



**Evaluation du comportement mécanique des matériaux
composites chanvre- PP sous traitement plasma =
Evaluation of mechanical behaviour of Hemp-PP
composites materials under plasmatic surface
modification**

Mohamed Ragoubi, Stéphane Molina, Béatrice Georges, André Merlin

► **To cite this version:**

Mohamed Ragoubi, Stéphane Molina, Béatrice Georges, André Merlin. Evaluation du comportement mécanique des matériaux composites chanvre- PP sous traitement plasma = Evaluation of mechanical behaviour of Hemp-PP composites materials under plasmatic surface modification. JNC 16, Jun 2009, Toulouse, France. 7 p. hal-00392697

HAL Id: hal-00392697

<https://hal.science/hal-00392697>

Submitted on 11 Jun 2009

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Evaluation du comportement mécanique des matériaux composites chanvre- PP sous traitement plasma

Evaluation of mechanical behaviour of Hemp-PP composites materials under plasmatic surface modification

RAGOUBI. Mohamed ¹, MOLINA. Stéphane ¹, GEORGE. Beatrice, MERLIN André.

Mohamed.ragoubi@lermab.uhp-nancy.fr, stephane.molina@lermab.uhp-nancy.fr,

Nancy université, LERMAB, Faculté des sciences et techniques, Boulevard des aiguillettes, BP70239 54506 Vandoeuvre cedex, France.

Résumé

L'effet du traitement Corona a été étudié pour comprendre les modifications entraînées à la surface des fibres naturelles et sur les propriétés d'adhésion au sein des matériaux composites. Différentes techniques d'analyses ont été utilisées. La spectroscopie des électrons X (XPS), la microscopie à balayage électronique (MEB) et les mesures d'angles de contact par goniométrie. Les analyses XPS montrent une augmentation du rapport O/C due à l'oxydation de la surface des fibres. Les mesures d'angles de contact diminuent en fonction du temps du traitement et augmentent en fonction du vieillissement de ce dernier. Les photos du MEB exhibent un accroissement de la rugosité et des micros cavités du à l'effet de gravure. Les composites chanvre/polypropylène ont été mis en forme par extrusion et thermo-compression. Le comportement mécanique de ces composites dépend fortement de l'adhésion entre la fibre de renfort et la matrice polymère. Les propriétés des composites montrent une amélioration significative et la force à la rupture est plus importante dans le cas où les fibres sont traitées. On note aussi un accroissement du module de Young de 30%. Cet aboutissement est dû principalement à l'amélioration de l'interaction entre la matrice et les fibres de renfort après traitement Corona causé essentiellement par un arrangement des macromolécules de surface permettant ainsi une meilleure compatibilité d'interface.

Mots Clés : fibres naturelles, traitement Corona, extrusion, composites, propriétés mécaniques

Abstract

Effects of corona treatment were investigated to understand the modifications on natural fibres surface and the adhesion performance on composites materials. Different analytical techniques was used, X-ray photoelectron spectroscopic (XPS), Scanning electron microscopy SEM and contact angle measurements. XPS findings revealed that corona treatment increases the O/C ratio by oxidation of the surface sample. The measured contact angle decreases after treatment and increases with aging. SEM images show an increase in the surface roughness and micro pits by etching effect due to the electron bombardment.

Hemp fibres/polypropylene resin composites were manufactured by extrusion and thermo-compression processes. The mechanical behaviour of composites materials depend greatly on the adhesion between the reinforcing fibre and the surrounding matrix. The mechanical behaviour of composites materials shows very much improved properties and the tensile strength was higher in the case of treated hemp fibres/PP composites only. We notice mainly the increase of the elastic modulus by 30% in this case. This result is due to the improvement of the interaction between matrix and fibres after corona treatment which caused a surface rearrangement of macromolecules allowing a better adhesion.

Keywords: natural's fibres, Corona treatment, extrusion, composites materials, mechanical properties.

Introduction:

Natural fibres such as industrial hemp or flax have been identified as attractive reinforcement for thermoplastic polymers. They are cheap, abundant and renewable, and have good specific properties due to their low densities. Unlike brittle synthetic fibres, natural fibres are flexible and are less likely to fracture as a result of harsh composites fabrication methods such as extrusion and injection moulding. This durability during processing allows natural fibres to maintain high aspect ratio required for good composite reinforcements. Despite these potential capabilities, they have not been used extensively in industry. Some of the problems associated with these composites include poor interfacial adhesion between the cellulosic fibres and the thermoplastic matrices, limited thermal stability of the composite and poor fibre separation and dispersion within the composite.

The incompatibility of polar cellulose fibres and non polar thermoplastic matrix leads to poor adhesion, which then results in a composite material with poor mechanical properties [1]. The adhesion between the fibres and matrix can be improved by either modifying the surface of fibres to make them more compatible with the matrix, or by modifying the matrix with a coupling agent that adheres well to both the fibres and matrix [2].

For our study, physical corona discharge treatment was selected. It is a non polluting technique based on the production of a plasma media at ambient pressure and temperature. Corona technology has a wide industrial application in the terms of polymeric products such as plastics [3] but also in fibres industries (wood, textile): dye ability, smart textiles, grafting, compatibilization [4].

The media induced by an electric corona discharge consists of a complex mixture of neutral particles, ions, radicals, electrons and photons. The interactions and the collisions of these particles with any introduced substrate produce new very reactive species with a capacity to be involved in further reactions.

Corona discharge can be a route to modify different types of fibre products. It has been used to increase the dye ability of textiles fabrics [5], to generate novel chemical functions at the surface of paper fibres in order to conduct subsequent grafting reactions and to improve the wettability of jute fibres [6].

The aims of this paper are to investigate the physical and chemical characteristics of corona treated natural fibres (flax, hemp) and evaluate the mechanical behaviour of composites materials made thereby. Scanning Electron Microscopy (SEM) was used to provide information about the morphology of the treated material surface. X-ray Photoelectron Spectroscopy (XPS) allows the study and the identification of the composition modifications at the surface of each sample. Wettability was characterized from contact angle measurements.

2. Experimental

2.1. Sample specification

In this study two kinds of fibres, flax and hemp were used as received. Flax consists in a plain weave and hemp fibres were compressed in the form of pellets for surface analysis.

2.2. Composites Samples preparations:

Composites were moulded for tensile tests. For their manufacturing, only the corona treated and untreated hemp fibers were used as reinforcements and the thermoplastic matrix was a commercially available polypropylene. Test specimens containing 20 wt% hemp fibres have been formed by extrusion mixing using a conical mono-screw extruder, WERNER PFLEIDERER. Fibres were crushed before extrusion process.

2.3. Corona discharge treatment (CDT)

The system consists of a horizontal cylindrically shaped glass reactor 10 cm in diameter and 30 cm length. It is fitted with three inlets and three outlets assuring the possible alimentation of inert gas or vacuum pump. In this reactor are disposed two planar rectangular (10cm x 8cm) electrodes positioned in the centre of the reaction chamber (distance between electrodes: 5.5 mm). The corona discharge is assured by a low frequency high voltage generator (typically 15 kV, 50 Hz). Two glass plates (130 X 110 mm²) are used as dielectric barriers to avoid arc discharge (Cf.fig1). The samples are disposed between the electrodes and treated for 5, 15, 30 or 45 minutes under 15Kv.

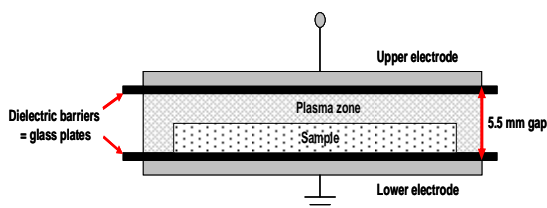


Fig1: Corona system

2.4. Contact angle measurement

The contact angles were measured with a Krüss Drop Shape Analyser DSA 10 in isothermal conditions with different reference liquids deposited onto modified or not modified hemp or flax surface. Glycerol (99,99%) and castor oil were chosen for these experiments. Micro-droplets of the chosen liquid (6 μ L) were delivered with a calibrated syringe and deposited on the surface of the material by casual contact.

2.5. XPS surface chemical analysis

X-ray photoelectron spectroscopy (XPS) analyses were carried out with a KRATOS Axis Ultra (KRATOS Analytical, UK) spectrometer using a monochromatic AlK α source. Spectra were analysed using the Vision software from KRATOS. A Shirley base line allows the subtraction of the background whereas Gaussian (70%) Lorentzian (30%) peaks were used for spectral decomposition. Quantification was performed using the photoemission cross sections and the transmission coefficients given in the Vision package.

2.6. SEM morphological study

Scanning electron microscopy observations were made using a HITACHI S 4800 model microscope. Dry samples were coated with a thin layer of carbon before observations under the microscope mark, in order to increase the sample conductivity.

2.7. Mechanical analysis

The specimen were tested using Instron testing machine fitted with a 10KN load cell, and operated at a rate of 5mm/min. Composite specimen were tested to failure. Mainly, the tensile behaviour was investigated. The average sample dimensions were 100*10*4mm. The results presented here are the average values of five tests.

Results and discussion

3. Surface modification

3.1. XPS Analysis

The XPS wide spectra of treated and untreated flax fabric show two peaks at 284.6 and 532.6 eV attributed respectively to C_{1s} and O_{1s}. The results obtained evidenced an increase in oxygen content and a decrease in carbon one with the treatment time (Cf. Table 1). XPS C_{1s} spectrum is composed of four mean peaks such C-C or C-H at 284.5eV, C-OH at 286.2eV, C=O at 287.69 eV, O-C=O at 289eV and the O_{1s} spectrum is composed of three mean peaks such O=C at 531.5eV, O-H at 532.5eV and H₂O at 533eV. Figures 2 and 3 shows the spectra decomposition of the oxygen and carbon peaks before and after 30min treatment.

Under most treatment conditions, there were peak area increases for C=O, C-OH, O-C=O, whereas peak area of O-H, -C-C and C-H decreased (Cf. Table 1).

Table1. Proportions of oxygen and carbon functional groups before and after corona treatment.

Sample treatment	Raw flax	15min treatment	30min treatment	45min treatment
% O	27.25	40.58	37.64	40.12
O=C	7.47	13.14	8.77	12.78
O-H	81.82	73.30	72.83	69.75
H ₂ O	10.71	13.55	18.39	17.47
%C	70.51	58.12	60.94	57.97
C-C or C-H	43.60	21.05	23.85	24.78
C-OH	45.05	49.46	48.03	48.58
C=O	9.49	22.66	19.59	17.57
O-C=O	1.87	6.83	8.53	9.07
O/C	0.39	0.70	0.62	0.69

We can assume the formation of oxygen containing functional groups such as esters, carboxyl and carbonyl, by reaction with oxygen present in fabric surface and atmosphere. So it is expected that the adhesive properties of fibres increased with the content of these groups on the surface.

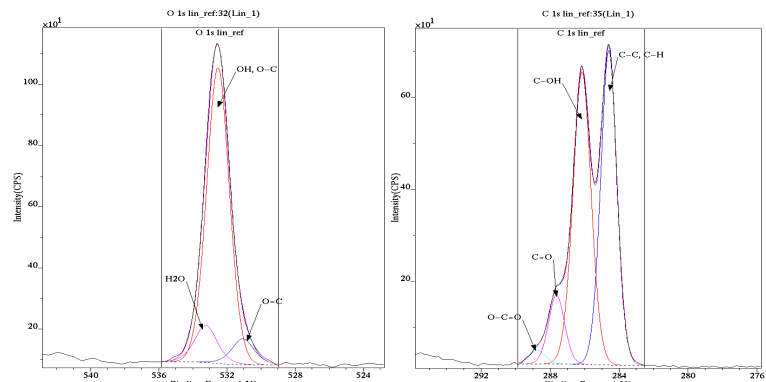


Fig 2 : Elementary surface decomposition from XPS survey spectra and relative amounts of differently bound carbon and oxygen determined from high resolution XPS spectra for raw fabric flax.

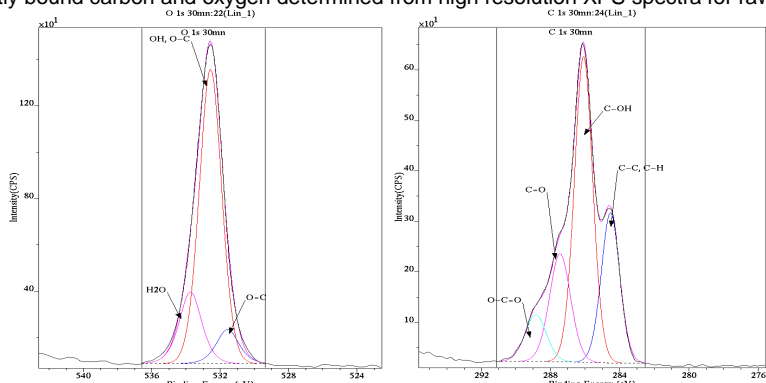


Fig3 : Elementary surface decomposition from XPS survey spectra and relative amounts of differently bound carbon and oxygen determined from high resolution XPS spectra for fabric flax treated 30min.

In the case of hemp fibers, the same trends as those obtained for flax samples were obtained (Cf. Table 2).

Table2 : Proportions of oxygen and carbon functional groups before and after corona treatment.

Sample treatment	Raw Hemp	15min treatment	30min treatment	45min treatment
% O	18.14	32.23	31.31	31.89
O=C	19.95	20.30	20.51	22.9
O-H	63.35	62.1	59.5	57.6
H ₂ O	16.70	17.5	19.91	19.47
% C	78.04	61.12	63.22	62.37
C-C or C-H	59.89	38.31	43.79	44.11
C-OH	29.09	36.45	32.22	31.74
C=O	7.70	14.9	12.58	12.03
O-C=O	3.35	10.26	11.41	12.12
O/C	0.23	0.53	0.50	0.51

3.2 Contact angle measurements:

The measured values of the solvent contact angle decrease with corona treatment time (Cf. Fig 4). This increase in the polarity can be explained by an increase of the carboxyl and hydroxyl groups due to a surface oxidation as previously mentioned.

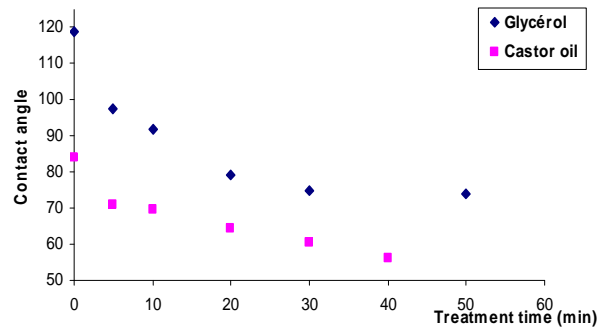


Fig4: Evaluation of the contact angle on flax samples.

The contact angles increase as a result of treatment aging and reach the original values after around 6 days (Cf. Fig 5). This can be attributed to a rearrangement of macromolecules: the polar groups are progressively buried inside the bulk in agreement with the findings of Garbassi and al. [7].

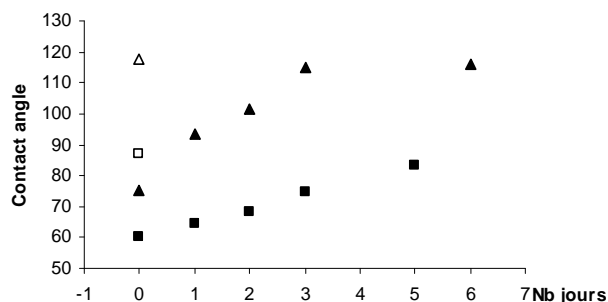


Fig5: Effect of aging onto corona treatment. Probe solvent : Glycerol.
open symbols for untreated and full symbols for 30 min treated samples. ■ hemp ; ▲ flax

3.3. SEM morphology study

SEM images of treated and untreated flax fibres are shown. The surface for the untreated sample appears smooth whereas holes are appearing on the sample surface as the treatment time increases. The size and number of these micro-pits increased with an increase of the discharge time According to Sun [8], this result can be attributed to the ablation effect caused by the bombardment of the oxygen plasma species on the fabric surface. It can be assumed that over the surface of the long polymeric chains, corona discharge produce many activated sites that could react with oxygen to give etching. This phenomenon has been observed by Zheng et al. [9] on polyethylene fibres.

Mechanical analysis

1- Tensile test

Tensile test allowed investigating the tensile behaviour of composites materials made with 20% of hemp fibre, as reinforcement, and 80% of polypropylene as polymer matrix.

The tensile curve (Cf.fig6) show the mechanical behaviour of different composites materials prepared for this study, like specimen with non treated hemp fibres (PP/ NTF), specimen with 15min treated fibres only (PP/ TF), and samples with 15min treated polypropylene only (TPP/ NTF). The results for thermoplastic polymer PP only are given for comparative results.

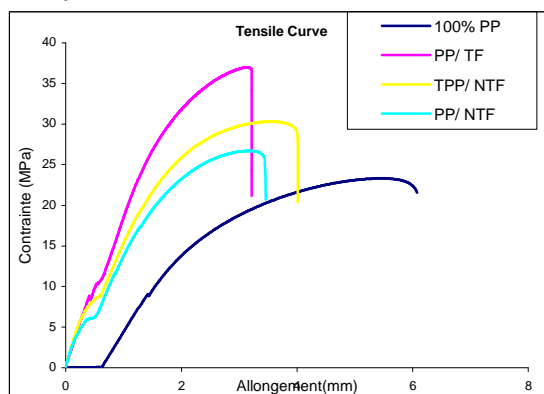


Fig6: Tensile curve for composites materials with 20% content hemp fibres.

Firstly, as we can observe, the addition of hemp fibres increases by 30% the failure tensile compared to the 100% polypropylene matrix and reduces significantly the deformation at break (until 50% of reduction).

It can be seen also that all composites showed an increase in tensile strength when we treated the compounds fibre or matrix.

For composites containing treated fibres, there was a significant increase in strength tensile compared to the other composites which can be explained by an improvement in the adhesion between the fibre and matrix compounds.

Also, the elastic modulus shows a great increase 30% in case of (PP/ TF) composites treated fibres (Cf.table3). The effects of corona are particularly noticeable in composites where cellulose fibres were so modified.

The values of elastic modulus E and strength tensile of the different composites are given in table 3. Mechanical properties of composites increase with the treatment time of fibres [10]. This improvement can be explained by:

- The increase of fibres wettability which allows a better interfacial adhesion through Van der Waals forces,
- The increase of the roughness hence the specific area of fibres caused by the formation of micro-pits which constitute cavities favouring mechanical anchoring. When the resin intruded and subsequently cured into these micro pits, an interlocking structure developed upon the fibre surface [6, 7].

Table3: Mechanical properties of composites materials
(20% reinforcement+80% PP)

composite	Strength (N)	Elastic modulus(MPa)
C-20% TF	1479	946
C-20% NTF	1148	544
C-20% TPP	1365	601
100% PP	979	322

2. Surface failure analysis with MEB

Scanning electron microscopy was used to monitor the fracture surface of composites are shown in (Cf.fig7 a et b).

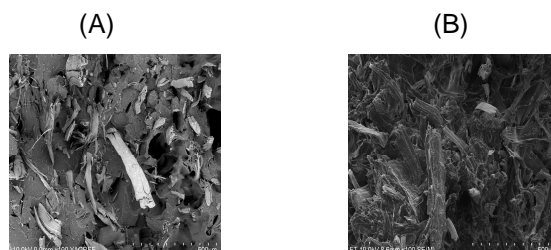


Fig7 : Scanning electron microscopy(*500) of the fracture composites
(A) with non treated fibres (B) with treated fibre.

For the composites with non treated fibres, there is much fibre pullout, as evident by the large number of unbroken fibres sticking out of the fracture surfaces, as well as the large number of holes present in the matrix from which the fibres were pulled out. The protruding fibres which are visible in the micrographs appear smooth and clean and there is no evidence of polypropylene adhering to the fibre surface. This composite appears to fail by means of debonding and tensile failure of matrix.

The view of composites with treated fibres showed that the fibres were covered with PP matrix to a larger extent. In addition there were almost no signs of fibre pull out and most of those fibres were closely associated to the matrix. This is evidence of good interfacial adhesion between the cellulose and polypropylene matrix. These micrographs show that the PP matrix containing composites fail mostly by local shear yielding of the matrix around the fibre, rather than tensile failure of the fibres or fibre debonding.

Conclusion

Corona treatment represents a valuable technique for the surface modification of cellulosic fibres used for manufacturing composite materials. It has been shown to exert varying effects on chemical composition (surface oxidation), wettability and microstructure (morphology) which contribute to the enhancement of the mechanical properties. In addition, the fracture surface of the composites revealed that the corona treatment improved the interfacial adhesion between cellulose fibres and PP matrix.

We now propose to study the thermo-mechanical behaviour of these samples and mainly study the effect of aging in order to better understand interfacial phenomena and extend our studies to other systems.

Acknowledgements:

- The authors would like to thank Jacques Lambert from LCPME, Nancy for XPS experiments.
- They are also grateful to CETELOR and APOLLOR companies for their help in the composites manufacture.

References:

- [1]. G. W. Beckermann; K. L. Pickering. Engineering and evaluation of hemp reinforced polypropylène composites: Fibre treatment and matrix modification.
- [2]. A. K. BLEDZKI , S. REIHMANE, J. GASSAN , Properties and modification methods for vegetable fibers for natural fiber composites, *journal of applied polymer science*, 1996, 59,1329-1336.
- [3]. R. Krüger; H. Potente., Corona - discharge treatment of polypropylene films—effects of process parameters. *Journal of Adhesion*, 1980, 11, 113-124
- [4]. L. Podgorski; B. Chevet; L. Onic; A. Merlin., Modification of wood wettability by plasma and corona treatments. *International Journal of Adhesion and Adhesives*, 2000, 20, 103-111
- [5]. N. Carneiro, A. P. Souto, E. Silva, A. Marimba, B. Tena, H. Ferreira and V. Magalhaes. Dyeability of corona treated fabrics. *Color Technology*, **117** (2001) 298
- [6]. J. Gassan, V. S. Gutowski and A. K. Bledzki, *Macromolecular Mater. Eng*, **283**, 132 (2000).
- [7]. F. Garbassi; M. Morra; L. Barino; Dynamics of macromolecules: A challenge for surface analysis *Surface and Interface Analysis*. vol. 14, pp. 585-589 1989.
- [8]. D. Sun, G. K. Stylios, Fabric surface properties affected by low temperature plasma treatment. *Journal of Materials Processing Technology*, **173**, 172 (2006)
- [9]. Z Zheng, X. Tang, M. Shi and G. Zhou, A Study of the influence of controlled corona treatment on UHMWPE fibers in reinforced vinylester composites. *Polymer. International*. Vol 52, 1833 (2003).