

# Development of temperature indicator prototype: Cardpaper coated with chitosan intelligent films

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Received October 2013

## ABSTRACT

An intelligent and biodegradable material packaging was developed based on a natural and thermal-sensitive pigment. Anthocyanin (ATH, 0.50 g/100g) was incorporated into chitosan matrix films (2 g/100g) forming a chitosan intelligent film (C-ATH). The system is able to indicate the variation of temperature during distribution and storage chain of industrial products. The novelty of this work was an alternative packaging material that it is biodegradable and could inform any temperature variations on the range of 40°C - 70°C, by irreversible visual colour changes. The effects of temperature (10°C, 30°C and 50°C) and luminosity (0, 500 and 1000 lx) were analyzed on C-ATH using an experimental design of 2 variables, measuring the colour parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) and mechanical properties (tensile strength, elongation break and Young's modulus) as responses. C-ATH suspensions were applied as a coating on cardpaper surface forming a temperature indicator prototype (TIP). C-ATH darkened after being exposed to temperatures above 50°C and luminosity of 1000 lx for 72 hours. TIP was obtained, without bubbles or defects, with reduced water absorption capacity. Irreversible visual colour change was verified on TIP exposed at 40°C independently of luminosity, turned gradually yellow. Chitosan suspensions containing ATH and applied as a coated on card paper sheets could be an alternative of biodegradable material for packaging system that indicates efficiently temperature changes. This indicator system has potential application temperature range of 40°C to 70°C, such as food, pharmaceuticals, biological, agricultural and others products, that are highly dependent of storage temperature conditions.

## KEYWORDS

Chitosan; Anthocyanin; Temperature Indicator; Coating; Card Paper

## 1. INTRODUCTION

The natural polymer films application in the packaging sector has been investigated due to their biodegradability and ability to retard the transport of moisture, gas, flavour and lipids. Films based on natural macromolecules, have been described in literature; however, industrial applications are still scarce. Among the natural polymers, chitosan forms resistant films with an efficient oxygen barrier [1,2].

Intelligent packaging is designed to monitor and communicate information about packed product quality and safety. Examples include time-temperature indicators, ripeness indicators, biosensors, radio frequency identification, etc. Colourimetric indicators can detect and monitor changes in the conditions of packed products [3] by visual colour variations.

Temperature greatly affects the quality and safety of thermal-sensitive products such as food, drugs and biological compounds. Variations in temperature conditions could promote undesirable physical and chemical deteriorations [4]. Time-temperature indicators (TTIs) are defined as simple, cost-effective and user-friendly devices to monitor, record and cumulatively indicate the overall influence of temperature traceability on the quality of the food product from the manufacturer to the consumer [5]. TTIs could be present as small self-adhesive labels that provide visual indications of temperature history during distribution and storage [6]. New types of TTIs have recently been studied; one example is a system based on the growth and metabolic activity of a strain of *Lactobacillus sakei*, which monitored food quality throughout the chilled-food chain [7]. Yan *et al.* [8] developed a new amylase-type TTI based on the reaction between amylase and starch solution, changing the colour from blue to

yellow after temperature exposure from 4°C to 37°C. Kato, Yoshida, Reis, Melo and Franco [9] developed a fast and colorimetric indicator system by combining chitosan as a three-dimensional biopolymer matrix and ferric sulfate ( $\text{FeSO}_4$ ) as a colorimetric indicator of hydrogen sulfide ( $\text{H}_2\text{S}$ ) gas. Maciel, Yoshida and Franco [10] developed an intelligent and biodegradable temperature indicator packaging material based on a natural and heat-sensitive pigment and chitosan solution dispersing on card paper.

In this study, the objective was to develop an intelligent and biodegradable alternative packaging material based on a natural polymer, chitosan, and thermal-sensitive pigment (anthocyanin, ATH) that visually change the colour after temperature exposition in a specific range. The efficiency response of this system was analysed by the changes in colour parameters. The mechanical properties were measured.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Chitosan (Primex, Iceland; degree of acetylation (DA) of 18% and molecular weight ( $M_w$ ) of  $238,000 \text{ g}\cdot\text{mol}^{-1}$ ), acetic acid (Synth, Brazil), anthocyanin (Christian Hansen, Brazil) and card paper triplex TP 250  $\text{g}\cdot\text{m}^{-2}$  (Suzano Papel e Celulose Ltd., Brazil) were used.

### 2.2. Chitosan Intelligent Films (C-ATH)

Film suspensions were prepared by dispersing chitosan (2.00 g/100g) in aqueous acetic acid [10]. The stoichiometric amount of acetic acid was calculated from sample weight, taking into account the value of DA to achieve the protonation of all the  $\text{NH}_2$  sites [2]. The suspensions were homogenized by magnetic stirring at room temperature for 45 minutes. The ATH (0.50 g/100g) was added to the filmogenic suspension and homogenized. Aliquots of 9.0 mL were poured into Petri dishes (9.5 cm) and dried at room temperature for 36 hours and then kept at 28°C in an incubator with forced air circulation for 24 hours. As the mass suspension used to cast the C-ATH was kept constant, the total solid content per gram of dried films was  $28.2 \text{ g}\cdot\text{m}^{-2}$ .

#### 2.2.1. Experimental Design

The experimental design was applied to study the temperature and luminosity effects on the colour of C-ATH (Table 1). The luminosity range was from dark exposure (0 lx) to simulation of supermarket light (1000 lx). The time of exposure to temperature and luminosity conditions established was 72 hours.

#### 2.2.2. Mechanical Properties

Tensile strength (TS), elongation at break ( $\epsilon$ ) and

**Table 1.** Values range used in experimental design of two variables.

Variables	-1	0	+1
Temperature (°C)	10	30	50
Luminosity (lx)	0	500	1000

Young's Modulus (E) were determined on C-ATH based on ASTM Standard method D882 [11]. Films were cut into  $25.4 \times 100.0 \text{ mm}$  strips and preconditioned at 50% relative humidity (RH) and  $25^\circ\text{C} \pm 2^\circ\text{C}$  for 48 hours. Measurements were made using a TA.XT2 texture analyzer (Stable Micro Systems, Godalming, UK). The initial grip separation was set at 50 mm and crosshead speed at  $1 \text{ mm}\cdot\text{s}^{-2}$ . There were at least ten replicates per experiment. Film thickness was measured using a micrometer (Mitutoyo Mfg Co. Ltd., Japan) and measurements were taken at five random positions on the film, using the average values to calculate film properties.

#### 2.2.3. Scanning Electron Microscopy (SEM)

SEM analysis was performed on fractured cross-sections and the surface of gold-sputtered C-ATH films using a LEO 440i scanning electron microscope (LEO Electron Microscopy Ltda., England), operating at 10 kV and 100 pA [10]. Chitosan films (CF) without anthocyanin was studied as reference.

### 2.3. Temperature Indicator Prototype (TIP)

Sheets of card paper ( $0.045 \text{ m}^2$ ) were coated with C-ATH suspensions. The C-ATH suspension was spread on the card paper surface using 80  $\mu\text{m}$  wire bar coater (TKB Erichsen, Brazil). The coated paper sheets were dried in an oven at 150°C for 90 s.

#### 2.3.1. Water Absorption—Cobb Test

Water absorption capacity was determined in accordance with standard ASTM D3285 [12]. T441om-90.27 The weight gain was measured using Mettler AE 163 analytical scales. The results are expressed in  $\text{g}\cdot\text{m}^{-2}$ . There were at least 15 replicates per experiment. Samples were preconditioned at 50 % RH and 25 °C for 48 hours in a desiccator.

#### 2.3.2. Taber Stiffness

Taber stiffness was determined using standard method ASTM D5342 [13]. Uncoated and coated cardpaper sheets were cut into samples of  $38 \times 70 \text{ mm}^2$  in the machine direction (MD) and the cross-machine direction (CD) using a guillotine (Regmed, Brazil). Taber stiffness was measured at an angle of 15° using Taber stiffness equipment (model RI 5000, Regmed, Brazil). Results are expressed in mN. There were at least 15 replicates per

experiment. Samples were preconditioned at 50% RH and 25°C for 48 hours in a desiccator.

## 2.4. Colour Response Efficiency Measurement

The colour parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) of C-ATH and TIP were measured at different periods of times after temperature and luminosity exposition. A Chroma Meter CR 400 colourimeter (Konica Minolta, Japan) was used. The parameter  $L^*$  represents the lightness of colours from 0 (dark) to 100 (light),  $a^*$  is a measure of greenness/redness and  $b^*$  is the grade of blueness/yellowness. Both  $a^*$  and  $b^*$  scales range from  $-60$  to  $+60$ . The transformation of  $a^*$  and  $b^*$  into geometric values (*hue angle* –  $h_{ab}$ ) for C-ATH is a better predictor variable of sensory perception in experimental design application. The  $h_{ab}$  ( $0^\circ$  -  $360^\circ$ ) was obtained by  $\arctan b^*/a^*$  and was used to express the characteristic/dominant colour [14]. According to several authors [14,15] this conversion is necessary to obtain results in the experimental design due to interaction between parameters  $a^*$  and  $b^*$ , where a change in one usually does not occur without changing the other. The C-ATH was exposed to experimental design conditions and the TIP was exposed to a range of temperatures ( $10^\circ\text{C}$  -  $70^\circ\text{C}$ ) and 0 and 1000 lx. There were three replicates per experiments.

## 2.5. Statistical Analysis

Statistical analysis was carried out with the Statistic version 7.0 program (Statistic Inc., USA) and differences between the means were detected by the Tukey multiple comparison test.

## 3. RESULTS AND DISCUSSION

Initially C-ATH was obtained to evaluate the colour response efficiency of the system as temperature indicator. Homogeneous, transparent, dark violet films were obtained and following drying, were easily removed from the support plates, forming a flexible and resistant matrix.

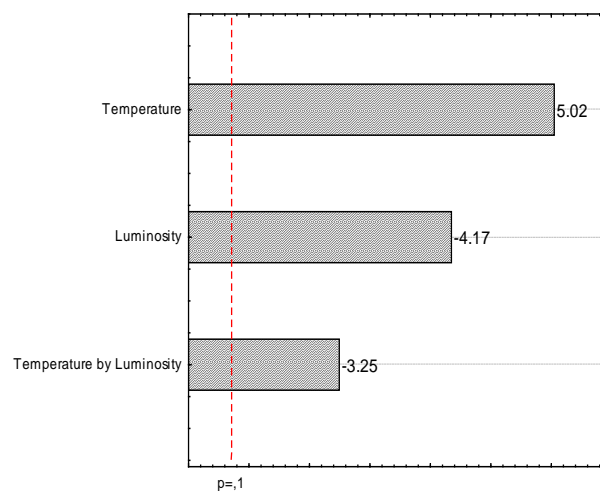
### 3.1. Experimental Design

The colour parameters  $L^*$  and  $h_{ab}$  of C-ATH were characterized after 72 h under exposure to temperatures and luminosities (Table 2).

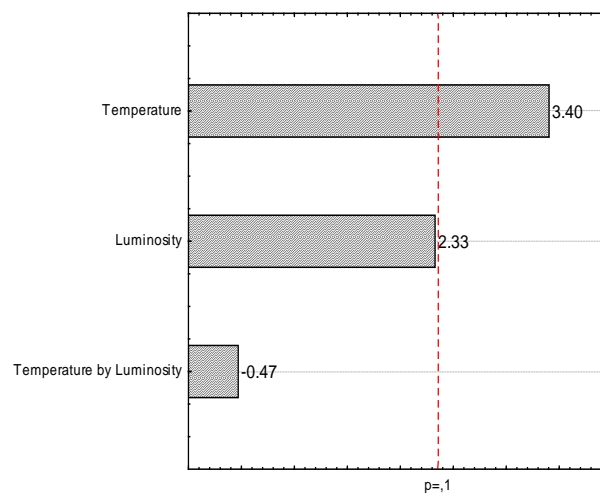
The effects of temperature and luminosity on colour variations of C-ATH were significant for a confidence level of 90% for parameters  $L^*$  and  $h_{ab}$  (Figure 1). The initial purple colour of the films gradually turned dark. Increasing the temperature from  $10^\circ\text{C}$  to  $50^\circ\text{C}$ , parameters  $L^*$  and  $h_{ab}$  increased to 5.02 and 3.40, respectively. Although increasing the luminosity from 0 to 1000 lx, a

**Table 2.** Matrix of experimental design  $2^2$ , colour parameters and mechanicals properties of C-ATH films.

Tests	Independent Variables		Properties				
	Temperature	Luminosity	$L^*$	$h_{ab}$ ( $^\circ$ )	$\epsilon$	TS	E
	( $^\circ\text{C}$ )	(lx)					
1	-1 (10)	-1 (0)	45.52	274.13	3.21	60.71	3.12
2	+1 (50)	-1 (0)	48.73	307.29	2.91	66.51	3.15
3	-1 (10)	+1 (1000)	45.16	298.08	3.61	60.62	2.50
4	+1 (50)	+1 (1000)	45.85	323.19	3.38	50.04	2.71
5	0 (30)	0 (500)	45.77	312.29	2.56	67.64	3.14
6	0 (30)	0 (500)	45.70	311.45	2.53	67.67	3.14
7	0 (30)	0 (500)	46.09	312.01	2.56	67.63	3.14



(a)



(b)

**Figure 1.** Effect of temperature and luminosity on variations in colour of C-ATH: (a) Parameter  $L^*$  and (b) Parameter  $h_{ab}$ .

process of discolouration was observed with the reduction in  $L^*$ . The combined temperature and luminosity decreased the  $L^*$  in 3.25 the C-ATH became lighter.

Shaked-Sachray, Weiss, Reuveni, Nissim-Levi and Oren-Shamir [16] studied the combined effect of elevated temperatures and metal concentrations on the accumulation of ATH in aster flowers and observed that the anthocyanin degraded and became discoloured at higher temperatures (higher than 30°C). Significant changes in  $b^*$  values were also found by Alighourchi and Barzegar [17] for anthocyanins in pasteurised pomegranate juice stored at 4°C, 20°C and 37°C for 210 days. In their study,  $L^*$ ,  $a^*$  and  $b^*$  values decreased and the most significant colour change was observed after storage at 20°C and 37°C. This change was attributed to the degradation of anthocyanin. According to Lauro and Francis [18], the anthocyanins could change with temperature, light, oxygen, presence of sugars and enzyme, pH and presence of proteins and metal ions [19-22], producing polymers with decreased stability.

Temperature and luminosity had not affected  $\epsilon$  and TS significantly (Table 2). For E, only the luminosity had a slightly significant effect ( $p \leq 0.1$ ). Increasing luminosity from 0 to 1000 lx, E decreased in order to 19.9% at 10°C and 14.0% at 50°C. These results are indicating that flexibility and strength of ATH-CF were maintained similar to the initial condition.

The good mechanical properties of CF and ATH-CF could be related with the microstructures (Figure 2). A compact and cohesive structure without pores or cracks was observed in CF (Figure 2(a)). No significant difference was observed between CF and ATH-CF structures (Figure 2(b)). ATH was entrapped in the tridimensional matrix forming a uniform structure films. Yoshida, Oliveira-Junior and Franco [1] found similar results for CF and CF with palmitic acid.

### 3.2. Film Card Paper System (TIP)

C-ATH suspensions were applied as a coating on card paper surface forming TIP system. The TIP drying process time was 90 s, which was faster than the total film drying process (60 h) that could be a commercial advantage.

C-ATH suspensions formed a homogeneous card paper coating without bubbles or defects. The systems were submitted to different temperature and luminosity conditions during 72 hours. An irreversible and gradual change in colour exposition of the TIP was visually observed after 72 hours at different temperature and luminosity conditions (Figure 3). A more pronounced colour change was observed after luminosity exposition. Studying the colour stability of berry anthocyanin, Rein [19] found that the exposition at higher luminosities accelerated ATH discolouration. The parameter  $b^*$  values increased

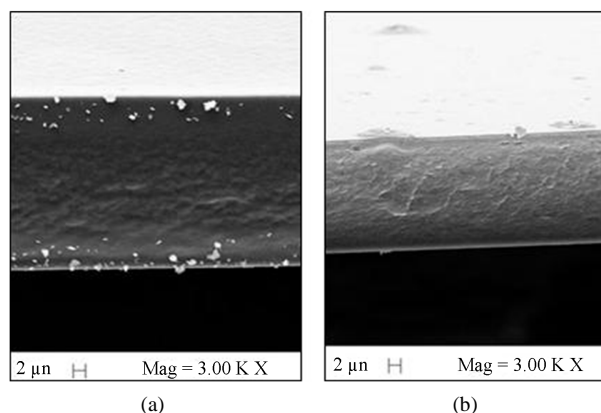
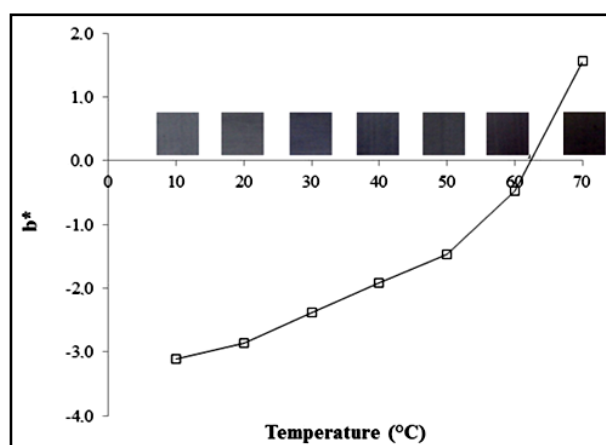
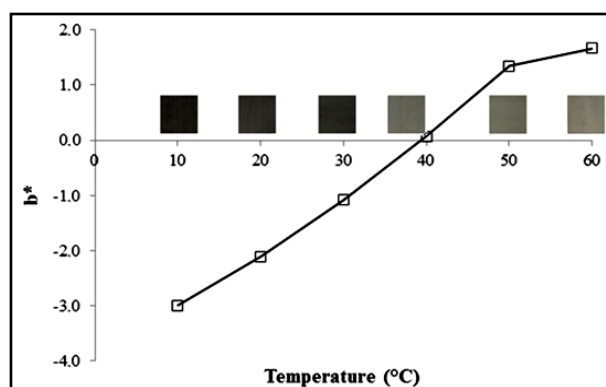


Figure 2. SEM Micrographs for (a) CF, (b) C-ATH containing 0.25% ATH.



(a)



(b)

Figure 3. The visual and  $b^*$  colour parameter changes on TIP system exposed to different temperatures and luminosities: (A) 0 lx and (b) 1000 lx.

in TIP after 0 and 1000 lx exposition.

Colour change on the TIP could be associated with ATH molecules chemical structure. Thermal degradation can produce changes in ATH structures that depend on the severity and heating conditions. The mechanisms of ATH degradation are still relatively unknown. Chemical

structures and the presence of other organic acids have a strong influence [22]. Markakis, Livingstone and Fillers [23] suggested that the pyrylium ring of ATH opens, forming a chalcone structure as a first degradation step. Chalcone is derived from three acetates and one cinnamic acid. It has a yellow pigmentation and is a precursor of the biosynthesis of flavonoid. Adams [24] reported that ATH could decompose upon heating into a chalcone structure and be further transformed into a coumarin glucoside derivative by the loss of the B-ring.

The ATH discolouration was observed in blue flowers [16], pomegranate juice [17], vegetables extracts [25] and fruits purees [26] after exposure to temperatures higher than 30°C. The discolouration process is usually accelerated with luminosity [23].

### 3.3. Properties of TIP

The grammage, water absorption capacity and Taber stiffness results for uncoated and coated card paper are shown in **Table 2**. The C-ATH coating did not significantly change the grammage of card paper. Water resistance is an important property which can determine the behaviour of card paper in various applications. The water absorption of the TIP decreased significantly applying C-ATH coating.

According to Aider [27], chitosan films have the ability to avoid moisture loss or water absorption and could act as a reinforcement layer. Bordenave, Grelier, Pichavant and Coma [28] studied the potentiality of bioactive food packaging based on chitosan-coated papers and show that chitosan film improved the water absorption of paper despite the very low amount of total solids. The incorporation of chitosan as a papermaking additive in paper and paperboard production or as a surface coating, had previously been investigated [29-32]. Different concentrations of chitosan were applied as a coating additive in paper and paperboard making, and it was observed that when increased chitosan concentration from 0.1 to 0.75% (w/w), the water absorption decreased significantly [29]. The greaseproof paper coated with chitosan films did not provide an extra barrier against water absorption [30]. The Taber stiffness values were statistically different when applied C-ATH coating on card paper surface as compared to uncoated card paper (**Table 3**). The resistance and flexibility of C-ATH strengthened the cellulose fiber interbonds. Chitosan films had a positive impact on the mechanical properties of coated paper [32].

## 4. CONCLUSION

An efficient and irreversible temperature indicator material was obtained for a specific range (from 40°C to 70°C) using biodegradable materials (chitosan, card paper and ATH). The TIP changed the colour from violet to yellow after temperature exposition. Luminosity acceler-

**Table 3.** Grammage, Cobb Test and Taber stiffness of TIP [10].

Samples	Grammage	Water absorption	Taber Stiffness (mN.m)	
	(g·m <sup>-2</sup> )	(g·m <sup>-2</sup> )	CD	MD
Uncoated cardpaper	252.71 ± 1.88 <sup>a</sup>	45.48 ± 1.76 <sup>a</sup>	5.60 ± 0.16 <sup>a</sup>	12.97 ± 0.21 <sup>a</sup>
TIP system	253.17 ± 1.71 <sup>a</sup>	35.41 ± 1.66 <sup>b</sup>	6.43 ± 0.17 <sup>b</sup>	14.15 ± 0.09 <sup>b</sup>

<sup>a, b</sup> Means in the same column with different superscripts differ significantly ( $p \leq 0.05$ ) in accordance with Tukey's test.

ated the ATH molecule degradation. The advantages of this temperature indicator were the simple manufacturing process, use of natural compounds that are food safety contact, the biodegradability and low cost. This indicator system has potential applications in different areas such as food, pharmaceuticals, biological, agricultural and others products, that are highly dependent of storage temperature conditions.

## ACKNOWLEDGEMENTS

The financial support of CNPq, FAPESP, CAPES and Suzano Papéis e Celulose Ltd.

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