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Preparation and Rheology of New Synthetic Thickeners Based on Polyacrylic Acid

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ABSTRACT

Four synthetic resins, viz. polyacrylic acid (PAA), polyacrylic acid/polyethylene glycol 1000 (PAA/PEG 1000), polyacrylic acid/polyethylene glycol 6000 (PAA/PEG 6000) and polyacrylic acid/polymethacrylic acid (PAA/PMA), were prepared, and the rheology of their pastes in comparison with that of sodium-alginate, at a concentration of 50 g/kg, was investigated. The results indicate that the pastes are characterized by a non-Newtonian, pseudoplastic flow under the studied conditions. The shear thinning index values of the pastes show that the flow properties of pastes of either PAA/PEG 1000 or PAA/PMA are approximately similar to those of sodium-alginate, and all are better than those of pastes of PAA and PAA/PEG 6000. It was also found that the apparent viscosities of the pastes increased on storing up to 8 days.

INTRODUCTION

It is well established that sodium alginate is the most suitable thickener for printing of cellulosic fabrics with reactive dyes.[1–5] Sodium alginate is extracted from seaweed, using an elaborate technique,[6] which is reflected in its relatively high price.

We are investigating low cost-efficient substitutes for sodium alginate, and this present work deals with the preparation of four synthetic resins,

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namely, polyacrylic acid (PAA), polyacrylic acid/polyethylene glycol 1000 (PAA/PEG 1000), polyacrylic acid/polyethylene glycol 6000 (PAA/PEG 6000) and polyacrylic acid/polymethacrylic acid (PAA/PMA), as well as the study of the rheological properties of pastes of these resins in comparison with those of sodium alginate.

A subsequent study will concern the use of these resins as reactive dyes–printing thickeners for cellulosic fabrics.

EXPERIMENTAL

Materials

Acrylic acid (AA) and methacrylic acid (MA), pure grade and containing 200 ppm of hydroquinone monomethyl ether, were used as commercially supplied without purification. Sodium peroxydisulphate, sodium sulphite, sodium hydroxide, polyethylene glycol 1000 (PEG 1000) and polyethylene glycol 6000 (PEG 6000) were all laboratory grade chemicals. A high viscosity sodium alginate (Cecalginate HV/KL 600), Ceca Kolloid Chemie, Paris), was used.

Preparation of the resins

AA or MA was first 20% neutralized with the equivalent amount of an aqueous solution of 500 g/litre NaOH. The polymerization was carried out (Abo-Shosha, M. H. & Ibrahim, N. A., unpublished) under atmospheric oxygen. A polymerization medium was first prepared and kept in a thermostatic water bath at 40°C, then 3·3 ml solution of 40 g/litre Na_2SO_3 and 12·2 ml solution of 330 g/litre $Na_2S_2O_8$ were successively added, with stirring. After an induction period, an exothermic polymerization reaction commenced, with the evolution of water vapour, followed by solidification of the polymerization medium. The latter was then cooled under ambient conditions, disintegrated, oven dried at 105°C for 2 h, cooled, ground and kept over P_2O_5 for at least 40 h before analysis.

The polymerization media were as follows:

(a) A PAA polymerization medium was prepared by 20% neutralizing of 157·5 g of AA as mentioned before.
(b) A PAA/PEG polymerization medium was prepared by 20% neutralizing of 115·5 g of AA, followed by dissolving 40 g of either PEG 1000 or PEG 6000.
(c) A PAA/PMA polymerization medium was prepared by 20%

neutralizing 115·5 g of AA and 42 g of MA separately, followed by mixing the resulting solutions.

Analysis and testing

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

A paste of sodium alginate (50 g/kg) was prepared by soaking overnight in distilled water followed by thorough mixing. A paste of each resin was prepared by soaking 50 g of the resin overnight in an aqueous solution of 100 g/litre NaOH (just enough to neutralize the free carboxyl groups of the resin); the total weight of the paste was then adjusted to 1 kg, using distilled water, followed by thorough mixing.

The rheological properties of each paste were measured at 20 ± 0·1°C, using a coaxial viscometer (Rheomat-15, Zurich, Switzerland). 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 shearing stress (dyne/cm^2), respectively.

RESULTS AND DISCUSSION

Polymerization

The decomposition of the persulphate/sulphite redox system to $SO_4^{-\bullet}$, $SO_3^{-\bullet}$ and $OH^\bullet$ free radical species[8] could stimulate the following set of polymerization reactions:

$$\text{AA (or MA)} + \text{R}^\bullet \rightarrow \text{RH} + \underset{\substack{\text{'activated AA or}\\ \text{MA molecules'}}}{\text{AA}^\bullet \text{ (or MA}^\bullet)} \qquad (1)$$

$$\text{AA}^\bullet \text{ (or MA}^\bullet) + n_1\text{AA (or } n_2\text{MA)} \rightarrow \text{PAA (or PMA)} \qquad (2)$$

$$\text{AA}^\bullet \text{ (or MA}^\bullet) + n_3\text{AA (or } n_4\text{MA)} \rightarrow \text{(AA/MA) copolymer} \qquad (3)$$

$$\text{PEG—OH} + \text{R}^\bullet \rightarrow \text{RH} + \underset{\text{'PEG macroradical'}}{\text{PEG—O}^\bullet} \qquad (4)$$

$$\text{PEG—O}^\bullet + \text{AA} \rightarrow \text{PEG—O—AA}^\bullet \xrightarrow{+n_5\,\text{AA}} \text{PEG–grafted–PAA} \qquad (5)$$

where $\text{R}^\bullet$ is a free radical species.

Logically, the constituent polymers of the resin obtained are in a state

TABLE 1
Effect of Polymerization Medium Composition on the ST, %TC and Visual Appearance of the Resins Obtained

Polymerization medium composition	*ST (s)*	*TC (%)*	*Resin appearance*[a]	*Resin designation*
AA	90	99·3	White powder	PAA
AA/MA	120	98·5	White powder	PAA/PMA
AA/PEG 1000	145	98·0	Pale yellow Waxy powder	PAA/PEG 1000
AA/PEG 6000	175	97·7	Pale yellow waxy powder	PAA/PEG 6000

[a] At 25°C.

of 'entanglement' and their types depend mainly on the composition of the corresponding polymerization medium, i.e.

(a) when the polymerization medium contains AA, the product obtained is mainly PAA.
(b) when the polymerization medium contains an AA/PEG mixture, the product obtained is most probably a mixture of PAA, PEG–grafted–PAA and unreacted PEG. This forms the so-called PAA/PEG resin.
(c) when the polymerization medium contains an AA/MA mixture, the product obtained is most probably a mixture of PAA, PMA and (AA/MA) copolymer. This forms the so-called PAA/PMA resin.

Table 1 shows the effect of polymerization medium composition on the solidification time (ST), percentage total conversion (%TC) and visual appearance of the resin obtained. It is clear that the STs are relatively short and the polymerization reactions proceed nearly to completion. However, a little increase (or decrease) in the ST (or %TC) is observed on going down Table 1. This could be associated with the accompanying decrease in the number of double bonds (active sites of polymerization) and/or the nature of the other compound mixed with AA.

Rheological properties

Figure 1 shows the effect of shearing rate on the shearing stress of a freshly prepared paste of the studied resins, in comparison with that of sodium alginate at a concentration of 50 g/kg. Evidently, the curves obtained are not linear, i.e. the shearing stress is not directly proportional

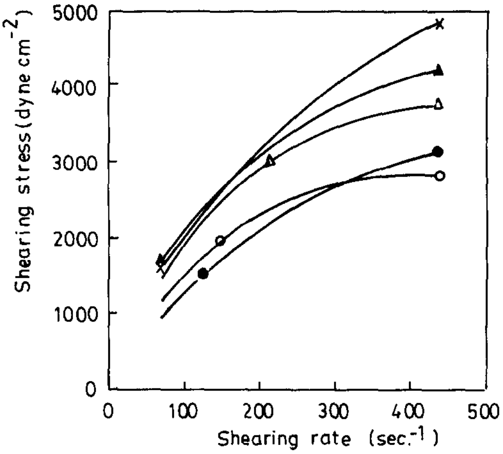

Fig. 1. Effect of shearing rate on shearing stress of pastes of PAA (▲), PAA/PEG 1000 (△), PAA/PEG 6000 (○), PAA/PMA (●) and sodium alginate (x); concentration, 50 g/kg; temp., 28 ± 0·1°C.

to the shearing rate, but are convex to the shear stress axis, i.e. shear thinning; no hysteresis is evident. The pastes, therefore, including sodium alginate, are characterized by a non-Newtonian, pseudoplastic flow under the conditions employed.

The apparent viscosities of the five pastes were calculated and plotted against the shearing rates as shown in Fig. 2. It can be seen, irrespective of the type of paste, that the viscosity decreases on increasing the shearing rate. This could be attributed to better orientation of the polymer particles in the direction of rotation at higher shearing rates, thereby

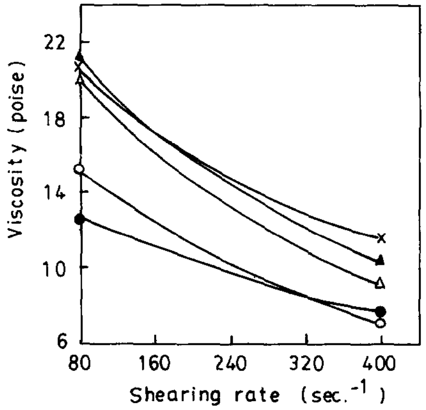

Fig. 2. Effect of shearing rate on the apparent viscosity of pastes of PAA (▲), PAA/PEG 1000 (△), PAA/PEG 6000 (○), PAA/PMA (●) and sodium alginate (x); concentration, 50 g/kg; temp., 28 ± 0·1°C.

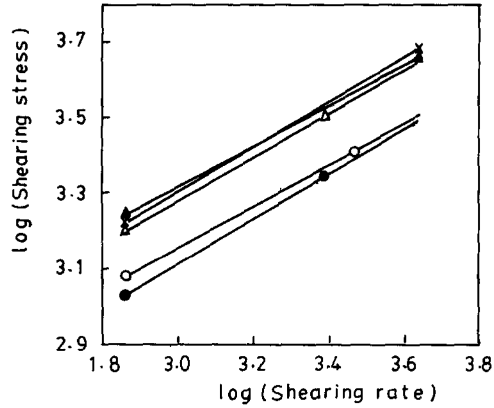

Fig. 3. A log—log plot of shearing stress vs. shearing rate of pastes of PAA (▲), PAA/PEG 1000 (△), PAA/PEG 6000 (○), PAA/PMA (●) and sodium alginate; concentration, 50 g/kg; temp., 28 ± 0·1°C.

offering less resistance to flow.[9] It is noticeable that the viscosities of PAA and sodium alginate are the highest, and those of PAA/PEG 6000 and PAA/PMA are the lowest; that of PAA/PEG 1000 lies in between. It is also apparent that the viscosity of PAA is slightly higher than that of sodium alginate in the range 80–160 s^{-1} shearing rate, after which the viscosity of sodium alginate becomes higher. In the case of PAA/PMA and PAA/PEG 6000, the viscosity of the first is lower in the range 80–320 s^{-1} shearing rate, then it becomes higher on increasing the shearing rate beyond 320 s^{-1} and up to 400 s^{-1}.

That the viscosity of PAA is higher than that of PAA/PMA, in spite of the presence of the pendant CH_3 groups in the latter (which could restrict the movements of the particles and reduce their internal flexibilities), suggests that the average length of the former is much higher than that of the latter. On the other hand, the lower viscosity of the longer chain PEG-based resin (i.e. PEG 6000) compared to that of resins based on a shorter chain (i.e. PEG 1000) suggests that the formed polymer chains of the latter are so long that their average particle size is larger than that of the former, and also that the amount of hydroxyl groups in the former is lower than that in the latter, which could result in less hydrogen bonding between the resin particles.

In order to compare the pseudoplastic nature of the pastes of the resins with that of sodium alginate, the logarithms of the shearing stresses were plotted against those of shearing rates,[10] as shown in Fig. 3; linear plots were obtained. The slopes of these plots, which represent the power of the Ostwald–de Waele equation,[10] were positive and less than unity. The values of the slopes influences the nature of these pastes; i.e.

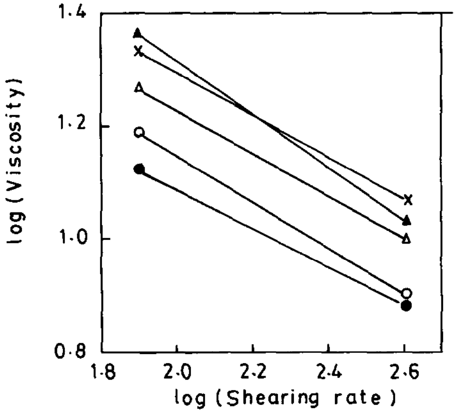

Fig. 4. A log—log plot of the apparent viscosity vs. shearing rate of pastes of PAA (▲), PAA/PEG 1000 (△), PAA/PEG 6000 (○), PAA/PMA (●) and sodium alginate; concentration, 50 g/kg; temp., 28 ± 0·1°C.

the pseudoplasticity increases with a decrease in the value of the slope.[10] Accordingly, the pastes can be classified into two groups, each group having approximately the same slope or the same pseudoplasticity. The first group consists of PAA and PAA/PEG 6000, and the second, sodium alginate, PAA/PEG 1000 and PAA/PMA. the slope of the first group is lower than that of the second, indicating that the pastes of PAA/PEG 1000 and PAA/PMA are as pseudoplastic as that of sodium alginate, and their pseudoplasticities are lower than those of PAA and PAA/PEG 6000.

The degree of pseudoplasticity can be obtained by determining the shear thinning index (STI) value of each paste as per the following relationship:[10]

$$\log \eta = \log K - (\text{STI}) \log D \qquad (6)$$

where K is a constant.

Hence, by plotting log η versus log D for different pastes, as shown in Fig. 4, the STI of each paste is the slope of the corresponding plot. The K values can then be estimated from the aforementioned relationship. The STI and K values are listed in Table 2; it is apparent that the STI of PAA is nearly the same as that of PAA/PEG 6000, that the STI of sodium alginate, PAA/PEG 1000 or PAA/PMA have approximately the same value, and that the STI of the first group is higher than that of the second group. Since the higher STI value, the poorer the flow properties, then the flow properties of the pastes follow the order:

PAA ≃ PAA/PEG 6000 < PAA/PMA ≃ PAA/PEG 1000 ≃ Na alginate

TABLE 2
STI and *K* Values of Pastes of Sodium Alginate and the Other Resins

Paste	*STI*	*K*
Sodium alginate	0·376	118·7
PAA	0·471	169·0
PAA/PMA	0·386	70·5
PAA/PEG 1000	0·380	77·4
PAA/PEG 6000	0·430	142·6

Paste concentration, 50 g/kg; temp., 28 ± 0·1°C.

When the applied rate of shear is 1 s^{-1}, then the *K* value is the observed apparent viscosity, as can be deduced from the relationship above. Subsequently, and as shown in Table 2, the viscosities of the five pastes, at a shearing rate of 1 s^{-1}, follow the decreasing order:

PAA < PAA/PEG 6000 < Na alginate < PAA/PEG 1000 < PAA/PMA

TABLE 3
Effect of Storing on the Apparent Viscosities (in poises) of the Pastes at Different Shearing Rates

Paste	*Storing time (days)*	*Shearing rate (s^{-1})*				
		80	*160*	*240*	*320*	*400*
Sodium alginate	0	20·6	17·2	14·8	13·0	11·6
	1	26·6	18·1	15·6	13·6	11·9
	8	28·8	19·5	15·9	13·8	12·0
PAA	0	21·25	17·2	14·6	12·2	10·5
	1	26·6	18·1	15·2	13·4	12·0
	8	28·3	19·4	15·6	13·8	12·4
PAA/PMA	0	12·5	11·6	10·0	8·6	7·1
	1	15·8	12·2	10·4	9·2	8·1
	8	17·5	12·8	11·0	9·5	8·6
PAA/PEG 1000	0	20·0	16·25	13·3	11·0	9·3
	1	23·8	17·5	14·9	12·0	10·3
	8	26·3	18·1	15·1	12·5	10·6
PAA/PEG 6000	0	15·0	12·8	10·4	8·6	7·8
	1	17·5	14·0	11·9	10·2	8·4
	8	19·8	14·2	12·5	10·6	8·8

Paste concentration, 50 g/kg; temp., 28 ± 0·1°C.

Storing

Table 3 shows the effect of storing on the apparent viscosities of the pastes in comparison with that of sodium alginate. It is noticed, regardless of the shearing rate, that all the pastes show an increase in their apparent viscosities and that the longer the storing time is, the higher the increase in the apparent viscosity; the greatest increase in viscosity occurs during the first day of storing. It is probable that storing permits better swelling, compatibility and uniformity of the macromolecules of the pastes, which in turn increases the apparent viscosities.

Data pertaining to the use of these resins as reactive dye printing thickeners in the coloration of cellulose will be reported later, together with a comparison with sodium alginate based thickeners.

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