



<Research Paper>

## Dyeing of Polyvinyl Alcohol Fibers in Filament Yarn Form with Reactive and Vat Dyes

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**Abstract**— As polyvinyl alcohol(PVA) filament yarn is commercially used in many fields due to its high strength and modulus properties. This research was carried out to study the dyeing behavior of PVA and to find out appropriate dye for better dyeing. As the dyeing behavior of PVA fiber is similar to cellulose due to the same functional group, reactive and vat dyes were selected for the dyeing. Color strength of PVA fibers treated with vat dyes was found to be better than those with reactive dyes, because of the low fixation of reactive dye on fibers. Most of the reactive dye may became hydrolyzed, and flushed away with water in washing. Colorfastness to laundering was shown to be very high for both of the reactive-dyed and vat-dyed PVA fibers.

**Keywords:** *dyeing, polyvinyl alcohol, vinylon, dyeing properties, vat dyeing*

### 1. Introduction

PVA fiber is very important among the synthetic fibers and now it is becoming more popular due to the general needs for the high strength fibers. In the past, dyeing of PVA fiber was not so important because its major use was for industrial purposes. But now needs for dyeing are going up due to its domestic use as towels, cosmetic towels, raincoats, covers of automobiles, for which people want to be colorful.

W. O. Herrmann and his collaborators, in 1931, stated that a fiber could be made from polyvinyl alcohol by the well-known wet and dry spinning methods, and also said that we could improve the properties of these fibers by some after treatments to make textile applications useful<sup>1</sup>. After that, Sakurada and his co-workers started working on the production of textile fiber from polyvinyl alcohol in 1938 at Kyoto University and prepared water insoluble PVA fibers by wet spinning by using a sodium sulphate as a coagulating bath<sup>2</sup>.

With the development of heat treatment of fiber in hot air and formalization, the commercial production of PVA fiber was started in 1950 in Japan by Kuraray company<sup>2</sup>. They produced staple fiber and tow by this technique. Staple fiber was converted into spun yarn by the usual spinning processes, and tow was applied to a stretch-break spinning process(Perlok system) to obtain strong spun yarn composed of relatively long staple fiber. The main purpose of producing the fiber at that time was to generate a new textile material for general use for overcoming the shortage of other textile materials<sup>3</sup>.

These fibers exhibit different structures and properties which depend upon the type of method used for its preparation and the type of after-treatment given to the fiber. Tenacity of fibers, for example, is 17g/d if it is prepared by wet spinning in an alkali coagulation bath, and tenacity is 14g/d if it is prepared by spinning in the presence of boric acid. Similarly hot water resistance of PVA fibers is to 95°C if coagulation bath is of sodium

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sulpahte solution, and if alkali solution is used as coagulation bath hot water resistance goes up to 110°C. Hot water resistance still can be increased up to 120°C and 140°C if fibers are further passed through the process of heat treatment and formalization<sup>4-5</sup>.

The structure of fibers consists of amorphous and crystalline region, but percentage of crystalline and amorphous region depends upon the method of the preparation and after treatment processes. The properties like water resistance, tenacity, modulus, water uptake depend upon the structure of fibers and after treatment process, i.e. heat treatment and formalization.

The heat treatment process can increase or decrease the crystallinity of polyvinyl alcohol through removal of residual water and formation of new hydrogen bonds. By increasing the crystallinity, the fibers become much stronger but dyeability goes towards lower side<sup>6</sup>.

Formalization generally improves not only hot water resistance and elastic recovery but also dyeability and other properties of the fibers. The effect of formalization on the dyeability of PVA fiber was checked in detail by K. Tanabe and O. Morimoto<sup>7</sup>.

## 2. Experimental

### 2.1 Materials

PVA filament yarn was supplied by Hyosung company, it was wet spun and heat treated, unformalized filament yarn. Degree of polymerization is 2099, and count is 1000 denier. Hydrogen peroxide and sodium hydrosulphite were reagent grade of Aldrich Chemicals Co. Also reagent grade of sodium carbonate, sodium chloride, and sodium hydroxide were purchased from Duksan Pure Chemicals Co. Sodium lauryl sulfate was reagent grade of Daejung. Kieralon B, a detergent for soaping, was obtained from BASF.

### 2.2 Dyestuff

Three reactive and three vat dyes supplied by Dystar Co. was used in the experiment.

- Remazol Brill. Blue R special
- Remazol Brill. Red F3B gran
- Remazol Brill. Yellow 4GL gran
- Indanthren Yellow C-GC plus
- Indanthren Blue BC
- Indanthren Red FBB

### 2.3 Samples Preparation

Total 18 samples were prepared and dyed to different shade named as under,

- Sample #1 : Remazol Brill. Blue R special, 2% owf
- Sample #2 : Remazol Brill. Blue R special, 3% owf
- Sample #3 : Remazol Brill. Blue R special 5% owf
- Sample #4 : Remazol Brill. Red F3B gran 2% owf
- Sample #5 : Remazol Brill. Red F3B gran 3% owf
- Sample #6 : Remazol Brill. Red F3B gran 5% owf
- Sample #7 : Remazol Brill. Yellow 4GL gran 2% owf
- Sample #8 : Remazol Brill. Yellow 4GL gran 3% owf
- Sample #9 : Remazol Brill. Yellow 4GL gran 5% owf
- Sample #10 : Indanthren Blue BC, 2% owf
- Sample #11 : Indanthren Blue BC, 3% owf
- Sample #12 : Indanthren Blue BC, 5% owf
- Sample #13 : Indanthren Red FBB, 2% owf
- Sample #14 : Indanthren Red FBB, 3% owf
- Sample #15 : Indanthren Red FBB, 5% owf
- Sample #16 : Indanthren Yellow C-GC, 2% owf
- Sample #17 : Indanthren Yellow C-GC, 3% owf
- Sample #18 : Indanthren Yellow C-GC, 5% owf

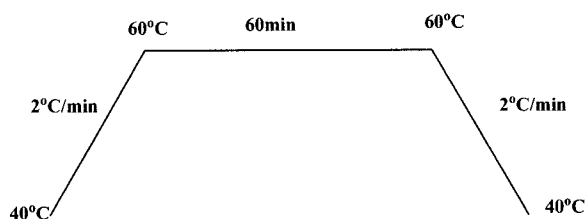
### 2.4 Dyeing method

Dyeing processes were carried out in IR-dyeing machine (Daelim Co., Korea).

#### 2.4.1 Dyeing with Reactive dyes

Dyeing with reactive dyes was done by raising the temperature of dye liquor from 40°C to 60°C at the rate of 2°C/min, and keeping at 60°C for 60 min, and then lowering temperature to 40°C at rate of 2°C/min. Auxiliaries were used according to the recommended recipes of Dystar Co. 50, 60, and 80g/lit. of neutral salt, sodium chloride, and 1.2, 1.5, and 2.0 ml/lit. of 50% sodium hydroxide solution was added to the 2%, 3%, and 5% owf of dye liquor respectively. Additionally 5g/lit. of sodium carbonate was added to the each dye bath.

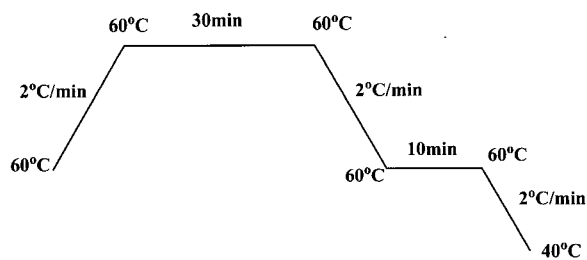
Liquor to fiber ratio of 10:1 was adopted in all the dyeing.



#### 2.4.2 Dyeing with vat dyes

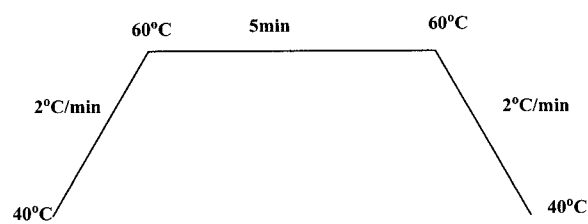
##### Reduction/dyeing

After putting the dye liquor and yarn in tubes and fixing on machine, the temperature was raised from room temp. to 80°C at the rate of 2°C/min, kept at 80°C for 30 min, and then lowered to 60°C and kept again for 10min, and then finally cooled to 40°C. Auxiliaries were used according to the recommended recipes of the Dystar Co. 30, 33, and 42ml/lit of 38°Bé sodium hydroxide solution, and 13, 15, and 20g/lit of sodium hydrosulphite was added to the 2%, 3%, and 5% owf of dye liquor respectively. Liquor to fiber ratio of 10:1 was also adopted in all the dyeing.



##### Oxidation and soaping

Now after reduction/dyeing process, yarn was taken from the liquor and put into the tubes with oxidation liquor. The temperature was raised from 40°C to 60°C at the rate of 2°C/min and maintained for 5 min, and then again cooled to 40°C at the same rate. The concentration of the hydrogen peroxide in oxidation liquor was 2ml/lit of 50% hydrogen peroxide, and liquor to fiber ratio was 10:1. After oxidation dyed fiber was soaped in hot detergent solution (1g/lit, Kieralon B) for 10 min.



## 2.5 Determination of Color Strength

### 2.5.1 By vision

After dyeing the all samples were observed by eye vision to see the difference in color strengths.

### 2.5.2 By colorimeter

After dyeing the K/S value of all the samples were measured by colorimeter CCM(X-rite 8200) to check the color strength of different dyed samples before washing and after washing as shown in Table 2 and 3.

## 2.6 Determination of fixation yield

To determine the fixation of dye on fibers after washing with detergent, i.e., percentage fixation (% F) was calculated by measuring the K/S values for the dyed samples before washing and after washing<sup>8)</sup> and putting in the equation 1 as shown here,

$$\% F = (K/S)_1 / (K/S)_2 \times 100 \quad (1)$$

Where,  $(K/S)_1$  = color yield value of the sample before washing, and  $(K/S)_2$  = color yield value of the sample after washing.

### 2.6.1 Washing Method

AATCC 61-1A washing method without steel balls was used to check the fixation of dye on the fiber.

Method description is as under

Total liquor : 200ml

Detergent used : 0.37% sodium lauryl sulfate

Temperature : 40°C

Time : 45min.

## 2.7 Colorfastness to laundering

Colorfastness to laundering of each sample was evaluated using the AATCC 61-1A test to check the color change and staining of adjacent multifibers.

### 3. Result and Discussion

#### 3.1 Comparison of color strength

PVA yarn was dyed by usual exhaustion dyeing method. When observed simply by naked eye vision, it was apparent that shade depth of the samples of PVA yarn dyed with vat dyes was greater than the samples dyed with reactive dyes, but to make it clear the samples were tested by colorimeter (X-rite 8200). The measured K/S value of each sample before and after washing is shown in Table 1 and 2. It is clear from the tables that the samples dyed with vat dyes have high K/S value, i.e., high color strength, as compared with the samples dyed by reactive dyes. It can be said that indanthren vat dye dyes PVA fiber better than Remazol reactive dye.

The color strength data of PVA fiber dyed in different concentrations is plotted as in the Fig.1 and Fig. 2. K/S value increases with the concentration of dye for both of reactive and vat dye, but the magnitude of the K/S value of the PVA fiber dyed with reactive dyes is much lower than that with vat dyes.

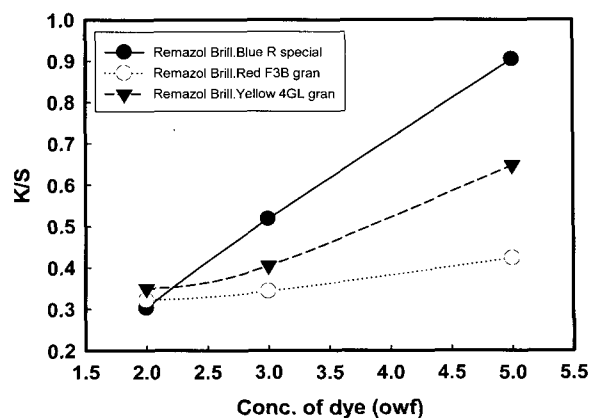


Fig. 1. K/S value of PVA fibers dyed in different concentrations of reactive dyes.

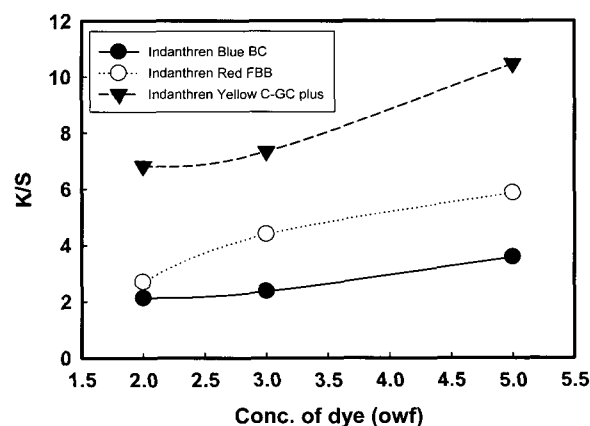


Fig. 2. K/S values of PVA fiber dyed at different concentrations of vat dyes.

Table 1. K/S value of dyed PVA fibers before washing

Reactive Dyes								
Remazol Brill. Blue R special			Remazol Brill. Red F3B gran			Remazol Brill. Yellow 4GL gran		
Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
0.30	0.52	0.90	0.32	0.34	0.42	0.35	0.40	0.65
Vat dyes								
Indanthren Blue BC			Indanthren Red FBB			Indanthren Yellow C-GC plus		
Sample 10	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15	Sample 16	Sample 17	Sample 18
2.13	2.37	3.58	2.70	4.39	5.86	6.83	7.34	10.46

Table 2. K/S value of dyed PVA fibers after washing

Reactive Dyes								
Remazol Brill. Blue R special			Remazol Brill. Red F3B gran			Remazol Brill. Yellow 4GL gran		
Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
0.16	0.22	0.12	0.12	0.19	0.23	0.20	0.30	0.24
Vat Dyes								
Indanthren Blue BC			Indanthren Red FBB			Indanthren Yellow C-GC plus		
Sample 10	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15	Sample 16	Sample 17	Sample 18
2.12	1.88	2.90	2.32	3.16	3.96	5.11	5.78	6.16

Although the functional groups related with dyeing in the PVA fiber are the same hydroxyl groups (-OH) as is in the cellulose, PVA fiber does not show the same color strength as the cotton fiber shows in dyeing with Remazol reactive dyes. It may be thought that dyeing depends not only on the reacting functional group, but also on the overall structure and composition of fiber, so that the dyeing mechanism is not always the same as in cellulose fiber. The reactivity of the secondary hydroxyl group in PVA may affect the dyeability when compared cotton cellulose where primary and secondary hydroxyl groups coexist<sup>9)</sup>. Besides, the low stability of PVA fiber in hot water limits the use of reactive dyes of high temperature types which might show better dyeabilities.

Differently from Remazol reactive dyes, Indanthren vat dyes show relatively high color strength. PVA fibers have low degree of crystallinity, and vat dyes penetrate deep into the amorphous region of PVA fiber during the reduction and dyeing step. By oxidation the dye becomes insoluble again and trapped within the fiber. The dye could not come out of fibers, which results in better fixation. Although PVA is rather hydrophilic as compared with the general hydrophobic synthetic fibers, its behavior in dyeing and finishing is different from that of hydrophilic fibers such as cellulose, and is also different from that of hydrophobic fibers such as polyester.

It is known that, because the formalization predominantly occurs in amorphous region in the PVA fibers, the crystalline part of Vinylon consists of vinyl alcohol units, and vinyl formal and unreacted vinyl alcohol units consist amorphous region. The changes in structure and the composition of amorphous region, and its percentage to crystalline part in fiber affect the dyeabilities of the fiber because dyeing occurs mostly in the amorphous part of the fibers<sup>10)</sup>.

The color depth of wet spun PVA fibers, as is used in this experiment, is inferior to that of dry spun fibers as the structure of dry spun fibers is not spongy and is fairly transparent<sup>11)</sup>.

### 3.2 Comparison of fixation

The percentage fixation was calculated from the K/S value of both PVA fibers of before and after detergent washing, as shown in Table 3.

It is clear that the fixation percentage of Indanthren vat dyes is far better than that of Remazol reactive dyes. Remazol reactive dyes are adsorbed on PVA fiber to some extent, but most of them are flushed away in detergent washing steps (Table 1 and 2). From this it might be thought that Remazol reactive dyes have some affinity with the PVA fiber, but the reaction with the PVA hydroxyl group is not sufficient to make a meaning. The high fixation of Indanthren vat dyes may be due to the deep penetration of the dyes into amorphous region of PVA fibers and low solubility of dyes in water.

### 3.3 Colorfastness to laundering

The colorfastness to laundering of each sample dyed with reactive dyes and vat dyes is shown in Table 4 and 5. The colorfastness to laundering of the vat-dyed PVA was satisfactory, 4-5 grades of color change and also 4-5 grades of staining. The colorfastness of reactive-dyed PVA fiber was expected to be very low because most of the reactive dyes on PVA fiber was flushed away by washing with detergent (Table 1 and 2). But, unexpectedly, the colorfastness of reactive-dyed PVA fiber was shown to be very high, 4-5 grades of color change and 5 grades of staining. This means that reactive dyes have some degree of affinity with PVA fiber and adsorb on PVA, but they can not react with PVA hydroxyl groups efficiently.

Table 3. Percentage fixation of dyes on PVA fiber at 5% owf dyeing

Dye	% Fixation
Remazol Brill. Blue R special	24
Remazol Brill. Red F3B gran	53
Remazol Brill. Yellow 4GL gran	37
Indanthren Blue BC	53
Indanthren Red FBB	82
Indanthren Yellow C-GC plus	59

Table 4. Colorfastness to laundering of PVA fibers dyed with reactive dyes

Sample No.	1	2	3	4	5	6	7	8	9
Color Change	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
Staining									
acetate	5	5	5	5	5	5	5	5	5
cotton	5	-	5	5	5	5	5	5	5
nylon	5	5	5	5	5	5	5	5	5
polyester	5	5	5	5	5	5	5	5	5
acrylic	5	5	5	5	5	5	5	5	5
wool	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5

Table 5. Colorfastness to laundering of PVA fibers dyed with vat dyes

Sample No.	10	11	12	13	14	15	16	17	18
Color Change	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
Staining									
acetate	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
cotton	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
nylon	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
polyester	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
acrylic	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5	4~5
wool	4~5	4~5	4~5	4	4	4	4	4	4

But the dyes that reacted with PVA hydroxyl, although being very small portion, form very stable covalent links, and do not leach out even at the severe conditions of laundering.

#### 4. Conclusions

The dyeabilities of Remazol reactive dyes and Indanthren vat dyes on PVA fiber were investigated. Vat dyes were more suitable than reactive dyes for exhaust dyeing of PVA fiber, giving much better color strength, and fixation properties than reactive dyes. Reactive dyes were also exhausted on PVA fiber, but fixation yields were very low. They flushed away by simple detergent-washing.

The colorfastness to laundering of PVA fiber dyed with vat dyes were good enough to show 4-5 grade of color change and staining as is usual with vat dyes. That of PVA fiber dyed with reactive dyes were also shown sufficient with 4-5 grades of color change and 5 grade of staining.

From these results it was concluded that, for PVA fiber, vat dyes are more suitable than reactive dyes, and that reactive dye form very stable linkage

with PVA fiber although fixation yield is much lower.

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