Catalyzation of Alkaline Hydrolysis of Polyester by Oxidizing Agents for Surface Modification

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Abstract

In the literature alkaline hydrolysis to bring hydrophilicity of polyester fabric is well. Various auxiliary chemicals such as hydrogen peroxide and sodium perborate are used along with NaOH to catalyze or facilitated the surface modification of polyester. Present paper describes the use of oxidizing agents such as H_2O_2 and NaBO3 to accelerate the alkaline hydrolysis of polyester. The results indicated that although the loss in strength due to weight loss cannot be totally eliminated, there is considerable improvement in fabric wettability measured by water drop absorption, sinking time and capillary rise methods. The FTIR study indicated the introduction of hydrophilic groups like -COOH and –OH responsible for improvement in hydrophilic character and comfort properties. The DSC study indicates decrease in crystallinity and glass transition temperature when the alkaline hydrolysis was carried out in presence of oxidizing agents compared to control. There was considerable improvement in disperse and cationic dye dyeability of modified polyester in presence of both the oxidizing agents compared to control using NaOH alone for alkaline hydrolysis. The effect of sodium perborate appeared to be more predominant compared to hydrogen peroxide which is interpreted in terms corresponding slow release of H_2O_2 form sodium perborate against rapid decomposition of H_2O_2 in presence of strong alkali like NaOH.

Keywords: alkaline hydrolysis; hydrophilicity; weight loss; Polyethylene terephthalat,dyeability.

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1. Introduction

PET fibers have outstanding chemical, physical, and mechanical properties but suffer from certain drawbacks due to the intrinsic hydrophobic and inert nature. Low moisture regain and poor wettability cause a variety of problems both during manufacturing (accumulation of static electricity) and consumer use (clinging to the body, accumulation of fluff and soil) [1,2,3].These problems can be overcome by alkaline hydrolysis of polyester, which converts hydrophobic PET into hydrophilic due to fibre surface modification. Polyester undergoes nucleophilic substitution and is hydrolysed by aqueous sodium hydroxide. The hydroxyl ions attack the electron-deficient carbonyl carbons of the polyester to form an intermediate anion [5]. Due to hydrolysis there is an increase of hydrophilic groups on the surface of PET fibers. The nucleophilic attack of NaOH on PET chains causes chain scissions at the ester linkages, producing carboxyl and hydroxyl polar groups, which lead to improved polarity and hydrogen bonding capacity with water molecules, and thus better water wettability [4].Alkaline attack is confined to the PET surface, because highly ionized compounds like aqueous sodium hydroxide are not allowed to diffuse into the bulk due to the strongly non-polar characteristic of PET. Many polymeric textile materials are known to be susceptible to moisture sorption and, if H_2O_2 vapor is similarly absorbed by these materials, their engineering properties could be seriously degraded. Polyester could be among the most vulnerable materials to potential hydrogen peroxide attack. These polymeric materials consist of long chain carbon-carbon backbones with side chain functional groups, as well as intermolecular cross-links that might be degraded by oxidation from the hydrogen peroxide [5].Treating polyester fabric with a treatment solution containing a synergistic combination of hydrogen peroxides (or compounds which produce hydrogen peroxide in solution like sodium perborate) for sufficient time makes polyester fabric hydrophilic. This process also can make available polyester material cationically dyeable, and improving its hand without affecting the excellent cloth making property of the fabric [6].Oxidation of polyester fabric brought –COOH functional groups which provide wettability as well as creating dye cites [7]. Oxidizing agents like H_2O_2 and $NaBO_3$ are one the chemicals that release active oxygen or act as oxidizing agent. Hydrogen peroxide is not stable over time; it is possible to get a fresh solution of hydrogen peroxide by using chemicals that contain hydrogen peroxide seemingly indirectly like sodium perborate. Hydrolysis reaction of NaOH with PET is initiated by the hydroxylation attack on the electron deficient carboxyl carbon atom of the ester linkages. The carboxyl group formed is immediately converted into carboxylate anion and the reaction goes to completion in the direction of hydrolysis. It is assumed that the alkali randomly attacks the carboxyl groups of the polymer molecule present on the surface and removes them as short chains. Finally, the short chains are hydrolyzed to disodium terephthalate [8].With the progressive alkaline hydrolysis, the PET chains on the surface are etched away and the diameter is reduced, producing fabrics with a softer and silkier hand. Surface hydrolysis does not impose significant changes on the overall geometry or pore structure of the material [8].As hydrolysis progresses, surfaces are etched away and alteration of fabric pore structure with increased severity of hydrolysis is expected. By varying the extent of hydrolysis, modification of surface wettability alone or improved surface wettability combined with altered fabric pore structure is possible [9].Alkali attacks PET chains (preferentially from the end groups) and removes hydrolyzed PET material, thus leading to the formation and exposition of new surfaces which is confirmed by the progressive weight loss and decrease in size of PET fibers and are accompanied by the negligible changes in the degree of polymerization and crystallinity. One of the most

peculiar morphological features of alkali-treated PET materials is the presence of pits on the surface, i.e., voids which are thought to play a significant role in surface-related phenomena [1]. Modification of PET material is important, because PET is un-reactive so that it difficult to attach other functional groups without modification. To increase its hydrophilic properties and enlarge the application field of PET material, proper modification is needed. Lots of research has been done on the modification of PET materials. Normal methods use sodium hydroxide or amines.

When polyester fabric is modified with sodium hydroxide there could be a reduction of glass transition temperature and a formation of carboxylic groups (COO-) which is responsible for accepting cationic dyes to the fabric [10].

Chemical modification of PET polyester permits a substantial change in its dyeability with out and significant changes in their physico-mechanical properties [10].

Polyester fabric is widely used in the textile industry due its simple manufacturing process and low cost of manufacturing. But polyester possess very serious drawback due to its hydrophobic character. This hydrophobic character of polyester has an effect on it comfort property during wearing and has limited dyeability character (it is not possible to dye polyester using different dyes except disperse dyes.) Despite its hydrophobic property despite the fact that polyester fiber is extremely hydrophobic, it has a bright future, particularly in the fashion industry, as consumers increasingly are attracted by its easy care properties. While research continues to develop an ideal hydrophilic polyester solution, this article examines ways to increase the hydrophilicity of polyester via processing routes (such as denier reduction and microfibers) and chemical routes (topical finishes).Now polyester is the world's leading fibre in manufacturing, so many researches has to be done and this is one the key researches which improves the hydrophobic character of polyester.

When the textile industries uses the hydrophilic polyester the following properties are improved like ease of soling ,static charge build up, tendency to pill and lack of dye receptor sites especially for cationic dyes so, for easy processing and use of variety of dyes for polyester is improved.

The present paper described the use of oxidizing agent like hydrogen peroxide and sodium perborate to catalyze the alkaline hydrolysis for surface modification of PET.

Differential Scanning Calorimetry, DSC, is a thermal analytical technique which measures thermal events, such as phase transition like glass transition temperature, crystallization temperature, specific heat and melting points of the polymer [11].

Fourier transform infrared spectroscopy is unique to polymer molecule which is used to determine the structure, and also by comparing it with spectra of known materials confirm the presence and absence of functional groups.FTIR spectroscopic measurements can be performed using FTIR instrument, model 460.in the transmission technique, the IR radiation passed directly through the sample contained within a potassium bromide (KBr) pallets [11].

2. Materials and Methods

1.1. Materials

Commercially bleached 100% polyester fabric procured from the market in Addis Ababa with 46picks/inch, 44ends/inch, and 200 GSM specifications was used.

2.1.1 Chemicals

Laboratory grade caustic soda, hydrogen peroxide, sodium perborate ,sodium sulphate, acetic acid ammonium sulphate were used. Commercially available Dispersing agent, cationic dye (BEZACRYL Blue GRL 300) supplied by Benzema, disperse dye (Dianix blue AM-2G) from Afro Germen were used.

2.1.2 Equipments used

For the experiment purpose Laundrometer (MESDAN LAB), GretagMacbeth colour-eye 3100 spectrophotometer, Differential scanning calorimetry 4000 Perkin-Elmer, USA thermal analyzer and Fourier transform infrared 460 were used.

2.2 Experimental methods

Alkaline hydrolysis experiments were performed according to general factorial single factor experimental design ,using design experts software Dx8.0.7.1, in the replication of three experiments and the data were analyzed using design experts Dx8.0.7.1 software, and Microsoft office excel 2007.

2.2.1 Treatment with caustic soda

Strength of laboratory grade caustic soda was determined by titration with standard sulpheric acid using phenolphthalein indicator. The concentrations of caustic soda taken for experiments were adjusted to 98% pure caustic soda strength. The strengths of hydrogen peroxide and sodium perborate were determined by titration with potassium permanganate. The strengths of H_2O_2 and sodium perborate were found to be 21% and 14% respectively.

2.2.2 Alkaline hydrolysis of polyester

Commercially bleached polyester fabric was treated with caustic soda solution of concentrations of varying from 0.5N -2N at 0.5N intervals containing 3.57, 7.14 and 14.28 g/l of H_2O_2 and 2.8, 5.6 and 11.2 g/l of sodium perborate (NaBO3) were used. The alkaline treatment of polyester fabrics was carried out using a high temperature, high pressure laboratory dyeing machine.

Required amount of alkali solution along with auxiliary chemicals were placed in stainless steel tubes, fabric samples were immersed in alkali solutions, and the sealed tubes were rotated in the closed bath containing NaOH along with H_2O_2 and $NaBO_3$ separately at 100 ^{o}c for 60 minutes. The material to liquor ratio was 1:20.

After the predetermined durations, the samples were removed from the bath, rinsed repeatedly with cold water, neutralized with a solution of 1% acetic acid and rinsed. The samples were then dried at room temperature conditioned and weighed. In separate bath, similar treatment was carried out on polyester fabric with sodium hydroxide only as a control sample.

2.2.3 Determination of weight loss

The percentage of weight loss was calculated with the following formula:

Weight loss (%) = [(W1 -W2)]/W1 x100.

Where, W1 and W2 are the weights of fabric before and after treatment, respectively.

2.2.4 Determination of tensile strength

Tensile strength and extension at break was determined using H5KS universal tensile strength testing machine according to ASTM D 2209; 1995. The measurements were carried out in triplicate and average values are reported.

For comparison purposes this test has been carried out for the untreated polyester fabric also.

2.2.5 Determination of wettability

Water drop absorbency: Water absorbency test was performed by putting a drop of water using dropper on the fabric surface and visually noting down time for the water absorption.

Sinking time: Three pieces from each sample (2.5cmx2.5cm) were taken. The samples were carefully placed (each piece separately) in to glass beaker filled with water and time required for the sample to sink at the bottom of the beaker was noted. Average of three tests is reported.

Capillary rise: The hydrophilic properties were tested as follows: one end of the sample was immersed vertically along its length in a water reservoir and water diffused into the sample by capillary action. The height climbed by the water in the sample (the so called wicking height), was measured after 5 minutes.

In this case each specimen was cut vertically into a 20 x 2cm strip, hung length way with the bottom end dipped in water stained with acid dye (for visibility)[12].

2.2.6 Determination of stiffness and thickness

Drapability was checked by measuring the bending length of the sample. Shirley stiffness tester was used for the bending length measurement. The stiffness tester is used for determining the stiffness of a fabric according to BS 3356 BS 9073 part 7 and ASTM D1388. The fabric thickness before and after treatment was measured using fabric thickness tester according to ASTM D 1777-96/97 and ISO 3616/5084/9073.

2.2.7 Dyeing with cationic and disperse dyes

Dyeing was performed using HTHP dyeing machine. The dyeing conditions are: MLR 1:20, at 100oc for 60 minutes under acid pH of 5-6 adjusted with acetic acid.

Dyeing with cationic dye

The treated samples were subjected to dyeing using cationic dye (Bezacryl blue GRL 300).

Dye bath composition

  Dye   2 % owf

  Sodium sulphate   10g/l

Dyeing was started at boil, firstly all dye bath additions were mixed at room temperature and machine was started after the temperature of the machine reaches at 100^oc. After dyeing the samples were taken out from the sample holder and rinsed with cold water and dried.

Dyeing with disperse dye

In the case of disperse dye similar to basic dye the treated fabrics were subjected to dyeing with disperse dye (Dianix blue AM-2G).

Dye bath composition

Dye   2 % owf

Ammonium sulphate   1 g/l

Dispersing agent   2g/l

Similar to cationic dye, dyeing was started at boil, firstly all dye bath additions were mixed at room temperature and machine was started after the temperature of the machine reaches at 100oc.After dyeing, the sample were washed with hot water and soaped at boil using 2 g/l commercial synthetic detergent for 5 minutes and rinsing with cold water.

2.2.8 Colour yield measurement

The colour yield was determined by measurement of the K/S value of the dyed samples on GretagMacbeth colour-eye 3100 spectrophotometer. Before measuring (K/S), samples were pressed with hot iron and left to cool down. Then, samples were made into four folds to ensure opacity. For each sample, K/S values were taken as averages of three different values at three places at the wave length of maximum K/S. The color intensity

expressed as K/S values of the dyed samples was determined by applying the Kubelka– Munk equation:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)}{2R_o}$$

Where R is the decimal fraction of the reflectance of the dyed sample, Ro is the decimal fraction of the reflectance of the undyed sample. K is the absorption coefficient and S is the scattering coefficient.

The relative color intensity is calculated using following equation:

$$\text{The relative color intnsity} = \frac{\text{K/S of treates sample}}{\text{K/S of untreated sample}} *100\%$$

2.2.9 Wash fastness

The wash fastness test has been carried out according ISO 105 C10:2006 part D to investigate efficiency of cationic dye and disperse dyes after surface modification. The test has been carried out in triplicate   for all samples. For comparison purposes the test has been carried out for the untreated fabric samples also.

Laundrometer (MESDAN LAB) was used.

Samples of size 10cm × 4 cm were cut and covered with a white (bleached) polyester fabric on both sides by stitching at the four edges. Then these samples were put in test jars of wash liquor.

Samples were rinsed with tap water 5 (five) times and air dried before assessing color loss. The color loss because of washing was assessed in terms of fading and staining. For determining color fade the color difference between treated and original sample was compared. Similarly for staining the color difference between stained and original white polyester fabrics was compared. Spectrophotometer has been used for determining the color difference both for color fade and staining tests.

2.2.10 Differential scanning calorimetry (DSC) Characterization

 The differential scanning calorimetry (DSC) for untreated and treated polyester fabrics was carried out using DSC 4000 Perkin-Elmer, USA thermal analyzer. The rate of heating was adjusted at 30oc/min. Thermograms were recorded from 50oc to 300 ^{o}c under nitrogen atmosphere.

2.2.11 Fourier Transform Infra Red (FTIR) Characterization

In the case of Fourier transform-infrared spectroscopy (FTIR) measurements were performed on FTIR 460 spectrophotometer employing a total transmittance mode. The wave number scale was adjusted from 400 cm-1 to 4000 cm-1. The treated samples were cut into pieces and well sandwiched with potassium bromide pallets and put into a sample holder.

3. Results and Discussions

3.1 Effect of hydrolysis on weight loss of polyester fabric

The weight reduction of polyester ranging between 15 and 30% gives a silky handle, luster, soil repellency and anti static properties to the polyester fabric, and its stiffness, tenacity and elongation are decreased [4].

Almost all the studies on alkaline hydrolysis of polyester indicate weight loss. However, the extent of weight loss varies depending on the hydrolytic conditions and the agents used. In the present study the alkaline hydrolysis of polyester was carried out using 0.5N, 1 N and 1.5N NaOH at boil for 1 h in the absence and in presence of H_2O_2 (7.14 g/l) and $NaBO_3$ (5.6 g/l). The experiments were carried out in triplicate and the results were analyzed using design experts software Dx8.0.7.1,

It was observed that the alkaline treatment of PET fabrics leads to a loss in weight of the fabrics. The weight loss increased with increasing concentrations of NaOH as shown in the table 1

Table 1: Effect of NaOH concentration on weight loss of PET fabric

Run #	NaOH conc. (N)	Wt loss (%)
1	1.0	12.40
2	0.5	5.740
3	1.0	13.52
4	1.0	12.54
5	0.5	5.520
6	1.5	19.86
7	0.5	4.960
8	1.5	21.52
9	1.5	20.60

It can be seen that with increasing caustic concentration the rate of hydrolysis increases [3]. It can be seen that at constant treatment time and temperature the weight loss increases with increasing the concentration of NaOH solution. The weight loss increased with the increase of the concentration of sodium hydroxide. Sodium hydroxide had an oxidative effect on the surface of the polyester fiber, and destroyed/remove the surface. This is evident from the obviously ridge and uneven rough trench structure formed, resulting in an increase of the contact areas between fiber and NaOH which in turn led to an improvement of the adhesive property. This was also confirmed by the following figure taken by DOE software [12].

However, weight loss at each concentration of NaOH was higher in presence of H_2O_2 and $NaBO_3$ indicating that the presence of these oxidizing gents accelerated the alkaline hydrolysis. The alkaline hydrolysis of polyester is well documented in the literature.

Hydrolysis of polyethylene terephthalate (PET) by alkali metal hydroxides, the hydroxide ions attacks C=O, C-O and C-O-C functional groups i.e. the ester group and removes as short chains. Low molecular segment of the chains is removed, resulting in weight loss and a decrease in the thickness of the fabric. The extent of attack and the removal of short chain segments increases with the increase in concentration of NaOH and it appears that the process is accelerated by the presence of oxidizing agents.

In order to see the effect of caustic soda concentration on the weight loss of polyester fabric single factor ANOVA test were performed by using design experts software.
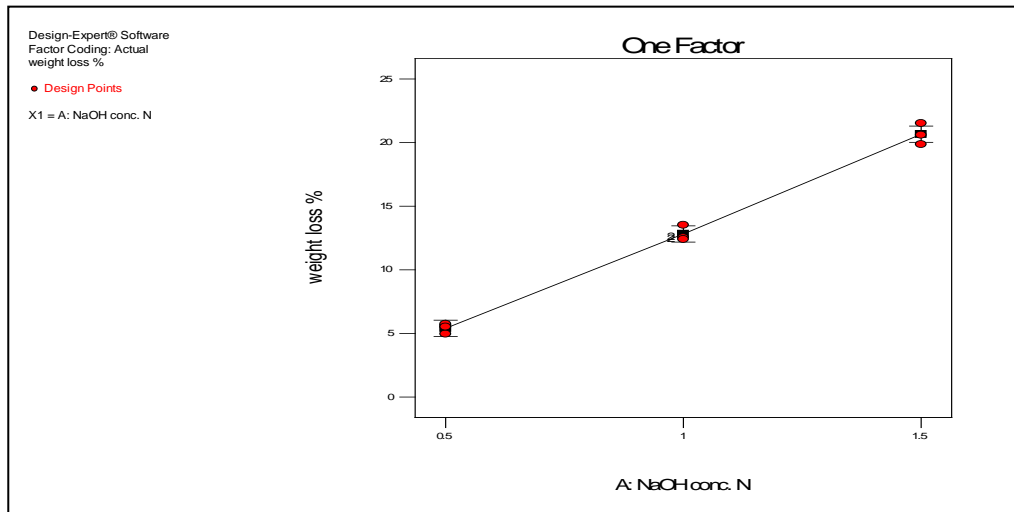

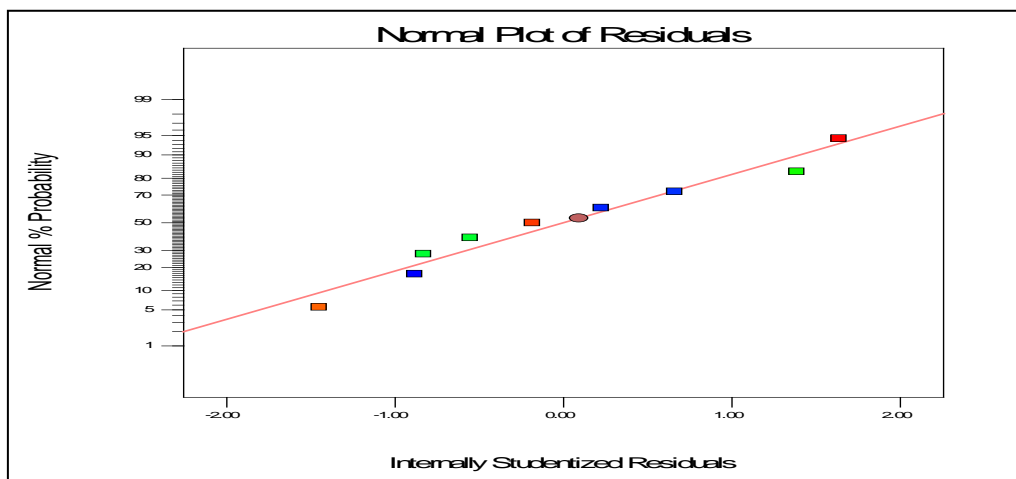**Figure 1:** effect of NaOH concentration on weight loss of PET fabric

Figure 2: Normal probability plot of residuals for NaOH concentration

Here the effects of caustic soda concentration on weight loss were found to be consistent and significant. This was confirmed from the normal probability plot of residuals, plotted by design expert software. As shown in figure 2, the points are fairly close to a straight line indicating the validity of the experimental data. Here a residual means differences in the observed value and predicted value. The normal probability plot of residuals is

used to check the residuals are normally distributed.

In order to see the effect of hydrogen peroxide and sodium perborate on weight loss of polyester fabric the same study was conducted like that of sodium hydroxide.

Table 2: Effect of H_2O_2 concentration on weight loss of PET fabric

Run #	H_2O_2 conc. (g/l)	Wt loss (%)
1	14.28	19.61
2	7.14	15.52
3	3.57	8.60
4	7.14	15.20
5	14.28	19.96
6	3.57	8.97
7	14.28	20.40
8	3.57	09.10
9	7.14	16.50

The results indicated that up to 1 N concentration of H2O2 and NaBO3 the weight loss was rapid and beyond this concentration the   weight loss was slowed down optimum concentration of H2O2 and NaBO3 was 7.14g/l and 5.6g/l respectively which give optimum weight loss and strength loss.
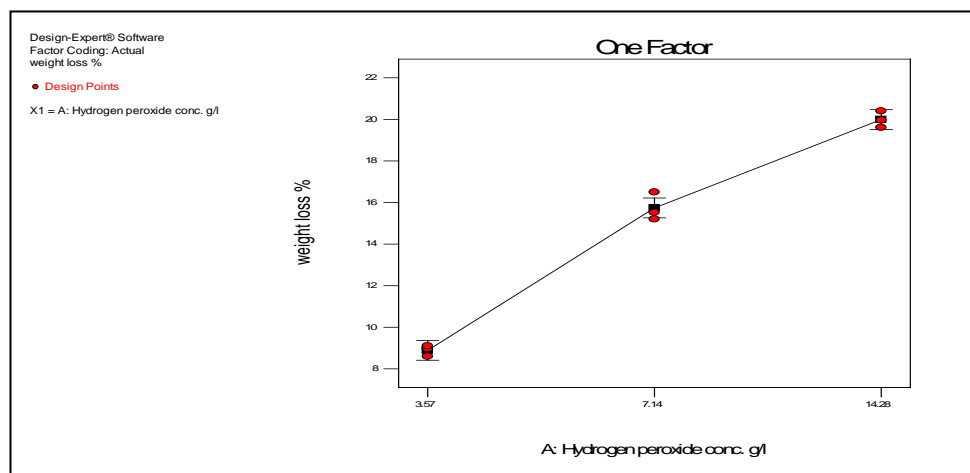

Figure 3: effect of H_2O_2 con. On weight loss

Many polymeric textile materials are known to be susceptible to moisture sorption and, if H_2O_2 vapor is similarly absorbed by these materials, their engineering properties could be seriously deteriorated. Polyester could be vulnerable to potential hydrogen peroxide attack. These polymeric materials consist of long chain carbon-carbon backbones with side chain functional groups, as well as intermolecular cross-links that might be degraded by oxidation from the hydrogen peroxide. Sodium perborate when combined with water, librates

hydrogen peroxide and active oxygen and the effect is indirectly similar to hydrogen peroxide when applied directly. The oxygen radical may facilitate the degradation of polyester during hydrolysis [5].

Table 3: Effect of $NaBO_3$ concentration on weight loss of PET fabric

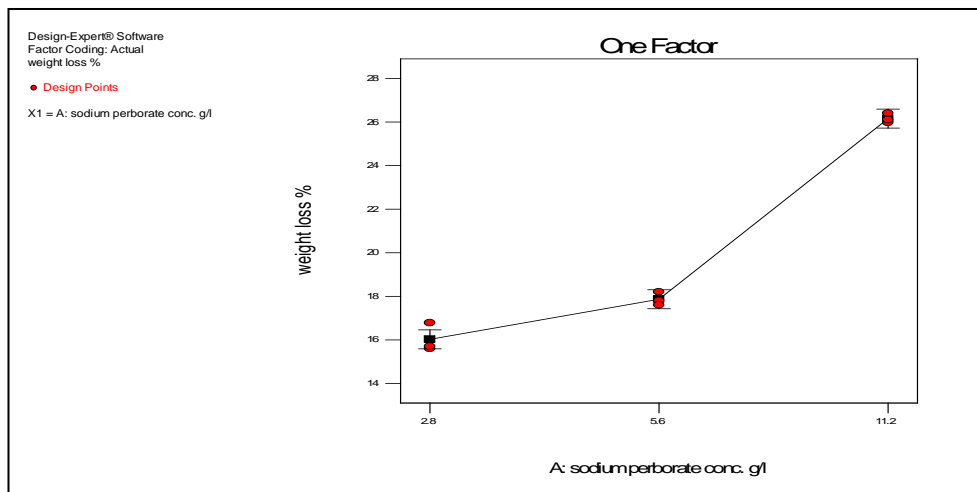| Run #	$NaBO_3$ conc. (g/l)	Wt loss (%)
1	2.8	15.70
2	2.8	16.78
3	5.6	18.20
4	5.6	17.20
5	11.2	26.40
6	5.6	17.80
7	11.2	26.10
8	2.8	15.60
9	11.2	25.97

Figure 4: effect of $NaBO_3$ conc. On weight loss

Generally, when polyester fabric is treated in a caustic solution with conventional hydrolysis the fabric weight is not so quickly reduced [3].

However, with oxidizing agents the treated fabric shows high weight loss in the same period of time, indicating that oxidizing agents like hydrogen peroxide and sodium perborate can increase the rate of hydrolysis at the fibre surface. This is mostly due to the catalyzing effect of oxidizing agents that the conventional hydrolysis system. In using oxidizing agents the caustic agent solution can degrade more highly and speeding up the hydrolysis on the polyester surface, bring more weight loss.
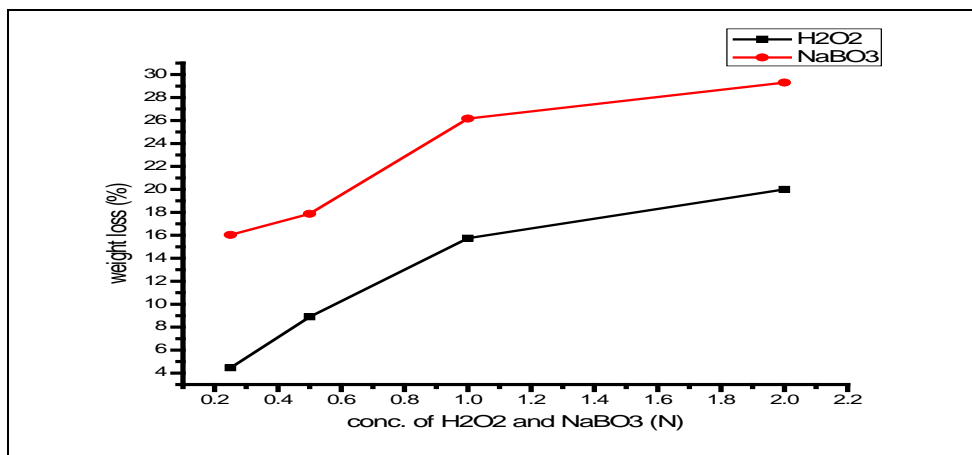
Figure 5: effect of H_2O_2 and $NaBO_3$ concentration on weight loss of PET

In terms of actual oxidizing agent in the treatment bath, the H2O2 concentration was higher compared to NaBO3 concentration. In spite of this the weight loss was higher in case of NaBO3 at each concentration. This may be accounted to the rapid decomposition of H2O2 under alkaline conditions at boil as a result of which effective H2O2 was not available over a period of 1 hour of alkaline hydrolysis. Whereas in case of NaBO3, hydrogen peroxide was slowly released during the treatment period and effective hydrogen peroxide was available over a period of 1 hr of alkaline hydrolysis. Therefore, alkaline catalyzation in case of NaBO3 was better resulting in higher weight loss. In order to check the validity of the experiment normal plot of residuals was drawn
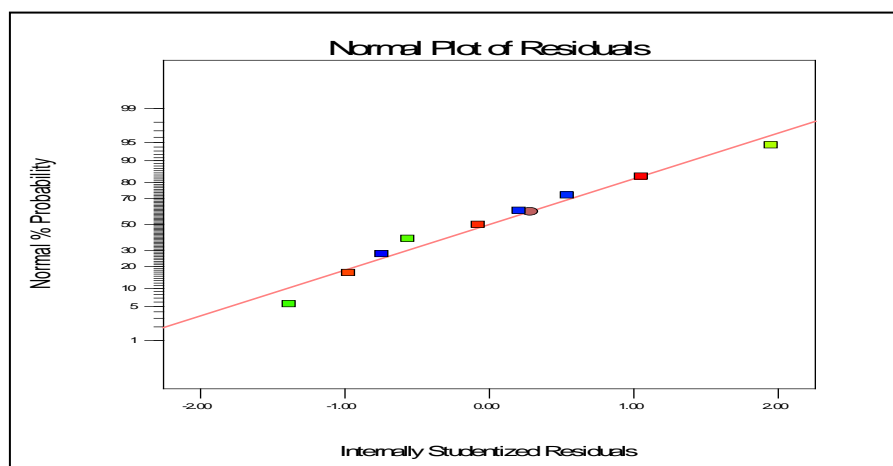

Figure 6: normal probability plot of residuals for H_2O_2 concentration

For both concentrations of hydrogen peroxide and sodium perborate, the consistency of data for weight loss was confirmed from normal probability plot of residuals, plotted by design expert software. As shown in figure 4&5, the points are fairly close to a straight line indicating the validity the experimental data. Residuals mean difference in the observed value (experimental value) and the predicted value or fitted value (by the software). In order to check that the residuals are normally disturbed, the mostly used technique is to plot normal probability plot of residuals. If the residuals fall approximately along a straight line, the residuals are considered

to be normally distributed i.e. the experiment is valid. In contrast, if the residuals do not fall fairly close to a straight line, the residuals are not normally distributed and hence the data do not come from a normal population i.e. the data is not valid.
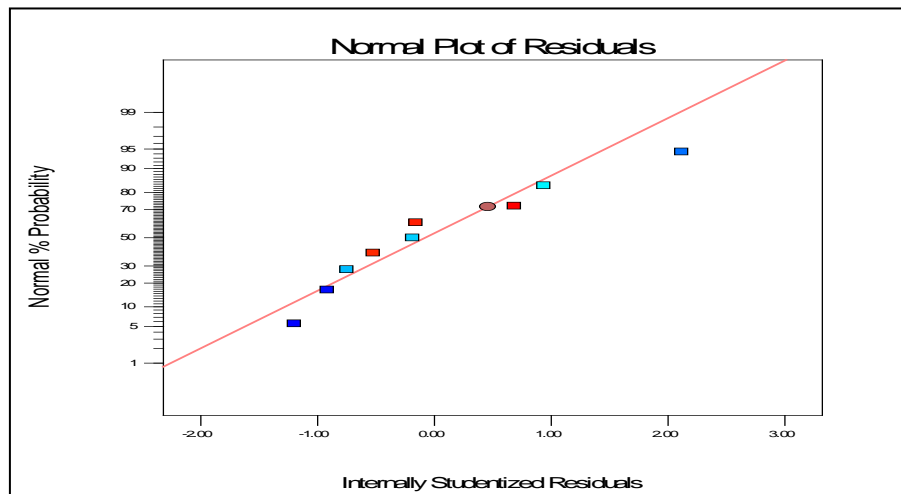

Figure 7: Normal probability plot of residuals for $NaBO_3$ concentration

3.2 Measurements of tensile strength

The weight loss due to alkaline hydrolysis of polyester is bound to result in strength loss.   Even though there is a debate among the researchers, the acceptable limit of tensile strength loss is from 5-10% [2].

Table 4: Effect of PET hydrolysis on tensile strength

Treatment	Strength loss (%) warp/weft	Extension loss (%) warp/weft
NaOH only	4.2/4.0	3.93/4.06
H_2O_2 and NaOH	5.2/4.9	4.82/4.98
$NaBO_3$ and NaOH	5.4/5.1	7.87/6.82

As shown in table 4, there is a decrease in breaking strength and extension at break. This could have been due to polyester hydrolysis and reduction of crystallinity. Due to weight loss   there is also a formation of pits on the surface which probably act as weak points when fabric is elongated under stress.

3.3 Fabric wettability

Fabric wettability was tested by measurement of water drop absorbency, sinking time and capillary rise methods. The results are shown in Table 5

Table 5: Effect of hydrolysis on absorbency, sinking time & capillary rise

Treatment	water absorbency	Sinking time	Capillary rise height/% incr
Untreated	5 sec.	4.5 sec	5cm/-
NaOH	Instantaneous	Instantaneous	7cm/40
H_2O_2 and NaOH	Instantaneous	instantaneous	9.5cm/90
$NaBO_3$ and NaOH	Instantaneous	Instantaneous	10/100

Concentrations of NaOH, H2O2, and NaBO3 were 1N, 5.6g/l, and 7.14 g/l respectively.

Results in table 5 showed that there is an increase in the water absorption capacity of the treated samples due to the formations of pits or voids or increase in porosity on the surface of the hydrolysed fabric that is created during hydrolysis. On the other hand, during this process the short chains of the fabric were removed by the attacking of hydroxyl groups.

The results also showed that alkali treatment led to a significant decrease in the time of water drop absorption, sinking time and an increase in the capillary height on the fabric surface.

The improvement of wettability may be attributed to the possibility of formation of hydrophilic groups like -OH and -COOH due to hydrolysis. In the case of capillary rise is higher when using oxidizing agents than NaOH only. This indicates that the presence of oxidizing agents has a significant effect in fabric wettability.

It can be seen that the wicking ability of the treated fabric increased with hydrolysis. This is ascribed to two reasons, firstly, the fabric hydrophilicity was improved after the treatment and thus the affinity of the fibre surface to water was improved.

Secondly, the fibre fineness was reduced and thus its porosity was improved, increasing the moisture uptake of the fabric.

3.4 Measurement of bending length and thickness

Bending length of the fabric gives an idea about the stiffness or fabric drapability. The measurement of bending length was carried out in both warp and weft directions. The results of average of 3 measurements are shown in table 6.

There is also a decrease in the bending length of the fabric due to weight reduction process. This happens due to the formation of pits or voids on the surface of the fabric. In addition, a decrease in bending length of treated fabric might be due to the reduced diameter of fibers and thickness of fabric.

This effect imparts the fabric a soft feel. The decreased bending length could be also a result of the reduced

diameter/thickness of fibers from the process of alkaline treatment.

Table 6: Effect of hydrolysis on bending length

Treatment	Warp		Weft	
	cm	%shift	cm	% shift
Untreated	2.6	--	2.5	--
NaOH	1.9	27	1.85	26
H_2O_2 and NaOH	1.5	42.31	1.45	42
$NaBO_3$ and NaOH	1.25	51.92	1.2	52

Table 7: Effect of PET hydrolysis on thickness of the fabric

Treatment	Thickness (mm)	%shift
NaOH only	0.44	4.3
H_2O_2 and NaOH	0.43	6.5
$NaBO_3$ and NaOH	0.43	6.5
Control	0.46	--

3.5 Dyeability

The PET fabric samples were dyed using basic dye Bezacryl blue GRL 300 and disperse dye Dianix AM-2G. The color strength is expressed in terms of K/S value. The results are shown in table 9 &10.

Dyeing with cationic dye

The K/S values were recorded at the wavelength of maximum value. The wavelengths of maximum K/S were 520 nm and 500 nm respectively for dyeing carried out under acid pH. The results are shown in Table 8.

Hydrolysed PET was subsequently dyed with cationic dyes. Cationic dyes develop a positive charge in the dye bath. Hydrolysis produces a significant amount of carboxylic groups on the fibre. The net negative charge on the fibre attracts the positively charged dye molecules, which get attached to the fibre with the help of ionic bonds.

The basic dye binds well with carboxylic group present in the polyester fabric. The K/S value can be taken as an indication of the amount of carboxylic groups present in the PET fabric. As result of the interaction of carboxylic functional group to the basic dye, the dye uptake is improved.

Table 8: Effect of PET hydrolysis on strength of cationic dye

Treatment	K/S value	Color intensity (%)
H_2O_2 and NaOH	8.49	132.04
$NaBO_3$ and NaOH	7.78	169.87

In general %colour intensity increase is more in acid pH compared to basic pH. The interpretation increased colour strength of cationic dye under alkaline pH would be different than for dyeing under acid pH. Under alkaline condition the positive charge on dye will diminish due to deprotonation resulting in no charge on dye molecule. Under such situation the cationic dye will behave like a disperse dye. The hydrolysed polyester will be more amorphous, this change in fibre structure will facilitate easy penetration of non-ionized dye under alkaline pH resulting in higher colour strength compared to untreated polyester.

The cationic dyes under acid pH form electrovalent bonds with the carboxyl groups of the fibre formed during hydrolysis and the amount of dye sorbed by the fibre is dependent on the number and accessibility of this groups.

Dyeing with disperse dye

The alkali treated PET samples adsorbed more dye and were dyed to deeper depths of shades and slightly different shades than was the untreated PET. It was noticed that when progressive amounts of the fibre surface were removed; the fibre interior became more dyeable than the fibre as a whole, suggesting that there are difference in morphology (crystallinity and amorphous) across the fibre cross-section.

Hydrolyzed polyester was dyed with disperse dye. The results of K/S and %increase in colour intensity are shown in Table 9. Maximum K/S was obtained at the wavelength of 620 nm.

Table 9: Effect of PET hydrolysis on strength of disperse dye

Treatment	K/S value	Color intensity (%)
H_2O_2 and NaOH	7.06	158.30
$NaBO_3$ and NaOH	7.78	174.44

Alkali hydrolysis occurs at the surface of the fabric and it creates pits or voids on the surface of the fabric.

Hence, dye uptake increased with alkali hydrolysis for PET fabrics. Additionally, alkaline hydrolysis decreases the crystallinity of the fiber hence increases the amorphous areas as a result diffusion of the dye to the fabric was increased. The K/s value of alkaline hydrolyzed sample and that of with carrier is almost the same value. Therefore, alkaline hydrolysis not only brings surface modification.

Modification of polyester by alkaline hydrolysis makes the fabric dyeing at or below 100 Oc even without the addition of carrier. The hydrolyzed polyester fabric showed low crystallinity and low glass transition temperature as indicated by DSC characterization. Due to their having low Tg the segmental motion of the polymer chains allows the dye to penetrated the fiber structure easily even at or below boiling.

The cationic and disperse dyed samples were subjected to wash fastness test. The results are shown in Table 10.

3.6 Wash fastness of dyed samples

In order to investigate the effect of hydrolysis, wash fastness test has been carried out. And the result is shown in table 10.

Table 10: wash fastness of dyed polyester

Treatment	Color change	Staining
Basic dye	4	5
Control	3/4	5
Disperse dye	4/5	5
control	4	5

It can be seen that both cationic and disperse dyes showed extremely good wash fastness both in terms of colour change and degree of staining.

3.6 Differential scanning calorimetry study

Thermo-physical properties of the PET fabric samples were studied by using differential scanning calorimeter. Thermal curves of untreated, NaOH treated, PVA+NaOH treated H2O2 + NaOH and NaBO3+NaOH are given in figure 4. The peak value indicates the melting temperature.

Differential Scanning Calorimetry (DSC) can measure crystallinity and molecular orientation within the fibers. This type of analysis is based on distinctly different values of the heats of fusion for crystalline and noncrystalline forms of the polymer.

Thermal analysis by DSC can give some insight into the structure and properties of the polymer by determination of the glass transition temperature (Tg), the melting temperature (Tm) and the degree of
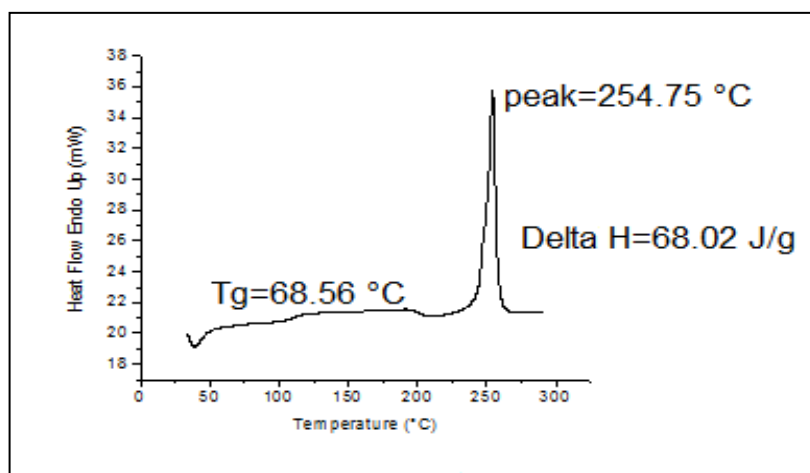
crystallinity (XDSC).The degree of crystallinity of polyester fibre is determined by integrating the peak area of a differential scanning calorimetry curve.
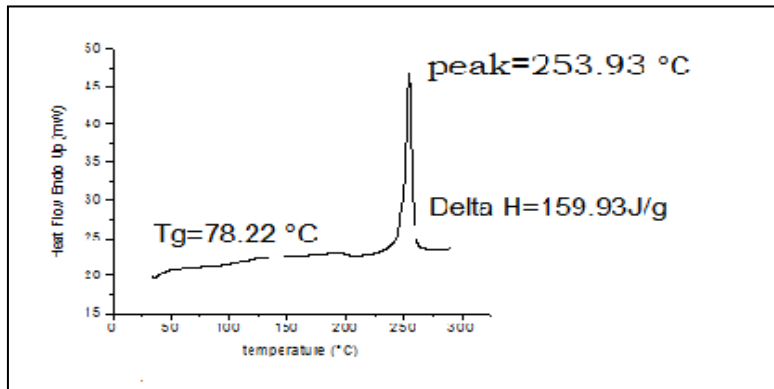
a) Untreated PET fabric
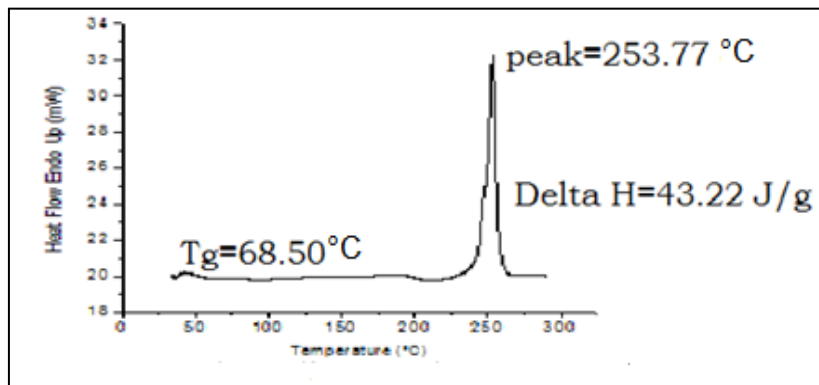
b) NaBO3 and NAOH treated PET fabric

c) H_2O_2 and NaOH treated fabric

Figure 8(a; b; c): Effect of hydrolysis on thermal property (DSC) of PET

Table 11: DSC results

Treatment	Tm(^{o}c)	Tg(^{o}c)	Δf(J/g)
Untreated	253.93	78.22	159.53
H$_2$O$_2$ + NaOH	254.75	68.56	68.02
NaBO$_3$ + NaOH	253.77	68.50	43.22

As shown in table 11, the heat of fusion and glass transition temperature is decreased due to treatment. Heat of fusion is the energy involved in the formation and melting of crystalline regions.

Heat of fusion and Tg are proportional to % crystallinity of PET. The heat of fusion is decreasing after treatment of fabric with alkali. The loss in Tg and heat of fusion indicates that a loss in the degree of crystallinity of the fabric and losing of compact structure of PET.

3.7 Fourier transform infrared study

The FTIR spectra of untreated, H2O2+NaOH treated and NaBO3+NaOH treated fabrics are shown in the table 15. The high peaks from around 1700cm-1 indicate the original signals, such as characteristics spectra of stretching vibration band of C=O at around 1730 cm-1 and C-O-C stretching vibration band at around 1097 to 1300 cm-1. All these peaks confirm the existence of ester linkages [13].

Table 12: FTIR results

Treatment	basic functional group	Band (cm-[1])
Untreated	C-O-C;C-O and benzene	1097-1300; 700-900
H$_2$O$_2$ + NaOH	benzene;COOH	700-900;2359
NaBO$_3$ + NaOH	benzene;COOH	700-900;2359

Infrared spectroscopy can be used to identify functional groups present in polymer layers. By using FTIR 460, it was possible to determine or characterize functional groups in modified polyester fabric.

The FTIR spectra of untreated, H2O2+NaOH treated and NaBO3+NaOH treated fabrics are shown in the table 15. Sodium hydroxide treated fabric showed reduction of strong peak to weak peak peaks at around 1097-1700 cm-1 which shows the elimination of short chains in the ester linkage and also shows an additional peak at around 2359 cm-1.

This additional peak attributed to the formation of carboxylic groups (-COOH), introduced on the surface due

to hydrolysis of the ester linkage.

4. Conclusions

- The results of surface modification of polyester fabric can be summarized as follows:
- Surface modification with sodium hydroxide brought a weight loss of polyester fabric and it doesn't affect the strength above the optimum value.
- The optimum concentration of NaOH is 1N.
- As concentration of NaOH increases, the weight loss also increases almost linearly.
- Surface modification in the presence of polyvinyl alcohol, hydrogen per oxide and sodium perborate was high as compared to that of NaOH only. This could be concluded that the presence of these chemicals facilitates the deterioration of ester linkage in polyester chain.
- Tensile strength decreased by an average of 5.2% in the warp direction and 5 % in the weft direction from the untreated fabric.
- Water absorbency test, sinking time test and capillary rise measurement all these indicates there was an increase in wettability/absorbency of hydrolyzed PET.
- Bending length of pre-treated fabrics samples has registered decreasing trend with increasing in concentration of NaOH leading to a better drape and handle (softness and feel). The hydrolyzed polyester samples showed considerable increase in color strength when dyed with selected cationic (acid and basic pH) and disperse dyes.
- DSC results shows that the fabric exhibits a decrease of glass transition by 10oc and lower value of heat of fusion compared to the untreated one, leading to higher segmental mobility and decreased in crystallinity of PET.
- The presence of hydroxyl and carboxyl group was confirmed by FTIR studies.

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