Cold plasma assisted modification of the cellulose/chitin fibres for their use as fillers in biocomposites and for food packaging application

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ACTIVE AND INTELLIGENT FIBRE-BASED PACKAGING – INNOVATION AND MARKET INTRODUCTION

EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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PURPOSE

Obtain functional fibers with antimicrobial and antioxidant properties

Grafting cellulose/chitin (CC) mix substrate with Eugenol (Eu) , p-hydroxybenzoic acid (HBA) and gallic acid (GA) - using a two steps process

I) Activation of the substrate with high frequency cold plasma

II) Reaction with different modifiers by subsequent coupling reaction

Activation procedure

The exposure to high-frequency plasma :

- **discharge gas - air or N_2**
- pressure - 0.4 mbar (40 Pa)
- **frequency - 1.3 MHz**
- discharge power - 100 W
- activation time - 15 minutes

Modification procedure

- After activation, the cellulosic substrates were removed from the treatment chamber and immediately (less than 30 s) immersed in the treatment solutions (10 wt%) of eugenol (Eu), galic acid (GA) and p-hydroxybenzoic acid (HBA) for 60 minutes, by mechanic stirring.
- The solutions used contain two chemical coupling agents: 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC), used as a carboxyl group activator incorporated by plasma activation for the coupling of primary amines to yield amide bonds; and N-hydroxysuccinimide (NHS) was used to increase coupling efficiency and create a stable amine-reactive product.
- The cellulosic substrates were then dried at 60 ºC, and after that extracted for 25 h in a Soxhlet extractor with methanol, in order to remove the physically adsorbed unreacted chemicals.
- The modified cellulosic substrates (CC/Eu, CC/GA and CC/HBA) were dried and analyzed.

Investigation Methods

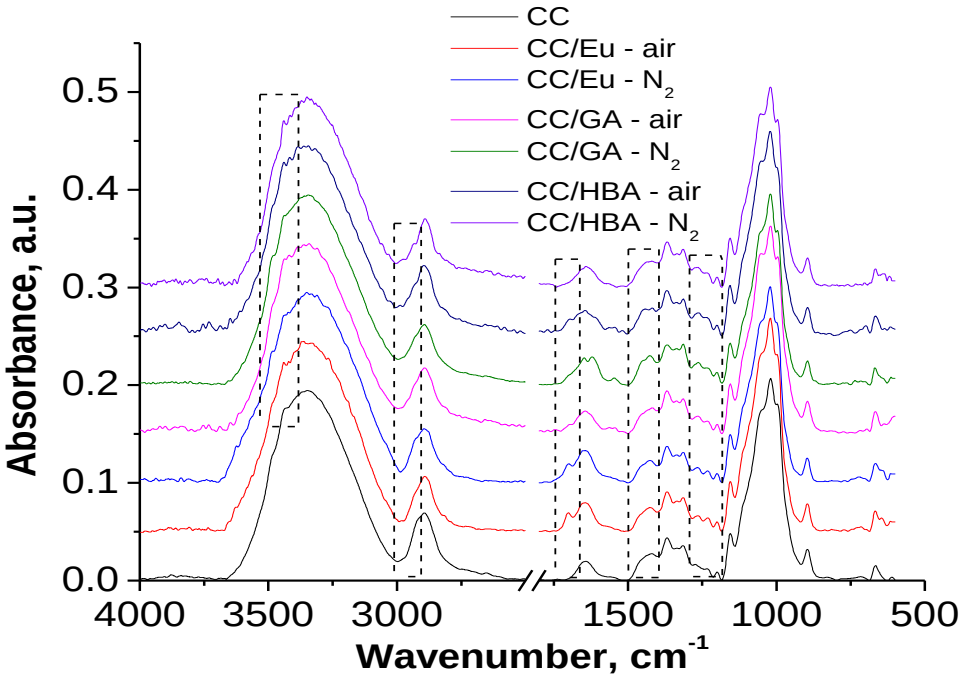
- ***The ATR-FTIR spectra***
- ***The X-ray photoelectron spectroscopy (XPS)*** *measurements*
- ***SEM analysis***
- ***Antimicrobial tests*** *have been performed by well-known standard methods such as:*

(1) SR EN ISO 6579/2003/AC/2004/AC/2006, 2007- Horizontal method for detection of Salmonella spp. Bacteria;

(2) SR ISO 16649-2/2007 – Horizontal method for counting the bacteria Escherichia coli β - positive glucuronidase, at 44 0C, using 5-bromo-4-chloro-3 Indolyl β-D-glucuronid medium;

(3) SR EN ISO 11290-1:2000/A1:2005 Part I - Horizontal method for detection and counting of Listeria monocytogenes.

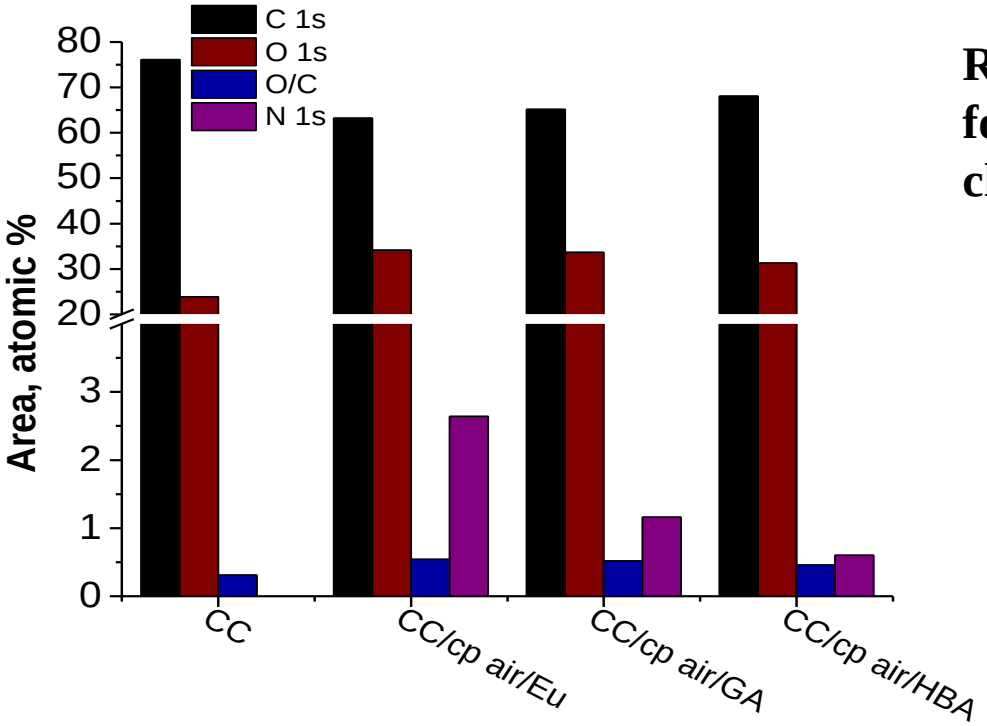
Surface properties – ATR-FTIR



Normalized ATR-FTIR spectra of the modified cellulose /chitin fibers

3440 - 3415 cm^{-1} - OH intramolecular H – bond
2932 - 2835 cm^{-1} - COOH group, OH stretching vibrations
1706 - 1693 cm^{-1} - COOH group, C=O stretching vibrations
1570 - 1565 cm^{-1} - COOH group, asymmetric C=O stretching vibrations
1238 - 1228 cm^{-1} and 1055 – 1050 cm^{-1} - -OC-O-CO- group, C-O stretching vibrations

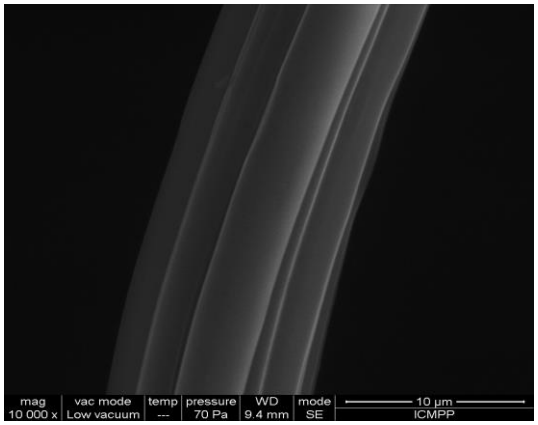
XPS



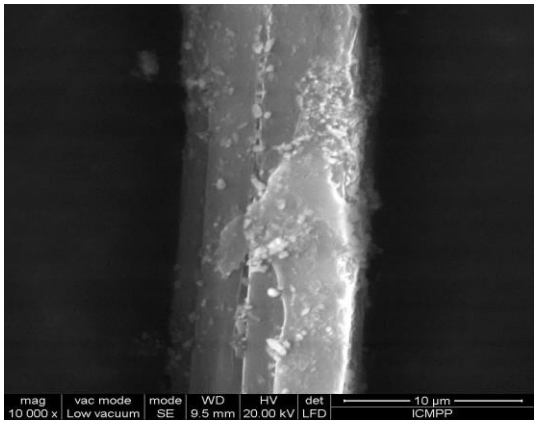
Relative surface atomic concentration for untreated and plasma treated and chemical modified samples

- C and O are the predominant species
- Nitrogen was found after plasma activation and further modification because of etching and cleaning of surface.
- The modification/grafting degree estimated from XPS data was 31.1 % for CC/Eu, 32.6 % for CC/GA and 37.8 % for CC/HBA.

SEM results

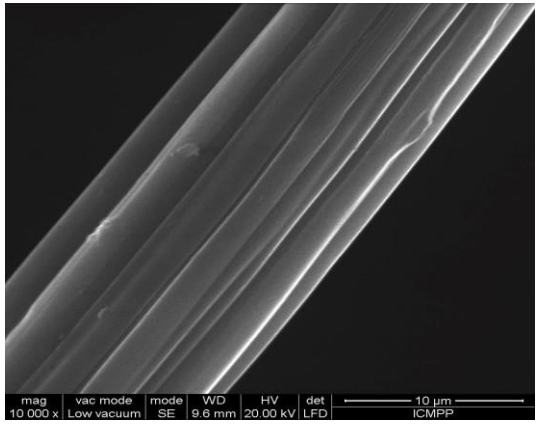


(a)

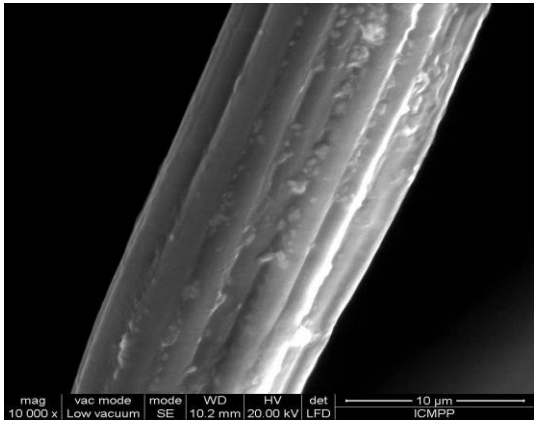


(b)

SEM images of the samples:
(a) CC,
(b) CC/Eu,
(c) CC/GA and
(d) CC/HBA



(c)



(d)

• The surface morphology of untreated substrate was quite homogenous and the individual fibers were intact (a), while modified cellulosic substrates pre-activated by plasma exposure with Eu, GA and HBA (b-d), show a rougher surface and also a thin layer of deposits seems to cover the whole surface.

Antimicrobial activity

Antimicrobial activity (%) of untreated, plasma treated CC substrate further modified with different compounds

Sample	Escherichia coli		Listeria monocytogenes		Salmonella enteritidis	
	24 h	48 h	24 h	48 h	24 h	48 h
CC	24	51	40	68	29	45
CC/Eu	77	79	83	100	76	86
CC/GA	38	78	64	100	76	86
CC/HBA	53	89	26	74	90	95

- Using plasma the surface of CC substrate is cleaned and etched and so more chitin is available at the surface to impart better antimicrobial properties.
- Further modification with phenolic compounds also improves the antimicrobial properties.
- The antimicrobial activity reached up to 100 %.

Conclusions

- Cellulosic substrate has been modified with eugenol, gallic acid and p-hydrohybenzoic acid, using cold plasma for the activation.
- The modification/grafting degree estimated from XPS data was between 31 and 38%.
- The antimicrobial activity was imparted.
- These materials could find practical applications in medical textiles, food packaging and also as reinforcements in polymer matrices used in the similar fields.

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