A novel approach in pigment printing using nano-keratin based binder

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This study is devoted to preparation and characterization of nano-keratin based binder (NKBB) from cheap renewable natural resources, namely coarse Egyptian wool or feather. The prepared NKBB is utilized as a biodegradable, environment-friendly and relatively cheap binder in textile pigment printing of polyester, pure polyacrylic, viscose, polyester/viscose, and polyester/acrylic fabrics. Different concentrations of the prepared NKBB as well as its mixture with commercially produced one are used in the pigment printing paste. The colour strength of the printed fabrics as well as their fastness properties to light, washing, and perspiration are evaluated. The effect of the used binder on the bending stiffness of the printed fabrics is also assessed. Results show that the NKBB gives almost the same colour strength and fastness properties as the commercial binder with improved stiffness of the printed samples in relation to that printed with commercial one.

Keywords: Acrylic, Binder, Nano-keratin, Poultry feather, Polyester, Pigment printing, Viscose, Wool

1 Introduction

Nano-particles technology is known to be a suitable tool to improve physical properties of conventional textiles in areas such as flame retardancy, anti-infrared, dyeability, soil-resistance, water repellency, anti-microbial properties, and strength⁵. Nano-sized materials can be prepared by several physico-chemical methods such as vapor phase reaction, chemical vapor deposition, inert gas condensation, laser ablation, plasma spraying, spray conversion and sputtering.

In some textile finishing applications, nano-particles can change surface properties and also give different functions to the textile materials ⁶. The nano-sized particles offer a larger surface area compared to bigger particles and also being in the nano-size the particles are transparent. Hence they do not alter the original colour or the brightness of either the product containing the nano-particles or the textile substrates. Moreover, having large surface area to volume ratio, nanoparticles are easily attached to the fabrics, and have increased functional durability imparted by the particles. Also use of nano-particles does not affect the breathability and hand feel of the textile ⁶. Pigment printing is not only the oldest, but likewise the easiest printing method as far as ease of application is concerned. More than 80% of the printed goods are based on pigment printing due to its obvious advantages such as versatility and ease of near final print at the printing stage itself ⁷.

Pigment printing differs from other methods of printing in that the colour is made by finely ground insoluble pigments which have no affinity for the fibre ⁸. Unlike printing with fibre affinitive dyes, the pigment is fixed to the fabric by a binder which adheres to the fibre and forms a continuous film on the fabric enclosing the pigment particles ⁹.

Binders are high molecular weight film forming agents. They are present initially as aqueous polymer solutions (dissolved binders) or aqueous polymer dispersions. Aqueous binder dispersions are the most common formula of binders ¹⁰. Binders employed in pigment printing of textile are polymer or copolymer of unsaturated monomer such as ethyl acrylate, butyl acrylate, styrene, acrylonitrile, vinyl acetate, butadiene, etc. ¹¹,¹².

Keratin is a natural polymers of high relative molecular weight. They are very widespread in nature, being essential components of animal and plant tissue. Like other proteins, the basic structural units of proteins are α-amino acids, which have the general formula: H₂N–CH (R) – COOH ¹³. It has been reported that the mass spectra of the keratinous materials clarify that the molecular mass of soluble keratin exceeds 2
kDa and the number of amino acid residues along any oligopeptide chain is at least 20 amino acid residues.

In the present study, keratin (nano-sized) is prepared from cheap renewable natural resources using simple and environment-friendly process. The prepared nanokeratin has been utilized as a binder in pigment printing of polyester, poly acrylic, viscose, viscose/polyester, and viscose/poly acrylic fabric, to replace the commercially available binder which is highly expensive and environment unfriendly imported one.

2 Materials and Methods

2.1 Materials

100% scoured polyester fabric, 100% acrylic fabric, 100% viscose fabric, polyester/viscose (60/40) fabric and acrylic/polyester (40/60) fabrics were supplied by Misr Co. for spinning and weaving, El-Melahla El-Kubra, Egypt. Raw Egyptian wool fleece (Barki) and chicken feather were collected from local market.

2.2 Pigments and Reagents

Two pigments, namely Print M.D. Blue 2G and Red GRL were supplied by DAICO for chemical industry, Egypt. The commercial binder SME-2 (Acrylate – based), and thickener Daicothick 1600 (based on polyacrylate) of DAICO for chemical industry, Egypt were used in this study. Sodium hydroxide and thiourea were purchased from El-Nasr pharmaceutical chemicals company, Egypt. Urea was supplied by Merck, Germany. Glutardialdehyde (25 % aqueous solution w/w) was purchased from Aldrich, Steinheim, Germany. All other chemicals used in this investigation are of laboratory grade.

2.3 Methods

2.3.1 Scouring

Coarse wool and chicken feather were scoured using 2 g/L sodium carbonate and 1 g/L non-ionic detergent at 60 °C for 15 min followed by thorough rinsing with cold water, then squeezing and finally air drying at ambient temperature.

2.3.2 Preparation of Nano-keratin Binders and Printing Paste

Coarse wool and chicken feather were dissolved in a mixture of 2% NaOH, 8% urea and 6.58% thiourea for 10 min at 50 °C. The obtained soluble keratin was then precipitated in a coagulating bath containing 6% H2SO4 and 12% NH4Cl (w/v) \(^{15,16}\), and the precipitate was filtered through polyester cloth and washed extensively with distilled water until pH 7. The precipitate was then left to dry overnight and then ground using a ball milling machine to obtain nano-sized keratin. The printing pastes were prepared according to the following formulation (total 100 g):

- Ammonia (25%) : 0.5 g
- Binder (NKBB) : 1, 3, 5, or 8 g
- Thickener : 3 g
- Diammonium hydrogen phosphate : 0.5 g
- Urea : 4 g
- Pigment : 5 g
- Water : 86, 84, 82, or 79 mL

Ammonia, urea, ammonium phosphate monobasic and the binder were mixed together. The thickener was then introduced and the paste was stirred using a high shear mixer for 10 min to allow full viscosity to develop. The pigment was then added to the mixture with stirring using a high shear mixer for 15 min. In another experiment, we used glutardialdehyde as across-linker for the NKBB (nano-keratin based binder) to the fabric.

2.3.3 Printing

All printing pastes were applied to the selected fabrics using the flat screen printing technique. Prints were air dried, and then fixed at different temperatures (120 °C - 160 °C) for different period of times (2 — 5 min) in an automatic thermostatic oven (Wermer Mathis Co., Switzerland).

2.4 Measurements

2.4.1 Colour Strength Measurements

The K/S of the printed fabrics was measured using a UV-Vis spectrophotometer with pulsed xenon lamps as light source (Ultra-Scan Pro, Hunter Lab, USA) 10° observer with D65 illuminant, d/2 viewing geometry and measurement area of 2 mm. The measurements of printed fabrics with blue pigment were occurred at λ\(_{560}\) nm, and those printed with red pigment occurred at λ\(_{510}\) nm wavelength. The corresponding colour strength value (K/S) was assessed by applying the Kubelka Munk \(^{17}\) equation.

2.4.2 Fastness Properties

The wet and dry rubbing fastness of printed samples was determined according to AATCC test method 8, (1989).

The colorfastness to washing was determined according to the AATCC test method 36, (1972) using Lunder Ometer. The wash fastness was assessed using the grey scale reference for colour change.

Fastness to perspiration was determined with acidic and alkaline perspiration solutions according to AATCC test method 15 (1989). The effect on the
colour of the test specimen was expressed and defined by reference to grey scale for colour change.

Colorfastness to light was determined according to AATCC test method 16 A (1989). The evaluation was established using the blue scale as reference of colour change.

2.4.3 Stiffness Properties

Stiffness of printed and unprinted samples was determined according to ASTM test method D 1388 – 96 using the cantilever apparatus.

2.4.4 Rheological Properties of Printing Pastes

The rheological properties of the pastes were measured using a rotary viscometer (Rheomat – 15, Zurich, Switzerland).

2.4.5 TGA and DSC Measurement

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured using SDT Q 600 with rate of heating 10 °C/min.

3 Results and Discussion

In order to attain the optimum conditions for pigment printing, different concentrations of NKBB (nano-keratin based binder) as well as thermo-fixation temperatures and times have been used to monitor their influence on the colour strength and fastness properties of the fabric printed by pigment paste containing NKBB.

3.1 Effect of NKBB Concentration

The effect of NKBB concentration extracted from wool on the colour strength and rub fastness of the printed fabrics has been studied at fixation temperature 140 °C and fixation time 4 min. Results of this investigation are summarized in Table 1.

It is observed that the printing of said fabrics using 1% NKBB results in satisfactory K/S values for the printed fabrics as compared to that obtained in presence of commercial binder (CB). The proposed reaction mechanism of NKBB with M.D. blue 2G is shown in Scheme 1.

Lower concentrations of NKBB within the printing paste led to lower viscosity and hence bleeding of the colorant. On the other hand, as the concentration of NKBB in the pigment paste increases, the colour strength and the rub fastness values decrease. This might be attributed to the fact that the additional amount of keratin is more suitable candidate to bind with keratin-pigment composite more than in polyester, poly acrylic and viscose fabrics, by virtue of its functional groups, viz. amino group (amidification reaction) or hydroxyl group (esterification reaction), as shown in Schemes 2 and 3. It is worthy to mention that the rub fastness is acceptable commercially starting from ranking 3.

<table>
<thead>
<tr>
<th>NKBB conc %</th>
<th>Substrate</th>
<th>K/S</th>
<th>Rub fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>1</td>
<td>Acrylic</td>
<td>14.5</td>
<td>2 1-2</td>
</tr>
<tr>
<td>2</td>
<td>Polyester</td>
<td>15.17</td>
<td>2-3 2</td>
</tr>
<tr>
<td>3</td>
<td>Viscose</td>
<td>13.3</td>
<td>3 2-3</td>
</tr>
<tr>
<td>4</td>
<td>Acrylic</td>
<td>13.5</td>
<td>2 1-2</td>
</tr>
<tr>
<td>5</td>
<td>Polyester</td>
<td>14.38</td>
<td>2-3 2</td>
</tr>
<tr>
<td>6</td>
<td>Viscose</td>
<td>12.5</td>
<td>3 2-3</td>
</tr>
<tr>
<td>7</td>
<td>Acrylic</td>
<td>12.4</td>
<td>1-2 1</td>
</tr>
<tr>
<td>8</td>
<td>Polyester</td>
<td>12.2</td>
<td>1-2 1</td>
</tr>
<tr>
<td>9</td>
<td>Viscose</td>
<td>11.5</td>
<td>2-3 2</td>
</tr>
</tbody>
</table>

Table 1 — Effect of different concentrations of NKBB on the colour strength and rubbing fastness of printed fabrics

Scheme 1 — Proposed reaction mechanism between M.D. Blue 2G pigment and keratin

Scheme 2 — Proposed mechanism for amide formation reaction between keratin-pigment composite and excess nano-keratin
3.2 Effect of Thermo-fixation Temperature

The influence of fixation temperature on the colour strength and rub fastness of the printed fabrics has been studied with 1% concentration of NKBB and at 4 min thermo-fixation time to attain the proper temperature for thermo-fixation. Results of this study are given in Table 2. The table shows that, the thermo-fixation of printed samples by curing at 150 °C, give higher K/S values and rub fastness than those cured at lower temperatures or at 160 °C. This could be correlated with the results of the thermal analyses, which show that the initial decomposition temperature of the NKBB is around 180 °C. Nearby this temperature, NKBB starts decomposing and losing its effective binding action as a long chain polymer. From Tables 1 and 2 it is noticed that the polyester and acrylic samples printed with the blue pigment show colour strength values more than that of viscose samples. This could be explained in terms of the triboelectric series, which implies that upon rubbing polyester and acrylic fabrics with other materials, their tendency to attract electrons increases. Thus, it is easy for the lone pair of electrons, of the secondary amino group of the prepared NKBB/pigment composite, to be attracted towards the surface of the polyester and acrylic fabrics. On the other hand, viscose is neutral and binds with the said composite chemically by virtue of its hydroxyl groups (Scheme 4). Consequently, the rub fastness of the printed viscose fabrics is better than those of polyester and acrylic samples.

The slight differences in the K/S values of printed polyester and acrylic samples could be attributed to the chemical composition structures of the samples. Polyester has more withdrawing groups than acrylic, namely benzene rings and carboxylic groups.

3.3 Effect of Thermo-fixation Time

Different fixation times are also studied to reach the optimum condition for the printing process. The effect of fixation time on colour strength and fastness properties has been studied with 1% concentration of NKBB at 150 °C and the results are given in Table 3. It is found that the K/S values and rub fastness increase with the increase in time of thermo-fixation. This may be due to the enhanced extent of cross-linking between the binder and the fabric by time. Further increase in fixation time led to decrease in the K/S values and fastness properties of the printed fabrics. This may be due to the thermal degradation of NKBB by exposing at high temperature for long time.

It has been proved that the optimum conditions of using NKBB in the pigment printing paste are 1% NKBB, 150 °C thermo-fixation temperature and 4 min treatment time (Tables 1-3). These optimum conditions are then adopted in printing of man-made fibres and their blends with and without a cross-linking agent.

3.4 Effect of Cross-linking Agent

Gluterdialdehyde has been used as a cross-linker for the prepared NKBB in the pigment paste to improve its durability to wet treatment and thus enhances the fastness properties of the printed samples. Results are tabulated in Table 4. The K/S values and fastness properties of the printed samples in presence of gluterdialdehyde as a cross linker are lower than those in absence of it.
Table 3 — Effect of different times of thermo fixation on colour strength and rubbing fastness of the printed fabrics

<table>
<thead>
<tr>
<th>Time of fixation min</th>
<th>Substrate</th>
<th>K/S</th>
<th>Rub fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>2</td>
<td>Acrylic</td>
<td>12.37</td>
<td>1-2</td>
</tr>
<tr>
<td></td>
<td>Polyester</td>
<td>12.4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Viscose</td>
<td>13.7</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Acrylic</td>
<td>12.8</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>Polyester</td>
<td>12.85</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Viscose</td>
<td>14.42</td>
<td>2-3</td>
</tr>
<tr>
<td>4</td>
<td>Acrylic</td>
<td>15.27</td>
<td>3-4</td>
</tr>
<tr>
<td></td>
<td>Polyester</td>
<td>15.58</td>
<td>3-4</td>
</tr>
<tr>
<td></td>
<td>Viscose</td>
<td>16.18</td>
<td>3-4</td>
</tr>
<tr>
<td>5</td>
<td>Acrylic</td>
<td>12.55</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Polyester</td>
<td>15.09</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Viscose</td>
<td>14.88</td>
<td>3</td>
</tr>
</tbody>
</table>

This may be rationalized in terms of the fact that gluteraldialdehyde causes cross-linking of the prepared NKBB within the pigment paste before the fixation step, by virtue of the active sites along keratin macromolecules. Pyridinium crosslink structure has been proposed to be derived from gluteraldialdehyde and proteins as shown in Fig. 1.

3.5 Rheological Properties of Printing Pastes

The rheological properties of the pigment printing pastes containing NKBB, CB (commercial binder) and their mixtures of them are assessed. The pastes were:

(i) Paste containing NKBB, prepared with optimum condition (such as 1% NKBB, 150°C fixation temperature and 4 min treatment time)

(ii) Paste containing commercially available binder CB (SME-2 acrylate-based), under the conditions (20% of the pigment paste, 150°C fixation temperature and 4 min treatment time)

(iii) Pastes containing different amounts of NKBB and CB:
   - 75% CB + 25% NKBB (15 g CB + 0.25 g NKBB)
   - 50% CB + 50% NKBB (10 g CB + 0.5 g NKBB)
   - 25% CB + 75% NKBB (5 g CB + 0.75 g NKBB)

It is clear, from the rheograms (Fig. 2) that, the analyzed samples were designated by a non-Newtonian pseudo plastic, since the up and down flow curves are coincident. This means that if these pastes are subjected to a shear force, their viscosities decrease. However, this is not permanent where, on the removal of the shear forces, the original viscosity is recovered again. This may enable the use of extremely fine screen gauges and roller engraving to give fine designs. Varied locations of rheograms with respect to rate of shear axis show differences in their viscosity.

The apparent viscosities at various rates of shear are calculated from the values of shearing stress and rate of shear. It can be seen that the apparent viscosity decreases as the rate of shear increases (Pastes show thinning down). On the other hand, it is noticed that the shear rates of all the pastes containing NKBB binder show viscosity values lower than that given by the CB. This is due to the use of a low concentration of NKBB which gives fastness properties better than the high concentration of it.

Different CB mixtures were made with NKBB to avoid the drawbacks of CB, like high price, importing
from abroad, being petrochemical substances and non ecofriendly nature, and that of NKBB which gives prints with relatively low rub fastness.

The colour strength and fastness properties of the printed fabric with pigment pastes containing NKBB, CB and their mixtures are summarized in Table 5.

The colour strength and the fastness properties of NKBB, CB and their mixtures are almost comparable to each other. However, small differences in these properties are monitored in case of printing on polyester fabric. It is also noticed that the samples containing the CB are stiffer than that containing the NKBB. So, the mixing process helps in minimizing the drawbacks of CB and NKBB.

### 3.6 NKBB Extracted from Feather

Adopting the optimum conditions of NKBB extraction from wool, a NKBB derived from feather

![Fig. 1 — Reaction mechanism for pyridinium crosslinks (NH₂ – R is the protein of interest, B is the base used)](image)

![Fig. 2 — Rheograms of CB, NKBB and their mixtures](image)
has been utilized in this study and the data are shown in Table 4.

Another pigment (Red GRL) is also used with the optimum conditions, as shown in Structure 1.

Results of both NKBB extracted from wool and feather are found almost similar to those of the blue pigment and show the same trend.

3.7 Thermal Properties

The thermal behaviour (DSC and TGA) of the NKBB extracted from wool and feather as well as the CB has been assessed. The findings are shown in Table 6. Also the glass transition temperatures of the NKBB extracted from wool and feathers as well as the CB are shown in the DSC charts (Fig. 3)

<table>
<thead>
<tr>
<th>Table 5 — Effect of mixing CB with NKBB on fastness properties of pigment using Print M.D. Blue 2G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition of preparation of binder</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>CB (20%)</td>
</tr>
<tr>
<td>Polyester</td>
</tr>
<tr>
<td>Viscose</td>
</tr>
<tr>
<td>Mix of (75% CB and 25% NKBB)</td>
</tr>
<tr>
<td>Mix of (50% CB and 50% NKBB)</td>
</tr>
<tr>
<td>Mix of (25% CB and 75% NKBB)</td>
</tr>
<tr>
<td>1% NKBB</td>
</tr>
<tr>
<td>Polyester / Acrylic</td>
</tr>
<tr>
<td>Polyester / Acrylic</td>
</tr>
<tr>
<td>Polyester / Acrylic</td>
</tr>
<tr>
<td>Polyester / Acrylic</td>
</tr>
<tr>
<td>Polyester / Acrylic</td>
</tr>
</tbody>
</table>

Alt. = Alteration in color.
Table 6 — Thermal properties of CB and NKBB extracted from wool and feather

<table>
<thead>
<tr>
<th>Binder type</th>
<th>IDT, °C</th>
<th>Maximum rate of decomposition</th>
<th>( T_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
<td>Weight loss</td>
<td>Rate of decomposition</td>
</tr>
<tr>
<td>CB</td>
<td>238</td>
<td>349.5</td>
<td>46.45</td>
</tr>
<tr>
<td>NKBB from wool</td>
<td>180</td>
<td>327</td>
<td>50.25</td>
</tr>
<tr>
<td>NKBB from feather</td>
<td>200</td>
<td>326</td>
<td>51.95</td>
</tr>
</tbody>
</table>

IDT – Initial decomposition temperature.

Table 6 elucidates that the CB exhibits high thermal stability. It has been reported that poly acrylate based polymer develop anhydride ring structures in the chain as a result of a dehydration process at high temperatures (Scheme 5)\(^{23}\). A further increase in the temperature of degradation causes the formation of chain fragments with anhydride rings or acid groups, together with various minor volatile products\(^{24}\).

On the other hand, the used NKBB exhibits lower thermal stability than the CB at low temperatures. But at higher temperatures the thermal stability of both approaches to each other. This could be explained by the presence of several active groups in the NKBB, viz. Carboxylic, amino, and hydroxyl groups which at high temperatures form new cross-links causing its degradation at higher temperatures.

Table 6 shows that the initial decomposition temperature of the CB is higher than that of the NKBB, indicating that the thermal stability of the CB is more than that of NKBB, as it is proved from the results of TGA. It is also noticed that the maximum rate of decomposition and the maximum weight loss of all the binders are comparable to each other. This is in harmony with the data of TGA, where at high temperatures the rate of decomposition of both binders approaches at high temperatures.

Charts of DSC (Fig. 3) shows that the \( T_g \) of the CB as well as the NKBB extracted from wool and feather are 59.7°C, 58.9°C and 79.2°C respectively which are almost comparable to each other and exist in the range of firm binders.

4 Conclusion

Coarse wool and feathers can be solubilized in dilute solutions of alkali metal hydroxides in presence of swelling and reducing agents without severe degradation of the keratin macromolecules. The solubilized keratin is precipitated in a coagulating bath, and the precipitate is collected by filtration with polyester cloth. The precipitate is dried overnight and grounded to the nano-sized scale. The nano-keratin obtained can be used as a binder in the process of the pigment printing. The data of the colour strength as well as fastness properties of the printed fabric with the NKBB (nano-keratin based binder) and the CB (commercial binder) are comparable to each other. Mixing of NKBB and CB avoids some disadvantages of the CB and reduces the stiffness of the printed fabrics with the CB. It is also noticed that using gluteraldialdehyde as a cross-linker gives lower colour strength and fastness properties than in its absence, so that, nano-keratin based binder could be used in pigment printing process without using cross-linker.

References

13 Lewis D M, Wool Dyeing (Society of Dyers and Colourists, West Yorkshire), 1992, Chap 1, 6.