CHAPTER IV

Result and Discussion

4.1 FT-IR Study of Hydroxyalkyl Dye

Fourior transform infrared spectroscopy (FT-IR) was carried out to identify the characteristic of hydroxyalkyl dye. The FT-IR spectra of the parent reactive dye and hydroxyalkyl dye are shown in Figure 4.1 and Figure 4.2, respectively.

From Figure 4.1, it can be observed that the main characteristic IR absorption band of the parent reactive dye can be found in the region of 797 cm^{-1} which is assigned to the presence of C-Cl functional group of reactive dye[28]. On the other hand, this absorption band completely disappears from the spectrum of the modified reactive dye. The disappearance of the C-Cl absorption band indicates that the reaction between parent reactive dye with hydroxyethylamine has occurred. The broad absorption band in the region of 2999 cm^{-1} is also found, corresponding to the presence $-CH_2$ group on the hydroxyalkyl residue of the modified dye. It is clearly confirmed that the reaction between parent reactive dye and hydroxylamine gave the hydroxyethyl dye which had the structure as shown in Figure 4.2.

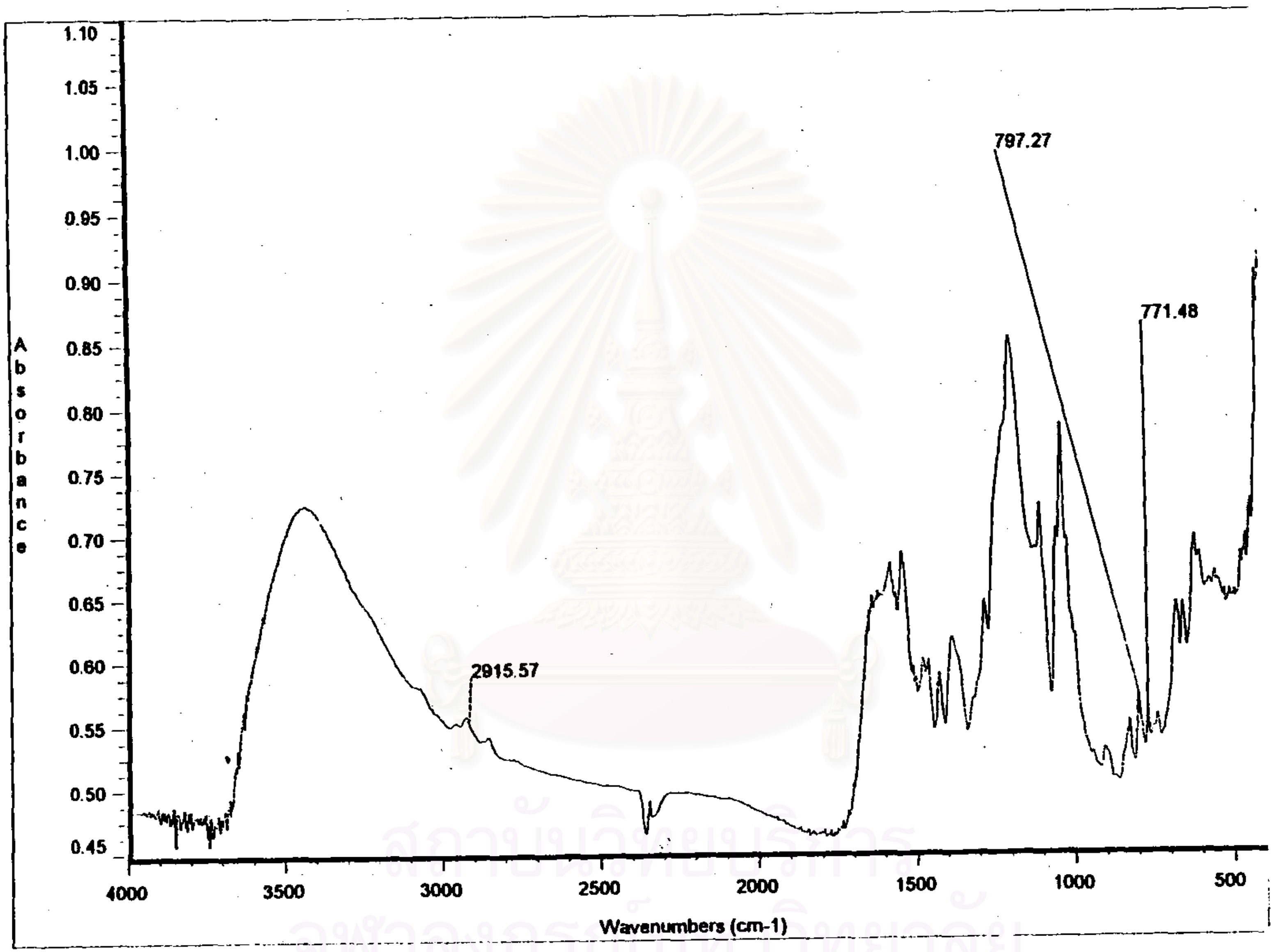

Figure 4.1 FT-IR spectrum of parent reactive dye; Cibacron blue P-B.

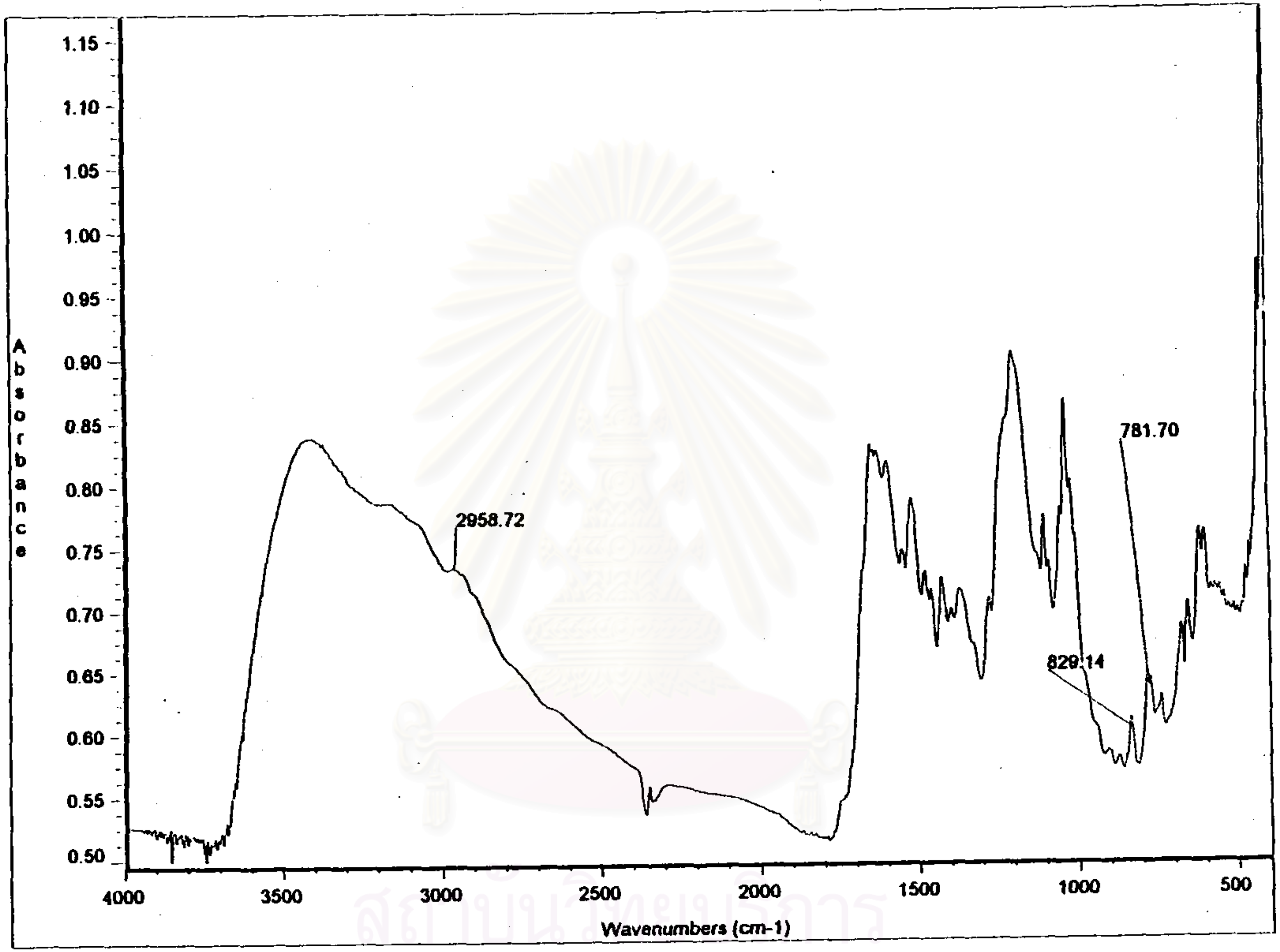

Figure 4.2 FT-IR spectrum of modified reactive dye; Cibacron blue P-B.

4.2 The use of FT-IR to investigate the reaction between crosslinking agent and cotton cellulose

The reaction between hydroxyl group of cellulose and carboxyl group of BTCA was investigated by FT-IR. The FT-IR spectrum of cotton fabric treated with BTCA and catalyst at temperature of 180°C is shown in Figure4.3. The evidence of absorption band of carbonyl group found at 1729 cm^{-1} confirms that the reaction has took place.

The cotton fabric was treated with BTCA and NaH_2PO_2 as a catalyst at a temperature of 180°C for 5 minutes. The treated fabric was rinsed in tap water to remove unreacted BTCA. FT-IR spectrum of treated fabric was collected and as shown in Figure 4.3. The evidence of absorption band of BTCA carbonyl group found at 1729 cm^{-1} indicates that the BTCA is present in the cotton fabric. The peak at 1729 cm^{-1} may represent the carbonyl carboxyl group or carbonyl carboxylate ester group; the later one is bonded to cellulose. To confirm this peak represent to the carbonyl carboxylate ester group. The treated fabric was neutralized with 0.1 N NaOH to convert all free carboxylic group present to carboxylate. The neutralized fabric was subjected to FT-IR analysis again. The FT-IR spectrum obtained is shown in Figure 4.4. It can be seen that the intensity of absorbance at 1729 cm^{-1} clearly decreases whilst the intensity of absorbance at 1586 cm^{-1} strongly increases. Since only free carboxylic groups that can be neutralized by NaOH, the strong absorbance found at 1586 cm^{-1} is believed to be attributable to the presence of carbonyl carboxyl group, indicating some carboxylic groups did not react with cellulose hydroxyl group. The weak absorbance remaining at 1729 cm^{-1} illustrates that the carbonyl carboxylate ester bond is present which confirms that BTCA did react with cellulose hydroxyl group.[29]

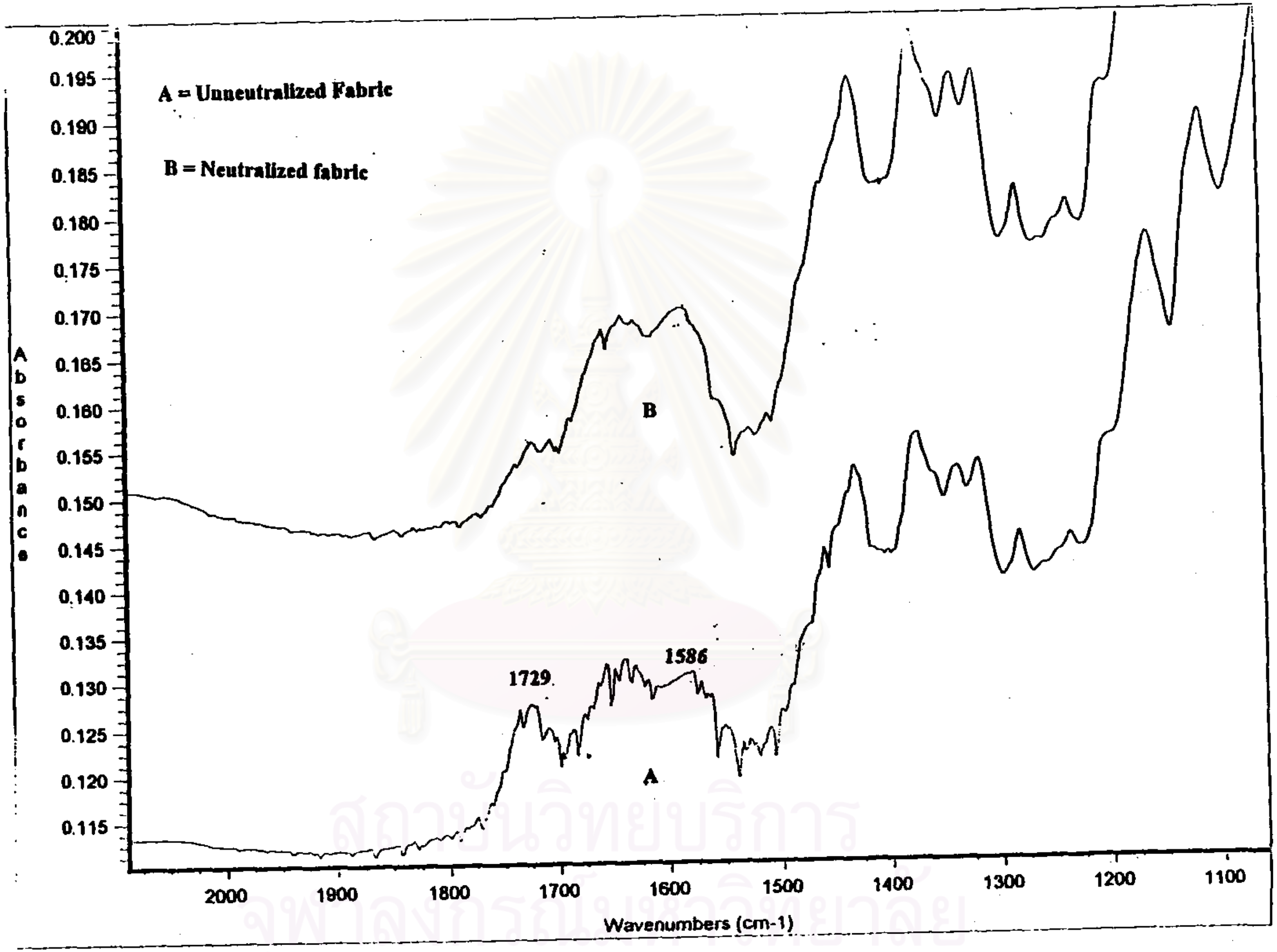

Figure 4.3 FT-IR spectrum of treated fabrics by using modified dye and crosslinking agent.

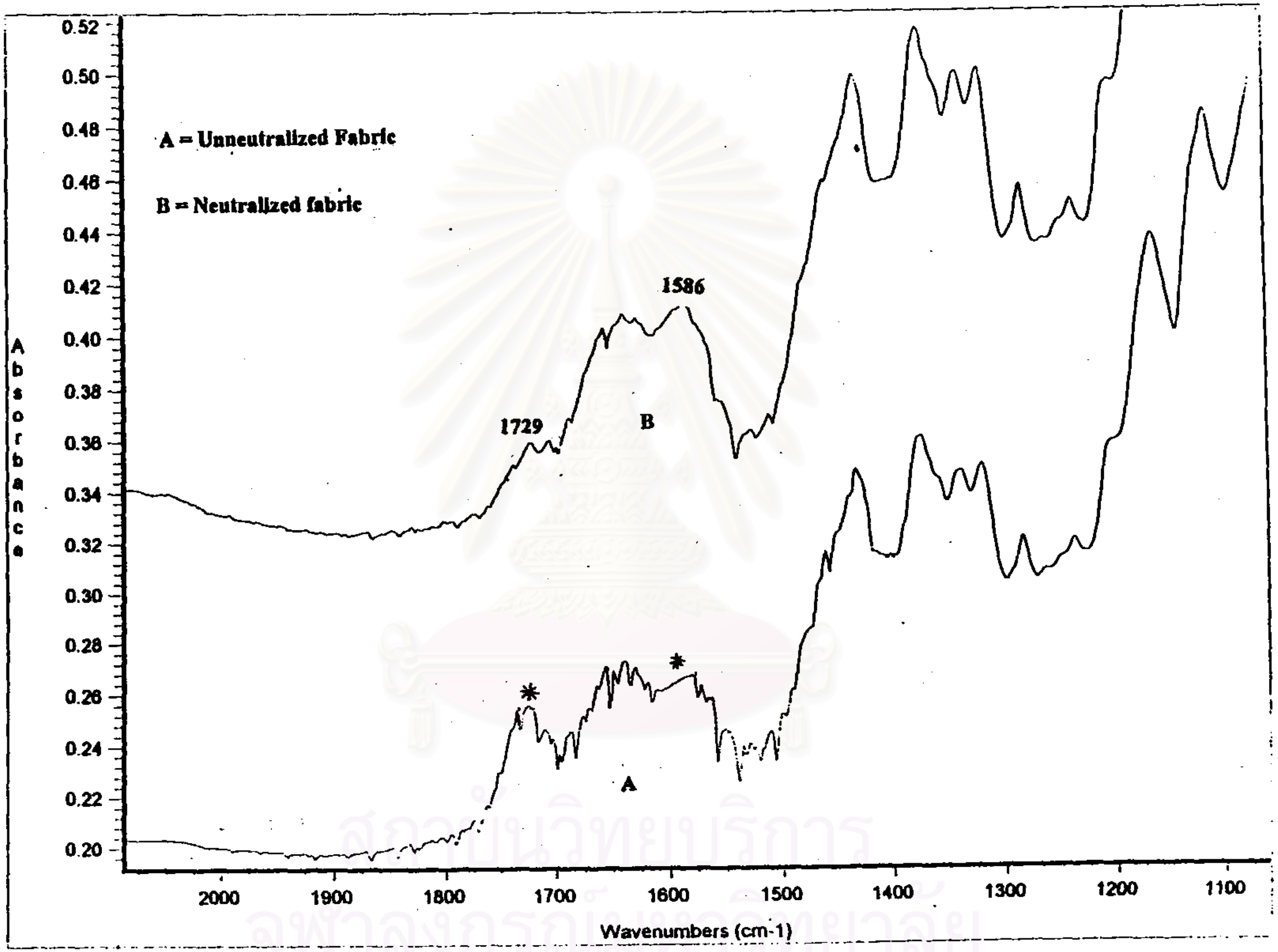

Figure 4.4 FT-IR spectrum of neutralized fabrics by using 0.1 N NaOH.

4.3 Application of the hydroxyalkyl dye to the cotton cellulose in the presence of BTCA as a crosslinking agent

4.3.1 The effect of $NaH_2PO_2.H_2O$ concentrations on the degree of dye Fixation

In all dyeings, concentrations of hydroxyalkyl dye and BTCA crosslinking agent were fixed at 10 g/l and 50 g/l, respectively. Concentrations of NaH_2PO_2. H_2O were varied ranging from 0 to 60 g/l. The pH values of all pad liquors were adjusted to pH 3 prior to padding. Padding was carried out by using the pad mangle to give 80% wet pick-up, then dried and cured at 100°C for 5 minutes and 180°C for 5 minutes in the minidryer stenter. The cured fabrics were soaped using 2 g/l nonionic detergent at 100 °C for 15 minutes and dried. The results of the colour yield and the degree of dye fixation were measured and given in Table 4.1.

Table 4.1 The degree of dye fixation of modified dye at various concentrations of catalyst by using pad-dry-cure method.

Concentrations of BTCA (g/l)	Concentrations of $NaH_2PO_2.H_2O$ (g/l)	%Dye Fixation
50	0	48.42
50	10	51.93
50	20	59.82
50	30	58.47
50	40	59.64
50	50	62.40
50	60	precipitation

From above results, it can be seen that the percentages of dye *fixation slight* increases as the concentrations of catalyst increases and the maximum %fixation *is 62.40* at concentration of catalyst is 50 g/l. At concentration of catalyst is 60 g/l occured precipitation of the modified dye, so %fixation can not be measured. From this experiment, conclusion is that at the concentration of BTCA of 50 g/l, the most appropriate catalyst concentration is 50 g/l because of it gives the maximum %fixation and at excess catalyst concentration, the accumulation of the modified dye is resulted from the higher crosslinking concentration. The concentrations of catalyst and %fixation are compared as Figure 4.5.

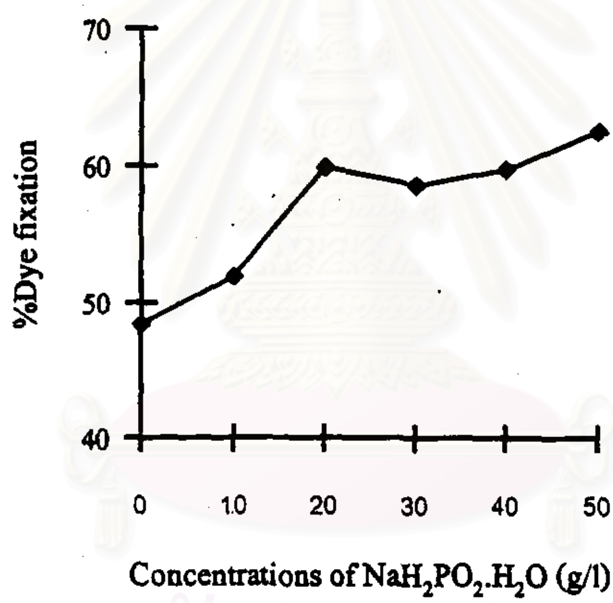

Figure 4.5 Comparison of catalyst concentrations and % dye fixation by pad-dry-cure method.

4.3.2 The effect of curing time and curing temperature on the degree of dye fixation

The pad liquor containing 10 g/l modified dye, 50 g/l BTCA and 50 g/l $NaH_2PO_2.H_2O$ catalyst was prepared. The solution was adjusted to pH 3.0 using 1.0 M NaOH. Cotton fabrics were padded with prepared-pad solutions on the pad mangle to give wet pick-up 80% and were then dried on the same machine and condition as described in 4.3.1. After drying, the fabrics were cured at temperature and time which varied from 160 to 180°C and 1 to 5 minutes respectively. The cured fabrics were soaped using detergent and dried in condition as described in 4.3.1. The resultant fixation values were shown in Table 4.2.

Table 4.2. %Dye fixation at various curing temperatures and curing times

Curing temperature (°C)	%Dye fixation at different curing time (min.)				
	1	2	3	4	5
160	29.20	30.85	43.94	44.96	45.65
170	36.43	46.49	49.68	53.88	56.97
180	48.93	49.90	53.36	54.14	57.31

From Table 4.2 and Figure4.6, percentages of dye fixation tend to increase with an increase of curing time and curing temperature. These may be assumed that the crosslinking reaction is energy-intensive. However, further increase in reaction temperature over 180°C and longer time than 5 minutes was not attempted since it was likely to cause a serious damage to the cotton fiber. Therefore, in this experiment, the curing temperature of 180°C and curing time for 5 minutes could be tolerated and were used through out this work.

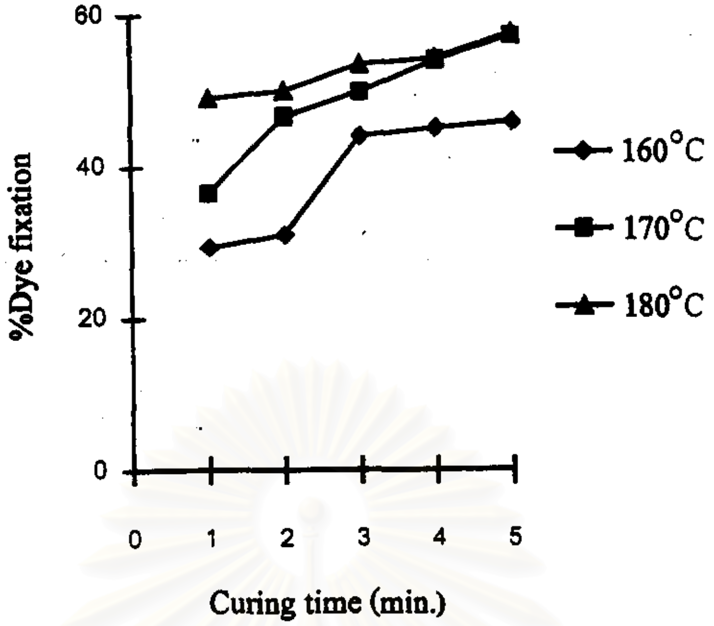

Figure 4.6 The plot of % dye fixation against curing temperature and curing time.

4.3.3 The effect of pH on the degree of dye fixation

Five cotton fabric samples were treated in five solutions containing 10 g/l modified dye, 50 g/l BTCA and 50 g/l $NaH_2PO_2.H_2O$ catalyst with pH values ranging from 2.0 to 4.0. From this experiment, using pad-dry-cure method, the fabrics were dried at 100°C for 5 minutes and cured at 180°C for 5 minutes. The cured fabrics were washed in tap water to remove unreacted dye, unreacted BTCA and catalyst, and then soaped in 2 g/l nonionic detergent at 100°C for 15 minutes. The results of dye fixation values were shown in Table 4.3.

Table 4.3. % Dye fixations of fabrics at various pH values

pH value	% Dye fixation
2.0	55.85
2.5	59.22
3.0	53.45
3.5	54.45
4.0	38.36

From Table 4.3 and Figure 4.7, it can be described that BTCA reacts with modified dye and cotton cellulose under strong acid condition. The suitable pH values which gave the highest dye fixation value were in the range of pH 2 and pH 3.5. Above pH 3.5, it resulted in the significant reduction in the degree of dye fixation. The application of dye to cotton fiber at such very low pH can bring about a serious drawback. This is because the strength of the fiber is substantially lost due to the fiber degradation catalysted by acid. The assessment of the loss of fiber strength will be given in details later.

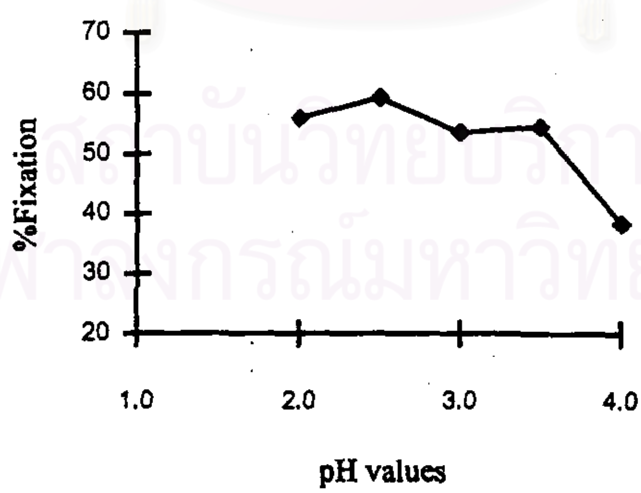

Figure 4.7 Effect of pH on % dye fixation.

4.3.4 The effect of increasing hydroxyalkyl dye concentrations on the degree of dye fixation

With pH values between 2.5 and 3, pad- solutions containing 50 g/l BTCA , 50 g/l $NaH_2PO_2.H_2O$ and modified dye which the concentrations were varied from 10 to 40 g/l were prepared. Fabrics were padded with prepared pad-solutions, then the padded fabrics were dried, cured at 180 °C for 5 minutes and soaped in the boiling soaping solution. The results of the degree of dye fixation were measured and shown in Table 4.4.

Table 4.4 Build-up of hydroxyalkyl dye on cotton fabrics.

Concentrations of dye (g/l)	%Dye fixation
10	58.27
20	46.84
30	Precipitation
40	Precipitation

It was experienced that an attempt to prepare pad solutions of dye concentrations above 30 g/l was failed due to the precipitation of dye. The problem of dye precipitation, especially in the case of high concentration, arised from the ionic repulsion between the dye and the BTCA crosslinking agent, thus forcing the dye molecules to close to each other and then accumulation occured.

The results from Table 4.4 show that increasing dye concentration from 10 g/l to 20 g/l tend to cause the decrease in the degree of dye fixation. In general, the degree of dye fixation obtained is about 50 % in average which is still unsatisfactory. The poor dye fixation value obtained might reflect that the condition used in this experiment was not effective enough or it was because the reactivity of BTCA was too low.

4.4 The evaluation of easy-care properties of dyed fabrics

4.4.1 The effect of curing temperature and curing time on the wrinkle recovery angle property

Fabrics were immersed in the solutions containing 10 g/l modified dye, 50 g/l BTCA and 50 g/l $NaH_2PO_2.H_2O$ catalyst. The fabrics were padded using pad-mangle and then dried at 100°C for 5 minutes followed by curing at various temperatures from 160 to 180°C. The curing times were varied from 1 to 5 minutes for each curing temperature. The results of wrinkle recovery angles were shown in Table 4.5.

Table 4.5 The effect of curing temperatures and curing times on wrinkle recovery angle property

Curing Temperature(°C)	Wrinkle recovery angle at time(min.)				
	1	2	3	4	5
160	228	235	239	259	265
170	243	258	266	268	271
180	247	268	270	273	282
Untreated cotton	223				

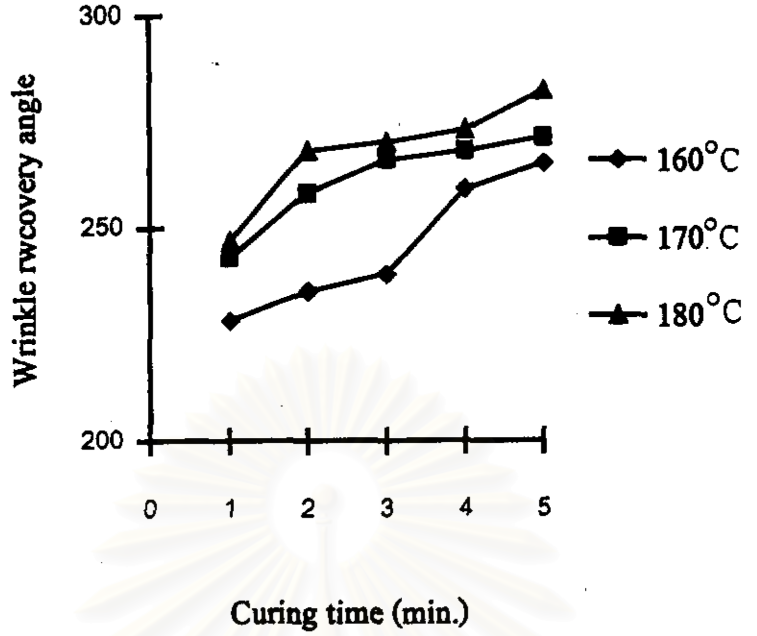

Figure 4.8 Wrinkle recovery angle at different curing temperatures are plotted against curing times.

BTCA is polycarboxylic acid which could improve the crease resistance of cotton fabric through the formation of ester linkages with adjacent cellulose chain molecules. Evaluation of easy care properties was carried out by measuring the wrinkle recovery angle. It can be seen from the results that wrinkle recovery angle increases as curing temperature increases as well as the duration of curing time at each curing temperature is extended. The higher wrinkle recovery angle value means that the treated fabric is resistant to crease. The highest wrinkle recovery value obtained in this experiment was 282 ^{o} compared to 223 ^{o} obtained from control fabric. It is expected that crease recovery angle value higher than 282 ^{o} would be obtained if curing temperature is higher than 180 ^{o}C. However, such a high temperature may greatly affect the tensile strength properties of treated fabric beyond an acceptable level.

4.4.1.2 The effect of pH values on the wrinkle recovery angle property

Cotton fabrics were dyed with 10 g/l modified dye, 50 g/l BTCA, 50 g/l $NaH_2PO_2.H_2O$ catalyst and pH values were varied from 2.0 to 4.0. The fabrics were padded on pad mangle to about 80% wet pick-up. The padded fabrics were dried at 100°C for 5 minutes and cured at 180°C for 5 minutes. After soaping with 2 g/l nonionic detergent, the dried fabrics were tested wrinkle recovery angle and the results were given in table 4.6.

Table 4.6 The effect of pH on the wrinkle recovery angle property

pH value	wrinkle recovery angle
2.0	272
2.5	265
3.0	260
3.5	245
4.0	238
Untreated cotton	223

As shown in Table 4.6 and Figure 4.9, wrinkle recovery angle at pH 2.0 is highest. The trend of wrinkle recovery values decreases as pH value increases. These results may imply that the crosslinking reaction requires acid catalyst in order to achieve the good result. However, the strong pH value may greatly affect the tensile property and elongation at break of treated fabric. Therefore, in this experiment pH values between 2.0-3.0 are sufficient enough to give a good result at acceptable loss in tensile properties.

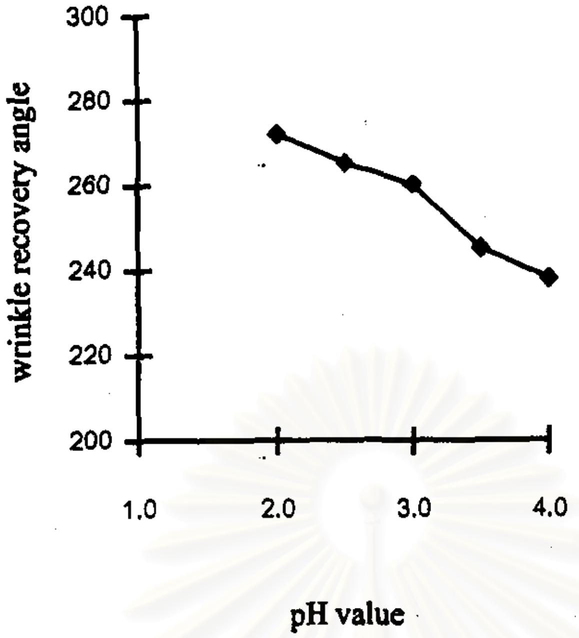

Figure 4.9 Wrinkle recovery angle properties are plotted against pH value.

4.4.2 The evaluation of the strength of dye-fiber bond by washing fastness test.(ISO 105-C04)

4.4.2.1 The effect of curing temperatures and curing times on washing fastness property

Fabrics were immersed with pad-solutions containing 10 g/l modified dye, 50 g/l BTCA and 50 g/l $NaH_2PO_2.H_2O$ catalyst. The pH values were adjusted to 2.5-3.0. Then fabrics were squeezed using pad mangle machine. The padded fabrics were dried at 100°C for 5 minutes. Curing time of the fabrics were varied from 1 to 5 minutes and curing temperatures were varied from 160 to 180°C. The cured fabrics were soaped and dried again as described in 4.4.1.2. After dried fabrics were subjected to wash fastness test the results are given in Table 4.7.

Table 4.7 Wash fastness test of dyed fabric at different curing times and temperatures.

Curing Time (°C)	Wash fastness at different curing times (min.)				
	1	2	3	4	5
160	5	5	5	5	5
170	5	5	5	5	5
180	5	5	5	5	5

Washing fastness test was carried out in order to assess the dye-fiber bond stability. Colour change before and after washing test was compared with standard grey scale level; the higher the level number the better the fastness properties to washing. It can be seen from the results that, according to ISO 105-C04 standard washing test, colour changes before and after washings were compared to number 5 on grey scale for the whole range of dyed samples. The number 5 read on grey scale means that there was not change in colour before and after washing test. It can be said that washing fastness of this dyeing system would be acceptable under mild washing test.

4.4.3 The determination of the loss of tensile strength of dyed fabrics

4.4.3.1 The effect of temperatures and times on the loss of tensile strength of dyed fabrics

Fabric were immersed with pad solutions containing 10 g/l modified dye, 50 g/l BTCA and 50 g/l $NaH_2PO_2.H_2O$ catalyst. The pH values were adjusted to 2.5-3.0. The fabrics were squeezed using pad mangle machine. The padded fabrics were dried at

100°C for 5 minutes. Curing time and curing temperature were varied from 160 to 180°C and 1 to 5 minutes respectively. %Loss strength of the fabrics were measured and the results were shown in Table 4.8.

Table 4.8 %Loss strength at various curing temperatures and curing times.

Curing Temperature (°C)	%Loss strength at different curing times (min.)				
	1	2	3	4	5
160	16.21	21.66	31.75	33.77	35.90
170	24.40	28.34	34.60	35.02	45.79
180	30.24	33.67	34.82	36.31	47.15

It can be seen from these results that the degree of the loss of tensile strength is highly dependent on both the duration and the temperature of curing. The degree of the loss of tensile strength increase as the curing temperature increases. At each curing temperature, the degree of the loss of tensile strength increases as the duration of curing time was extended. It is strongly required that the loss of tensile strength should be as small as possible by controlling the curing temperature and duration of curing times.

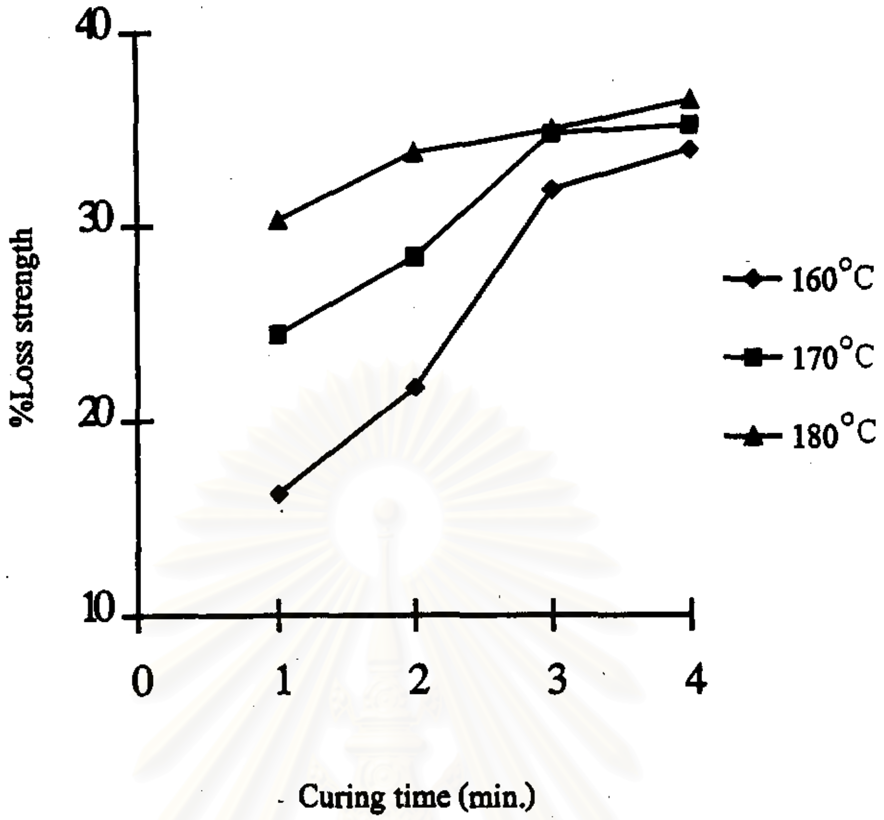

Figure 4.10 %Loss strength at times were plotted against temperatures.

4.4.3.2 %Loss strength at various pH of the dyed fabrics

Fabrics were immersed in solutions containing 10 g/l modified dye, 50 g/l BTCA and 50g/l $NaH_2PO_2.H_2O$ catalyst. The pH values were varied from 2.0 to 4.0. The fabrics were passed between the squeeze rolls of pad mangle and were then dried at 100°C for 5 minutes. The fabrics were cured at 180°C for 5 minutes, soaped at 100°C for 15 minutes with 2 g/l nonionic detergent. After soaping, the fabric were dried at 100°C for 5 minutes and measured %loss strength and the results were shown in Table 4.9.

Table 4.9 %Loss strength of dyed fabrics at various pH

pH value	%Loss strength
2.0	44.71
2.5	39.52
3.0	34.19
3.5	33.56
4.0	16.21

From Table 4.9 and Figure 4.11, the results of this experiment that are %loss strength of the fabric decreases as pH values increases. The maximum of %loss strength is 44.71 at pH 2.0 and the minimum is 16.21 at pH 4.0. It can be summarized that the pH value of pad liquor affect the strength of dyed fabrics, the dyed fabrics can be reduced the strength when padded with strong acid liquor.

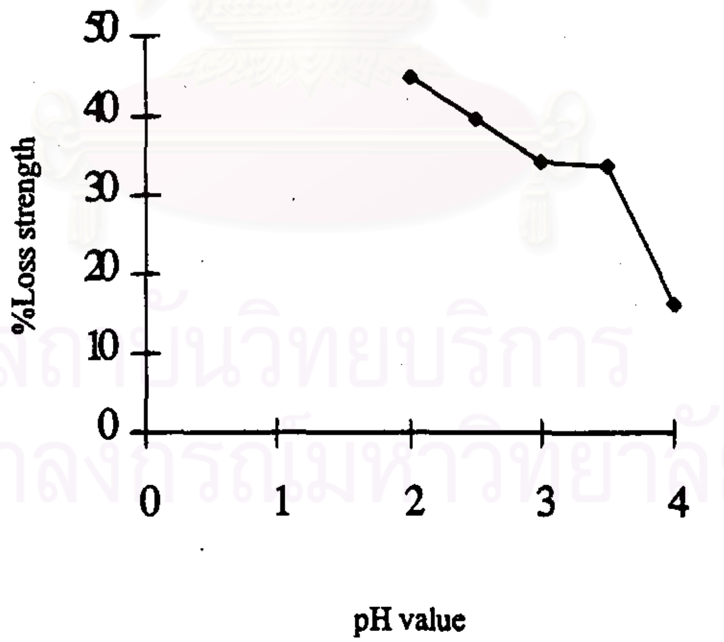

Figure 4.11 %Loss strength are plotted against pH value.