The esterification and dyeing properties of raw wool fibers

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Abstract. The reaction of raw wool fibers (RWFs) with methanol, ethanol and n-propanol catalyzed by HCl has been found to modify carboxyl side chains. The effect of esterification of wool on its behavior toward acid dye has been studied. Esterified wool fibers (EWFs) showed an increase in acid dye affinity, and dyed esterified wool shows an increase in dye fastness to washing. The process of esterification with alcohols/hydrogen chloride caused some modification of carboxyl and other groups. The surface modification of wool fibers was determined by FTIR, modification rate of carboxyl groups and the acid dye distribution of RWFs and EWFs with various alcohols was evaluated by Datacolor.

Keywords: Carboxyl groups, acid dye, methanol, ethanol, n-propanol

1. Introduction

Blackburn & Phillips (1944) informed that a combination of methanol and acetic anhydride esterified the carboxyl groups, in part at least, but that some of the terminal amino groups in lysine and the peptide imino linkage were simultaneously acetylated. Fraenkel-Conrat & Olcott (1945) attested that anhydrous alcohols containing a catalytic quantity of mineral acid reacted precisely with the carboxyl groups in proteins without modifying any other group[1, 2]. Methanol containing 0,1M hydrochloric acid was used by Blackburn & Lindley (1948) to introduce 0,8% of methyl groups into wool; this is equivalent to masking 65 % of the carboxyl groups [3, 4].

The present investigation shows an increase in dye affinity with esterified wool fibers, it appears that the basis of this increase, in this case, was the conversion of anionic carboxylate groups into ionizable ester groups and it was also confirmed by the increased rate of dye uptake [1, 4], especially from a neutral dye bath. Furthermore, a hypothesis was made by Alexander that by blocking the carboxylate groups in wool, acid dyes should be more resistant to washing[1, 5]. Kilpatrick and Maclaren (1969) found that amide groups, in addition to carboxyl groups, are modified during treatment of wool with boiling methanol containing hydrogen chloride, which cast doubts over the specificity of the esterification procedure by Alexander [4, 6, 7]. Esterification with boiling methanol has been used by numerous workers, who measured the changes in fiber properties (such as, water sorption stability and dyeing behavior) which resulted on esterification and then rationalized them in terms of changes in carboxyl content[1, 3]. It is therefore important to know the nature and extent of any side reactions accompanying the modification of carboxyl groups by esterification. We have studied the esterification of wool with three alcohols and this work describes the side reactions resulting from the modification of carboxyl groups.

2. Materials and Methods

2.1 Esterification and dyeing
The raw wool fibers (RWFs) were cleaned by a washing process in a Soxhlet apparatus with distilled water for 6 cycles. RWFs were esterified with methanol (65°C), ethanol (75°C) and n-propanol (97°C), containing hydrogen chloride (introduced as concentrated HCl); the liquor/wool ratio was 50/1. Reactions were carried out in a water bath with a reflux heating from 3h to 48h and the EWFs were then rinsed with acetone.

The RWF and EWFs dyeing was performed by a commercial acid dye (blue BEMACID) in the water bath; the samples were introduced in pots, under heating and manual stirring to a temperature from 45°C to 98°C in acid medium, then the samples were washed and dried.

2.2 Modification rate of carboxyl groups
50mg of each sample (RWFs and EWFs with various alcohols) was added to 50 ml of NaOH (0.05M). The mixte was stirred for 1h, then filtered and titrated with HCl (0.05M). (HCl and NaOH are purshased from Sigma Aldrich). The consumed NaOH by samples should be corresponding to the extent of fibers carboxylic groups. Thus, the modified amount of carboxylic groups is calculated as below (1) [8]:

\[
\frac{C_b (M) \cdot V_b (ml) - C_a (M) \cdot V_a (ml)}{m (g)} \text{ mmols}
\]

Where \(C_b\), \(V_b\), \(C_a\) and \(V_a\) are the concentration and volume of the initial base and the acid solution (titration), and \(m\) represents the amount of samples used in the titration. To calculate the modification rate of the carboxylic groups, we proceed as follows (2):

\[
\frac{\text{mmols (RWFs)-mmols (EWFs)}}{\text{mmols (RWFs)}} \times 100
\]

2.3 FTIR analysis
Fourier transform infrared spectra of the investigated samples were realized using Nicolet iS10FTIR-ATR spectrophotometer, connected with the Golden Gate single attenuated total reflection (ATR) accessory.

2.4 Color Measurement
For the study and characterization of the dyed wool samples with blue BEMACIDE, measurements are made using DATACOLOR spectrocolorimeter and they are systematically conducted along with visual observations, the experimental results are then listed in form of tables.

3. Results and discussions

3.1 Modification rate of Carboxyl groups
Although esterification with methanol containing 0.1 M hydrogen chloride took place rapidly at 3h and 2h with carboxyl groups modification of 38% and 73% respectively. Meanwhile, the esterification with higher alcohols, especially n-propanol, was slower (Table 1); it took 48h to esterify only 33% of carboxylic groups. Therefore, the modification rate of carboxyl groups significantly decreased as the size of the alcohol increased. As a result, methanol is preferable over ethanol or n-propanol when it comes to esterification with a maximum modification of carboxyl groups [1, 5].

| Alcohol   | Reaction time (h) | Carboxyl groups % |
|------------|-------------------|-------------------|
| Methanol   | 6                 | 38                |
|            | 24                | 73                |
| Ethanol    | 3                 | 23                |
|            | 6                 | 42                |
|            | 24                | 47                |
| n-propanol | 6                 | 17                |
|            | 24                | 31                |
|            | 48                | 33                |
3.2 FTIR analysis
In the following spectrum (Figure 1), the additional bands are attributed to the newly formed esters groups indicating the successful surface modification of RWFs with various alcohols especially the methanol. Therefore, the modification rates of carboxyl groups significantly decreased as the size of the alcohol increased [1, 5]. Thus, methanol is preferred over ethanol and propanol for esterification of carboxyl groups.

An analogy is noted between the IR spectrum of RWFs and methanol EWFs, with the appearance of a peak at 1730.88 cm\(^{-1}\), this peak corresponds to the carbonyl group[2, 9]. This observation allows us to say that the treatment of wool with an alcohol, such as methanol, leads to the penetration of the latter and creating a new function "-CO"[2, 9]. It should be noted that the carbonyl peak also appears using other alcohols, but it is not as significant as the methanol’s.

![Figure 1. Infrared-Raw and Esterified wool fibers with various alcohols.](image)

3.3 Color differences DATA
The spectropolarimeter allowed us to determine the parameters \(L^*\), \(a^*\) and \(b^*\) of the colored samples[10, 11]. Knowing the properties, \(L^*, a^*\) and \(b^*\) corresponding to the two samples [11], it is possible to evaluate the difference between the color 1 and the color 2 as below (3):

\[
\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{\frac{1}{2}} \quad (3)
\]

if the color (1) is considered as reference, (4), (5) and (6) will be:

\[
\Delta L^* = L^*2 - L^*1 \quad (4)
\]
\[
\Delta a^* = a^*2 - a^*1 \quad (5)
\]
\[
\Delta b^* = b^*2 - b^*1 \quad (6)
\]

The signification of color differences is shown in (Table 2)[11]. In our case, the sample reference is the raw wool fibers (Table 3).

| Color Differences | Positive | Negative |
|-------------------|----------|----------|
| \(\Delta L^*\)    | The sample is clearer | The sample is darker |
| \(\Delta a^*\)    | The sample is redder or less green | The sample is greener and less red |
| \(\Delta b^*\)    | The sample is yellower or less | The sample is bluer and less yellow |
The color differences (Table 4, 5 and 6) in the samples shows that the wool treated with the various alcohols has a greater affinity for the acid dye than the RWFs. Hence, EWFs are 6, 4, 2 times darker than RWFs for methanol, ethanol and propanol respectively (Figure 2). These results indicate that the ester functions are not largely reactive compared to the carboxyl groups of wool.

**Table 3.** Color Differences obtained for RWFs and EWFs.

| Parameters | RWFs  | Methanol EWFs | Ethanol EWFs | Propanol EWFs |
|------------|-------|---------------|--------------|---------------|
| \(L^*\)   | 30.31 | 26.19         | 27.39        | 29.98         |
| \(a^*\)   | -4.50 | -1.30         | -1.19        | -2.83         |
| \(b^*\)   | -30.99| -33.50        | -34.20       | -32.78        |

**Table 4.** Comparison with methanol EWFs.

| Differences  | Value | Comment                                |
|--------------|-------|----------------------------------------|
| \(\Delta L^*\) | -4.12 | Methanol EWFs is darker than RWFs      |
| \(\Delta a^*\) | 3.2   | Methanol EWFs is redder                |
| \(\Delta b^*\) | -2.51 | Methanol EWFs is bluer                 |
| \(\Delta E\)  | 5.82  | Methanol EWFs is almost 6 times darker than RWFs |

**Table 5.** Comparison with ethanol EWFs.

| Differences  | Value | Comment                                |
|--------------|-------|----------------------------------------|
| \(\Delta L^*\) | -2.92 | Ethanol EWFs is darker than RWFs       |
| \(\Delta a^*\) | 3.31  | Ethanol EWFs is redder                 |
| \(\Delta b^*\) | -0.21 | Ethanol EWFs is bluer                  |
| \(\Delta E\)  | 4.41  | Ethanol EWFs is 4 times darker than RWFs |

**Table 6.** Comparison with n-propanol EWFs.

| Differences  | Value | Comment                                |
|--------------|-------|----------------------------------------|
| \(\Delta L^*\) | -0.33 | n-propanol EWFs is darker than RWFs    |
| \(\Delta a^*\) | 1.67  | n-propanol EWFs is redder              |
| \(\Delta b^*\) | -1.79 | n-propanol EWFs is bluer               |
| \(\Delta E\)  | 2.47  | n-propanol EWFs is 2 times darker than RWFs |
Figure 2. a) RWFs, b) Methanol EWFS, c) Ethanol EWF and d) n-propanol EWFs colored with acid dye.

4. Conclusion
The effect of the wool esterification and its behavior towards the acid dye was studied. EWFs with various alcohols have an increased affinity for the dye especially Methanol EWFs. It seems that the basis of this affinity in the wool was the conversion of anionic carboxylate groups into nonionizable ester groups. In contrast to the acidic groups, these ester groups are no longer in competition with the coloring anions for the basic cationic groups of the wool and, therefore, the increase of the dye affinity was successfully confirmed by the modification rate of carboxyl groups.

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References
[1] Holt L A, Leach S J and Milligan B 1969. Textile Research Journal 39(3) pp.290-293..
[2] Pasquini D, Belgacem M.N and Gandini A, 2006. Aprigio da Sliva Curvelo A. J. Colloid Interface Sci, 295, pp.79-83..
[3] Kilpatrick D J and Maclaren J A, 1969. The Dyeing Properties of Esterified Wools. Textile Research Journal 39(3) pp.279-283..
[4] Robert S 1943 Dyeing cellulose esters. U.S. Patent 2,328,682.
[5] Alexander P, Carter D, Earland C and Ford O E 1951 Esterification of the carboxyl groups in wool. Biochemical Journal 48(5) p.629..
[6] Ammayappan L 2013 Eco-friendly surface modifications of wool fiber for its improved functionality: An overview Asian journal of textile 3(1) pp.15-28..
[7] Kilpatrick D J and Maclaren J A 1969 The Dyeing Properties of Esterified Wools. Textile Research Journal 39(3) pp.279-283..
[8] Moaseri E, Baniadam M, Maghrebi M and Karimi M 2013 A simple recoverable titration method for quantitative characterization of amine-functionalized carbon nanotubes Chemical Physics Letters 555 pp.164-7.
[9] Gomez N, Julia M R, Lewis D M and Erra P 1995. The use of FTIR to investigate modifications to wool treated with sodium sulphite and cationic protein hydrolysate. Journal of the Society
of Dyers and Colourists 111(9) pp.281-284.

[10] Equipment: 2012 Datacolor launches handheld spectrophotometer for colour measurement, Additives for Polymers 2012(4) p.10.

[11] Pathare P B, Opara U L and Al-Said F A J 2013 Colour measurement and analysis in fresh and processed foods: a review. Food and bioprocess technology 6(1) pp.36-60.