THERMAL ANALYSES STUDIES ON THE INTERACTIONS BETWEEN EUCALYPTUS KRAFT PULP COMPONENTS AND OFFSET PRINTING INKS

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ABSTRACT

Thermal and infrared spectroscopic analyzes were accomplished in order to study the kind of interaction between the anatomical components of the bleached eucalyptus kraft pulp with offset inks. A Bauer-McNett fiber classifier was used in order to obtain the anatomical components of the pulp, separately. The determinations of the enthalpy of the processes occurring in the samples of inks and pulp, as well as the enthalpy of these components interactions were obtained by Differential Scanning Calorimetry. In the interaction between pulp and offset ink, the reduced enthalpy values of the endothermic peak were interpreted as due to the released energy for adhesion of the ink pigment to the substratum. The low enthalpy value, 58 to 121 $cal.g^{-}$,[1] indicate that the settling of the ink occurs by physical interactions. The pulp fraction enriched with vessel elements cause a higher energy release during the adherence of the pigment into the pulp.

Key-words: differential scanning calorimetry, thermogravimetry, kraft pulping, cellulose, interaction, and *eucalyptus* sp.

INTRODUCTION

The pulps proceeding from the tropical forest species may cause problems in the papermaking process, because the structure of their chemical and anatomical components, a well-known fact in the graphic and papermaking medium. The vessel elements may be stored in the lumen, mainly in the tylosis, extractives**.** These extractives may unfasten during the production of the paper, therefore causing depositions on the equipments as well as spots in the paper. Some problems such as the vessel picking might occur during the printing process. The vessel picking is related to a phenomenon in which some vessel elements found on the surface of the paper rather tend to be removed through the process of adhesion with the printing ink, so creating some defective points on the printed surface.

The vessel elements are shown under shapes forms that vary according the species and the widest and shortest shapes are the ones causing problems during the offset printing process of both coated and uncoated papers. These elements found on the surface are visibly noticed for presenting a higher shine, when exposed towards the light. In certain printed materials, one may observe that the printing faults are much more pronounced in some colors than in other ones. Some authors have been mentioning that these faults may be due to the differentiated interaction of the pulp components, fibers, and vessel elements with the printing inks.

One follow-up accomplished in the industry is to measure the dimensions of the vessel elements (length-L and width-D) and the percent rate of fibers and vessel elements. The company's genetic improvement program has been searching for a high width/length relationship and low fiber/vessel rate, in order to minimize the printing problems of the eucalyptus papers. Another method used in reducing the picking is the increased refine degree of the pulp for papermaking.

In the graphic industry, the printing techniques require a careful control on the interaction of the ink components with the printing system and the paper. In the development of the printing inks it is necessary to take several factors into account such as the adhesion work among their components and the plate, blanket, dampening water and the paper. There is a scarce knowledge on those interactions, although several observations have shown their importance. One way to obtaining better quality in the printed paper is getting better adhesion between the ink and paper, by determining the thermodynamic parameters involved in the process. Thus, the reactions or the phase changing process with enthalpies depending on the temperature might be followed by DSC.

In this study, thermal and spectroscopy analyses were carried out in order to determine the interaction between the anatomical components of the bleached eucalyptus kraft pulp of with the offset printing inks.

MATERIAL AND METHODS

Material

The industrial Kraft pulp of *Eucalyptus* spp was bleached by ECF technology, proceeding from the industrial unit Suzano Papel e Celulose - Mucuri-BA.

The offset inks were supplied by the company Lorigraf JF Tintas Especiais Ltda located in Juiz de Fora county, MG. For this experiment, the manufacturer prepared three europa-blue colored inks with similar chemical composition (Table 1) and three tack ranges: low - 120 to 160 g.m.; medium - 161 to 200 g.m. and high - 201 to 250 g.m.

Table 1 - Composition of the used offset inks

Composite	Type
Resins	phenolic, alkydic and hydrocarbonic
Vegetal oil	soybean, linseed, and alky-refined
Mineral oil	deodorized aliphatic
Pigment	organic
Others	modifiers**,** waxes, antioxidants, drier agents

Methods

Pulp classification in Bauer-McNett

In order to separate the anatomical elements found in the bleached pulp, the fiber classifier Bauer-McNett provided with a system of sieves with 20, 48, 100 and 200 mesh that is able to separate fiber samples into fractions or groups was used.
A pulp sample equivalent to 10g o.d. (over dry) was weighed and quantitatively transferred at 4% consistence to a laboratory hydrapulper. After desagregation at 30.000 rpm, the water-suspended pulp was introduced into the highest tank of the classifier, from which it feeds by gravity the four inferior classification tanks for a 15 min period. After classification, the fractions retained in those four qualifying sieves of the tanks were discharged into centrifuge until reaching a consistence around 40%, in order to determine the fiber/vessel rate.

The fiber/vessel rate of the pulp

After classification of the pulp in Bauer-McNett, an amount of 10g o. d**.** pulp from each fraction were randomly sampled for determination of the fiber/vessel rate. Each fraction was moistened for 24 hours approximately; then, it was disintegrated at 30.000 rpm in a laboratory hydrapulper at 25% consistence. Later, these pulp fractions were subjected to two successive dilutions. The first dilution resulted into 0.05% consistence and the second one into 0.0025%. The dilutions were accomplished by agitation. An amount of 250 mL from each fractional sample were collected under constant homogenization, and the paper sheet was formed in a Tappi former. The hand sheet was dried at 105 ± 3 ^{o}C temperature for 20 minutes. After drying, four distinct areas of the sheet were sampled with transparent adhesive tape and allocated on microscope glass plate in order to be quantified in computerized microscopy system. Eight glass plates from each fractional sample were quantified, by counting of 1,500 fibers by plate and the respective amount of the vessel elements present in this quantification.
In order to standardizing the nomenclature of the fractions of the classified pulps used in the subsequent stages, those fractions were named in relation to the analysis of the fiber/vessel rate, therefore being classified into low, medium and high pulps for the fiber/vessel rate.

Chemical and physical characteristics of the pulp

The characterization of the pulp was accomplished in triplicate, by evaluating the fibers count/grams (million), average length of the fibrous material (mm), average diameter of the fibrous material (mm), coarseness (mg/100g), fines (%) of the pulp. The pulp suspensions were prepared in distilled water, at 0.001% consistence and added dispersant (2.0% pulp base) to them. The analysis was accomplished, by using the image analyzer (GALAI CIS-100) with its respective software Wshape. For calculation of the percent fine occurrences, the dimensions equal or lower than 0.07 mm were considered. The air resistance (s/100cm^3 air) was accomplished according to the norm TAPPI T536 om-96, whereas the carbohydrate analyses followed the norm TAPPI T249 cm-00 modified.

Analyses by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA)

In these analyses was used hand sheet made in a laboratorial former according to Tappi T205 sp-95.
For determination of the thermodynamic parameters, three types of pulp samples (low, medium and high fiber/vessel rate) were taken, by using a perforator with a diameter around 6.4 mm, so resulting into 4.5 ± 0.2 mg weight for each sample. For inks with low, medium, and high tack, 9 ± 0.2 mg were used. Finally, for determining the thermodynamic parameters of the interaction between pulp and ink, an amount of 5.3 ± 0.2 mg of each ink were manually added to each pulp sample. The samples were transferred to a stainless steel crucibles that it was sealed at 2-tons pressure for 1 minute. The DSC thermograms were obtained in a Differential Scanning Calorimeter SHIMADZU DSC-50, under nitrogen atmosphere at a constant flow rate of 50 ml/min. The variation of the temperature from 25 ºC up to 500 ºC was performed, by adopting three heating rates of 10, 15, and 20 °C/min for the inks as well as 15, 20 and 25 °C/min either for pulps and the interaction between pulps and inks. The kinetic parameters (activation energy and reaction order) were calculated, by using Ozawa's kinetic model available in the program contained in the proper device. For obtaining the enthalpy of the endothermic and exothermic peaks, the heating rate of 15 °C/min was used for the inks, pulps and the interaction between pulps and inks. The equipment was previously calibrated for temperature using a standard melting point of indium (156.4 °C), 99.99% pure, and the energy calibration was done by using of the enthalpy of melting point ($\Delta H = 28.5$ J g^{-1}) of this same metal.
The TGA thermograms were obtained through the device SHIMADZU model TGA-50. A sample of 6 ± 2 mg inks with low, medium and high tack, as well as 4 ± 2 mg of the pulps with low, medium, and high

fiber/vessel rate were taken. The scanning was performed at heating rate of 15 °C/min at the temperature range from 25 ºC up to 500 ºC.

Analyses by infrared spectroscopy (FT-IR)

The FT-IR spectra were obtained in a spectrophotometer Perkin Elmer FT-IR 1000 by the diffuse reflectance method, for investigating a representative sample of the offset inks. The spectrum FT-IR of the inks at room temperature, 200 °C, 400 °C and 500 °C were measured, by preparing a thin ink layer under a cesium Iodide cell (CsI). All spectra were measured at 4000-500 cm^{-1} range, with 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

The Differential Scanning Calorimetry analysis (DSC)

Results of the offset ink samples

The thermograms obtained from DSC of the offset ink samples at the heating rate of 15 °C/min, from 25ºC to 500 ºC temperature, are presented in Figure 1. The peak areas under the obtained curves are the enthalpy ($cal.g^{-1}$) involved into thermodynamic processes that occur at each temperature range. The thermograms of the ink samples show an endothermic phenomenon (ascendant peak) with the maximum peak temperature ranging from 108 to 116 °C, following an exothermic phenomenon (descending peak) from 425º to 432 °C.

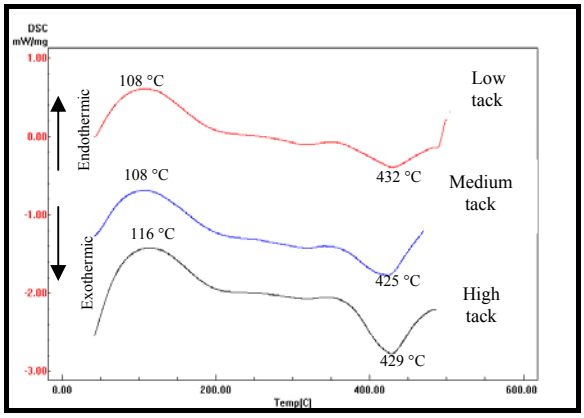

Figure 1 - Thermograms obtained from DSC of the offset inks

To assigning a molecular interpretation to each peak of DSC, it was necessary to accomplish the infrared spectrum analyses of a sample that would be representative for offset ink and its respective pigment isolated, at room temperatures**,** 200 °C, 400 °C and 500 °C. To exemplify, Figure 2 shows a typical spectrum of the ink at different temperatures. The ink spectrum at room temperature (Figure 2) showed the presence of bands corresponding to the oils that constitute one of their main components. This spectrum presented the same characteristic bands found by Blayo et al. (2001) who studied the oils from linseed, soybean, and rape.

When observing the Figure 2, it is inferred that the offset blue ink probably contains the copper pigments so-called phthalocyanine with typical absorption bands in the infrared at 2936, 2870, 1607, 1505, 1460, 1419, 1375, 1334, 1288, 1166, 1120, 1091, 998, 900, 786, 778, 726, 571 and 506 cm^{-1} (Havlínová et al. 2002; Newman, 1979). Newman (1979) adds that the phthalocyanines show very distinct spectrum (particularly near 1700 cm^{-1}) in the medium infrared region, as containing well defined narrow bands due to the stretching system of the aromatic ring carbon-carbon bonds, as well as hydrogen-carbon bonds of the rings at the plane and outside the plane.

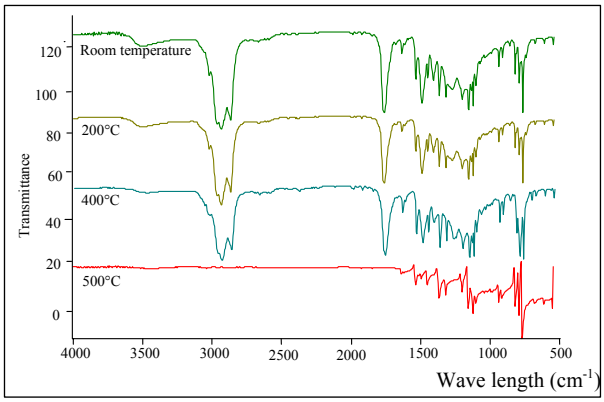

Figure 2 - Spectra obtained by infrared representing the offset inks at room temperature, 200 °C, 400 °C and 500 °C.

The infrared spectra of the offset ink show that no alteration occurred at the temperature range corresponding to the interval from 25 ºC to 200 ºC, relative to the structural relationship of its components, so indicating no chemical reactions to occur there. Thus, it can be concluded that the endothermic peak observed in the DSC analyses of the inks was due to evaporation of the solvent. The enthalpy values found in the endothermic peaks for both low tack and medium tack inks were 53.05 ± 2.0 $cal.g^{-1}$, respectively, therefore indicating a similar solvent content in both inks. On the contrary, the high tack ink that probably contains a higher solvent content showed a higher enthalpy value (88.86 ± 2.0 $cal.g^{-1}$).

As observed in the infrared spectroscopy analyses (Figures 2), from 400 °C some modifications began in the profile of the ink spectrum, whereas at 500 °C a great degradation of some parts of the ink components occurred due to the disappearance of the bands corresponding to the oils and resins. Therefore, it may be inferred that the exothermic peak observed in the ink DSC analyses (Figure 1) was due to the total degradation of their component parts, such as the oils and resins, and partially of the pigment. For the values of the exothermic peak enthalpy, as there occurred an increased ink tack (Table 2), the enthalpy values also

increased, therefore suggesting a gradual increase in the content of the solid components such as resins and pigments

Results of the pulp samples

Figure 3 shows the thermograms obtained from DSC of the pulp samples at the heating rate of 15 °C/min, from 25 ºC up to 500 ºC. It is possible to observe the presence of two different phenomena for those three pulp samples under study. The endothermic phenomenon happened at the maximum temperature range from 122 to 133 °C, and the exothermic from 314 to 340 °C. Liu et al. (2004) evaluated the pyrolysis of wood derivatives, by thermogravimetry associated with mass spectrometry. The first detected peak appeared at the temperature range from 80 to 220 ºC, with maximum peak at 125 °C that was due to the physical desorption of the water. It was observed that between 300 and 400 ºC, the depolymerization of glucose units occurs with formation of levoglucosans and decomposition of the remaining water into carbon monoxide, carbon dioxide and char.

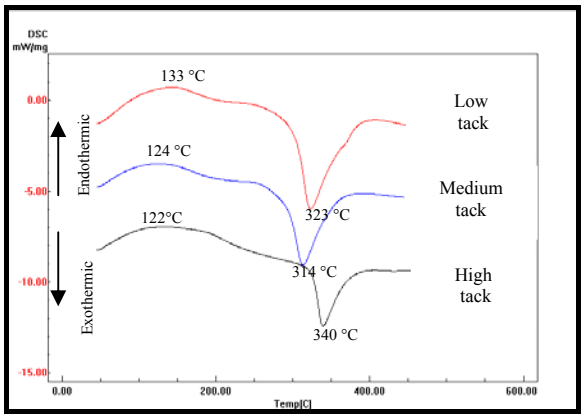

Figure 3 – The thermograms obtained from DSC of the pulp samples.

It was observed in our experiment an endothermic phenomenon in the pulp samples at the temperature range of 25 ºC to 200 °C. The enthalpy values for the endothermic phenomenon of the samples with low, medium, and high fiber/vessel rate were: 122.34 cal.g^{-1}, 92.05 cal.g^{-1}, and 65.09 cal.g^{-1}, respectively. It is known that this endothermic phenomenon is due to water desorption. Despite all samples have been tested with the same moisture content (6%) a higher energy was needed for desorption of water molecules on the pulp with low fiber/vessel rate. In order to explain this difference in the consumption of energy, the pulp samples under the form of handsheets were submitted to the air-resistance test, as described in the item 'materials and methods'. This test constitutes a measure related to the porosity of the paper. The following values were found for the pulp with low and high fiber/vessel rate: 4.05s and 0.97 s/100cm^3 air, respectively. Based on this result, one may infer that as higher is the resistance to the passage of air, the higher will be the necessary energy to occur the evaporation of the water molecules kept in the pulp structure, during the heating process, when analyzing DSC. This behavior is probably explained due to the highest contents of fines found in the pulp with low fiber/vessel rate, which supply a higher superficial area for the adsorption of the water molecules.

In addition, it was found an exothermic phenomenon in our pulp samples. It is cited on the literature as a depolymerization of glucose units. The enthalpy values found in the exothermic phenomenon for the samples of low, medium, and high fiber/vessel rate were: -125.2; -118; and –108.6 cal.g^{-1}, respectively. Although the pulp samples with low and high rate have basically presented the same polymerization degree, which was shown by the proximity of the values for their viscosities (15.2 and 16.0 cP, respectively), it is observed that the energy released during the depolymerization of the cellulose chains are different among the pulps.

The enthalpy values found in the exothermic reactions for the samples of low, medium, and high fiber/vessel rate were: -125.2; -118; and –108.6 cal.g^{-1}, respectively. Although the pulp samples with low and high rate have basically presented the same polymerization degree, which was shown by the proximity of the values for their viscosities (15.2 and 16.0 cP, respectively), it is observed that the energy released during the depolymerization of the cellulose chains are different among the pulps.

The results from the technological characterization of the pulps showed that the samples with high fiber/vessel rate presented higher values for the average length of the fibrous material (0.84 mm), coarseness (4.8 mg/100m) and fine contents (4.98%), when compared to the pulp with low fiber/vessel rate that presented average length of the fibrous material (0.49 mm), coarseness (2.2 mg/100m) and fine contents (13.44%). This fact caused the formation of more porous handsheets and the pulp with high fiber/vessel rate probably leading to a higher accessibility for breaking of the glycosidic bonds of the chains, therefore generating a lower release of energy (exothermal reaction) during the chemical linkage breaking process.

Results from the pulp and ink interaction

According to Hartus (1999), the interactions between inks and fibers in the DSC analysis can be detected by changes in the consumption of energy and/or in peak temperature corresponding to a determined thermal transition. One may observe in the interaction between pulps and inks (Figure 4) that both the endothermic and exothermic phenomena were presented (Figure 3). For the endothermic phenomenon, the maximum temperature range from 120 to 134 °C is observed.

Table 2 shows the thermodynamic parameters for the samples of the inks, pulp and interaction between ink and pulp. It may be observed that the values for enthalpy in the interactions between pulp and ink for

all samples were always lower, compared with the values found in the pulp samples.

Aiming at the investigation of the causes of the decreased enthalpy, the Thermogravimetric analysis was accomplished in order to evaluate the amount of matter that participates into each endothermic and exothermic transition

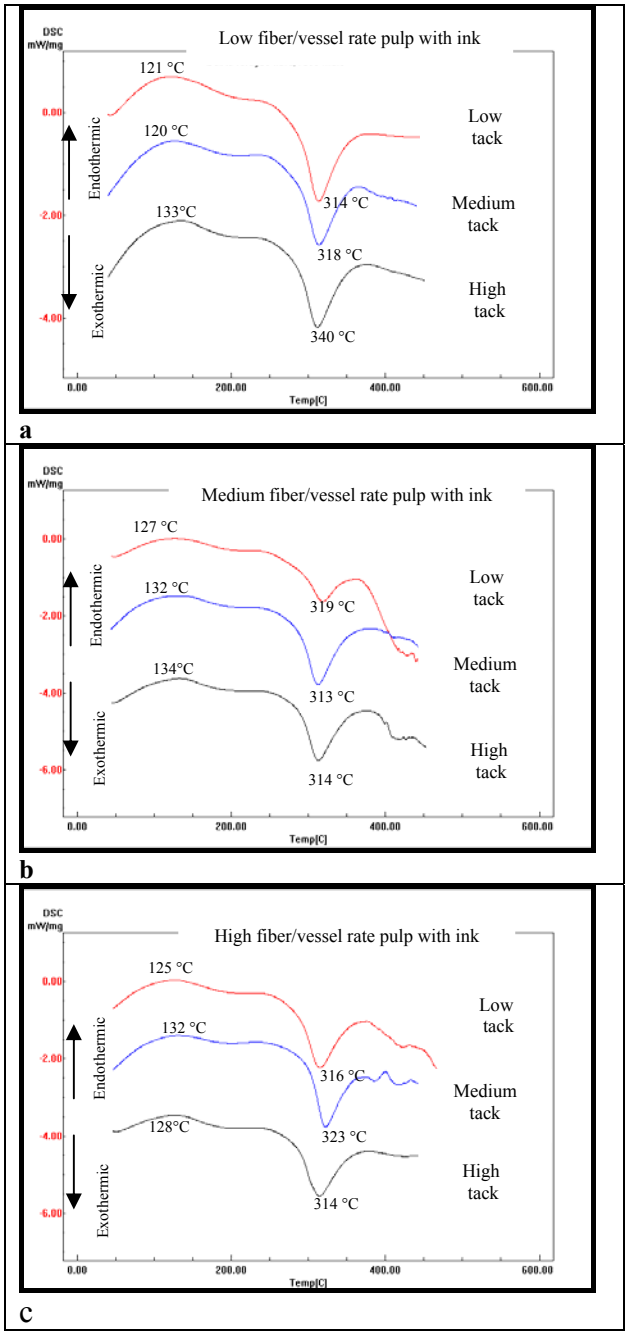

Figure 4 – Thermograms of the interaction between pulp and offset ink obtained from DSC. A) Interaction between the low fiber/vessel rate pulp and inks; b) Interaction between the medium fiber/vessel rate pulp and inks; and c) Interaction between the high fiber/vessel rate pulp and inks.

Table 2 - DSC parameters of the samples for the endothermic peak

Sample	T_{peak} (°C)	ΔH ($cal.g^{-1}$)	E_a ($kJ.mol^{-1}$)	N
LT	108	53.05	24.06	2.1
MT	108	51.76	31.32	2.5
HT	116	88.86	25.75	1.5
LR	122	122.34	20.38	1.8
MR	124	92.05	28.38	2.8
HR	133	65.09	19.10	1.0
LR LT	121	39.86	20.66	1.5
LR MT	126	52.20	16.91	2.1
LR HT	133	52.58	24.22	1.1
MR LT	127	25.03	21.26	1.4
MR MT	132	46.64	26.12	1.6
MR HT	134	28.73	26.63	1.5
HR LT	125	39.61	24.24	1.4
HR MT	132	39.28	17.95	1.5
HR HT	128	22.48	24.56	1.7

T = peak temperature; ΔH = enthalpy; Ea = activation energy; N = reaction order.

Where: LT = low tack ink; MT = medium tack ink; HT = high tack ink; LR = low fiber/vessel rate pulp; MR = average fiber/vessel rate pulp; and HR = high fiber/vessel rate pulp.

Thermogravimetry analyses (TGA)

According to Hartus (1999), the interactions among ink and the fiber components in TGA will occur with changes in weight loss at determined temperature range, changes in the weight loss rate taxes, or changes in temperature corresponding to the highest rate of mass loss.

In the thermograms obtained from the interaction between pulp samples and inks, an initial weight loss was observed at the range from 25 to 200 °C, which corresponds to the sum of the water evaporation molecules of the pulp samples and the ink solvent molecules, as well as a higher weight loss as those found in the analyses accomplished in DSC at the range from 300 to 500 ºC, which corresponds to degradation of either the cellulose chains and ink components.

The matter amount foreseen for the endothermic transition in interaction between pulp and ink was given by the sum of the weight loss due to evaporation of the water molecules in the pulp plus the weight loss of the ink solvent molecules. These foreseen values and those experimentally obtained in TGA are shown in Figure 5.

It was observed that the amount of both water and solvent molecules evaporated in the interaction were superior to the foreseen amount, for all samples under study. Based on these results, one may infer that the decreased enthalpy values of the endothermic peak in the DSC analysis were not due to a decreased matter in the pulp and/or ink samples. So, this decreased energy can only be attributed to the released energy

(exothermal process) during absorption of the ink pigment to the surface of the pulp.

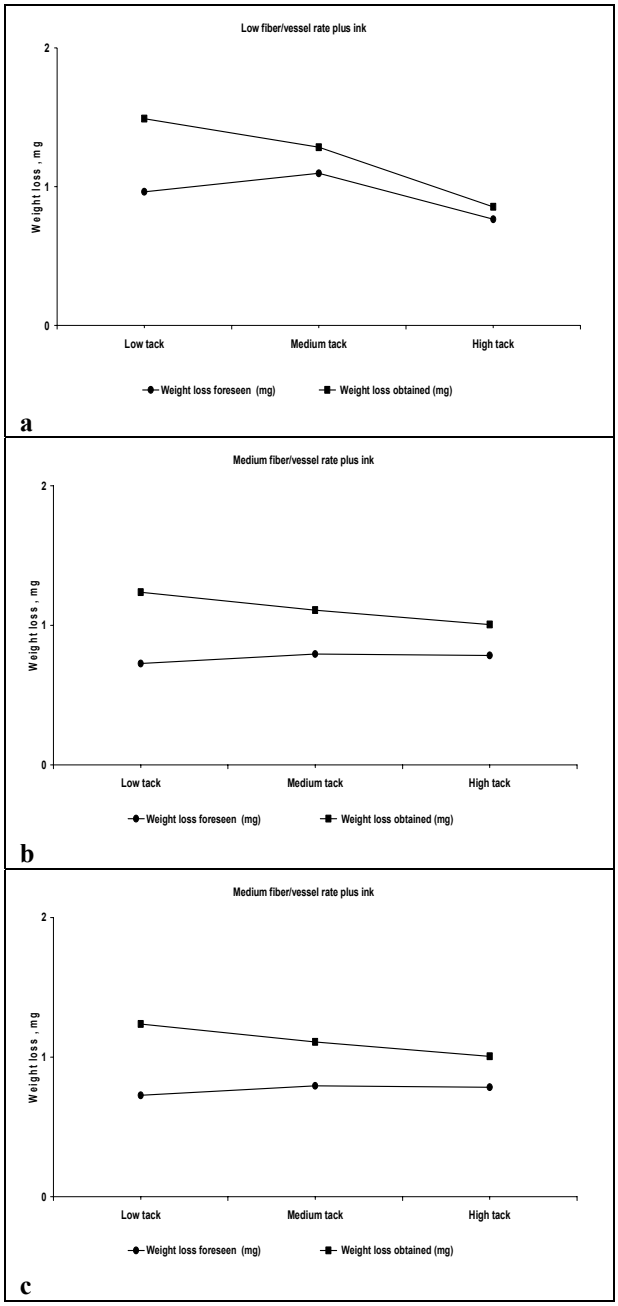

Figure 5 - Results of the weight loss obtained from TGA of the interaction between pulp and offset ink. a) Interaction between low fiber/vessel rate pulp and inks; b) Interaction between medium fiber/vessel rate pulp and inks; and c) Interaction between high fiber/vessel rate pulp and inks.

Interaction between fibers and vessel elements with offset printing inks

The enthalpy values ($cal.g^{-1}$) foreseen for the endothermic phenomenon in the interaction of pulps and inks correspond to the sum of water molecule evaporations in the pulp substratum plus the ink solvent molecules. The real values obtained by Differential Scanning Calorimetry (DSC) for this phenomenon and the difference found between the foreseen enthalpy and the real enthalpy for all samples are represented by Figure 6.

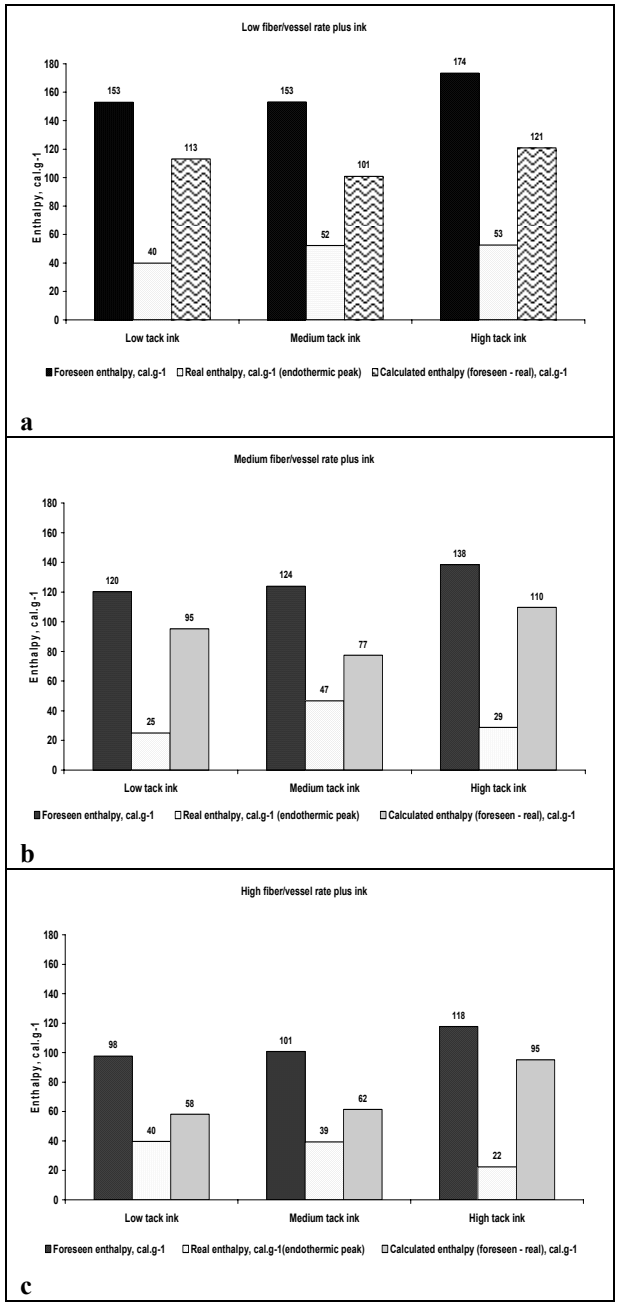

Figure 6 – Enthalpy values obtained from DSC of the interaction between the pulp and ink samples. a) Interaction between the low fiber/vessel rate pulp and the low, medium and high tack inks; b) Interaction between the medium fiber/vessel rate pulp and the low, medium and high tack inks; and c) Interaction between the high fiber/vessel rate pulp and the low, medium and high tack ink.

The enthalpy values obtained by adhesion of the ink pigments on the pulps ranged from 58.1 to 121.0 $cal.g^{-1}$ (Table 3). According to the enthalpy values, it can be inferred that this adhesion did not happen by covalent bonds, where the energy from 4000 to 5000 $cal.g^{-1}$ is needed, but it probably occurred through physical adsorption (hydrogen bonds, van der Waals forces, electrostatic attraction) and penetration of the ink pigment molecules through the capillaries of the fibers

Table 3 – Enthalpy values obtained from DSC in the interaction of the ink samples with the samples of low, medium and high fiber/vessel rate

Fiber/vessel rate	Enthalpy, $cal.g^{-1}$		
	Low tack ink	Medium tack ink	High tack ink
Low	113.1	101.7	121.0
Medium	95.2	77.4	109.7
High	58.1	61.5	95.2

Johansonn et al. (1989) studied the way the alkyd resins are kept on the surface of cellulose. They concluded that chemical interactions could occur between the carboxylic acid groups in the alkyd resins and the reactive sites of the cellulose surface. The resin will adhere to the surface of the fibers by an exothermal phenomenon (ΔH: -9.4 $kJ.mol^{-1}$) determined by intermolecular interactions of the van der Walls forces, but not by chemical bonds.

In Table 3, one may observe that as smaller the fiber/vessel rate pulp the higher will be the content of vessel elements in the fraction, as well as there will be a tendency for increasing the energy released for adhesion of the pigment into substratum, for all ink samples. Thus, those enthalpy differences between the fractions with higher contents of vessel elements and higher fiber contents may be due to both chemical and physical nature of the samples.

The carbohydrate analyses in the low fiber/vessel rate sample showed higher content of xylan (14.4%) and lower glucans (77.6%), whereas in the sample with high fiber/vessel rate showed lower xylan contents (13.8%) and higher glucans (81.4%). It is well-known that xylans are the main hemicelluloses in hardwood. For each 10 xylose units, these hardwoods present 7 units of acetyl groups as well as from 1 to 2 units of 4-0-metylglucuronic acid. Cellulose that is the main carbohydrate found in the wood, which is called as glucans, presents the alcoholic and hemiacetalic groups and carboxylic groups as functional ones.

It is known the reactivity of the hemicelluloses to be higher than the cellulose due to both chemical and physical differences of these components. Concerning to chemical characteristic, the hemicelluloses present a higher number of functional groups, such as acetyl, carboxyl, and methoxyl, as well as their monomers are less stable for presenting five-carbon rings, besides having a lower molecular weight, which leads to a lower stability of the molecule. Concerning to the physical characteristic, they are shown under ramified chains and consequently amorphous, therefore leading to a higher accessibility within their chain.

So, it is inferred that the highest content of hemicelluloses in the sample enriched with vessel elements might have increased the reactivity of the substratum, since they present higher number of possible reaction sites, besides leading a higher accessibility to these reactive groups due to the presence of the ramified chains. On the contrary, the fiber-enriched sample (higher fiber/vessel rate) presented higher glucan contents that show more crystalline chains as well as a lower amount of reactive sites for adhesion of the ink pigment. The vessel elements also present a highly different anatomical characteristic compared to the fibers since, their diameters are much larger than those fibers. The most common shape to the eucalyptus wood is popularly called as barrel wooden shape that is shorter and broader cells.

The studies concerning to separation of the non-fibrous components in oak wood accomplished by Klungness & Sanyer (1981) showed that the specific surface of the vessel elements was almost 50% higher than that of the fibers, and the specific volume twice as higher. So, the low fiber/vessel rate fraction, that is that most enriched with vessel elements, probably released a higher energy amount in the adhesion of the pigment on the pulp because it has a broader specific surface compared to the fibers. Thus, besides the vessel elements to possessing a chemical structure with higher amount of reactive sites, the vessel elements also have a higher specific area for a possible interaction.

The energy liberated from the adhesion of the pigment into substratum (pulp) was higher for all pulps samples under study, when using the high tack ink (Table 3). This phenomenon may be explained by the amount of the pigment used in formulating this ink type. With the results for loss of the ink weight obtained by TGA, a higher mass was observed in the exothermic peak, which corresponded to degradation of both resins and pigments for the high tack ink. This occurrence leads to the conviction that a higher pigment quantity was used in the formulation of the high tack ink, therefore increasing the number of particles by area that adhered to the substratum, thus releasing higher energy.

CONCLUSIONS

Molecular interactions among the components of pulp and offset printing inks were determined by thermal analyzes of DSC and TGA. These analyses showed an evaporation of the solvent to occur at the temperature range from 25° C to 200° C, whereas the degradation of some ink component parts is began above 300° C. So, the settling of the ink will be easier with the increased temperature since it does not surpass 300° C. However, thermogravimetric analyzes of the pulp have shown its thermal stability to occur only until 200° C temperature, which leads to suggest this temperature as

the maximum assurance level for the printing with those offset inks.

The adsorption of the pigment to the pulp occurs exothermically at enthalpy values related to physical interactions, such as: hydrogen bonds, van der Waals forces and electrostatic attractions, in which higher interaction was also observed among the ink pigments with vessel elements

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