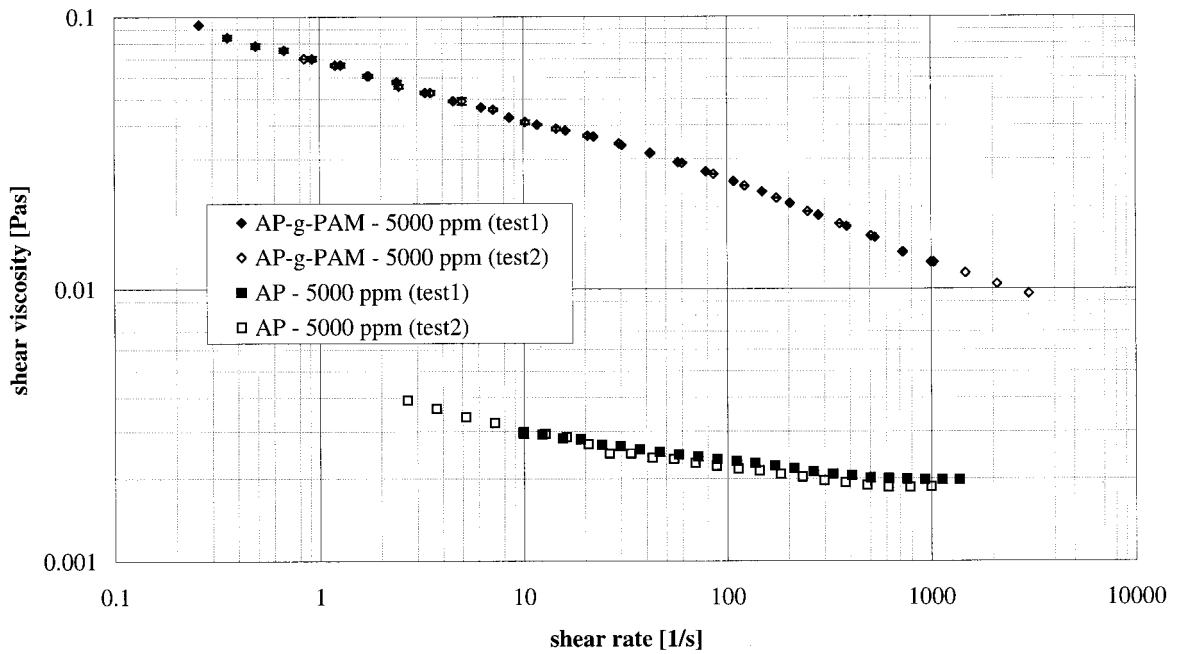
The intrinsic viscosity of amylopectin-g-PAM was measured by an Ubbelohde viscometer in 1M NaNO<sub>3</sub> solutions, as given in Table I. The intrinsic viscosities of amylopectin, as well as amylopectin-g-PAM, were measured by the device, giving

almost zero shear rate in deionized water (Fig. 1). Comparing the intrinsic viscosity of amylopectin-g-PAM with that of amylopectin, there is a drastic difference. The reason being due to charge neutralization and an appreciable shear rate in the Ubbelohde viscometer, the values in the first case are much lower. This has also been observed in the case of graftcopolymers of amylose, where the values of intrinsic viscosities are of the same order as found in the present latter case.<sup>23</sup>

The viscosity at various shear rates was measured in aqueous solutions of polyacrylamide (AP-273) (Figs. 3 and 4), amylopectin and amylopectin-g-PAM (Figs. 5 and 6) at the concentrations of 5000 and 1000 ppm. At both concentrations, aqueous solutions of polyacrylamide and amylopectin-g-PAM are evidently non-Newtonian and shear thinning. The aqueous solutions of amylopectin also exhibit a slight shear thinning behavior. The same behavior is indicated when the complex viscosity  $\eta'$ , shear elastic modulus  $G'$ , and loss shear modulus  $G''$  are measured for varying frequency at a 5000-ppm concentration of Ap-g-PAM, as shown in Figure 7. The grafting of polyacrylamide chains on amylopectin enhances the viscosity of its aqueous solutions towards that of polyacrylamide solutions over all shear rates. Be-

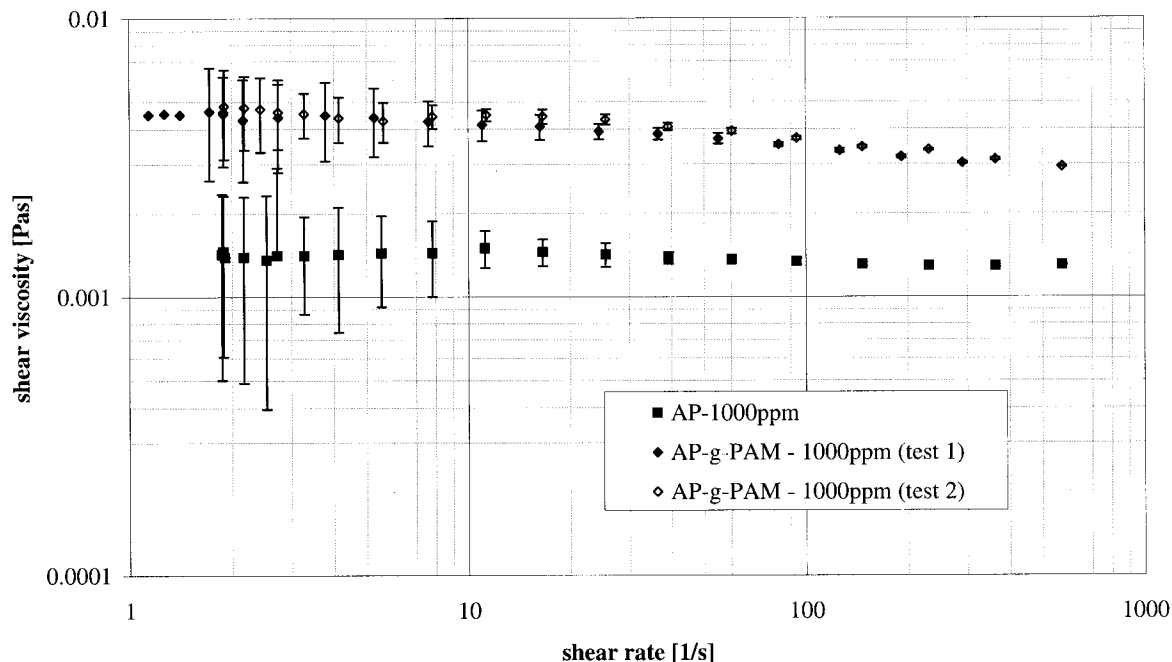


**Figure 4** Dependence of the apparent shear viscosity ( $\eta$ ) on the shear rate ( $\dot{\gamma}$ ) for a 1000-ppm solution of Polyacrylamide (AP-273). The data sets termed “test 1” through “test 3” are repeated measurements at the same conditions, indicating very good repeatability.



**Figure 5** Dependence of the apparent shear viscosity ( $\eta$ ) on the shear rate ( $\dot{\gamma}$ ) for 5000-ppm solutions of amylopectin-g-polyacrylamide and amylopectin. The data sets termed “test 1” and “test 2” are repeated measurements at the same conditions, indicating very good repeatability.

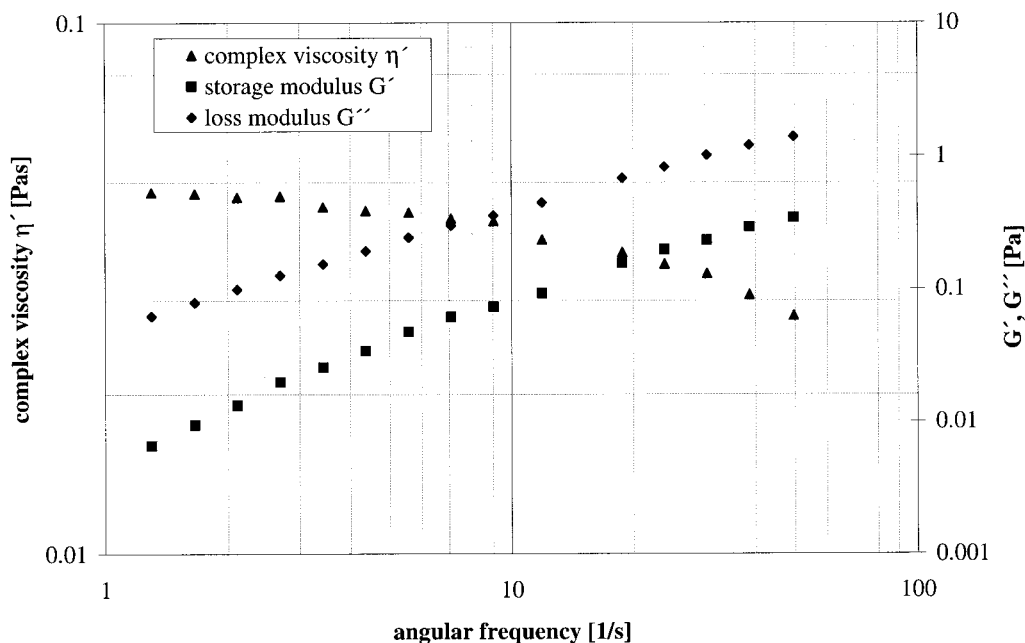




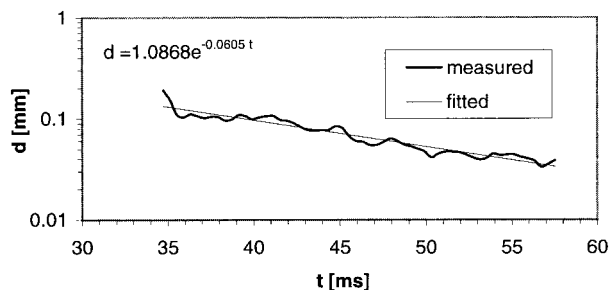
**Figure 6** Dependence of the apparent shear viscosity ( $\eta$ ) on the shear rate ( $\dot{\gamma}$ ) for 1000 ppm solutions of amylopectin-*g*-polyacrylamide and amylopectin. The data sets termed “test 1” and “test 2” are repeated measurements at the same conditions, indicating very good repeatability.

cause of the limited shear rate range available due to experimental constraints, no attempt has been made to curve-fitting by suitable rheological

models. Measurements of the modulus  $G$  were not carried out for the AP-273 solutions. Conclusions on its magnitude in polyacrylamide solutions for



**Figure 7** Dependence of the dynamic viscosity  $\eta'$ , storage shear modulus  $G'$ , and loss shear modulus  $G''$  on the angular frequency  $\omega$  for a 5000-ppm solution of AP-*g*-PAM.

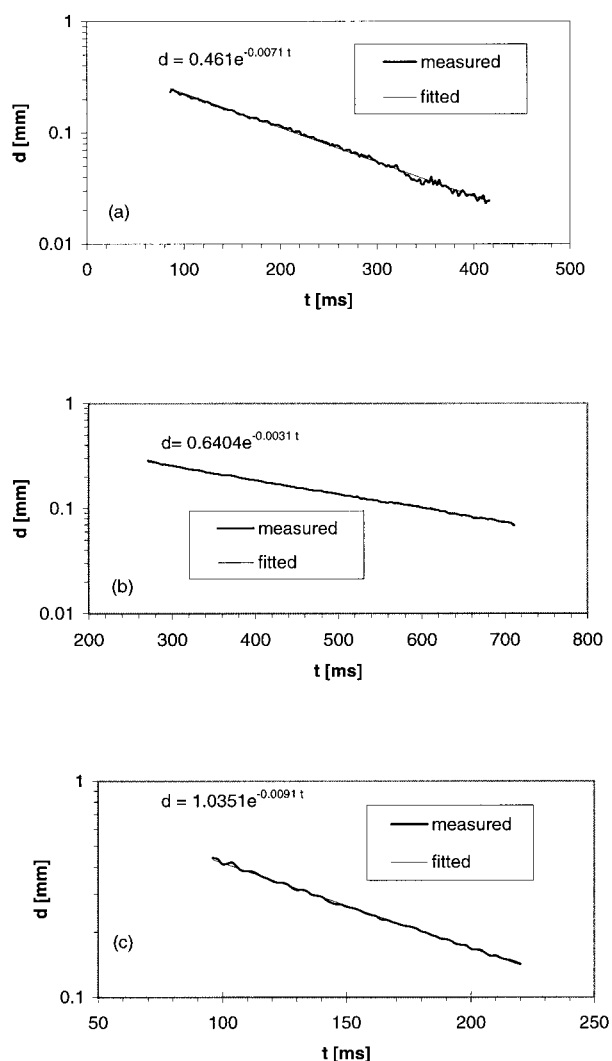


**Figure 8** Variation of the thread diameter with time in the stretching device (Yarin<sup>11</sup>) for a 1000-ppm solution of Ap-g-PAM at  $T = 26^\circ\text{C}$ . The measured relaxation time is  $\theta = 5.5$  ms.

different concentrations are therefore not presented here.

Table II depicts the extensional relaxation time as evaluated from eq. (1) on the basis of the measurements of the diameter of the thread versus time using the elongational rheometer for grafted polysaccharide and three samples of polyacrylamide. In Figures 8 and 9, the evolution of the thread diameter with time is depicted. From these data, the relaxation time  $\theta$  was evaluated by fitting the measured curves with an exponential function. The equations of the fit functions are given in the subfigures, with the diameter in mm and time in ms. Ungrafted and grafted starch, as well as ungrafted amylopectin, did not exhibit any thread formation and were, therefore, not measurable with the stretching device. On the other hand, grafted amylopectin showed thread formation at the concentration of 1000 ppm. Grafted amylopectin has fewer but longer grafted branches of polyacrylamide and is of high molecular weight, as evidenced from the higher intrinsic viscosity. Amylopectin itself shows crystallization,<sup>1,24</sup> which indicates that the branches are parallel to the backbone and do not hinder cohesiveness. On grafting with polyacrylamide, the cohesiveness increases, which ushers in thread formation. Grafted amylopectin becomes semiflexible due to grafted flexible polyacrylamide branches and the ring opening of AGU. This also increases the cohesiveness and orientation of the molecules for thread formation. In the case of polyacrylamide (linear flexible and anionic), there is more cohesiveness due to an increase of concentration of the droplet put into the stretching device and resultant lesser tendency of thinning of the thread and consequent increase in relaxation time. Among the two Praestol samples, Praestol 2500 and Praestol 2540, the latter is a rigid one

and oriented with higher molecular weight. Its intermolecular interaction is also stronger due to hydrogen bonding. Hence, it shows the least tendency of thinning and the largest relaxation time. Both Praestol 2500 and polyacrylamide AP-273 are flexible and exhibit relaxation times of the same order at 1000 ppm concentration. Though grafted amylopectin is amenable to thread formation and of semiflexible nature due to the branched nature of amylopectin, cohesion is less; hence, its relaxation time is almost one-tenth of the flexible polyacrylamide samples. Due to the combination of low molecular weight, rigidity,



**Figure 9** Variation of the thread diameter with time in the stretching device (Yarin<sup>11</sup>) for 1000-ppm solutions of the polyacrylamides (a) Praestol 2500, (b) Praestol 2540, and (c) AP-273 at  $T = 24, 23,$  and  $26^\circ\text{C}$ , respectively. The measured relaxation times are  $\theta = 47, 107.5,$  and  $36.6$  ms, respectively.



and small cohesion, the grafted and ungrafted starch polymers are not amenable to thread formation. The grafted amylopectin shows enhanced drag reduction and flocculation characteristics, which are partly due to its extensibility and semiflexible nature, as evidenced from the above investigation.

## CONCLUSIONS

The grafted amylopectin, which is endowed with drag reduction and flocculation characteristics, also exhibits viscosifying attributes. The solutions of grafted amylopectin show shear thinning behavior. Their viscosities lie in between those of amylopectin and polyacrylamide. The solutions of grafted amylopectin show extensional behavior akin to those of high-molecular-weight polyacrylamide. Grafted amylopectin becomes semiflexible due to ring opening during the grafting mechanism and due to grafted flexible polyacrylamide chains. These two factors, along with its high molecular weight, are responsible for thread formation in the extensional experiment. The stretching device applied for the present experiments is a valuable tool for quantifying the relaxation behavior of threads of dilute viscoelastic fluids.

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## APPENDIX

The stretching device shown in Figure 2 is based on the following theoretical considerations. In the uniaxial elongational flow, the longitudinal component of the orientation–deformation tensor  $L_{XX}$  is much larger than the radial one,  $L_{YY}$ . It is also much larger than its equilibrium value based on

the undeformed macromolecular coil size,  $r = b_1 N_{01}^{1/2}$  ( $b_1$  is the Kuhn segment, and  $N_{01}$  is the number of Kuhn segments in a macromolecule), and it is much less than its value based on the length of the fully stretched macromolecule,  $b_1 N_{01}$ . So,

$$L_{XX} \gg L_{YY} \quad (\text{A.1a})$$

$$\frac{r^2}{3} \ll L_{XX} \ll (b_1 N_{01})^2 \quad (\text{A.1b})$$

Also  $\partial L_{XX}/\partial X = 0$  since the deformation in the central part of the thread is uniform. Therefore, from the third equation of (3.2) in Yarin,<sup>12</sup> we obtain,

$$\frac{dL_{XX}}{dt} = 2L_{XX} \frac{\partial V}{\partial X} - \frac{1}{\theta} L_{XX} \quad (\text{A.2})$$

where  $\theta$  is an effective relaxation time,  $X$  is the longitudinal axial coordinate in the thread,  $t$  is time, and  $V$  is the longitudinal velocity. We also assume that the deviatoric elastic stress related with stretching of the macromolecular coils in uniaxial elongational flow,  $\tau_{XX} = CkL_{XX}$  ( $C$  is the polymer concentration, and  $k$  is the elastic constant of the coiled macromolecule), as well as its driving capillary stress,  $\alpha/a$ , are much larger than the stress related with the solvent  $3\mu_1 \partial V/\partial X$ . Here,  $\alpha$  is the surface tension coefficient,  $a$  is the cross-sectional radius of the thread, and  $\mu_1$  is the solvent viscosity. Therefore, from the first equation of (3.2) Yarin<sup>12</sup> in a uniform part of the thread, where  $\partial a/\partial X = 0$ , we find the stress in the thread cross section as

$$\Sigma_{XX} = -\frac{\alpha}{a} + CkL_{XX} \quad (\text{A.3})$$

From the momentum balance equation [the second one in (3.1) in Yarin,<sup>12</sup>] it follows that in the uniform part of the thread  $\Sigma_{XX} = 0$ . Thus, from (A.3), we arrive at

$$L_{XX} = \frac{\alpha}{Cka} \quad (\text{A.4})$$

Also from the continuity equation [the first one in (3.1) in Yarin<sup>12</sup>], it follows that the rate of stretching of the thread is related with the rate of its thinning as per

$$\frac{\partial V}{\partial X} = -\frac{2}{a} \frac{da}{dt} \quad (\text{A.5})$$

Substituting (A.4) and (A.5) in (A.2), we arrive at the following equation:

$$\frac{d}{dt} \left( \frac{1}{a} \right) = 2 \frac{1}{a} \left( -\frac{2}{a} \frac{da}{dt} \right) - \frac{1}{\theta} \frac{1}{a} \quad (\text{A.6})$$

This is transformed to

$$\frac{3}{a} \frac{da}{dt} = -\frac{1}{\theta} \quad (\text{A.7})$$

which yields

$$a = a_0 e^{-t/3\theta} \quad (\text{A.8})$$

where  $a_0$  is the initial thread radius.

Therefore, measuring the slope of an experimental curve in the plane  $(\ln a, t)$ , we find  $\theta/3$ , and as a result, the relaxation time  $\theta$ .