효소를 이용한 wool의 염색

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Enzymatic Dyeing for Wool

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1. Introduction

Oxydoreductase enzymes such as laccases (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) and horseradish peroxidase (donor: hydrogen peroxide oxidoreductase, HRP, EC 1.11.1.7) can provide novel ways for wool coloration in the face of actual state of the art of these enzymes[1]. HRP has been reported as a very useful enzyme for the synthesis of phenolic polymers[2]. Many enzymatic polymerised phenolic compounds tend to have a characterized colour because polyphenol forms a big conjugated structure along the main chain. This phenomenon is interesting because the colour can be obtained easily from enzymatic reaction and therefore can be available for textile dyeing. In this study, we tried to dye wool fabric in an enzymatic method. We investigate the effects of dyeing conditions such as phenolic compound concentration, enzyme concentration and hydrogen peroxide concentration on enzymatic dyeing towards wool fabric.

2. Experimental

2.1 Materials

Raw wool fabric was used in this study. Hydroquinone, catechol, dopamine, guaiacol and ferulic acid from Sigma were used as phenolic compounds. Peroxidase from horseradish (Type VI-A) (HRP, EC 1.11.1.7) was purchased from Sigma. 30% of hydrogen peroxide solution was used as oxidizing agent. The buffer systems used in this study were sodium phosphate - disodium hydrogen phosphate (0.1 M) for pH 7.0 and acetic acid sodium acetate (0.1 M) for pH 5.0. HRP was diluted in the buffer solution (pH 7.0) and kept in a refrigerator as stock solution. This stock solution contains 5000 units/ml. 29.4 g/l of potassium dichromate solution was prepared for mordant processing.

2.2 Enzymatic dyeing

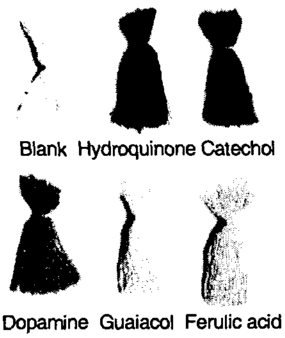
1 g of hydroquinone was dissolved in 20 ml of water for 1 g of a wool fabric (8 cm x 8 cm). The fabric was immersed in a hydroquinone solution for 1 hour at room temperature and padded in 100% pick up ratio. This was prepared with 0.1 ml of the HRP stock solution, 0.1 ml of the hydrogen peroxide solution and 20 ml of the buffer solution (pH 7.0). The wool fabrics were dipped in the enzyme solution without stirring for 1 hour at room temperature. After the enzymatic reaction, the fabrics were slightly with water rinsed to remove residual compounds on the fabrics. 20 ml of the potassium dichromate solutions were employed to mordant the fabrics for 1 hour at room temperature. The coloured fabrics were thoroughly rinsed with water at 85°C for 15 minutes to remove residual compounds.

2.3 Colour measurement

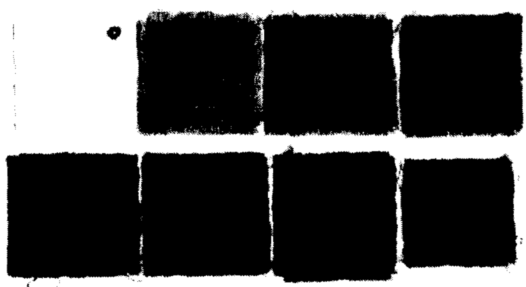
Colour depth was evaluated in terms of K/S values and these were calculated using Kubelca-Munk's equation. The reflectance values were measured with a Spectraflash SF600+CT of Datacolor International with illuminating D65 at 10° observer.

3. Results and Discussion

Colour in wool can be developed using several phenolic compounds such as hydroquinone, catechol, dopamine, guaiacol and ferulic acid after treatment with



Scheme 1. Enzymatic dyed wool samples



Scheme 2. Enzymatic dyed wool samples with hydroquinone

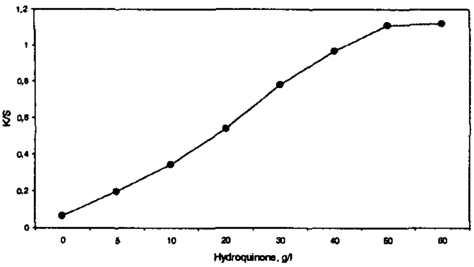


Figure 1. Colour depths of enzymatic dyed wool fabric on various concentrations of hydroquinone

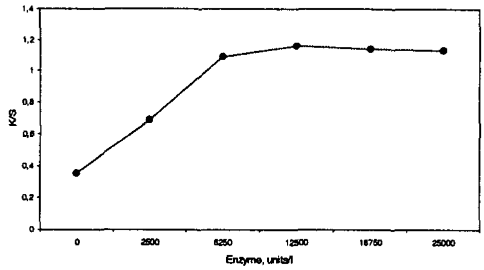


Figure 2. Colour depths of enzymatic dyed wool fabric on various activities of HRP

HRP. The results are shown in Scheme 1. They show that each of these samples have different characterized colours which depends on the different phenolic compounds chosen for the enzymatic dyeing. This result indicates that different kind of colourations can be performed by selection of phenolic compounds.

Wool fabric used for enzymatic treatment has been padded with hydroquinone previously. The colour of wool fabric changed to brown during enzymatic treatment as shown in Scheme 2. This colour change may be explained by the fact that hydroquinone on the fabric is oxidized by enzymatic oxidation and then forming dimmer, oligomer and polymer.

The diagram in Figure 1 shows the colour depths of wool fabrics that were padded previously with hydroquinone solutions in several concentrations and treated with HRP solution under the concentration of 25000 units/l. The concentration of hydroquinone solution is in the range of saturation, that is, to 60 g/l. This figure shows that the colour depth of wool fabric increases with increasing concentration of hydroquinone in the padding solution, indicating that colour depth of fabric can be controlled by the concentration of hydroquinone padded on the wool fabric.

The colour depth of wool fabric is also shown against enzyme concentration at the same time in Figure 2. Wool fabric has been padded previously with hydroquinone solution in the concentration of 60 g/l. Colour depth increases remarkably with increasing enzyme activity to 6250 units/l, and then the plot is nearly getting flat in the subsequent activity. This indicates that 6250 units/l is sufficient activity to oxidize almost all hydroquinone padded on the fabric, for 1 hour dyeing process. The K/S value of the untreated fabric is about 4.0. This value is higher than the value of the untreated fabric shown on the other plot, which is about 0.1, because this untreated fabric has been padded with hydroquinone previously.

In Figure 3, the colour depth of wool fabric is shown against concentration of added hydrogen peroxide in enzyme solution. The concentration of hydroquinone

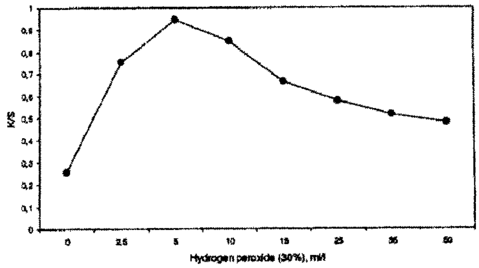


Figure 3. Colour depths of enzymatic dyed wool fabrics on various concentrations of hydrogen peroxide

solution used for padding wool fabric was 40 g/l. Colour depth of wool fabric increases with increasing concentrations of hydrogen peroxide until 5 ml/l. The colour depth, however, starts to decrease in the subsequent concentration of hydrogen peroxide. This indicates that a lot of hydrogen peroxide apparently inhibits the HRP reaction, although hydrogen peroxide is necessary for HRP catalytic reaction. In this case, it seems that enzyme loses its activity because hydrogen peroxide may oxidize and may inhibit the protein enzyme. Suitable concentration of hydrogen peroxide should be applied in order to increase the colour depth obtained in the enzymatic reaction without damage the protein enzyme.

4. Conclusion

We have attempted to obtain new dyeing methods using enzymatic reaction that contributes to colouration for wool. We knew that particular phenolic compounds such as hydroquinone, catechol, dopamine, guaiacol and ferulic acid could be used for the enzymatic dyeing of wool. It was expected that various characterized colour of wool fabric could be obtained by selection of phenolic compounds. To obtain higher colour depth, dyeing conditions such as concentration of enzyme and concentration of hydrogen peroxide should be appropriate.

5. References

1) Hoonsik Shin, Artur Cavaco-Paulo, *Macromol. Rapid Commun.* accepted.
2) T. Oguchi, S. Tawaki, H. Uyama, S. Kobayashi, *Macromol. Rapid Comr* 20, 401(1999).