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Development of ecofriendly binders for pigment printing of all types of textile fabrics

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Abstract

For many years, improving the quality of pigment prints was the main goal in product development. Lately, economic, environmental and toxicological considerations have become more important. Using more environmentally friendly pigment preparations and auxiliary products, for example to reduce or to eliminate formaldehyde on the fabric, is currently one of the major concerns in the textile printing industry. The curable oligomers take the place of the organic solvents and work as the binder of pigments. Some novel prepared aqueous binder of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate having zero volatile organic compounds was used for preparing printing paste for screen printing of all types of textile fabrics using pigment dyes.

The highest color strength is obtained and fastness properties range between good and excellent for samples printed using polyurethane acrylate based on glycerol ethoxylate-*co*-propoxylate as a binder, this is true irrespective of the type of fabric used. While lower value of color strength is obtained for samples printed using Ebecryl 2002 as a commercial binder, and polyurethane acrylate based on PEG_{2000} is better than polyurethane acrylate based on $PEG_{1000+2000}$, unless in case of screen printed wool, the inverse is true.

Keywords: Development; Ecofriendly; Binders; Pigment; Pigment printing; Textile fabrics

1. Introduction

Pigment printing is not only the oldest but also the easiest printing method as far as simplicity of application is concerned [1–5]. More than 80% of the printed goods are based on pigment printing due to its obvious advantages, such as versatility, ease of near final print at the printing stage itself, etc. This pigment printing makes use of kerosene or mineral turpentine which is involved in making emulsion thickeners. In this system, the kerosene in the emulsion gets evaporated to the atmosphere at the time of curing of the pigment printed fabric [6].

It is almost impossible to reclaim this kerosene. In spite of the superior thickening properties of kerosene/water emulsion which also contribute towards a soft hand of the print, good fastness properties, ease of application methods, and economy, and several other factors have compelled the search for a replacement for kerosene; some of these are [7]:

1. The ongoing oil crisis, both in terms of cost and availability makes it imperative to minimize kerosene use.
2. When printed fabrics are dried and cured in ovens, the surrounding atmosphere in the oven must contain enough excess of air volume in relation to the volatile hydrocarbon volume to ensure that the mixture is below the explosion point. A number of

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fatal accidents caused by explosions in curing ovens proved that this system is highly risky.
3. The emission of high percentage of hydrocarbons through the curing exhausts is considered to be posing a very serious problem.

The use of synthetic thickening agents and new developments in printing auxiliaries have also contributed to the increasing importance of pigment printing, since here, too, environmental aspects such as minimization of formaldehyde emissions and carbon dioxide content must be taken into account. At the same time, novel binder systems allow a much softer handle to be attained [8]. Formaldehyde emissions and clogging on the screens during the actual printing process must also be taken into account [9–11]. These disadvantages are related to the binders used.

The aim of this work was to examine some novel prepared aqueous binders having low viscosity and zero volatile organic emissions of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate in pigment printing, and the new idea is not only fixation of the pigment dye through the polymerization process of the binder but also printing all types of fabrics using pigment dyes.

2. Experimental

2.1. Materials

- Aqueous binders of polyurethane acrylate based on either polyethylene glycol 2000 and 2000 mixed with 1000 or glycerol ethoxylate-*co*-propoxylate had been prepared [12–14] and commercial binder was supplied under the commercial name Ebecryl 2002 by UCb, Belgium.
- Sodium alginate (HV) from *Macrocystis pyrifera* (Kelp) SIGMA chemical Co., Germany.
- Helizarin Brilliant red BBT, BASF, Germany.
- Ammonium persulfate $(NH_4)_2S_2O_8$, MERCK, Germany.
- Mill scoured, bleached and mercerized plain wave cotton fabric (135 g/m^2), viscose fabric [100% viscose] of 140 g/m^2, wool fabric [100% wool] of 145 g/m^2, polyamide fabric [100% nylon 66] of 110 g/m^2, and polyester fabric [100% PES, satin] of 85 g/m^2 supplied by private sector Co.

3. Methods

3.1. Preparation of printing pastes

The pigment printing pastes were prepared according to the following recipe:

Ingredients	By weight (%)
Binder*	40
Pigment dye	3 or 5
Sodium alginate	1
Ammonium persulfate	2
Distilled water	up to 100%

* The binder used was either polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate and/or Ebecryl 2002.

3.2. Printing technique

The fabrics' printing was carried out using screen printing machine, Type VP-AL-500, Germany, the printed fabrics were dried in air, the goods were subjected to thermal treatment in a thermostatic oven (Mathis, Switzerland) to fix the color through the polymerization process. After that the printed goods were subjected to washing, via, rinsing thoroughly with cold water, then treated with hot water to remove the residual unfixed dye and also the remains of sodium alginate.

4. Testing and analysis

4.1. Rheological properties

The rheological properties and apparent viscosity of the printing pastes were measured using fluids spectrometer RFS II (Rheometrics CO 1483), Germany at 25 °C and at different shear rates.

4.2. Color measurements

The relative color strength of the prints, expressed as K/S value [15] of the printed samples was determined by reflection measurements using data color international model SF 500, USA.

4.3. Fastness properties

Fastness to washing [16], rubbing [17], and perspiration [18] was assessed according to the standard methods.

5. Results and discussion

This work was carried out with the following three main objectives in mind:

- Elimination of either kerosene/water emulsion or formaldehyde emissions in pigment printing by using some novel prepared binder containing unsaturation sites which is responsible for fixation of the pigment through polymerization process.

- Evaluation of the prepared binder [7–9] of polyurethane acrylate based on either ethylene glycol or glycerol ethoxylate-*co*-propoxylate as a binder used in preparation of printing paste.
- Printing of all types of fabrics using the pigment dye, through this new technique, which is dependent on the fixation of the dye through the polymerization process that happened to the binder used under the effect of the temperature of fixation.

Since the rheological properties of the printing pastes and their viscosity are responsible for controlling dye penetration, depth of shade, sharpness of the print and levelness, it is of great interest to investigate the rheological properties of the printing pastes.

The rheological properties and apparent viscosity of freshly prepared printing pastes using 1% sodium alginate and 40% of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate and/or commercial binder Ebecryl 2002 on using 3 and/or 5% Helizarin Brilliant red BBT are shown in Figs. 1 and 2, respectively.

It is clear from Figs. 1 and 2 that all samples examined were characterized by non-Newtonian pseudo plastic behavior, where the up and down flow curves are coincident. It is also clear from Figs. 1 and 2 that the location of the rheogram and its slope seems to be dependent not only on the type of binder used but also on the concentration of dye used, which indicates a variation in the apparent viscosity. The rheogram curve of the commercial binder used (Ebecryl 2002 containing 3% dye) was shifted nearest to the axis of the rate of shear indicating a decrease in its apparent viscosity as shown in Fig. 1, while on using 5% dye, the rheogram curve was shifted far from the axis of the rate of shear indicating an increase in its apparent viscosity

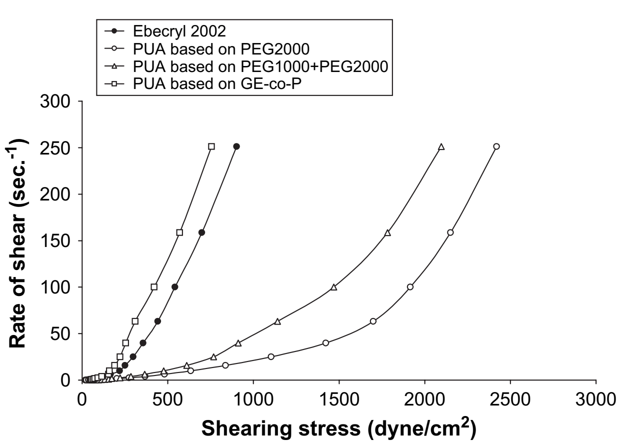

Fig. 1. Rheological properties of freshly prepared printing pastes using 1% sodium alginate and 40% of prepared binder of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate (GE-*co*-P) and/or commercial binder Ebecryl 2002 on using 3% Helizarin Brilliant red BBT.

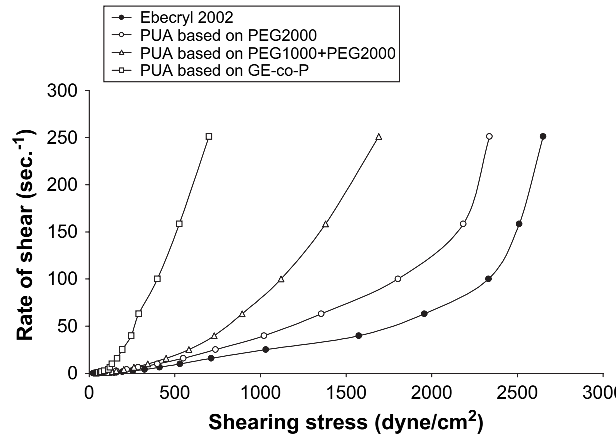

Fig. 2. Rheological properties of freshly prepared printing pastes using 1% sodium alginate and 40% of prepared binder of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate (GE-*co*-P) and/or commercial binder Ebecryl 2002 on using 5% Helizarin Brilliant red BBT.

as shown in Fig. 2. But vice versa in case of using the prepared binder of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate. For example, at a rate of shear 10.0007 s^{-1}, the apparent viscosity of Ebecryl 2002 increased from 2.19 to 5.303 Pa s, while it decreased from 6.348, 4.757 and 1.593 to 3.984, 3.425 and 1.327 Pa s in case of using polyurethane acrylate based on PEG_{2000}, $PEG_{1000+2000}$ and GE-*co*-P, respectively, by increasing the amount of dye used from 3 to 5%. This may be due to the difference in the chemical constituent of prepared binder and the commercial binder used, may be the dispersant medium of the pigment dye containing some groups which make cross-links or form hydrogen bonding with the Ebecryl 2002 which lead to an increase in its molecular weight and leads to increase in its viscosity.

5.1. Effect of either dye concentration and/or type of binder used

5.1.1. Screen printed cotton and polyester fabrics

The effect of increasing the fixation temperature on the color strength of screen printed on either cotton (natural fabric) or polyester (synthetic fabric) upon using Ebecryl 2002 as a commercial binder and/or prepared binders of polyurethane acrylate based on PEG_{2000}, $PEG_{1000} + PEG_{2000}$ and based on glycerol ethoxylate-*co*-propoxylate containing Helizarin Brilliant red BBT of different concentrations 3 and 5% and the time of fixation of 2 min are represented in Figs. 3–6, respectively.

It is clear from the Figs. 3–6 that the color strength of the printed fabrics (using either 3% or 5% dye) are nearly comparable. This may be attributed to the increase in the

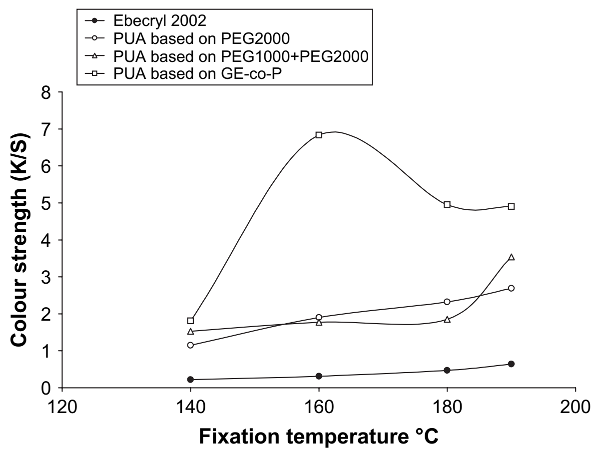

Fig. 3. The effect of the type of binder used on the color strength of screen printed cotton fabrics using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

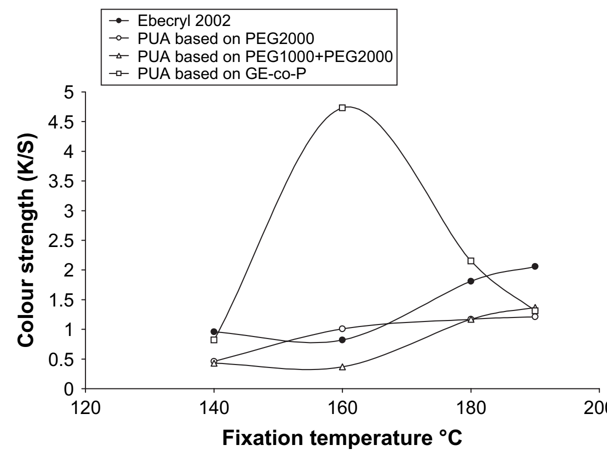

Fig. 5. The effect of the type of binder used on the color strength of screen printed polyester fabrics using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

dye concentration needed to increase in the binder concentration to make fixation to this dye through the polymerization process to this binder.

It is also clear from Figs. 3–6 that the highest color strength values were obtained in case of using polyurethane acrylate based on glycerol ethoxylate-*co*-propoxylate [PUA based on GE-*co*-P] as a binder in the printing paste as compared to the results obtained upon using the commercial binder of Ebecryl 2002, which gives the lowest value of color strength in case of screen printed cotton fabrics, while in case of using PUA based on PEG_{2000}, the K/S values were better than the values obtained in case of using PUA based on $PEG_{1000} + PEG_{2000}$. For example, the K/S values of screen printed cotton and polyester fabrics fixed at temperature 160 °C were 0.31, 1.9, 1.77, 6.83 and 0.85, 1.01, 0.65, 4.73 by using Ebecryl 2002, PUA based on PEG_{2000}, PUA based on $PEG_{1000} + PEG_{2000}$, PUA based on GE-*co*-P as a binder in printing paste containing 3% Helizarin red BBT, respectively. This may be due to either the difference in the structure of the binder used or the amount of unsaturation groups found in the binders which is responsible for fixation of the dye through the polymerization process that happened to these oligomers i.e. binders.

5.1.2. Screen printed viscose, wool, and nylon 66 fabrics

The effect of increasing the fixation temperature on the K/S of screen printed viscose, wool and nylon 66 fabrics upon using Ebecryl 2002 as a commercial binder and/or prepared binders of PUA based on PEG_{2000}, $PEG_{1000\ +\ 2000}$ and based on GE-*co*-P containing 3% of Helizarin Brilliant red BBT, the time of fixation of 2 min are represented by Figs. 7–9, respectively.

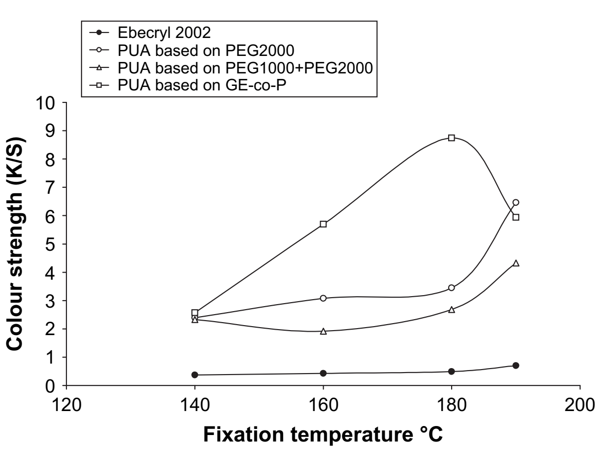

Fig. 4. The effect of the type of binder used on the color strength of screen printed cotton fabrics using 5% Helizarin Brilliant red BBT, the time of fixation is 2 min.

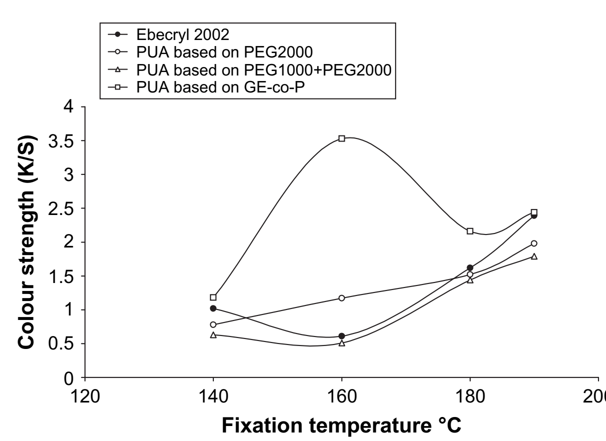

Fig. 6. The effect of the type of binder used on the color strength of screen printed polyester fabrics using 5% Helizarin Brilliant red BBT, the time of fixation is 2 min.

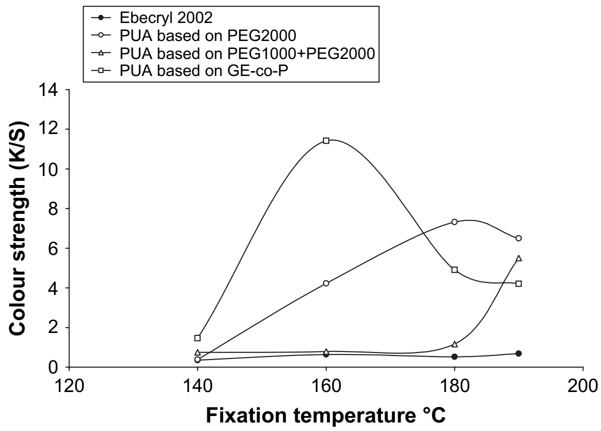

Fig. 7. The effect of the type of binder used on the color strength of screen printed viscose fabrics using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

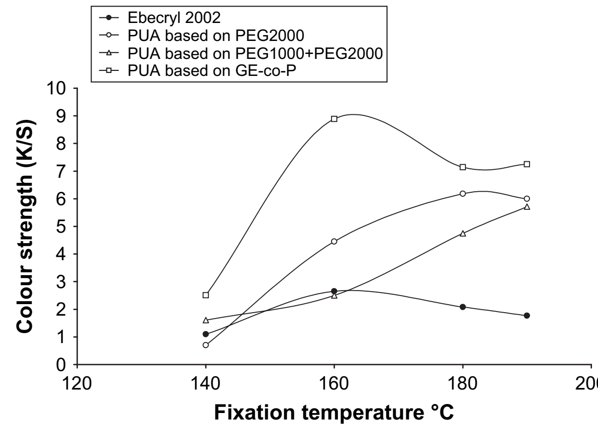

Fig. 9. The effect of the type of binder used on the color strength of screen printed nylon 66 fabrics using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

It is clear from Figs. 7–9 that the highest color strength values were obtained in case of using polyurethane acrylate based on GE-*co*-P as a binder in printing paste while lower values were obtained upon using Ebecryl 2002 in case of screen printed viscose fabrics, and in case of using PUA based on PEG_{2000}, the K/S values were better than the values obtained in case of using PUA based on $PEG_{1000\,+\,2000}$, in case of screen printed viscose and nylon 66 but the inverse was true in case of screen printed wool fabrics. For example, the K/S values of screen printed viscose, wool, and nylon 66 fabrics fixed at temperature 160 °C were 0.64, 4.23, 0.79, 11.42, 1.96, 0.93, 1.84, 6.8 and 2.65, 4.45, 2.5, 8.89 by using Ebecryl 2002, PUA based on PEG_{2000}, PUA based on $PEG_{1000\,+\,2000}$, PUA based on GE-*co*-P as a binder in printing paste containing 3% Helizarin red BBT, respectively. The highest values of K/S in case of using PUA based on GE-*co*-P may be due to the presence of free hydroxyl besides the unsaturation site in the chemical composition of this type of binder, which leads to increase in the fixation of the pigment dye through either the hydrogen bond which can happen between this binder and the fabrics or cross-linking of the binder, this cross-linkage is essential for physical adhesion of the binder to the textile fiber and to give the pigment print optimum fastness properties.

5.2. *Effect of type of fabric used*

The effect of increasing the fixation temperature on the K/S of screen printed fabrics upon using Ebecryl 2002, PUA based on PEG_{2000}, PUA based on $PEG_{1000\,+\,2000}$ and PUA based on GE-*co*-P as a binder in printing paste containing 3% Helizarin Brilliant red BBT, the time of fixation of 2 min are represented by Figs. 10–13, respectively.

It is clear from Figs. 10 and 13 that in case of used Ebecryl 2002 and PUA based on GE-*co*-P the highest color strength is obtained at fixation temperature 160 °C, while in case of used PUA based on PEG_{2000}

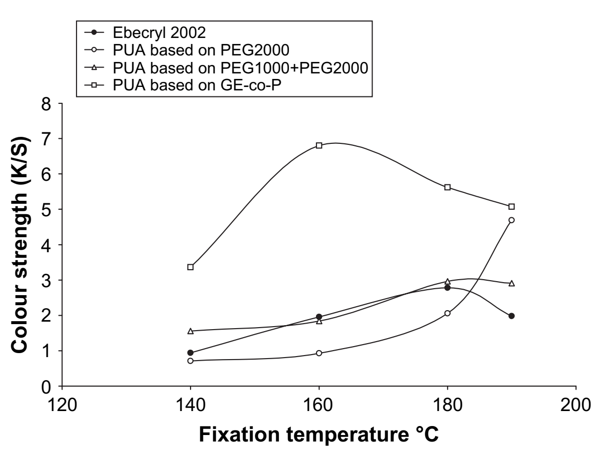

Fig. 8. The effect of the type of binder used on the color strength of screen printed wool fabrics using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

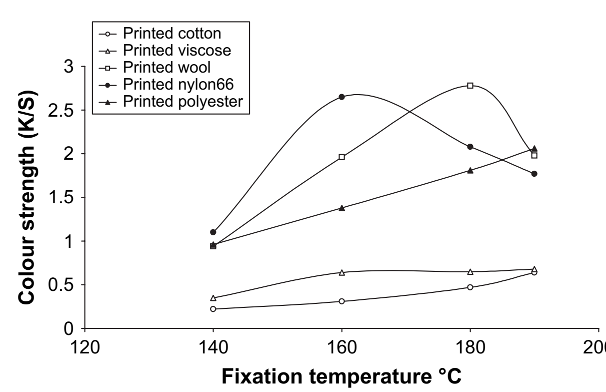

Fig. 10. The effect of the fixation temperature on the color strength of screen printed fabrics using Ebecryl 2002 as a binder on using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

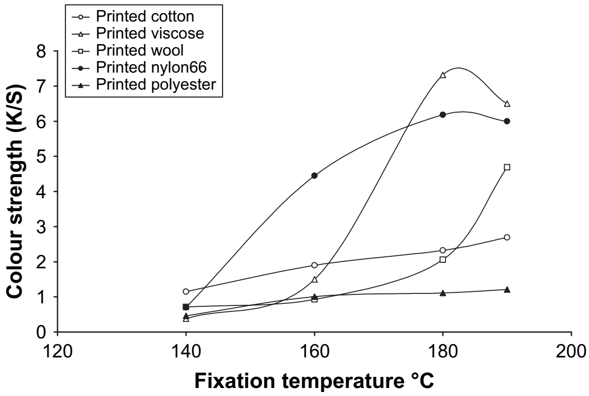

Fig. 11. The effect of the fixation temperature on the color strength of screen printed fabrics using polyurethane acrylate based on polyethylene glycol 2000 as a binder on using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

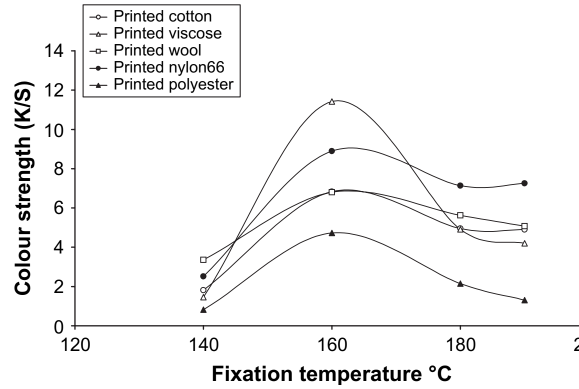

Fig. 13. The effect of the fixation temperature on the color strength of screen printed fabrics using polyurethane acrylate based on glycerol ethoxylate-*co*-propoxylate as a binder on using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

as shown in Fig. 11 the highest color strength is obtained at fixation temperature 180 °C and in case of used PUA based on $PEG_{1000 + 2000}$ the highest color strength is obtained at fixation temperature 190 °C as shown in Fig. 12, this is true irrespective of the type of fabric used.

It is also clear from Fig. 10 that the highest color strength value was obtained upon using Ebecryl 2002 in case of screen printed nylon 66, wool and polyester, while the lowest K/S value was obtained in case of screen printed cotton and viscose. But in case of using PUA based on PEG_{2000}, PUA based on $PEG_{1000 + 2000}$ and PUA based on GE-*co*-P as shown in Figs. 11–13, respectively, the highest color strength value was obtained in case of screen printed viscose, nylon, cotton and wool while the lowest K/S value was obtained in case of screen printed polyester fabric, this may be due to the difference in the chemical structure and the number of the unsaturated site in each binder used in prepared printing paste.

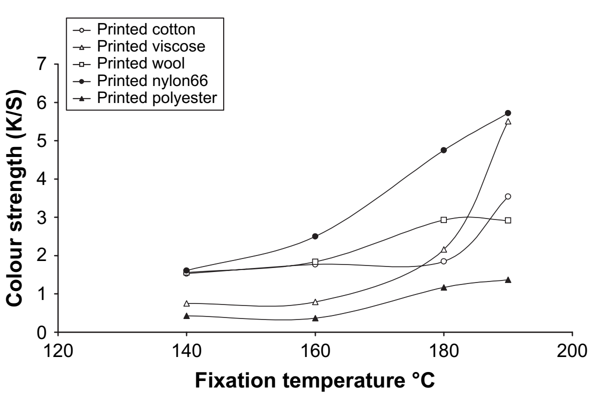

Fig. 12. The effect of the fixation temperature on the color strength of screen printed fabrics using polyurethane acrylate based on polyethylene glycol 1000 + 2000 as a binder on using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min.

5.3. Fastness properties

Tables 1 and 2 show the color strength and overall fastness properties of screen printed natural and synthetic fabrics using prepared polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate and/or Ebecryl 2002 as a thermal curable binder used in prepared printing paste containing 3% Helizarin Brilliant red BBT.

It is clear from the data in Tables 1 and 2 that the K/S and overall fastness properties not only depend on the type of binder used in printing paste but also on the type of textile fabric printed. The highest color strength for all the types of printed fabric was obtained upon using PUA based on GE-*co*-P as a binder in printing paste and the fixation temperature was 160 °C for 2 min, and the lowest color strength in case of cotton and viscose printed fabrics upon using Ebecryl 2002 and the change in color due to washing ranged from poor to good for all printed fabrics. The rubbing, washing and perspiration fastness ranged from good to excellent in case of using prepared binder. This was true irrespective of the nature of the binder used and/or the type of fabric printed.

6. Conclusions

- These results show that some novel prepared aqueous oligomers (binder) of polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate having zero volatile organic compounds can be used safely for preparing printing paste for screen printing of all types of textile fabrics using pigment dyes.

Table 1
Color strength and overall fastness properties of screen printed natural and man-made fabrics using prepared polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate and/or Ebecryl 2002 as thermal curable binders in printing paste using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min

Binder used	Type of fabric	Color strength	Rubbing fastness		Washing fastness			Perspiration fastness					
								Acidic			Alkaline		
			Dry	Wet	Staining		Alt.	Staining		Alt.	Staining		Alt.
					Cotton	Wool		Cotton	Wool		Cotton	Wool	
Ebecryl 2002[a]	Cotton	0.31	4	4	3	4	2	4	4	3	4	4	3
PUA based on PEG$_{2000}$[b]		2.32	4–5	3–4	4	4	4	5	5	5	5	5	5
PUA based on PEG$_{1000+2000}$[c]		1.85	3–4	3	4	4	4	5	5	5	5	5	5
PUA based on GE-*co*-P[a]		6.83	3	3	4	4	4	5	5	5	5	5	5
Ebecryl 2002[a]	Viscose	0.64	3–4	3–4	3	4	2	4	4	3	4	4	3
PUA based on PEG$_{2000}$[b]		7.32	3–4	3	3	4	3	5	5	5	5	5	5
PUA based on PEG$_{1000+2000}$[c]		5.51	3–4	3	4	4	3	5	5	5	5	5	5
PUA based on GE-*co*-P[a]		11.42	3–4	3	4	5	5	5	5	5	5	5	5
Ebecryl 2002[a]	Wool	1.96	2–3	3–4	4	4	3	4	4	4	4	4	4
PUA based on PEG$_{2000}$[b]		2.06	2–3	3	4	4	3	4	4	4	4	4	4
PUA based on PEG$_{1000+2000}$[c]		2.91	3	3	4	4	3	4	4	4	4	4	4
PUA based on GE-*co*-P[a]		6.8	3–4	3–4	4	5	5	4	5	5	4	5	5

The washing fastness in case of cotton and viscose is at 60 °C, but in case of wool at 40 °C. All samples showed soft handling. Alt. = alteration.
[a] Fixation temperature at 160 °C.
[b] Fixation temperature at 180 °C.
[c] Fixation temperature at 190 °C.

- The highest K/S is obtained and the fastness properties range between good and excellent for samples printed using polyurethane acrylate based on glycerol ethoxylate-*co*-propoxylate, this is true irrespective of the type of printed fabric.
- The lowest K/S is obtained in case of using Ebecryl 2002 as a commercial binder.
- The binder of PUA based on PEG$_{2000}$ gives K/S better than the binder of PUA based on PEG$_{1000+2000}$ for all the types of printed fabrics unless in case of printed wool, the inverse is true.
- The fastness properties of goods printed with this system were satisfactory and the hand of printed goods was soft.

Table 2
Color strength and overall fastness properties of screen printed synthetic fabrics using prepared polyurethane acrylate based on either polyethylene glycol or glycerol ethoxylate-*co*-propoxylate and/or Ebecryl 2002 as a thermal curable binders in printing paste using 3% Helizarin Brilliant red BBT, the time of fixation is 2 min

Binder used	Type of fabrics	Color strength	Rubbing fastness		Washing fastness			Perspiration fastness					
								Acidic			Alkaline		
			Dry	Wet	Staining on		Alt.	Staining on		Alt.	Staining on		Alt.
					Cotton	Wool		Nylon 66	Wool		Nylon 66	Wool	
Ebecryl 2002[a]	Nylon 66	2.65	4	3–4	3	3	1	3	4	4	3	4	4
PUA based on PEG$_{2000}$[b]		6.18	4–5	3–4	4	4	3	4	4	5	4	4	5
PUA based on PEG$_{1000+2000}$[c]		5.72	4–5	3	4	4	3	5	5	5	5	5	5
PUA based on GE-*co*-P[a]		8.89	3	2–3	4	4	4	5	5	5	5	5	5
								Polyester	Wool		Polyester	Wool	
Ebecryl 2002[a]	Polyester	1.38	4	3–4	3	4	1	4	4	4	4	4	4
PUA based on PEG$_{2000}$[b]		1.11	4	3–4	4	4	2	4	4	4	4	4	4
PUA based on PEG$_{1000+2000}$[c]		1.37	4	4	4	4	3	4	4	4	4	4	4
PUA based on GE-*co*-P[a]		4.73	5	4	4	5	5	5	5	5	5	5	5

The washing fastness at 40 °C. All samples showed soft handling. Alt. = Alteration.
[a] Fixation temperature at 160 °C.
[b] Fixation temperature at 180 °C.
[c] Fixation temperature at 190 °C.

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