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THE MECHANICAL PROPERTIES AND BIODEGRADABILITY STUDY OF CHITOSAN FILM-COATED KRAFT PAPER SHEETS

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Abstract.
Different recyclable materials for packaging have been studied, including cellulosic packaging such as cardboard, paperboard, kraft paper, among others. The kraft paper, the main component of making sheets of cardboard has good mechanical properties but low resistance to moisture. The use of natural polymers is an alternative to petroleum-derived polymers that can reduce industrial waste and contribute to environmental protection. The application of natural polymers in the packaging has been studied, due to the biodegradable nature of same. Among the possible biodegradable polymers can cite chitosan, which has the property of forming films and these in turn can be used as cover. The objective of this study was to evaluate the degradation process and mechanical properties from the junction of two different materials, and polymer sheets. Chitosan coated sheets of kraft paper (KC-Kraft Chitosan), both compared to the uncoated sheet Kraft (KCF-Kraft Chitosan free). The study was tensile mechanical properties tensile tests. The biodegradability study was based on analysis of biomass carbon Gravimetry, and microbiological evaluation of biofilm formation by scanning electron microscopy (SEM).

Keywords*:Chitosan, Kraft, Mechanical Properties, Biodegradability.*

1. INTRODUCTION

Paper is a biodegradable material widely applied on packaging sector "Sothornovit *et al*. (1997)". Paper is essentially comprises spontaneous crosslinks between cellulose fibers by hydrogen bondings. Kraft paper is widely used in packaging applications but its porous structure makes it highly permeable to gases "Despond *et al*. (2005)" and it is formed of a structural matrix that connects cellulose and non cellulose chains (hemicellulose and lignin) by H-bondings. Its low cost favors its application in the packaging sector (electronics, food, pharmaceuticals, etc.). It is still necessary to search for solutions to improve mechanical properties, moisture, gas barrier and water absorption capacity. These properties directly influence the integrity and quality of packed products.

A good example of such efforts is the packaging industry that, steadily growing in the market, prioritizes the development of new technologies intended to mitigate recycling, environmental pollution and biodegradation problems, among others. Within this context, the replacement of synthetic polymers for biopolymers is an alternative reduce the use of non-renewable materials.

Polymers are considered biodegradable when degradation results from microbial activity, such as fungi, bacteria and algae, generating water, CO_2, CH_4, cellular components and other products "Melo, 2008". There are several biodegradable polymers; one of them is chitosan, which consists of a linear sequence of -(1- -4)2-acetamide-2-deoxy-D-glucose (N-acetylglucosamine) monomeric sugars and glucosamine from chitin deacetylation "Muzzarelli *et al*. (1996)".

The application of chitosan as a coating on Kraft paper sheets could be an alternative to bilayer commercial systems that often use synthetic polymers as coating. Advantages are its biodegradability and recyclability, which could reduce the amount of waste "Cárdenas *et al*. 2008" , and is readily compatible with paper matrix. The combination of chitosan with paper is not new. It has been used as an additive of papermaking and for surface treatments improving the paper properties.

The long degradation period of currently used packaging materials is a major environmental problem that encourages the conduction of studies on the application of biodegradable materials "Massadier-Nageotte, (2006)". Non-degradable compounds added to the paper manufacturing process, such as synthetic polymers resistant to enzymatic and

microbial action are produced worldwide. The use of non-degradable compound has been turning into a problem in which the search for solutions is based on the exploration of new packaging materials.

This study has assessed the biodegradability of chitosan film-coated Kraft paper sheets, emulsified chitosan film-coated chitosan sheets, as well as uncoated Kraft paper sheets. In order to assess mechanical properties was tensile tests and the biodegradability, analyses on Scanning Electron Microscopy (SEM), gravimetry, Microbial Biomass Carbon were performed.

2. MATERIALS AND METHODS

Materials

Chitosan (Primex, ChitoClear®, lot TM 2227, Iceland), acetic acid (Synth, Brazil) and Kraft paper sheet having a grammage of 200g/m^2 (RIGESA, Brazil) were used.

Methods

Chitosan solubilization

The chitosan filmogenic suspensions were prepared by dispersing 4.0% chitosan (w/w) in aqueous acetic acid under continuous agitation. The stoichiometric amount of acetic acid was calculated from the weight of the sample, taking account of the degree of acetylation of the chitosan (DA=18%), to achieve protonation of all the NH_2 sites. The dispersion was stirred until the chitosan was fully dissolved.

Kraft Paper/Film Packaging Systems

Sheets of Kraft paper (0.045m^2) were coated with filmogenic suspensions of chitosan equivalent to 5,33 g/m^2 (each coated sheet) using a 80µm wire bar coater (TKB Erichsen, Brazil). The coated paper sheets were dried at over T=200ºC for 1 minute.

Scanning Electron Microscopy

The samples received gold deposition for three minutes under a 25,000 Ampere current and then had their structure and biofilm formation analyzed by a Gemini Leo 982 Leica Zeiss high resolution scanning microscope from the laboratory of Environmental Microbiology of *Embrapa Meio Ambiente*, under the following conditions: voltage = 10Kv; working distance = 16mm.

Pre-conditioning

The uncoated and coated Kraft paper sheets were previously conditioned at 23±1ºC and 50±2% relative humidity had been before analysis, in accordance with ASTM D685-93 standard method "ASTM D 685-93, (2007)".

Tensile Properties

The tensile properties were determined as specified in ASTM D823-95, "ASTM D823-95, (2007)". Uncoated and coated Kraft paper were cut into sheets with a width of 15.0±0.1mm and a length of 180.0±0.1mm, machine direction (MD) and cross direction (CD), using a guillotine (Regmed, Brazil). Tensile properties were measured by a dynamometer (Mod. D-21, Regmed, Brazil) using a 500N load cell and a speed of 20mm/min. Tensile initial grip separation was set at 180 mm. The tensile strength was expressed in kgf/15mm and elongation was calculated from the difference in distance between grips holding the samples before and after break. There were at least ten replicates per experiment.

Scanning Electron Microscopy

The analysis of scanning electron microscopy was done on equipment high resolution scanning microscopea Gemini Leo 982 Leica Zeiss from the laboratory of Environmental Microbiology of Embrapa Meio Ambiente, under the following conditions: voltage = 10Kv; working distance = 16mm

Microbial Biomass Carbon

The analysis of microbial biomass carbon was bases on the method fumigation-extraction (Vance et al., 1987; Wu et al., 1990), in which microbial biomass is estimated by the difference in CO_2 flux from soil samples fumigated with chloroform (F) and non-fumigated (NF)

Gravimetric Analysis

The gravimetric analysis, according to NBR 10004 (ABNT, 1987), consists of KCF and KC in bags made of nylon. The same were prepare containing approximately 0.80g dry sample at 105ºC , then buried in deep furrows with 10cm of common ground (without treatment).

3. RESULTS AND DISCUSSIONS

Mechanical Properties

The mechanical properties of bilayer Kraft paper were analyzed by elongation and maximum force at break. The tensile tests were performed on the KCF, KC, as show in Table 1. Tensile strength (TS) is an important property of packaging materials that measures the ability of cellulose based package resist before break under tension. Statistically significant differences in tensile strength were not seen in either the machine direction or the cross direction. Statistically significant differences in elongation were not seen in the machine direction (MD) of the fiber of fabrication.The decrease could be associated to the lower strength between fiber-fiber interactions on paper matrix, which may be partially due to the coated material impregnated into cellulose structure. The mechanical properties of chitosan-Kraft paper systems were still controlled by the cellulose fiber matrix which is dependent on the strength of fibers, their surface area and length and the bonding strength between them "Rhim *et al*. (2007)". Similar results were obtained by Bordenave *et al.*(2007) and Kjellgren *et al.*(2006), who found that the mechanical properties of chitosan-coated paper remained almost unchanged or slightly reduced the Young modulus. Matsui *et al*. (2004). did not observe significant differences in the mechanical properties of uncoated and coated acetate starch-Kraft paper.

Table 1: Mechanical properties content, maximum force and elongation at break of uncoated Kraft CF and Kraft C in the machine (MD) and cross directions (CD) of paper manufacturing.

Samples	Force (Kgf/15mm)		Elongation (mm)	
	(MD)	(CD)	(MD)	(CD)
Kraft CF	19,33 ± 0,94 [a]	9,05 ±1,10 [a]	3,30 ± 0,21 [a]	4,09 ± 1,06 [a]
Kraft C	21,11 ± 1,85 [b]	10,54 ± 1,41 [b]	3,74 ± 0,39 [b]	4,82 ± 1,25 [ab]

[a-b] Means in the same column with different superscripts differ significantly ($p \leq 0.05$) according to Tukey's test.
CD - Cross direction
MD - Machine direction

Scanning Electron Microscopy

The scanning electron microscopy analyses showed the surface of each sample (KCF and KC), whether with or without coating, in pictures taken in crescent time intervals in order to follow-up the formation of films throughout the soil microorganisms and to view bacteria colonies (Figure 1). The greater evidence of biofilm formation was seen in the KC samples (8h), what may be related to the beginning of the paper degradation process in soil. It was possible to visualize a greater formation of bacterial cells in the KC samples until 72h, indicating that the chitosan film coating acted a substrate for the cellular reproduction, also noticed by the increase of bacterial cell formation during the collection periods when compared to the KCF samples (times: 8, 12 and 72 hours). As the number of cells increased, the times of collection were increased.

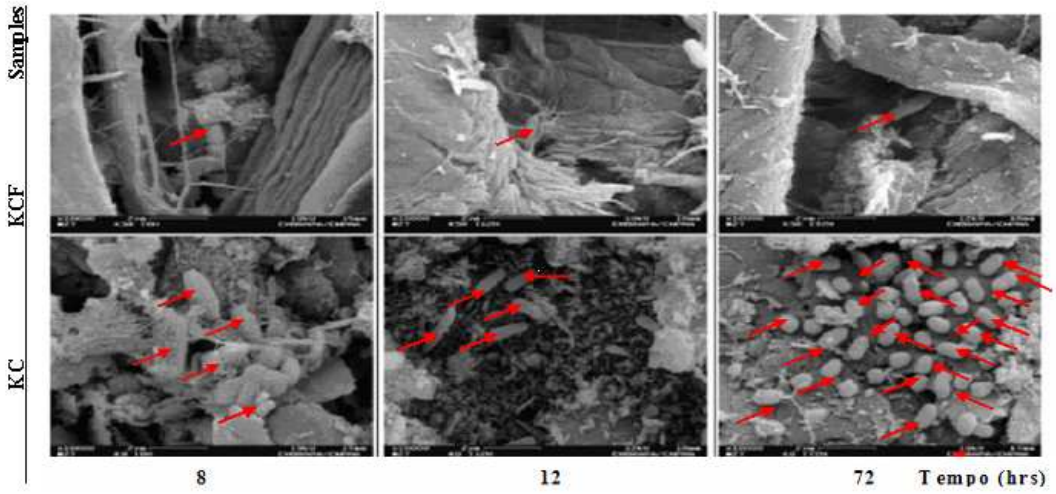


Figure 1 – SEM pictures of Kraft paper sheets: KSR, KQ and KAP.

Gravimetric Analysis

The gravimetric analysis of soil degradation and consisted in the difference of mass of the samples buried in soil (initial weight) and the samples weight after a certain period (final weight). The collections were performed at: 1, 3, 7, 15, 30 and 60 days for the KCF and KC samples (Table 2). It was observed in all samples the gradual reduction of masses in relation to the times of collection and even more in the degradation.

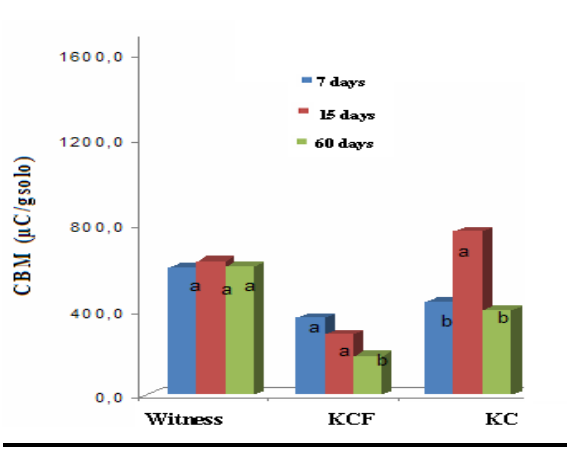
Table 2 – Porcentage of the degradation of de degradação in soil of KCF and KC.

	% Degradation					
Time (days)	**1**	**3**	**7**	**15**	**30**	**60**
KCF	5.56	4.84	12.10	21.57	38.54	62.7
KC	4.72	4.96	13.94	21.52	42.80	67.63

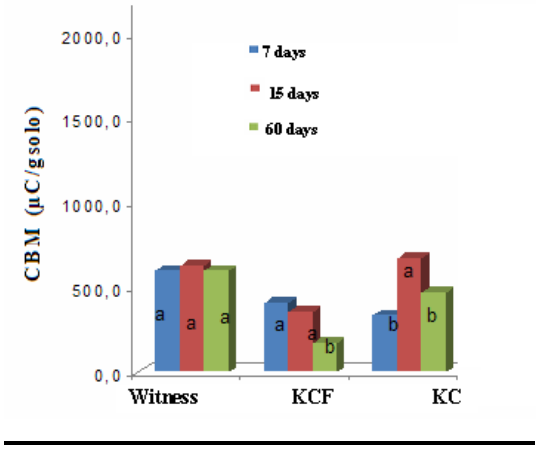
Microbial Biomass Carbon

The microbial biomass is one of the components that control the decomposition and the accumulation of organic matter in soil. It is a remarkable reserve of nutrients that are continuously assimilated to the cycles of growth of several organisms that comprise the ecosystem (Gregorich *et al*., 1994).

The bags containing the samples were buried in 10cm deep common soil furrows (without treatment). In soil, the furrows were moulded by establishing the distance of 40cm between samples with similar concentrations and 100cm between samples with different concentrations. In the Microbial Biomass Carbon (MBC) performed with the KCF and KC samples in the 0.5 and 2.5g masses, the term 'witness' was used to identify the white, reference point and, therefore, the soil samples in which no analyzed samples were buried (Figure 2).



0.5 g masses of the soil



2.5 g masses of the soil

Figure 2: Microbial biomass carbon analysis of KCF, KC whith 0.5 and 2.5 masses of the soil.

4. CONCLUSIONS

- It was possible to see in MEV analyses the formation of microbial biofilms in 8h in KC samples and during the collecting periods (8, 12 and 72h) it was possible to see the gradual growth of KC bacterial cells when

compared to the KCF samples, indicating that the chitosan film coating act as a substrate to the microorganisms, inducing their growth.

- It was observed in all samples the gradual reduction of masses in relation to the times of collection and even more in the degradation behavior regarding the KC and KCF samples. The KSR, KC samples presented increasing degradation percentage, indicating that they were degraded.
- In relation to mechanical properties, the coating did not significantly change the properties of elongation and tensile strength of the Kraft paper sheets.

5- ACKNOWLEDGEMENTS

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5- REFERENCES

- ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **ABNT NBR 10.004** Sistema Nacional de Metrologia, Normalização e Qualidade Industrial, -Classificação de Resíduos Sólidos, 1987.
- ASTM D685-93(2007) Standard Practice for Conditioning Paper and Paper Products for Testing (**Withdrawn 2010**)
-ASTM D823-93- Standard test method for tensile properties of paper and paperboard using constant-rate-of-elongation apparatus, ***ASTM Book of Standards***, Philadelphia, PA, 1997.
- Bordenave, N., Grelier, S., Pichavent, F., Coma, V. Water and moisture susceptibility of chitosan and paper-based materials: Structure-property relationships. ***Journal of Agriculture Food Chemistry*** 2007. 55(23), pp 9479-9488.
- Cárdenas, G., Amaya, P., Plessing, C., Rojas, C., Sepúlveda, J. Chitosan composite films. Biomedical applications. ***Journal of Material Science: Material Medical*** 2008, 19, pp. 2397-2405.
- Despond, S., Espuche, E., Cartier, N., Domard, A., Barrier properties of paper-chitosan and paper-chitosan-carnauda wax films. ***Journal of Applied Polymer Science*** 2005, 98, pp 704-710.
- Gregorich, E.G.; Carter, M.R.; Angers, D.A.; Monreall, C.M.; Ellert, B.H. Towards a minimum data set to assess soil organic-matter quality in agricultural soils. ***Canadian Journal of Soil Science***, Montreal, v.74, p.367-385, 1994.
- Kjellgren, H., Gällstedt, M., Engström, G., Järnström, L. Barrier and surface properties of chitosan-coated greaseproof paper. ***Carbohydrate Polymers*** 2006, 65, pp 453-460.
- Matsui, K.N., Lorotonda, F.D.S., Paes, S.S., Luiz, D.B., Pires, A.T.N., Laurindo, J.B. Cassava bagasse-Kraft paper composites: Analysis of influence of impregnation with starch acetate on tensile strength and water absorption properties. ***Carbohydrate Polymers*** 2004, 55, pp 237-243.
- Melo, I. S. Microbiologia Ambiental. 2ª ed. – Embrapa Meio Ambiente – Jaguariúna/SP, 2008. Laboratory of ***Environmental Microbiology of Embrapa Meio Ambiente***.
- Muzzarelli, R.A.A. Chitosan-based dietary foods. ***Carbohydrate Polymers***,v.29,p.309-316, 1996.
- Massadier-Nageotte, V., Pestre, C., Cruard-Pradet, T., Bayard, R. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. ***Polymer degradation and stability***, v.91, p.620-627, 2006.
- Rhim, J.W., Lee, J.H., Hong, S.I. Increase Water Resistance Paperboard by Coating with poly(lactide). ***Packaging Technology and Science*** 2007, 20, pp 393-402.
- Sothornovit, R. Effect of hydroxypropyl methylcellulose and lipid on mechanical properties and water vapor permeability of coated paper.
- VANCE, E.D.; ROOKES, P.C.; JENKINSON, D.S. An extraction method for measuring soil microbial biomass C. **Soil Biology & Biochemistry**, Oxford, v.19, p.703-707, 1987.
- Wu, J.; Joergensen, R.G.; Pommerening, B.; Chaussod, R.; Brookes, P.C. Measurement of soil microbial biomass C by fumigation-extration-an automated procedure. **Soil Biology Biochemistry**, 22, 1167-1169, 1990.