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The Influence of Different Substitution Levels of Guar on the Quality of Viscose Prints with VS Monoreactive Dye

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The basic problem of reactive printing on viscose with polysaccharide guar thickeners is the capability of dye molecule to react with the hydroxyl groups of cellulose (binding of the dye) as well as with the hydroxyl groups of water (the dye hydrolyzes) or the thickener (binding of the dye) [1, 2]. This latter is most clearly expressed in combination of the polysaccharide unmodified guar thickener and the bifunctional reactive dye where the bifunctional dye forms, due to the presence of two reactive groups, a bridge between the cellulose fibre and the guar thickener [3]. The unmodified guar has a large number of free hydroxyl groups which cause crosslinking with cellulose and hinder the thickener to wash off, thus increasing the stiffness of the printing fabric. The further investigation has shown that this undesireous reaction with the guar molecules can be partly diminished by the suitable selection of chemically modified guar thickener or by lowering the dry substance content [4, 5].

In this paper the influence of nonsubstituted and different substituted guar thickeners with monoreactive (vinylsulphone) dyes on the changing of fabric stiffness will be shown.

Keywords: Viscose; printing paste; polysaccharide thickener; guar gum; reactive dye; chemical reactions; stiffness; colour; penetration

INTRODUCTION

The distribution of the reactive dye and its binding controls, beside different reactivity of hydroxyl groups on cellulose fibre and respectively on the guar molecules, also ability of the reactive dyes to react.

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It is known that reactive OH-groups on primary C(6) atoms are much more reactive because of spherically more accessible position in comparison with OH-groups on secondary C(2) and/or C(3) atoms. In the case of guar thickener, where on every second mannose molecule is bound one free mobile galactose molecule (Fig. 2.1), OH-groups on C(6) and on C(2) atoms on galactose molecules are, in comparison with OH-groups on same position on mannose molecules, much more reactive. In comparison with other OH-groups on C(3) atoms are the least reactive [3, 6, 7].

The most important demand in printing process is the diffusion capability [1, 2, 8] of reactive dye or its crosslinking from the printing paste on/in substrate and its chemical binding during fixation process. The diffusion of reactive dye is at the most important criteria dependent on reactivity of the dye and on its affinity to cellulose fibre, at which, for successful reaction of the dye with substrate the affinity of the reactive dye [8, 9] to cellulose fibre must be higher than to polysaccharide guar thickener. The diffusion properties are also dependent on physical properties, above all on capability of swelling of the thickener which influences the depth of colour and the penetration of the dye.

In this paper the influence of nonsubstituted and with different substitution levels of carboxymethyl guar thickeners on results of viscose prints shown. For preparing the printing pastes we used different monofunctional monovinylsulphonic (VS) reactive dyes, C.I. Reactive Blue 19 and C.I. Reactive Violet 5. At the same time concentrations (1.5, 3.0 and 5.0%) of the dyes were varied. We evaluated the results of prints with determination of the fabric stiffness (bending rigidity), the depth of colour and the penetration of the dye.

EXPERIMENTAL PART

Substrate

All experiments were made on viscose textiles with a mass per unit area of 126,1 g/m².

Thickeners

Nonsubstituted guar gum (Fig. 1) and carboxymethylised guar gum (Fig. 2) of different substitution levels were used as polysaccharide thickeners [4, 10]. The used thickeners can be seen in Table I.

Reactive Dyes

The used monofunctional reactive dyes are shown in Table II and on Figures 3 and 4.

Printing Paste and Printing Process

Printing pastes were made according to the recipe shown in Table III and the flat screen printing technique was used in according to the conditions set in Table IV.

Evaluation of Depth of Colour and Penetration

The reflectance values of all printed samples were measured by a spectrophotometer Texflash DC 3881 (Datacolor, Germany). The

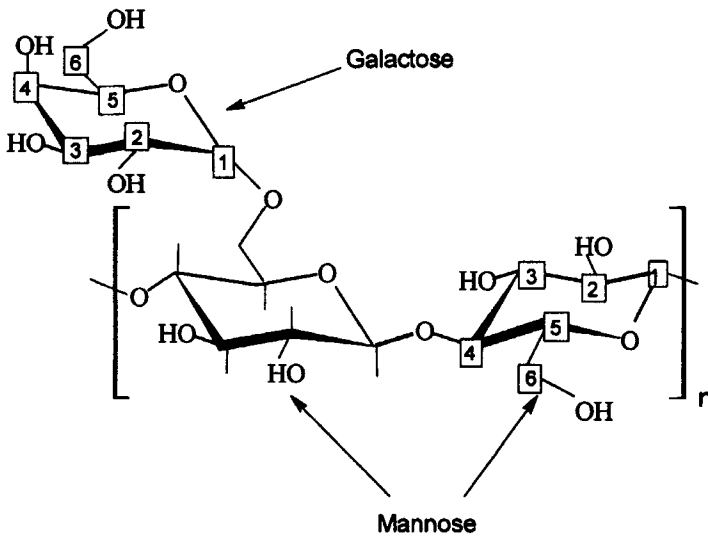


FIGURE 1 Chemical structure of nonsubstituted guar gum (NSG).

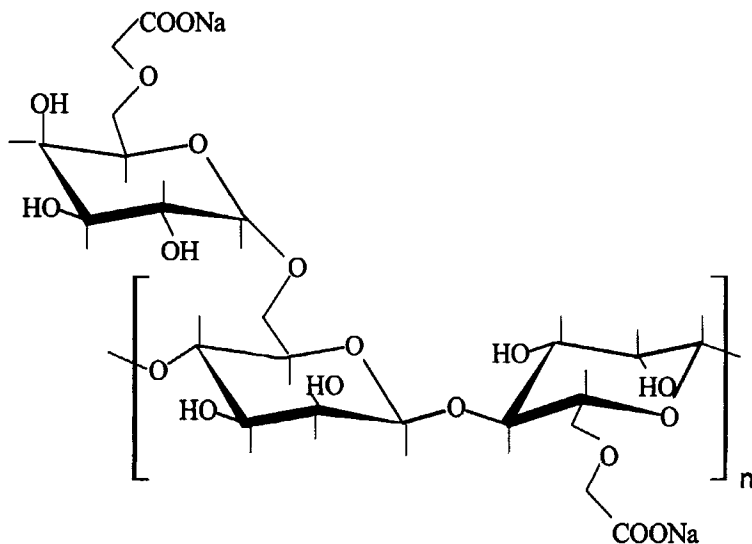


FIGURE 2 Chemical structure of carboxymethylised guar gum (CMG).

TABLE I Thickener, substitution level and sign of abbreviation

Nr.	Thickener	Substitution level-DS	Sign of abbreviation
1.	Nonsubstituted guar gum	0	NSG/0
2.	Carboxymethylised guar gum	0.13	CMG/13
3.	Carboxymethylised guar gum	0.26	CMG/26

TABLE II Monofunctional reactive dyes

Nr.	C.I.	Chromogen	Reactive system	Molekular weight	Sign of abbreviation
1.	Reactive Blue 19	Anthraquinone	VS	624	B19
2.	Reactive Violet 5	Monoazo	VS	735	V5

results of measurements were expressed by K/S values and the penetration calculated by Eq. (1)

$$\text{Penetration (through print)} = \frac{K/S_f}{K/S_b} \times 100[\%] \quad (1)$$

K —the absorption constant depending on the dye,

S —the light scattering constant depending on the substrate,

R – the degree of reflectance at a certain wavelength,
 K/S_f – depth of colour on the front side of the substrate,
 K/S_b – depth of colour on the back side of the substrate.

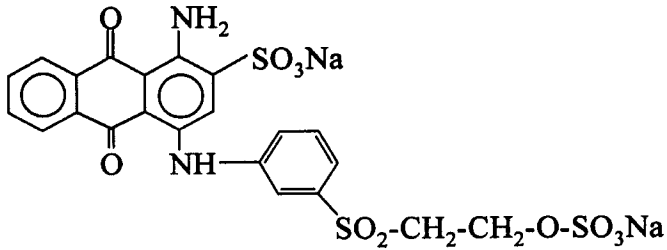


FIGURE 3 Chemical structure of C.I. Reactive Blue 19 dye – B19.

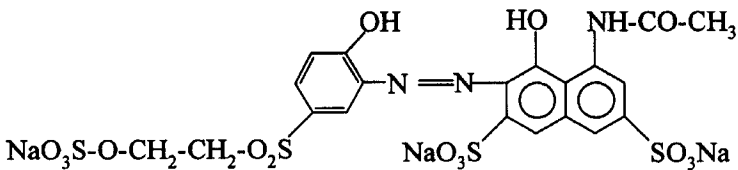


FIGURE 4 Chemical structure of C.I. Reactive Violet 5 dye – V5.

TABLE III The recipe for printing pastes

Substance	Amount [%]
Thickener	60.0
NaHCO ₃	2.5
Reactive dye	1.5, 3.0, 5.0
Water	36.0, 34.5, 32.5

TABLE IV Printing conditions

Stages of work	Condition for work
Printing	<ul style="list-style-type: none"> • Laboratory printing machine (J. Zimmer) Typ VP-RSF • Flat printing screen: finess 77 thread/cm, 80 μm open area • Squeegee diameter: 15 mm • Speed: 5 m/min • Pressure grade: 3
Drying	<ul style="list-style-type: none"> • 5 minutes in drying machine at $T = 40^{\circ}\text{C}$ (W. Mathis)
Steaming	<ul style="list-style-type: none"> • Steamer (W. Mathis) Typ DHE 15973 • Saturated steam: 15 minutes at $T = 102^{\circ}\text{C}$
Washing	<ul style="list-style-type: none"> • Washing 5 times at $T = 95^{\circ}\text{C}$ with demineralized water

Evaluation of Fabric Stiffness by Determining the Bending Rigidity

In order to determine fabric handle, the stiffness of washed and climatized printed samples was measured according to DIN 53212 by determining the bending rigidity. The measurements were performed by using a fabric stiffness measuring apparatus Type 58963 of the firm Frank GmbH.

RESULTS AND DISCUSSION

The Influence of Guar Thickeners on Printing Paste Add-on

Owing to different chemical constitution, the used guar thickeners for preparing printing pastes on equally viscosity ($\eta = 7000 \pm 500$ mPas at shear rate $\dot{\gamma} = 10$ s⁻¹ and $T = 25^\circ\text{C}$), the different concentrations of solid content were required, which influenced the printing paste add-on at constant printing conditions.

Because the type or the concentration of the reactive dye did not influence the printing paste add-on in Figure 5, the add-on of printings pastes without the reactive dye and with all the used guar thickeners are shown. As we see CMG/26 and CMG/13 guar thickeners with highly solid content (33.6 g/kg and 39.6 g/kg) give almost three times

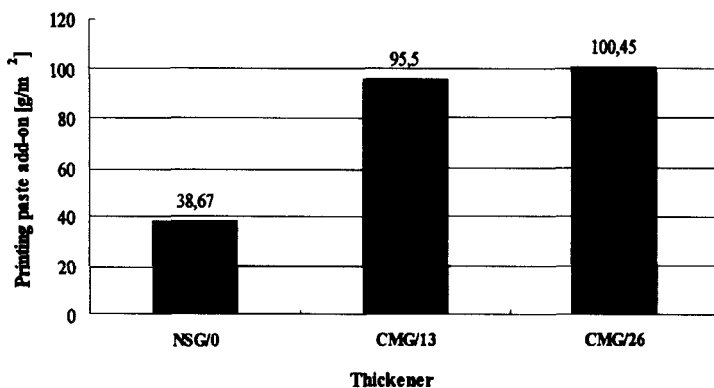


FIGURE 5 The printing paste add-on dependent on the type of guar thickener.

highest add-on of the printing pastes without dye in comparison with NSG/0 thickener with lowest solid content (12 g/kg).

The Influence of Guar Thickeners and Monoreactive Dye on Bending Rigidity of Viscose

In Figure 6 the influence of concentration of reactive dye and of substitution level of the guar thickeners on bending rigidity viscose printed with different monofunctional monovinylsulphone reactive dyes is shown.

The bending rigidity is at every prints higher than the bending rigidity of viscose fabric. This confirms that at binding of the reactive dye with cellulose fibre also the binding of guar thickeners takes place.

Because the bending rigidity at all the used guar thickeners and the concentrations used is instantly greater with V5 than B19 reactive dye the structure of reactive dye also has an important role. Upon previous theory the monofunctional monoreactive dyes does not cause the highest bending rigidity in case of guar thickeners [5]. But as we can see from the results, the bending rigidity at all samples printed with B19 dye is independent from the concentration of the dye, while with decreasing substitution level the guar thickener loosely decreases. With the V5 reactive dye the bending rigidity differently increases with carboxymethylised guar thickeners with increasing of concentration of the dye. From this we can infer that V5 reactive dye can make covalent

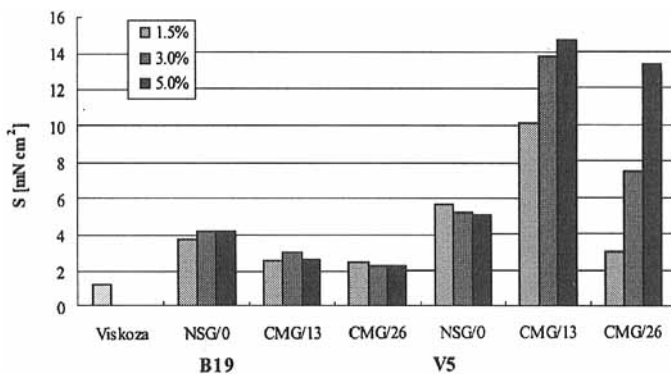


FIGURE 6 The influence of guar thickeners and monoreactive dyes on bending rigidity of viscose.

bond with its functional (VS) group on viscose fibre and at the same time through OH-group forms hydrogen bond with guar thickener. At lower concentrations of the dye it is less probable that this kind of binding occurs, because of high substantivity of the dye on cellulose fibre and according to this the quicker binding with cellulose fibre and because of smaller number of free groups capable of reaction. The probability is higher at high concentrations of the dye where the bending rigidity is very increased. The probability for this kind of binding is seen if we compare the bending rigidity of these samples with samples printed with B19 dye (Fig. 3) which does not have OH-groups.

Because the interactions between polysaccharide guar thickener, reactive dye and viscose are determined by the thickener, by its solid content and the number of free OH-groups on guar molecule, the solid content and the substitutional level of thickener have the strongest influence on bending rigidity. Nonsubstituted guar (NSG/0) causes certain stiffness which does not change considerably with different reactive dyes, while the bending rigidity in the case of CMG/12 and CMG/26 guar thickeners, dependent on the kind of the dye used, increases considerably. The bending rigidity, very increased with V5 reactive dye and CMG/13 thickener and again decreases with CMG/26 because of higher substitutional level. Higher number of free OH-groups with CMG/13 thickener in comparison with CMG/26 gives more chances for binding of guar molecules. Negative charge in CMG/26 thickener, which is made with dissociation of carboxyl groups in water by guar's macromolecules, lowers the probability of interactions between reactive dye and polysaccharide guar.

In order to confirm the binding of polysaccharide guar with cellulose fibre we calculated the quantity of remaining add-on by difference of mass samples, determined before printing and after the finished technological procedure. In Figure 7 the different add-on on printed cellulose fibre, which confirms the crosslinking of guar on viscose, is shown.

The Influence of Thickeners on Colour Depth of K/S Printed Viscose

Different depth of colour is the result of mutual effect between reactive dye and polysaccharide thickener and is dependent on their chemical

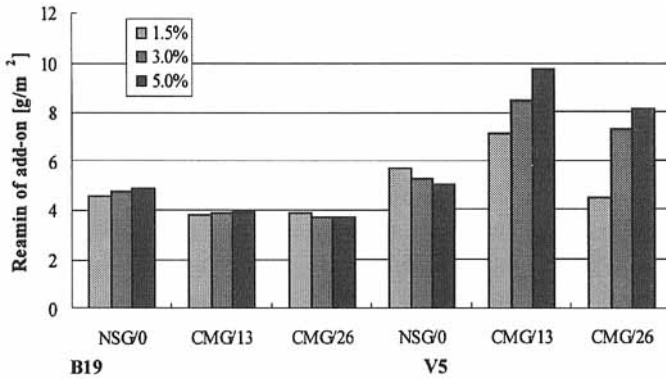


FIGURE 7 The remain of add-on on printed viscose.

constitution and physico chemical properties [2, 6–9]. In concentrated solution the polysaccharide macromolecules form certain crosslinking structure which is dependent on macromolecular structure and quantity of solid content. Nonsubstituted guar with a low solid content form in the solution, because of high molecular mass of long polymers, a loos crosslinking structure, while carboxymethylised guar with a high solid content forms, because of short low molecular polymers, very dense crosslinking structure [10].

As seen in Figure 8 the K/S_1 values in both dyes are extremely high in printing with CMG/13 and CMG/26 guar, which is connected with

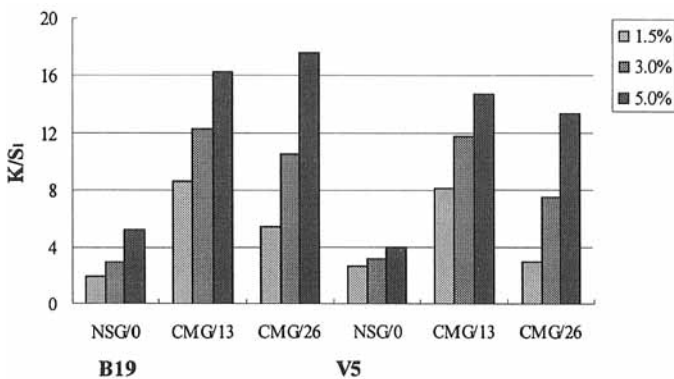


FIGURE 8 The influence of guar thickener and monoreactive dye on the depth of colour.

high print paste add-on (Fig. 5) and then also with high add-on of the dye on the surface of the fibre. Because of that the K/S_f values are quite lower at samples with NSG/0 thickener. Different K/S_f value in different dyes is the result of different reactivity and affinity of reactive dye to a viscose fibre or to a polysaccharide guar thickener. The strongest influence on the affinity of reactive dye has chromogen. Slightly higher K/S_f values in the case of B19 dye at all concentrations of dye and used guar thickeners are connected with anthraquinone chromogen, which has influence on higher affinity of the dye to cellulose fibre than azo chromogen (V5 dye).

The Influence of Thickeners on Penetration of Printed Viscose

The penetration is seen in the depth of colour of print and represents the relation between the depth of colour on the front and the back side of the fibre. During the fixation phase the molecules of dye diffuse through diffusive medium from printing paste into the fibre where they have higher affinity to viscose fibre than to polysaccharide guar thickener. The condensed water causes the swelling of printing paste on the surface of substrate and the diffusion of the dye from add-on film into the fibre. Due to quick diffusion there is less contact and because of that the reactive time between the reactive dye and the guar thickener is shorter and that influences the lowest bending rigidity. The diffusion of reactive dye is therefore dependent on the swelling capability of guar thickener and viscose fibre, the size of molecule of dye and its substantivity to substrate.

In Figure 9 the level of penetration at both monoreactive dyes in dependence with the kind of guar thickener is seen. Among all used guar thickeners we can see the highest penetration with NSG/0 thickener, which is a result of good swelling of thickener. Slightly lower level of penetration in the case of printing with carboxymethylised guar thickeners CMG/13 and CMG/26 is connected with higher content of solid content of thickeners and therefore with not so good capability of swelling. Penetration does not differ substantially from the kind but it does from the concentration of reactive dye. The higher concentration of dye causes the solution of dye on the surface of fibre, which hinders the diffusion through porous surface of fibre [8,9].

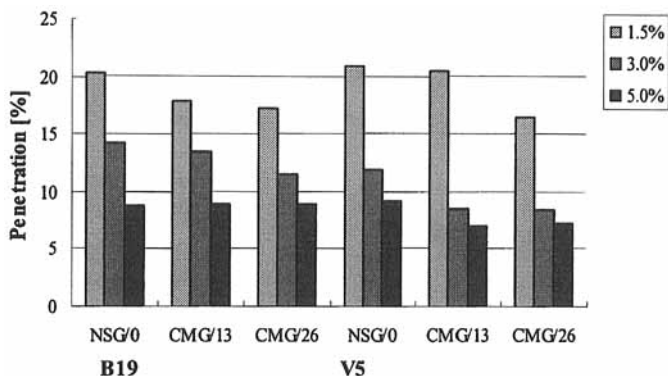


FIGURE 9 The influence of guar thickener and monoreactive dye on penetration of the dye.

Because of that we can see at higher concentrations of dye (at 3.0% and 5.0%) considerably lower level of penetration, which is in the case of V5 dye because of lower affinity and slower diffusion of this dye, more distinctive. With this dye we cause stronger binding on the surface of substrate.

CONCLUSION

Based on the results of the experiment we can conclude that the increased stiffness in printing on viscose with guar thickener occurs also in the case of monoreactive vinylsulphone dyes and that this increasing depends on the structure, mainly on the presence of hydroxyl groups and affinity of reactive dye. We can also see that the nonsubstituted guar causes certain bending rigidity, which is in the case of carboxymethylised guar because of higher solid content and therefore higher number of hydroxyl groups, capable to react, very increases and with higher substitutional level again decreases. The highest level of penetration gives, because of the low solid content of the nonsubstituted guar thickener, capable of good swelling, which again because of low print paste add-on, influences on a low quantity of binding of dye and the bad depth of colour. With carboxymethylised guar thickener the depth of colour is therefore much higher and

increases with increasing concentration of the dye while the penetration of the dye strongly decreases.

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