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Rheological properties of printing pastes and their influence on quality-determining parameters in screen printing of cotton with reactive dyes using recycled polysaccharide thickeners

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ABSTRACT

Alginate, carboxymethylated guar gum and carboxymethylated cellulose, used as thickeners in printing pastes for monoreactive dyes, were recycled from wastewater concentrates (separated by ultrafiltration from wastewater after screen printing of cotton), and from printing paste residues (obtained from the cleaning of printing equipment and application systems in the printing machine). The printing performance, using original and recycled polymers, was studied via rheological properties of printing pastes and quality-determining parameters of printing.

A quantitative interpretation of the flow and the viscoelastic properties, which are strongly connected to the qualitative parameters of printing, was obtained using rheological models (Cross and Friedrich–Braun model). Recycled thickeners are easily reused for screen printing of cotton with monoreactive dyes, provided that the printing paste recipe fits a rheological constraint of equal viscosity in the steady shear conditions. The results of quality-determining parameters of prints using recycled thickeners are comparable to those obtained with the original thickeners.

1. Introduction

Textile printing is the most versatile and important of the methods used for introducing colour and design to textile fabrics. Considered analytically it is a process of bringing together a design idea, one or more colorants, and a textile substrate, using a technique for applying the colorants with some precision (Miles, 1994). Today some 89% of all printed textiles are produced with flat or rotary screens (Lacasse & Baumann, 2004).

Thickening agents play a paramount role in the formulation of printing pastes, ensuring through the modulation of the rheological properties, sharp and clean drawing patterns, by preventing dye migration, a homogenous distribution of the printing paste on the screen and its uniform flow through the screen openings. The selection of the thickening agent, which in most cases is confined to polysaccharides and their derivatives with high molecular weight, is determined by the fabric to be printed, the printing conditions, and, above all, the type of dye used. Depending on their chemical structure, dyes may interact with thickening agents, to form complexes or to give a chemical reaction, so causing a variation of the rheological properties of the printing pastes and, hence, of their application characteristics (Kokol, 2002; Lapasin & Pricl, 1995; Šostar & Schneider, 1999). Sodium alginates have become very important for printing paste thickening because of their ready solubility, even after high-temperature fixation treatments. They are especially important for pastes of reactive dyes (McLachlan, 1985), because the extent of interaction is very small, due to the absence of primary hydroxyl groups and due to the repulsion of dye anions by the ionised carboxyl groups of the polymer under alkaline conditions. The repulsion promotes migration of the dye from the thickener into the fabric during steaming, which results in good colour yields. The alginate film after drying and dye fixation is washed out easily, therefore less dye is removed during washing and the printed fabric has a "soft handle" due to complete removal of the hydrocolloid. Because of the relatively high cost and limited supply of alginates, attention has been paid to finding alternatives (McLaughlin, 1998; Miles, 1994; Whistler & BeMiller, 1993). The use of modified polysaccharides as thickening agents in reactive dye printing constitutes an interesting alternative. Based on quality-determining parameters authors have shown that carboxymethylated derivatives of cellulose, guar and starch are equally suitable for reactive printing and actually increase the technical printing and colouristic possibilities with reactive dyes (Kokol & Šostar, 2000; Kumbasar & Bide, 2000; Schneider, Belz, Šostar, & Oppermann, 1995). In view of the price the most interesting alternative natural thickener is shown to be guar gum. Application of nonsubstituted guar gum in the presence of bifunctional

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reactive dyes in cellulose printing has its disadvantage in direct or indirect (via reactive dye) chemical covalent binding of guar gum macromolecules with the cellulose substrate, causing increased fabric stiffness and decreased colour yield. The chemical cross-linking of guar gum macromolecules with the cellulose substrate can be decreased with higher degree of substitution of free primary hydroxyl groups with different substituents, contributing to softer fabric handle. Detailed studies on chemical modification of guar gum and their correlation to printing performance have been published (Abdel-Thalouth, Elzairy, & Hebeish, 1986; Kokol, 2002; Kokol & Šostar, 2000; Kokol, Šostar-Turk, & Schneider, 2002; Lapasin, De Lorenzi, Pricl, & Torriano, 1995; Lapasin, Pricl, Graziosi, & Molteni, 1988; Lapasin, Pricl, & Tracanelli, 1991; Welinga, 1986; Šostar & Schneider, 1998, 1999; Šostar-Turk & Schneider, 2000). The application and rheological behaviour of some chemically modified natural printing thickeners in textile printing, such as carboxymethylcellulose, hydroxyethylcellulose, carboxymethyl-hydroxyethylcellulose, methylcellulose and cellulose ethers has been studied by several authors (Abdel-Thalouth et al., 1986; Guion, Foushee, Pak, & Somerville, 1984; Guion & Hood, 1985; Lapasin et al., 1988). Carboxymethylcellulose has received considerable attention in the textile industry because of its readily solubility and excellent film-forming characteristics and has thus been used successfully for many years as a thickener for textile printing pastes. It is stable to acids and alkalines within the pH range of these pastes and can therefore be used with a variety of dyes (Whistler & BeMiller, 1993).

In the present research a study of rheological properties of printing pastes in relation to quality-determining parameters in screen printing of cotton with monoreactive dyes is performed using different polysaccharide thickeners previously recycled from printing paste residues and wastewater concentrates. A detailed study of rheological and molecular weight properties of recycled polysaccharides is presented in Fijan et al. (2009). The recycling of printing thickeners is aimed to reduce solid wastes and wastewater pollution in the textile printing industry.

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 dyestuff C.I. (colour index) Reactive Yellow 95; produced by Dystar, Germany) and a vinylsulphone reactive group (Yvs), namely Benzactiv Yellow V-GR 133 (contains dyestuff C.I. Reactive Yellow 15; produced by Bezema AG, Switzerland) were used for the preparation of printing pastes.

Printing paste additives (Table 1), namely salts and urea were provided by Sigma–Aldrich (Germany) and Rapidoprint XRN Pearls (sodium-*m*-nitrobenzene sulphonate) were supplied by Bezema AG (Switzerland).

The printing experiments were performed on 100% cotton fabric (supplied by a Slovenian textile factory (Tekstilna tovarna Prebold d.d.)), which was already desized, scoured, bleached (without optical whiteners) and mercerised. Fabric specifications: weight 115 g/m^2, thread density tex = 20 mg/m, warp 30 threads/cm, weft 25 threads/cm, plain weave.

2.2. Preparation of printing pastes; recycling of thickeners from printing paste residues and wastewater concentrates

The recipes of textile printing pastes are shown in Table 1. The thickener stock solution was prepared by adding the thickener (original or recycled) to demineralised water, stirred with a mixer and left in a refrigerator overnight to attain full swelling. Printing paste additives and dyestuff were added to the thickener stock solution at ambient temperature and stirred for 15–20 min. All printing pastes were adjusted to an equal viscosity (at 25 °C) in the range of (7.3 ± 0.8) Pas at shear rate 10 s^{-1} by the amount of water addition (Kokol & Šostar, 2000; Šostar & Schneider, 1999).

Printing paste residues, having the same recipes as printing pastes (with original A, CMG or CMC and primarily recycled A, CMG or CMC thickeners), were obtained after cleaning of the printing equipment and the application systems in the printing machine (dipper, mixer, screen, squeegee, etc.).

Wastewater concentrates were separated with ultrafiltration of synthetically prepared wastewater as described in Fijan et al. (2009), which was adapted from the cleaning-up operations by diluting the printing pastes (containing original A, CMG or CMC thickeners) with distilled water at ratio 1:6.

Recycling of thickeners was performed according to the processing principle proposed by Marte and Meyer (Marte & Meyer, 1995; Schneider, 1997) and is described in Fijan et al. (2009).

Table 1
Printing paste recipes and function of printing paste additives

Thickener[a]		A	CMG	CMC
	Original thickeners	6*	6*	8*
	Thickeners recycled 1×	6*	5*	8*
	Thickeners recycled 2×	6*	5*	–
		*X*** (thickener stock solution)		
Oxidative agent[b]		1**		
Alkali[c]	Sodium carbonate or	2.5**		
	Sodium bicarbonate	3**		
Urea[d]		15** (with sodium carbonate)		
		10** (with sodium bicarbonate)		
Dyestuff	Ymct Or Yvs	3**		
Water		*Y***		

* The amount of thickener solid content in thickener stock solution expressed as % w/w.
** The amount of printing paste additive in printing paste expressed as % w/w. The amount of thickener stock solution (*X*) and water (*Y*) is 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}.
[a] Thickeners acts as a rheological medium.
[b] Oxidative agent Rapidoprint XRN Pearls (sodium-m-nitrobenzene sulphonate) is added to offset the reactive dye's sensitivity to reduction during steaming.
[c] Alkali produces ionization of accessible cellulose hydroxyl groups of the fibre that react with the reactive dye.
[d] Urea is required for optimal fixation of the reactive dye in superheated steam. It increases the solubility of the reactive dye and accelerates migration of the dye from the thickener film into the fibre.

2.3. Textile printing process

Textile printing on cotton was performed with a laboratory printing machine type MDF-R-237 (J. Zimmer), using flat printing screen (fineness 120 thread/cm, 45 μm screen open area, 34 μm thread diameter) and a magnetic-rod squeegee (10 mm i.d.), at printing speed 4 m/min, with pressure grade 6 and 1 squeegee passage. Drying (2 min at 80 °C) and fixation (10 min at 102 °C in saturated steam) of the printed fabrics were performed with a laboratory steamer type DHE 43687 (W. Mathis). Washing was obtained with demineralised water in 5 washing baths (15 min at 95 °C with bath ratio = 1:40).

2.4. Rheological characterization

Rheological characterization was performed for thickener stock solutions, prepared with original or recycled thickeners and for the corresponding printing pastes. The concentration of the thickener stock solution was chosen to fit the rheological constraint of equal viscosity (at 25 °C) of the corresponding printing pastes: $\eta = (7.3 \pm 0.8)$ Pas at $\dot{\gamma} = 10\ s^{-1}$.

Rheological measurements, namely rotational and oscillatory measurements, were carried out at 25 °C and performed with a rotational controlled stress rheometer Haake RS150 using cone-and-plate (C60/1) measuring device. 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.

2.5. Quality-determining parameters

Printing paste add-on was determined gravimetrically from the differences in the mass of cotton fabric samples determined before

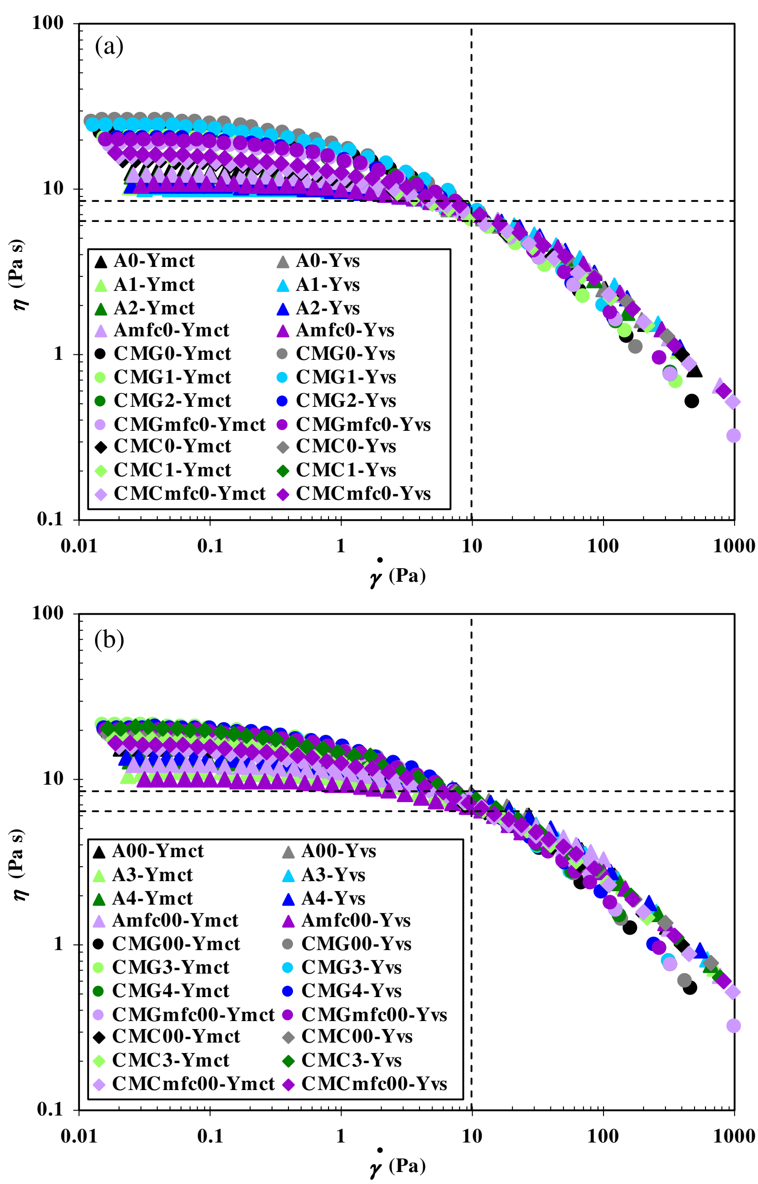

Fig. 1. Flow curves of printing pastes using A, CMG and CMC thickeners prepared with sodium carbonate (a) or sodium bicarbonate (b) as alkali. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

printing and immediately after the application of the printing paste.

The reflectance measurements of the prints were determined using a Datacolor SF 600 PLUS spectrophotometer with d/8 measurement geometry under the following conditions: measurement wavelength range from 400 nm to 700 nm, measurement area of 9 mm in diameter (SAV-small area view), and SIN-specular included measurement mode. The CIE L^*, a^*, b^*, C^* and h co-ordinates (CIELAB 1976), and colour depth values K/S (K is the absorption coefficient depending on the dye and S is the scattering coefficient depending on the substrate (Kubelka & Munk, 1931)) at the wavelength of maximum absorption were calculated using Datacolor Datamaster software.

The dye concentration in the washing baths was determined by absorbance measurements using UV/VIS spectrometer Lambda 2 (Perkin-Elmer).

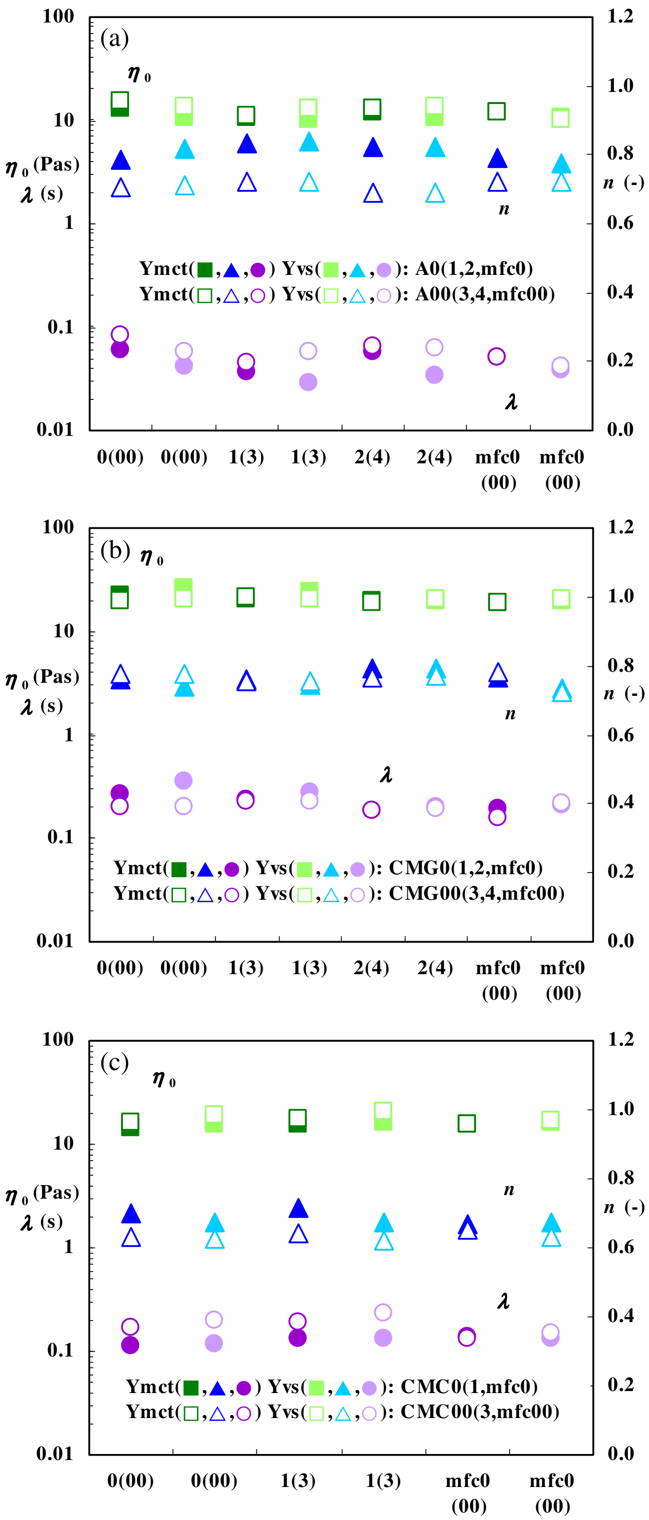

Fig. 2. Cross model parameters of printing pastes using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

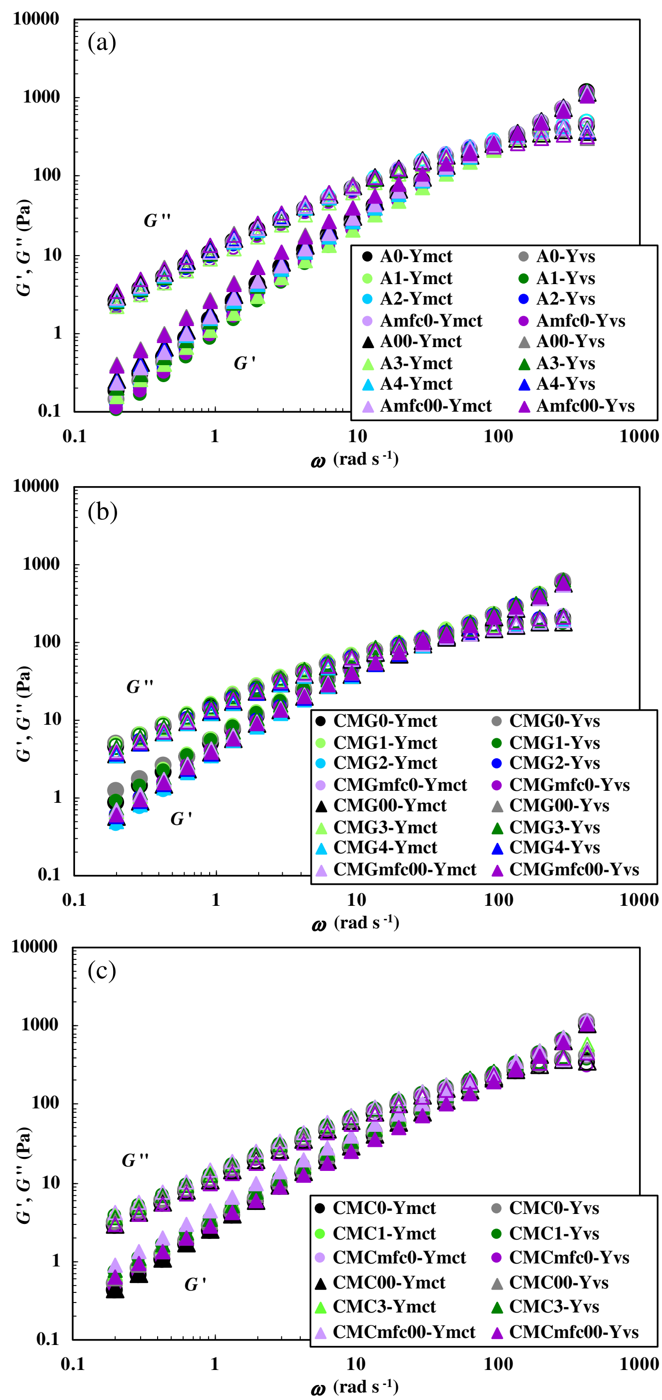

Fig. 3. Mechanical spectra of printing pastes using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

The colour fastness to washing and dry/wet rubbing of the prints were determined by the conventional methods according to SIST EN 20105-CO3:1992 (ISO 105-CO3:1989) and ISO 105-X12:1993, respectively. The grey scale assessment of the change in colour of the printed samples and the staining of adjacent specimens were determined according to visual assessment described in ISO 105-A02:1993 and ISO 105-A03:1993, respectively.

3. Results and discussion

3.1. Rheological properties of printing pastes

The rheological properties of printing pastes were investigated under steady and oscillatory shear conditions. The ingredients for printing paste preparation are (see printing paste recipes in Table 1) distinguished by using different symbols for: thickeners A, CMG and CMC (original thickeners (marked as 0 or 00), primarily (marked as 1,3), secondarily (marked as 2,4) recycled thickeners from printing paste residues or thickeners recycled from membrane filtration concentrates (marked as mfc)), dye (yellow shaded monoreactive dye, with a monochlorotrizine (marked as Ymct) or a vinylsulphone reactive group (marked as Yvs)) and alkali (sodium carbonate (indicated with 0, 1, 2, mfc0) or sodium bicarbonate (indicated with 00, 3, 4, mfc00).

3.1.1. Steady shear properties

As seen from the results in the steady shear conditions (Fig. 1), the printing pastes prepared with different thickeners exhibit shear-thinning behaviour. Data fitting of flow curves was obtained using the Cross equation (Cross, 1965):

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

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 fitting parameters η_0, n and λ of printing pastes prepared with different thickeners, shown in Fig. 2, were obtained as described in Fijan et al. (2009).

From the flow curves (Fig. 1) and the model parameters (Fig. 2) it is evident that despite the shared viscosity constraint at $\dot{\gamma} = 10\ s^{-1}$ the printing pastes prepared with different types of thickeners exhibit differences in the shear-thinning properties. The zero-shear viscosity (η_0) is evidently (Fig. 1) highest for printing pastes prepared with CMG as thickener and lowest for A based printing pastes and accordingly printing pastes based on CMG display a more distinctive shear-thinning behaviour than CMC and A based printing pastes. These findings are in good agreement with the rheological properties of concentrated A, CMG and CMC thickener solutions reported in Fijan et al. (2009), indicating that the flow properties of the corresponding printing pastes are primarily governed by the polymer content. The addition of the dye does not produce a qualitative change in the flow behaviour, but only slight changes in the rheological quantities. The influence of alkali shows slight changes in the rheological quantities, seen as less pronounced power-law dependence (lower n values), evidently in A and CMC based printing pastes, when using sodium bicarbonate as alkali.

3.1.2. Linear viscoelastic properties

The viscoelastic properties of printing pastes were examined by dynamic tests in the linear viscoelastic regime, whose extension was determined by strain sweep tests. The critical strain values γ_c^0 were obtained from strain sweep data (at 1 Hz), using the Soskey–Winter (1984) equation under the conditions described in Fijan et al. (2009). The γ_c^0 for A, CMG and CMC based printing pastes are in the ranges: 0.7–1.1, 0.6–0.8 and 0.2–0.4, respectively.

Linear viscoelastic properties, expressed in terms of mechanical spectra (frequency dependence of storage $G'(\omega)$ and loss $G''(\omega)$ moduli) (Fig. 3) were correlated with the Friedrich–Braun viscoelastic model based on fractional derivatives (Friedrich & Braun,

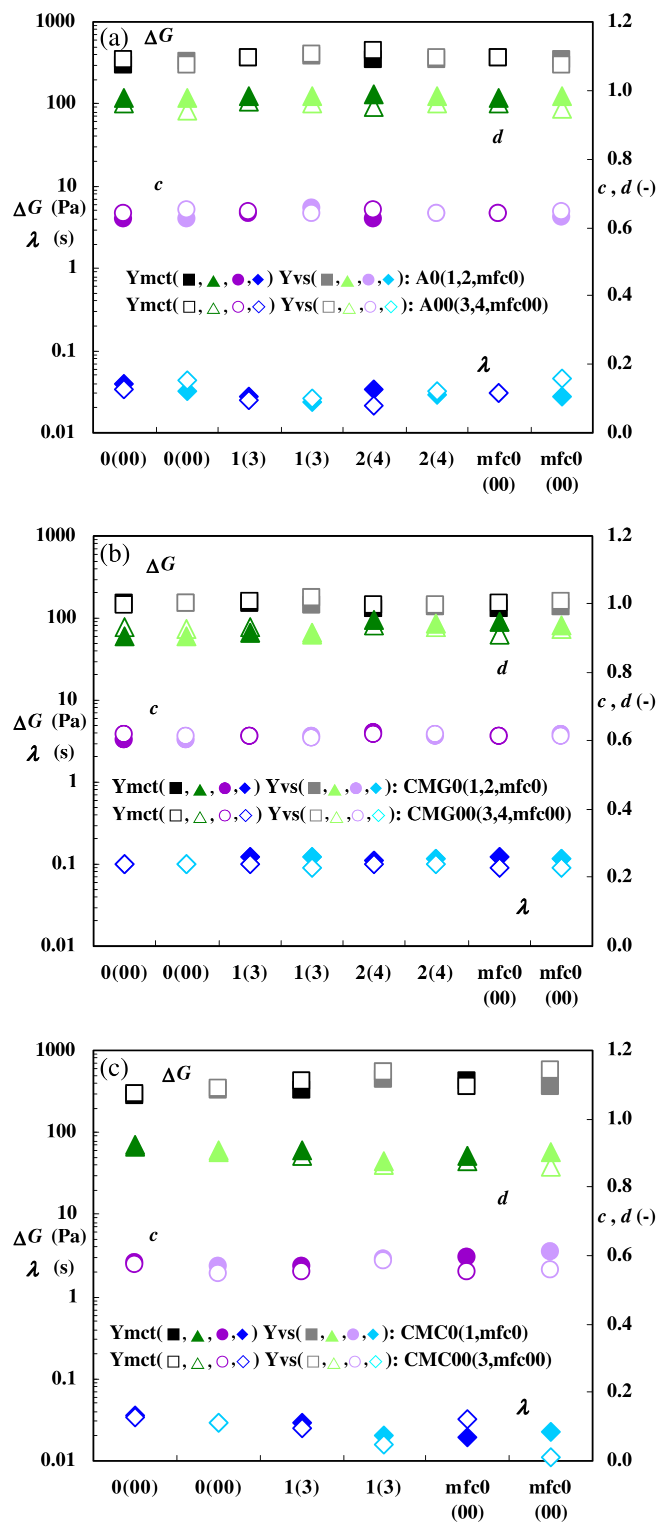

Fig. 4. Friedrich–Braun model parameters of printing pastes using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

1992). The results from oscillatory measurements show similar patterns of both moduli for the printing pastes prepared with the same thickener and the dynamic properties of printing pastes are primarily influenced by the polymer content, which imparts viscoelastic behaviour to the printing pastes (Fijan et al., 2009). The Friedrich–Braun model (Friedrich & Braun, 1992) provides adequate correlation of $G'(\omega)$ and $G''(\omega)$ for all printing pastes:

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

$$G''(\omega) = \Delta G \frac{(\lambda\omega)^d \left[\sin\frac{\pi}{2}d + (\lambda\omega)^c \sin\frac{\pi}{2}(d-c)\right]}{1 + 2(\lambda\omega)^c \cos\frac{\pi}{2}c + (\lambda\omega)^{2c}} \quad (3)$$

where λ is a characteristic relaxation time, G_e is the equilibrium modulus, ΔG is a parameter which rules the magnitude of the viscoelastic response and c and d are the derivation orders of fractional derivatives of the model. The frequency dependence of the dynamic moduli is well described through the variation of the 4 parameters: ΔG, λ, c and d (presented in Fig. 4), when applying the fitting procedure simultaneously for both moduli under the yielding conditions described in Fijan et al. (2009). The results of the fitting procedure show only slight differences in the model parameters for printing pastes prepared with the same thickener. In the case of parameter ΔG they are related to minimal variations in the magnitude of both moduli; however slight differences in the derivation orders, c and d, of the differential operators, affect the shape of the curve $G'(\omega)$ in the whole frequency range, whereas the material function $G''(\omega)$ is slightly modified only at higher frequencies (see Fig. 3).

For comparison of different viscoelastic behaviour of the printing pastes, data are shown in terms of frequency dependence of complex modulus $|G^*| = \sqrt{G'^2 + G''^2}$ and loss tangent

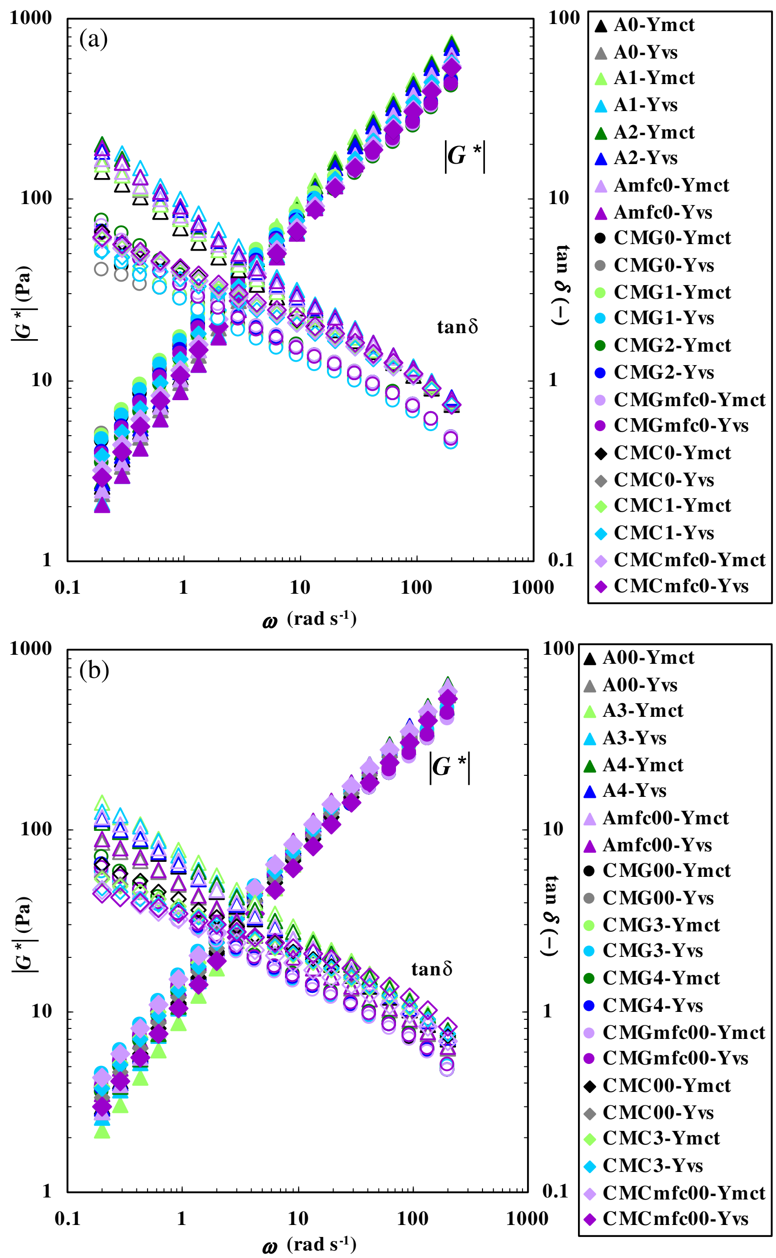

Fig. 5. Frequency dependence of $|G^*|$ and tan δ of printing pastes using A, CMG and CMC thickeners prepared with sodium carbonate (a) or sodium bicarbonate (b) as alkali. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

$G''/G' = \tan\delta$ (Fig. 5), where the variation in the loss tangent and the complex modulus reflect differences in the relative and absolute contributions of elastic and viscous components of the printing pastes, respectively. The frequency dependence of the loss tangent shows that the elastic contribution is highest for CMG based printing pastes (lowest $\tan\delta$) over the whole frequency region; while higher loss tangent values of A based printing pastes indicate a higher viscous contribution. CMC based printing pastes exhibit a viscoelastic behaviour in between A and CMG based printing pastes: in the low frequency region the viscoelastic response in closer to CMG based printing pastes and in the high frequency region the behaviour becomes like that of printing paste prepared with A thickeners.

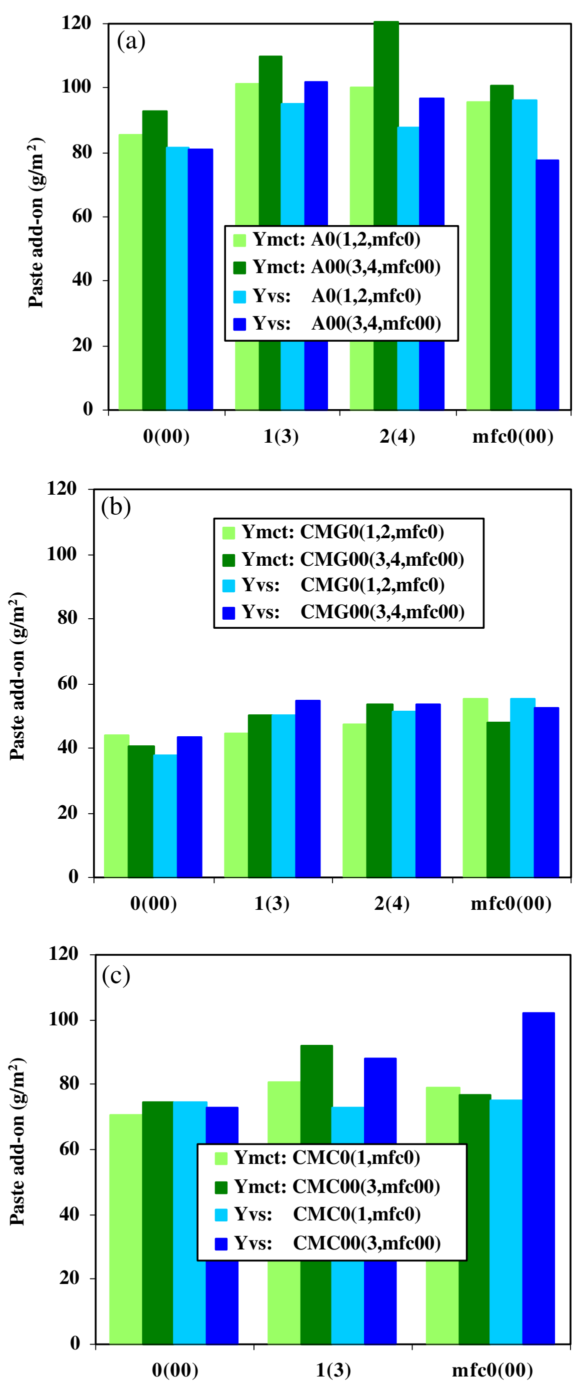

Fig. 6. Paste add-on for printed samples using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

3.2. Quality-determining parameters and the relevance of printing paste rheology

3.2.1. Printing paste add-on

The paste add-on occurs during the printing process immediately after the printing paste is forced through the screen openings, during which high shear rates are present. Simultaneously the flow behaviour of the paste through the screen openings is also affected by elasticity, governing possible recovery of the paste immediately after its application and the onset of normal stresses hindering the passing of the paste through the screen openings.

The results presented in Fig. 6 in general show that the least deposit of the printing paste on the fabric is seen in case of samples printed with CMG, while samples printed with A thickeners have the highest amount of paste add-on. These properties are attributed to the relative contribution of elastic and viscous components, described as the loss tangent $G''/G' = \tan\delta$ (determined from the Friedrich–Braun model parameters), of the printing pastes. As depicted in Fig. 7 an increasing $\tan\delta$ (at $\omega = 30\ s^{-1}$) signifies a higher viscous contribution, therefore paste add-on is higher, such as in the case of A and CMC based printing pastes. Meanwhile, an increasing elasticity in the case of CMG based printing pastes denotes lower loss tangent values, thus less paste is forced through the screen openings and deposited on the fabric. Within the same alkali group printing pastes of recycled thickeners as rheological media exhibit slightly higher paste add-on values resulting from a decreased elasticity, in comparison to the printing pastes prepared with the original thickeners (see Fig. 6).

3.2.2. Colour depth and penetration

The colour depth K/S was used for measuring the colour value of the printed fabrics. As presented in Fig. 8, independently of the dye, samples printed with A and CMC thickeners that give higher add-on exhibit higher colour depth values comparing to prints prepared with CMG thickener. A slight increase in the colour depth is seen when using the recycled thickeners.

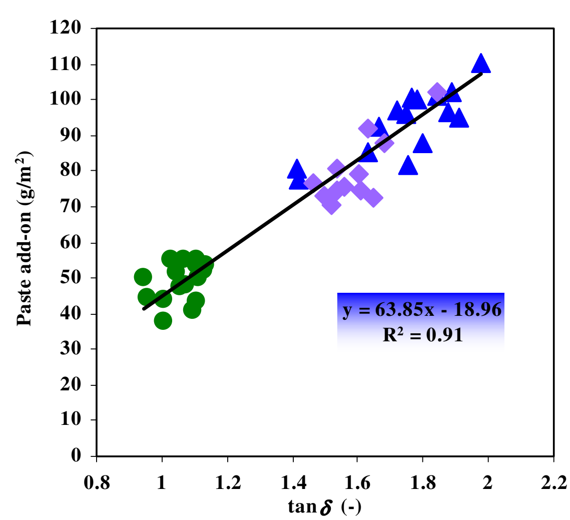

Fig. 7. Relation between paste add-on of prints and $\tan\delta$ (calculated with the Friedrich–Braun model) at frequency $\omega = 30$ rad/s (A thickeners: ▲ (blue); CMG thickeners: ● (green); CMC thickeners: ◆ (violet)). (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

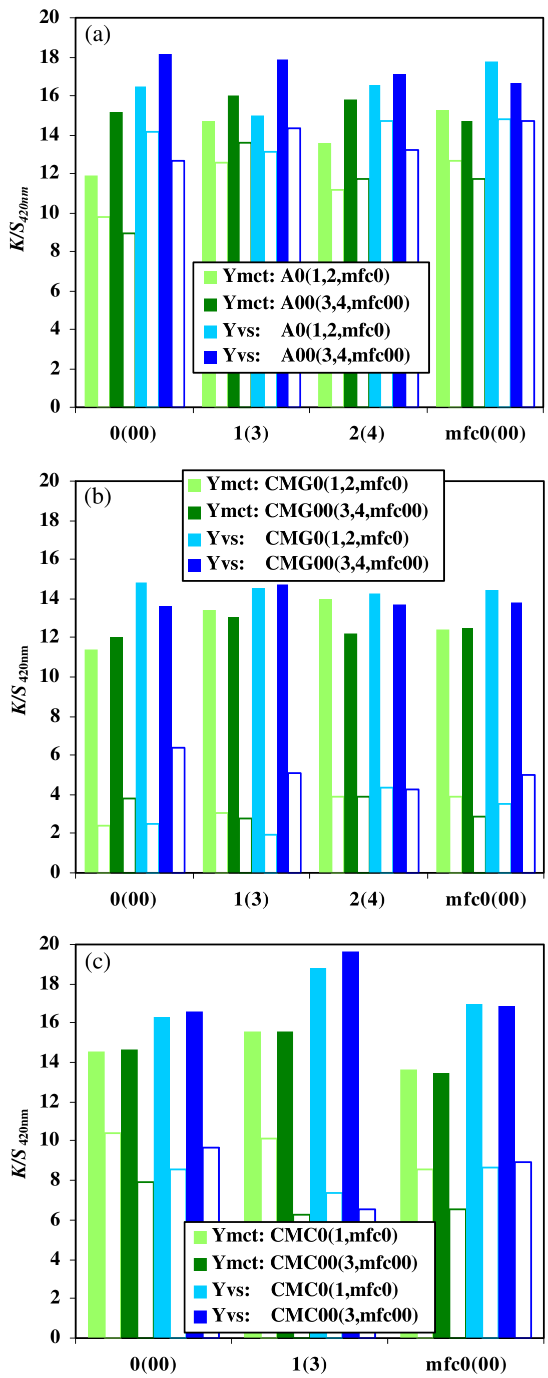

Fig. 8. K/S values for the face $(K/S)_f$ (filled columns) and back $(K/S)_b$ (non-filled columns) of the fabric at 420 nm for printed samples using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

The relation between K/S values of the face $(K/S)_f$ and back $(K/S)_b$ of the printed fabric are reflected through penetration, determined as (Kumbasar & Bide, 2000):

$$\text{Penetration}(\%) = \frac{(K/S)_b}{0.5((K/S)_f + (K/S)_b)} \times 100 \tag{4}$$

As seen in Fig. 9 the penetration is highest when using A thickener as rheological media and lowest when using CMG as thickener. During the application process, after the printing paste is forced through the screen openings and deposited on the fabric, the paste will continue to flow through the fibres at very low shear rates and thus the differences in the penetration values are closely related to the zero-shear viscosity of the printing paste. As depicted in Fig. 10, with increasing η_0 the extent of penetration decreases. The dependence of penetration is well described with a sigmoid function, which presumes complete penetration at $\eta_0 = 0$ and zero penetration at $\eta_0 = \infty$, written as:

$$y = y_\infty + \frac{y_o - y_\infty}{1 + \left(\frac{\eta_0}{a}\right)^b} \tag{5}$$

where y is the penetration as defined by Eq. (4), y_0 and y_∞ are set to 100 and 0, respectively; and a and b, with values 19.9 and 3.9,

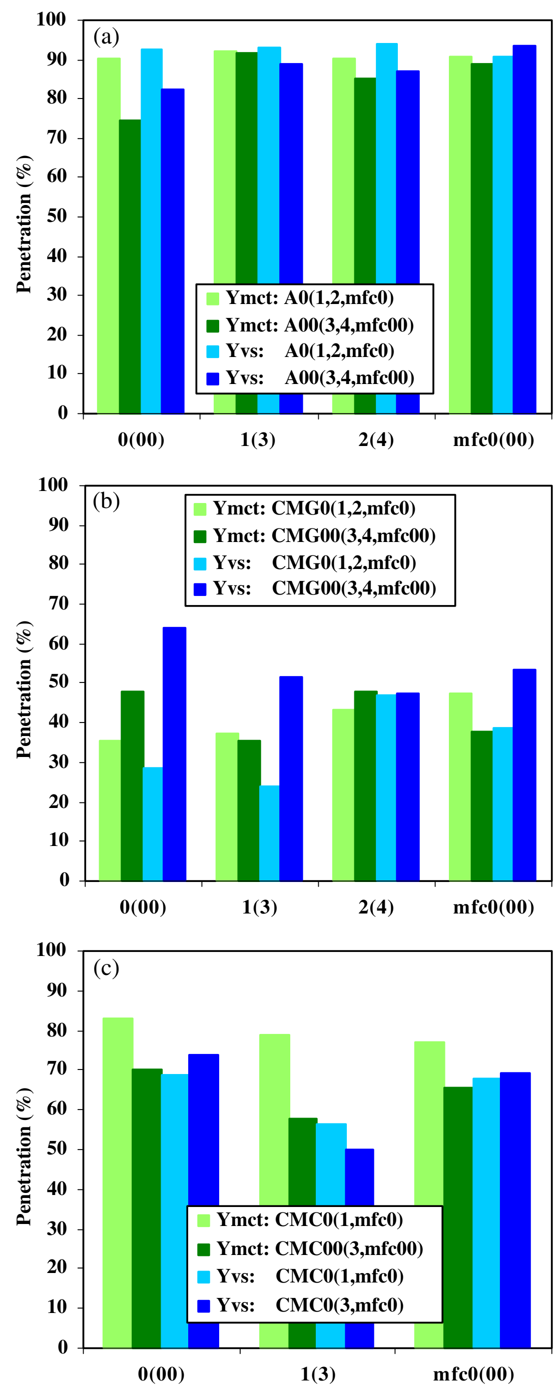

Fig. 9. Penetration for printed samples using A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

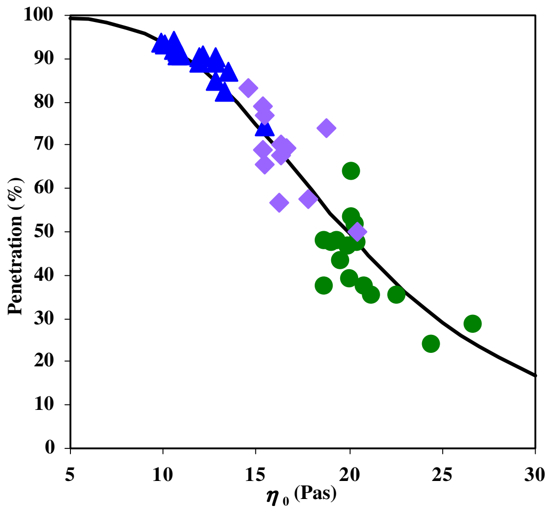

Fig. 10. Sigmoid relation between η_0 of printing pastes and penetration of the prints (A thickeners: ▲ (blue); CMG thickeners: ● (green); CMC thickeners: ◆ (violet)). (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

respectively, are parameters determined through regression analysis.

3.2.3. Dye concentration in washing baths

During the wash-off process the unfixed dye is rinsed directly into the wastewater. In Fig. 11 the rinsing quantity of the dyes are given depending on the type of dye and the number of washing baths. The results show that the majority of the hydrolysed dye is washed out in the first washing bath, irrespective of the thickener. The absolute values however depend on the deposit of the printing paste on the fabric, being least in the case of samples printed with CMG thickener, which accounts for the lower amount of the hydrolysed dye in the washing baths. The removal properties of the dye in case of original and recycled thickeners are similar; therefore the degree of dye fixation is comparable.

3.2.4. Colour fastness properties

Colour fastness properties, which are a measure of the stability of the dye–fibre system, present an interesting property for quality printing in terms of serviceability. For the determination of colour fastness properties of the printed samples, colour fastness to dry and wet rubbing and to washing at 60 °C were evaluated. As seen from the results in Table 2, there are no changes exhibited in the shade of the printed samples and simultaneously no staining on the adjacent cotton in case of dry rubbing and washing at 60 °C. Moderate staining is seen on adjacent cotton in case of wet rubbing and on adjacent wool in case of washing at 60 °C. Colour fastness properties of all printed samples thus show excellent dye–fibre stability and no decrease in the quality is observed when using the recycled thickeners.

4. Conclusions

The study of flow and viscoelastic properties of printing pastes, which are primarily governed by the polymer content, show differences in the rheological behaviour, when using different types of

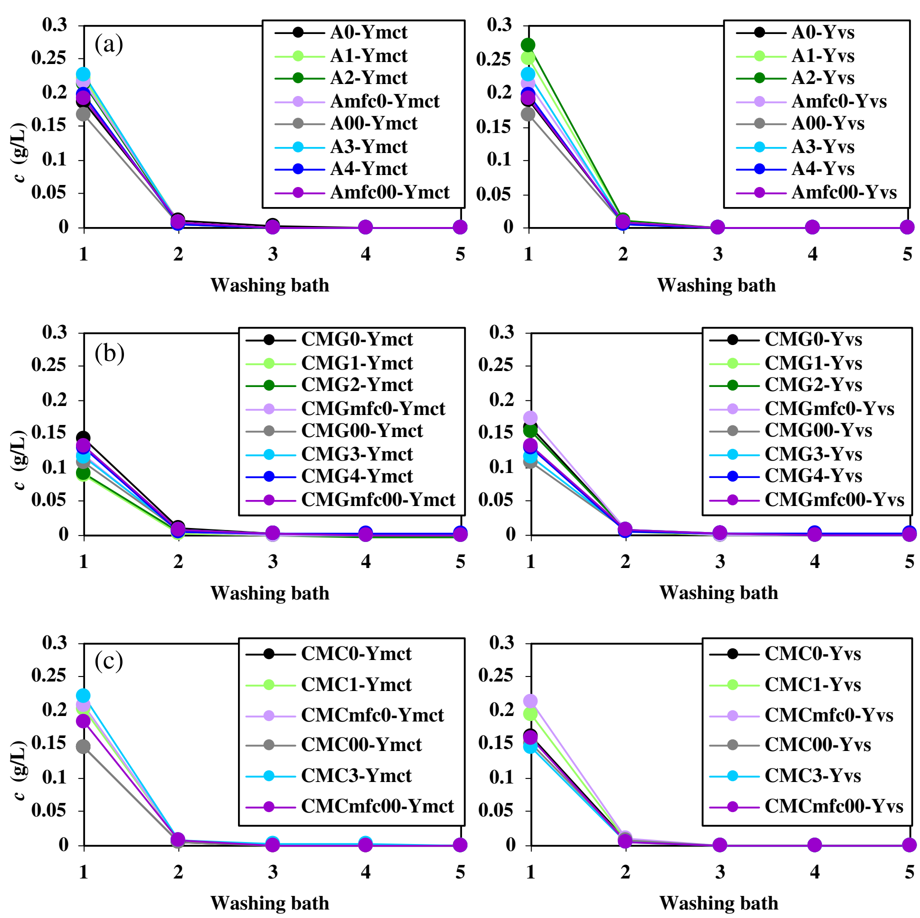

Fig. 11. Dye concentration of Ymct and Yvs in the washing baths after washing of samples printed with A (a), CMG (b) and CMC (c) thickeners. (For interpretation of color mentioned in this figure legend the reader is referred to the web version of the article.)

Table 2
Colour fastness to dry and wet rubbing and to washing at 60 °C.

Printed sample	Colour fastness to rubbing								Colour fastness to washing at 60 °C		
	Warp				Weft						
	Dry		Wet		Dry		Wet				
	S*	C**	S*	C**	S*	C**	S*	C**	S*	W**	C**
A0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A1-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A2-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
Amfc0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A3-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A4-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
Amfc00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A1-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A2-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
Amfc0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A3-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
A4-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
Amfc00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG1-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG2-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMGmfc0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG3-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG4-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMGmfc00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG1-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG2-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMGmfc0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG3-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMG4—Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMGmfc00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC1-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMCmfc0-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC3-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMCmfc00-Ymct	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC1-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMCmfc0-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMC3-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5
CMCmfc00-Yvs	5	5	5	4–5	5	5	5	4–5	5	4–5	5

Scale: the assessment of change in shade of the printed sample and staining on wool or cotton is based on grey scale that ranges from 1 to 5; a grade of 5 is given when there is no perceived difference in colour or contrast between the original and the tested specimen.
* The results are assessed according to the grey scale for colour change, where S is change in the shade of the printed sample.
** The results are assessed according to the grey scale for staining, where W and C are staining on wool and cotton, respectively.

original and recycled thickeners (A, CMG or CMC). These changes, quantitatively described with rheological models (Cross and Friedrich–Braun model), are exhibited as differences in the low shear viscosity, the power-law dependence and in the elastic character of the printing pastes.

The results of quality-determining parameters in screen printing of cotton with reactive dyes show that recycled polysaccharide thickeners can be easily reused as rheological media in reactive dye printing pastes, provided that the printing paste recipe is adjusted to a rheological constraint of equal viscosity ((7.3 ± 0.8) Pas) at shear rate $10\ s^{-1}$ ($T = 25$ °C). The amount of paste add-on, penetration and colour depth resulting from the application of recycled thickeners are comparable to the results obtained with the original thickeners, while the colour fastness levels remain unchanged. The differences in the qualitative parameters of printing, such as printing paste add-on and penetration of printing pastes prepared with different thickeners arise from the diversities in the rheological behaviour of printing pastes, which also have an indirect impact on the colour depth and the degree of dye fixation. Printing pastes containing CMG thickeners that possess a stronger elastic character, exhibit higher zero-shear viscosity and thus display lower paste add-on and penetration compared to A and CMC based printing pastes. Therefore they are also applicable for binary thickener mixtures, aiming at maximization of beneficial behaviours and minimization of advantages.

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