Carbohydrate Polymers 76 (2009) 8–16

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

A study of rheological and molecular weight properties of recycled polysaccharides used as thickeners in textile printing

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ARTICLE INFO

Article history:
Received 17 July 2008
Received in revised form 8 September 2008
Accepted 15 September 2008
Available online 30 September 2008

Keywords:
Polysaccharides
Reactive dye printing pastes
Thickener recycling
Rheology
Molecular weight averages and molecular weight distribution

ABSTRACT

Polysaccharide thickeners (alginate, carboxymethylated guar gum and carboxymethylated cellulose) used for the preparation of printing pastes, were recycled from printing paste residues and from wastewater concentrates, which were separated by ultrafiltration technique from wastewater after screen printing of cotton with reactive dyes. Concentrated aqueous polysaccharide solutions were studied via rheological measurements under steady and oscillatory shear conditions. Molecular weight averages and molecular weight distribution of thickeners were determined by size exclusion chromatography.

A satisfactory fitting of viscosity data is obtained with the Cross equation and mechanical spectra are described with satisfactory approximation with the Friedrich–Braun model. The obtained parameters enable a quantitative interpretation of the changes in rheological properties. Moderate changes produced by thickener recycling on the shear-thinning and viscoelastic behaviour of polymers are a direct result of changes in molecular weight averages (MWA) and molecular weight distribution (MWD).

1. Introduction

Thickeners are components of a printing paste that impart a printable, pasty consistency to an aqueous solution containing dye(s) and other printing paste additives. Thickeners are used in textile screen printing to obtain sharp, clean drawing patterns by preventing dye migration. In other words thickeners modulate adequate rheological properties that ensure a homogenous distribution of the printing paste on the screen and its uniform flow through the screen openings. During the first step of the application process, high strain rate conditions are present, while after being forced through the screen openings and deposited on the fabric, the paste will continue to flow at very low shear rates. Elasticity affects both the flow behaviour of the paste through the screen openings to the fabric and the following step (flow through the fibers) by governing possible recovery of the paste immediately after its application (Lapasin & Pricl, 1995; Lapasin, Pricl, Graziosi, & Molteni, 1988).

During textile printing large amounts of paste residues are produced after cleaning of application systems in the printing machines (drums, screens, squeegees, etc.) and of colour kitchen equipment after each colour change. In this way considerable amounts of residual printing pastes have to be tackled and a lot are still discharged to the effluent. The substances, which are removed to the wastewater, are thickener, unfixed dye and auxiliaries applied to the material as part of the printing process, and thus cause severe wastewater problems by appreciably increasing the COD (50,000–300,000 mg O_2/L), nitrogen and dye loads. The concentration of these components in the wastewater depends on the component concentration in the printing paste formulation (Lacasse & Baumann, 2004).

Printing pastes that adhere to every implement due to their high viscosity can be removed before rinsing with water by dry capture systems. In this way, these residues can at least be disposed off in segregated form, thus minimizing water consumption. Considering a separate collection of printing pastes residues at a printing factory might allow for their treatment and disposal by more suitable processes, such as incineration, landfilling after drying or anaerobic treatment (Bonomo, Rozzi, & Malpei, 1997; Malpei, Andreoni, Daffonchio, & Rozzi, 1998a; Malpei, Bonomo, & Rozzi, 1998b).

Separate collection of printing pastes enables also the opportunity of recycling. Considering the reuse the composition of every residual printing paste is saved and the formulation of new printing pastes is calculated. In this way the quantity of residual printing pastes to be disposed off is significantly reduced both in wastewater and solid waste. The amount of residual printing paste is reduced to 50% at least, in many cases to about 70% (Lacasse & Baumann, 2004). Conversely, recycling of storage printing pastes

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doi:10.1016/j.carbpol.2008.09.027

brings disadvantages, such as decrease of colour depth due to partial hydrolysis of the dye in the presence of alkali (sodium carbonate or sodium bicarbonate) and/or changes in the thickener structure brought about by its interactions with other components of the printing paste. As a result, the extent of dye fixation and fastness properties of the printed samples decrease marginally (Ibrahim, El-Zairy, & Abo-Shosha, 1994; Ibrahim, Abo-Shosha, El-Zairy, Allam, & El-Zairy, 2006).

A promising perspective for reducing wastewater loads in textile printing and treatment of printing paste residues is the recycling of thickener, proposed by Marte and Meyer (1995). The patented processing principle (tested on sodium alginate and polyacrylate based reactive printing pastes with sodium bicarbonate as alkali) works according to the extrusion process of wastewater concentrates and printing paste residues, where the thickener is precipitated in a water-solvent mixture at a defined pH. Subsequent extraction of the dyestuff from the thickener threads is performed in the following extraction baths to achieve a quantitative dye removal. Schneider (1997) studied the precipitation and properties of alginate thickener recycled from concentrates of washing water after reactive printing (with sodium bicarbonate as alkali), which can be separated by using ultrafiltration technique. The thickener can be eliminated from washing water and almost quantitatively recycled.

The recycling of printing thickeners from printing paste residues and wastewater concentrates represents an important step in solving ecological problems in the textile printing industry by reducing solid wastes and wastewater pollution. The results of this research provide a complete characterization of rheological and molecular weight properties of recycled thickeners, which are strongly connected to the printing performance of screen printing on cellulosic fibres with reactive dyes.

2. Experimental

2.1. Materials

Three types of medium viscous industrial thickeners were used in this research, namely alginate (A), carboxymethylated guar gum (CMG) with degree of substitution DS = 0.3 and carboxymethylated cellulose (CMC) with DS = 1.1. The polymers were produced and supplied by a specialized industrial manufacturer of natural thickeners for textile printing Lamberti S.p.a. (Italy).

Two commercially available monofunctional dyes, with a monochlorotriazine reactive group (Ymct), namely Procion Yellow PX-6GN (contains C.I. Reactive Yellow 95; produced by Dystar, Germany) and a vinylsulphone reactive group (Yvs), namely Benzactiv Yellow V-GR 133 (contains C.I. Reactive Yellow 15; produced by Bezema AG, Switzerland) were used for the preparation of printing paste residues.

Other printing paste additives (Table 1), namely salts and urea were provided by Sigma–Aldrich (Germany) and were of pure grade; rapidoprint XRN Pearls (sodium-m-nitrobenzene sulphonate) was supplied by Bezema AG (Switzerland). Alkali, namely sodium carbonate or sodium bicarbonate, are used to produce ionization of accessible cellulose hydroxyl groups of the fibre, which can then react with the reactive dye. Urea is added to increase the solubility of the reactive dye in the printing paste, to accelerate migration of the dye from the thickener film into the fibre and most importantly for optimal fixation of the reactive dye in superheated steam. Sodium-*m*-nitrobenzene sulphonate is used as a weak oxidizing agent in the printing paste to offset the reactive dye's sensitivity to reduction during steaming.

2.2. Preparation of printing paste residues and wastewater after reactive dye printing

The thickener (original or recycled) was added to demineralised water, stirred with a mixer and left in a refrigerator overnight to attain full swelling. For preparation of the printing pastes residues, printing paste additives and dyestuff were added to the thickener solution at ambient temperature and stirred for further 15–20 min. All printing pastes were adjusted to an equal viscosity in the range of (7.3 ± 0.8) Pas at shear rate 10 s^{-1} (at 25 °C) by the amount of water addition. The recipes of textile printing paste residues used for thickener recycling are shown in Table 1.

The synthetically prepared wastewater was adapted from the cleaning-up operations by diluting printing paste residues (containing original thickeners of A, CMG or CMC) with distilled water at ratio 1:6.

2.3. Preparation of wastewater concentrates with ultrafiltration technique

Separation of wastewater concentrates from synthetically prepared wastewater was performed with flat sheet polysulphone ultrafiltration membranes (pressure range 1–10 bars, pH range 1–13 and temperature range 0–75 °C; Alfa Laval, Denmark). Separation of wastewater concentrates from synthetically prepared wastewater with CMG thickener was performed with GR40PP membrane (molecular weight cut-off 100,000). Wastewater concentrates containing A and CMC thickeners were separated with membrane GR51PP (molecular weight cut-off 50,000).

The experiments were carried out in a modified DDS Lab 20 in a cross-flow mode of filtration, where membranes of the same type were installed in pair. The system was operated in a batch mode. A volume of 5.5 L of synthetically prepared wastewater was treated and the filtrations were performed in a concentration mode. The volume of removed permeate was 80% V/V of the initial feed volume.

Table 1
Printing paste recipes

Printing paste additive		Original thickener			Thickener recycled 1x	
		A	CMG	CMC % w/w	A	CMG
Thickener stock solution				X[a]		
(thickener content in stock solution)		6	6	8	6	5
Oxidative agent				1		
Alkali	Sodium carbonate or			2.5		
	Sodium bicarbonate			3		
Urea				15 (with sodium carbonate)		
				10 (with sodium bicarbonate)		
Dyestuff: Ymct or Yvs				3		
Water				Y[a]		

[a] The amount of thickener stock solution (X) and water (Y) was adjusted to fit the commonly used rheological constraint of equal viscosity (at 25 °C) in the range of (7.3 ± 0.8) Pas at shear rate $10_s{}^{-1}$

For the determination of operational conditions experiments were carried out in the total recycle mode where permeate (representing the portion of the feed solution passing through the membrane) along with the concentrate (representing the portion of the feed solution that is retained on the high-pressure side of the membrane) were recycled back into the feed tank. Permeate was only periodically collected at pressures from 1 to 8 bar, when steady-state was reached. The filtrations were carried out at cross-flow velocity 0.6 m/s. The determined operational pressure of GR40PP membrane was 2 bars and of GR51PP membrane 4 bars. A single pump was employed to provide both cross-flow flush and operational pressure for permeate production.

2.4. Recycling of thickeners from printing paste residues and wastewater concentrates and thickener cleaning

"Cleaning" of the printing paste residues was obtained by extrusion (with a syringe) of the prepared printing paste into an ethanol–water mixture at pH 4–5 (60% w/w for A and CMG and 85% w/w for CMC based printing paste residues; 90% w/w for A, CMG and CMC based wastewater concentrates). The mass ratio of the ethanol–water mixture to the printing paste residues was 3:1. While the polymer precipitated, the dyestuff and other chemical additives present in the printing paste were removed. The procedure was performed in an ultrasonic bath (Elmasonic S 30 H (Elma, Germany)) to accelerate the migration of the dye from the precipitated thickener threads to the solvent mixture. The thickener threads were collected and adequate extraction (in 60% w/w ethanol–water solution) of the remained dyestuff was achieved in subsequent extraction baths (4–5 for A thickeners; 5–6 for CMG thickeners; 9 for CMC thickeners from printing paste residues and 5–6 for CMC thickeners from wastewater concentrates). At the end of the "cleaning" cycle thickener threads were dried at room temperature (2 days), milled and subsequently dried in a drier at 40 °C (2 days). The procedure was repeated for "cleaning" of printing paste residues prepared with the primarily recycled A and CMG thickeners and thus secondarily recycled thickeners were obtained. Due to difficulty of cleaning CMC precipitates, the secondary recycled thickeners were not obtained.

Aqueous solutions of original A, CMG and CMC thickeners were purified by precipitation and subsequent cleaning in ethanol–water solution as described above (3–4 washing baths).

2.5. Rheological measurements

Rheological characterization was performed for concentrated solutions of original thickeners, cleaned original thickeners, thickeners recycled from printing paste residues and from membrane filtration concentrates. Polymer aqueous systems were prepared by adding the dry polymer into distilled water during stirring. The aqueous solution concentration of the thickener stock solution was chosen to fit the rheological constrain of equal viscosity (at 25 °C) of the corresponding printing pastes: $\eta = (7.3 \pm 0.8)$ Pas at $\dot{\gamma} = 10\,\mathrm{s}^{-1}$. CMG thickeners were studied at 5% w/w of polymer stock solution concentration, A thickeners at 6% w/w stock solution concentration and CMC thickeners at 8% w/w stock solution concentration. All the systems were left overnight in the refrigerator to attain full swelling.

Rheological measurements, namely rotational and oscillatory measurements, were carried out at 25 °C and performed with a rotational controlled stress rheometer Haake RS150 (Searle system) using cone-and-plate (C60/1) measuring device, where a non-contact motor applied a known torque to a sample through the measuring system supported on a virtually zero friction air bearing provided by an air supply unit. The resultant displacement (strain or strain rate) was measured. The apparatus was computer controlled (RheoWin software program) and the temperature was maintained with a thermostat HAAKE TC500.

Rotational measurements, namely flow curves ($\eta = f(\dot{\gamma})$) were performed setting $\sigma = 0.1 - 1000$ Pa. Oscillatory measurements, namely frequency sweep tests ($G', G'' = f(\omega)$), were performed at $f = 100$–0.01 Hz setting the limit of viscoelastic region at $\gamma = 0.1$, that was previously determined with stress sweep tests ($G', G'' = f(\sigma)$) in the range of 0.1–300 Pa at $f = 1$ Hz.

2.6. Size exclusion chromatography (SEC)

Molecular weight averages (MWA) and molecular weight distribution (MWD) of original thickeners, cleaned original thickeners, thickeners recycled from printing paste residues and from membrane filtration concentrates were determined by relative method SEC. SEC measurements were performed at room temperature using a Hewlett Packard 1100 series pump and detector Agilent 1100 series differential refractometer operating at 30 °C. Separations were carried out using 8 μm PL aquagel-OH mixed column (300 mm length and 7.5 mm i.d., Polymer Laboratories, UK) with a precolumn in 0.2 M solution of $NaNO_3$ in bidistilled water. The pH of the solution was adjusted to 9.8. The nominal flow rate of the eluent was 1.0 mL/min. The mass of the samples injected into the column was typically 1.25×10^{-4} g, whereas the solution concentration was approximately 2.5×10^{-3} g/mL (injection volume: 50 μL). Data acquisition and evaluation was utilized with WinGPC Unity software (Polymer Standards Service, PSS, Germany). MWA of samples were calculated based on polysaccharide calibration curve constructed from pullulan standards with weight average molecular weights: 1,660,000; 788,000; 404,000; 112,000; 11,800; 180 (Polymer Laboratories, UK) and narrow MWD using polynomial regression of the third order.

3. Results and discussion

3.1. Steady shear properties

The influence of primary (A, CMG and CMC thickeners; marked as 1 and 3) and secondary (A and CMG thickeners; marked as 2 and 4) recycling of thickeners obtained from printing paste residues, using sodium carbonate (marked as 1 and 2) or sodium bicarbonate as alkali (marked as 3 and 4) was investigated. In addition, research was performed on thickeners recycled from waste water concentrates, which were separated from synthetically prepared wastewater by using ultrafiltration technique (A, CMG and CMC thickeners recycled from membrane filtration concentrates; marked as mfc).

The results presented in Fig. 1 show that concentrated solutions of thickeners exhibit non-Newtonian pseudoplastic behaviour. The shear-thinning behaviour is similar within each group of polymer systems prepared with the same thickener. Data fitting of shear thinning behaviour was obtained using a 4 parameter model, namely Cross equation (Cross, 1965):

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\dot{\gamma})^n} \tag{1}$$

where η_0 and η_∞ are the asymptotic values of the viscosity at zero and infinite shear rates, respectively, λ is the characteristic time and n rules the shear dependence in the power law region. The objective function (OF) used in the minimization procedure is given as:

$$\mathrm{OF} = \sum_{i=1}^{N} \left(1 - \frac{\eta_{i,\mathrm{cal}}}{\eta_{i,\mathrm{exp}}}\right)^2 \tag{2}$$

where N is the number of measurements and $\eta_{i,\mathrm{cal}}$, $\eta_{i,\mathrm{exp}}$ are calculated and experimental viscosity, respectively. The number of

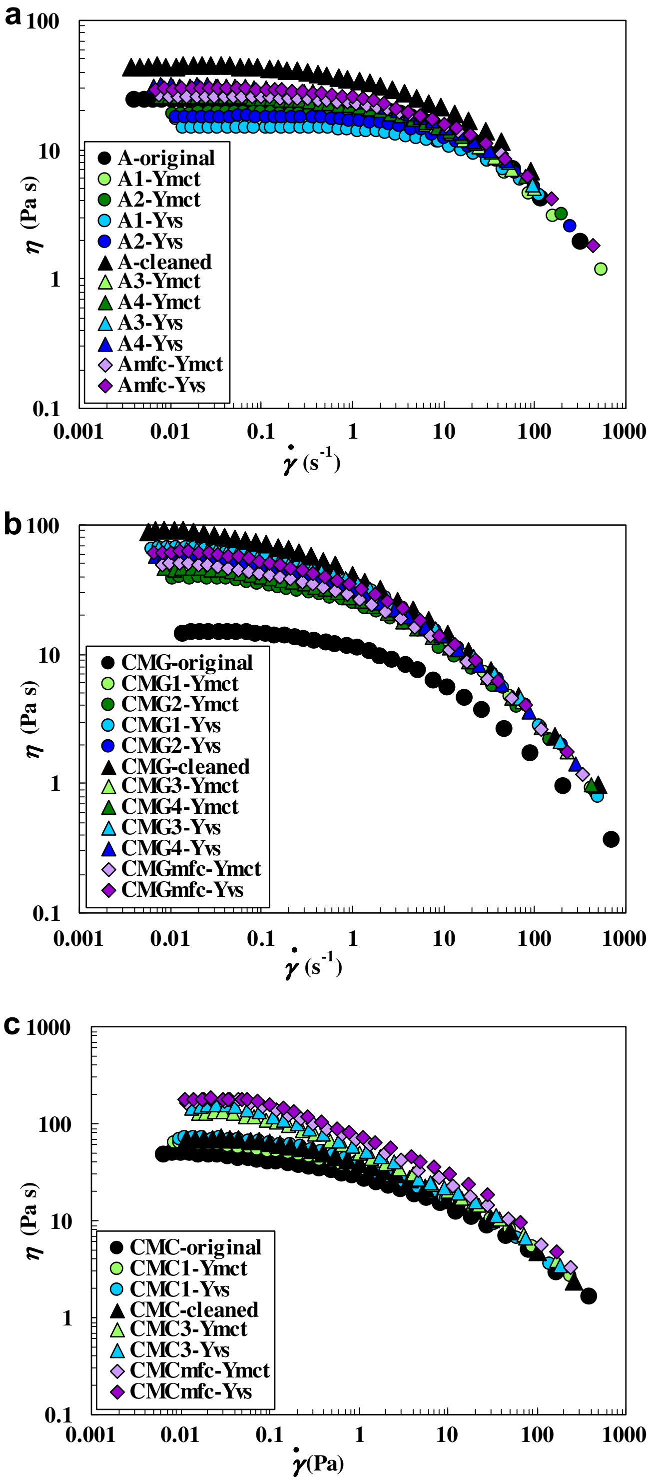

Fig. 1. Flow curves (a) A, (b) CMG and (c) CMC thickeners.

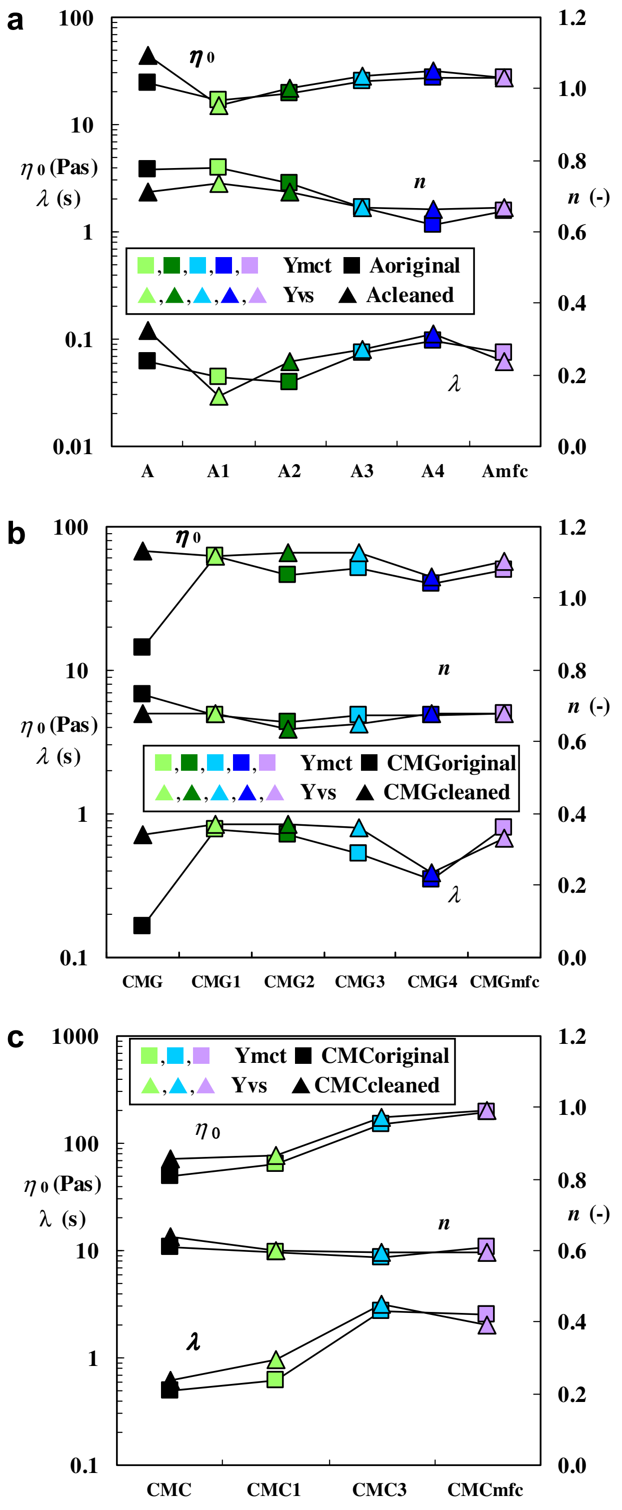

Fig. 2. Cross model parameters (a) A, (b) CMG and (c) CMC thickeners.

adjustable parameters is reduced to 3 by arbitrarily setting η_∞ to 8.9×10^{-4} Pa s (the viscosity of water solvent at the corresponding temperature, 25 °C). The model parameters η_0, n and λ, obtained with data fitting are gathered in Fig. 2.

The critical shear rate $\dot{\gamma}_c$ that marks the transition from the Newtonian plateau to the power-law region, was arbitrarily derived from the following criterion: $\dot{\gamma} = \dot{\gamma}_c$ when $\eta/\eta_0 = 0.90$. Table 2 shows the critical shear rate values calculated with the Cross parameters.

The flow curves and the model parameters of the different sets of polymer systems clearly show discrepancies in the rheological behaviour produced by the recycling procedure. The results obtained for recycled A thickeners (Figs. 1 and 2a) show a drop in viscosity over the whole experimental shear rate range, if thickeners recycled from paste residues prepared with sodium carbonate are compared to the original thickener, which is used as such in the printing process. For such systems the transition from the first

Table 2
Critical shear rates for the thickeners calculated with the Cross model; crossover frequency, crossover storage and loss moduli, and shifting factors calculated with the Friedrich–Braun model

	Critical shear rate (s^{-1})	Crossover ω (rad/s)	Horizontal shift factor a	Crossover G',G'' (Pa)	Vertical shift factor b
A-original	0.939	182.31	1.000	692.0	1.000
A1-Ymct	1.368	200.34	0.910	612.1	1.131
A2-Ymct	1.269	219.80	0.829	702.0	0.986
A1-Yvs	1.738	181.85	1.003	544.7	1.271
A2-Yvs	0.725	189.99	0.960	605.3	1.143
A-cleaned	0.379	94.92	1.921	568.5	1.217
A3-Ymct	0.499	188.61	0.967	635.1	1.090
A4-Ymct	0.299	207.41	0.879	681.5	1.016
A3-Yvs	0.462	158.77	1.148	616.7	1.122
A4-Yvs	0.321	126.12	1.446	555.8	1.245
Amfc-Ymct	0.475	113.19	1.611	570.2	1.214
Amfc-Yvs	0.616	161.21	1.131	661.3	1.046
CMG-original	0.306	43.72	1.000	113.0	1.000
CMG1-Ymct	0.049	19.52	2.240	180.8	0.625
CMG2-Ymct	0.049	31.37	1.394	183.1	0.617
CMG1-Yvs	0.047	20.20	2.164	173.1	0.653
CMG2-Yvs	0.037	27.06	1.616	188.9	0.598
CMG-cleaned	0.054	18.02	2.426	193.4	0.584
CMG3-Ymct	0.073	24.96	1.752	193.4	0.585
CMG4-Ymct	0.113	27.50	1.590	190.5	0.593
CMG3-Yvs	0.042	24.37	1.794	201.7	0.560
CMG4-Yvs	0.101	24.58	1.779	203.1	0.557
CMGmfc-Ymct	0.050	28.11	1.555	183.6	0.615
CMGmfc-Yvs	0.059	20.75	2.107	191.0	0.592
CMC-original	0.055	111.60	1.000	483.0	1.000
CMC1-Ymct	0.041	103.48	1.079	470.5	1.027
CMC1-Yvs	0.027	99.63	1.120	514.4	0.939
CMC-cleaned	0.051	99.48	1.122	551.5	0.876
CMC3-Ymct	0.008	71.07	1.570	522.9	0.924
CMC3-Yvs	0.008	68.81	1.622	526.2	0.918
CMCmfc-Ymct	0.011	80.09	1.393	584.9	0.826
CMCmfc-Yvs	0.012	58.86	1.896	561.7	0.860

Newtonian region to the power-law region is slightly shifted to higher shear rates (Table 2). The opposite effect is observed for thickeners recycled from printing paste residues prepared with sodium bicarbonate as alkali and thickeners recycled from membrane filtration concentrates. Accordingly, the departure from zero-shear viscosity is slightly displaced to lower shear rates (Table 2). Compared to the cleaned original thickener the recycled thickeners and the original thickener show a viscosity drop over the whole shearing region.

The results of recycled CMG (Figs. 1 and 2b) and CMC (Figs. 1 and 2c) thickeners show an increase in the viscosity over the whole shear region comparing to the original thickener. The transition from the first Newtonian region to the power-law region is thus shifted towards lower shear rates (Table 2).

The effect of primary and secondary recycling shows slight decrease in the viscosity properties of secondary recycled thickeners (compared to primary) from printing paste residues prepared with CMG as thickener, whilst the opposite effect is seen for secondary recycled A thickeners.

3.2. Linear viscoelastic properties

The viscoelastic properties of concentrated polymer solutions were examined by dynamic tests in the linear viscoelastic regime, whose extension was determined by strain sweep tests. The Soskey and Winter (1984) equation was used to describe the strain dependence of the complex modulus $G^*(\gamma)$:

$$\frac{G^*}{G^*_0} = \frac{1}{1 + b\gamma^n} \tag{3}$$

where G^*_0 is the complex modulus in the linear viscoelastic regime, and b and n are adjustable parameters.

The critical strain amplitude γ^0_c which marks the upper limit of the linear viscoelastic regime, is arbitrarily derived from the following criterion: $\gamma^0 = \gamma^0_c$ when $G^*/G^*_0 = 0.95$. The objective function used in the minimization procedure is given as:

$$\mathrm{OF} = \sum_{i=1}^{N} \left(1 - \frac{G^*_{i,\mathrm{cal}}}{G^*_{i,\mathrm{exp}}}\right)^2 \tag{4}$$

where N is the number of measurements and $G^*_{i,\mathrm{cal}}$, $G^*_{i,\mathrm{exp}}$ are calculated and experimental complex modulus, respectively.

The critical strain values from strain sweep data at 1 Hz, obtained from data fitting with the Soskey–Winter equation, are typical of ordinary polymer solutions. For A and CMC systems the values are in the range of 0.7–1.1, while γ^0_c varies between 0.2 and 0.4 for CMG systems.

The results of oscillatory shear presented in terms of mechanical spectra show that within the group of systems prepared with the same thickener similar viscoelastic properties are exhibited. As seen from the mechanical spectra (Fig. 3), in the low frequency region a predominantly liquid like behaviour is observed, G' increases more rapidly with respect to G''. As ω increases, the crossover of the $G'(\omega)$ and $G''(\omega)$ curves can be observed within the experimental window. Beyond the intersection of G' and G'', a region then appears where the solution exhibits predominant elastic properties. Such patterns of mechanical spectra are typical of ordinary polymer solutions where the temporary topological constraints (entanglements) between the polymer chains govern the rheological responses of the systems.

The mechanical spectra were fitted with the Friedrich–Braun model (Friedrich & Braun, 1992):

$$\underline{\underline{\sigma}} + \lambda^c D^c[\underline{\underline{\sigma}}] = G_e\{D^0[\underline{\underline{\gamma}}] + \lambda^c D^c[\underline{\underline{\gamma}}]\} + \Delta G \lambda^d D^d[\underline{\underline{\gamma}}] \tag{5}$$

where $\underline{\underline{\gamma}}$ is the deformation tensor, $\underline{\underline{\sigma}}$ is the stress tensor, λ is a characteristic relaxation time, G_e is the equilibrium modulus, ΔG is a parameter which rules the magnitude of the viscoelastic response,

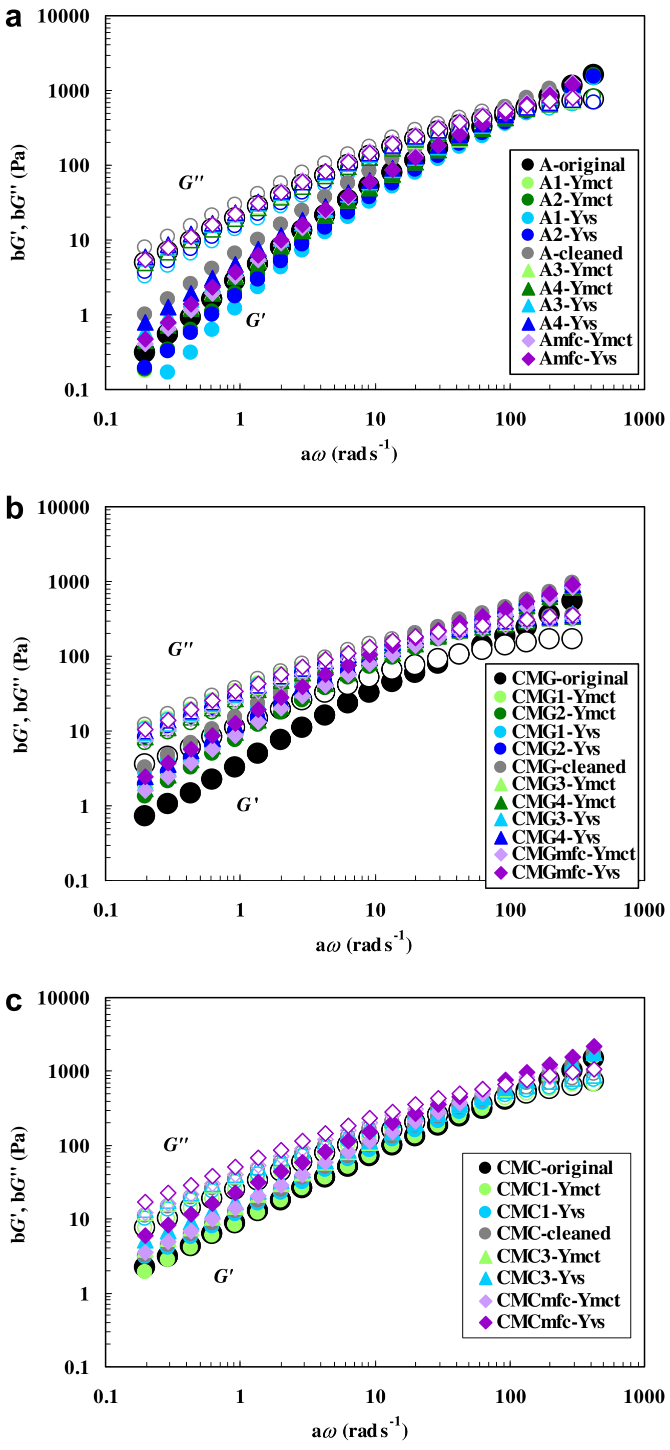

Fig. 3. Mechanical spectra (a) A, (b) CMG and (c) CMC thickeners.

and c and d are the derivation orders of fractional derivatives D^c and D^d. The model provides adequate correlation of loss (Eq. (6)) and storage (Eq. (7)) moduli as the function of frequency for all polymer systems:

$$G'(\omega) = G_e + \Delta G \frac{(\lambda\omega)^d \left[\cos\frac{\pi}{2}d + (\lambda\omega)^c \cos\frac{\pi}{2}(d-c)\right]}{1 + 2(\lambda\omega)^c \cos\frac{\pi}{2}c + (\lambda\omega)^{2c}} \tag{6}$$

$$G''(\omega) = \Delta G \frac{(\lambda\omega)^d \left[\sin\frac{\pi}{2}d + (\lambda\omega)^c \sin\frac{\pi}{2}(d-c)\right]}{1 + 2(\lambda\omega)^c \cos\frac{\pi}{2}c + (\lambda\omega)^{2c}} \tag{7}$$

The yielding conditions $0 < c < d \leqslant 1$ and $G_e \geqslant 0$ must be satisfied in order to satisfy physical constraints. The model parameters were determined by applying the fitting procedure simultaneously to both $G'(\omega)$ and $G''(\omega)$ data: so doing, for all the polymer systems under examination G_e converges to the limiting condition ($G_e = 0$). Consequently, the frequency dependence of the viscoelastic moduli is described by resorting to only four adjustable parameters (ΔG, λ, c and d), whose values can be conveniently compared in order to detect the differences between the polymer systems examined, as shown in Fig. 4. The objective function used in the minimization procedure is given as:

$$\mathrm{OF} = \sum_{i=1}^{N} \left(\left(1 - \frac{G'_{i,\mathrm{cal}}}{G'_{i,\mathrm{exp}}}\right)^2 + \left(1 - \frac{G''_{i,\mathrm{cal}}}{G''_{i,\mathrm{exp}}}\right)^2 \right) \tag{8}$$

where N is the number of measurements and $G'_{i,\mathrm{exp}}$, $G''_{i,\mathrm{exp}}$ are experimental storage and loss modulus, and $G'_{i,\mathrm{cal}}$, $G''_{i,\mathrm{cal}}$ are calculated storage and loss modulus, respectively.

Comparing the original, cleaned and recycled polymers a variation of model parameters is seen in all polymer systems. The derivation orders, c and d, of the differential operators, regulate the profiles of $G'(\omega)$ and $G''(\omega)$. The changes in the parameters c and d affect the shape of the curve $G'(\omega)$ (markedly in A and CMG systems, see master curves in Fig. 5a and b) in the whole frequency range, whereas the material function $G''(\omega)$ is slightly modified only at higher frequencies. These observations are clearly discernible in relative master curves obtained by superimposing the dynamic properties of the recycled (and cleaned original) thickener solutions with regard to the corresponding original thickener solution (Fig. 5). The crossover condition ($G'(\omega)$=$G''(\omega)$) calculated with the Friedrich–Braun model (Table 2) of the material can be explicitly determined from the following equation:

$$(\lambda\omega)^c = \frac{\sin\left(\frac{\pi}{2}d\right) - \cos\left(\frac{\pi}{2}d\right)}{\cos\left(\frac{\pi}{2}(c-d)\right) - \sin\left(\frac{\pi}{2}(c-d)\right)} \tag{9}$$

The differences in parameter ΔG show variations in the magnitude of both moduli. The patterns of the mechanical spectra for recycled A thickeners slightly differ from the original thickener solution. A decrease of the viscoelastic properties (the decrease in parameter ΔG, Fig. 4a) is noticed for the thickeners recycled from printing paste residues prepared with sodium carbonate as alkali, whilst an increase of both moduli (increase of ΔG values, Fig. 4a) is evident in the case of thickeners recycled from printing paste residues prepared with sodium bicarbonate and thickeners recycled from membrane filtration concentrates, as well as for the cleaned original thickener.

Mechanical spectra of recycled CMG thickeners and CMC thickeners as well as the cleaned original thickeners show an increase of viscoelastic properties (increase in ΔG, Fig. 4b and c) with respect to the original thickener solution, which is highlighted by the shifting of the crossover condition towards higher G' and G'' values and lower frequencies (Table 2).

3.3. Molecular weight properties and rheological parameters

MWA and MWD of the investigated thickeners were determined with reference to pullulan polysaccharide standards and are presented in Table 3. Owing to different chemical structure of pullulan standards and investigated polymer thickeners the MWA values obtained for A, CMG and CMC polymers are useful for relative comparisons rather than for absolute considerations. The results show moderate changes in molecular weight properties produced by cleaning and recycling treatments with no influence of the type of dye used, however changes in MWA of different sign are associated to different polymer-alkali combinations and to the

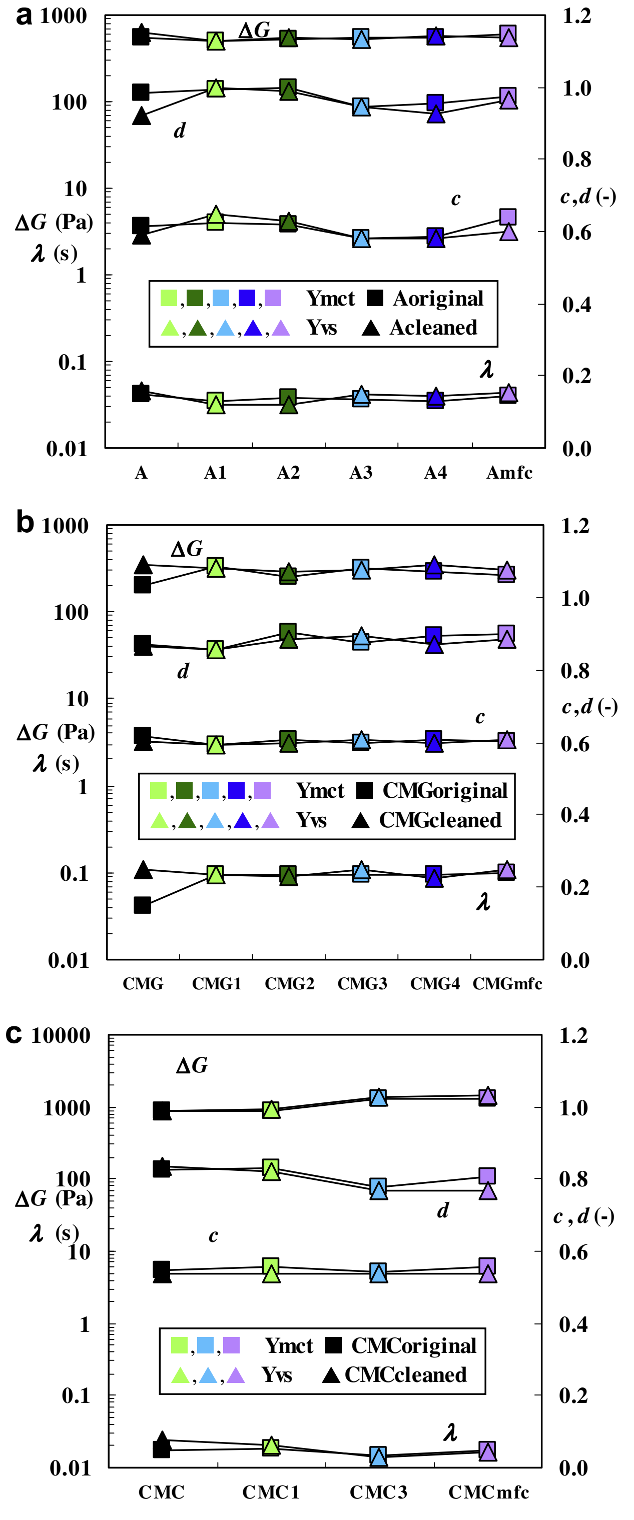

Fig. 4. Friedrich–Braun model parameters (a) A, (b) CMG and (c) CMC thickeners.

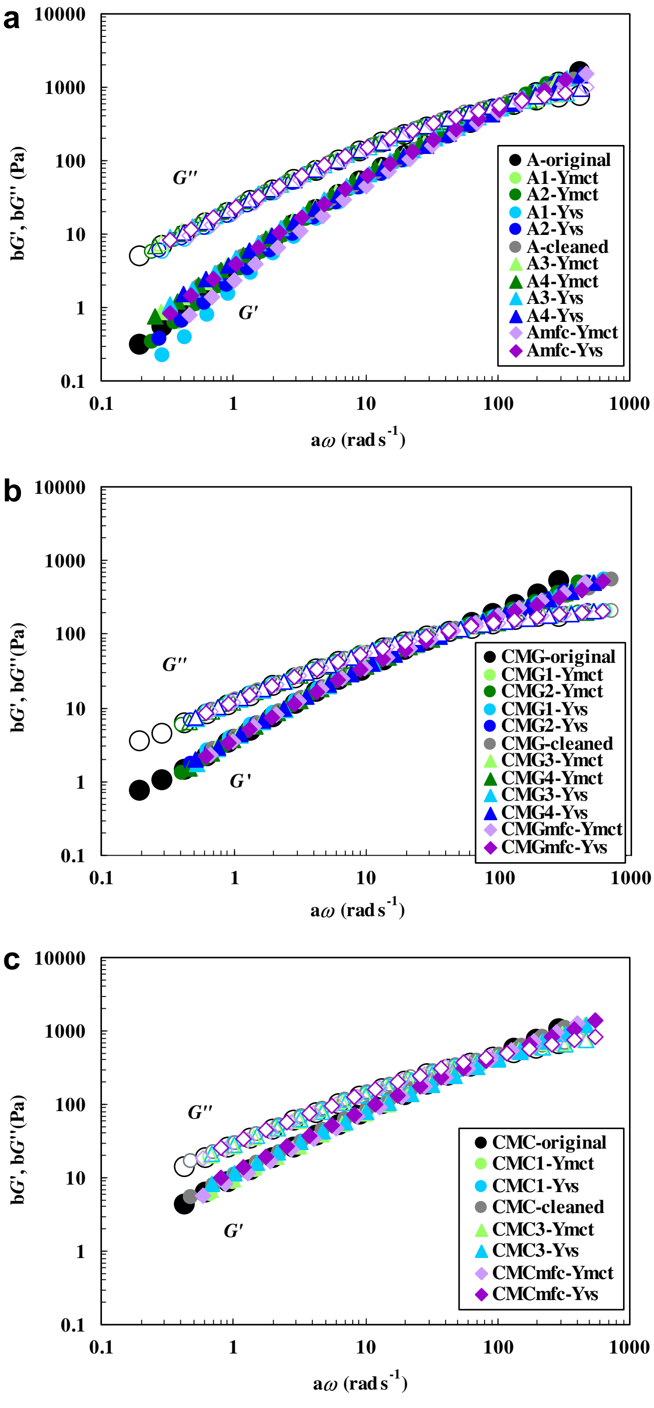

Fig. 5. Master plots (a) A, (b) CMG and (c) CMC thickeners.

origin of the recycled polymers, namely printing paste residues or wastewater concentrates.

In comparison to the cleaned original polymer the recycling procedure narrows the polymer MWD. A and CMG recycled thickeners are generally characterized by lower MWA, whilst the opposite is seen in the case of CMC thickeners. The effect of secondary recycling produces an increase in the weight average molecular weights of A thickeners, a decrease of the weight average molecular weights of CMG thickeners and leads to broader MWD (higher values of polydispersity indices).

Rheological parameters, such as η_0, $\dot{\gamma}_c$, ΔG and ω_c obtained from data fitting are strongly connected to the weight average molecular weight, $\overline{M}_w$. It is observed that with increasing $\overline{M}_w$ the zero-shear viscosity, η_0, increases (see Fig. 2) and simultaneously the critical shear rate, $\dot{\gamma}_c$, corresponding to the onset of the non-Newtonian behaviour (see Table 2) shifts towards lower values, as presented in Fig. 6a. In the oscillatory flow, data obtained from dynamic tests show that ΔG, the indicator of the magnitude of both moduli (see Fig. 4), increases with increasing $\overline{M}_w$ and the crossover frequency,

Table 3
Molecular weight averages ($\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$) and polydispersity indices ($\overline{M}_w/\overline{M}_n$, $\overline{M}_z/\overline{M}_w$) of polysaccharide thickeners

	$\overline{M}_n \cdot 10^{-5}$	$\overline{M}_w \cdot 10^{-6}$	$\overline{M}_z \cdot 10^{-7}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$
A-original	2.08	1.49	1.05	7.14	7.07
A-cleaned	1.78	1.58	1.43	8.88	9.06
A1-Ymct	1.61	1.04	0.78	6.44	7.55
A2-Ymct	1.75	1.15	0.87	6.55	7.60
A1-Yvs	1.57	1.04	0.78	6.60	7.49
A2-Yvs	1.99	1.43	1.28	7.19	8.94
A3-Ymct	1.91	1.28	0.85	6.73	6.62
A4-Ymct	2.36	1.54	1.30	6.53	8.40
A3-Yvs	1.88	1.27	0.92	6.74	7.28
A4-Yvs	1.20	1.49	1.20	7.45	8.06
Amfc-Ymct	1.59	1.39	1.51	8.71	10.86
Amfc-Yvs	1.67	1.24	1.00	7.40	8.11
CMG-original	4.69	4.45	2.41	9.48	5.42
CMG-cleaned	3.48	3.85	2.49	11.05	6.47
CMG1-Ymct	3.92	3.86	2.33	9.86	6.04
CMG2-Ymct	3.59	3.69	2.35	10.29	6.37
CMG1-Yvs	3.78	3.84	2.40	10.16	6.27
CMG2-Yvs	3.45	3.80	2.34	11.03	6.16
CMG3-Ymct	3.68	3.66	2.34	9.95	6.39
CMG4-Ymct	3.75	3.50	2.24	9.35	6.40
CMG3-Yvs	3.86	3.86	2.30	10.01	5.97
CMG4-Yvs	3.41	3.43	2.20	10.06	6.40
CMGmfc-Ymct	3.11	3.53	2.50	11.34	7.09
CMGmfc-Yvs	3.55	3.70	2.31	10.41	6.24
CMC-original	1.34	1.56	1.64	11.65	10.50
CMC-cleaned	1.32	1.41	1.41	10.70	9.98
CMC1-Ymct	1.51	1.47	1.53	9.76	10.41
CMC1-Yvs	1.72	1.49	1.43	8.64	9.63
CMC3-Ymct	1.52	1.54	1.59	10.10	10.35
CMC3-Yvs	1.52	1.52	1.47	10.01	9.64
CMCmfc-Ymct	1.78	1.55	1.48	8.67	9.56
CMCmfc-Yvs	1.95	1.62	1.68	8.30	10.38

ω_c, i.e. the frequency at which the intersection of G' and G'' occurs (see Table 2), shifts towards lower values as seen in Fig. 6b.

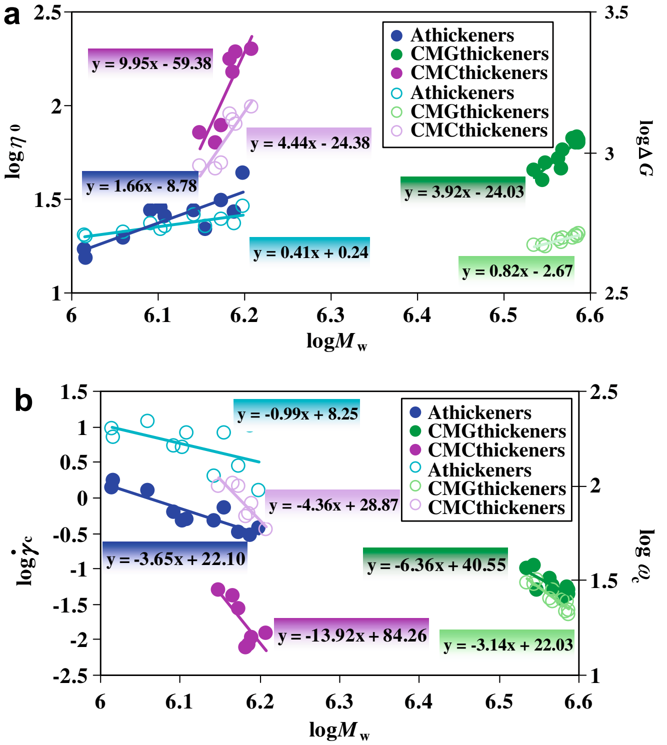

Fig. 6. Dependence between $\overline{M}_w$ and (a) η_0 (full circles), ΔG (open circles), (b) $\dot{\gamma}_c$ (full circles), ω_c (open circles) for A, CMG and CMC thickeners.

3.4. Viscosity - molecular weight relationships

The well known power-law relationship between the weight average molecular weight, $\overline{M}_w$, and the zero-shear viscosity, η_0, researched in detail for polymer melts (Fox & Flory, 1951):

$$\eta_0 = K \cdot \overline{M}_w^a \tag{10}$$

can also be established for ordinary polymer solutions, since the motion of chains are subjected to the same topological boundaries which affect polymer melts. By taking into account the Mark–Houwink–Sakurada equation:

$$[\eta] = KM^a \tag{11}$$

where K and a are constants and $[\eta]$ intrinsic viscosity; a correlation between η_0 and $\overline{M}_w$ is established with different scaling laws in the diluted and in the concentrated region. The concentration dependence of viscosity for polymer solutions is usually referred to the specific viscosity, $\eta_{sp,0}$, instead of to η_0 in order to remove the contribution of solvent viscosity, and expressed through the following scaling law:

$$\eta_{sp,0} \approx a \cdot c^b \tag{12}$$

where the scaling law exponent b is comprised between 1 and 1.4 for dilute solutions and more frequently lies in the range 3.2–4 in the concentrated regime (Lapasin & Pricl, 1995). Even higher scaling law exponents (up to 5.5) are reported for some aqueous solutions of neutral polysaccharides, such as guar gum, locust bean gum (Morris, Cutler, Ross-Murphy, & Rees J. Price, 1981) and for aqueous solutions of sodium carboxymethyl cellulose (Kästner, Hoffmann, Dönges, & Hilbig, 1997).

The above scaling law can be transformed in a generalized relation valid for polymers with similar conformational features using the reduced concentration, $\tilde{c}$, (Simha & Utracki, 1967; Utracki & Simha, 1981):

$$\tilde{c} = c/\gamma(M) \tag{13}$$

where γ is a scaling concentration factor; accounting for the polymer molecular weight. The intrinsic viscosity $[\eta]$ represents the most appropriate reference to define the scaling factor γ as:

$$\gamma = 1/[\eta] \tag{14}$$

and, hence, the generalized relation is:

$$\eta_{sp,0} = f(\tilde{c}) = f(c[\eta]) \tag{15}$$

Accordingly, the dependence of $\eta_{sp,0}$ from $\overline{M}_w$ is thus expressed by scaling laws whose exponent is between a and $1.4a$ and $3.2a$ and $5.5a$ in the diluted and concentrated regimes, respectively, where a represents the exponent of the Mark–Houwink–Sakurada equation for a given polymer-solvent pair.

Looking at the correlations between $\overline{M}_w$ and η_0 for the investigated polysaccharide aqueous systems (Table 4), it is difficult to establish a scaling law for the different polysaccharide groups, since the obtained data are restricted to a very narrow range of molecular weights. The low power law exponent in case of A polymers approximates towards the diluted region. Much higher power law exponent for CMC polymers is evidence of interchain association by formation of specific junctions, in addition to physical entanglements of overlapping coils. Such specific chain-chain interactions ("hyperentaglements") denotes that the entities involved in the motion are not the individual chains, but rather entities created by the associations between the chains and thus the scaling law is no longer valid.

Indeed the shear dependence of the viscosity is also sensitive to the polymer MWD, which induces changes in the profile of the relative flow curves. The range of shear rates over which the transi-

Table 4
Parameter values of equations 10, 16 and 17

η_0=	$K \cdot \bar{M}_w^a$		$K \cdot \overline{M}_w^p \cdot \left(\frac{\overline{M}_w}{\overline{M}_n}\right)^q$			$K \cdot \overline{M}_w^p \cdot \left(\frac{\overline{M}_w}{\overline{M}_n}\right)^q \cdot \left(\frac{\overline{M}_z}{\overline{M}_w}\right)^r$			
Polymer group	a	R_1^2	p	q	R_2^2	p	q	r	R_3^2
A	1.66	0.70	1.24	0.84	0.76	1.39	1.97	−1.28	0.92
CMG	3.92	0.79	3.78	0.92	0.89	2.85	1.47	−1.21	0.90
CMC	9.95	0.72	13.53	2.09	0.75	15.36	2.99	−5.08	0.92

tion from the upper Newtonian plateau to the power-law region occurs depends mainly on the polymer MWD described by polydispersity indices ($\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$). Polydispersity, particularly the presence of a high molecular tail in polymer MWD, widens the transition region, and the decrease of viscosity with increasing shear rate is more gradual (Cross, 1969; Graessley, 1974). Locati and Gargani (Locati & Gargani, 1973) proposed to include a polydispersity modifier in the power-law dependence of η_0 on $\overline{M}_w$ for compensating the effect of high molecular weight tail in MWD of polymers, by the following empirical molecular weight distribution scaling, with parameterization K, p and q for polydisperse polyethylenes:

$$\eta_0 = K \cdot \overline{M}_w^p \cdot \left(\frac{\overline{M}_w}{\overline{M}_n}\right)^q \tag{16}$$

where $p = 3.46$ and $q = 0.51$.

The fitting of the power-law dependence of η_0 on $\overline{M}_w$ corrected by the polydispersity index, $\overline{M}_w/\overline{M}_n$, for the investigated polysaccharide polymers shows an improved correlation. The parameter values and the coefficient of determination (R_2^2) determined from regression analysis are shown in Table 4.

Steeman (Steeman, 1998) showed that zero-shear viscosity depends besides on the weight average molecular weight, also on both polydispersity indices $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$:

$$\eta_0 = K \cdot \overline{M}_w^p \cdot \left(\frac{\overline{M}_w}{\overline{M}_n}\right)^q \cdot \left(\frac{\overline{M}_z}{\overline{M}_w}\right)^r \tag{17}$$

with $q = 0.24$ and $r = 0.44$ for polypropylene homopolymers, derived with linear regression analysis, however, it is not known whether these values are universal. For the exponent p no conclusions were drawn since only a single value of $\overline{M}_w$ was studied. Application of Eq. (17) shows a significant improvement of the correlations for the investigated polysaccharide systems with the coefficient of determination being above 0.90 and parameter values as shown in Table 4.

4. Conclusions

The rheological investigation of thickeners recycled from printing paste residues and wastewater concentrates in general shows marked shear thinning and viscoelastic properties. Moderate changes of the rheological quantities of different sign detected in steady and oscillatory shear conditions are associated to different polymer-alkali combinations. In general a more marked increase in the viscosity and viscoelastic properties of CMG and CMC recycled thickeners are exhibited compared to A recycled thickeners that show only slight changes in rheological properties.

Rheological models, which provide a satisfactory data fitting, enable a quantitative interpretation of the changes in rheological properties, which are strictly related to the changes in the polymer molecular weight averages and its molecular weight distribution. Rheological parameters, such as η_0 and ΔG, $\dot{\gamma}_c$ and ω_c are strongly connected to $\overline{M}_w$. Besides being dependent on $\overline{M}_w$, η_0 depends also on polymer molecular weight distribution described by polydispersity indices $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$.

Acknowledgements

The authors thank Lamberti S.p.a. for supplying the thickeners, and Dystar and Bezema for dyestuff samples used in this research. Financial support given by the Slovenian Research Agency for young researchers and by the EU project COOP-CT-2004-005864 is gratefully acknowledged.

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