INVESTIGAÇÃO EXPERIMENTAL SOBRE CORANTES NATURAIS / REVESTIMENTOS DE QUITOSANA APLICADOS EM EMBALAGEM CELULÓSICA

EXPERIMENTAL RESEARCH ON NATURAL COLORS / COATINGS OF CHITOSAN APPLIED IN CELLULOSIC PACKAGING

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RESUMO

A indústria de embalagem é um dos setores mais importantes da economia, reconhecido e diagnosticado como estratégico para a sociedade. Com isso, tecnologias têm surgido visando o desenvolvimento sustentável e a procura por materiais que minimizem os danos ao meio ambiente. Paralelamente à necessidade de inovação, garantia de qualidade e praticidade a ser propiciada ao consumidor, existe a preocupação com seu destino final de forma econômica e ambientalmente correta. Inseridos nesse contexto, estão as embalagens celulósicas e a substituição de revestimentos à base de polímeros sintéticos por polímeros naturais. No presente trabalho, foram desenvolvidos revestimentos à base do biopolímero quitosana com a adição dos corantes naturais: antocianina e urucum (*Bixa Orellana* L.), intitulados PCA2 e PCU2, respectivamente. Amostras de papel (277 g/m²) foram revestidas e caracterizadas quanto à Microscopia Eletrônica de Varredura (MEV), espessura, gramatura e propriedades de barreira: WVPR, COBB e resistência à tração. As análises de gramatura e resistência à tração não apresentaram diferenças estatísticas. Houve redução de WVPR da ordem de 38,6% e 24,2% para as amostras de PCA2 e PCU2, respectivamente, quando comparadas às amostras sem revestimento (PU). Fato semelhante ocorreu com a análise COBB, houve redução da ordem de 14,8% e 29,62%.

Palavras-chave: Embalagens, Quitosana, Corantes Naturais, Revestimento

ABSTRACT

The packaging industry is one of the most important sectors of the economy, recognized and diagnosed as strategic for society. With this, technologies have arisen aiming at sustainable development and the search for materials that minimize damages to the environment. At the same time, the need for innovation, quality assurance and practicality to be offered to the consumer, there is concern about its final destination in an economical and environmentally correct way. Included in this context are the cellulosic packaging and the substitution of coatings based on synthetic polymers by natural polymers. In the present work, coatings based on the chitosan biopolymer were developed with the addition of natural dyes: anthocyanin and urucum (*Bixa Orellana* L.), entitled PCA2 and PCU2, respectively. Samples of paper (277 g/m²) were coated and characterized as Scanning Electron Microscopy (SEM), thickness, weight and barrier properties: WVPR, COBB and tensile strength. Weight and tensile strength analyzes showed no statistical differences. There was a reduction of WVPR of the order of 38.6% and 24.2% for the PCA2 and PCU2 samples, respectively, when compared to uncoated samples (PU). Similar fact occurred with the COBB analysis, there was reduction of the order of 14.8% and 29.62%.

1. INTRODUCTION

The growth of the global packaging market is being driven by a number of general trends such as increasing urbanization, construction investments, health sector expansion and the rapid development still evident in emerging economies (Sarantópoulos & Rego, 2012). In the packaging segment, the main factors of influence are: the consumer, the new distribution channels and the environmental aspects (Madi, 2000). Concerns about the environment has been discussed in this sector, at the same time, issues of inadequate disposal also cover this aspect, since the design of the packaging itself to its disposal. Various types of compounds are widely used in a paper production process. For instance, fillers, adhesives, plasticizers, dyes and other additives which are used to improve the functional and visual properties of the final product (Nowacka *et al.*, 2018).

In this case, it can be stated that the concern with the discard of synthetic packaging, the reduction of oil reserves, the search for new objective, feasible and cost effective methods, which besides maintaining the integrity of the product, confers quality, safety and consumer confidence (Aider, 2010). Another way to ensure consumer safety is to make sure that your product after used will not collaborate with the already high level of environmental pollution, even if visually, when disposed of in landfills and dumps control and / or reliable information about its final destination. In this context, the use of natural polymers in the development of flexible packaging have been studied as a way of guaranteeing sustainability of the same, as well as coatings based on biopolymers, applied in cellulose packaging. Biodegradable polymers derived from renewable resources are highlighted as the future generation of packaging materials, like Poly (lactic acid) (PLA), starch, cellulose, chitosan, agar, alginate, proteins are some of the biopolymers that can be named in this large class of materials (Souza & Fernando, 2016).

Among the natural polymers, chitosan has aroused interest, since it is biodegradable indeed, it comes from renewable sources, besides being able to form filmogenic solutions that can be used as coatings, mainly due to the performance of its functional groups. In their work, Fráguas *et al.*

(2015) produced chitosan films from the 0.5% concentration, and observed that they were homogeneous, thin, transparent and flexible, in addition to having basically the same functional groups. Muzzarelli (2001) states that acidic aqueous solutions of chitin form films or coatings of chitosan and can be used for coating surfaces. In this way, it is possible to assure that many applications of chitosan have been suggested. The most studied topics are: protein removal, metal ion removal, effluent treatment and applications in the textile and paper industry (Peter, 2002). It can also be used as a protective film in the application of packages (Kittur *et al.*, 1998). Second, Tan *et al.*, (2015), affirmed the introduction of hydrophobic substituents into the glycosidic groups can improve the overall hydrophobicity of chitosan. This will increase your surface activity which plays a huge role in the incorporation and controlled release of insoluble water and therefore may be of great importance in packaging applications.

In this context, the structural interaction of chitosan is determined by the amine group. The electron double that is free on the nitrogen atom of amine group. The more the deacetylation, more is the number of free amine groups for interactions. The interaction is dependent on several properties such as pH, concentration of metallic ions, the size, solvents, nature of chitosan (whether protonated or deprotonated) etc. Stronger interactions lead to multi layers from oriented fibres. Further modifications in interactions can be modulated by chemical conjugation of chitosan with other groups (Annapoorna *et al.*, 2018).

Another advantage of using the chitosan biopolymer in the packaging sector is the use of the polymer matrix as coatings that can be used in several areas, such as obtaining intelligent packaging, which acts as an indicator of the internal characteristics of the packaged product. Coating with natural dyes is still poorly studied, but it has been found in the literature tests of barrier properties in coatings in the researches of Kuusipalo *et al.*, (2005) studying the effects of chitosan films applied as coating on sheets of paper (90 g / m²), found a slight improvement of the mechanical properties and reduction of water absorption. Ham-Pichavant *et al.*, (2005) researching the use of chitosan as a coating on

sheets of Kraft paper, found good barrier to fat.

Studies can be carried-out for establishing new protocols of chitosan film processing involving economical and natural ingredients avoiding the use of costly chemicals. The availability of chitosan sources is still constrained which limits the mass production of chitosan at industrial scale, so in this context, the studies should be focused on exploring new and easily accessible sources of chitosan. Research can be undertaken for finding novel sources of plant extract, as many novel plant extracts with possible desirable attributes are still unexplained in terms of their applications in chitosan blend films (Mujtaba *et al.*, 2018).

On the other hand, the use as a coating on the packaging is advantageous and promising application. On the packaging coating is commonly used to add a thin layer of a plastic on to the surface of another plastic film or, more commonly, onto a nonplastic substrate, such as paper, cellophane, or foil. The Coating can improve barrier properties and also helps to avoid the base material directly contacting the product, helps to impart heat sealability for plastics that are not heat sealed easily, and protects base materials, such as paper or cellophane from moisture. These coating is usually in the form of a solution, a suspension, or a melt (Fellows, 2016), (Mangaraj *et al.*, 2009).

As a way of exemplifying, we can include the cellulosic packages coated with polymer solutions composed of biopolymer + dyes and, in the case of dyes, aiming sustainability of the obtained packages, nothing more indicated than replacing the dyes commonly found in the market, such as natural dyes. Several researches are being developed to evaluate the application of chitosan films to the surface or even during the papermaking process; as well as the characteristic of the biopolymer chitosan with its ability to act as a vehicle for addition of various additives, such as lipids, dyes and others. That researches aim to improve the mechanical and barrier properties, and to reduce the amount of chemical additives in packaging and paper-based packaging systems. Wiczorek & Mucha (1997) studied the application of chitosan solution in Canson paper sheets (brand CO, France) and observed an increase in mechanical properties (tension at rupture and elongation).

The same result was obtained by Kamel *et al.*, (2004), by immersing sheets of paper in chitosan solution, observing an increase in tear

stress and tearing factor, results attributed to the greater number of interfiber bonds and the compatibility between chitosan and paper sheet fibers. Bordenave *et al.*, (2007) found no statistically significant differences for the paper coated with chitosan. Novel polymer blend combinations can be investigated for blending chitosan-based film, which will enable the chitosan-based films to compete for the commercially available packaging materials (Mujtaba *et al.*, 2018).

The substitution of these synthetic compounds on the packaging surface and the use of natural dyes. These can be derived from plants, animals and microorganisms presenting the different colors and functional properties (Hasler, 2000). Among the natural dyes that stand out most for industrial application are anthocyanins, urucum (*Bixa Orellana* L.), cochineal carmine, curcumin, betalains and chlorophylls, which due to their natural characteristics and their specifics can be used in the development of active and intelligent packaging. Demczuk *et al.*, (2015) relatam que após a industrialização do urucum, são gerados em média 96% de resíduos, que depois de secos e triturados podem ser reutilizados. a diversidade de produtos que podem ser obtidos a partir das sementes de urucum é útil para satisfazer a necessidade de aplicação em vários tipos de alimentos industrializados.

Demczuk *et al.*, (2015) report that after the industrialization of annatto, 96% of the residues are generated, which after drying and crushing can be reused. the diversity of products that can be obtained from urucum seeds is useful to meet the need for application in various types of industrialized foods. Silva *et al.*, (2006) reported that the urucum seed improves the egg yolk pigmentation of laying hens fed with high levels of sorghum in the feed, assigning to the by-product up to 12% inclusion in the feed. Albach *et al.*, (2016), extracted norbixin dye from urucum seeds via alkaline hydrolysis and then used as a graft in poly-ethylene-vinyl alcohol copolymer (EVAL). This guarantees the increase of applications, since EVAL is already widely used in packaging. Choi *et al.*, (2017) developed potato starch films with anthocyanins, resulting in a colorimetric non-toxic pH indicator film, denoting their potential for applications in intelligent food packaging materials.

Dyes derived from urucum are extensively used in the food industry. Its peculiar

characteristics such as the one that makes it possible to obtain water soluble or liposoluble dyes from small changes in the production processes was one of the success factors of this pigment. Medina-Flores *et al.*, (2016) study results partially validate the *Bixa Orellana* L. applications in the odontology field, with antimicrobial properties and a non-toxic profile. It is observed recently, on the last five years; efforts have been devoted to the study of physicochemical characteristics of the different structures of carotenoids that participate in the so-called annatto dye (Von Elbe, 2000). Anthocyanins are compounds of the flavonoid family and constitute a group of pigments responsible for most of the colors in flowers, fruits, leaves, stems and plant roots (Markakis, 1982). Anthocyanins are natural water-soluble pigments that have wide response ranges to pH variation (Zhai *et al.*, 2017). Among plant-based natural dyes, anthocyanins have a sensitive color reaction to wide pH ranges (Choi 2017). Zhai *et al.*, (2017), developed a pH sensing film by incorporating anthocyanins extracted from *Bauhinia blakeana* Dunn with chitosan and the pH sensing film presented a distinguishable color change from purple to green due to the basic volatile gases generated from the fish, suggesting that the anthocyanins-based colorimetric films were good candidates of gas sensors for monitoring fish freshness.

In this context, in the present work two types of coatings were developed: one chitosan based coating containing the natural urucum (*Bixa Orellana* L.) dye and other chitosan based coating containing the anthocyanin natural dye, were studied. In order to do so, two types of coatings titled PCA2 and PCU2 were produced, corresponding to the coatings: Chitosan 1%+Anthocyanin 2% and Chitosan 1%+Urucum 2%, respectively. Both coating were applied on sheets of 277 g/m² card paper, in the proportion of 0.752 mL_{solution}/mm². After coating, the sheets of card paper were subjected to the characterization of the barrier properties from packaging system. The objective was to evaluate the performance of coated papers compared to uncoated paper.

2. MATERIAL AND METHODS

2.1 Material

For the accomplishment of the present

work the following materials were used: Chitosan (Polymar-Brazil); Acetic Acid (Shynth); Anthocyanin AC 12r WSP donated by CHR HANSEN; Urucum A-720-WS-AP donated by CHR HANSEN and sheets of bleached Kraft paper, 277 g/m² weights supplied by Klabin. Monte Alegre/PR-Brazil.

2.2 Methods

2.2.1 Preparation of chitosan film-forming solution

The preparation of the film-forming solution was carried out by dispersing 1% chitosan (by mass) in acidic aqueous solution under continuous agitation for 60 minutes and heating to 50 °C.

2.2.2 Preparation of chitosan film-forming solution with addition of dyes

After preparation of the fimogenic solution of chitosan, natural dyes were added in proportions of 2% (by mass), both for the addition of anthocyanin and urucum (Table 1).

Table 1. Composition and abbreviations of chitosan film-forming solution

Initials	Coating	(%)
CA2	Chitosan solution with anthocyanin	1.0 chitosan + 2.0 anthocyanin
CU2	Chitosan solution with urucum	1.0 chitosan + 2.0 urucum

2.2.3 Application of coatings

The application of the film-forming solution, that is, of the coatings, on the sheets of card paper was carried out with the aid of a 40.0 µm stainless steel extension bar (TKB Ericken, Brazil). The sheets of paperboard were fixed to a metal support and then 4.0 mL of film-forming solution were distributed, yielding a distribution of 0.752mL_{solution}/mm², and then the sheets of paperboard already coated were subjected to the oven drying process at 100 °C for a period equal to 90 seconds. At the end of the application process of the different types of coating, in order to facilitate the discussion of the results, the nomenclatures were determined: PU, PCA2, PCU2 (Table 2).

Table 2. Composition and abbreviations of chitosan coatings

Initials	Coating	(%)
PU	Uncoated Paper	-
PCA2	Coated paper with chitosan solution and anthocyanin	1.0 chitosan + 2.0 anthocyanin
PCU2	Coated paper with chitosan solution and urucum	1.0 chitosan + 2.0 urucum

2.2.4 Characterization of sheets of paper

The sheets of card paper were characterized as the analyzes of: thickness, weight, and barrier properties: rate water vapor permeability and water absorption (COBB method).

2.2.5 SEM - Scanning Electron Microscopy

The Scanning Electron Microscopy SEM analysis was performed at the Chemistry Institute of the Federal University of the Jequitinhonha Valleys and the Mucuri-Campus JK-Diamantina / MG. The samples were cut with a stylet of 1cm x 1cm dimensions, submitted to a gold bath and then analyzed using the Shimatzu benchtop SEM equipment.

2.2.6 Thickness

The thickness was determined according to the NBR NM-ISO 534 (2011). A micrometer of the Lorentzen & Wettre brand was used, with contact area equal to $200 \pm 10 \text{ mm}^2$ and pressure exerted on the sample of $100 \pm 10 \text{ kPa}$. Five specimens of each sample were evaluated. The results were expressed as μm .

2.2.7 Grammage

The weight test was based on the methodology described in the standard ASTM D 646-96 (1997). The specimens were cut in size $130 \times 130 \text{ mm}$ with the aid of a standard device and weighed in the Mettler model AE 163 analytical balance. Ten specimens were evaluated for each sample analyzed. The results were expressed in g/m^2 .

2.2.8 Barrier properties

A determinant parameter in the barrier properties is the structural characteristic of the polymer matrix. Matrices formed by simple linear polymer chains lead to increased packaging and consequently to films with low permeability, whereas polymer chains formed by bulky side groups lead to a poorly packed matrix (increase in free spaces) and an increase in permeability McHugh et al., (1994), Robertson, (1993). The barrier properties of plastic films can be varied by changing the film thickness, orientation of polymer molecules, and amount and type of additives, and by coating, lamination, and so on (Alavi et al., 2015). Packaging materials with sufficient barrier properties need to be used according to the shelf life and storage temperature characteristics of the specific products (Tajeddin et al., 2018). On the packaging Coating is commonly used to add a thin layer of a plastic onto the surface of another plastic film or, more commonly, onto a nonplastic substrate, such as paper, cellophane, or foil.

The Coating can improve barrier properties and also helps to avoid the base material directly contacting the product, helps to impart heat sealability for plastics that are not heat sealed easily, and protects base materials, such as paper or cellophane from moisture. These coating is usually in the form of a solution, a suspension, or a melt (Tajeddin et al., 2018).

2.2.8.1 Water Vapor Permeability Rate (WVPR)

The water vapor permeability rate was determined for the $23^\circ\text{C} / 75\% \text{ RH}$ condition by the gravimetric method, based on ASTM methodology ASTM E96-05, 96M-05 (2005). This method is based on weight gain of anhydrous calcium chloride (desiccant agent), placed inside an aluminum cap and isolated from the conditioning environment by the material whose WVPR is to be known. The effective permeation area of each specimen was 50 cm^2 . The weight gain was quantified in the Mettler analytical balance, model AT 400, with a resolution of 10^{-4} g . The conditioning was done in Patra chamber. Four specimens of each sample were analyzed. The results were expressed in $\text{g} \cdot \text{water} \cdot \text{m}^{-2} \cdot \text{dia}^{-1}$ and calculated according to equation 1.

$$WVPR = \frac{\Delta m}{\Delta t} \times \frac{1}{A} \quad (\text{Eq.1})$$

At where: WVPR = Water Vapor Permeability Rate to water vapor ($\text{g} / \text{m}^2 \cdot \text{day}$); Δm = mass of water absorbed by hygroscopic material at time "t" (g); A = area of exposed specimen (m^2); Δt = permeation time (days).

2.2.8.2 Water Absorption (COBB)

The water absorption test was determined according to the norm ISO 535, (2014). The weight gain was monitored on an analytical balance Mettler AE 163. The results were expressed in g/m^2 . This test was performed with five specimens of each sample, using the mean as the final result, calculated by equation 2.

$$Abs = (M_f - M_i) \times 100 \quad (\text{Eq.2})$$

At where: Abs = water absorption (g/m^2); M_i = initial mass of the specimen; M_f = final mass of the specimen.

2.2.9 Mechanical properties

The mechanical properties define the behavior of the material when subjected to external loads, its ability to resist or transmit these forces without fracture or uncontrolled deformation.

Films and coatings that have good barrier properties may be rendered inefficient if the mechanical properties do not maintain their integrity during handling, packaging, transport and commercialization Debeaufort *et al.*, (1998). According to Von Elbe, (2000), the mechanical and barrier properties of films and edible coatings are highly associated with the polarity of the constituents of the film-forming solutions. In the present study, tensile strength tests analyzes were performed according to the standard norm ASTM D774-96a (1997).

3. RESULT AND DISCUSSION

3.1 Films after drying period

As a way of illustrating the characterization of the coatings applied on the sheets of paper, after the homogenization of the chitosan filmogenic solutions containing the dyes, these were distributed in petri dishes and exposed to drying for 48hrs in a forced circulation chamber at 40°C , Chitosan films with the addition

of anthocyanin and urucum dyes, titled CA2 and CU2, respectively (Figure 1).

Figure 1. Chitosan films with addition of dyes

For the evaluation of the thickness of the coating applied in the packaging systems cardboard, scanning electron microscopy taken with side view and view in the interface.

3.1.1 Scanning Electron Microscopy

Scanning Electron Microscopy analysis offers advantages in the investigation of both rough and smooth surfaces, from flat, lateral views or to particular fractures. In the present work, lateral-view analyzes were performed on samples CA2 and CU2 (Figure 1) and on samples PU, PCA2 and PCU2 (Figure 2), both at 200-fold magnifications.

Figure 2. SEM analyses side view of samples: CA2, CU2 (films) and PU, PCA2, PCU2 (Coatings).

As shown in Figure 2, in the PU sample, it was possible to view the paper fibers more loosely, probably after the stylus sample was cut, there was a change in the uncoated paper structure. Differently, in the samples PCA2 and PCU2, it can be seen that the fibers remained grouped even after being cut with stylus.

Also in Figures PCA2 and PCU2 it was possible to visualize the coatings layer (CA2 and CU2) applied to the sheets of paper. As shown in Table 3, it is possible to observe such occurrence by the results obtained in the thickness analysis: 407 μ m, 416 μ m, 420 μ m corresponding to the samples PU, PCA2 and PCU2, respectively.

3.1.2 Grammage and Thickness Analysis

The grammage and thickness analyzes were determined in the samples with and without coatings (Table 3), with results referring to 10 determinations. Coating application showed a statistically significant increase in paper grammage, on the order of 1.1% over uncoated paper (PU Sample). However, the type of coating did not present significant difference in the value of the grammage.

As shown in Table 3, there were no statistically significant differences between the PU, PCA2 and PCU2 samples. According to Sarantópoulos *et al.*, (2002), this test is a useful determination for evaluation and quality control, as it allows obtaining information about the performance of a packaging material. Bordenave *et al.*, (2007) evaluated paper packaging systems with different weights (40 g/m² e 320 g/m²) containing chitosan as a coating and observed that chitosan when applied as a coating promoted improved barrier properties.

Table 3. Grammage and Thickness analysis results

Samples	Average	
	Grammage (g/m ²)	Thickness (μ m)
PU	282.0 ^a	407 ^a
PCA2	284.7 ^b	416 ^{b,c}
PCU2	284.9 ^b	420 ^c

Note: different letters (a-b) in the same column represent a significant difference ($p < 0.05$) between the means obtained by the Tukey test.

As shown in Table 3, there was an increase in thickness, of the order of 2.21% and 3.19% in the samples PCA2 and PCU2, respectively, when compared with the PU sample. According to the Tukey test, the results obtained showed that the average coat thickness increased significantly in relation to the PU sample. Comparing the coatings, only the PCA2 and PCU2 samples did not present statistically significant differences. Chitosan solution prepared by dissolving 2g chitosan in 100 ml of 2% malic acid had the highest thickness, which is resulting from the protruded structure of CR (Brodnjak, 2017). In this case, the components in blend coating solutions affected the alignment and compacting the molecules during the drying of the papers and consequently causing the differences in thickness.

The thickness is an important parameter, since this analysis is directly related to the homogeneity of the material. According to Garcia, *et al.*, (1989), little variation in thickness guarantees a uniform mechanical performance, besides minimizing irregularities in the barrier properties. Besides that, the interactions between different polymeric chains in coatings can be promote a change in a bulk. Changes in moisture and water barrier properties proved retained water in coating structure. The thickness of a paper coating has a strong influence on many properties such as tensile properties, moisture, water vapor permeability and water absorption capacity (Brodnjak, 2017). In present work as for the properties of the paper, the weight and thickness have undergone significant changes with application of the coatings.

3.2 BARRIER PROPERTIES

3.2.1 Water Vapor Permeability Rate (WVPR)

The moisture barrier is measured as the water vapor permeability rate, which is the

amount of water passing through a unit area of the package per unit time at a given temperature and relative humidity. The water vapor permeability rate was determined under the conditions in the papers with and without coating, 23°C / 75% RH. (Table 4).

Table 4. Results of WVPR analysis

Samples	WVPR (g.água.m ⁻² .dia ⁻¹)
	Average
PU	500 ^a
PCA2	307 ^b
PCU2	379 ^c

Note: Different letters (a-b-c) in the same column represent a significant difference (p <0.05) between the means obtained by the Tukey test.

3.2.2 Water Absorption (COBB)

The water absorption of the paper is a parameter that measures the ability of the sheet to absorb water when exposed to direct contact. According to Noletto, (2010), a low absorption value means a greater difficulty of penetration of water, preventing the loss of mechanical resistance of the material. The water absorption test was performed on the inside of the sheets of paperboard (uncoated) and on the outside of the coated and uncoated samples (Table 5).

The properties of paperboard are adversely affected by moisture, weakening the highly porous paper fibres, and consequently reducing paperboard strength. During the production of paperboard, inaccurate control of moisture content can lead to many problems. Too much moisture content could cause the softening of the paperboard leading to collapse and flute exposure after production while low moisture content could lead to the paperboard being crisp and easy to breakdown (Fadiji *et al.*, 2018). According Dang *et al.*, (2018), Because of the large surface pores and high swelling potential of the highly beaten fibers, the base paper is prompted to absorb water.

Table 5. Results of COBB analysis

Samples	Water Absorption (g/m ²) Internal / External	
	Average Internal	Average External
PU	38 ^a	27 ^a
PCA2	36 ^a	23 ^b
PCU2	37 ^a	19 ^c

Note: different letters (a-b-c) in the same column represent a significant difference (p <0.05) between the means obtained by the Tukey test.

As Table 5 shows, the COBB analysis did not show statistically significant differences in the internal direction. However, for the analyzes carried out in the external direction, the PCA2 and PCU2 samples showed a reduction of the absorption capacity of the order of 14.81% and 29.62%, respectively, when compared with the PU sample.

In this test, no statistically significant changes in water absorption were observed, since the inner part of the analyzed samples was not coated. Thus, it can be said that the coating applied on the outside of the paper did not influence the absorption of water in the part under analysis. A significant reduction in the water absorption of the coated samples was observed. The PCA2 sample reduced water absorption capacity by 15% and the PCU2 sample showed reductions of 33 and 30%, respectively, when compared to the PU sample.

Regarding the performance between the dyes, it was observed in this test that the anthocyanin had a higher water absorption, which may be associated with the chemical structure of this, since this dye is a phenolic compound, soluble in water, contributing to the formation of hydrogen bonds with water molecules. The coatings provided a decrease in the water absorbency of the paperboard. Urucum was the dye that presented better performance in this analysis with reduction above 30% when compared to the PU sample.

3.3 MECHANICAL PROPERTIES

3.3.1 Tensile Strength (internal and external)

The tensile strength test was based on the methodology described in the standard norm ASTM D774-96a (1997). The guillotine was used

to obtain specimens with a width of $15.0 \pm 0.1\text{mm}$ and 200mm in length. The assay was performed in an Instron Universal Test Machine model 5500R, using a 1kN load cell and clamp spacing speed of 20mm/min. The initial distance between the claws used was 180mm. Ten specimens from each sample were analyzed. The tensile strength was expressed in kgf /15mm. As paper is considered an anisotropic material, since fibres are aligned in the direction of travel in the papermaking machine (i.e. MD direction) and across the fibre alignment called cross-machine direction (i.e. CD direction), tests were performed in both directions (Table 6).

Table 6 - Results of the tensile strength test (kgf/15mm)

Sample	Direction	Average
PU	MD	26 ^a
	CD	15 ^a
PCA2	MD	27 ^a
	CD	16 ^a
PCU2	MD	27 ^a
	CD	16 ^a

MD=Machine Direction; CD= Cross-machine Direction.

Note: different letters (a-b-c) in the same column represent a significant difference ($p < 0.05$) between the means obtained by the Tukey test.

When evaluating the tensile strength, the extension and the tensile energy absorption for these parameters can aid in predicting the performance of paper and paperboard, particularly when the material (paper and paperboard) is subjected to uneven stress (Fadiji *et al.*, 2018). Tensile strength at break are very important for packaging materials, due to the specific handling and shipping of the products. The reason is also in the interface of the coating materials with molecular interactions among the fibres (Khwaldia, 2013).

An increase in the mechanical properties of CNF-coated samples especially at higher coat weight compared to the uncoated samples is observed, however this improvement is not considerable. The improvement in tensile index in MD and CD is around 10% and 20% at maximum, respectively and for bending stiffness an increase about 15% at maximum in both directions (Mousavi *et al.*, 2018). In the present work the addition of colors in the solution of chitosan has not affected the properties tensile

strength.

4. STATISTICAL ANALYSIS

For statistical analysis, the Tukey's test was used in order to evaluate the difference between means, with significance level $p < 0.05$.

5. CONCLUSIONS

Based on the results obtained in the analyzes of TPVA, Cobb, Weight, Thickness it was possible to conclude that natural dye based coatings are innovative developments that can be a real alternative with great potential of application and partial substitution of synthetic additives in sheets of card paper.

The PCA2 and PCU2 coatings presented visible adhesion when applied to the sheets of paper, which can be confirmed by SEM and thickness analyzes. By the formation of the layer on the sheets of paper, as well as by the increase of thickness, when compared to the sample PU.

In addition, being a system made up of natural materials, the technology adopted is environmentally and economically viable. Another perspective is to use such coatings as supporting in the development of active and intelligent packaging. However, further results are still needed, such as mechanical properties analysis.

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7. REFERENCES

1. Aider, M. Chitosan application for active bio-based films production and potential in the food industry. *Food Science and Technology*, **2010**, 43, 837-842.
2. Alavi, S., Thomas, S., Sandeep, K.P., Kalarikkal, N., Varghese, J., Yaragalla, S. "Polymers for Packaging Applications". Apple Academic Press, Oakville, Canadá.

2015.

3. Albach, B., da Silva, T. A., Barbosa, R. V. Síntese do Eval-g-norbixina: Aplicação como um Pigmento em Polímeros. *Rev. Virtual Quim.* **2016**, 8, No. 5, 1550-1559.
4. American Society for Testing and Materials - ASTM Book of Standards, Philadelphia, PA. ASTM D646-96 - Standard test method for grammage of paper and paperboard (weight per unit area), **1997**.
5. American Society for Testing and Materials - ASTM Book of Standards, Philadelphia, PA ASTM D774-96a-Standard test method for bursting strength of paper, **1997**.
6. American Society for Testing and Materials - ASTM Book of Standards, Philadelphia, PA. ASTM E96/E 96M-05. Standard Test Methods for water vapor transmission of materials, **2005**.
7. Bordenave, N., Grelier, S., Pichavant, F., Coma, V. Water and Moisture Susceptibility of Chitosan and Paper-Based Materials: Structure–Property Relationships. *Journal of Agricultural and Food Chemistry*, v. 55, **2007**, 9479-9488.
8. Brodnjak, U.V. Experimental investigation of novel curdlan/chitosan coatings on packaging paper. *Progress in Organic Coatings*. 112, **2017**, 86–92.
9. Choi, I., Lee, J. Y., Lacroix, M., Han, J. Intelligent pH indicator film composed of agar/potato starch and anthocyanin extracts from purple sweet potato. *Food Chemistry*. 218, **2017**, 122–128.
10. Tan, C., Zhang, Y., Abbas, S., Feng, B., Zhang, X., Xia, W., Xia, S. Biopolymer–Lipid Bilayer Interaction Modulates the Physical Properties of Liposomes: Mechanism and Structure, *Journal of Agricultural and Food Chemistry*. 63, 32, **2015** 7277-7285.
11. Dang, C., Yin, Y., Xu, M., Pu, J. Hydrophobic noncrystalline porous starch (NCPS): Dispersed silver nanoparticles suspension as an antibacterial coating for packaging paper. *BioResources*. 13,1. **2018**, 192-207.
12. Demczuk, B. Jr., Ribani, R. H. Atualidades sobre a química e a utilização do urucum (*Bixa orellana* L.). *Revista Brasileira de Pesquisa em Alimentos*. 6,1, **2015**, 37-50.
13. Debeaufort, F., Quezada-Gallo, J. A., Voilley, A. Edible films and coatings, tomorrow's packagings: A Review, *Critical Reviews in Food Science*. 38, **1998**, 299-313.
14. Fadji, T., Berry, T. M., Coetzee, C. J., Opara, U. L. Mechanical design and performance testing of corrugated paperboard packaging for the postharvest handling of horticultural produce. *Biosystems Engineering* 171, **2018**, 220-244.
15. Fellows, P.J. *Food Processing Technology: Principles and Practice*. Woodhead Publishing, Cambridge, UK. **2016**.
16. Fernando, A.L., Souza, V.G. Nanoparticles in food packaging: Biodegradability and potential migration to food—A review. *Food Packaging and Shelf Life*. 8, **2016**, 63–70.
17. Fráguas, R. M., Simão, A. A., Faria, P. V., Queiroz, E.R.Q., Junior, E. N. O., Abreu, C. M. P. Preparo e caracterização de filmes comestíveis de quitosana. *Polímeros*. 25, **2015**, 48-53.
18. Garcia, E.E.C; Padula, M.; Sarantópoulos, C.I.G.L. *Embalagens Plásticas: Propriedade de barreira*, **1989**, 44p.
19. Ham-Pichavant, F., Sèbe, G., Pardon, P., Coma, V. Fat resistance properties of chitosan-based paper packaging for food applications. *Carbohydrate Polymers*, 61, **2005**, 259-265.
20. Hasler, C. M. The Changing Face of Functional Foods. *Journal of the American College of Nutrition*. 19,5, **2000**, 499S-506S.
21. ISO 535 “Paper and board”. Determination of water absorptiveness-COBB method, “International Organization for Standardization, Geneva, Switzerland. **2014**.
22. ISO 534 “Paper and board”. Determination of thickness, density and specific volume. **2011**.

23. Kamel, S., El-Sakhawy, M., Nada, A.M.A. Mechanical properties of the paper sheets treated with different polymers, *Thermochimica Acta.* 421, **2004**, 81-85.
24. Khwaldia, K.Arab-Tehrany, E., Desobry, S. Biopolymer coatings on paper packaging materials. *Comprehensive reviews in food science and food safety.* 9, **2010**, 82-92.
25. Khwaldia, K. Physical and mechanical properties of hydroxypropyl methylcellulose-Coated paper as affected by coating weight and coating composition. *BioResources.* 8, **2013**, 338–352.
26. Kittur, F. S., Kumar, K. R., Tharanathan, R.N. Funcional packaging properties of chitosan films, *Z. Lebensm Unters Forsch.* 206, **1998**, 44-47.
27. Kuusipalo, J., Kaunisto, M., Laine, A., Kellomaki, M. Chitosan as a coating additive in paper and paperboard. *Tappi Journal.* 4, **2005**, 17-21.
28. Lima, L.R.P., Oliveira, T.T., Nagem, T.J., Pinto, A.S., Stringheta, P.C., Tinco, A.L.A., Silva, J.F. Bixina, norbixina e quercetina e seus efeitos no metabolismo lipídico de coelhos. *Brazilian Journal of Veterinary Research and Animal Science.* 38, 4, **2001**, 196- 200.
29. Lopes, T. J., Xavier, M. F., Quadri, M. G. N., Marinho B. Q. Anthocyanins: A brief review of structural characteristics and stability. *R. Bras. Agrociência, Pelotas,* 13, 3, **2007**, 291-297.
30. López, O.P., Jiménez, A.R., Vargas, F.D. Natural pigments: carotenoids, anthocyanins, and betalains – characteristics, biosynthesis, processing, and stability. *Critical Reviews Food Science Nutrition.* 40, 3, **2000**, 173-289.
31. Madi, L. A embalagem no século XXI – Perspectivas e Tendências. In *Brasil Pack Trends 2005: Embalagem, distribuição e consumo.* CETEA/ITAL. **2000**.
32. Mangaraj, S., Goswami, T., Mahajan, P. Applications of plastic films for modified atmosphere packaging of fruits and vegetables: a review. *Food Eng. Rev.* 1, **2009**, 133–158.
33. Markakis, P. Stability of anthocyanins in foods”. In: Markakis P (Ed) *Anthocyanins in color foods.* New York, Academic Press. **1982**, 163-180.
34. McHugh, T.H., Krochta, J.M. Permeability properties of edible films, in *Edible Coatings to Improve Food Quality.* Lancaster, Eds. J.M. Krochta, E.A. Balwin e M.O. Nisperos-Carriedo, Technomic Publishing Company, Ch.7, **1994**, 139-187.
35. Medina-Flores, D., Ulloa-Urizar, G., Camere-Colarossi¹, R., Caballero-García¹, S., Mayta-Tovalino, F., Valle-Mendoza, J. Del. Antibacterial activity of *Bixa orellana* L. (achiote) against *Streptococcus mutans* and *Streptococcus sanguinis*. *Asian Pac J Trop Biomed.* 6, 5, **2016**, 400-403.
36. Mohandas, A., Deepthi, S., Biswas, R , Jayakumar, R. Chitosan based metallic nanocomposite scaffolds as antimicrobial wound dressings. *Bioactive Materials.* **2018**, 267-277.
37. Mousavi, S. M. M., Afra, E., Tajvidi, M., Bousfield, D.W., Dehghani-Firouzabadi, M. Application of cellulose nanofibril (CNF) as coating on paperboard at moderate solids content and high coating speed using blade coater. *Progress in Organic Coatings.* 122, **2018**, 207-218.
38. Mujtaba, M., Morsi, R. E. Kerch, G., Elsabee, M. Z., Kaya, M., Labidi, J., Khawar, K. M. Current advancements in chitosan-based film production for food technology; A review. *Biomac.* **2018**.
39. Muzzarelli, R. A. A., Biagini, A., Mengucci, P., MAJNI, G., TOSI, G. Chitosan-oxychitin coatings for prosthetic materials. *Carbohydrate Polymers,* 45, **2001**, 35-41.
40. Noletto, A. P. R. Embalagens de Papelão Ondulado: Propriedades e Avaliação da Qualidade. *ITAL/CETEA.* **2010**, 62-64.
41. Nowacka, M. K. ,Rybak, A., Wiktor, A., Mika, P., Boruszewski, J., Woch, K., Przybysz, D., Witrowa-Rajchert. The quality and safety of food contact materials – paper and cardboard coated with paraffin emulsion. *Food Control,* **2018**.

42. Peter, M. G. Chitin and chitosan in Fungi chitin and chitosan from animal sources. University of Potsdam, Instituto of Organic Chemistry and Structure Analysis, Wiley-UCH, Weinheim. 6, **2002**.
43. Robertson, G. L. Optical and mechanical properties of thermoplastic polymers, in Food Packaging: Principles and Practice. New York, Marcel Dekker. **1993**. 63-107.
44. Sarantópoulos, C. I. G. L., Regos, R. A. O Mercado de Embalagem no Brasil. (Brasil pack trends 2020). ITAL/Brasil. **2012**. 231.
45. Sarantópoulos, C.I.G.L., Oliveira, L.M., Padula, M., Coltro, L., Alves, R.M.V., Garcia, E.E.C. Embalagens plásticas flexíveis - principais polímeros e avaliação de propriedades. ITAL/CETEA, **2002**, 267.
46. Si W., Wang, W., Yan, K., Ding, F., Shi, X., Deng, H., Du, Y. Electrochemical writing on edible polysaccharide films for intelligent food Packaging. Carbohydrate Polymers. 186, **2018**. 236-242.
47. Silva, J. H. V., Silva, E. L., Jordão, F. J., Ribeiro, M. L. G., Costa, F. G. P. Resíduo da semente de urucum (*Bixa orellana* L.) como corante da gema, pele, bico e ovário de poedeiras avaliado por dois métodos analíticos. Ciência e Agrotecnologia, Lavras. 30, 5, **2006**, 988-994.
48. Tajeddin, B., Ahmadi, B., Sohrab, F., Chenarbon, H. A. Polymers for Modified Atmosphere Packaging Applications. Agricultural Engineering Research Institute (AERI), Agricultural Research, Education, and Extension Organization (AREEO), Karaj, Iran, Islamic Azad University, Varamin - Pishva, Iran. **2018**.
49. Von Elbe J.H. Colorantes. In: FENNEMA, O.W. Química de los alimentos. 2ª.ed. Zaragoza: Wisconsin – Madison. 10, **2000**. 782-799.
50. Wieczoreck, A., Mucha, M. Application of chitin derivatives and their composites to biodegradable paper coatings. Faculty of process and environmental engineering, Technical University of Wólezanska, Poland, **1997**, 890-896.
51. Zhai, X., Shi, J., Zou, X., Wang, S., Jiang, C., Zhang, J., Huang, X., Zhang, W., Holmes, M. Novel colorimetric films based on starch/polyvinyl alcohol incorporated with roselle anthocyanins for fish freshness monitoring. Food Hydrocolloids, 69, **2017**, 308-317.