Functionality of Textile Surfaces Using Plasma

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Scientific Book: Young scientist in the protective textiles research

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Within the activity T.6.4 of the EU project FP7–REGPOT-2008-1: **Unlocking the Croatian Textile Research Potentials** under the auspices of the **Textile-Science Research Centre (TSRC)** the competition for the award for the most successful scientific or artistic research work in the field of textiles - paper titled *APPLICATION OF ARGON PLASMA TREATMENT FOR IMPROVING FIXATION PROCESS, won the First Award* in category for the best student work and was published in scientific book - *Young scientist in the protective textiles research*.

Introduction

• Modern textile technology processes attribute great importance to the increasing demands the environment - where the more compliant material processing agents that are acceptable from an ecological but economical aspect.

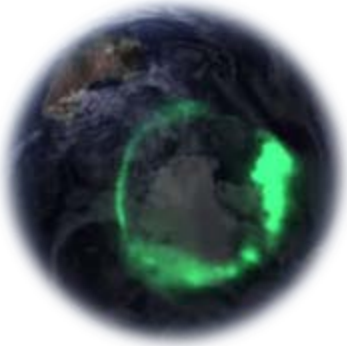
• Increasing research are related to the application of cold plasma as an environmentally acceptable physical agents.

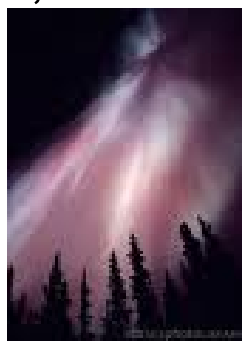
• The most common application of plasma in the textile industry in the processes pretreatment and finishing of textile materials $\Rightarrow$ multifunctional textile products.

• The plasma is carried out for surface treatment of materials in order to achieving the targeted modification of material properties.

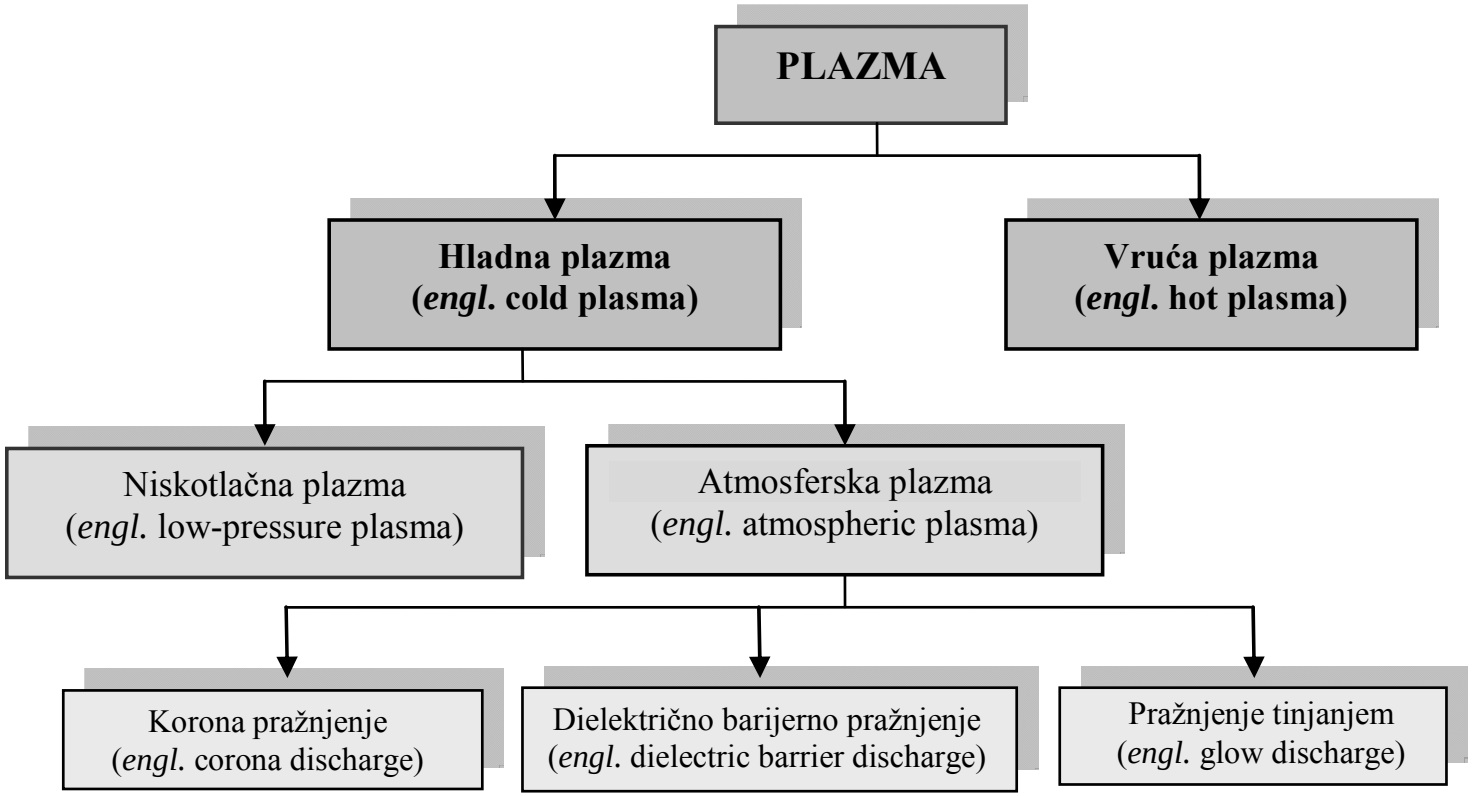
What is plasma?

- It comes from greek words - *plasso* , “self forming materials”.
- In physics and chemistry, plasma is defined as an almost completely ionized gas, mainly composed of the free charge particles, such as ions and electrons.
- In Nature - Plasma is widespread state of matter (99% of visible matter in the universe) - Sun, Stars, Ionosphere, ...
- It can be observed from Earth: lightning and other forms of electrical discharge of the atmosphere, polar lights (eg. Aurora Borealis, Aurora





Classification of the plasmas



Characteristics of Low-pressure plasma system application

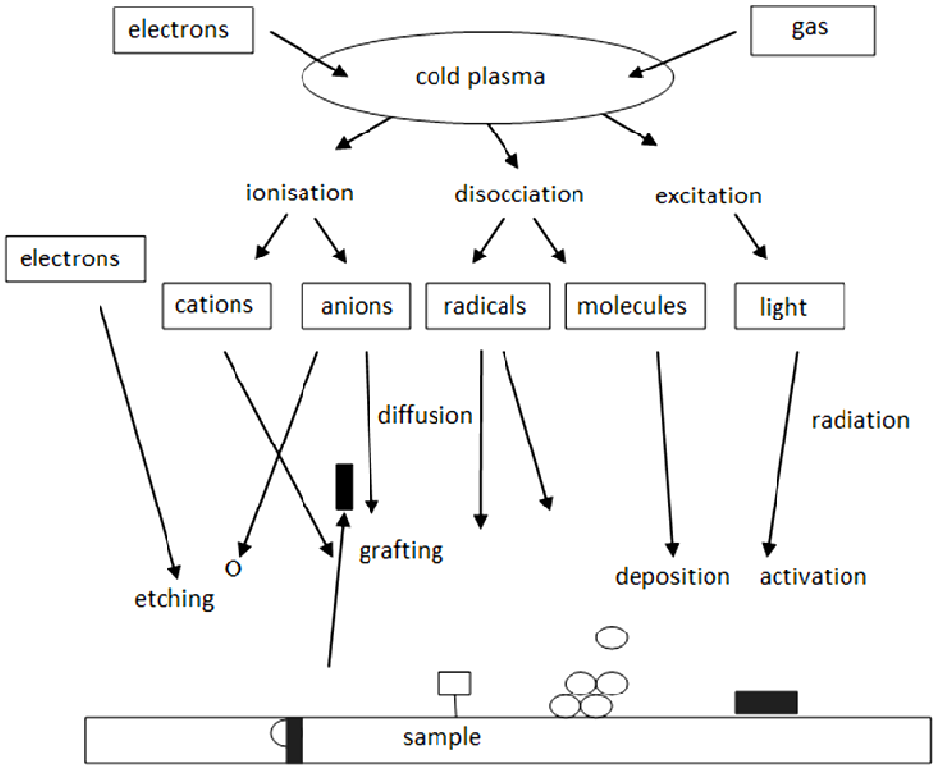
- Applicable for treatment of different substrate surfaces;

- Using optimal process parameters, new desirable surfaces properties of treated materials were achieved without significant changes of their bulk properties ;

- Applicable for polymers where the modification of surface properties by using chemical wet processes not appropriate ;

- Treatment processes were achieved in dry, closed and safe systems;

Reaction and mechanism of plasma acting on the substrate



Cleaning and etching of the surfaces

→ Removing of organic layer from treated surface

→ Breaking of covalent bonds in polymer chain

Surface activation and modification

→ Reaction between chemical groups on the substrate surfaces and chemical particles in plasma → generating of new functional groups

- wettability improving of textile materials

Plasma polymerization or deposition

→ Deposition of nanolayers of different agents (fluorocarbons, hydrocarbons , organosilicones,…) on the different material surfaces.

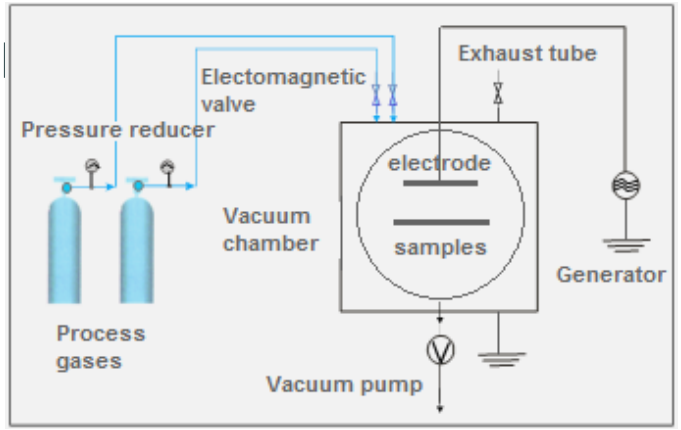
→ Use of monomer gases or vapour is needed, which contains C, S, Si atoms in working gas

Parameters of the plasma efficiency depending about frequency

f (Hz)	Field of freq.	Effects
10 – 50 kHz	Corona discharge	Activation and modifications of surfaces
50 – 450 kHz	Low-frequency (lf)	Surface activation and low rate of deposition in process of polymerization
13,56 or 27,12 MHz	Radio frequency (rf)	Surface activation and high rate of deposition in process of polymerization
915 MHz or 2,45 GHz	Microwave (mw)	Surface microetching, polymerization

Parameters of plasma system

- working gases - different non corrosive gases,
- gas flow rate - from 0 to 400 sccm,
- working pressure - from 0.1 to 10 mbar,
- working frequency of system - 40 kHz,
- treatment time - adjustable (depending on the treatment



Low-pressure plasma system typ NANO, LF-40kHz, by Diener Electronic

Because of their sizable temperature and density ranges, plasmas find applications in many fields of research, technology and industry.

For example, in:

- Automotive industry,
- Medicine (catheters, contact lenses, biocompatible materials for sterilizations)
- Electronics (microelectronic elements, semiconductors, senzors),
- Solar cells productions, plasma monitors,
- Plastic industry and elastomeric materials ,
- Metal industry (technological process of welding),
- Source of artificial light (lamps),
- Deposition of organic polymers using metal alloys ,
- Composite production(laminates),
- Biology and microbiology sciences ,
- Membrane technology and environment technology (elimination of hazardous

… last 15 years application in textile industry also …

- Desizing process,
- Improving of dyeing process,
- Increased hydrophilicity/hydrophobicity,
- Improving oleophobicity,
- Improving of adhesion properties,
- Antimicrobial properties,
- Resistance on UV degradation, self-cleaning
- Flame resistance,
- Antistatic properties,
- Resistance to shrinkage by felting,
- Dimensional stability of material,…

Scope of this research:

- *The purpose of this research is mainly to evaluate how the different plasma processes influence to the better fixation of carboxylic groups of succinic acid with the cellulose functional groups*.

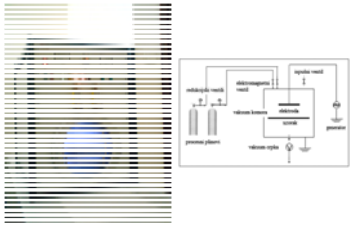
- *Is it the possible the replacing of conventional technological processes with environmentally more favorable ones.*

Experimental procedure

Untreated cotton fabric

Surface activation by Oxygen plasma

Working gas: oxygen (O_2)
Pressure: 0,34 mbar
Power: 300 W
Gas flow rate: 40 sccm
Treatment time: 5 min
Working frequency: 40 kHz



ACTIVATED SURFACE

0,6 M Succinic acid with NaH_2PO_2

0,6 M Succinic acid without catalyst

Exhaustion method
Bath ratio 1:20; 1 hour ; pH 2,2; 22 °C
Drying : 100 °C, 10 min

Plasma fixation

Working gas : argon (Ar)
Pressure : 0,30 mbar
Power : 300 W
Gas flow rate : 40 sccm
Treatment time : 5 min

Curing

Curing : 170 °C, 3 min

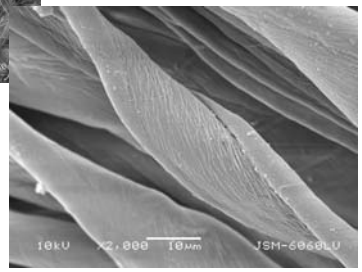
After treatment all the samples were scoured in dest. water at 40 °C for 10 min and dryed at 100 °C for 10 min.

Material

Cotton fabric:

- mass per unit area: **130.6 g/m²**
- number of threads per cm: **warp25/weft20**
- thickness: **0.35 mm**
- plain woven fabric

SEM, magnification 40x



SEM, magnification 2000x

Methods of analysis

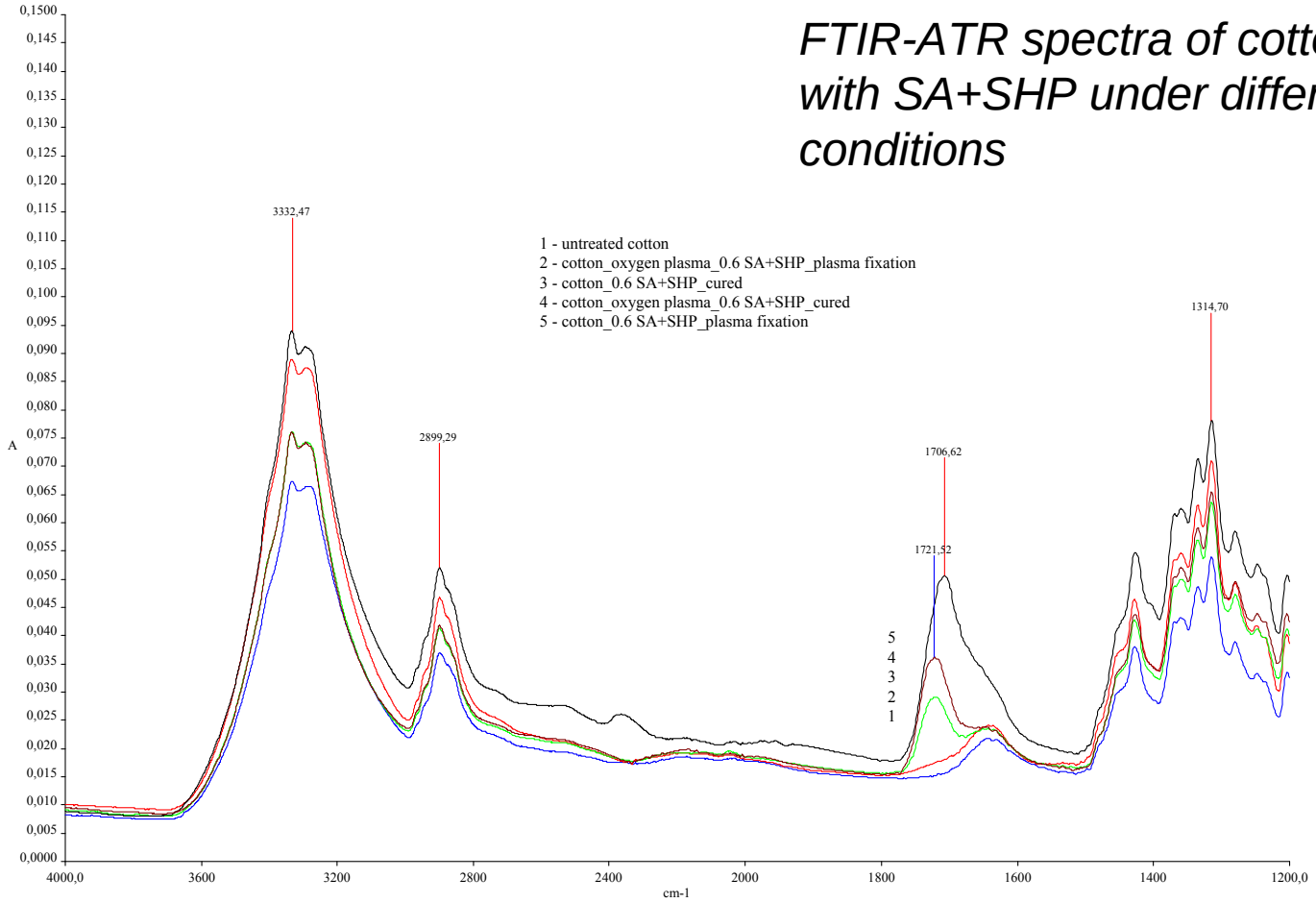
FTIR-ATR analysis

A Fourier transform infrared spectrometer Spectrum 100 FT-IR (Perkin Elmer) with attenuated total reflectance (ATR) detector, was used in this experiment. The spectra were recorded over the range of 4000-500 cm^{-1}, with resolution of 4 cm^{-1} and per 32 scans. The FTIR spectra were normalized to the absorption band at 1314 cm^{-1}.

Strength Tester

A tensile testing machine Strength Tester 3000 (Mesdan, Italy) is used for testing the mechanical properties of cotton fabrics. Measurements were performed on cotton woven fabric samples which were prepared according the standard HRN EN ISO 13934-1:2008. For every fabric sample, three tests were performed.

Results and discussion



FTIR-ATR spectra of cottons treated with SA+SHP under different process conditions

Results and discussion

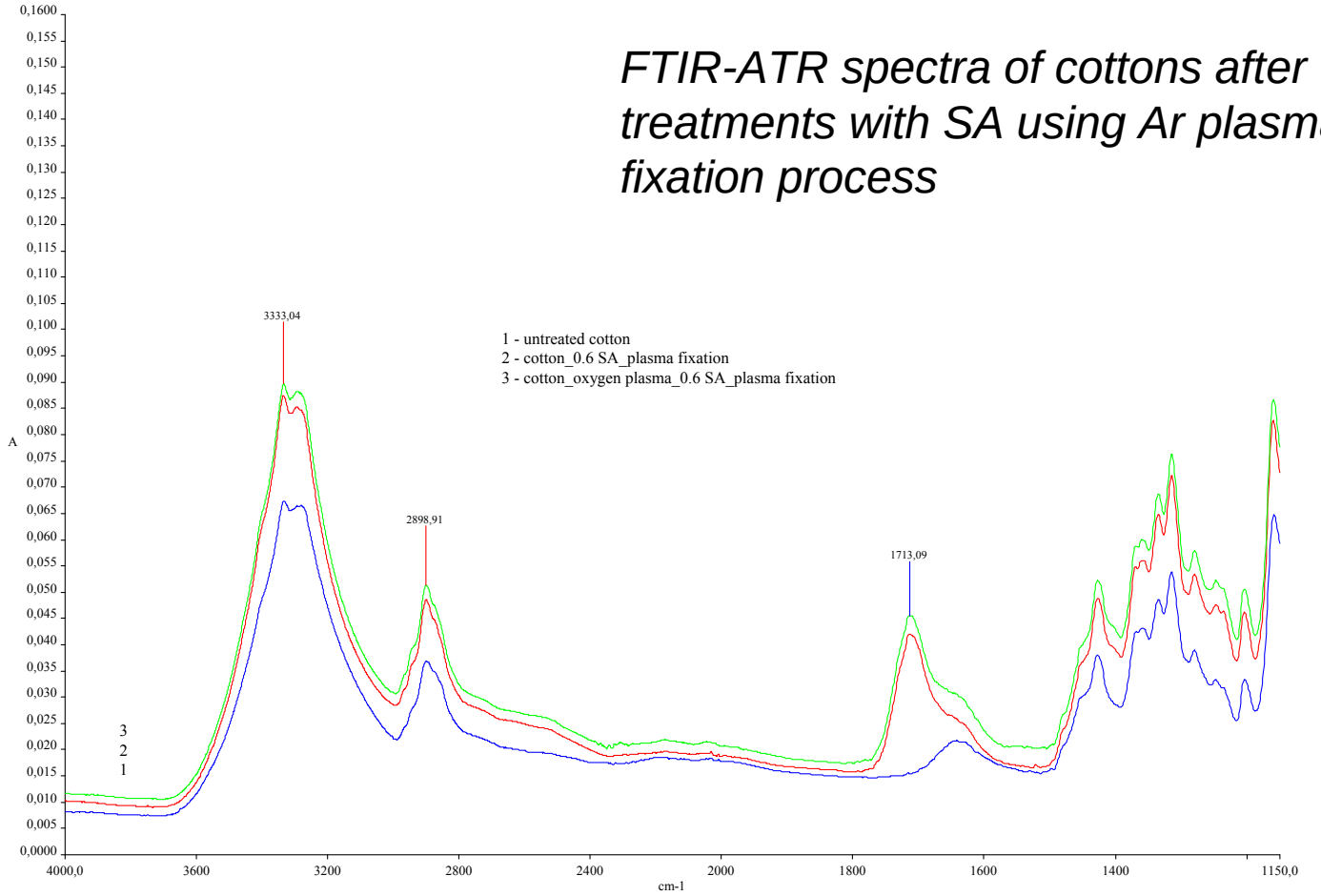
- Spectra shown in Figure 1 reveals the presence of absorption bands at 1706 cm^{-1} and 1721 cm^{-1}, attributed to the carbonyl group of the ester and/or carboxyl groups.

- The intensity of this absorption bands indicate on the amount of generated ester linkages between the hydroxyl groups of the cellulose and the carboxyl groups of the carboxylic acid such modified cellulose.

- Additionally, the intensity of the absorption band at 1721 cm^{-1} of pretreated oxygen plasma samples was higher in relation to the sample without oxygen plasma pretreatment.

- According to this approach it can be assumed that the processing of succinic acid anhydride with a curing catalyst under conventional cure process have proved to be the

Results and discussion



FTIR-ATR spectra of cottons after treatments with SA using Ar plasma for fixation process

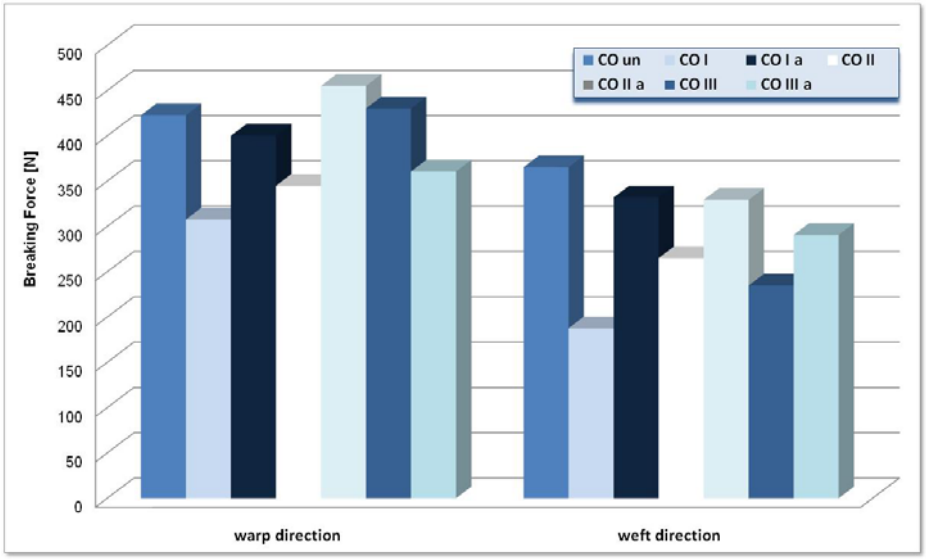
Results and discussion

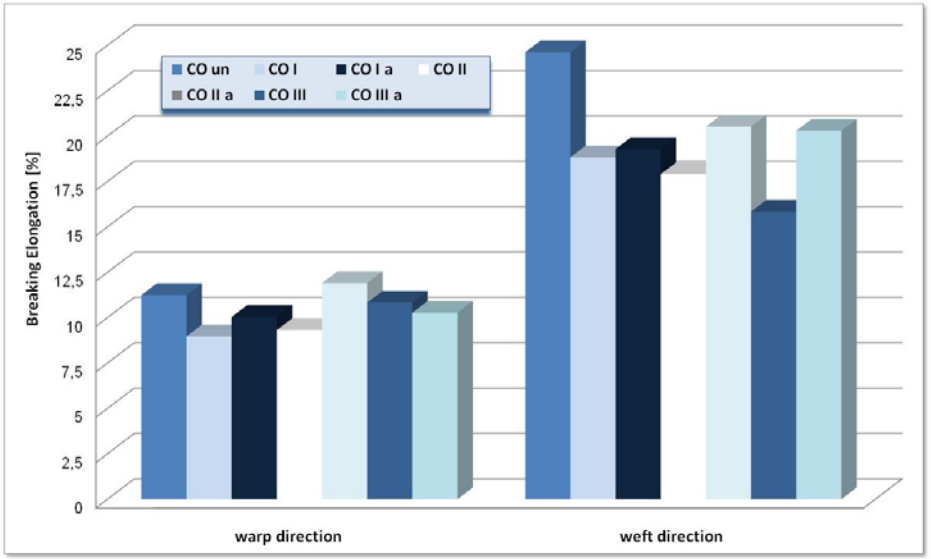
• Figure 2 shows the spectra obtained for the samples treated with SA without catalyst and fixed using Ar plasma, were compared to the untreated cotton sample.

• Additionally, one cotton sample was pretreated using oxygen plasma. The spectra in spectral region between 1800-1500 cm^{-1} is of high interest. The band at 1713 cm^{-1} is attributed to the carbonyl band of the free carboxylic acid.

• Based on these results, it can be presumed a higher efficiency of the plasma acting, as a pretreatment and as a fixation process, and representing a new

Results and discussion





Graphs of results of breaking strength [N] *and breaking elongation* [%] *of tested samples*

Results and discussion

- The results of mechanical properties presented on the graphs indicate the lower reduction of breaking strength and breaking elongation after plasma fixation process, in relation to the curing process where the reduction of breaking strength and elongation is evident, both in warp and weft direction.

- It is believed that oxygen plasma treatment caused etching and ablation action on the substrate surface, resulting in roughening effect on the fabric surface. The rougher surface resulting in enhanced inter-yarn and fiber friction and contributing to increased of mechanical properties, as well as physical properties at macrostructure level (e.g. increased of thickness, mass per unit area, number of threads and reducing of volume porosity).

- Additionally, the Ar plasma treatment was expected to affect the crosslinking structure and agent distribution to improve the physical-chemical properties of the finished fabrics, with less or no reduction of mechanical properties of the treated fabrics, as well.

Conclusions

- The results of FTIR-ATR analysis indicate that the argon plasma treatment certainly improved fixation process of carboxylic groups of succinic acid on the cotton supstrate in comparison to the thermofixation process.

- Oxygen plasma pretreatment increase the intensity of the absorption band at 1721 cm^{-1} which indicate on the amount of generated ester linkages between the hydroxyl groups of the cellulose and the carboxyl groups of the carboxylic acid such modified cellulose.

Conclusions

• Results of mechanical properties indicate on the lower reduction of breaking strength and breaking elongation after plasma fixation process (reduction of breaking strength amounts approx. from 5% to 15%), in relation to the thermofixation process where the reduction of breaking strength and breaking elongation is evident (reduction of breaking strength amounts approx. from 15% to 40%).

• If the processes of plasma fixation were durable in application conditions, it would be a good basis for the substitution of conventional method with environmentally more favorable one.

Thank you for attention !

Authors:

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