Shear and Extensional Rheological Investigations in Solutions of Grafted and Ungrafted Polysaccharides

T. WUNDERLICH,[1] M. STELTER,[1] T. TRIPATHY,[2] B. R. NAYAK,[2] G. BRENN,[1] A. L. YARIN,[3] R. P. SINGH,[2] P. O. BRUNN,[1] F. DURST[1]

[1] Lehrstuhl für Strömungsmechanik (LSTM), University of Erlangen-Nürnberg, D-91058 Erlangen, Germany

[2] Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

[3] Faculty of Mechanical Engineering, Technion–Israel Institute of Technology, Haifa 32000, Israel

ABSTRACT: Many polysaccharides with varying shear stability have been grafted with polyacrylamide branches to enhance their turbulent drag-reducing and flocculating characteristics. Their aqueous solutions have been studied by shear and extensional rheometric techniques. All the solutions of grafted carboxymethyl cellulose, guar gum, starch, and sodium alginate exhibit shear-thinning non-Newtonian behavior. The viscosities are higher than those of ungrafted polysaccharides. The solutions of grafted carboxymethyl cellulose, guar gum and sodium alginate are spinnable. When subjected to uniaxial stretching in a stretching device, the formation of a thread and reduction of the thread diameter with time were observed. The stretching device was used to measure the relaxation time, which was found to be the largest ($\sim$26 ms), on the order of flexible polyacrylamide, for the grafted carboxymethyl cellulose. Though a polyacrylamide solution degrades through nozzle flow and completely loses its extensional properties, a solution of grafted carboxymethyl cellulose retains about half its relaxation time because of the shear stability of polysaccharide chains and their structure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3200–3209, 2000

INTRODUCTION

Polysaccharides are used both as drag-reducing[1] and flocculating agents.[2] Their aqueous solutions are prone to biodegradation but are fairly shear stable.[3] A high dose of polysaccharide is needed for both flocculation and drag reduction. On the other hand, synthetic polymers such as polyacrylamides provide very efficient drag reduction and flocculation at concentrations of only a few parts per million.[4,5] However, they have poor shear stability and lose their drag reduction and flocculation characteristics quickly in turbulent and high-shear conditions. Singh et al.[6–16] have established that by grafting polyacrylamide branches on polysaccharides, a wide variety of efficient and shear-stable graft copolymers can be developed. These copolymers are efficient drag reducers and flocculating agents that have controlled biodegradation and are highly efficient at low concentrations (30–50 ppm). For both these phenomena and, in particular, for nozzle flows, shear and extensional rheological characteristics influence their behavior. Hence, an attempt has been made to study the shear and extensional rheological behavior of these solutions.

Recently it has been observed that solutions of graft copolymers of amylopectin and polyacrylamide exhibit extensional effects when subjected

Table I   Synthesis Details of Graft Copolymers

Polymer	Polysaccharide (g)	Acrylamide (g)	Conc. of CAN (mol $\times 10^3$)	% Conversion	Intrinsic Viscosity[a] (cm^3/g)
CMC-*g*-PAM (Carboxymethyl cellulose-*graft*-polyacrylamide)	2	15	8.75	89	762
St-*g*-PAM (Starch-*graft*-polyacrylamide)	2.5	10	0.1003	89.33	686
GG-*g*-PAM (Guar gum-*graft*-polyacrylamide)	1	10	0.08	79.6	830
SAG-*g*-PAM (Sodium alginate-*graft*-polyacrylamide)	2.5	10	0.2006	84.58	782

The percentage conversion is calculated according to the relation:
% Conversion = [(Wt. of graftcopolymer − Wt. of polysaccharide)/Amount of acrylamide] ×100.
[a] The intrinsic viscosity was obtained in 1*M* NaNO3. The details of the intrinsic viscosity measurement are given in Ref. 10.

to a stretching device.[12] However, their relaxation time is about one-tenth that of flexible polyacrylamide. It appears that if the main chain of the polysaccharide has a tendency to align and crystallize, the grafting may impart extensibility in such a way that the graft copolymer may have a relaxation time (~50 ms) on the same order as that of a flexible polyacrylamide.

In our earlier investigation,[13] it was found that in turbulent flows the solutions of carboxymethyl cellulose (CMC) are most stable, followed by those of guar gum (GG). It is expected that graft copolymers of CMC/GG and polyacrylamide (PAM) may have a relaxation time on the order of that of polyacrylamide and may have a fairly high shear stability. Sodium alginate is a linear polymer; its graft copolymer may also provide requisite characteristics. The

graft copolymers of starch (st) and its constituents are very effective flocculants. Hence, in the present investigation, graft copolymers of carboxymethyl cellulose, guar gum, starch, and sodium alginate were studied. The shear and extensional rheological characteristics of grafted and ungrafted carboxymethyl cellulose, guar gum, starch, and sodium alginate aqueous solutions are reported in this article. An effort has been made to correlate the rheological properties to the structures and dimensions of these polysaccharides. It has been shown that higher relaxation times in graft copolymers of carboxymethyl cellulose result from a combined effect of main-chain characteristics and grafting. Furthermore, for a manifestation of spinnability, a certain minimum molecular dimension seems to be necessary. The importance of these investi-

Table II   Comparison of Measurement Results from Zimm–Crothers Viscometer and from Stretching Device for Different Polymers

Fluid	Temperature [°C]	Molecular Weight $\times 10^{-6}$	Intrinsic Viscosity [η] [cm^3/g]	Relaxation Time [ms]	Notes
Starch	26	0.45	396		branched
SAG	25		2000		linear, ionic
Guargum	23		433		linear, flexible
CMC	24		1150		linear, ionic
St-*g*-PAM	26	0.35	423.5		semirigid
SAG-*g*-PAM	25	1.19	1128	3.24	semirigid
GG-*g*-PAM	23	0.96	955	6.68	semirigid
CMC-*g*-PAM	24	16.88	9440	26	semirigid
Praestol 2500	25	14	8135	47	linear, flexible
Praestol 2540	23	14	127000	107	anionic

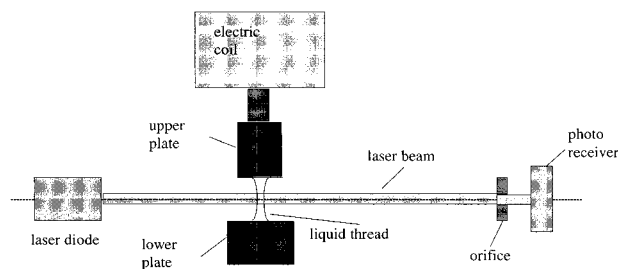The relaxation time measurements were carried out at the concentration of 1000 ppm.

Figure 1   Sketch of the stretching device used for the relaxation time measurements.

EXPERIMENTAL

Materials

Four graft copolymers and their base polysaccharides were studied in the present investigation: carboxymethyl cellulose, guar gum, starch, and sodium alginate. They were grafted with polyacrylamide side chains.

Sodium carboxymethyl cellulose was procured from Supertex Ltd., Mumbai, India. It is produced by carboxymethylation of cellulose. In the present case, the degree of substitution was 0.8. Guar gum was procured from Hindustan Gums and High Chemicals, Bhiwani, India. Soluble starch was purchased from E. Merck, Germany, and sodium alginate was procured from Aldrich Chemical Company, United States. Guar gum was subjected to Soxlet extraction with 95% ethanol for 5 days to remove protein and fat impurities. Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate (CAN) was procured from Loba Chemie, Mumbai, India. Hydroquinone, sodium nitrate, and acetone (Analar grade) were obtained from E. Merck, Mumbai, India. Doubly distilled water was used for synthesis.

Synthesis

The grafting reaction was carried out by the ceric ion–induced redox initiation method.[14,15] The details of the procedure are given elsewhere.[6–11,16,17] The synthesis details are given in Table I.

Viscosity Measurement

Viscosity measurements of all the grafted polysaccharide solutions were carried out by an Ub-

belohde capillary viscometer (Const. 0.00527 mm^2/s^2). The temperatures were 30°C for CMC-*g*-PAM, 27°C for St-*g*-PAM, and 26°C for SAG-*g*-PAM. The details are given elsewhere.[6–11,16,17] The intrinsic viscosity was measured by a Zimm–Crothers viscometer, as described in our previous article.[12] The intrinsic viscosity values thus obtained are given in Table II. The flow curves of the solutions were measured with the rotational viscometers Paar Physica UDS 200, Paar Physica LS 100, and Haake CV 100.

The molecular weights of the polymers listed in the table were calculated from the measured in-
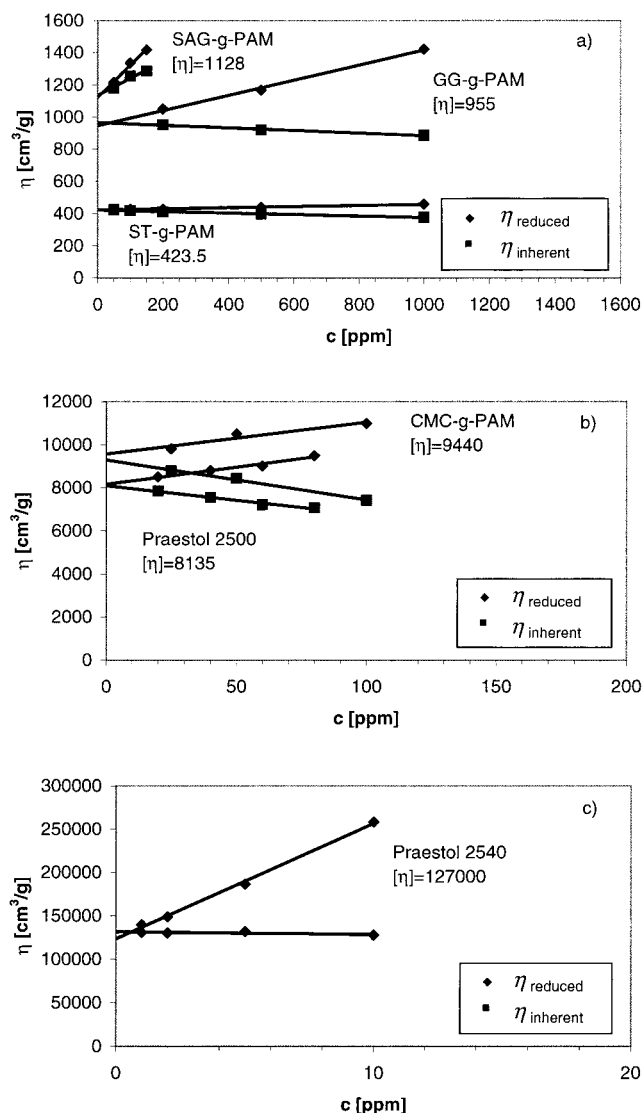

Figure 2   Results of intrinsic viscosity measurements with the six polymer solutions investigated. The concentrations of the polymers in the solutions were very low, so that the measurements were carried out in the dilute regime of the polymers.
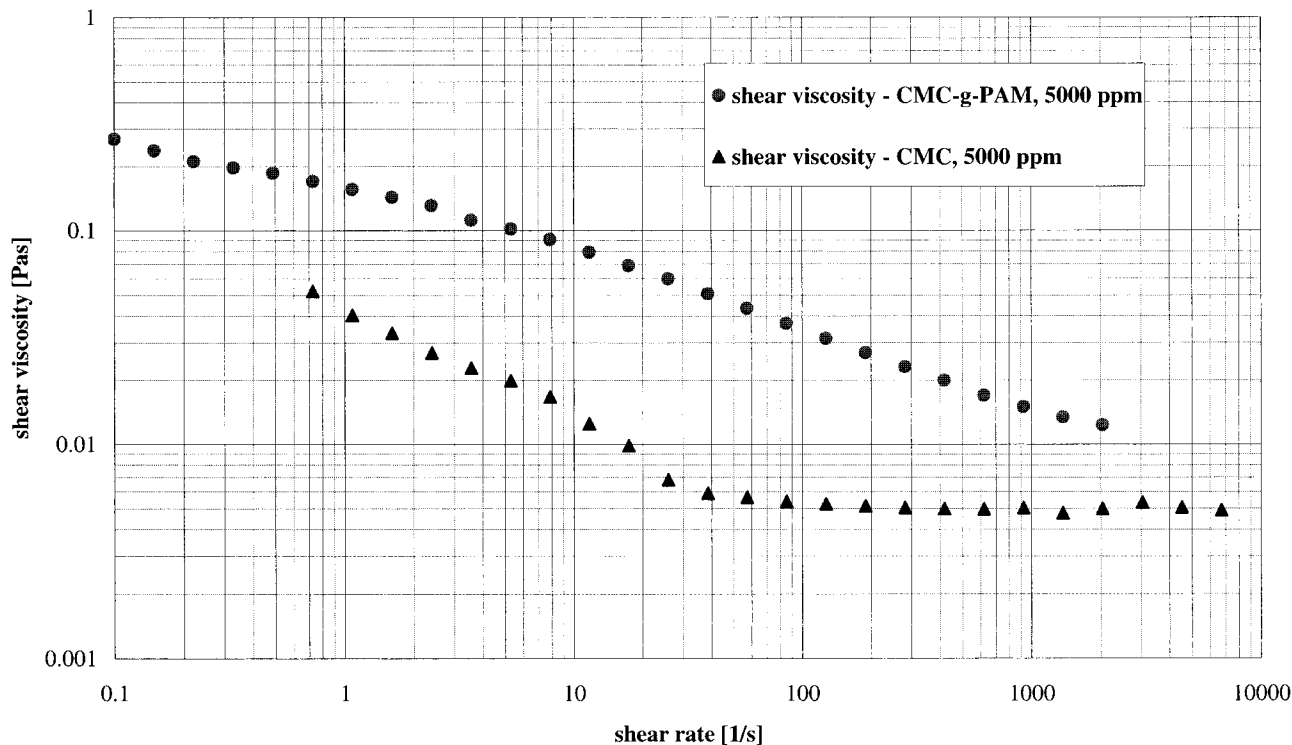
Figure 3   Variation of the shear viscosity with shear rate for 5000-ppm solutions of grafted and ungrafted carboxymethyl cellulose, measured with a Paar Physica UDS 200 in configuration MK24.

trinsic viscosity according to the Mark–Houwink relation $M_w = ([\eta]/K)^{1/\alpha}$, using the appropriate values of the parameters K and α for each polymer.
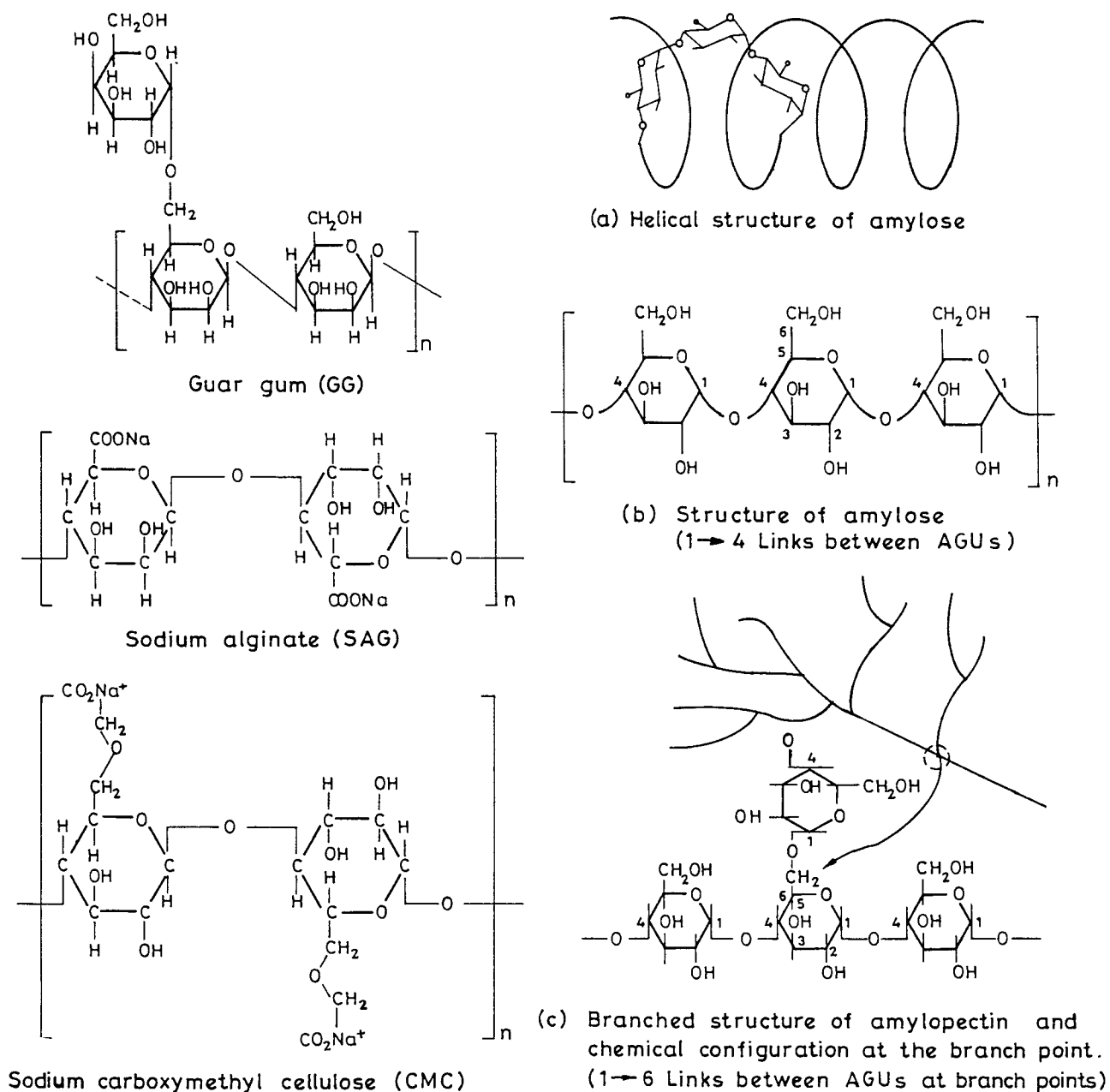
A novel elongational rheometer has been developed for dilute polymer solutions, where a small quantity of liquid is stretched abruptly to form a thread between two plane solid surfaces.[12] This elongational rheometer for dilute solutions is based on the self-thinning of the liquid thread under the action of surface tension. In this 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. More details of this device have been described elsewhere.[12] The device is sketched in Figure 1.

RESULTS AND DISCUSSION

The structural details of all the polysaccharides are given in Table III. Apart from starch and amylopectin, the rest of the polysaccharides are linear. Starch consists of amylose, a linear polysaccharide with a low molecular weight ($M_w \approx 6 \times 10^5$), and amylopectin, a branched polysaccharide with a high molecular weight ($M_w \approx 20 \times 10^6$). The relative weight percentages of amylose and amylopectin in starch range between 72% and 82% amylopectin and 18% and 28% amylose.[18] However, the side branches are organized in a discrete cluster structure, with a high proportion of branches running parallel to each other, leading to considerable crystallinity.[19,20] CMC and sodium alginate are both classified as water-soluble anionic polymers.

A measure of viscosity was obtained from a Zimm–Crothers viscometer at an apparent shear rate of $2\ s^{-1}$, in which case deionized water was used. Hence, the intrinsic viscosities of all the systems are larger than those obtained by the Ubbelohde viscometer in a $1M$ NaNO$_3$ solution. In the Ubbelohde viscometer, the viscosity was

Table III   Molecular Structures of the Polymers studied

Guar gum (GG)

Sodium alginate (SAG)

Sodium carboxymethyl cellulose (CMC)

(a) Helical structure of amylose

(b) Structure of amylose
(1→4 Links between AGUs)

(c) Branched structure of amylopectin and chemical configuration at the branch point. (1→6 Links between AGUs at branch points)

measured at higher shear rates, and $1M$ NaNO$_3$ solutions tend to neutralize charge on the main and side chains, causing a decrement in chain straightening. Understandably, intrinsic viscosity measures are higher from the Zimm–Crothers viscometer. The shear rate encountered in the Zimm–Crothers viscometer is almost zero. For the measurements of the intrinsic viscosity, the concentrations of the solutions were chosen according to the rule of thumb that zero-shear viscosity should be about 1.2–2 times larger than the

solvent's shear viscosity. Therefore, the solutions were in the dilute polymer region, that is, the inequality $[\eta]\,c < 1$ holds. Typical examples are given in Figure 2. The graft copolymers do not show any polyelectrolyte behavior, as evidenced by viscosity measurements at low concentrations. Here η_{sp}/c decreases monotonically with decreasing concentration.

The present study used the Mark–Houwink relationship with parameters for polyacrylamide for graft copolymers in which the ratio of poly-
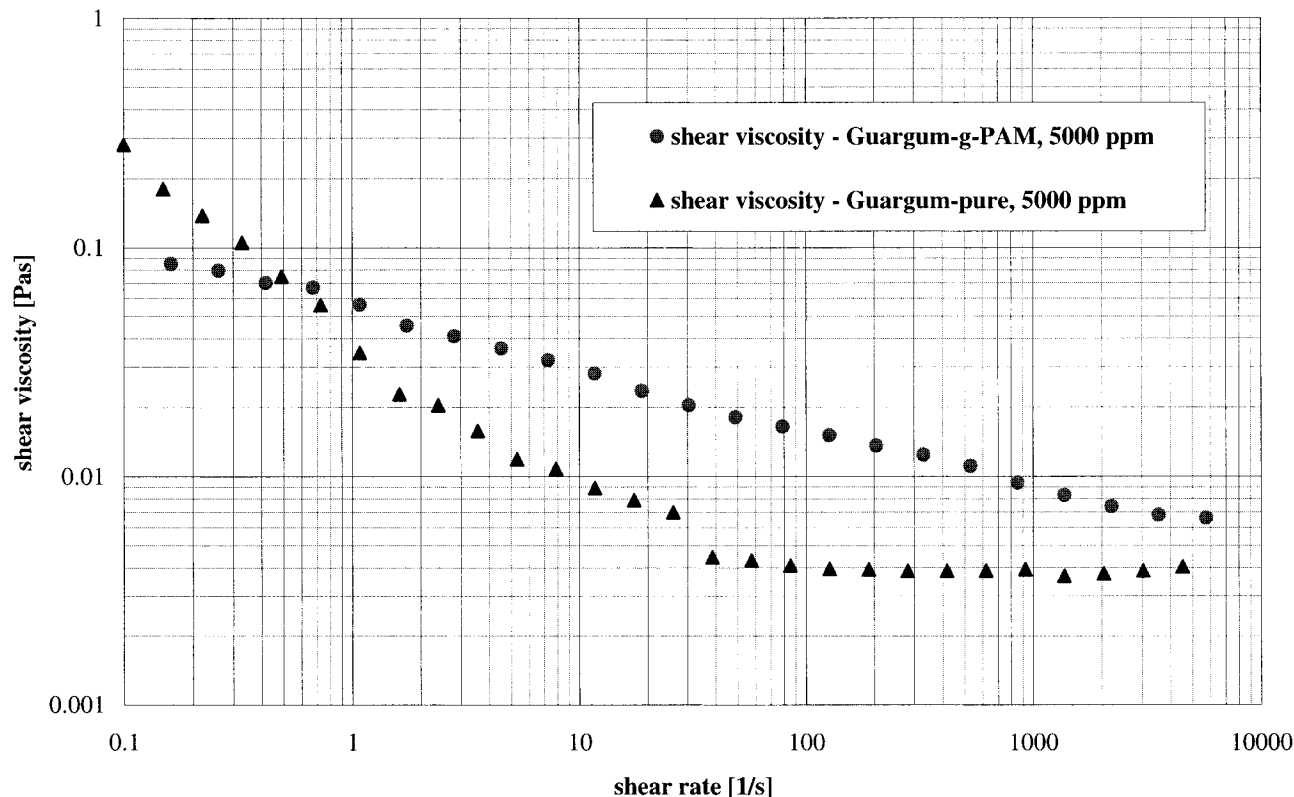
Figure 4 Variation of the shear viscosity with shear rate for 5000-ppm solutions of grafted and ungrafted guar gum, measured with a Paar Physica UDS 200 in configuration MK24.

acrylamide to polysaccharides is about 10 : 1, a method also used by several other researchers.[21,22] However, the evaluated molecular weights from the Mark–Houwink relation give only a coarse idea of the molecular weight of the polymers. The calculated results must therefore be interpreted with care.

The extensional relaxation time has been obtained from the reduction of the thread radius in the stretching device on the basis of the following equation:

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

where a is the radius of the thread at time t, a_0 is the initial radius, and θ is the relaxation time. The derivation of this equation was explained in our previous article.[12] The results of the investigation are summarized in Table II.

The structures of the various polysaccharides are given in Table III. The grafted CMC shows the maximum shear stability, mainly because CMC presents modified cellulose, and cellulose

is insoluble in water because of a high level of intermolecular interaction and crystallization. The remnant of cellulose structure in CMC gives its observed shear stability. Similarly, starch is also crystalline. Its constituent linear amylose dissolves with difficulty in water and has considerable crystallinity. The other constituent, amylopectin, has, in spite of its branched structure, some level of crystallinity. The grafting reduces the crystallinity of starch, amylose, and amylopectin.[23,24] The Guar gum and sodium alginate have slightly branched and linear structures, respectively, with hydroxyl groups. Their molecules are supposed to have high intermolecular interaction and consequent shear stability. In the graft copolymers the molecular weight, the temperature, and the intermolecular interaction provide elasticity and shear stability for their solutions.

The grafted polysaccharides exhibit higher relaxation times. It is well known that the elasticity of polymer solutions is proportional to the molecular weight and intermolecular interaction.
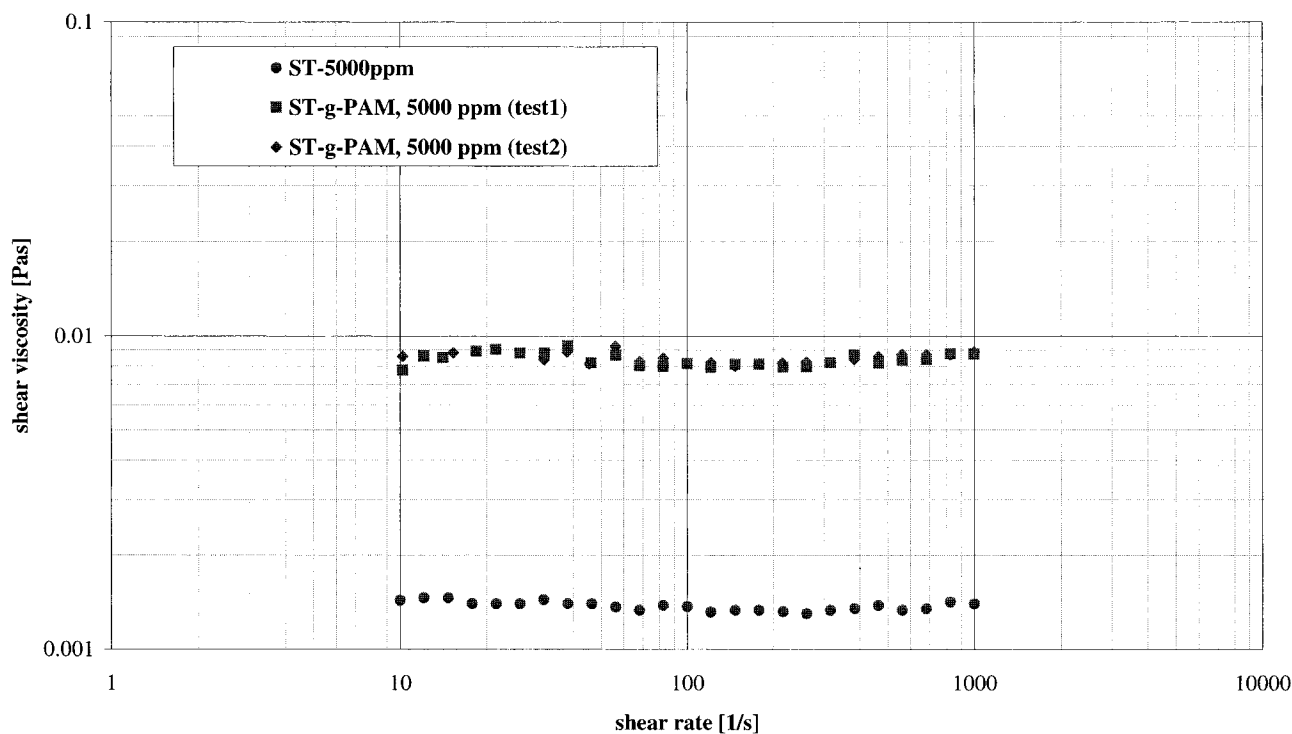
Figure 5 Variation of the shear viscosity with shear rate for 5000-ppm solutions of grafted and ungrafted starch, measured with a Paar Physica UDS 200 in configuration cone-plate CP 501. The data marked "test 1" and "test 2" are repeated measurements.

Hence, low-molecular-weight polymers do not exhibit any extensional effects or thread formation, that is, they are not spinnable. With increasing intermolecular interaction, the thinning of a thread becomes more difficult, resulting in an increase of relaxation time. Very high-molecular-weight anionic polyacrylamide, therefore, exhibits the highest relaxation time, followed by the flexible nonionic PAM and high-molecular-weight anionic carboxymethyl cellulose-*g*-acrylamide. Among the solutions of SAG-*g*-PAM and GG-*g*-PAM, the order of relaxation time does not exactly follow the order of molecular weight. Here the relaxation times have not been measured at the same temperature because the stretching device cannot be run at thermostatic conditions. The experiments were carried out during the summer months of 1998 at LSTM Erlangen. The measurements for the solutions of GG-*g*-PAM were carried out at the lowest temperature, 23°C, and those of SAG-*g*-PAM at the higher temperature, 25°C. A rise in temperature weakens the intermolecular interaction. Hence, the measured relaxation times must be interpreted in the light of these experimental conditions. SAG-*g*-PAM has the higher molecular weight, but the relaxation time has been measured at the higher temperature. The gain in relaxation time from the molecular weight is upset by the rise in temperature. Similar arguments can explain the relatively high relaxation time of the GG-*g*-PAM solution, which was measured at the lower temperature and therefore seems to be in contradiction to what would be expected from the molecular weight. Also, in this interpretation it must be kept in mind that the molecular weight of the polymers determined from the Mark–Houwink relationship may be very inaccurate and gives only a coarse idea of the real molecular weight.

The results of the investigation of shear rheology using the cone-plate configuration of the Physica UDS 200 Universal Dynamic Spectrometer for cases of 5000 ppm solutions of CMC-*g*-PAM and GG-*g*-PAM are given in Figures 3 and 4. The solutions are shear thinning. The grafting of acrylamide branches onto a polysaccharide backbone increases the viscosity in both cases. A similar conclusion can be drawn in cases of starch, both at 5000 ppm and at 1000 ppm, and for SAG at 5000 ppm. These results were obtained using a Paar
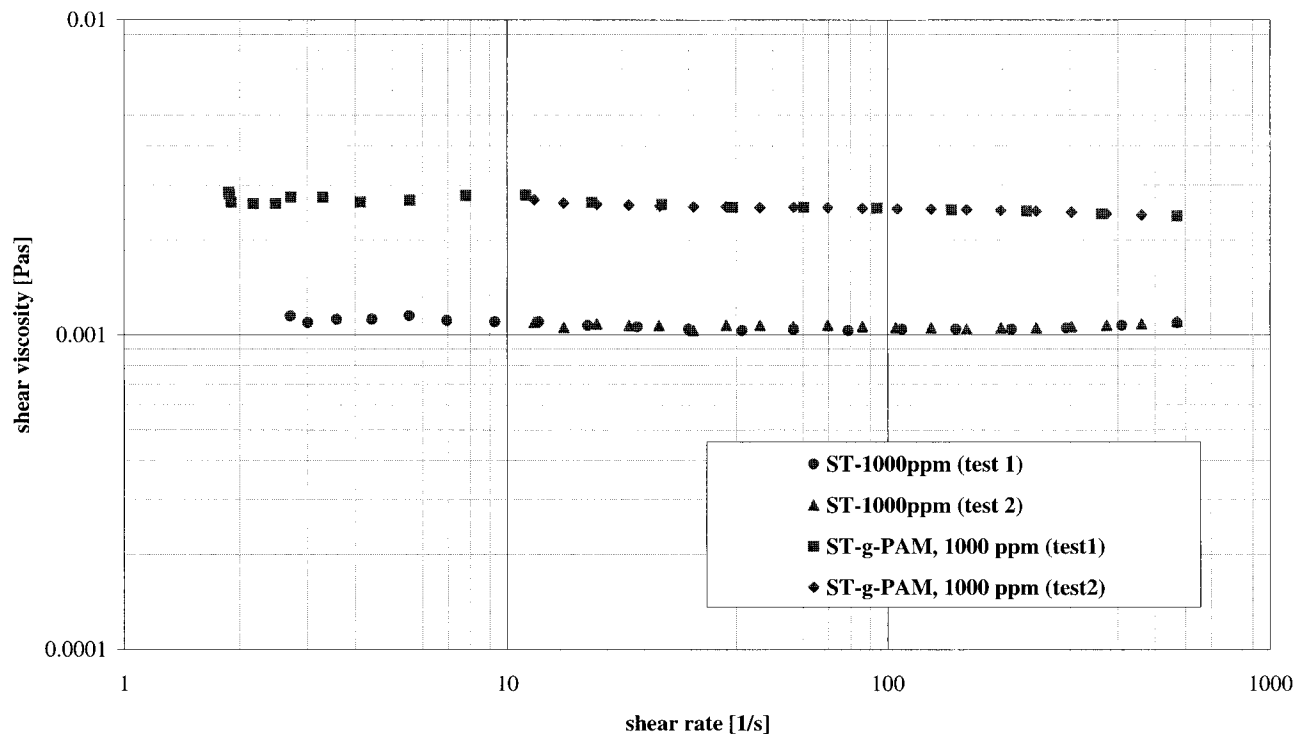
Figure 6 Variation of the shear viscosity with shear rate for 1000-ppm solutions of grafted and ungrafted starch, measured with a Haake CV100 in configuration ME46. The data marked "test 1" and "test 2" are repeated measurements.

Physica UDS 200 and LS100 in cone-plate configuration (Figs. 5 and 7) and a Haake CV 100 (Fig. 6).

Some preliminary experiments on nozzle flows were conducted with 200 ppm Praestol 2540 and with ≈300 ppm CMC-*g*-PAM solutions. The flow rate was 40 l/h, and the ratio of main pipe to nozzle inner diameter was 10:1, with a nozzle hydraulic diameter of 0.79 mm. In the case of the anionic Praestol 2540, the relaxation time of the undegraded solution was ≈38 ms, but it was impossible to measure the relaxation time in solutions that had run through the nozzle. Since these degraded solutions were not spinnable, thread formation was impossible with these degraded solutions, indicating strong changes in the molecular structure from mechanical degradation caused by the nozzle flow. In the case of a fresh CMC-*g*-PAM solution, the relaxation time was 5.23 ms, and in degraded solutions the relaxation time was 2.36 ms. From these results it is evident that CMC-*g*-PAM does not degrade considerably, while polyacrylamide solutions degrade more. From our earlier studies on drag reduction,[13] CMC is known to be the most stable polysaccharide, followed by guar gum. Thus CMC-*g*-PAM

may be a suitable candidate as an additive to liquids in order to, for example, enhance their performance as an anti-wind-drift agent in agricultural applications, where the agent should avoid small droplet formation during atomization from pressure nozzles.

CONCLUSIONS

Aqueous solutions of grafted CMC, guar gum, sodium alginate, and starch exhibit viscosifying attributes. Solutions of grafted CMC and guar gum show distinct shear-thinning behavior. The same behavior is observed for solutions of grafted sodium alginate and starch, although not as prominent. The aqueous solutions of grafted CMC, guar gum, and sodium alginate exhibit spinnability. The relaxation times of various grafted polysaccharide solutions obtained by a uniaxial stretching device depend on their molecular weight, chemical structure, and ambient temperature. The relaxation times of grafted CMC solutions are on the order of the polyacrylamide relaxation time. They retain their spinna-
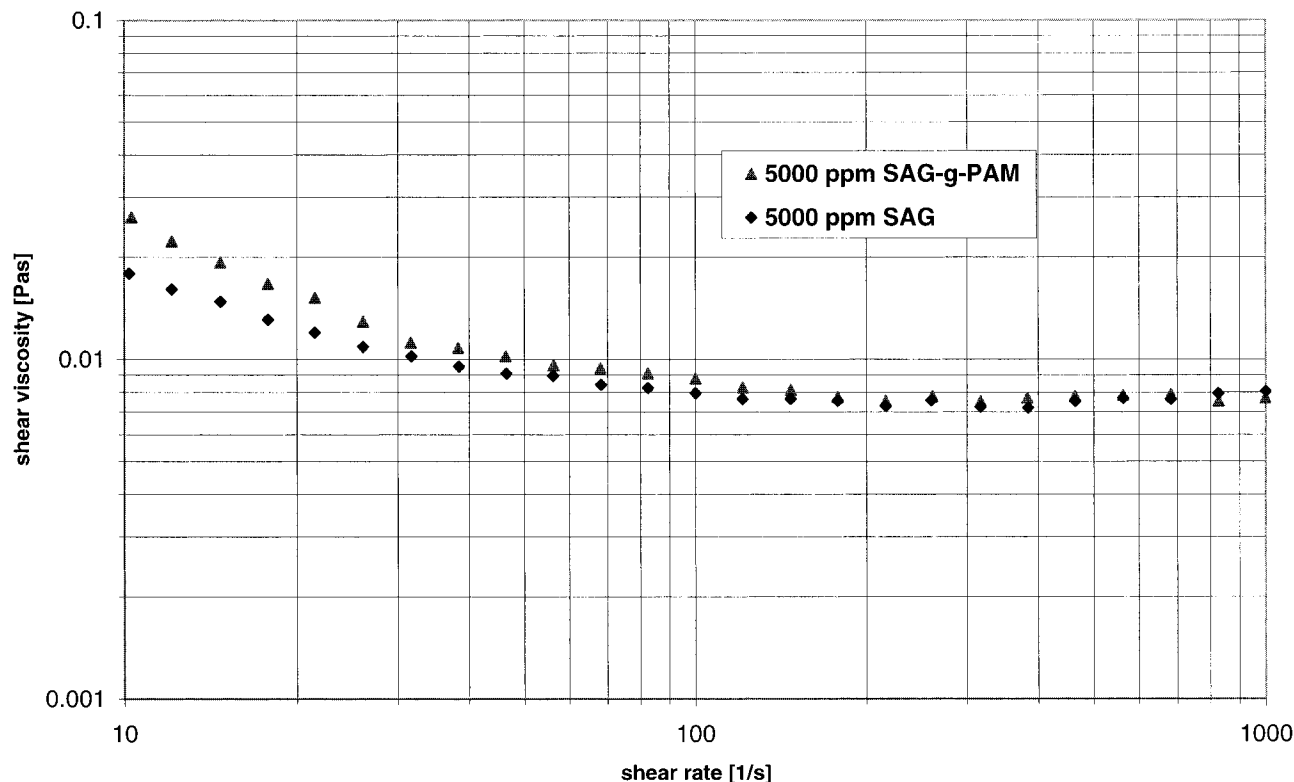
Figure 7   Variation of the shear viscosity with shear rate for 5000-ppm solutions of grafted and ungrafted sodium alginate, measured with a Paar Physica LS100 in configuration CP 501.

bility even in nozzle flows, in which polyacrylamide solutions cease to do so.

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