Carbohydrate Polymers 74 (2008) 241–249

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Preparation and characterization of polyacrylic acid/karaya gum and polyacrylic acid/tamarind seed gum adducts and utilization in textile printing

M.H. Abo-Shosha [a,*], N.A. Ibrahim [a], E. Allam [b], E. El-Zairy [b]

[a] *Textile Research Division, National Research Center, Dokki, Cairo, Egypt*
[b] *Faculty of Applied Arts, Helwan University, Cairo, Egypt*

ARTICLE INFO

*Article history:*
Received 22 January 2008
Received in revised form 7 February 2008
Accepted 20 February 2008
Available online 29 February 2008

*Keywords:*
Karaya gum
Tamarind seed gum
Acrylic acid
Polymerization
Thickeners
Rheology
Reactive printing
Acid printing

ABSTRACT

Polymerization of 20% neutralized acrylic acid (Na form), AA, in presence of Karaya gum, KG, or tamarind seed gum, TG, at AA/gum weight ratio of 1/1 and 2/1 results in PAA/KG1, PAA/KG2, PAA/TG1 and PAA/TG2 adducts, respectively (where the suffix 1 or 2 stands for AA/gum ratios of 1/1 or 2/1). Infra red spectra of adducts are examined. Aqueous pastes of adducts, native gums and GG are of non-Newtonian thixotropic flow within a shear rate range of 4–40 $s^{-1}$. Adduct pastes (7.5% w/v) are of higher apparent viscosities ($\eta$) than their native gums or GG, and pastes of TG adducts are of higher $\eta$ than KG adducts. Except for PAA/TG2 adduct, the power law does not correlate well to the other pastes. Preliminary trials showed that adducts are excellent thickeners for reactive and acid printing on wool, silk and nylon 6. Prints by adducts are of higher color strength than those by native gums or GG. GG paste was completely destroyed after storing for 7 days, whereas $\eta$ of pastes of adducts and native gums were noticeably decreased upon storing.

## 1. Introduction

Karaya gum, KG, and tamarind gum, TG, are water soluble polysaccharides of vegetable origin. TG is the purified from of a powder obtained by pulverizing the kernels of tamarind pulp after the removal of the taste. It has a branched structure consisting of a main chain of β-D (1→4) linked glucopyranosyl units, with a side chain consisting of a single xylopyranosyl unit attached to every second, third and fourth D-glucopyranosyl unit through an α-D (1→6) linkage (Davidson, 1980). One D-galacotopyransoyl units is attached to one of the xylopyranosyl unit through a β-D (1→2) linkage. TG is used as a sizing agent for jute and cotton warps due to its excellent binding and film forming properties (Davidson, 1980). It has replaced starch in many formulation in India due to its lower cost and similar or better weaving efficiency (Srivastava, Gharia, & Mudis, 1972). It can be used alone or in admixtures with tragacanth gum as economic thickeners in printing pastes of textiles (Savur, 1956). However, it can not be used in reactive printing because it interferes with the dye.

KG is a partially acetylated complex having around 8% acetyl group and about 37% uronic acid residues (Davidson, 1980). Before utilization as a thickener in textile printing, its solubility is increased either by cooking a water suspension of the gum under pressure or oxidizing it with some oxidants such as persulfale or persilicate (Davidson, 1980). It can be then used in direct printing of cotton fabric.

This study aims at improving the thickening properties of both of TG and KG and to extend their application to involve other dyestuffs and textile substrates. Previous studies revealed that free radical polymerization of suitable vinyl monomers in presence of some gums produced adducts of superior thickening properties than the native gum in textile printing. Examples are: (a) polyacrylic acid/British gum (BG) adduct that produced higher color strength than BG upon acid, reactive or metal complex printing on wool fabric (Abbas, 2004), (b) polyacrylamide/guar gum adduct which proved to be of better thickening properties upon reactive printing of wool and nylon 6 than those of guar gum (Ibrahim, Rashad, & Abo-Shosha, 2003), and (c) polyacrylic acid/gum Arabic or dextrin that had enhanced reactive printing on cellulosics than those obtained by the native gum (Abo-Shosha, Ibrahim, Allam, El- Zairy, & EL-Zairy, 2006; Ibrahim, Abo- Shosha, Allam, EL- Zairy, & El. Zairy, 2006).

Based on these studies and to achieve the objective cited, partially neutralized acrylic acid (20%, Na form) is polymerized in presence of either TG or KG using ammonium persulfate/sodium thiouslfate

---

* Corresponding author. Tel.: +2 010 721 60 79; fax: +2 02 33 70 931.
*E-mail address:* mshoshal@yahoo.com (M.H. Abo-Shosha).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.02.011

redox system to prepare two adducts of each of TG and KG (using two different ratios of acrylic acid-to-gum). The four adducts are characterized by investigating their FT-IR spectrum, thermogrvimetric analysis, and rheology. Preliminary trials of utilizing these adducts in comparison with guar gum as thickeners for reactive or acid printing of wool, silk and nylon-6 fabrics is reported.

## 2. Experimental

### 2.1. Materials

Mill-scoured chlorinated plain woven merino wool fabric of 290 g/m$^2$, degummed/bleached plain woven silk fabric of 48 g/m$^2$ and mill-scoured Nylon 6 fabric (210 denier/35 filament) were used.

Karaya gum, KG, was locally purchased from Al Haraz co., Cairo. Tamarind seed gum, TG, was supplied by Noveon UK Ltd. Diagum A8 8%, guar gum, GG, depolymerized glactomannans, was supplied by BF Goodrich Diamalt GmbH, Munich, Germany. All gums were ground before use. Hostapal® CV, a technical grade nonionic wetting agent of Clariant, was used.

Acrylic acid, AA, pure grade and containing 200 ppm hydroquinon monomethylether, supplied by Fluka Chemika, Switzerland, sodium persulfate, sodium hydroxide, sodium thiosulfate, citric acid, urea, sodium hydroxide, laboratory grade chemicals, supplied by Merck, were used.

Isolan® Red 2GLN and Levafix® Golden Yellow PN-GR an acid and reactive dyes, respectively, and supplied by Dystar, were used.

### 2.2. Methods

### 2.2.1. Preparation of adducts

Adducts were prepared by polymerizing AA in presence of any of KG or TG based on a method developed by Abo-Shosha and Ibraim (Abo-Shosha, El Zairy, & Ibrahim, 1994; Ibrahim et al., 2003) under atmospheric oxygen as follows. AA was 20% neutralized with aqueous solution of NaOH (32% w/v). Aqueous solutions of $Na_2S_2O_8$ ($34.9 \times 10^{-3}$ mol/L) and $Na_2S_2O_3{\cdot}H_2O$ ($26.87 \times 10^{-3}$ mol/L) were consequently added with stirring to a 2 L polypropylene beaker containing AA (20% neutralized and having a concentration of 11.46 mole/L at 90 °C). The gum was then added to the beaker with rapid mixing to form a uniform paste. AA/gum weight ratios were adjusted to 1/1 and 2/1. The beaker was kept in a thermostatic water bath at 90 °C. After an induction period, an exothermic reaction began with the rise of water vapor, followed by solidification of the paste. The time elapsed between keeping the beaker in the bath and solidification is called solidification time, ST, and found to be 6, 4, 5 and 3 min in cases of PAA/KG1, PAA/KG2, PAA/TG1 and PAA/TG2 adducts, respectively. The suffixes 1 and 2 stand for AA/gum ratios of 1/1 and 2/1, respectively. The beaker was left in the bath for an extra 10 min. after solidification, then cooled to ambient temperature, disintegrated, ground and dried at 60 °C/5 h, then kept over $P_2O_5$ for 48 h before analysis.

### 2.2.2. Printing paste

The composition of acid printing paste is as follows.

| | |
|---|---|
| Isolan® Red 2GLN | 30 g/Kg |
| Stock thickening (7.5%) | 500 g/Kg |
| Urea | 100 g/Kg |
| Citric acid | 30 g/Kg |
| Water | 340 g/Kg |
| Total weight | 1000 g |

The composition of reactive printing paste is as follows.

| | |
|---|---|
| Levafix® Golden Yellow PN-GR | 30 g/Kg |
| Stock thickening (7.5%) | 500 g/Kg |
| Urea | 100 g/Kg |
| Citric acid | 10 g/Kg |
| Water | 360 g/Kg |
| Total weight | 1000 g |

### 2.2.3. Printing

Printing was performed using flat screen technique. Printed fabric samples were dried at 85 °C/5 min then steam fixed at 105 °C/30 min using Ariolt® CSL Steamer – Italia. After fixation, the prints were rinsed thoroughly with cold water, soaped for 15 min. at 60 °C in presence of Hostapal® CV (2 g/l), and then thoroughly rinsed with warm water followed by cold water then dried at ambient conditions.

### 2.3. Analysis and testing

The extent of polymerization, expressed as percentage total conversion, % TC, was determined by assessing the unsaturation content before and after polymerization (Welcher, 1965). FT-IR spectra were done using Perkin Elmer spectrum one FT-IR with optical system that gives data collection over a total range 7800–370 cm$^{-1}$ using KBr disc technique.

Thermogravimetric analysis (TGA) was carried out on Shimadzu TGA-SOH detector using platinum cell in nitrogen atmosphere at a rate of flow of 30 ml/min, up to a temperature of 500 °C at a heating rate of 10 °C/min.

The rheological properties of the adduct pastes (7.5%w/v) were measured at 25 ± 0.1 °C using a co-axial rotary viscometer (HAAKE RV20), Germany. The apparent viscosity ($\eta$) was calculated using the formula:

$$\eta = \tau / D \text{ Pa s}$$

where, $D$ and $\tau$ are the rate of shear (s$^{-1}$) and shear stress (Pa), respectively.

Depth of the acid or reactive prints, expressed as K/S, was measured at the wavelength of maximum absorbance using an automatic filter spectrophotometer. The spectrophotometer used was of model ICS-Texicon limited, Kennetside park, Newbury, Berkshire R.G145 TE, England.

## 3. Results and discussion

### 3.1. Preparation of the adducts

Under the conditions employed $SO_4^{-\cdot}$, and $S_2O_3^{-\cdot}$ free radical species are generated from the decomposition of sodium persulfate/sodium thiouslfate redox system (Ghosh, Chadha, & Palit, 1964; Sorum & Edwards, 1952). These radical species ($R^{\cdot}$) can effect a set of reactions (Abbas, 2004; Abo-Shosha et al., 2006; Ghosh et al., 1964) as shown in Scheme 1. In reaction 1, activated AA monomer ($AA^{\cdot}$) is generated, in reactions 2 or 3, either KG or TG macroradicals are formed, in reaction 4, AA is homopolymerized, and in reaction 5 or 6, PAA-g-KG or PAA-g-TG is formed. Furthermore, the persulfate ions can also oxidize either KG or TG to variable extents.

The mixture of products of reactions 4–6, i.e. PAA, PAA-g-KG and PAA-g-TG, in addition to ungrafted (intact and oxidized) KG or TG, all in a state of intimate entanglement with each other is called PAA/KG or PAA/TG adduct.

Four types of adducts were prepared based on KG and TG using AA/gum weight ratios of 1/1 or 2/1. Table 1 shows the % TC, ST,

$$\mathrm{R^{\cdot} + AA \longrightarrow AA^{\cdot}} \tag{1}$$

$$\mathrm{KG\text{-}OH + R^{\cdot} \longrightarrow KG\text{-}O\,R^{\cdot} + RH} \tag{2}$$

$$\mathrm{TG\text{-}OH + R^{\cdot} \longrightarrow TG\text{-}O^{\cdot} + RH} \tag{3}$$

$$\mathrm{n\,AA^{\cdot} \longrightarrow PAA} \tag{4}$$

$$\mathrm{KG\text{-}O^{\cdot} + n_1\,AA \longrightarrow PAA\text{-}g\text{-}KG} \tag{5}$$

$$\mathrm{TG\text{-}O^{\cdot} + n_2\,AA \longrightarrow PAA\text{-}g\text{-}TG} \tag{6}$$

**Scheme 1.** Suggested reaction mechanism.

**Table 1**
%TC, ST, appearance and water solubility of adducts prepared at different AA/gum ratios

| Property | Gum type | | | |
|---|---|---|---|---|
| | KG | | TG | |
| | AA/Gum ratio | | | |
| | 1/1 | 2/1 | 1/1 | 2/1 |
| %TC | 99.72 | 99.80 | 98.6 | 99.9 |
| ST (min) | 6 | 4 | 5 | 3 |
| Appearance | Beige powder | | Off-white powder | |
| Water solubility | S | S | S | S |
| Designation | PAA/KG1 | PAA/KG2 | PAA/TG1 | PAA/TG2 |

[AA], 6.75 mol/L; degree of neutralization, 20% (Na salt); [$Na_2S_2O_8$], $34.9 \times 10^{-3}$ mol/L; [$Na_2S_2O_3.H_2O$], $26.87 \times 10^{-3}$ mol/L; temp., 90°C; S: mixed with water in all proportions at room temp.

appearance and water solubility of these adducts. It is clear that the % TC is very high for all adducts (>98%), reflecting the high affinity of free radical species to AA/gum system under the conditions employed. Increasing AA/gum ratio from 1/1 to 2/1 slightly improves the % TC and noticeably shortens the ST, regardless of gum type. This can be associated with enhancing the continuity of the liquid phase in the pastes (Ibrahim et al., 2006). It is also depicted from Table 1 that all adducts formed are water soluble in all proportions at room temperature, which is an essential property of a thickening agent.

### 3.2. *Characterization of the adducts*

The four adducts shown in Table 1 are characterized by investigating their infrared spectra and TGA. Since they are intended for use as thickeners in printing pastes, characterization extends to involve their rheology. Given hereafter are the results obtained with relevant discussion.

#### 3.2.1. *Infrared specra*

Fig. 1 shows FTIR spectra of TG, PAA/TG1 and PAA/TG2. The summary of bands position and their assignments (Dean, 1995; Pavia, Lampman, & Kriz, 2001) for each spectrum are set out in Table 2. Fig. 1 and Table 1 depict common bands, which can be summarized as follows:

1. A broad strong peak at 3250–3000 $cm^{-1}$ and medium peak at 612 $cm^{-1}$ belonging to stretching and out of plan bending of alcoholic —OH, respectively.
2. Medium peaks at 2900 and at 1430–1480 $cm^{-1}$ belonging to asymmetric stretching and bending vibration respectively of —CH2- groups.
3. A band at 1700–1850 $cm^{-1}$ belonging to stretching vibration of —C═O in cyclic or open chain aldehyde.
4. The bands near 1200 $cm^{-1}$ are attributed to in-plan deformation of O—H groups.
5. A medium peak at 1163 $cm^{-1}$ that is attributed to —C—O—C— asymmetric stretching vibration of glucopyranosyl and xylopyranosyl units.
6. A small peak at 613 $cm^{-1}$ that is attributed to alcoholic —OH out of plan bending.

Polymerization of AA in presence of TG added substantially higher amount of —COOH groups onto the final adducts. The higher the AA/TG ratio, the higher the carboxyl content. This in turn reflected on the three spectra shown in Fig. 1. Obviously, the intensity of the band, at 1750 $cm^{-1}$ corresponding to C═O, is higher in case of PAA/TG2 than in case PAA/TG1 adduct and both are much higher than in case of native TG.

Fig. 2 shows the IR spectra of KG, PAA/KG1, and PAA/KG2 adducts. It is clear that IR spectrum of KG are of close similarity to

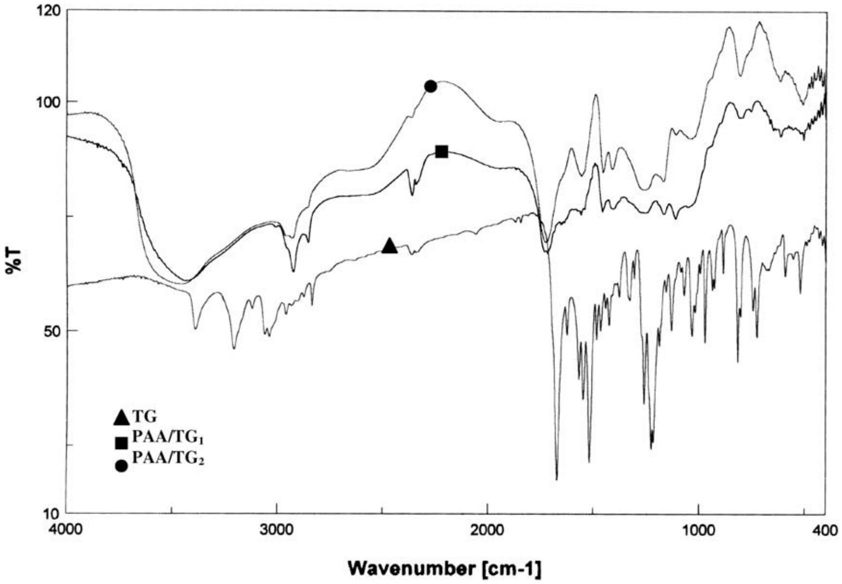

**Fig. 1.** IR spectrum of TG, PAA/TG1 and PAA/TG2.

**Table 2**
FTIR analysis; position of bands (cm$^{-1}$) and their assignments (Dean, 1995; Pavia et al., 2001)

| Functional groups | TG | PAA/TG1 | PAA/TG2 |
|---|---|---|---|
| —OH Stretching vibration | 3450 | 3400 | 3400 |
| Aliphatic —CH2 stretching | 2902 | 2900 | 2900 |
| Adsorbed water | 1632 | 1614 | 1636 |
| Aliphatic —CH2 bending | 1432 | 1471 | 1482 |
| O—H in plan deformation | 1369 | 1365 | 1353 |
| Asymmetric stretching vibration of —C—O—C— bond | 1163 | 1007 | 1139 |
| —C—O—C— bending vibration | 1116 | 1115 | 1115 |
| —C—O stretching | 1060 | 1080 | 1088 |
| Alcoholic —OH out of plan bending | 613 | 579 | 600 |
| C=O stretching vibration (Its Intensity) | 1750 (low) | 1750 (high) | 1750 (Very high) |

that obtained previously with of TG and can be explained on similar assignments. The little shift in some bands position in KG adducts are attributed to the difference in molecular structure between TG and KG.

### 3.2.2. Thermal gravimetric analysis (TGA)

Fig. 3 or Fig. 4 shows TGA of adducts of KG or TG up to 500 °C. It is obvious that TG adducts are thermally stable than their native gum, and the higher the AA/TG ratio is the higher the stability. That is within the range studied, the stability can be arranged descendingly according to the order:

PAA/TG2 > PAA/TG1 > TG

On the other hand, KG adducts behave differently, where the stability can be divided into three regions. The first is within the range of up to 210 °C, where the stability can be arranged descendingly as follows:

PAA/KG2 ≈ KG > PAA/KG1

The second is between 210° and up to 260 °C, where the stability can be arranged descendingly as follows:

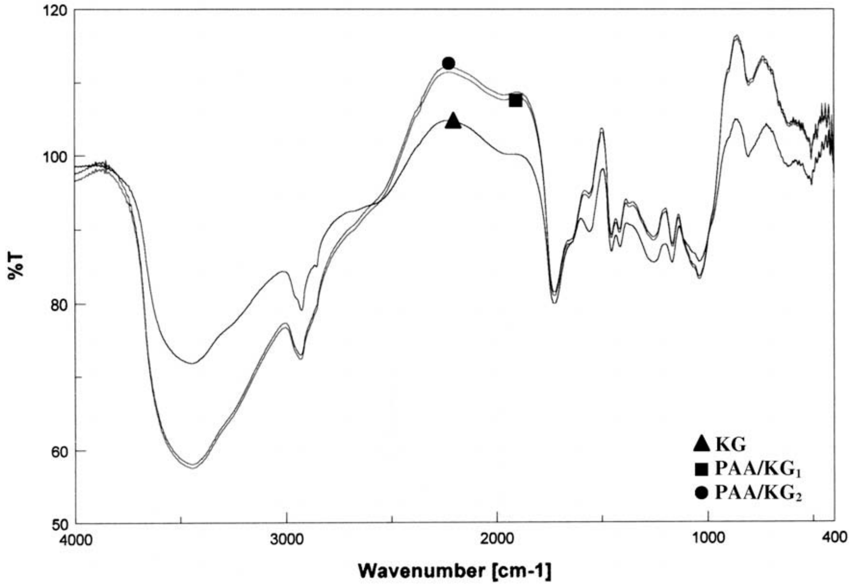

**Fig. 2.** IR spectrum of KG, PAA/KG1 and PAA/KG2.

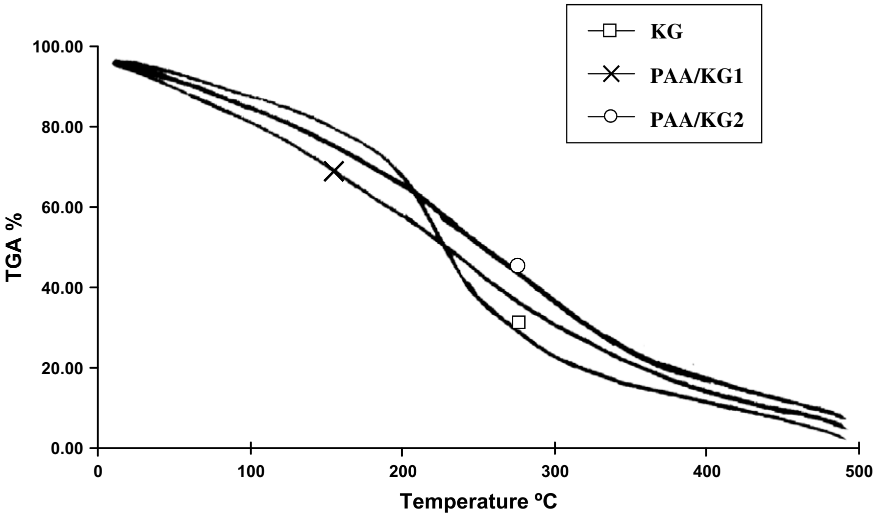

**Fig. 3.** Thermal gravimetric analysis of KG, PAA/KG$_1$ and PAA/KG$_2$.

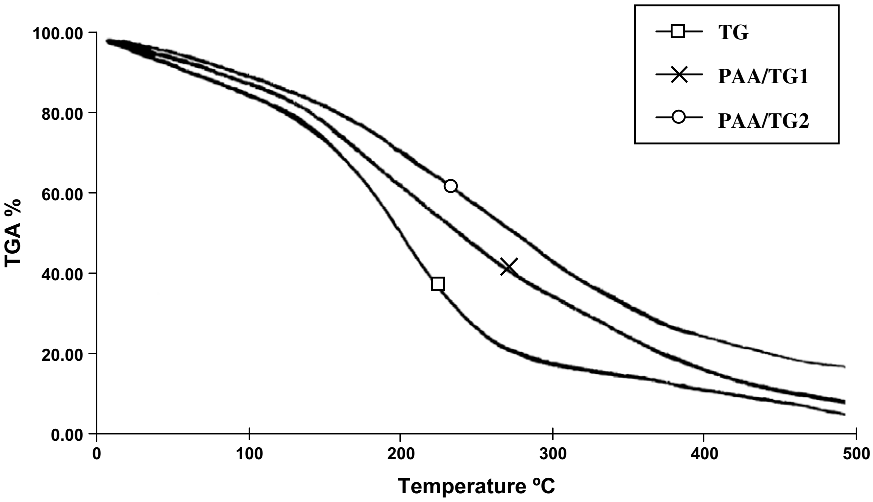

**Fig. 4.** Thermal gravimetric analysis of TG, PAA/$TG_1$ and PAA/$TG_2$.

PAA/KG2 > KG > PAA/KG1

The third is beyond 260° and up to 500 °C, where the stability follows the descending order:

PAA/KG2 > PAA/KG1 > KG

It can be concluded that any of the adducts behaves as one phase, and shows approximately one step decrease in weight upon increasing the temperature. This is a result of the presence of PAA, as a homopolymer and/or graft, along with the native gum in intimate blending. Moreover, the thermal stability of the adducts is different from that of a native gum. That is, (a) the thermal stability is enhanced in case of TG adducts, and the extent of enhancement increases by increasing AA/TG ratio from 1 to 2, and (b) the thermal stability of PAA/KG2 is the highest among those of KG and PAA/TG1 within the whole range of temperature studied, and KG has a higher a thermal stability than that of PAA/KG1 up to a temperature of 260 °C, beyond which the opposite holds true.

### 3.2.3. Rheological properties

Since the adducts are intended for use as thickeners in reactive and acid printing on wool, silk and nylon 6 fabrics, therefore guar gum (GG) is selected as a reference thickener. The rheograms of 7.5% (wt/v) aqueous pastes of adducts, native gums and GG are shown in Figs. 5 and 6. It can be seen, that the pastes are of a non-Newtonian, shear thinning (pseudoplastic) flow with a clear thixotropy (Hebeish, Ibrahim, Fahmy, & Abo-Shosha, 1996). The area between the up and down curves is a measure of the extent of thixotropy (Ragheb, Abdel Thalouth, El Sayed, & Hebeish, 1991) and follows the descending order:

PAA/TG2 ≈ PAA/TG1 > PAA/KG2 ≈ PAA/KG1 > GG > TG ⩾ KG

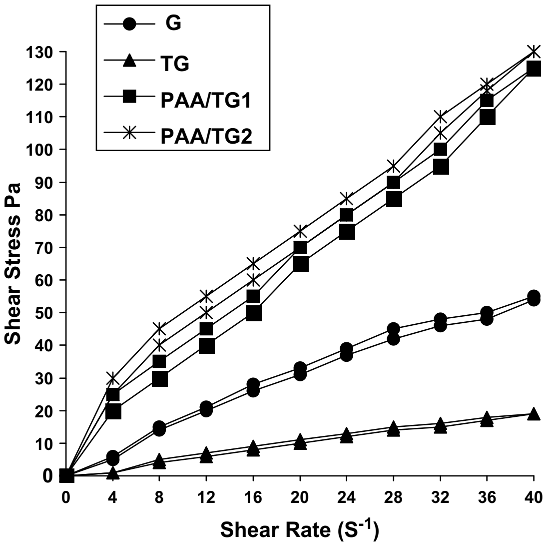

**Fig. 6.** Effect of shear rate on shear stress of 7.5% (w/v) aqueous pastes of TG and adducts as well as GG at 25 ± 0.1 °C.

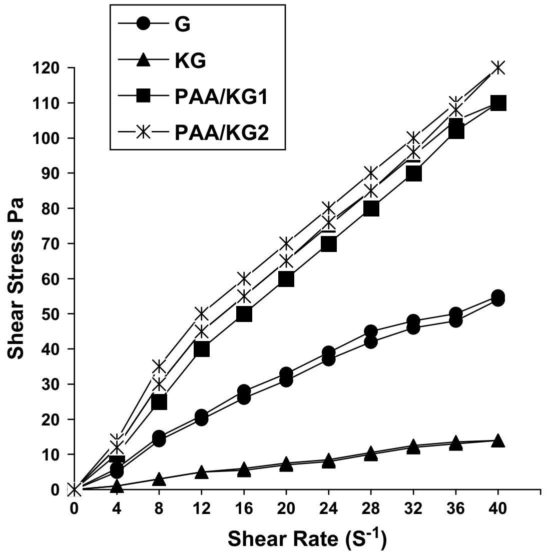

**Fig. 5.** Effect of shear rate on shear stress of 7.5% (w/v) aqueous pastes of KG and adducts as well as GG at 25 ± 0.1 °C.

Obviously, these pastes need some time to rebuild their internal structure that has been deformed during shear, which explains their thixotropic nature. The lower the extent of thixotropy is, the higher the elasticity of a solution will be. Accordingly, the rebuilding of the paste internal structures follows an opposite order of the extent of thixotropy. That is KG and TG pastes are more elastic than those of GG and other adducts. Moreover, KG adducts are more elastic than TG adducts.

The up curves, Figs. 5 and 6, represent the contour of the ceilings of resistance to shearing. So, the viscosity at the up curves should be taken into consideration in investigating these pastes for more understanding of thinning behaviors of these solutions. Therefore the apparent viscosities ($\eta$), at the up curves, of each of the pastes were calculated and plotted against shear rate as shown in Fig. 7. Close examination of Fig. 7 shows that $\eta$ decreases by increasing shear rate, under the conditions studied, regardless of gum type. This can be associated with better orientation (Hebeish et al., 1996) of polymer molecules and/or particles in the direction of rotation, which results in reducing their resistance to flow. The apparent viscosity follows the descending orders:

a. Within the shear rate range of 4–13 $s^{-1}$:

PAA/TG2 > PAA/TG1 > PAA/KG2 > PAA/KG1 > GG > TG > KG

a. Within the range of >13 and up to 40 $s^{-1}$:

PAA/TG1 > PAA/TG2 > PAA/KG2 > PAA/KG1 > GG > TG > KG

This order manifests that (a) all adducts obtained are of higher $\eta$ than those of their parent gums and guar gum, regardless of shear rate, (b) TG adducts are of higher $\eta$ than those of KG adducts, regardless of both of AA/gum ratio and shear rate, and (c) except for TG adducts beyond a shear rate of 13 $s^{-1}$, $\eta$ increases by increasing AA/gum ratio from 1 to 2.

That an adduct is of higher $\eta$ than its native gum is due to the complex nature of its ingredients, where it is a mixture of PAA, PAA-g-gum as well as intact and oxidized gum; all in a state of intimate entanglement. Increasing AA/gum ratio is logically reflected on increasing $\eta$. The latter is true for TG adducts up to a shear rate of 13 $s^{-1}$, and for KG adducts within the whole shear rate range studied. Beyond a shear rate of 13 $s^{-1}$, TG adducts behave abnormally. That is $\eta$ of PAA/TG2 is lower than that of PAA/TG1. This is not quite understandable. However a close look at Fig. 7 shows that PAA/TG2 curve is extremely steeper than that of PAA/TG1. This means that, upon shearing the first yields more and its particles orient themselves much better in the direction of rotation than the latter. This suggests that (a) the extent of entanglement in the first is lower than that in the latter, and/or (b) the extent of grafting (and hence branching) onto TG is higher in the first than that in the latter.

### 3.2.4. The power law

The power law is an empirical relationship describing the flow behavior of non-Newtonian fluids. The simplest forms of which are (Dearly & Wiss, 1990, chap. 10):

$$\tau = KD^n$$

$$\eta = KD^{n-1}$$

where $K$ and $n$ are constants at a given temperature and concentration and termed as the non-Newtonian consistency and the flow behavior index (FBI). The power law is checked on the up curves of Figs. 5 and 6, at the maximum shear stress and viscosity, which should be considered to conduct good printing performance and design of processing machinery.

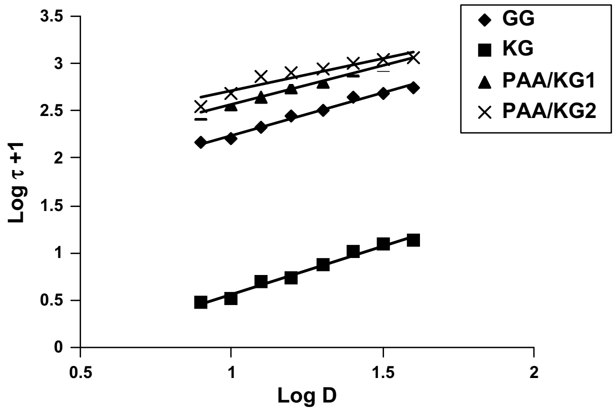

**Fig. 8.** Logarithmic plot of shear stress vs. shear rate for 7.5% (w/v) aqueous pastes of KG and adducts as well as GG at 25 + 0.1 °C.

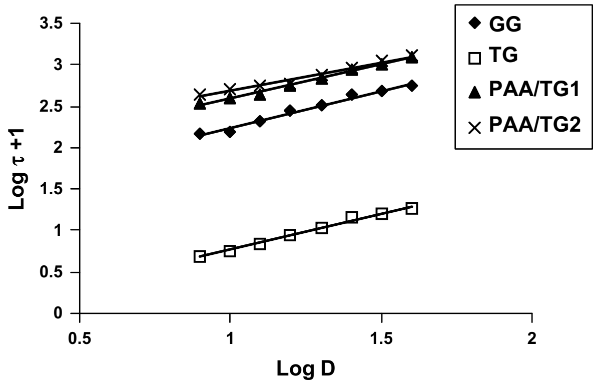

**Fig. 9.** Logarithmic plot of shear stress vs. shear rate for 7.5% (w/v) aqueous pastes of TG and adducts as well as GG at 25 + 0.1 °C.

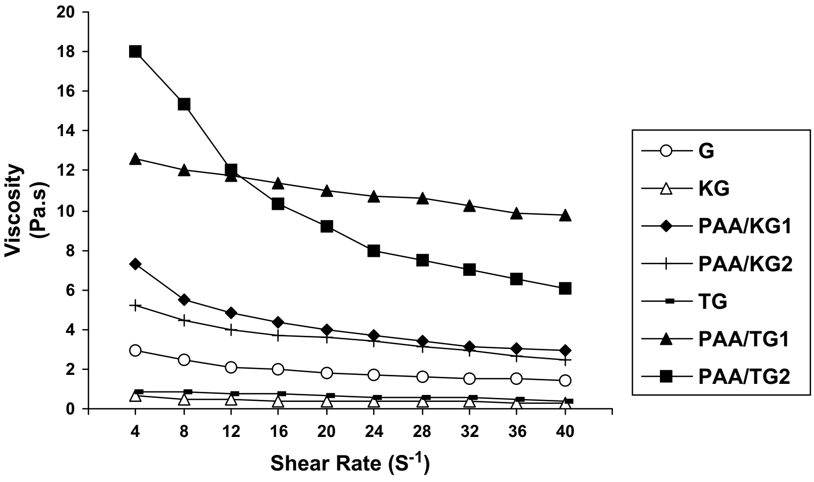

**Fig. 7.** Dependence of the apparent viscosity on shear rate of 7.5% aqueous pastes of adducts, native gums and GG at 25 ± 0.1 °C.

**Table 3**
FBI (flow behavior index) and STI (shear thinning index) values of 7.5% (w/v) pastes of adducts, native gums and GG

| Adducts | STI | FBI | FBI + STI |
|---|---|---|---|
| GG | 0.33 | 0.88 | 1.21 |
| KG | 0.26 | 0.93 | 1.19 |
| PAA/KG1 | 0.35 | 0.82 | 1.17 |
| PAA/KG2 | 0.41 | 0.82 | 1.23 |
| TG | 0.43 | 0.84 | 1.27 |
| PAA/TG1 | 0.20 | 0.81 | 1.01 |
| PAA/TG2 | 0.58 | 0.67 | 1.25 |

Fig. 8 or 9 are the logarithmic plots of shear stress vs. shear rate of the up curves of Fig. 5 or Fig. 6. Straight lines of positive slopes were obtained; the values of which are the FBIs of the pastes studied and their values are less than one as can be seen in Table 3, indicating that these solutions are pseudoplastic (Dearly & Wiss, 1990; Teli & Vyas, 1990) as has already been concluded before. The lower the FBI than unity is the more the deviation from Newtonian flow and the higher the pseudoplasticity is. Accordingly, the pseudoplasticity of the pastes follows the descending order:

- TG adducts:

$\text{PAA/TG2} > \text{PAA/TG1} \approx \text{TG} \geqslant \text{GG}$

- KG adducts:

$\text{PAA/KG2} = \text{PAA/KG1} \geqslant \text{GG} \geqslant \text{KG}$

Figs. 10 and 11 are logarithmic plots of $\eta$ vs. shear rate, where each paste is represented by a straight line of negative slope, the value of it equals to "$n - 1$". The absolute value of a slope, or $1 - n$, is termed as the shear thinning index (STI). The values of STI and FBI are listed in Table 3. The sum of FBI and STI of a paste should equal to one, however this is not the case as shown in Table 3, where only PAA/TG$_2$ correlates well to the power law by virtue of having a difference of 1%. The other pastes are of differences between 17% and 27% which means that they do not correlate well to the power law.

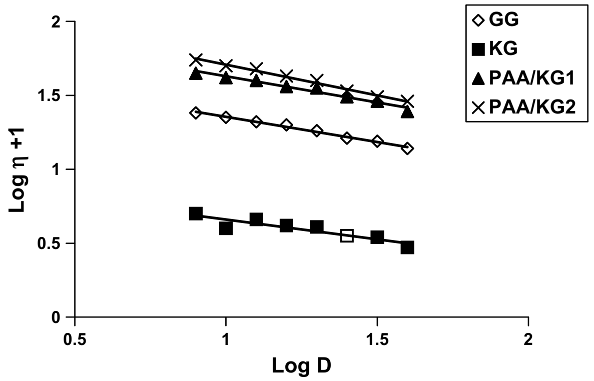

**Fig. 10.** Logarithmic plot of viscosity vs. shear rate for 7.5% (w/v) aqueous pastes of KG and adducts as well as GG at 25 + 0.1 °C.

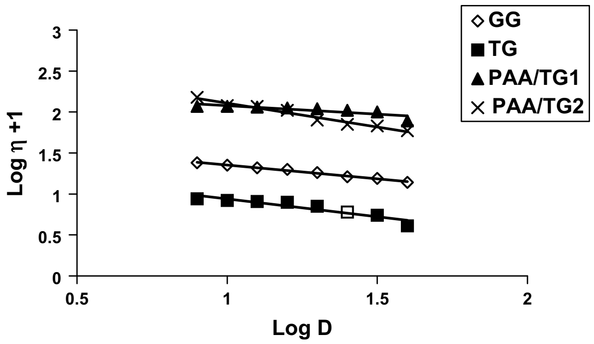

**Fig. 11.** Logarithmic plot of viscosity vs. shear rate for 7.5% (w/v) aqueous pastes of TG and adducts as well as GG at 25 + 0.1 °C.

Nevertheless, and keeping in mind that the lower the STI is, the lower the deviation from Newtonian behavior and the better the flow property is (Teli & Vyas, 1990), then the flow properties of the seven pastes follow the descending order (from

- TG adducts.

$\text{PAA/TG1} > \text{GG} > \text{TG} > \text{PAA/TG2}$

- KG adducts:

$\text{KG} > \text{GG} > \text{PAA/KG1} > \text{PAA/KG2}$

Comparing these orders with those based on FBI's reveals that either of them is not the negative image of the other. According to the power law the order of decreased pseudoplasticity should be opposite to that of increased STI values. The reason behind this is unequivocally due to the fact that the power law does not correlate well to all pastes studied. However, in printing pastes the flow properties is not only governed by pseudoplasticity, but also governed by other factors such as thixotropy, $\eta$ and interaction of thickener with other ingredients (dyestuff, catalyst, humectants, oxidizing agents, etc.) as well as storing behavior. Study of flow property of pastes of a new thickener is only a first step towards preliminary judging of its suitability to use in printing. The second step is a preliminary checking of its ability to perform sharp prints with good depth of colors. Since the majority of the function groups of these adducts are the carboxyl groups, then they are suitable for anionic printing on substrates such as wool, silk and nylon 6. This is given in the following section.

### 3.2.5. *Preliminary utilization of the adducts in anionic printing on wool, silk and nylon 6*

A reactive dye (Levafix® Golden Yellow BN) and an acid dye (Isolan® Red 2GLN), were used for printing of wool, silk and nylon 6 fabrics using a printing paste containing 75 g/k of any of the four adducts, native gums or GG. It was observed that all prints are of sharp edges; however the depth of color (K/S) depends on the type of dye, fabric and thickener as shown in Tables 4 and 5. For the same set of conditions, K/S obtained by an adduct is higher than that obtained by its native gum or GG, while TG adducts results in prints of higher K/S than those of KG adducts. It is also observed, Tables 4 and 5, for given set of conditions that: (a) increasing AA/gum ratio is accompanied by decreasing (or increasing) K/S of prints thickened by KG (or TG) adducts, (b) in case of reactive printing, K/S on nylon 6 is higher than that on wool or silk upon utilizing the same adduct and, (c) in case of acid printing, K/S obtained on wool by an adduct is higher than that obtained on silk or nylon 6 by the same adduct.

This preliminary study implicates the following: (a) the pseudoplasticity of adduct pastes results in reducing their viscosity upon shearing, allowing them to pass throw the openings of the screens in adequate flux to ensure enough loading of paste films on the fabric, and (b) both of thixotropy and pseudoplasticity allows films to rebuild their internal structures and regain their initial $\eta$ upon shear release. The net result of (a) and (b) above is a suitable film on the fabric with enough amount of dye to ensure high depth of color, and well defined edges to ensure sharpness of color. Moreover, the presence of surplus carboxyl groups in the adduct results in repelling the anionic dyes away of the films to the fabric, giving rise to high color strength.

**Table 4**
Utilization of any of the adducts, native gums or GG as thickeners in reactive printing of wool, silk, and nylon 6

| Type of fabrics | Type of thickener | | | | | | |
|---|---|---|---|---|---|---|---|
| | GG | KG | PAA/KG2 | PAA/KG2 | TG | PAA/TG1 | PAA/TG2 |
| | Depth of color (K/S) | | | | | | |
| Wool | 16.97 | 1.05 | 21.75 | 19.84 | 5.34 | 25.84 | 28.17 |
| Silk | 7.40 | 0.81 | 14.44 | 13.73 | 1.07 | 16.02 | 18.99 |
| Nylon6 | 10.63 | 6.31 | 15.96 | 14.55 | 9.15 | 16.07 | 17.81 |

Levafix® Golden Yellow BN (30 g/k); urea (100 g/k); citric acid (10 g/k); thickener (75 g/k); drying at 85 °C/5 min; steaming at (105 °C/30 min).

**Table 5**
Utilization of any of the adducts, native gums or GG as thickeners in acid printing of wool, silk, and nylon 6

| Type of fabrics | Type of thickener | | | | | | |
|---|---|---|---|---|---|---|---|
| | GG | KG | PAA/KG1 | PAA/KG2 | TG | PAA/TG1 | PAA/TG2 |
| | Depth of color (K/S) | | | | | | |
| Wool | 20.12 | 10.20 | 22.60 | 22.15 | 12.03 | 23.19 | 24.95 |
| Silk | 8.62 | 2.61 | 14.68 | 14.12 | 10.69 | 15.62 | 15.90 |
| Nylon6 | 2.84 | 9.32 | 15.22 | 8.89 | 9.64 | 18.96 | 20.21 |

Isolan® Red 2 GLN (30 g/k); urea (100 g/k); citric acid (10 g/k); Thickener (75 g/k); drying at 85 °C/5 min; steaming at (105 °C/30 min)

Correlating the flow properties, predicted by STI, to the color strength, shown in Tables 4 and 5, shows that:

- In case of TG adducts: (1) though the flow properties of TG and GG lie in between PAA/TG1 and PAA/TG2 adducts, their prints on a fabric are of lower color strength than any of the adducts on the same fabric, (2) though the flow property of PAA/TG1 adduct is better than that of PAA/TG2 adduct, the first results in lower K/S than the latter. Factors 1 and 2 suggest that the precedence in flow properties does not prevail both of the increase in $\eta$ and carboxyl content in governing the improvement in K/S, because of the fact that both of adducts are of higher $\eta$ and carboxyl content than those of TG and GG, besides PAA/TG2 is of higher carboxyl content than PAA/TG1.
- In case of KG adducts: (a) though the flow properties of both of KG and GG are better than those of the adducts, the latter are of higher color strength than either of them; it seems that the higher carboxyl content and $\eta$ of the adducts prevail the effect of enhanced flow properties of either of KG or GG, and (b) the flow properties prevails the effect of carboxyl content and $\eta$ in enhancing the color strength in the case of adducts, since PAA/TG1 is of better flow property but of lower $\eta$ and carboxyl content than those of PAA/TG2.

### 3.3. Stability to storing

Pastes of adducts (7.5% w/v), native gum and GG were stored in tightly closed containers for 3 and 7 days, then $\eta$ of each was determined and compared to that of freshly prepared pastes. The results are depicted in Table 6. In case of KG, TG and GG, it can be observed that (a) GG is completely deteriorated with the evolution of unpleasant odor after 3 days storing time, whereas KG and TG show progressive decrease in viscosity by prolonging storing time,

**Table 6**
Effect of storing time on the apparent viscosity of printing pastes

| Thickening agent used | Storing time (day) | Shear rate ($S^{-1}$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 | 8 | 12 | 16 | 18 | 24 | 28 | 32 | 36 | 40 |
| | | Viscosity (Pa.s) | | | | | | | | | |
| GG | I | 2.94 | 2.43 | 2.11 | 2.00 | 1.82 | 1.75 | 1.61 | 1.56 | 1.48 | 1.40 |
| | II | Deteriorated by fermentation | | | | | | | | | |
| | III | | | | | | | | | | |
| KG | I | 0.62 | 0.50 | 0.45 | 0.41 | 0.40 | 0.38 | 0.35 | 0.34 | 0.32 | 0.29 |
| | II | 0.56 | 0.42 | 0.34 | 0.32 | 0.31 | 0.30 | 0.28 | 0.27 | 0.26 | 0.25 |
| | III | 0.42 | 0.32 | 0.29 | 0.28 | 0.27 | 0.26 | 0.23 | 0.22 | 0.21 | 0.20 |
| PAA/KG1 | I | 5.0 | 4.50 | 4.0 | 3.72 | 3.60 | 3.40 | 3.10 | 2.90 | 2.70 | 2.50 |
| | II | 4.60 | 4.0 | 3.60 | 3.41 | 3.0 | 2.76 | 2.62 | 2.50 | 2.31 | 2.10 |
| | III | 4.40 | 3.40 | 2.80 | 2.50 | 2.21 | 2.0 | 1.93 | 1.80 | 1.76 | 1.51 |
| PAA/KG2 | I | 7.0 | 5.50 | 4.80 | 4.32 | 4.0 | 3.73 | 3.57 | 3.10 | 3.0 | 2.90 |
| | II | 4.6 | 3.86 | 3.10 | 3.0 | 2.68 | 2.50 | 2.44 | 2.20 | 2.0 | 1.99 |
| | III | 4.0 | 3.20 | 2.82 | 2.61 | 2.40 | 2.22 | 2.10 | 2.0 | 1.90 | 1.82 |
| TG | I | 0.90 | 0.86 | 0.80 | 0.78 | 0.70 | 0.60 | 0.59 | 0.54 | 0.51 | 0.40 |
| | II | 0.70 | 0.68 | 0.62 | 0.60 | 0.58 | 0.50 | 0.45 | 0.40 | 0.30 | 0.29 |
| | III | 0.26 | 0.25 | 0.24 | 0.23 | 0.22 | 0.21 | 0.20 | 0.18 | 0.16 | 0.13 |
| PAA/TG1 | I | 12.0 | 11.80 | 11.75 | 11.68 | 11.60 | 10.50 | 10.41 | 10.35 | 9.90 | 9.75 |
| | II | 11.50 | 11.0 | 10.90 | 10.81 | 10.74 | 10.32 | 9.89 | 9.75 | 9.70 | 9.60 |
| | III | 11.0 | 10.48 | 10.40 | 9.53 | 9.31 | 9.29 | 8.26 | 8.0 | 7.82 | 7.18 |
| PAA/TG2 | I | 18.2 | 16.86 | 15.20 | 11.50 | 9.32 | 8.50 | 8.20 | 7.10 | 6.80 | 6.12 |
| | II | 17.0 | 15.40 | 12.0 | 11.50 | 8.0 | 7.60 | 7.20 | 6.80 | 6.50 | 6.0 |
| | III | 14.0 | 12.50 | 10.30 | 10.0 | 7.50 | 7.30 | 6.83 | 6.30 | 5.40 | 5.0 |

I = freshly prepared; II = Stored for 3 days; III = Stored for 7 days.

(b) the extent of decrease in $\eta$ of TG is higher than that of KG, irrespective of storing time and shear rate and, (c) the major loss in $\eta$ of GG, TG and KG is due to biological fermentation and enzymatic degradation.

On the other hand, in case of adducts, Table 6 shows that storing also decreases their $\eta$ and the decrease is higher after 7 days than that after 3 days. It is probable that storing allows better swelling; compatibility and uniformity of macromolecules and/or particles of adduct, which results, more or less, in releasing entanglement, thereby decreasing the viscosity.

## 4. Conclusion

PAA/TG1, PAA/TG2, PAA/KG1 and PAA/KG2 water-soluble adducts resulted from the polymerization of 20% neutralized AA (Na form) in presence of TG or KG at AA/gum ratios 1 or 2. Infra red spectra proved the structure of these adducts. Thermal gravimetric analysis (up to 500 °C) revealed that the presence of PAA, as a homopolymer and/or graft, along with the native gum changed the thermal stability of the latter. That is: (a) the thermal stability is enhanced in case of TG adducts, and the extent of enhancement increased by increasing AA/TG ratio from 1 to 2, and (b) the thermal stability of PAA/KG2 is the highest among those of KG and PAA/TG1 within the whole range of temperature studied, and KG has a higher a thermal stability than that of PAA/KG1 up to a temperature of 260 °C, beyond which the opposite holds true. Aqueous pastes (7.5% w/v) of adducts, native gums and GG are of non-Newtonian thixotropic flow within a shear rate range of $4\text{–}40\,\mathrm{s}^{-1}$. Pastes of adducts are of higher apparent viscosities than their native gums or GG, and pastes of TG adducts are of higher apparent viscosities than KG adducts. Except for PAA/TG2 adduct, the power law does not correlate well to the aqueous pastes of other adducts, native gums or GG. Preliminary trials showed that adducts are excellent thickeners for reactive and acid printing on wool, silk and nylon 6. Color strength on prints are higher in case of adducts than that in case of native gum or GG; and TG adducts results in prints of higher color strength than those of KG adducts. Aqueous pastes of GG was completely destroyed after storing up to 7 days, whereas the apparent viscosities of pastes of adducts and native gums were noticeably decreased upon storing.

## References

Abbas, M. A. M. (2004). Printing of wool fabrics with anionic dyes using new thickeners. Ph.D. Thesis, Helwan University, Cairo.

Abo-Shosha, M. H., El Zairy, M. R., & Ibrahim, N. A. (1994). Preparation and rheology of new synthetic thickeners based on polyacrylic acid. *Dyes and Pigments, 24*, 24.

Abo-Shosha, M. H., Ibrahim, N. A., Allam, E., El-Zairy, M. R., & El-Zairy, E. (2006). Synthesis and characterization of poly acrylic acid/dexy 85 and polyacrylic acid/gum arabic adducts. *Journal of Applied Polymer Science, 101*(6), 4290.

Davidson, R. L. (1980). *Handbook of water-soluble gums and resins*. New York: McGraw-Hill. pp. 10-1, 23-1.

Dean, J. A. (1995). *Analytical chemistry handbook*. New York: McGraw-Hill.

Dearly, J. M., & Wiss, K. I. (1990). *Melt rheology and its role in plastic processing: Theory and applications*. New York: Van Nostrand Reinhold. p. 365.

Ghosh, P., Chadha, S. C., & Palit, S. R. (1964). Incorporation of hydroxyl end groups in a vinyl polymer. *Journal of Polymer Science (Part A), 2*, 441.

Hebeish, H., Ibrahim, N. A., Fahmy, H. M., & Abo-Shosha, M. H. (1996). Reheological behavior of some polymeric sizing agents alone and in admixtures. *Polymer Plastics Technology and Engineering, 35*(4), 517.

Ibrahim, N. A., Rashad, M. M., & Abo-Shosha, M. H. (2003). Polyacrylamide guar gum adducts as a new thickener for reactive printing of wool and nylon 6. *Polymer Plastics Technology and Engineering, 42*(5), 757.

Ibrahim, N. A., Abo-Shosha, M. H., Allam, E., El-Zairy, M. R., & El- Zairy, E. (2006). New thickening agents for reactive printing of cellulosic fabrics. *Journal of Applied Polymer Science, 101*(6), 4430.

Pavia, D. L., Lampman, G. M., & Kriz, G. S. (2001). *Introduction to spectroscopy* (3rd ed.). San Diego, New York: Harcourt College Publisher.

Ragheb, A., Abdel Thalouth, I. A., El Sayed, H., & Hebeish, A. (1991). Preparation and characterization of carboxymethyl cellulose from jute wastes. *Indian Journal of Fiber & Textile Research, 16*(3), 263.

Savur, G. R. (1956). Mellian Textilber, Use of pectin from tamarind seeds in the textile industry. *Chemical Abstracts 37,* 588; (*50,* 15091).

Sorum, C. H., & Edwards, J. O. (1952). Oxidation of thiosulfate ion by peroxydisulfate ion. *Journal of American Chemical Society, 74*, 1204.

Srivastava, H. C., Gharia, S. M., & Mudis, G. P. (1972). Synthesis of chlorodeoxy cellulose and its conversion to 5,6-cellulosene. *Journal of the Textile Association, 33*, 139.

Teli, M. D., & Vyas, U. V. (1990). Rheological behavior of textile thickeners. *American Dyestuff Reporter, 79*(2), 15.

Welcher, F. G. (1965). *Standard methods of chemical analysis, Part A*. New York: Van Nostrand. p. 475.