Synthesis and Characterization of Polyacrylic Acid/Dexy 85 and Polyacrylic Acid/Gum Arabic Adducts

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ABSTRACT: Polyacrylic acid/gum arabic or polyacrylic acid/dextrin (PAA/GA or PAA/D) adducts were prepared by free radical polymerization of highly concentrated, partially neutralized AA using $Na_2S_2O_8/Na_2S_2O_3$ redox system in the presence of GA or D. Optimum reaction conditions, viz., AA, 6.76 mol/L; $Na_2S_2O_3$, 26.87×10^{-3} mol/L; $Na_2S_2O_8$, 34.9×10^{-3} mol/L; degree of neutralization, 20%; temperature, 90°C; and time 30 min, were utilized in preparing two adducts of each substrate (GA or D) at two liquor ratios (LRs; 1.25/1 and 6.3/1 *L*/*K*). The four adducts formed, viz., PAA/GA_1, PAA/GA_2, PAA/D_1, and PAA/D_2 (where 1 and 2 refer to the low and high LR, respectively) were found to be water soluble at all proportions. IR spectrum of these adducts confirmed the introduction of the COOH group onto their structures. Rheological properties of 7% aqueous solutions of these adducts, including Na-alginate (Alg), showed that all are characterized by a non-Newtonian, shear-thinning, thixotropic behavior. Within the range of shear rate studied, the apparent viscosities of these solutions followed the descending order: $PAA/D_2 > PAA/D_1 > Alg > GA_1 = PAA/GA_2$. Completing neutralization (Na form) of adducts to 100% results in a remarkable enhancement of their apparent viscosities, so that they follow the descending order, depending on the shear rate:

$$\text{At } 2\ s^{-1} \text{ shear rate:} PAA/D_2 > PAA/D_1 = PAA/GA_1 > PAA/GA_2 > Alg$$

$$\text{At } 18.89\ s^{-1} \text{ shear rate:} PAA/D_2 > PAA/D_1 = PAA/GA_1 > Alg \geq PAA/GA_2$$

$$\text{At } 40\ s^{-1} \text{ shear rate:} PAA/D_2 > PAA/D_1 = PAA/GA_1 > PAA/GA_2 = Alg$$

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Key words: adduct; monomers; polymerization; redox-system; rheology

INTRODUCTION

The most versatile thickener for reactive printing of cellulose fabric is, by far, sodium alginate.[1–4] However, the latter suffers from some disadvantages, such as high price and limited supply.

Previous reports[5] presented new synthetic thickeners based on polyacrylic acid (PAA) as substitutes to alginate.

Following them, a comprehensive work is carried out in our laboratories, aiming at investigating some PAA adducts as suitable substitutes to sodium alginate. The present study aims at preparing and characterizing some of these adducts; and in a subsequent study, their utilization as thickeners in reactive printing of cellulose fabric is going to be examined.

Preparation of these adducts is carried out by free-radical polymerization of highly concentrated partially neutralized acrylic acid (AA) in presence of two substrates, viz., gum Arabic (GA) and dexy 85 (a commercial dextrin), using $Na_2S_2O_8/Na_2S_2O_3$ redox system. The adducts prepared are characterized by investigating their IR spectrum and rheological properties.

EXPERIMENTAL

Materials

Dexy 85, a powder pyrodextrin, kindly supplied by Starch and Glucose Co., Mostorod, Cairo, was used. It is based on Egyptian maize starch that was heat treated for 5 h in the presence of an acid. GA locally purchased from Al Haraz Co., Cairo, was ground before used. AA (pure grade and containing 200 ppm hydroquinon monomethylether) supplied by Fluka Chemika, Switzerland, sodium persulfate ($Na_2S_2O_8$), sodium hydroxide, sodium thiosulfate ($Na_2S_2O_3$) laboratory-grade chemicals, supplied by Merck, and Na-alginate of medium viscosity, Na-Alg, (cecalginate HV/KL-600, Ceca KolloidChemie, Paris) were used.

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Polymerization reaction

Adducts of PAA with either dexy 85 or GA were prepared by polymerizing AA in presence of each of them, based on a method developed by Abo-Shosha et al. and Ibrahim et al. as follows.[2,6] AA was first partially neutralized with equivalent amounts of an aqueous solution of NaOH (32% w/v). Polymerizations were carried out under atmospheric oxygen in 30-mL polypropylene beakers. Aqueous solutions of $Na_2S_2O_8$ and $Na_2S_2O_3$ were added with stirring to a thermostated aqueous solution of partially neutralized AA contained in the beaker. A substrate (either dexy 85 or GA) was added to the beaker with rapid mixing to form a uniform paste. The beaker was kept in a thermostatic water bath. After an induction period, an exothermic reaction commenced with evolution of water vapor, followed by solidification of the paste. The sample was then cooled at ambient conditions, disintegrated, ground, dried at 60°C for 5 h, and then kept over P_2O_2 for at least 48 h before analysis.

Analysis and testing

The extent of polymerization, expressed as percentage total conversion (% TC), was determined by assessing the unsaturation (double bonds) content before and after polymerization.[7]

The rheological properties of the solutions of adducts (7% w/v) were measured at 25°C + 0.1°C, using a coaxial rotary viscometer (HAAK V20), Germany.

The apparent viscosity (η) was calculated using the following formula:

$$\eta = \tau / D \text{ Poise}$$

where, D and τ are the rate of shear (s^{-1}) and shear stress (dyn/cm), respectively.

RESULTS AND DISCUSSION

Preparation of polyacrylic acid/dexy 85 and polyacrylic acid/gum arabic adducts

Reaction mechanism

The decomposition of $Na_2S_2O_8/Na_2S_2O_3$ redox system result in the formation of $SO_4^{-\cdot}$, $HO^{\cdot}$, and $S_2O_3^{-\cdot}$ free radical species.[8–10] These radical species ($R^{\cdot}$) are capable of initiating the following set of reactions:

1. Formation of AA activated monomer[11]

$$R^{\cdot} + AA \rightarrow AA^{\cdot} \qquad (1)$$

2. Abstracting hydrogen atoms from the hydroxyls of either D or AG, to form the corresponding macroradical

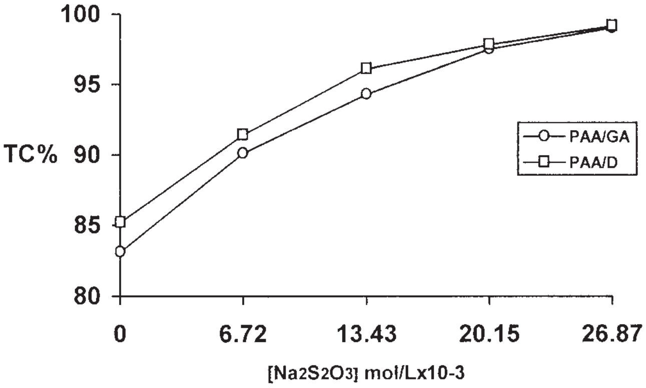

Figure 1 Effect of sodium thiosulfate concentration on the formation of PAA/D and PAA/GA adducts. AA, 6.76 mol/L; $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; DN, 10%; LR, 1.25 *L/K* (GA) or 2.1 *L/K* (D); temperature 80°C; time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

$$D{-}OH + R^{\cdot} \rightarrow D{-}O^{\cdot} + RH \qquad (2)$$

$$GA{-}OH + R^{\cdot} \rightarrow GA{—}O^{\cdot} + RH \qquad (3)$$

3. AA homopolymerization

$$nAA^{\cdot} \rightarrow PAA \qquad (4)$$

4. Grafting of PAA on either D or GA

$$D{-}O^{\cdot} + n_1AA \rightarrow PAA\text{-}g\text{-}D \qquad (5)$$

$$GA.O^{\cdot} + n_2AA \rightarrow PAA - g - GA \qquad (6)$$

Moreover, the persulfate ions can also oxidize either D or GA to varied extents.

The product obtained from these polymerization reactions is a mixture of PAA homopolymer, PAA-*g*-D, PAA-*g*-GA, and ungrafted D or GA, intact and oxidized, all in a state of intimate entanglement with each other. This mixture is referred to as polyacrylic acid/dexy 85 (PAA/D) or polyacrylic acid/gum arabic (PAA/GA) adduct. Given below are the results obtained with relevant discussions of studying major factors affecting the preparation of these adducts. These include the concentrations of either sodium persulfate or sodium thiosulfate, temperature, degree of neutralization (DN), time, and AA/substrate ratio.

Sodium thiosulfate concentration

Figure 1 shows the effect of sodium thiosulfate (reductant) concentration on the formation of adducts based on dexy 85 and GA. It is obvious that at zero reductant concentration, a high % TC (85.2% in case of dexy 85 and 83.1% in case of GA) is attained. This is unequiv-

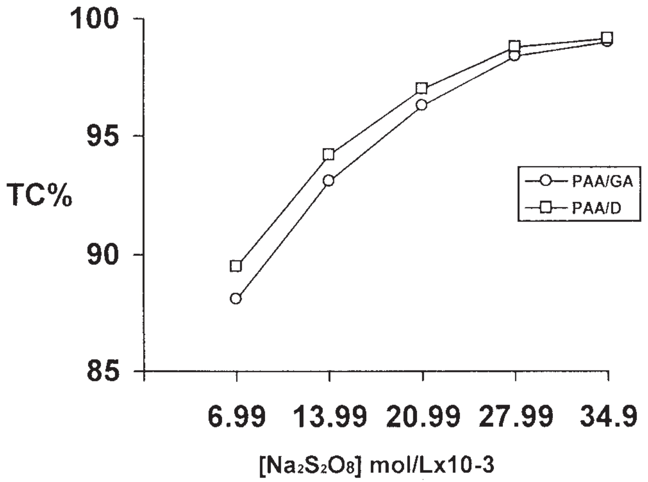

Figure 2 Effect of sodium persulfate concentration on the formation of PAA/D and PAA/GA adducts. AA, 26.87 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} mol/L; DN, 10%; LR, 1.25 *L*/*K* (GA) or 2.1 *L*/*K* (D); temperature 80°C; time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

ocally, due to the decomposition of the oxidant (sodium persulfate), giving rise to $SO_4^{-\cdot}$ and $HO^{\cdot}$ free radical species[12] capable of initiating polymerization reactions.[13] Introducing sodium thiosulfate into the system at a concentration of 6.72 × 10^{-3} mol/L is accompanied by a reasonable increase in the % TC for the two adducts. This can be associated with faster rate of oxidant decomposition in presence than in absence of the reductant.[9] Increasing the reductant concentration in the range studied is accompanied by an increase in the % TC, but with a decreasing gradient. This is more pronounced after a concentration of 20.15 × 10^{-3}, where leveling off tends to appear. At any rate, however, the % TC almost approaches completion at the final concentration of thiosulfate used. It is also obvious that, for a given set of conditions, the % TC is slightly higher in case of dexy 85 than that in case of GA; this can be associated with differences in chemical and physical nature, reactivity, and stereochemistry of both substrates.

Sodium persulfate concentration

Figure 2 shows the effect of sodium persulfate (oxidant) concentration on the adducts formation. It can be seen that, though AA used with its content of the inhibitor, the % TC starts at a high value (more than 88%) for the lowest oxidant concentration used, which indicates the higher affinity of the radical species to AA in its mixture with GA or dexy 85. Increasing the concentration, in the range examined under the conditions employed, up to 27.99 × 10^{-3} mol/L is accompanied by an increase in the % TC for both adducts. This can be ascribed to the accompanying increase in the amounts of free radical species capable of enhancing: (a) the consumption of hydroquinone monomethyl ether and (b) formation of substrates macroradicals and AA-activated monomer, and resulting in promotion of graft copolymerization and homopolymerization reactions. It can be also observed that the % TC tends to level off in the concentration range from 27.99 × 10^{-3} to 34.9 × 10^{-3} mol/L. This can be attributed to the accompanying (a) depletion of AA monomer in the reaction medium and (b) increase in the steric hindrance (due to the solid nature of the adducts formed) to the diffusing species (i.e., free radicals and activated AA monomer).

Temperature

Figure 3 shows the effect of temperature on the formation of the adducts expressed as % TC. It is clear that, for both adducts under the conditions employed, raising the temperature from 60 to 80°C is accompanied by a noticeable enhancement in the % TC. This can be ascribed[14] to the favorable effect of temperature on: (a) faster decomposition of the initiating system, giving rise to higher density of free radicals, (b) promoting the mobility of free radicals and AA molecules, thereby enhancing the probability of their collisions, (c) improving the swellability of both dexy 85 and GA, and subsequently promoting the diffusion of free radicals and AA-activated monomer inside their structures, and (d) supplying the system with enough energy to overcome the activation energy barrier of homopolymerization and graft copolymerization reactions. The % TC tends to level off in the range of 80 to 90°C, which suggests that formation of free radicals in

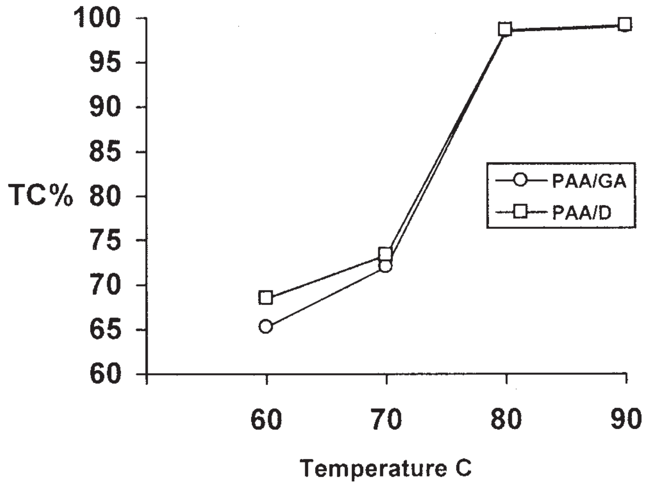

Figure 3 Effect of temperature on the formation of PAA/D and PAA/GA adducts. AA, 26.87 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} and $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; DN 10%; LR, 1.25 *L*/*K* (GA) or 2.1 *L*/*K* (D); time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

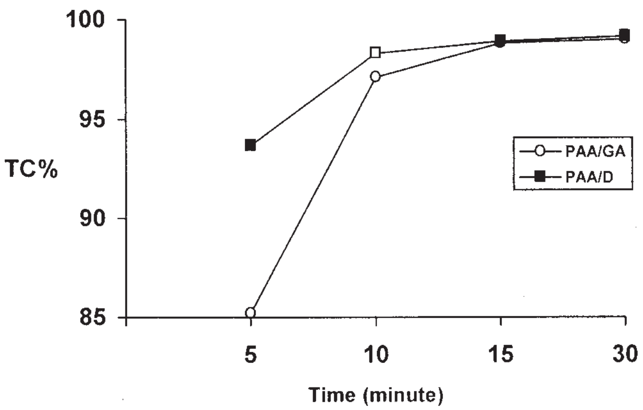

Figure 4 Effect of time on the formation of PAA/D and PAA/GA adducts. AA, 26.87 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} and $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; DN, 10%; LR, 1.25 *L*/*K* (GA) or 2.1 *L*/*K* (D); temperature 90°C. All concentrations are based on the liquid phase before the addition of substrates.

abundance makes a balance between polymerization (homo and copolymerization), propagation, and termination in the mentioned range. It is also clear that the gap in % TC value between dexy 85 and GA decreases by increasing the temperature.

Time

Figure 4 shows the impact of time on the adducts formation. Obviously, prolonging the reaction time, under the conditions used for both adducts, from 5 to 15 min, is accompanied by a remarkable increase in the % TC. This can be associated with the favorable effect of time on: (a) supplying the system with more energy, (b) diffusion of active species (radicals) inside the structure of substrates, and (c) initiation and propagation of polymerization.

Prolonging the time beyond 15 min (and up to 30 min) keeps the % TC almost unchanged for both adducts, which can be associated with the depletion of reacting species and/or higher steric hindrance, as has already been mentioned.

Degree of neutralization

Figure 5 shows the effect of DN of AA (Na-form) on the formation of the adducts, where it can be seen that the %TC remains constant by increasing the DN from 10 to 20%. Increasing the DN beyond 20%, in the range examined, is accompanied by a sharp decrease in the % TC. This can be generally attributed to the inhibiting effect of Na cations on the polymerization process.[10] It seems that in the range from 10 to 20%, the inhibiting effect of Na^+ is balanced by the highly exothermic nature of the reactions (as polymerization was carried out at every high concentration of AA), which favors the formation of more energetic free radicals capable of initiating and propagating polymerization, and in the mean time, able to compensate the inhibiting effect of Na^+. In the range behind a DN of 20%, it seems that the presence of Na^+ in surplus favors inhibition rather than initiation and propagation of polymerization.

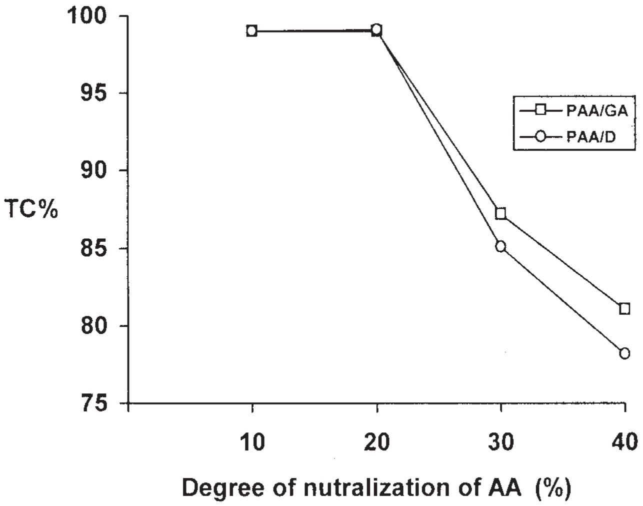

Figure 5 Effect of DN of AA on the formation of PAA/D and PAA/GA adducts. AA, 26.87 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} and $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; LR, 1.25 *L*/*K* (GA) or 2.1 *L*/*K* (D); temperature 90°C; time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

Liquor-to-substrate ratio

Figure 6 shows the effect of liquor-to-substrate ratio (LR) on the adducts formation. It is clear that polymerization

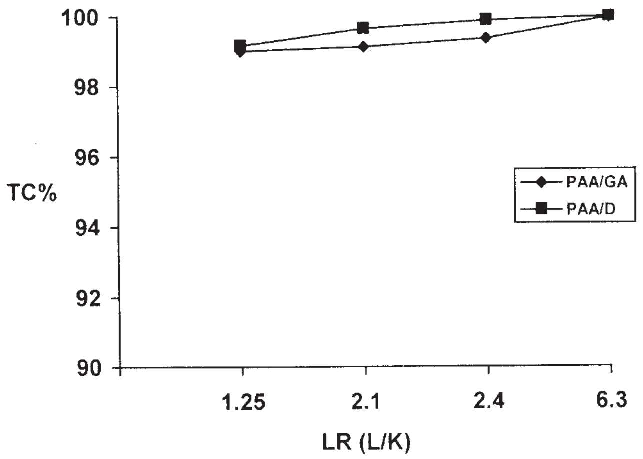

Figure 6 Effect of LR on the formation of PAA/D and PAA/GA adducts. AA, 26.87 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} and $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; DN, 20%; temperature 90°C; time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

TABLE I
Conditions of Preparation, % TC, Visual Appearance, and Water Solubility of Selected Adducts

Substrate	LR	% TC	Visual appearance	Water solubility	Designation
GA	1.25/1	99.01	Brownish white solid	The two adducts are mixed with water in all proportions	PAA/GA_1
	6.3/1	99.96	Brownish white solid		PAA/GA_2
Dexy 85 (D)	1.25/1	99.16	Yellowish white solid	The two adducts are mixed with water in all proportions	PAA/D_1
	6.3/1	99.98	Yellowish white solid		PAA/D_2

AA, 6.75 mol/L; $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} mol/L; degree of neutralization, 20% (Na salt); temperature, 90°C; time 30 min. All concentrations are based on the liquid phase before the addition of substrates.

proceeds nearly to completion, regardless of LR or substrates used. This reveals that (a) the conditions employed represent the optimum values under the circumstances examined and (b) the free radical species have a very high affinity to AA/substrate system studied.

Characterization

Adducts and some characteristics

Four types of adducts (based on the substrates studied) were prepared at the optimum conditions illustrated in Figure 6, at two LRs of 1.25/1 and 6.3/1. Table I shows the conditions of preparation, % TC, visual appearance, and water solubilities of these adducts. Regarding to the latter, it can be seen that all the four adducts are water soluble.

These adducts were further characterized by investigating their IR spectrum as well as the rheological properties of their aqueous solutions, in comparison with sodium alginate, which is a versatile thickener—highly recommended for reactive printing. Results obtained and appropriate discussions follow.

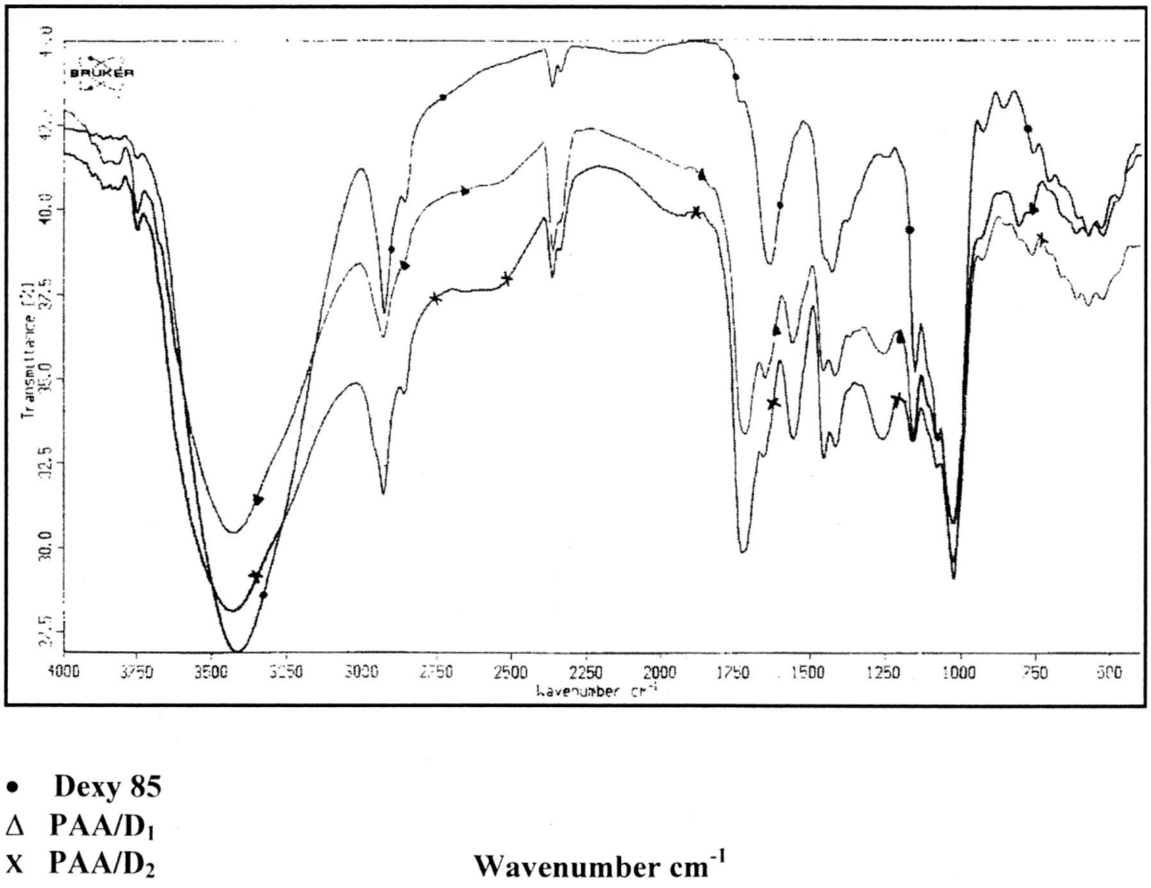

Figure 7 IR spectrum of dexy 85, PAA/D_1, and PAA/D_2. (●), dexy 85; (△), PAA/D_1; and ([multi]), PAA/D_2.

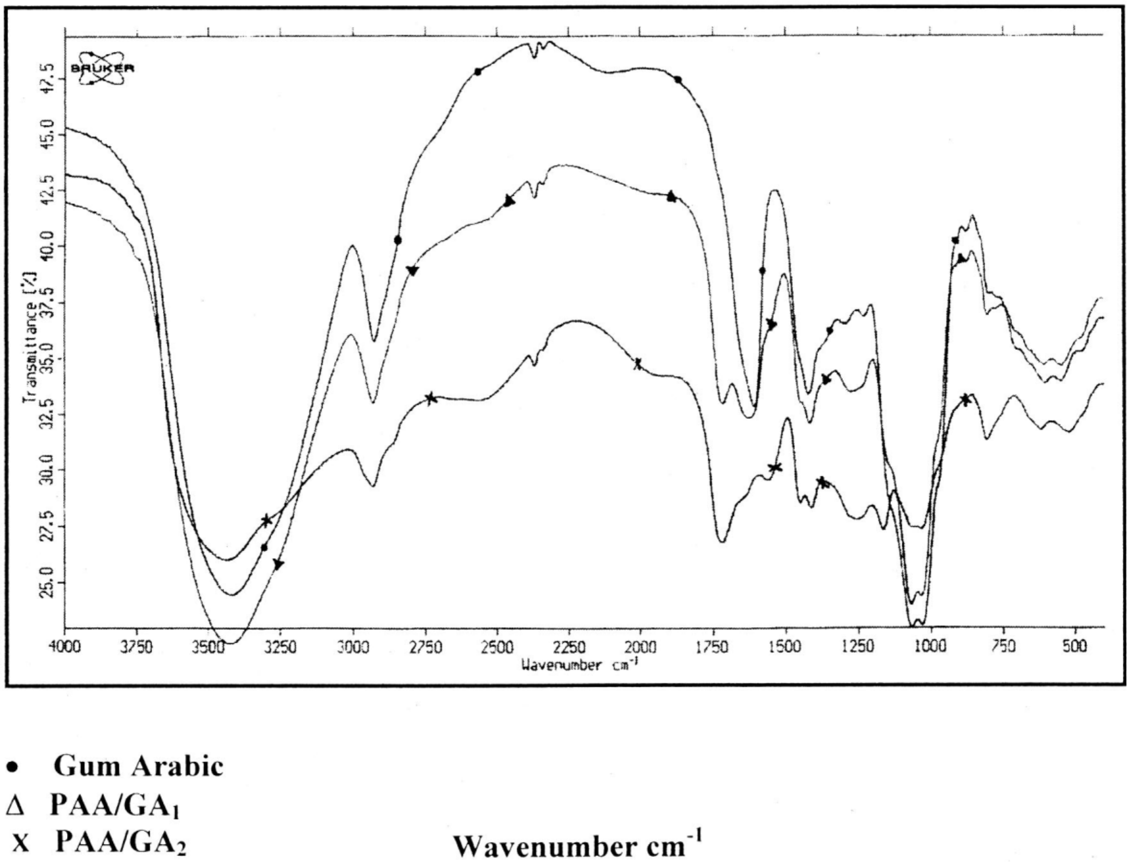

Figure 8 IR spectrum of GA, PAA/GA$_1$, PAA/AG$_2$. (●), GA; (△), PAA/GA$_1$; and ([multi]), PAA/GA$_2$.

Infrared spectrum

IR spectroscopy is a useful tool for investigating the fine structure of polysaccharides and chemically modified polysaccharides. Figure 7 shows the IR spectrum of dexy 85, PAA/D$_1$, and PAA/D$_2$. IR spectra of dextrin (dexy 85) shows 3600–3200 cm^{-1} wavelength band corresponding to OH of sugar or amylose, 2820–2980 cm^{-1} corresponding to aliphatic chain hydrogen

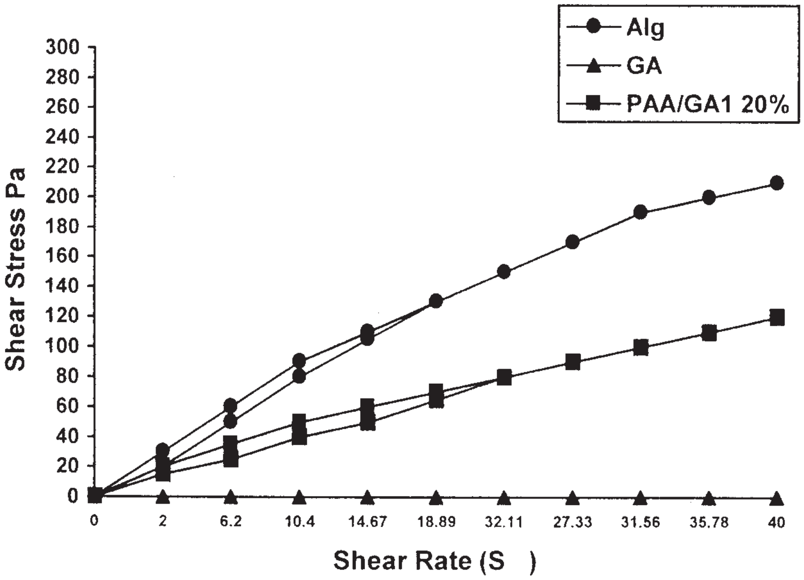

Figure 9 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, GA, and PAA/GA$_1$ (20% neutralized) at 25°C ± 1°C.

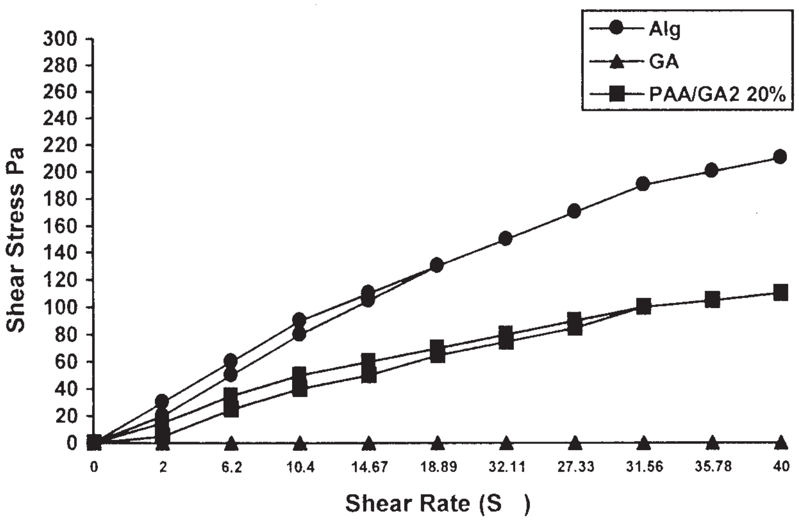

Figure 10 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, GA, and PAA/GA$_2$ (20% neutralized) at 25°C ± 1°C.

CH/CH$_2$ stretch, binding deformation; but C═O in cyclic or open chain aldehyde appears in the range 1710–1630 cm^{-1}.

Polymerization of AA in presence of dexy 85 results in the introduction of COOH groups onto the adducts formed, and the higher the LR, the higher the carboxyl content is. This is clearly shown in Figure 8, where the intensity of the band corresponding to C═O (or COOH) has its highest value for D$_2$ (in the range of 1700–1600 cm^{-1}) and lowest value for dexy 85 (in the range of 1700–1630 cm^{-1}), whereas an intermediate value (but it is much higher than that of dexy 85) for D$_1$ (in the range of 1745–1700).

Figure 8 shows the IR spectrum of GA and PAA/GA adducts. It can be seen that IR spectra of GA is similar to that of dexy 85, but it differs in the band range of 1730–1665 cm^{-1} corresponding to COOH and COO*R* of GA after treatments.

Investigating the rheological properties

PAA/GA adducts. The effect of shear rate on shear stress of 7% aqueous solutions of PAA/GA$_1$ and PAA/GA$_2$ in comparison with that of sodium alginate is shown in Figures 9 and 10, respectively. It can be seen that the curves obtained for each solution are not straight lines, rather, each forms a hysteresis loop, the upper and lower parts of each are convex to the shear stress axis. Accordingly, these solutions are character-

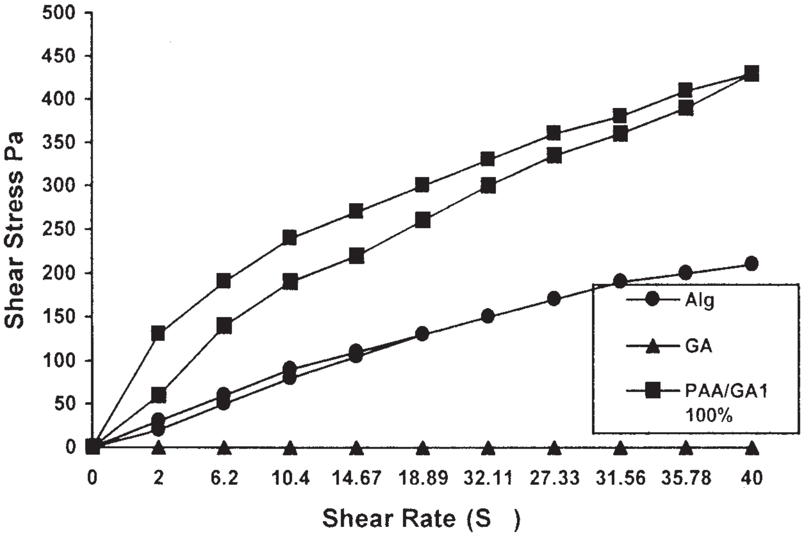

Figure 11 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, GA, and fully neutralized PAA/GA$_1$ at 25°C ± 1°C.

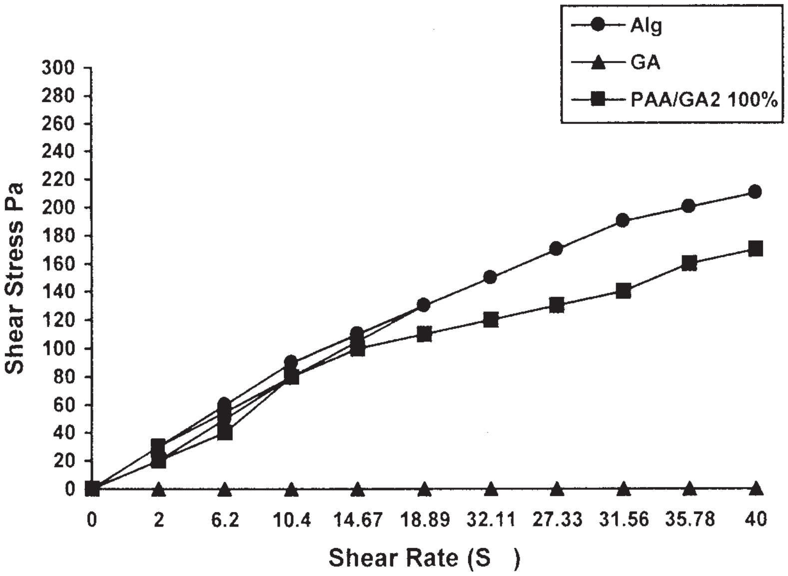

Figure 12 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, GA, and fully neutralized PAA/GA_2 at 25°C ± 1°C.

ized by a non-Newtonian, shear-thinning, thixotropic flow, under the conditions investigated.[15] Thixotropic behavior can be attributed to the time needed for the solution to recover its original structure after releasing of shear.[15]

The extent of thixotropy, or the area encountered in the hysteresis loop is higher in case of adducts than that in case of alginate, revealing that the latter is more elastic (i.e., its ability to recover its own structure after shear release) than the formers. It can be also observed that GA solution is characterized by a non-Newtonian pseudoplastic flow.

It is to be observed that PAA carboxyl groups of the adducts studied (Figs. 9 and 10) are 20% neutralized. Therefore, complete neutralization was accomplished (using NaOH), and the effect of shear rate on shear stress of fully neutralized solution (7%) was investigated. Results obtained are shown in Figures 11 and 12. It can be seen that the loops of fully neutralized adducts are shifted up in the vertical direction, in

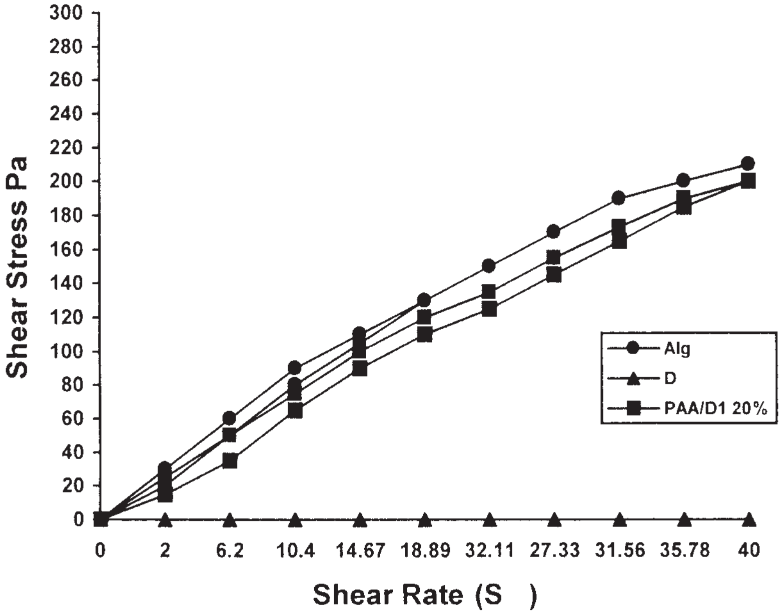

Figure 13 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, D, and PAA/D_1 (20% neutralized) at 25°C ± 1°C.

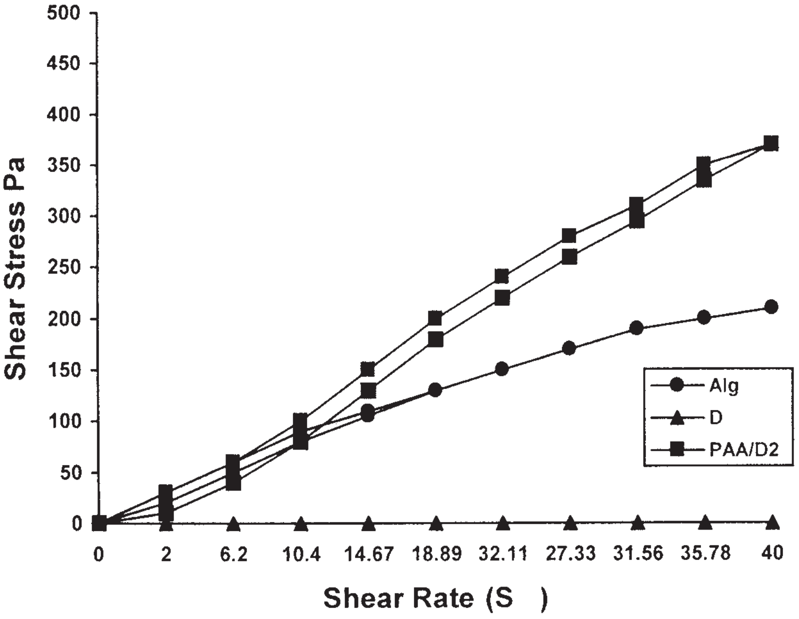

Figure 14 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, D, and PAA/D_2 (20% neutralized) at 25°C ± 1°C.

comparison to those of 20% neutralization. That is, more neutralization results in solutions that are more resistant to flow (in virtue of exerting higher shear stress). Obviously, neutralized PAA/GA_1 adduct loop is above that of Na-alginate; however, its thixotropic nature gets higher value than that at 20% neutralization.

PAA/D adducts. The effect of shear rate on shear stress of 7% aqueous solutions of PAA/D adducts in comparison with that of Na-alginate is shown in Figures 13 and 14, for PAA/D_1 and PAA/D_2, respectively. It can be seen that the general behavior of these adducts is similar to that of PAA/GA adducts. That is, all are characterized by a non-Newtonian, shear-thinning, thixotropic flow, and the extent of their thixotropy is higher than that of alginate.

It is also observed that 7% aqueous solution of dexy 85 is characterized by a non-Newtonian pseudoplastic flow.

Full neutralization (Na form) of the adducts results in increasing both of their thixotropic behavior and resistance to flow, as illustrated in Figures 15 and 16. This observation is more pronounced in case of PAA/D_1 than in case of PAA/D_2.

Comparison of apparent viscosities. In practical application, the apparent viscosities of the upper curves of

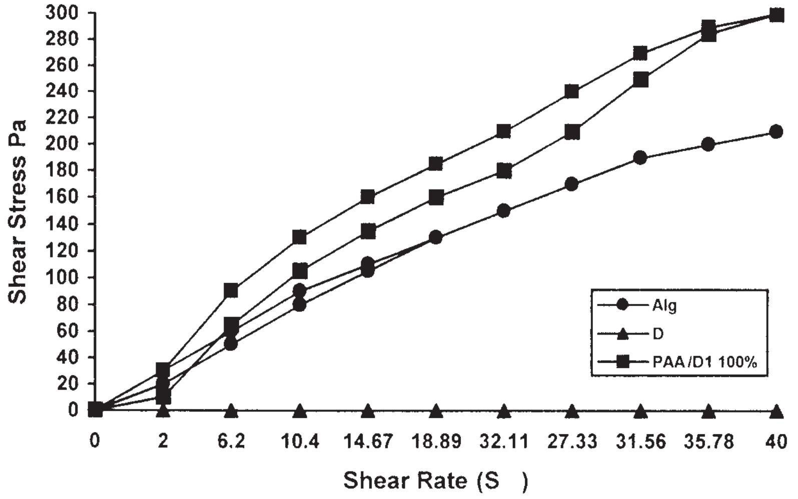

Figure 15 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, D, and fully neutralized PAA/D_1 at 25°C ± 1°C.

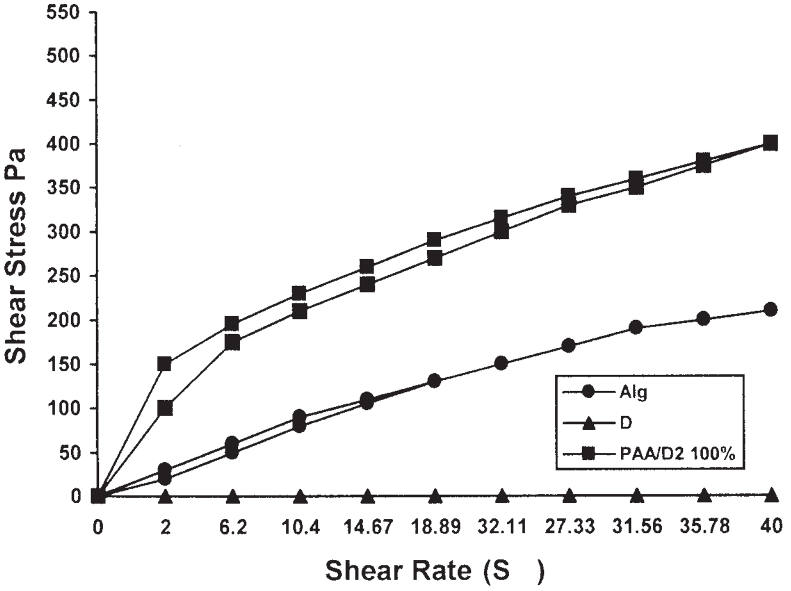

Figure 16 Effect of shear rate on shear stress of 7% (w/v) aqueous solutions of Na-alginate, D, and fully neutralized PAA/D_2 at 25°C ± 1°C.

rheograms (Figs. 9–16) have the greatest influence on printing, because they represent the highest resistance to applied shear exerted during printing process. Accordingly, these values were calculated for all adducts, partially or fully neutralized, including alginate, at three shear rates, viz., 2, 18.89, and 40 s^{-1}, and were tabulated in Table II. At a given set of conditions, Table II shows that:

a. The apparent viscosity decreases upon increasing the shear rate, regardless of solution studied, which can be associated with better orientation of polymer particles in the direction of rotation at higher shear rates, thereby offering less resistance to flow.[16]

b. The apparent viscosity of the adducts significantly increases upon increasing the extent of neutralization from 20 to 100%, which can be ascribed to the accompanying higher solubility of polymer macromolecules or particles. The apparent viscosities of the solution studied can be arranged descendingly, as shown in Table III, where it can be seen that:

i. At a DN of 20%, the viscosity order is almost the same, regardless the shear rate, and can be generalized as follows:

TABLE II
Comparison of Apparent Viscosity (Pa s) of PAA Adducts, Partially (20%) and Fully (100%) Neutralized at Different Shear Rates

Degree of neutralization (%)	Shear rate (s^{-1})		
	2	18.89	40
PAA/GA_1			
20	12	18.5	2.6
100	60	3.8	10
PAA/GA_2			
20	12	3.8	3
100	23	7	5
PAA/D_1			
20	14	9	6.8
100	60	18.9	10
PAA/D_2			
20	60	20.1	15
100	90	30	22
Alginate	13.1	7.3	5

TABLE III
Descending Arrangement of the Apparent Viscosities of Aqueous Solution (7% w/v) of Adducts Partially or Fully Neutralized, Including Alginate

Degree of neutralization (%)	Shear rate (s^{-1})	Apparent viscosity descending order
20	2	PAA/D_2 > PAA/D_1 > Alg > PAA/GA_1 = PAA/AG_2
	18.89	PAA/D_2 > PAA/D_1 > Alg > PAA/GA_1 = PAA/AG_2
	40	PAA/D_2 > PAA/D_1 > Alg > PAA/GA_1 = PAA/AG_2
100	2	PAA/D_2 > PAA/D_1 = PAA/GA_1 > PAA/AG_2 > Alg
	18.89	PAA/D_2 > PAA/D_1 ≥ PAA/GA_1 > Alg ≥ PAA/AG_2
	40	PAA/D_2 > PAA/D_1 = PAA/GA_1 > PAA/AG_2 = Alg

$$\text{PAA/D}_2 > \text{PAA/D}_a > \text{Alg} > \text{PAA/GA}_1 = \text{PAA/GA}_2$$

ii. At a DN of 100%, there is little difference in viscosity order at different shear rates. However PAA/D adducts ride the crest followed by PAA/GA_1, and then alginate follows, precedes or gets side by side the order of PAA/GA_2 depending on the shear rate. At any rate, however, differences in apparent viscosities of adducts studied reflect differences among them regarding to substrate used, ratio of homopolymer to copolymer, extent of branching, DN, molecular size and weight, and internal orientation of polymer particles in solutions.

CONCLUSIONS

Optimum reaction conditions, viz., AA, 6.76 mol/L; $Na_2S_2O_3$, 26.87 × 10^{-3} mol/L; $Na_2S_2O_8$, 34.9 × 10^{-3} mol/L; DN, 20%; temperature, 90°C; and time 30 min, were utilized in preparing two adducts of each substrate (GA or D) at two LRs (1.25/1 and 6.3/1 *L*/*K*). The four adducts formed were PAA/GA_1, PAA/GA_2, PAA/D_1, and PAA/D_2, (where 1 and 2 refers to the low and high LR, respectively) and were found to be water soluble at all proportions. IR spectrum of these adducts confirmed the introduction of the COOH group onto their structures. Rheological properties of 7% aqueous solutions of these adducts, including Na-alginate, showed that all are characterized by a non-Newtonian, shear-thinning, thixotropic behavior, within the range of shear rate studied. The apparent viscosities of these solutions followed the descending order:

$$\text{PAA/D}_2 > \text{PAA/D}_1 > \text{Alg} > \text{GA}_1 = \text{PAA/GA}_2$$

Full neutralization of adducts to 100% results in a remarkable enhancement of their apparent viscosities.

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