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Evaluation of enzymatic hydrolyzed starches in discharge, discharge-resist and burn-out printing styles

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Maize starch samples have been subjected to gelatinization at 70°C followed by enzymatic treatment using different concentrations of α-amylase enzyme (0.025, 0.050, 0.075 and 0.1 mL/50g starch) and then used in printing paste as thickener for discharge, discharge-resist and burn-out printing on cotton, wool/polyester and viscose/polyester/lucre fabrics. The results show that enzymatic treatment of maize starch converts the rheological properties of starch from thixotropic into pseudo-plastic. Increase in α-amylase enzyme concentration is accompanied by a decrease in the apparent viscosity. While enzyme-treated starches give better results when used as thickening agent in discharge-resist printing compared with sodium alginate, the opposite holds true in case of discharge printing. Enzyme-treated starches specially that prepared using 0.1 mL/50g starch could act successfully as thickening agent in burn-out printing of both wool/polyester and viscose/ polyester/lucre blends.

Keywords: α-amylase, Burn-out printing, Cotton, Discharge printing, Discharge-resist printing, Enzyme treatment, Wool/polyester blend, Viscose/polyester/lucre blend

1 Introduction

Textile printing is called localized dyeing. Unlike dyeing, in printing the dye penetrates into the selective areas of the substrate.[1] A distinction is usually made between printing methods and printing styles. Printing styles[2] are (i) direct printing where printing pastes come into contact with the fabric surface with no subsequent processing alterations; (ii) discharge printing in which subsequent processing of a printed fabric is carried out to bleach or destroy certain colours in the pattern; (iii) resist printing, where certain parts of the fabric are originally protected by waxes or other materials to resist colouration by printing pastes or inks; and (iv) burn-out printing where burn out style of printing is carried out using a paste containing chemicals capable of dissolving or destroying one of the fibre components of a blended fabric. This technique was developed in France in the early twentieth of the last century and was extremely popular in fashion design[3].

Printing is done by using a thickening agent along with the dye and the required chemicals. The thickening agents, also called the thickeners, restrict the spreading of the dye. Thickeners are generally high molecular weight polymeric compound, usually water soluble, swell able substances with colloidal character which are used in their thickened state as thickeners for printing with aqueous solution of dye and pigments[4]. Starch and its derivatives is one of the most important thickening agents used in textile printing. Starch is a homopolymer of glucose (D-glucopyranose) units, with most of the units jointed by α1:4 glucoside linkages[5-10].

Starch is a major storage product of many economically important crops such as wheat, rice, maize, tapioca, and potato. A large-scale starch processing industry has emerged in the last century. In the past decades, we have seen a shift from the acid hydrolysis of starch to the use of starch-converting enzymes in the production of maltodextrin, modified starches, or glucose and fructose syrups. Currently, these enzymes comprise about 30% of the world's enzyme production. Besides the use in starch hydrolysis, starch-converting enzymes are also used in a number of other industrial applications, such as laundry and porcelain detergents or as anti-staling agents in baking[11].

The present study aims to prepare starch derivatives via treatment with α-amylase under

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controlled conditions, and to investigate the rheological properties of their pastes. Furthermore, the suitability of the prepared derivatives as thickening agents in discharge, discharge-resist and burn-out printing on cotton, wool/polyester and viscose/polyester/lucre fabrics is also investigated.

2 Materials and Methods

2.1 Materials

Mill desized, bleached and mercerized cotton and wool/polyester (70/30) blended fabrics, produced by El-Mehalla for Spinning and Weaving Company, were used.

High viscosity sodium alginate from brown algae, manufactured by Fluka Chemical Company, was used as a thickening agent. British gum and starch, supplied by Misr Company for Starch and Glucose, Cairo, Egypt were used. Daico thickener PES, produced by Nadin Print Company, was used.

Reactive dyes, namely Sunzole Red F3B and Sunfix Yellow MF-D, were supplied by ICI Company, Cairo, Their reactive center is vinylsulphone.

Ethyl alcohol, sodium hydrosulphite, glucose, titanium dioxide, sodium hydroxide, sodium hydrogen sulphate and glycerin were also used.

Alpha amylase enzyme, supplied by Novozymes A/S Krogshoejvej 36 2880 Bagsvaerd Denmark, was used for the study.

2.2 Methods

2.2.1 Cooking and Enzymatic Treatment of Starch

Fifty grams (50 g) of starch powder was added to 250 mL water and then the starch was cooked at 70°C in a water bath for 30 min during mechanical stirring. The cooked starch samples were subjected to enzymatic using the following procedure

The aforementioned cooked starch was treated separately with different concentrations of α-amylase enzyme (0.025, 0.05, 0.075, 0.1 mL/50 g starch) at 40°C for 30 min at *p*H 5 under vigorous stirring. The *p*H was adjusted using acetic acid and sodium dihydrogen phosphate as buffer.

The prepared enzyme-treated derivatives were precipitated using commercial ethyl alcohol several times until free from the enzyme.

2.2.2 Dyeing of Cotton Fabric

The cotton fabric was padded in a solution containing 30 g/L dye, 35g/L sodium carbonate[12] and 2g/L wetting agent to pick up of 70% at room temperature.

2.2.3 Printing

White Discharge Printing

The printing paste was prepared according to the following recipe:

Sodium hydrosulphite + Glucose (2:1) (Reducing agent)	:	250 g
Titanium dioxide	:	100 g
Thickening agent	:	*Y* g
Water	:	*X*
Total	:	1000 g

Thickening agents used were either sodium alginate (30g) or enzymatic hydrolyzed starch (200g/kg). Sodium alginate was soaked in a small amount of water overnight at room temperature before commencing preparation of the corresponding printing paste. The reducing agent mixture was dissolved in water, and then poured on the thickener suspension followed by titanium dioxide under stirring. Finally, the total weight of the whole paste was adjusted to one kilogram with addition of the necessary amount of water. The same procedure was conducted in case of hydrolyzed starch, except it was subjected to cooking instead of soaking overnight.

Discharge-resist Printing

The recipe of the uncolored printing paste was as follows:

Sodium hydrosulphite + Glucose (2:1)	:	250 g
Titanium dioxide	:	100 g
Thickening agent	:	*Y* g
Water	:	*X*
Total	:	1000 g

Thickening agents used were either sodium alginate (30g/kg) or enzymatic hydrolyzed starch (200g/kg). The pastes were prepared as previously indicated.

The printed cotton samples were then over printed using printing pastes containing one of the aforementioned two reactive dyes, using the following recipes:

Reactive dye	:	30 g
Urea	:	100 g
Sodium alginate	:	30 g
Sodium bicarbonate	:	30 g
Water	:	*X* g
Total	:	1000 g

The dye was first mixed with urea and some hot water. Thorough stirring of this mixture was performed to homogenize the solution. The solution was poured on the alginate suspension and the whole mixture was thoroughly stirred with addition of the bicarbonate. Finally, the total weight of the whole paste was adjusted to one kilogram with addition of the necessary amount of water.

Fixation and Washing—The discharge and discharge-resist printed fabrics were fixed via steaming at 102°C for 15 min. The fixed discharge and discharge-resist printed fabrics were subjected to washing through five stages as given below:

- Rinsing thoroughly with cold water
- Treatment with hot water
- Treatment near the boiling temperature (90-95°C) with a solution containing 2 g/L Aspkon 1030
- Washing with hot water
- Rinsing with cold water

Burn-out Printing

Burn-out Printing of Wool/Polyester (70:30) Blend

The printing paste containing the following recipe was used

Thickening agents	:	*X* g
Sodium hydroxide	:	250 g
Glycerin	:	50 g
Water	:	*Y*
Total	:	1000 g

Thickening agents used were either British gum (400g) or enzymatic hydrolyzed starch (200g/kg). The British gum was first soaked in water overnight as it has been mentioned in case of sodium alginate.

Fixation and Washing—The burn-out printed wool/ polyester blended fabrics were fixed via steaming at 102°C for 10 min. After fixing, these fabrics were washed with cold water containing acetic acid solution (20%).

Burn-out Printing of Viscose/Polyester/Lucre (50:45:5) Blend

Burn-out printing of the viscose/polyester/lucre (50:45:5) blended fabrics was carried out using the printing pastes containing the following ingredients:

Thickening agents	:	575 g
Sodium hydrogen sulphate	:	125 g
Glycerin	:	50 g
Water	:	250 g
Total	:	1000 g

Thickening agents used were either Daico thickener PES (30g/kg) or enzymatic hydrolyzed starch (200g/kg). The thickener was dissolved in water under vigorous stirring followed by adding sodium hydrogen sulphate and glycerin.

Fixation and Washing—The burn-out printed viscose/polyester/lucre blended fabrics were fixed via thermo fixation at 150°C for 5 min. After printing, the fabric was given a thorough rinse with cold water , followed by hot water, then soaped at 90-95°C with an aqueous solution containing 5g/L Hostapal CV and 2g/L sodium carbonate for 15 min. At the end, the fabric was given a hot rinse, followed by a thorough wash with cold rinse.

2.3 Analysis and Measurements

The rheological properties of the printing pastes were measured using Rheomat-15 Zurich, Switzerland at 25°C and the apparent viscosity (η) at various rates of shear was calculated from the shearing stress (τ) and rates of shear (D) using the equation[13] $\eta = \tau/D$

The colour strength, expressed as *K/S*, was assessed according to a standard method[14].

3 Results and Discussion

In the present work, maize starch was treated with α-amylase enzyme using different concentrations of amylase viz. 0.025, 0.05, 0.075, 0.1 mL/50 g starch at 40°C and *p*H 5 for 30 min. The prepared samples were then purified via precipitation in commercial ethyl alcohol and air-dried. The treated starch samples were cooked again at 90°C for 30 min at a concentration of 20% in order to investigate the rheological properties of the prepared pastes and to investigate its suitability as thickening agent.

3.1 Rheological Properties

Pastes of the aforementioned cooked enzyme-treated starch were prepared at a concentration of 20%. The rheological properties were monitored before and after storing of the pastes for 3 days. The results obtained are shown in Fig. 1A.

It is clear from the rheograms (Fig. 1A) that native starch exhibits non-Newtonian thixotropic behavior, where the up and down rheograms are not coincident, while all of the enzyme-treated starch pastes are characterized by a non-Newtonian pseudo-plastic behavior, where the up and down flow curves are coincident. This reveals the homogeneity of the molecular structure of the enzyme-treated pastes,

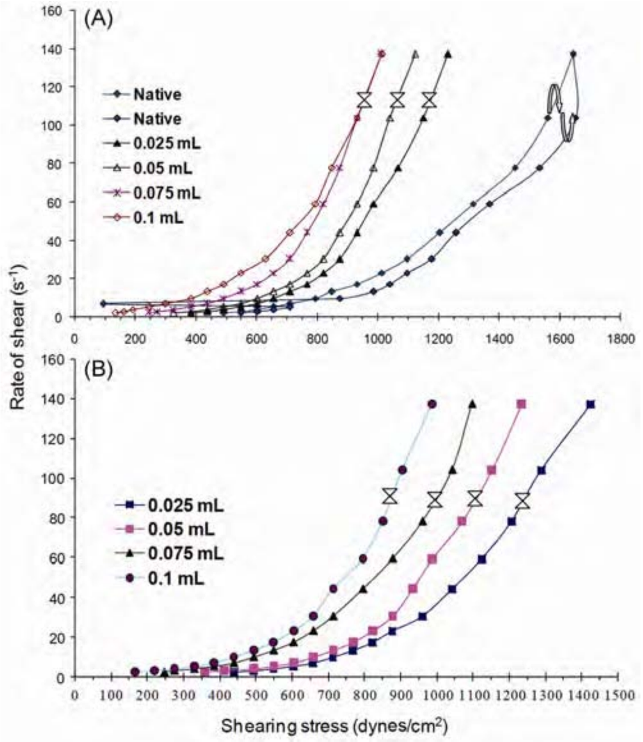

Fig. 1—Rheograms of (A) fresh enzyme-treated starch pastes and (B) enzyme-treated starch pastes after storing for 3 days

which are amenable to rebuild themselves and retain their original state immediately after removal of the acting force[15].

Figure 1A also shows that the location of the rheograms with respect to the rate of shear depends on the used concentration of α-amylase enzyme. As the latter increases, the rheogram is shifted near to the rate of shear axis, indicating a decrease in the apparent viscosity. A clearer picture about the apparent viscosity at various rates of shear is shown in Table 1. The pastes were stored for 3 days and their rheological properties were measured. The data are also given in Table 1.

It is worthy to mention that the untreated cooked maize starch is unstable for storing for 3 days, as fermentation takes place. Hence, we cannot measure its rheological properties after storing. However, the enzyme-treated starch pastes are found to be stable for three days, and hence their rheological properties can be measured. The rheograms obtained are illustrated in Fig. 1B.

It is clear from Fig. 1B that the rheological properties of enzyme-treated starches remain non-Newtonian pseudo-plastic after storing for 3 days. However, the rheograms are shifted far from the rate of shear axis, which indicates an increase in the apparent viscosity by storing.

A clearer picture about the apparent viscosity is shown in Table 1 before and after storing for 3 days. The apparent viscosity decreases as α-amylase concentration increases. For example, at the rate of shear 17.26 s^{-1} it decreases from 44.41 to 41.24, to 34.89 and finally to 28.55 poise as the α-amylase enzyme concentration increases from 0.025 to 0.05 to 0.075 and finally to 0.1 mL respectively. This may be due to enzymatic decomposition of starch polymers as the concentration of enzyme increases. The shorter the molecules chain the lesser is the viscosity of the product.

Table 1 also represents the data obtained after storing for 3 days. The apparent viscosity increases by storing for 3 days. The increase in the apparent viscosity by storing may be due to the increase in the adhesive power or the formation of some physic-chemical bonding, viz. hydrogen or Van der Waals forces.

3.2 Printing

In the present work, the suitability of starch samples treated with α-amylase enzyme as thickening agents in discharge, discharge-resist and burn-out printing was investigated. To achieve this goal, printing pastes thickened with α-amylase enzyme treated starch samples or sodium alginate or British gum or Daico thickener PES were prepared according to the recipes given in the experimental section. The values of *K/S*, weight loss, tensile strength and overall fastness properties of the printed fabrics were measured.

3.2.1 Discharge Printing on Cotton Fabrics

To investigate the effect of α-amylase enzyme-treated starches as thickening agents in discharge printing, different printing pastes thickened with starch samples treated with 0.025, 0.050, 0.075 and 0.100 mL of α-amylase enzyme/50g starch or commercial sodium alginate, were prepared as describe before. The latter was more safe and ecofriendly when compared with the traditional sodium or zinc sulphoxylate formaldehyde which is conventionally used for discharge printing[16]. Samples of cotton fabrics dyed with Sunzole Red F3B were printed with the aforementioned pastes. After printing, drying and steaming at 102°C for 15 min the samples were washed and assessed for *K/S* measurements (Table 2).

Table 1—Effect of α-amylase concentration on apparent viscosity at various rates of shear

Rate of shear s^{-1}	Apparent viscosity, poise									
	0.0 mL		0.025 mL		0.05 mL		0.075 mL		0.1 mL	
	Fresh	Stored for 3 days	Fresh	Stored for 3 days	Fresh	Stored for 3 days	Fresh	Stored for 3 days	Fresh	Stored for 3 days
2.18	226.07	-	175.83	200.95	150.71	163.27	113.03	113.03	62.79	75.35
2.93	186.89	-	149.51	168.2	130.82	140.17	93.44	93.44	56.06	74.75
3.85	156.45	-	128.01	142.23	113.78	128.01	85.34	85.34	49.78	71.11
5.14	127.84	-	106.53	117.19	95.88	106.53	74.57	74.57	47.94	63.92
6.78	104.99	-	88.84	96.92	80.76	88.84	64.61	64.61	44.42	56.53
9.77	81.27	-	67.25	72.86	61.65	67.58	50.44	50.44	39.23	44.83
13.12	64.69	-	54.25	58.43	50.08	54.22	41.73	41.73	33.39	37.56
17.26	53.93	-	44.41	47.58	41.24	44.41	34.89	34.89	28.55	31.72
23.03	43.98	-	35.66	38.04	33.28	35.66	28.53	28.53	23.77	26.15
30.38	36.05	-	28.84	31.54	27.03	28.84	23.43	23.43	20.72	21.63
44.1	27.31	-	21.1	23.59	19.86	21.1	17.38	18	16.14	16.14
59.22	22.19	-	16.64	18.95	15.71	16.64	13.87	14.9	13.4	13.4
77.92	18.62	-	13.7	15.46	12.64	13.7	11.24	12.29	10.89	10.89
103.9	15.02	-	11.06	12.38	10.01	11.06	8.95	10.01	8.95	8.69
137.1	12.38	-	8.98	10.38	8.18	8.98	7.38	7.89	7.38	7.18

Table 2—Effect of thickener type on % decrease in *K/S* of discharge and discharge resist printed samples

Thickener used	*K/S*			% decrease in *K/S*		
	Discharge printing	Discharge resist printed		Discharge printing	Discharge resist printed	
		Sunzole Red F3B	Sunfix Yellow MF-D		Sunzole Red F3B	Sunfix Yellow MF-D
Untreated	3.25	3	12	-	-	-
Sodium alginate	0.62	0.07	0.57	80.92	97.66	95.25
Starch treated with α amylase (0.025 mL/50g starch)	1.14	0.09	0.57	64.92	97	95.25
Starch treated with α amylase (0.05 mL/50g starch)	1.13	0.08	0.57	65.23	97.33	95.25
Starch treated with α amylase (0.075 mL/50g starch)	1.1	0.08	0.56	66.15	97.33	95.33
Starch treated with α amylase (0.1 mL/50g starch)	1.1	0.07	0.55	66.15	97.66	95.41

It is clear from the data that the samples printed using the prepared enzyme-treated starches acquire relatively low % decrease in the *K*/*S* compared with the samples printed using sodium alginate. This phenomenon holds true regardless of the concentration of the enzyme used. The current results may be due to the relatively higher solid content of the treated starches (20%) compared with sodium alginate (3%). Hence, the penetration in case of using sodium alginate seems to be better than that of enzyme-treated starches.

Samples were dyed via padding with Sunzole Red F3B or Sunfix Yellow MF-D and printed with sodium hydrosulphite: glucose ratio 2:1 (in 250g) and fixed via steaming.

3.2.2 Discharge-resist Printing

The prepared enzyme-treated starches were evaluated as thickening agents in discharge-resist printing. To achieve this goal, cotton fabrics were printed with uncolored printing pastes containing a mixture of sodium hydrosulphite/ glucose at a ratio of 2:1 and thickened with either enzyme-treated starches or sodium alginate. After printing and drying, the fabrics were subjected to overprinting using a colored printing pastes containing either Sunzole Red F3B or Sunfix Yellow MF-D. The dyed samples were then subjected to steaming at 102°C for 15 min followed by washing and air drying. The dried samples were assessed for *K/S*. The results obtained are given in Table 2.

It is clear from the results that enzyme-treated maize starches could be used successfully in discharge-resist printing especially using the highest concentration, i.e. 0.1 mL/50g starch.

The samples treated with 0.1 mL enzyme/50g starch give a % decrease of 97.99% which is equal to that obtained in case of sodium alginate in case of using Sunzole Red F3B, and slightly higher than that obtained in case of sodium alginate on using Sunfix Yellow MF-D (95.41 % decrease).

3.2.3 Burn-out Printing

Finally, the enzyme-treated starch samples were evaluated as thickening agents in burn-out printing style also. To achieve this goal, burn-out printing paste containing either sodium hydroxide[17] (250g/kg paste) or sodium hydrogen sulphate[16] (125g/kg paste) was thickened with either enzyme-treated starch samples, British gum or Daico thickener PES. The prepared pastes were used in printing wool/polyester (70:30) or viscose/polyester/lucre (50:45:5) blends.

After printing and drying, the samples were either steamed at 102°C for 15 min or thermofixed at 150°C for 5 min. After that, the samples were washed thoroughly, air dried and assessed for weight loss. The data obtained are represented in Fig. 2.

In case of wool/polyester (70/30) yarn, enzyme-treated starches are found to be better than British gum as thickening agent in burn-out printing. However as the concentration of enzyme increases the % weight loss increases too. The superiority of enzyme-hydrolyzed starch over British Gum in burn-out printing may be due to the high solid content in case of using British gum (40%) compared with hydrolyzed starch (20%). Hence, the thickness of the printed film is relatively higher which causes mechanical hindrance for discharging chemical to act on the fabric surface.

However, in case of viscous/polyester/lecra (50/45/5) blended yarn, Daico thickener PES is found to be better than the enzyme-treated starch samples using 0.025, 0.050, 0.075 mL α-amylase enzyme/50g. The sample treated with higher amount of enzyme (0.1 mL/50g starch) gives better results than Daico thickener PES. Also, as the viscosity of the enzyme-treated starch decreases the penetration of the printing paste increases and hence the per cent burnt-out also increases.

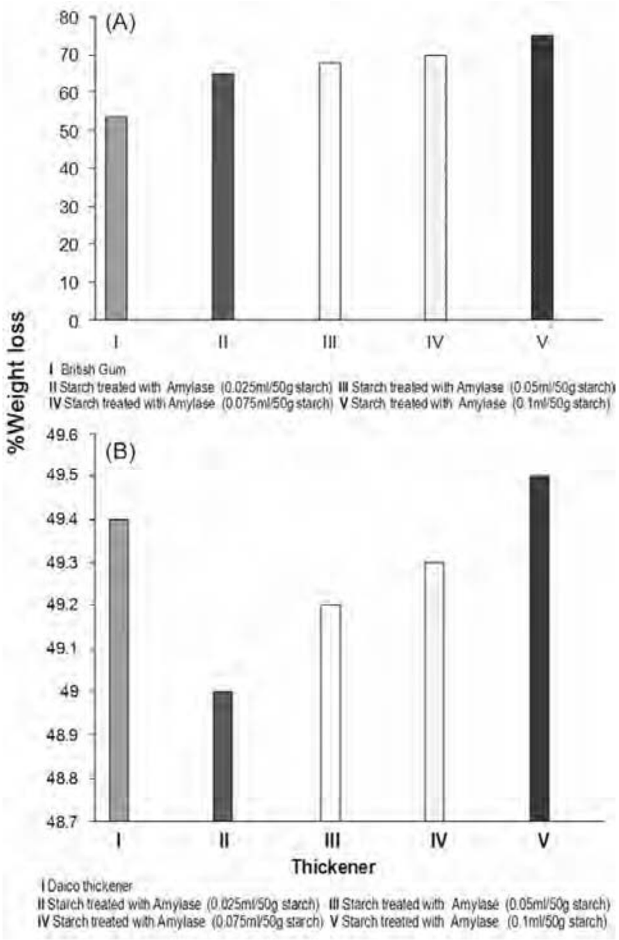

Fig. 2—Weight loss of (A) wool/polyester (70:30) and (B) viscose/polyester/lecra blended fabrics printed via burn-out style using starch derivatives treated with amylase enzyme

It can be concluded that enzyme-treated starch specially that prepared using 0.1 mL/50g starch could act successfully as thickening agent in burn-out printing of wool/polyester blend or viscose/polyester/lucre blend.

4 Conclusion

4.1 Enzymatic treatment of maize starch converts the rheological properties of starch from thixotropic to pseudo plastic.

4.2 At a constant rate of shear, increase in α-amylase enzyme concentration is accompanied by a decrease in the apparent viscosity.

4.3 Enzyme-treated starches give better results in discharge-resist printing using sodium alginate than in discharge printing. Enzyme-treated starch samples are used successfully in burn-out printing of both wool/polyester and viscose/ polyester/lucre blend.

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