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Surface Hydrophilization of Polyester

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SUMMARY OF THE THESIS

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Abstract

Polyester is the most widely used material for both textile and non-fibrous applications. The major potential applications are high mechanical strength, good stretchability, heat stability, rapid drying, wrinkle resistance and resistance to usual organic solvents. The inherent hydrophobic nature of the polyester products are lacking water and moisture wicking, poor adhesion properties and ability to develop static charge. The modification of surface of the polyester by low concentration alkaline hydrolysis with NaOH in aqueous finishing bath under hot drying conditions is explored in this study. Moreover the surface of polyester film is modified by synergistic effect of sulphuric acid and sodium hydroxide in order to achieve hydrophilic surface with improved adhesion. The use of chemicals allows the surface hydrophilization of polyester at conventional pad-dry stenters without use of any sophisticated equipment that is required by most of the physical modifications (like plasma, corona, ozone etc).

The surface hydrophilization of polyester fabric is done by low concentration of sodium hydroxide. The time of treatment, curing temperature and concentration of sodium hydroxide played very important role in getting better wicking rate and stability of the treatment. The weight loss of the fabric is minimized through the low liquor ratio pad-dry method of application. The use of hygroscopic agents like glycerin and urea at elevated temperatures has contributed to retain humidity during hot dry reaction conditions. The weight loss is far less than the high liquor ratio alkali treatment of polyester fabric. In this work optimization of parameters for getting higher vertical wicking rate and less surface scission through weight loss has been achieved by varying concentration of sodium hydroxide (20, 35 and 50 g/l), time of treatment (2,4, and 6 minutes) and drying temperature (130, 150 and 170 ˚C). Later the stability of the surface hydrophilization is evaluated at different temperatures by placing for longer times. The hydrophilized polyester fabric surface shows good stability at different temperatures and in comparison with plasma and ozone surface hydrophilic treatment. The activated polyester fabric shows good fastness against number of washing cycles. The surface morphology and chemical characterization of the hydrophilized polyester fabric is measured by Scanning Electron Microscope (SEM), X-ray Photoelectron spectroscopy (XPS) and Brunauer Emmett Teller (BET).

The polyester film is hydrophilized with strong sulphuric acid solution and followed by low concentration alkali solution to evaluate the surface wettability and adhesion properties. The super hydrophilic surface is obtained at 80 % sulphuric acid and 50 g/l sodium hydroxide aqueous solution treatment. These treatment conditions give the polyester film surface with lowest water contact angle and high SFE values with good adhesion properties. The presence of hydroxyl groups on the surface with significant decrease in the surface energy has been confirmed through contact angle measurements. The SEM, BET analysis and T-peel data obtained by the polyurethane resin has indicated the increase in adhesion strength after chemical treatment and improvement of adhesion by thermoset resin can be attributed to the increase in surface wettability and roughness due to the surface modification.

Key words: Polyester, hydrophilized surface, optimization, stability, vertical wicking, wettability, roughness

Anotace

Polyester je nejrozšířenějším materiálem jak pro textilní, tak pro nevlákenné aplikace. Hlavní potenciální aplikace předurčuje vysoká mechanická pevnost, dobrá tažnost, tepelná stabilita, rychlé sušení, nemačkavost a odolnost vůči obvyklým organickým rozpouštědlům. Vlastní hydrofobní povaha polyesterových výrobků bez přítomnosti vody a vlhkosti zapříčiňuje špatné adhezní vlastnosti a schopnost vytvářet statický náboj. Modifikace povrchu polyesteru alkalickou hydrolýzou s nízkou koncentrací NaOH ve vodné dokončovací lázni za podmínek sušení za tepla se zkoumá v této studii. Navíc je povrch polyesterové fólie modifikován synergickým účinkem kyseliny sírové a hydroxidu sodného, aby se dosáhlo hydrofilního povrchu se zlepšenou přilnavostí. Použití chemikálií umožňuje povrchovou hydrofilizaci polyesteru na konvenčních zařízeních bez použití sofistikovaného vybavení, které vyžaduje většina fyzikálních modifikací (jako je např. plazma, korona, ozón apod.)

Povrchová hydrofilizace polyesterové tkaniny se provádí nízkou koncentrací hydroxidu sodného. Doba úpravy, teplota sušení a koncentrace hydroxidu sodného hrály velmi důležitou roli při získávání vyšší vzlínací rychlosti a stability úpravy. Úbytek hmotnosti tkaniny je minimalizován aplikací suchého způsobu nanášení na suchý podklad. Použití hygroskopických činidel, jako je glycerin a močovina, při zvýšených teplotách přispělo k udržení vlhkosti při reakčních podmínkách sušení za zvýšených teplot. Ztráta hmotnosti je mnohem nižší, než je poměr vysokého obsahu alkoholu při alkalickém zpracování polyesterové tkaniny. V této práci byly optimalizovány procesní parametry pro dosažení vyšší vertikální rychlosti nasákavosti a nižšího narušení povrchu sledovaného prostřednictvím úbytku hmotnosti, a to pomocí změny koncentrace hydroxidu sodného (20, 35 a 50 g/l), doby zpracování (2, 4 a 6 minut) a teploty sušení (130, 150 a 170 °C). Stabilita povrchové hydrofilizace se sleduje po delší dobu, při různých teplotách. Hydrofilizovaný povrch polyesterové tkaniny vykazuje dobrou stabilitu při různých teplotách a ve srovnání s hydrofilním zpracováním povrchu plazmy a ozonu. Aktivovaná polyesterová tkanina vykazuje dobrou stálost vůči počtu pracích cyklů. Morfologie povrchu a chemická charakterizace hydrofilizované polyesterové tkaniny se měří pomocí skenovacího elektronového mikroskopu (SEM), rentgenové fotoelektronové spektroskopie (XPS) a Brunauer Emmett Teller (BET).

Polyesterová fólie se hydrofilizuje silným roztokem kyseliny sírové a následně působením alkalického roztoku o nízké koncentraci za účelem průzkumu povrchové smáčivosti a adhezních vlastností. Superhydrofilní povrch se získá při použití 80% roztoku kyseliny sírové a 50 g/l vodného roztoku hydroxidu sodného. Tyto podmínky zpracování poskytují polyesterovému povrchu fólie nejnižší kontaktní úhel smáčení vodou a vysoké hodnoty SFE s dobrými adhezními vlastnostmi. Přítomnost hydroxylových skupin na povrchu s výrazným poklesem povrchové energie byla potvrzena měřením kontaktního úhlu. SEM, BET analýza a T-Peel data získaná s využitím polyuretanové pryskyřice naznačila zvýšení adhezní síly po chemickém zpracování a zlepšení adheze termosetovou pryskyřicí lze přičítat nárůstu smáčivosti povrchu a zvýšení drsnosti díky povrchové modifikaci.

Klíčová slova: polyester, hydrofilizovaný povrch, optimalizace, stabilita, vertikální vznícení, smáčivost, drsnost

Table of Contents

1 Introduction

Polyethylene terephthalate (PET) is one of the most important and widely used material in both textile industry for its apparel applications and in nonfibrous applications. They have properties like easy care, high strength, suitability for blending with other hydrophilic fibers, dimensional stability, thermal and chemical resistance, these properties make polyester fibers useful for versatile applications in the textile industry. Polyester fibers have taken the major position in textiles all over the world but they have some drawbacks like low moisture regain, static electricity accumulation, poor soil release properties, formation of pills on the garment. Research work is done in order to minimize the abovementioned deficiencies in the polyester by the controlled alkali treatment of the polyester fibers and fabrics through exhaust method [1-3] and hydrolysis of PET by strong acid or alkali [4], amine treatment [5], alcholysis [6] and treatment by various radiations including plasma [7, 8].

The modification of polyester surface is field to achieve hydrophilicity and surface that has specific characteristics to be used to provide better suitability for the use of adhesives [9], biomaterials [10] and protective coatings [11]. The strong acid causes micro scale roughness on the surface of PET that can then be used for further treatment of the polyester. In this study the acid treatment of polyester is done and then followed by alkaline hydrolysis and its effect on contact angle and surface energy is studied.

Polyester is hydrolyzed by aqueous sodium hydroxide and undergoes nucleophilic substitution reaction as hydroxyl ion attacks carboxyl carbon of polyester following the chain scission results in production of hydroxyl and carboxylate end groups. This attack occurs at surface of fiber and loss in weight of fiber occurs [12]. The weight reduction of polyester fabric is usually done by the exhaust method under high liquor ratio [13, 14]. This leads to the longer cycle time and more weight loss of the polyester fabric. The padding technology is a well-known process in the field of polyester and cotton fabric processing. The padding and drying technology involve the use of less liquor and higher production rate at high temperature. The padding technology in dyeing and finishing of polyester is widely used in order to save the liquor and achieving more smooth fabric properties with high reproducibility [15]. The alkaline treatment of polyester fabric is carried out by padding method with the objective to study the effect of different treatment conditions on the wetting and physical characteristics of polyester fabric.

2 Purpose and aim of the thesis

The non-availability of surface polar groups in polyester leads to the high hydrophobicity, low moisture regain, static charge accumulation, low wettability and poor adhesion properties. The alkaline hydrolysis of polyester by sodium hydroxide is a well-known method in order to create some polar groups on the surface of polyester that leads to the improvement in the wettability of polyester fabric. This alkali treatment is usually done by exhaust method that leads to the longer time of treatment, high liquor ratio, more weight loss and low reproducibility. The control of conditions such as time, temperature and concentration of alkali is necessary for non-destructive modification of polyester. Padding and drying technology is used to for fabric alkaline hydrolysis and its effect on wetting properties is studied. The combined effect on wetting properties by strong acid followed by alkali treatment on polyester film is also studied. The main aims of the study are as follows:

- To study the effect of different hygroscopic agents on alkali treatment of polyester fabric by Pad-dry method
- To optimize parameters for surface hydrophilization of polyester fabric by dry heat fixation method
- Performance and durability of optimized pad-dry heat sodium hydroxide treated polyester fabric at different temperature conditions
- Development of super hydrophilic surface of polyester film by combined acid and alkali treatment

3 Overview of the current state of problem

The alkali treatment of the polyester fibers and fabrics by the use of caustic soda imparts hydrophilicity to the treated substrate but in the process the polyester losses weight due to the hydrolysis by caustic soda [16]. The caustic soda treatment of polyester fibers and yarns is usually done by exhaust method that involves treatment of polyester at boil and longer time of treatment. The hydrophilic properties are achieved by the controlling the conditions of treatment and concentration of the caustic soda. This treatment method contributes to the loss in weight and strength of the treated polyester substrates [17, 18]. The caustic treatment also contributes to the functionalization of the polyester fabric for in cooperation of the particles for improving properties like UV blocking etc [14]. H. Tavanai has thoroughly investigated the weight reduction phenomena of polyester fabric and its effects on the fabric handle properties [16].

Structural modification of polyester fiber can influence the hydrophilic properties due to efficient moisture transport and release mechanism. Moisture can remain in the cross-section of the fiber, in the void space within a yarn, and void space created by the yarn crossover in the woven and knitted fabrics. Moisture regain of fabric depends on the air permeability, independent of fiber type. However, capillary wicking of water largely depend on the degree of hydrophilicity of individual polyester fiber [19-21]. When the liquid wets the fibres, it reaches the spaces between the fibres and produces a capillary pressure. The liquid is forced by this pressure and is dragged along the capillary due to the curvature of the meniscus in the narrow confines of the pores [22]. The kinetics of wicking and liquid diffusivity in the porous textiles is determined by different models [23-27].

In addition to the chemical processing route, the hydrophilicity of polyester can also be increased by improved fiber or yarn design. Use of microfibers instead of regular fibers can significantly improve the moisture management of polyester. The improved design of polyester filament with a hollow structure, which significantly improved the breathability, water absorption, and release rate [28, 29].

The adhesive bonding of solids has been associated with their surface energies and an improvement of adhesion usually involves ways to increase surface energy, one of the most effective ways being to chemically change the functional groups at the polymer surface. The most common are surface grafting [30], UV irradiation [31] and wet chemical reaction.

Alkaline hydrolysis is one of the most rapid methods to modify the chemical and physical characteristics of a polyester.

4 Used Methods, study materials

The fabric used in this study was lab grade 100 % polyester with GSM 165 with equal warp and weft density of 20 threads per cm. The fabric was treated with hot water in order to remove any wax and dirt. Laboratory grade caustic soda flakes were used for caustic treatment of the samples and laboratory grade acetic acid was used to neutralize the fabric after the caustic treatment. Lab grade Glycerin and urea is obtained from Sigma Aldrich.

Commercial polyester film of 30 µm in thickness is selected. The film is Mylar™, supplied by DUPONT. The selected material has good properties high melting temperature (> 250 ˚C), good mechanical strength, plasticity and intrinsic low surface energy makes it a potential material for chemical surface modification. Caustic soda flakes, ethyl alcohol, acetic acid and sulphuric acid of highest purity are obtained from Sigma Aldrich and used as received.

4.1 Alkali surface hydrophilization of polyester fabric

Polyester samples were impregnated in caustic soda solution at concentrations (20 g/l and 50 g/l) and then padded at the pickup of 80%. The experiments are conducted, one to see the effect of concentration, time and temperature of treatment. The schematic diagram of the method for conduction of experiments is shown in figure 1. Second set of experiments are conducted with the addition of 50 g/l urea with 50 g/l NaOH at 150 °C for different times. Standard treatment (NaOH 50 g/l, time 30 minutes and temperature at 90 °C) is also done for comparison. The glycerin treatment is also carried out by pad dry method in the similar way as the sodium hydroxide treatment is done. The technique used for alkali treatment is the impregnation of polyester fabric in padding bath and then drying under tension state at fixed width. The purpose of fixing the width of fabric is to minimize the effect of shrinkage that can occur during high temperature hot drying. After padding and drying the fabric samples were rinsed and neutralized with acetic acid until all the caustic soda is removed from the samples. All the treated samples were dried in ambient air followed by conditioning and testing.

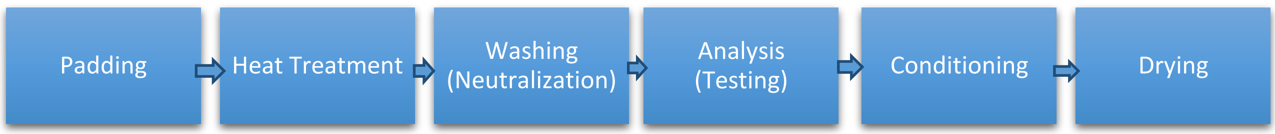


Figure 1. Scheme of treatment for polyester fabric

4.2 Optimization of treatment parameters for alkali Hydrophilized polyester

The polyester fabric is first treated with non-ionic detergent followed by hot water in order to remove any dirt, dust and wax. The fabric was then dried, stabilized and conditioned. The sodium hydroxide treatment effect is studied under three variables.

- Sodium Hydroxide Concentration (SHC)
- Time of Treatment (TIME)
- Temperature for treatment (TEMP)

Three levels of sodium hydroxide concentration are selected that are 20 g/l, 35 g/l and 50 g/l. Three different levels of treatment time (2, 4 and 6 minutes) and three different levels of treatment temperature (130 ˚C, 150 ˚C and 170 ˚C). The optimization was performed using Box-Behnken design and response surface modeling under three levels and three factors as mentioned in table 1. The mathematical relationship between the three independent variables and the response is approximated by the second order polynomial as given in equation (1) and equation (2).

Table 1. Selected factors and levels for sodium hydroxide treatment of polyester fabric

Number of Factors	Levels		
	[-]	[0]	[+]
SHC (g/l)	20	35	50
TIME (min)	2	4	6
TEMP (˚C)	130	150	170

$$\boldsymbol{Percentage\ weight\ loss} = X_0 - X_1.SHC - X_2.TIME + X_3.TEMP + X_{11}.SHC^2 - X_{22}.TIME^2 - X_{33}.\ TEMP^2 + X_{12}.SHC.TIME + X_{13}.SHC.TEMP + X_{23}.TIME.TEMP \quad (1)$$

$$\boldsymbol{Vertical\ Wicking} = -Y_0 + Y_1.SHC + Y_2.TIME + Y_3.TEMP - Y_{11}.SHC^2 + Y_{22}.TIME^2 - Y_{33}.\ TEMP^2 + Y_{12}.SHC.TIME + Y_{13}.SHC.TEMP - Y_{23}.TIME.TEMP \quad (2)$$

Where X_0 and Y_0 are model constant; X_1, X_2, X_3 and Y_1, Y_2, Y_3 are linear coefficients; X_{12}, X_{13}, $X_{23}$and Y_{12}, Y_{13}, Y_{23} are cross product coefficients and X_{11}, X_{22} , X_{33} and Y_{11}, Y_{22}, Y_{33} are the quadratic coefficients. The coefficients of main effect and two factor interaction effect are estimated from the experimental results using the mathematical software package MINITAB.

4.3 Characterization of hydrophilized polyester

Capillary rise measurements (Wicking)

The rise of liquid in the fabric is measured according to the AATCC 197 method. The samples were placed vertically with the lower end dipped in a thin layer of a 1 % solution of methylene blue dye that has no affinity towards synthetic fibers as shown in Figure 10. The apparatus was set in a closed chamber in order to keep a saturated vapor atmosphere. The blue coloration of dye solution on white fabric clearly indicated the height of capillary rise, and a ruler marked off in millimeters assembled along the fabric can make the height measurement easier. Height readings were recorded 20 minutes after the fabric was dipped in the liquid. Each measurement was carried out 5 times and the average height values were regarded as the final results.

Percentage weight loss

The weight of the fabric samples that were treated with the alkali were measured before and after the treatments using an electronic balance with an accuracy level of ± 0.001 g and the percentage weight loss was calculated using the following formula:

$$Percentage\ weight\ loss = \frac{W1-W2}{W1}\ 100 \qquad (3)$$

Where W_1 and W_2 are weights of the fabric samples before and after the alkali treatment respectively.

X-Ray photoelectron spectroscopy (XPS) analysis

XPS measurement is performed on machine by Omicron Technology. Monochromatic primary radiation is used. The measurement is done in CAE mode with constant pass energy for surveillance of 50 [eV] and 20 [eV] spectrum. It is done for detail measurement of individual line spectra.

4.4 Surface treatment of polyester film

The polyester film is immersed in alcohol water solution (1/1, v/v) for 2 hours in order to remove any dirt or oil for clean surface, rinsed with distilled water and then dried at room temperature for 24 hours. For hydrolysis reaction by acid the film is immersed in solution of sulphuric acid for specific time of treatment at room temperature. Two concentrations of sulphuric acid, 75 % and 80 %, are used for the treatment of film. The time of treatment for 80 % concentration of sulphuric acid is 3 sec and for 75 % concentration of sulphuric acid is 2 min. After this treatment the samples are rinsed and dried at room temperature for 12 hours. The acid treatment is followed by alkali treatment of samples for time of treatment (30 sec, 1, 2, 4, 6… 16min) at temperature of 90 ˚C. Alkali treatment is followed by neutralization of samples by 5 % solution of acetic acid followed by rinsing and drying at room temperature overnight. All the samples are conditioned and then measurements are carried out. The schematic diagram of treatment of samples is shown in figure 2.

4.5 Characterization of polyester film

Contact angle measurements

The surface wettability is evaluated using the sessile drop method and measurements are carried out on Advex instrument (figure 3) using 5 µl for liquid drop contact angle measurements. This measurement is used both to assess the wettability of the polymer film and critical surface energy measurements. Each sample is measured 10 times for liquid at room temperature and the contact angle (CA) values are averaged.

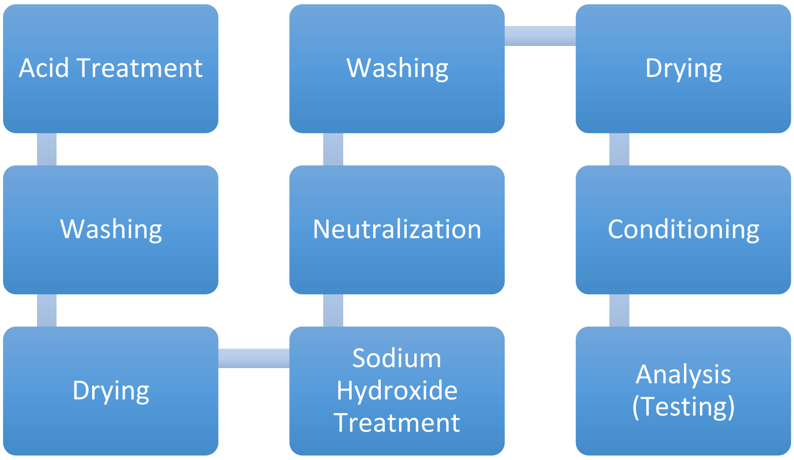


Figure 2. Scheme of treatment for polyester film

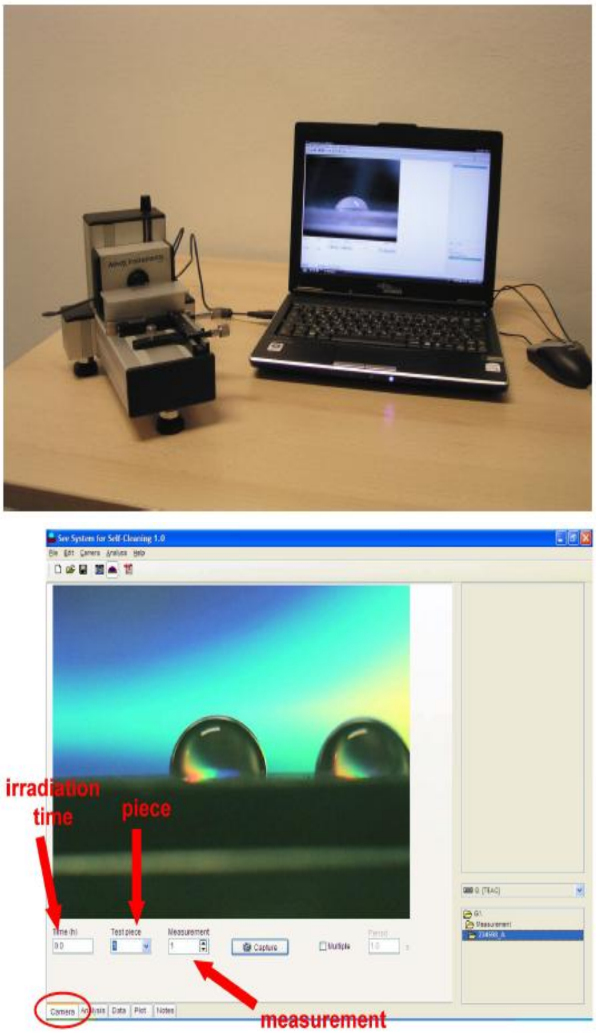


Figure 3. Advex instrument setup for contact angle measurement

Evaluation of surface free energy

The surface free energy of the modified polyester film is evaluated by using three liquids (distilled water, ethylene glycol, and diiodomethane) of known surface tension. The liquids are supplied by Aldrich and are used without further purification. Surface tension components of liquids are reported in Table 2. Surface free energy (SFE) and critical surface tension is calculated by using the models proposed by Owens-Wendt, Li-Neumann and Zisman. These methods allow to calculate the surface free energy using at least two liquids. The results obtained by one, two and three methods are combined according to the requirement of each method.

Table 2. Solvent surface tension components at 20 ˚C (mJ m^{-2})

Liquid	γ_d	γ_p	γ_t
Water	22.1	50.7	72.8
Ethylene Glycol	30.1	17.6	47.7
Diiodomethane	44.1	6.7	60.8

Evaluation of surface (Scanning Electron Microscope)

The surface changes after the treatment of acid and sodium hydroxide are observed by Scanning Electron Microscope (SEM) at high resolution. SEM is less surface sensitive as compared to other techniques and it is a well-established tool to observe the surface topography of the treated samples.

T-Peel test of adhesion

T-peel tests of adhesion are carried out on both untreated and treated samples on SANS universal testing machine with load cell of 30 kN and peel speed of 10 mm/min according to ASTM D 1876-01 on rectangular specimens. Polyurethane resin is applied in order to join the treated substrates. Polyurethane resin is selected in order to test the change in surface free energy of the polyester substrate. The isocyanate present in the resin can react with the carboxylate ions generated after the sodium hydroxide treatment on the polyester film surface. A static load is applied on the ends of the resin bonded substrates for a week at room temperature. The T-peel strength is determined on average of three samples.

Determination of specific surface area

The surface area is quantified by using the method developed by Brunauer, Emmett and Teller (BET method) which is an extension of Langmuir theory of monolayer adsorption to multilayer adsorption. The BET analysis is performed on Autosorb IQ, Quantachrome instrument, USA. The specific surface area is determined by N_2 absorption desorption isotherm at 77.35 K with relative pressure range P/P_o from 0.02 to 1, where P_o is the saturated pressure of nitrogen gas at 77.35 K (1 Atm). The samples are pre-treated in an oven at 45 ˚C for at least 5 hours and outgassed overnight at 150 ˚C.

Thermal properties

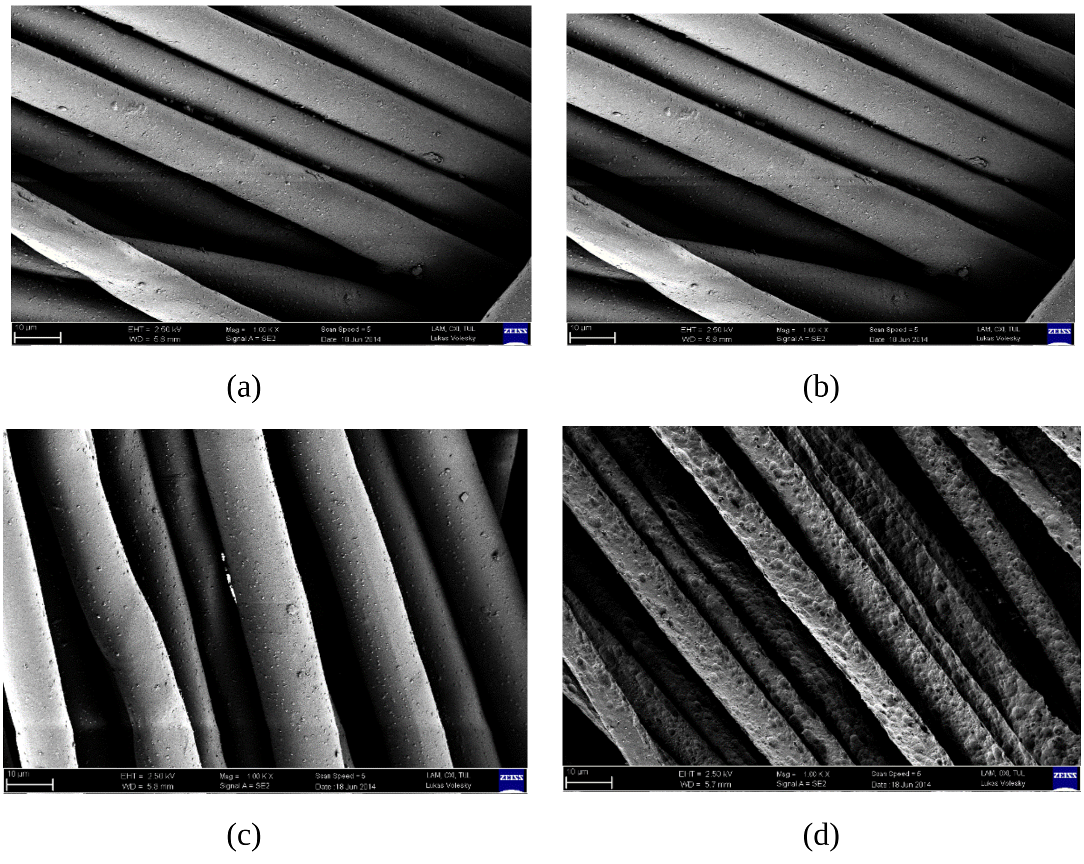
Thermal properties of the polyester film samples under investigation are evaluated in order to determine the thermal changes in the treated samples with heat flow. For the measurements a

DSC 220 high sensitivity Differential Scanning Calorimeter is used with temperature rise of 10 ˚C/min under nitrogen flow and temperature is raised from room temperature to 400 ˚C.

5 Summary of the results achieved

5.1 Alkaline hydrolysis (Polyester fabric sodium hydroxide and urea Treatment)

The figure 4 illustrates the surface morphology of the untreated and alkali treated polyester fabric samples. The SEM micrograph of untreated polyester fabric has almost the smooth surface. In the figure 4 (b) there is small pitting on the surface of the polyester fabric after the treatment with 20 g/l NaOH. In figure 4 (c) the pitting is more evident when saponification of polyester fabric is done with NaOH (50 g/l). The figure 4 (d) is the clear evidence of the alkaline hydrolysis of the polyester fabric after standard treatment for 30 min with caustic soda. The polyester fabric losses more weight as the yarns are thinned when treated at 90 °C with caustic soda as compared to the only small surface pitting when treated with caustic soda by padding method.



(a) (b) (c) (d)

Figure 4. (a) Untreated Polyester fabric, (b) Polyester fabric Pad-dry with NaOH (20 g/l) at 150 °C, (c) Polyester fabric Pad-dry with NaOH (50 g/l) at 150 °C, (d) Polyester fabric treated with NaOH (50 g/l) at 90 °C for 30 min

XPS is an extremely surface sensitive method allowing us to identify and quantify the chemical elements in the surface region of a solid and give information on the binding states of these elements, their oxidation numbers or functionalities. The spectra obtained by XPS measurement is the result of number of photoelectron incident on the specimen surface that are recorded as the function of binding energy with the groups present on the surface. There is change in the surface functionality and surface groups when polyester fabric is alkali treated. Figure 5 illustrates that the percentage of C-O groups in the surface are 40 % in the alkali treated polyester, which is the clear evidence of the surface hydrolysis of polyester fabric after alkali treatment.

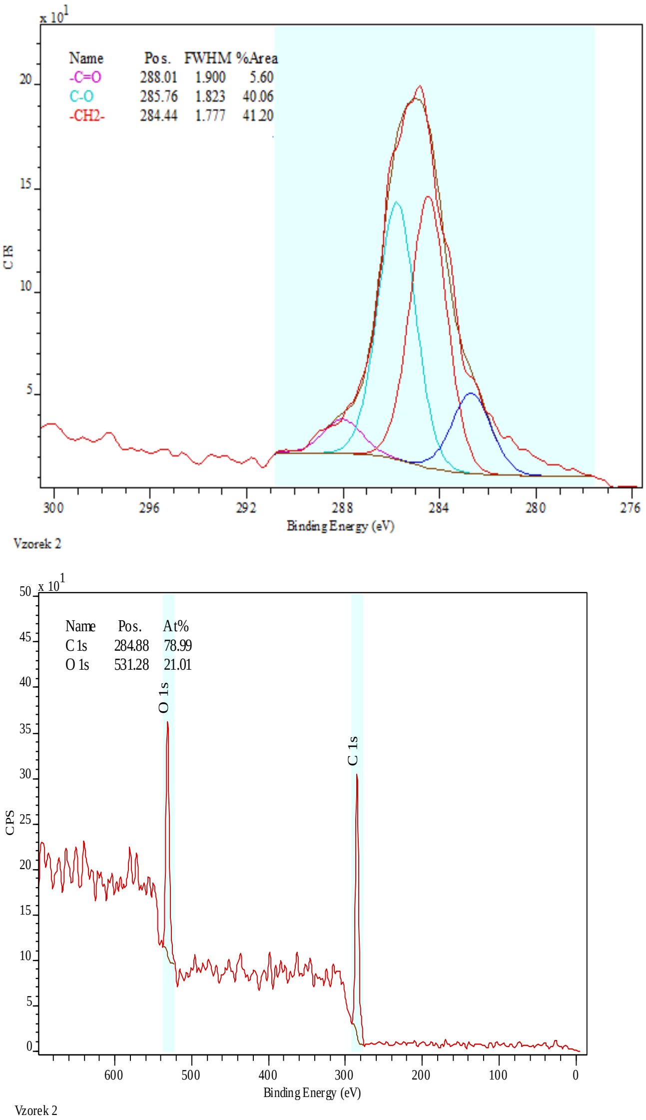


Figure 5. XPS micrograph of polyester fabric treated with 50 g/l NaOH at 150 °C for 4 min

Loss in weight

The results percentage weight loss *(%WL)* of 100 % polyester fabric treated with NaOH (50 g/l) are shown in figure 6. The results of the study show that the weight loss has registered an increasing trend as the treatment time and temperature increases. When the fabric is treated without the addition of urea the weight loss is slightly more as it is reached to 6.78 % at the treatment time of 8 min. The weight loss is higher when polyester fabric is treated with standard caustic treatment at boil with increase in time of treatment. The Pad-dry samples show very little weight loss when compared with the standard technique of polyester treatment with sodium hydroxide. The fabric weight loss also increases with the concentration of caustic soda increases from 20 g/l to 50 g/l.

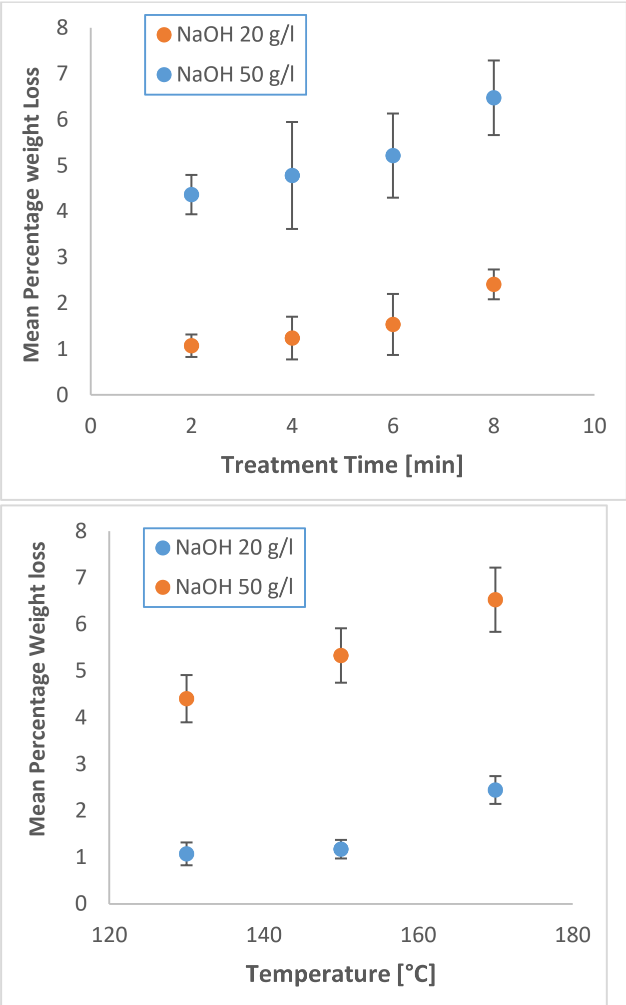


Figure 6. Effect of treatment time and temperature on Percentage Weight loss after NaOH treatment

Wicking

The wicking behaviour of polyester fabric treated with caustic soda is shown in figure 7. The wicking of untreated sample is only 15 mm. In figure 7 the wicking is related with the time of treatment of the fabric. It is quiet noticeable that the wicking height shows increasing trend as the wicking height shows increasing trend when concentration of sodium hydroxide is increased from 20 g/l to 50 g/l with the increasing treatment time. The maximum wicking height for both the samples whether caustic treated with padding method and by standard treatment is 90 mm and 95 mm respectively. The alkali treatment of the polyester fabric in both conditions causes partial hydrolysis of the polyester yarns which causes the capillary formation with in the bundle of fibers that may be the reason of better wickability than the untreated polyester fabric.

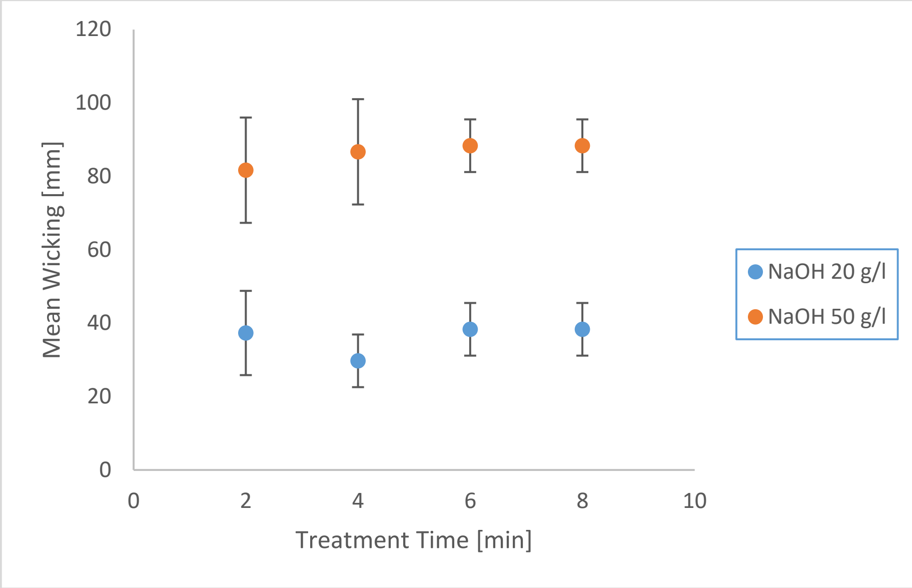


Figure 7. Effect of treatment time on wicking height of polyester fabric

5.2 Optimization of Alkali treatment parameters

The alkali treatment parameters are estimated by using the Box–Behnken experimental design, thirty runs with appropriate combinations of NaOH concentration, Time and temperature of treatment were conducted. The results for percentage weight loss and vertical wicking are given in table 3. The alkali like sodium hydroxide causes the surface hydrophilization of polyester fabric leading to the potential hydrophilic groups on the surface of the polyester. The low concentration alkali treatment by padding under controlled conditions causes the increase in the wicking and weight loss of the fabric. The weight loss by this padding method is far less than the general standard method at longer cycles of the alkali treatment. The experimental results in the table were fitted to a full quadratic second order model by applying multiple regression analysis using MINITAB software. The one repetition of the selected experiments is also include in the design in order to minimize the experimental errors that occurs during the performance of the experiment runs. The model equations representing percentage weight loss and wicking are expressed in terms of SHC, TIME and TEMP for actual values of variables as given in equation 4 and 5.

$$\boldsymbol{Percentage\ weight\ loss} = 1.35 - 0.0224.SHC - 0.706.TIME + 0.002.TEMP + 0.001.SHC^2 - 0.038.TIME^2 - 0.001.TEMP^2 + 0.003.SHC.TIME + 0.001.SHC.TEMP + 0.006.TIME.TEMP \quad (4)$$

$$\boldsymbol{Vertical\ Wicking} = -690 + 0.86.SHC + 26.21.TIME + 8.47.TEMP - 0.069.SHC^2 - 0.028.\ TEMP^2 + 0.034.SHC.TEMP - 0.172.TIME.TEMP \quad (5)$$

Table 3. Box-Behnken design showing obtained properties of hydrophilized polyeser fabric

Run	Sodium hydroxide concentration [g/l]	Time [min.]	Temperature [˚C]	Percentage weight loss	Vertical Wicking [mm]
1	20	6	150	1.25	40
2	20	4	130	1.09	35
3	35	2	130	2.16	45
4	35	6	170	3.43	75
5	20	2	150	1.18	40
6	50	6	150	4.92	90
7	35	2	170	2.24	75
8	35	2	170	2.3	75
9	20	6	150	1.25	40
10	20	4	170	1.48	40
11	35	4	150	2.76	80
12	35	2	130	2.52	45
13	50	4	170	5.38	90
14	20	4	130	1.1	35
15	50	6	150	5.06	90
16	35	6	130	2.67	75
17	50	4	130	4.45	43
18	35	4	150	2.94	80
19	20	2	150	1.14	40
20	35	4	150	3.02	80
21	35	6	170	3.38	80
22	50	2	150	4.52	85
23	35	4	150	2.97	80
24	50	2	150	4.47	85
25	35	4	150	3.04	80
26	35	4	150	2.9	75
27	35	6	130	2.36	75
28	20	4	170	1.45	40
29	50	4	170	5.32	90
30	50	4	130	4.4	45

For the estimation of significance of the model, the analysis of variance and the F-test were carried out. The corresponding variables would be more significant when the absolute F-value becomes greater and the p-value (significance probability value) becomes smaller. Using 95 % confidence level, a model is considered highly significant if the p-value is less than 0.05. From the p-value presented in table 4 and 5, it can be concluded that the linear, quadratic and interaction contributions for both percentage weight loss and vertical wicking are highly significant. The coefficient of determination is found to be 96.82 % for percentage weight loss model and 87.19 % for vertical wicking model, that means that the model could explain 96.82 % and 87.19 % of the total variations in the system.

Table 4. Estimation of significance of model for percentage weight loss

Source	Degree of Freedom [DF]	Sum of Squares [SS]	Mean Square [MS]	F-value	p-value
Regression	9	53.87	5.98	170.7	0.001
Linear	3	53.06	17.69	942.67	0.003
Quadratic	3	0.485	0.162	4.62	0.013
Interaction	3	0.787	0.26	7.49	0.002
Residual error	20	0.701	0.035		
Lack of fit	3	0.105	0.04	1.00	0.418
Pure error	17	0.59	0.035		
Total error	29	54.57			

Table 5. Estimation of significance of model for vertical wicking

Source	Degree of Freedom [DF]	Sum of Squares [SS]	Mean Square [MS]	F-value	p-value
Regression	9	11849.9	1316.66	41.54	0.001
Linear	3	8023.6	2674.54	84.38	0.001
Quadratic	3	2595.2	865.05	27.29	0.001
Interaction	3	1231.1	410.37	12.95	0.001
Residual error	20	634.0	31.70		
Lack of fit	3	598.6	199.54	96.01	0.001
Pure error	17	35.3	2.08		
Total error	29	12483.9			

The statistical significance of the each factor as a function of p-value (at 95 % confidence) based on the analysis of the variance of data is shown in table 6. From the analysis of variance it is evident that the percentage weight loss and wicking are significantly affected by the surface hydrophilization parameters for polyester fabric by pad-dry method under the tension state. The development of carboxyl groups after the alkali treatment of polyester fabric causes the hydrophilicity to increase and water to rise in the capillaries of the fabric in connection with water loving groups present on the surface of the polyester fabric. This behaviour is attributed to the gradual reaction of sodium hydroxide with the polyester that leads to the surface pitting to occur by hydrophilization reaction. The three factors under study have a pronounced effect on the weight loss and vertical wicking of the polyester fabric. The results has indicated that among the three concentrations of sodium hydroxide the 50 g/l gives the best results for the vertical wicking of the under study substrate.

Table 6. Analysis of variance for effect of input variables on response variables

Terms	Percentage weight loss		Vertical wicking [mm]	
	Coeff.	*p-value*	*Coeff.*	*p-value*
SHC	1.786	0.000	19.25	0.000
TIME	0.182	0.001	4.69	0.003
TEMP	0.253	0.000	10.44	0.000
SHC^2	0.188	0.013	-15.65	0.000
$TIME^2$	-0.152	0.038	0.23	0.913
$TEMP^2$	-0.042	0.540	-11.27	0.000
SHC.TIME	0.101	0.142	1.25	0.537
SHC.TEMP	0.138	0.049	10.25	0.000
TIME.TEMP	0.262	0.001	-6.88	0.003

With the help of response optimizer in MINITAB software, set of optimized parameters for both percentage weight loss and vertical wicking are calculated and given in Table 13.

Table 7. Optimum values of hydrophilization parameters

SHC (g/l)	TIME (min)	TEMP (˚C)	Percentage Weight Loss	Vertical Wicking [mm]
40.5	4	150	3.67	85.5

5.3 Durability of surface hydrophilization against washing cycles

Washing of textiles during service is a compulsory process and it is regulated by chemistry, mechanical agitation, temperature and time. The impact of particular factors can be represented by a washing cycle, within which is the circle dealing with water and fabric that can withstand the washing treatments. The effect of water on individual fibers varies greatly with their chemical constitution. Hydrogen bonding is perhaps the most important kind of bond between and within fibers that influences stabilization. Cellulose (in cotton), protein (in silk), and polyamide (in nylon) have strong hydrogen bonding networks. Hydrogen bonds that contribute to the transverse structure of the fibers are more or less readily broken and reformed with water molecules. Some fibers such as polyester are substantially unaffected by the absence or negligible presence of hydrogen bonds. The decrease in vertical wicking is only 12 mm from 90 mm to 78 mm, as depicted in figure 8 even after the 15 washing cycles. It indicates that the alkali treatment has the modification of the surface that do not tend to disappear during service.

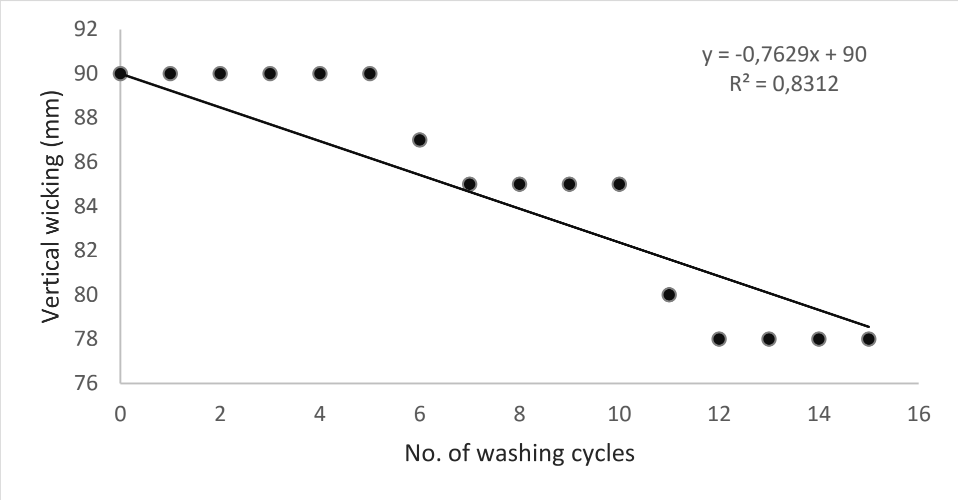


Figure 8. Effect of washing cycles on vertical wicking of surface hydrophilized polyester fabric

5.4 Surface hydrophilization of polyester film

Contact Angle

The ideal smooth surfaces that are flat and solid chemically and homogenously there is only one contact angle exists that is at the equilibrium. According to liquid surface tension theory the largest contact angles are measured for water and lower correspond to the diiodomethane. Figure 9 and 10 show the water CA changes for hydrolyzed polyester film as a function of NaOH treatment time for previously treated with 80 % and 75 % sulphuric acid respectively. The surface modification by strong acid causes roughness on the surface of the polymer film that provides a good surface for the alkaline modification of the polymer film. As the time of treatment of NaOH hydrolysis increases firstly the CA decreases but after some time the CA increases again reaching a value that is less than untreated polyester film.

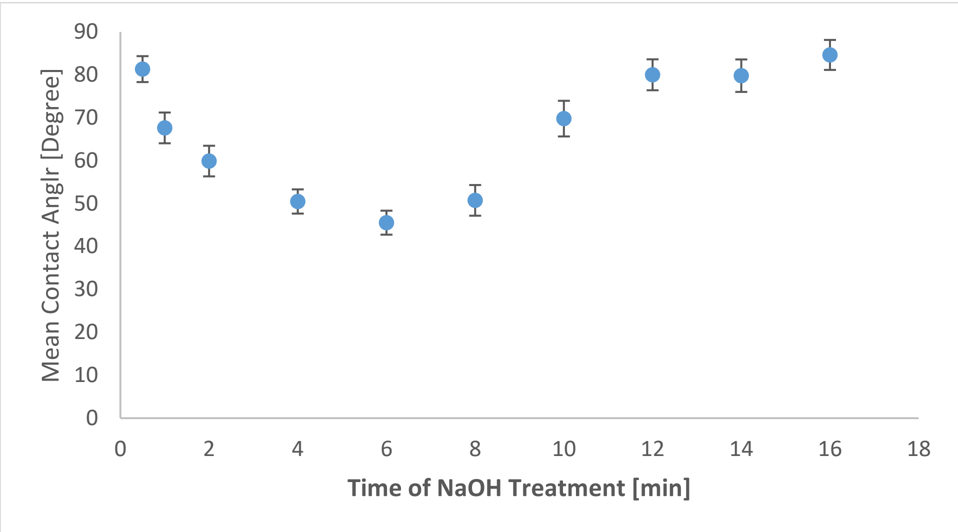


Figure 9. Effect of 50 g/l NaOH treatment time on mean contact angle

This may be due to the fact that surface treatment by strong acid causes surface activation of polyester film through redox reaction that provides an active surface for hydrolysis by sodium hydroxide but with the increase in the alkaline treatment time the peeling off the surface of polyester causes disappearance of strong acid activation so the hydrolysis is only limited to the alkali. The combined effect of acid and alkali disappears and CA again increases with time reaching a values around 84 that are less than the untreated CA values. This small decrease in CA is only caused by alkali treatment only. The combined acid and alkali treatment hydrolyze the surface of polyester as much that the 80 % sulphuric acid treated samples followed by alkali treatment lower the CA value to 45.50 degree after 6 min of treatment while 75 % sulphuric acid treatment lower CA to 57.23 degree. The surface modification increases the surface hydrophilicity of the all the treated samples.

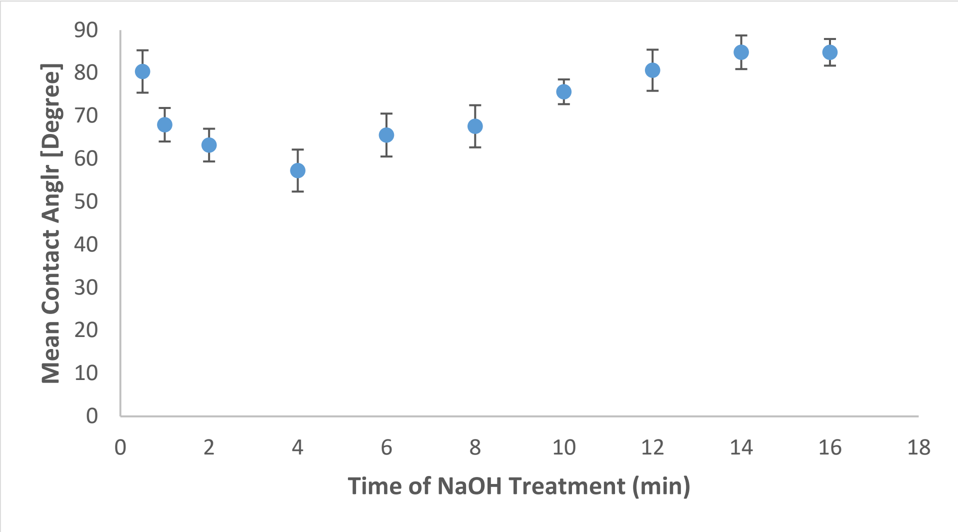


Figure 10. Effect of 50 g/l NaOH treatment time on contact angle of 75 % sulphuric acid treated polyester film

5.5 Surface free energy

In this study the CA measurements of three different liquids are further used to calculate the surface free energy of the treated polyester substrate. The surface tension components are given in Table 8.

Table 8. SFE components of polyester substrates untreated and modified with sulphuric acid and sodium hydroxide

[mJ m^{-2}]	Owens-Wendt			Zisman	Li-Neumann	Mean
	γ_S^p	γ_S^d	γ_s	γ_s	γ_s	γ_s
Untreated	0.73	44.10	44.83	36.57	41.79	41.06
S11	4.84	46.78	51.63	43.29	45.04	46.65
S15	16.28	49.01	65.29	47.76	50.75	54.60

When a drop of liquid rests on a solid surface, it makes an angle θ with the surface, the young explained it by the equation below:

$$\gamma_L \cos\theta = \gamma_s + \gamma_{SL} \qquad (6)$$

Where γ_s is the surface energy of the solid/air, γ_{SL} is the interfacial tension between solid and liquid and γ_L is the surface tension of liquid/air. Many different methods have been proposed in order to calculate the γ_s using values of contact angles formed by different liquids with known surface tension. The experimental values of CA at room temperature of water, ethylene glycol and diiodomethane are used to evaluate the SFE of substrates via Owens-Wendt, Zisman and Li-Neumann methods.

Zisman method shows that the cosines CA (θ) formed by drop of homologuos liquids on the solid surface varies linearly with their surface tension. The critical surface tension can then be found by extrapolating the linear function to cosθ = 1, indicating complete wetting ($\theta = 1$). Brethelot uses young equation in order to approximate the SFE by taking into account of work of adhesion for solid-liquid interface by geometric mean and obtained from young equation [92]:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}} \quad (7)$$

This equation (7) calculates the SFE by using data of CA from one liquid. The use of one liquid may not be reliable and this equation overestimates the pair values obtained from different liquids, usually largely deviating values are obtained by changing the liquids. The Neumann also worked on the transformation of the equation of state for interfacial tension. The SFE is also calculated by method proposed by Li-Neumann[93].

Fowkes approach focuses on the interactions between phases across interfaces and it is based on the theory that the type of forces working between the molecules act independently to each other. The total free energy is divided in two parts, dispersive part and polar part. Owen and Wendt method use this equation and combine the dispersion and polar force components [67]:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{\gamma_S^d\,\gamma_L^d} - 2\sqrt{\gamma_S^p\,\gamma_L^p} \quad (8)$$

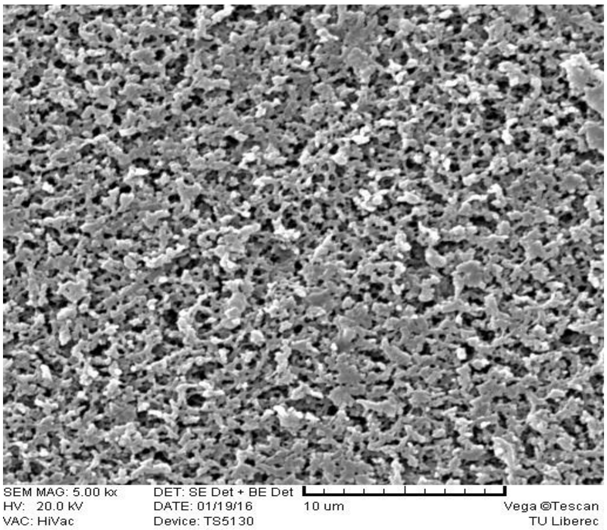
Dispersion force and polar components are indicated respectively by superscripts *d* and *p*. from the Young equation it follows that:

$$\gamma_L\,(1 + \cos\theta) = 2\sqrt{\gamma_S^d\,\gamma_L^d} + 2\sqrt{\gamma_S^p\,\gamma_L^p} \quad (9)$$

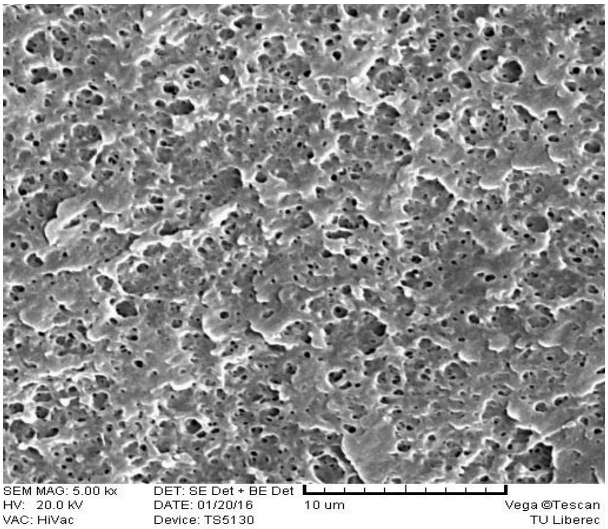
In order to obtain γ_S^d and γ_S^p of a solid surface, the CA measurement of atleast two liquids are required (polar and non-polar).

Table 8 shows the SFE energy values of the untreated samples and those which are treated by both sulphuric acid and sodium hydroxide. The critical surface energy values derived by Zisman are lower than that determined by other methods. It is assumed that use of two liquids one polar and other non-polar give better results in calculation of SFE. So the polarity difference between water and diiodomethane is high that gives the better results for SFE calculation. There is definite increase in the SFE of the treated samples. The SFE of the polyester sample treated for 6 min of sodium hydroxide and previously treated with 80 % sulphuric acid has measured to be increase from 41.06 mJ m^{-2} to 54.60 mJ m^{-2} on average of the all the methods used.

5.6 Scanning electron microscope (SEM) evaluation



(a)



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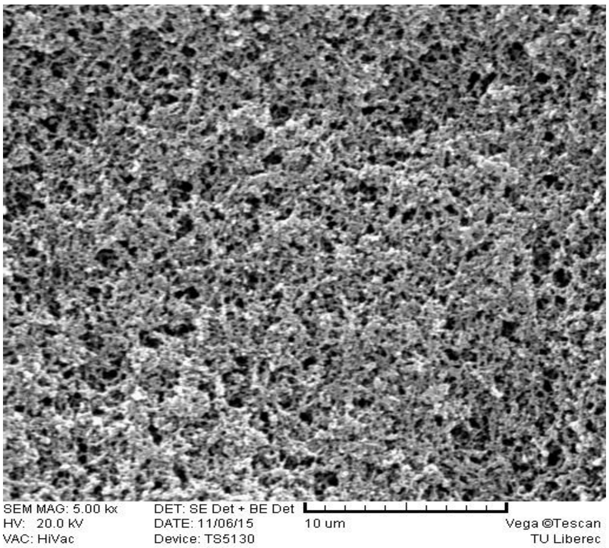

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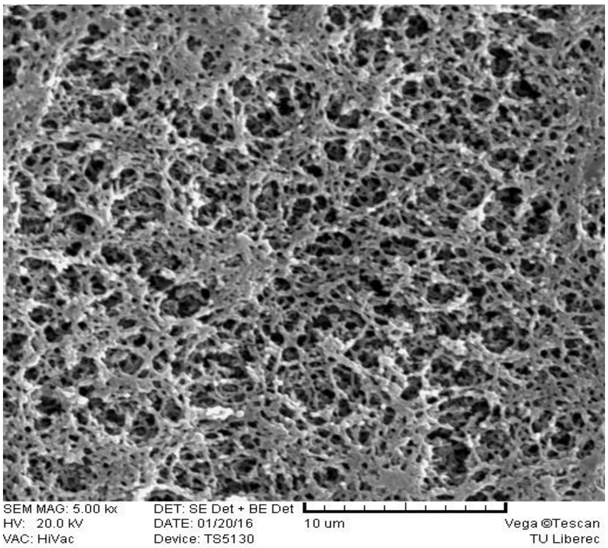

(d)

Figure 11. (a) SEM micrograph of polyester film after 80 % sulphuric acid treatment for 3 sec (b) SEM micrograph of polyester film after 80 % sulphuric acid treatment for 3 sec followed by 50 g/l NaOH treatment for 4 min(c) SEM micrograph of polyester film after

The figure 11 shows the surface topography of the polyester film after the acid treatment and then followed by alkali treatment for the surface hydrolysis of the polyester film. It is clearly evident that the sulphuric acid treatment creates the surface roughness through the acid easter reaction. This surface roughness allows the sodium hydroxide to penetrate in less time and hydrolyse the polyester for the improvement of water retention ability. The combine acid and alkali treatment causes the hydrolysis on the surface of the polyester film making it suitable for the hydrophilicity improvement.

5.7 T-PEEL test of adhesion

The effect of surface treatment of the polyester film with acid and alkali is tested through T-Peel test of adhesion by using polyurethane adhesive. The N=C=O group present in the adhesive is highly reactive with the –OH group of the treated polyester film. So the increase in the adhesion strength of the treated polyester film can be related to the increase in the surface –OH groups.

The values of the adhesion test is recorded in the force per unit width (kN/m) of the bonded specimen. The values are fluctuated because of the very small area at which the stress is localized during loading. A load curve of the treated and untreated polyester film samples is shown in Fig. 12 T-Peel strength is taken as an average of the center portion of the curve. The T-Peel strength of the treated polyester film is 1.8 times higher than that of the untreated film. This improvement in the adhesion strength shows that the surface modification of the polyester film by hydrolysis is effective in improving the adhesion between polyurethane and polyester film.

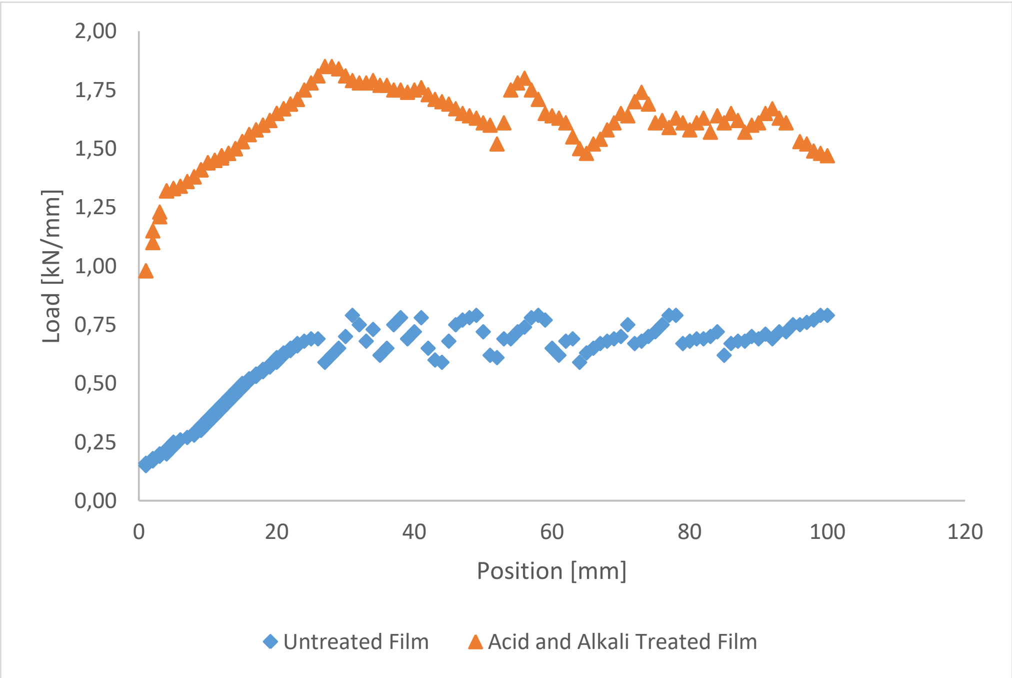

Figure 12. T-Peel test curve of untreated and polyester film treated with 80 % sulphuric acid followed by 50 g/l NaOH for 6 min

6 Evaluation of results and new findings

The following conclusions have been drawn from each study:

6.1 Surface hydrophilization by Pad-dry method

The surface of polyester fabric is successfully hydrophilized by Pad-dry method at low concentration of sodium hydroxide. The influence of sodium hydroxide treatment by Pad- dry method with different low concentrations of caustic soda is studied with different treatment times and compared with the standard caustic treatment at 90 °C with respect to surface morphology, weight loss and wicking height. Hydrolysis with 50 g/l sodium hydroxide using

Pad-dry technique causes less surface pitting and thinning of the polyester yarns in the fabric as compared to the standard caustic treatment for 30 minutes. The weight loss by Pad-dry treatment with sodium hydroxide is only 6.78 % with treatment time of 8 minutes while the weight loss by treating polyester fabric at 90 °C for 30 minutes is 27.1%. The time of treatment shows little effect on the wicking height of the polyester fabric treated by pad-dry method. The addition of urea and glycrin in the solution of NaOH for the treatment of polyester fabric has not improved the absorbency properties and also not hinders the alkaline hydrolysis of polyester fabric.

6.2 Optimization of hydrophilized parameters

The higher concentration of sodium hydroxide was found to have positive effect on the percentage weight loss and vertical wicking of the polyester fabric. The time of treatment and temperature of drying relate linearly to the percentage weight loss and vertical wicking of the polyester fabric. The pad dry method at optimized conditions is suitable for the development of surface hydrophilic groups on polyester that leads to the better hydrophilic properties and moisture transmission.

6.3 Durability against different temperature conditions of hydrophilized polyester fabric

The study of thermal stability of the hydrophilized polyester fabric under different performance temperature conditions and for longer periods of time has shown that the sodium hydroxide modified polyester fabric shows better retention of chemical modification at elevated temperatures. The physical treatments like plasma and ozone, that are successfully used to modify the surface of polyester, tends to reverse the hydrophilic groups as the temperature and time increases during the performance of stages of polyester fabric. The decrease in vertical wicking is 10 mm only even the temperature is increased to 120 ˚C and holding time is six days. The relationship is developed between the maximum suction height (vertical wicking) and holding time. The measured and predicted values shows good agreement when plotted against time.

6.4 Washing fastness properties of hydrophilized polyester fabric

The ability of performance fabrics to withstand the washing cycles is necessary to maintain the effect of surface hydrophilic property achieved by the sodium hydroxide modification of the polyester fabric. The hydrophilized polyester shows good fastness up to washing cycles. The washing of fabric only lowers the vertical wicking to lesser extent.

6.5 Development of hydrophilic polyester film surface by synergistic effect of sulphuric acid and sodium hydroxide

The polyester film is treated with strong sulphuric acid solution and followed by low concentration alkali solution in order to increase surface wettability and adhesion properties. The super hydrophilic surface is obtained by the combined action of acid and alkali at concentration of 80 % sulphuric acid and 50 g/l sodium hydroxide treatment for 6 min. These treatment conditions give the polyester film surface with lowest water contact angle and high

SFE values with good adhesion properties. The presence of hydroxyl groups on the surface with significant decrease in the surface energy has been confirmed through contact angle measurements. The SEM and BET analysis has confirmed the increase in roughness after chemical treatment of the polyester film. T-peel data obtained by the polyurethane resin has indicated the increase in adhesion strength after chemical treatment and improvement of adhesion by thermoset resin can be attributed to the increase in surface wettability and roughness due to the surface modification. Finally a super hydrophilic surface of the polyester film can be achieved through combined acid and alkali hydrolysis under controlled conditions.

6.6 Proposed applications and limitations

The proposed application is industrial usage of pad-dry treatment under controlled tension conditions that provides economical usage of water due to low liquor ratios and efficient recycling of the sodium hydroxide liquors from the padding equipment. It has also good application as longer runs can be processed in at higher speeds with less weight loss and more hydrophilization of the polyester surface. The porous morphology of the polyester film provides super hydrophilic surface that has potential application in the field of flexible electronics and antifogging surfaces where higher adhesion properties are required. The idea of polyester surface modification by synergistic effect of acid and alkali provides a good prospect for adhesion improvement as it requires no sophisticated equipment as most of the physical treatments need for modification.

6.7 Future work

- The moisture transmission rate studies by different methods to study the effect of hydrophilization by this new method.
- The one sided hydrophilization can be done by spray method and it evaluation of extent of hydrophilization.
- Effect of different wicking techniques on the moisture transmission through the polyester fabric.
- The deposition of Nano- cellulosic layers on polyester and their effect on surface wetting of the polymer.

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8 List of published papers by the author

8.1 List of publications in Impact factor Journals

- H. Tanveer, H. A. Abid, "Effect of caustic soda treatment on some comfort aspects of polyester/cotton workwear fabrics." INDUSTRIA TEXTILA 63.4 (2012): 183-189.
- Nazir, H. A. Abid, et al. "Modelling heat-setting of cotton/elastane knitted fabrics for optimum dimensional stability." Journal of Textile and Apparel, Technology and Management 9.2 (2015).
- H. A. Abid, J. Wiener, S. Q. Z. Gilani, "Low concentration alkaline modification of polyester fabric by Pad-dry method and its effect on surface properties of fabric." *Under Review in Fibers and Textiles in Eastern Europe.*
- H. A. Abid, J. Wiener, J. Saskova, S. Q. Z. Gilani., "Surface modification of commercial polyester film for improved adhesion and super hydrophilic surface." *Under Review in Fibers and Polymers.*
- Nazir, H. A. Abid, M. B. Qadir, A. Afzal, M. S. Fakhri, Z. Sarwar, "Combined easy-care and water repellent finishing of cotton fabrics using plasma treatment." TexTech, November 2017.

8.2 List of related publications in international conferences

- H. A. Abid, J. Wiener, S. Q. Z. Gilani, "The alkaline modification of polyester fabric by Pad-dry method and its effect on surface properties of fabric." Advances in Material Engineering, organized by KMI, FT, Technical University of Liberec, Czech Republic, 1-2 December 2015.
- H. A. Abid, J. Wiener, J. Saskova, S. Q. Z. Gilani., "The alkaline treatment of polyester fabric by pad-dry method and its effect on wetting properties of fabric." Proceedings of Workshop Pension Bila Voda Harrachov, 20-23 September 2016, 7-12.
- M. U. Javaid, J. Huang, H. A. Abid, J. Militky, D. kremenakova, "Radiation distribution characterization of fluorescent dyed polyester fabrics at 633 nm wavelength." Proceedings of workshop svetlanka, 22-25 September 2015, 73-76.
- H. A. Abid, J. Wiener, J. Saskova, S. Q. Z. Gilani, Z. Khaliq, A. Shehzad, A. Jabbar, "Chemical surface modification of commercial polyester film for improved hydrophilic and adhesion properties." Ist International Conference on Technical Textiles, 9-10 November, NTU Faisalabad.
- S. Q. Z. Gilani, M. S. Naeem, J. Wiener, H. A. Abid, J. Militky, "Use of CO_2 laser irradiation to carbonize acrylic coated glass mats." NANOCON, 18-20 October, Brno, Czech Republic.

8.3 Research Projects

- Member of the student grant completion (SGS) project 2014, titled, "Preparation of microporous CMC structure with help of lyophilization", Faculty of Textile, Technical University of Liberec, Czech Republic.

- Member of the student grant completion (SGS) project 2015, titled, "Materials for photodynamic therapy", Faculty of Textile, Technical University of Liberec, Czech Republic.

9 Curriculum Vitae

Hafiz Affan Abid

House No. 80 Sabir Pia Town Okara, Pakistan | +420776147243, +923006951382
affanabid2001@gmail.com

Education

PhD student | 2013-present | Technical University of Liberec, Czech Republic

- Major: Textile Technics and Material Engineering (in progress)

M.Sc. | 2009-2011 | National Textile university Faisalabad, Pakistan

- Major: Textile Engineering

B.Sc. | 2003-2007 | National Textile university Faisalabad, Pakistan

- Major: Textile chemistry

Honors and Awards

- Awarded Silver Medal on obtaining 2nd position in the M.Sc. Textile engineering class.

Work Experience

Lecturer | National Textile university Faisalabad, Pakistan | 2011-present

- Teaching and research activities related to textile processing.

R & D Manager | Be Be jan colors limited Raiwind, Pakistan | 2009-2010

- Product development and troubleshooting for the dyeing and finishing of cotton, polyester-cotton blends.

Assistant dyeing Manager | Chenab limited Faisalabad | 2007-2009

- Process control, planning and troubleshooting for the dyeing and finishing of cotton, polyester-cotton blends.

Journal publications

- H. Tanveer, A. Abid. "Effect of caustic soda treatment on some comfort aspects of polyester/cotton workwear fabrics." INDUSTRIA TEXTILA 63.4 (2012): 183-189.
- A. Nazir, et al. "Modelling Heat-Setting of Cotton/Elastane Knitted Fabrics for Optimum Dimensional Stability." Journal of Textile and Apparel, Technology and Management 9.2 (2015).
- H. A. Abid, J. Wiener, S. Q. Z. Gilani, Low concentration alkaline modification of polyester fabric by Pad-dry method and its effect on surface properties of fabric. *Under Review in Fibers and Textiles in Eastern Europe.*

Conference publications

- H. A. Abid, J. Wiener, S. Q. Z. Gilani. "The alkaline modification of polyester fabric by Pad-dry method and its effect on surface properties of fabric." Advances in Material Engineering, organized by KMI, FT, Technical University of Liberec, Czech Republic, 1-2 December 2015.
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- Member of the student grant completion (SGS) project 2014, titled, "Preparation of microporous CMC structure with help of lyophilization", Faculty of Textile, Technical University of Liberec, Czech Republic.
- Member of the student grant completion (SGS) project 2015, titled, "materials for photodynamic therapy", Faculty of Textile, Technical University of Liberec, Czech Republic.
- Research Assistant in HEC funded project 2011, titled, "Enhancing the cooling and comfort properties of textile clothing through chemical finishing", Faculty of Textile Engineering, National Textile University Faisalabad, Pakistan.

Record of the state exam

TECHNICKÁ UNIVERZITA V LIBERCI
Fakulta textilní

ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktoranda: **Hafiz Affan Abid, M.Sc.**

Datum narození: **16. 11. 1984**

Doktorský studijní program: **Textilní inženýrství**

Studijní obor: **Textile Technics and Material Engineering**

Termín konání SDZ: **2. 12. 2016**

prospěl **~~neprospěl~~**

Komise pro SDZ:

		Podpis
Předseda:	prof. Ing. Jiří Militký, CSc.	
Místopředseda:	doc. Ing. Maroš Tunák, Ph.D.	
Členové:	prof. Ing. Jaromír Šňupárek, DrSc.	
	prof. Ing. Jakub Wiener, Ph.D.	
	doc. Ing. Petr Exnar, CSc.	
	doc. Ing. Pavel Pokorný, Ph.D.	
	Ing. Michal Černý, Ph.D.	

V Liberci dne 2. 12. 2016

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Recommendation of the supervisor

Supervisor's opinion on PhD thesis of Hafiz Affan abid

Topic: Surface Hydrophilization of Polyester

I am writing this recommendation letter for Hafiz Affan Abid regarding his final defense. Mr. Hafiz Affan Abid has been studying and doing research work under my supervision for the last four years. He is intelligent, hardworking, positive minded and good in research work.

The main objective of this research work is to chemically hydrophilize the surface of polyester for hydrophilic properties with less weight loss and optimize the method of treatment. The optimization of parameters for getting higher values of vertical wicking and lower weight loss have been successfully performed. XPS, SEM, and BET analysis were performed to analyze change in structure and surface at different temperatures and time of treatment. Later the hydrophilized polyester is successfully employed for stability at different temperatures and durability against washing. The synergistic effect of acid and alkali is evaluated on polyester film for increased surface free energy and improved adhesion properties with good surface area.

The thesis is well written, concise and compact. His publications are quite worthy and good addition in the field of polyester hydrophilization. He has four presentations in international conferences. Three research papers are under review in impact factor journals for possible publications.

By concluding I can say that it is an industrial and novel method for surface hydrophilization of polyester. I strongly recommend him for the defense as he has completed all the necessary requirements and good work he has done.

31.10.2017

Ing. Jana Šašková, PhD.

Supervisor

Opponent's reviews

Oponentský posudek disertační práce.

Autor práce: Hafiz Affan Abid, M.Sc.

Název práce: Surface Hydrophilization of Polyester.

(Povrchová hydrofilizace polyestru.)

Předložená disertační práce se zabývá studiem stále aktuálního problému, jakým je zvýšení hydrofilního charakteru povrchu polyesterových textilních vláken povrchovou alkalickou hydrolýzou. Tento postup je v omezené míře používán i v průmyslové praxi, spíše ale ke zvýšení hedvábnického charakteru polyesterového hedvábí. Doktorand přistupuje ke studiu problému inovativním postupem za použití metody Pad-dry, kdy tkanina naklocovamá alkálií je krátkodobě zpracována při vyšší teplotě. Sleduje se vliv koncentrace alkálie, doby zpracování a vliv teploty na základní parametry, kterými je charakterizována hydrofilizace povrchu vlákna. Zajímavá je i studie sledující možnost zvýšení účinnosti alkálie spolupůsobením močoviny nebo glycerinu.

Možnost zvýšení hydrofilního charakteru povrchu polyesterového vlákna je zřejmě stále předmětem četných studií, jak o tom svědčí seznam použité literatury, kde více nežli polovina citovaných prací byla publikována po roce 2000.

Studiu hydrofilizace polyesterové tkaniny alkalickou povrchovou hydrolýzou byla rozšířena o studiu hydrofilizace polyesterové folie, kde pro modifikaci povrchu byla použita kombinace účinku 80% roztoku kyseliny sírové s následným zpracováním vodným roztokem hydroxidu sodného. Tato jiná forma polyesterového matriálu umožnila rozšířit použití metod pro hodnocení účinnosti hydrofilizace např. o měření kontaktního úhlu na povrchu folie nebo o studiu vlivu hydrofilizace na zvýšení adhezních vlastností polyesterové folie. Zvýšení adhezních schopností polyesterové folie však spíše souvisí se „zdrsněním“ povrchu účinkem hydrolýzy.

Autor prokázal výbornou schopnost aplikovat metody pro hodnocení hydrofilnsti povrchů textilií na hodnocení jím dosažených hydrofilních úprav polyesterových materiálů. Cíle práce byly splněny.

K práci mám některé dotazy a připomínky, které mohou být diskutovány v průběhu obhajoby:

1) Existuje kontakt na některý průmyslový podnik, který se alkalickou hydrolysou povrchu polyesterových vláken zabývá, kde by mohl být provozně ověřen navržený a studovaný postup Pad-dry alkalické hydrolýzy?

2) Byl někdy také studován vliv povrchové alkalické hydrolýzy polyesterových materiálů na jejich koloristické vlastnosti? Možno předpokládat vliv této úpravy na difuzní chování disperzních barviv a na remisní vlastnosti materiálu s ohledem na jeho změněný povrch?
3) Bylo by možno povrchovou hydrolýzu použít pro studiu strukturních změn v průběhu výroby PES vlákna, (např. dloužením, fixací apod.)? Je možno považovat změněnou strukturu povrchu vlákna nebo folie za zvýraznění semikrystalické struktury studovaných materiálů (viz. obr. 13 – str. 42 a obr. 38. str. 70, kde zřejmě schází dokončení popisu)?

Uvedené dotazy a připomínky nikterak nesnižují kvalitu předložení dizertační práce, která je zpracována na velmi vysoké odborné i formální úrovni.

Disertační práce představuje velký objem dobře provedené a vyhodnocené experimentální práce. Doktorand prokázal schopnost samostatné a systematické vědecké práce, výsledky zpracovat a předložit odborné veřejnosti formou přednášek na konferencích i publikací v odborném tisku. Velkým přínosem pro doktoranda také jistě bylo jeho zapojení do práce na výzkumných projektech řešených na Technické univerzitě Liberec.

Práce splňuje všechny nároky na ni kladené, doporučuji ji k obhajobě.

doc. Ing. Ladislav Burgert, CSc.
Ústav chemie a technologie makromolekulárních látek.
Fakulta chemicko-technologická.
Univerzita Pardubice.

Pardubice, 10. dubna 2018.

Referee´s report on PhD. thesis of

Hafiz Affan Abid

„ Surface Hydrophilization of Polyester“

Professor Miroslav Černík

The presented thesis consists of 85 pages divided into 6 major chapters plus References and List of publications. The thesis deals with chemical modification of polyester and its characterization.

Description of Phd chapters

Abstract summarizes content of the thesis with major results.It is written in English, Czech and Arabic. Czech version has some grammar errors (missing word breaking).

Chapter 1 (Introduction) describes basic characterization of PET and properties important for its application. The part summarizes different methods for PET treatment.

Chapter 2 (Research objectives) defines objectives of the thesis – investigation of different agents for PET treatment, especially hydrophilization.

Chapter 3 (Literature review) is a very illustrative introduction into the topic, different methods for man-made fiber treatment – alkali treatment, weight loss of polyester, moisture transmission through fabric, application of wetting and hydrophilic polymeric surfaces. In the chapter, there are figures probably taken from literature without specification of the sources. Also some of the equations are not properly written (e.g.16 and 17). Also Fig 8 is strange (it is a legend for Fig 7).

Chapter 4 (Materials and methods) deals with material modifications (e.g. surface hydrophilization, ozonization, plasma treatment) and subsequent characterization (weight loss, XPS, surface free energy, SEM, adhesion, specific surface area and thermal properties). Major part is a description of measurement of different properties of the fabrics, e.g. The methods are described in low details.

Chapter 5 (Results and discussion). The treatment with NaOH caused very different result compared to treatment at 90 °C, where weight loss is more than one order of magnitude higher. The discussion of this difference is missing. **Is it due to longer contact time or different alkali concentration or temperature? Too many parameters were changed simultaneously.**
SEM micrographs of untreated and NaOH treated polyester fabric is different according to the author (smooth x small pitting on the surface), but the pictures at Fig.13 (a and b) are identical! XPS method was also used for detailed study of the fabric surface.

Is the present model based on physical phenomena of is it just a fitting exercise? E.g. percentage of weight loss is negatively dependent on time (and time^2), which means that with increasing time, the weight loss is decreasing. I also do not see physical reason of mixed

members of the equation. Could you show example of calculation for selected runs (e.g. Run 1)?
Durability of surface hydrophilization against washing cycles showed step-like changes of vertical wicking (Fig. 35). Approximation by straight line is probably not feasible. Have you some explanation of such behavior?

Chapter 6 (Conclusions) summarizes the determined results of the thesis.
The author specifies that percentage of weight loss and vertical wicking are linearly related to temperature and time. Experimental error is so high, that such conclusion is very disputable.
The other results summarized are without acceptable, especially results about hydrophilic polyester film.

References. There is 95 references of previous work, but none of them was published after 2011, so the work present in the thesis was not compared with up-to-date literature.

Questions

1. Why percentage of weight loss and wicking are very different after NaOH treatment at different temperatures (5.1)?
2. Could you show example of calculation with equation percentage weight loss for selected runs (e.g. Run 1)?
3. Durability of surface hydrophilization against washing cycles showed step-like changes of vertical wicking (Fig. 35). Approximation by straight line is probably not feasible. Have you some explanation of such behavior?

Imperfections and recommendations

Language of the thesis is relatively good, but I did find some errors and mistypes. Some examples:

- 5.1 Polyester …..Treatment
- Pictures a) and b) at Fig.13 are identical
- Sometimes a number of decimal or valid numbers is very different in the same context (e.g. p. 43 10.66% to 40%, or 57.23 contact angle p. 66)
- Fig. 18 is twice in the thesis
- Colors are changing in one Figure (Fig. 17).

Referee´s conclusion

The presented thesis deal with modifications of polyester to improve its properties and applicability. Although, I consider some parts of the thesis not fully clarified, some results determined without sufficient details and with only little explanation, the thesis has all necessary parts and show the author understand his work and he is able to put results logically into appropriate parts. Moreover, I dislike the reference part, where all cited sources are very old and do not reflect present state of knowledge in the presented topic. Despite above mentioned weak points, I recommend the thesis for the defense.

In Liberec (Czech R.) on 24. 6. 2018

Prof. Dr. Ing. Miroslav Černík, CSc.