INTERFACE PHENOMENA OF CATIONIZED COTTON WITH EPTAC

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INTRODUCTION

- The most important phase in cotton pretreatment and finishing is adsorption of chemical substances and compounds on textile material surface and wet ability as well.
- Due to existing repulsion forces, adsorption of dyestuffs, fluorescent whitening agents and other textile auxiliaries is not easy to perform. This can be overcome with large amount of electrolyte addition, what is economically and ecologically unfavorable.



 One of cotton modification is cationization using amines and/or quaternary ammonium compounds.

 In this paper, modification of cotton fabric for achieving electropositive charge was carried out by cationization with 2,3-epoxy-propyl-trimethyl ammonium chloride (EPTAC) before, during and after the mercerization process.



- Different treatments, and mostly alkaline modifications, change surface charge and adsorption ability of fibers.
- Interface phenomena, which happen between liquid and solid phase, like water solution and textile material, result in change of textile surface free energy.
- Electrokinetic phenomena, as zeta potential and specific amount of surface charge, characterize electric charge of textile material, while contact angle characterize its wet-ability.
- The effect of modification on the change of fabric zeta potential, surface free energy, contact angle, specific amount of surface charge, ionic surfactant and dyestuff adsorption ability were discussed.



MATERIAL

Fabric	Pretreatment of cotton fabric
В	Standard adjacent bleached fabric of 100% cotton
ВМ	Mercerization (24% NaOH, 8 g/I Subitol MLF)
BE	Bleaching, cationization* (EPTAC)
BEM	Bleaching, cationization during the mercerization
BME	Bleaching, cationization after mercerization

*CATIONIZATION

50 g/l EPTAC (Sigma) 35 g/l 50% NaOH 8 g/l Subitol MLF (Bezema) LR 1:20 pH = 13,0 t = 120 s T = 18 °C



staying at the room temperature for 24 hours in a glass with plastic cover

rinsed and neutralized until pH 7



METHODS

 The effect of modification on the change of fabric interface phenomena were discussing. Firstly, the cotton fabrics modification by cationization was researched through structural properties of fabrics:

FTIR-ATR Fourier Transform Infrared Attenuated Total Reflection Spectrum GX FT-IR (Perkin-Elmer)









TGA

Thermogravimetric analysis SDT 2960 (TA Instruments) Temp. range: 25°C - 500°C Heating rate: 10°C/min Nitrogen atmosphere with a flow rate of 50 ml/min.







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TGA





- Interface phenomena was investigated throughout the change of:
 - Fabric hydrophilicity,
 - Contact angle
 - Pore volume distribution
 - Surface free energy
 - Water adsorption,
 - Ionic surfactant adsorption,
 - Dyestuff adsorption,
 - Zeta potential,
 - Isoelectric Point,
 - Point of Zero Charge,
 - Specific amount of surface charge







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METHODS

HYDROPHILICITY

Characteristic	Standard	Instrument		
	SNV 9858:1952	vertical test		
Hydrophilicity	Chibowski method	horizontal test		
	AATCC 79-2000 Absorbency of Bleached Textiles	Drop test		





HYDROPHILICITY

Fabric	t _{Drop Test} [S]	t _{vertical} [s/ 5 cm]	<i>t</i> _{horizontal} [s/ 5 cm]
В	0	348,8	44,2
ВМ	0	277,8	37,1
BE	0	300,0	39,4
BME	0	263,2	35,7
BEM	0	254,2	34,8







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• Contact angle, θ



- Good wetting
- 1. Hydrophobic surface
- 2. Border case
- 3. Hydrophilic surface









- Low wetting
 - θ >> 90°
 - **θ = 90°**
 - θ << 90°

Structural contact angle and pore volume distribution

(TRI auto-porosimeter)

$$\cos \theta_{test} = \frac{\gamma_{ref} \cdot \Delta P_{test}}{\gamma_{test} \cdot \Delta P_{ref}}$$

- θ structural contact angle within porous network
- γ_{ref} surface tension of the reference liquid (1% Triton X-100)
- γ_{test} surface tension of the test liquid (double distilled water)
- ∆P Laplace pressure difference across the liquid/air meniscus



CONTACT ANGLE measurements is a practical tool for surface characterization.







	Fabric	Contact angle [°]			SFE (acid-base model)					
Щ		$ heta_{water}$	$ heta_{ extsf{formamide}}$	$ heta_{diiodomethane}$	γ _s ^{LW} [mJ/m²]	γ _s ⁺ [mJ/m²]	γ _s - [mJ/m²]	γ _s ^{AB} [mJ/m²]	_{γs} ^{τοτ} [mJ/m²]	
gy, S	в	The surface free energy and pore volume distribution								
Ener	ВМ	(PVD) depends on contact angle measurement.								
Free	BE	Unfortunately, all the tested fabrics with all test liquids formed a zero contact angle; therefore it was								
ace	BME	not possible to calculate $\cos \theta$, pore radius and distribution or the components of surface free energy								
Sur	BEM	(SFE) according to acid-base, Owens-Wendt and Wu.								



Thin-layer wicking method according to Chibowski



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Thin-layer wicking method according to Chibowski

Surface Free Energy, SFE





ШЦ	Fabric	γ _s ^{LW} [mJ/m²]	γ _s + [mJ/m²]	γ _s - [mJ/m²]	γ _s ^{ΑΒ} [mJ/m²]	γ _s ^{τοτ} [mJ/m²]	<i>R</i> [μm]	W _s [mJ/m²]
·gy, S	В	34,21	1,29	51,68	16,33	50,54	11,35	-6,89
Enel	ВМ	43,03	0,13	58,45	5,57	48,60	7,05	-3,45
Free	BE	40,71	3,23	41,59	23,20	63,92	7,73	-2,71
rface	BME	41,44	4,37	37,43	25,58	67,02	10,23	-2,58
Sur	BEM	37,43	5,02	39,31	28,09	65,52	14,72	-2,52







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- part of the total potential drop intermediate surface layer solid/liquid phases consequence of ions distribution
- interface fiber/ aqueous solution electric double layer
- moving of two charged surfaces results by zeta potential



Streaming current/potential method Electro Kinetic Analyzer, EKA (A. Paar, Austria)





ZETA POTENTIAL vs. pH Isoelectric Point (IEP)

ZETA POTENTIAL vs. SURFACTANT ADDITION Point of Zero Charge (PZC)







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capillary system.

Helmholtz-Smoluchowsky





PCD, Muetek, Germany

 $q_{surfactant} = \frac{(V_0 - V) \cdot c \cdot F \cdot V_x}{V_w}$

 $\frac{q_{NDDS} + q_{N-CPC}}{m_{fiber}}$ q_{fiber}

Back titration method

- *q_{surfactant}* amount of fabric charge in a specific surfactant per 1 g of fabric
- c concentration of the titrant
- **F** Faraday constant
- V_0 used up volume of the titrant for the titration of the starting solution
- V used up volume of the titrant for the titration of the solution after the dwell process of fabric
- V_x total volume of the solution where fabric dwelt
- V_w taken volume of the solution after dwelling for the determination of charge













Zeta potential (ζ) of the cotton fabrics vs. pH of 0.001 M KCl





Zeta potential (ζ) of the cotton fabrics vs. N-CPC addition in 0.001 M KCl at pH 10



Fabric	ζat pH 9 [mV]	IEP [pH]	PZC [µg/ml]	<i>q</i> [C/g]
В	-20,9	<2,5	67,11	-2,26
ВМ	-24,7	<2,5	74,84	-1,39
BE	-1,5	5,4	1,34	2,16
ВМЕ	0,5	-	1,90	3,19
BEM	0,9	-	4,06	3,94







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ADSORPTION

- Water Retention Value (WRV)
- According to ASTM D 2402-90

$$WRV = \frac{G_f - G_{tr}}{G_{tr}} \cdot 100 [\%]$$

Water adsorption

 G_f – centrifuged mass test sample G_{tr} – dry mass of test sample





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ADSORPTION

- anionic surfactant sodium dodecyl sulfate (SDS)
- cationic surfactant dodecyltrimethylammonium bromide (DDTMAB)
 - in Linitest, Original (Hanau)
 - c = 0,001 M
 - T = 40 °C
 - t = 30 min
 - pH 7





Amount of adsorbed surfactants was determined indirectly from solution using potentiometric titration method on Titrino 736 (Metrohm).











Surfactant adsorption

ADSORPTION

DYEING

- 0,1 %; 1 %; 10 % owf Benzopurpurin 4B (Sigma; C.I. 2350; Direct Red 3)
- LR 1:30
- T = 100 °C
- t = 90 min
- in Linitest (Hanau)
- neutralization 1 % CH₃COOH
- rinsing until pH 7

Dyestuff concentration in the bath was monitored as absorbance on spectrophotometer Cary 50 (Varian)















CONCLUSION

- Systematic study of interface phenomena of modified cotton fabrics sets the base that can be used to predict the behavior of cotton in the wet finishing processes, and to some extent to assess the value and utilization characteristics, and environmental acceptability of the product for a particular application.
- By comparing mercerized and cationized cotton, it was concluded that cationization during the mercerization process with short chain cationic compounds results in new material and a new dimension to cotton pretreatment and finishing.



CONCLUSION

- The modified cotton retains all the beneficial properties of mercerized cotton with a change of surface charge that ensures further quality improvement.
- It was found that cationization with short chain cationic compounds completely change the system dyestuffcotton fiber and do not obey any known law, which indicates the necessity of further investigations of such modified cotton.
- Except the above, this modification presents an exceptional potential for environmental disposal of waste as well, since such modified cotton fully adsorbs anionic dyestuff.





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