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## Turning Used Frying Oil into a New Raw Material to Printing Inks

Vinícius M. Mello, Gustavo V. Oliveira and Paulo A. Z. Suarez\*

*Laboratório de Materiais e Combustíveis, INCT-Catálise, Universidade de Brasília,  
CP 4478, 70910-970 Brasília-DF, Brazil*

Óleo de fritura usado (OFU) foi obtido de indústrias responsáveis pelo preparo de alimentos e avaliado como matéria prima para a produção de resinas aglutinantes para serem usadas em tintas de impressão (impressoras offset e tipográfica). A polimerização do óleo de fritura foi comparada com a de óleos refinados já relatados na literatura para preparação de tintas. Após 3 h, a viscosidade do polímero obtido com óleo residual foi 80% superior ao óleo refinado de soja em condições reacionais similares. Este comportamento está possivelmente associado ao menor tempo de indução para óleo usado. A acidez devido à formação de ácidos carboxílicos aumentou na polimerização de todas as matérias primas estudadas. Utilizando complexos metálicos do tipo  $M(\text{carboxilato})_2$  ( $M = \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}$  e  $\text{Sn}^{2+}$ ) como catalisador, a viscosidade aumentou até 75% quando comparado com a reação sem catalisador.

Used frying oil (UFO) obtained from industrial food preparation was evaluated as raw material to produce biobased resins suitable to be used as binder in printing inks (offset or typographic printers). The polymerization of UFO was compared with selected refined oils described in the literature to produce printing inks. After 3 h, the UFO-polymer viscosity was up to 80% higher than using refined soybean oil in similar conditions. This behavior is possibly associated to a smaller induction time when using UFO. The polymerization increased the acid value in all feedstock used because of the formation of carboxylic acids. Using metal complex of the type  $M(\text{carboxylate})_2$  ( $M = \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}$  and  $\text{Sn}^{2+}$ ) as catalyst precursor for UFO polymerization, the viscosity increased up to 75% when compared with non-catalyzed reactions.

**Keywords:** thermal polymerization, printing ink, used frying oils

### Introduction

Along the human history, oils and fats have been used as food and also, as raw-material for the preparation of inks and paints. In the last century, fats and oils became important in the industry not only as a feedstock to produce different materials but also as a medium to prepare fried food.<sup>1</sup> Concerning the use of oils and fats to prepare deep fried aliments, it is well know that the food industry and restaurants produce a large amount of a waste residue composed essentially by degraded triacylglycerides after thermal polymerization and oxidative modification. This residue is associated with high environmental and economic impact due to its high oxygen depletion in the limnic system as well as plugging pumps and pipelines in the city sewer network.<sup>2</sup> Besides, used frying oil is difficult to transform into a less pollutant residue.<sup>2</sup> Government estimative

indicates that Brazil produces approximately 2.4 billion liters *per year* of UFO, and only from 2.5 to 3.5% of this total volume is recycled.<sup>3</sup> The low amount of recycling is associated with the low value of the products that are usually obtained from UFO (mainly soaps and biodiesel), not paying back all the recycling costs.<sup>2,4</sup> Thus, in order to expand the UFO recycling industry, it is mandatory to develop new and profitable recycling processes.

Recent researches in oil chemistry showed the possibility of producing high-value printing inks for newspapers and magazines (lithographic, typographic and offset)<sup>5,6</sup> using refined unsaturated vegetable oils. These biobased inks were quickly accepted in the USA market and are already replacing important amount of the petroleum based ones, which are composed by mineral oil (60%), petroleum-based resin (20%) and fillers (20%, usually pigments and additives).<sup>7</sup>

The development of biobased printing inks started during the 1970 decade due to the petroleum crises. Initially,

\*e-mail: psuarez@unb.br

gilsonite and tall oil were used as raw material to produce resins by thermal polymerization.<sup>5</sup> In the 1980s and 1990s, important improvements such as new feedstocks with lower prices and higher availability, specially soybean oil were achieved.<sup>6</sup> Indeed, it was obtained polymers with good quality to be used as binders in formulations of coatings, paints and inks. The new inks proved to have better attrition resistance, viscosity and adhesiveness than those obtained from petroleum derivatives.<sup>6</sup> Other technological advantages reported were greater compatibility of the material to the carbon black used as a pigment and a faster degradability than traditional ones, which improves the paper recycling process.<sup>7-12</sup> With refined soybean oil, biobased printing inks achieved competitive prices and the industrial production started up.

Thermal polymerization of oils and fats is characterized by a cross-link in the chains of triacylglycerides, forming high molecular weight polymers with variable physicochemical properties.<sup>13</sup> Several mechanisms have been proposed to explain this process, all related to the presence of double bonds. Many studies agree that the polymerization starts with the isomerization of the non-conjugated *cis-cis* linolenic chains into conjugated *trans-cis* or *trans-trans* isomers, and, thus, reacting via Diels-Alder mechanism to create tetra-substituted six-member ring.<sup>7,13,14</sup> More recently, studies showed evidences that the polymerization may also undergo via a radicalar process without the formation of six-member rings.<sup>15</sup> It is important to mention that during this process an increase in the viscosity was observed.<sup>7</sup>

Currently, studies are still trying to improve the polymerization process. For instance, it was recently proved that the use of metal-based catalysts is able to reduce the polymerization time up to 60% of the required to perform a non-catalyzed reaction.<sup>16</sup> It was also recently shown that it is possible to produce biobased inks from non-edible oils, such as refined karanja oil, avoiding the dilemma food supply security and sustainability.<sup>17</sup>

The aim of this work was to study the production of printing inks from UFOs and compare the obtained resins with those produced with refined vegetable oils. The main goal was to produce a high value product from UFO in order to improve its recyclability and, thus, diminishing their environmental impacts.

## Experimental

### Materials

Alkali-refined soybean, canola, corn and sunflower oils were obtained from Bunge Alimentos S.A. (Brazil) and used as received. UFO was obtained in fast-food restaurants

established in Brasilia City, Brazil. Reagents (FeCl<sub>2</sub>·4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, SnCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, HCl, NaOH, Na<sub>2</sub>SO<sub>4</sub> and hexane) were purchased from Vetec Química Fina Ltda (Brazil) and used as received.

### Preparation of metal complexes

Metal complexes used as catalysts were synthesized utilizing metal ions (M = Ni<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup>) and carboxylate ligands derived from palm oil fatty acids, with the generically structure M(carboxylate)<sub>2</sub>, as previously described by Mello *et al.*<sup>16</sup>

### Vegetable oil thermal polymerization

UFO or alkali-refined oil (500 g) was added in a 1.0 L five necked round bottom flask equipped with condenser, nitrogen inlet, mechanical stirring, a thermocouple and heating mantle. When evaluating the catalytic activity, the metal complex (2.5 mmol L<sup>-1</sup>) was also added. Samples were collected in the reaction times of 0.0, 1.0, 1.5, 2.0, 2.5 and 3.0 h under nitrogen flux. The acid value and iodine values of the samples were determined using, the AOCS Cd3d63 and AOCS Cd1-25 standard methods, respectively. The kinematic viscosities were determined according to ASTM D445 standard method. For each reaction, the apparent kinematic viscosity constant (k) was calculated plotting ln (kinematic viscosity) vs. time, according to the linear function  $\ln \eta = k t$ .

### Instrumental

Fourier transform infrared spectra (FTIR) were obtained using Shimadzu Prestige-21 equipped with attenuated total reflectance (Pike Technologies), optical way of 7 mm and 10 reflections, using nominal spectral resolution of 4 cm<sup>-1</sup>, and average of 32 interferograms was accumulated. Rancimat test was performed in a Metrohm 873 Biodiesel Rancimat apparatus according to the EN-14112 oxidation stability standard method. Thermogravimetry analysis (TGA) curves from the samples (2 mg) were obtained using a Shimadzu model DTG-60, under nitrogen flux at a rate of 50 mL min<sup>-1</sup> and temperature varying from 30 to 600 °C, using 10 °C min<sup>-1</sup> heating rate.

## Results and Discussion

### Used frying oil characterization

In this work, the UFO used was collected in only one batch in a fast food restaurant. According to that restaurant,

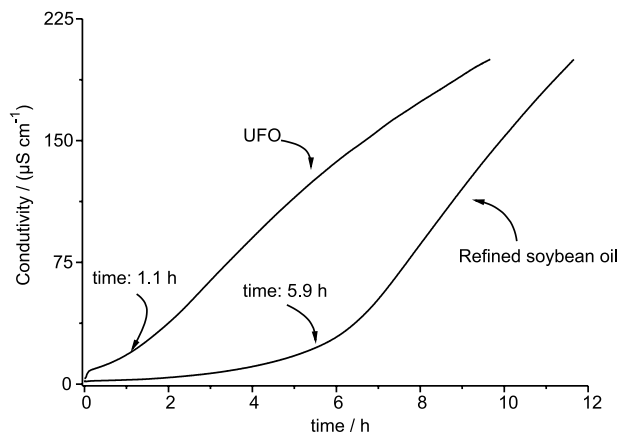
the UFO resulted from refined soybean oil used to fry different foods under the atmosphere and in temperatures above 100 °C for a maximum period of 6 h. The oil was filtrated to remove solid particles soon after the arrival in the laboratory.

In general, oils and fats submitted to prolonged frying process suffer considerable changes in their chemical structure. The contact with oxygen at high temperature results in a partial oxidation of the triacylglycerides, reducing the number of double bonds in their chains and forming carboxylic acids, epoxides, ketones, alcohols and ethers.<sup>18</sup> Both natural and added antioxidants are also oxidated during this process. Due to a large amount of water in foods, oils and fats can also undergo hydrolysis of the ester groups leading to the formation of carboxylic acids.<sup>18</sup>

To characterize UFO, it was evaluated the acid value, iodine value, FTIR spectra, TGA curves and oxidative stability. Thus, an increase in the acid value comparing refined soybean oil and UFO (from 0.5 to 1.5 mg KOH g<sup>-1</sup>, respectively) was observed probably due to the hydrolysis during the frying process. Iodine values showed a decrease from 150 to 139 mg I<sub>2</sub> g<sup>-1</sup> after the frying process, clearly indicating a decrease in the amount of double bonds present in the acilglyceride alkyd chains. FTIR analysis confirmed the consumption of double bonds, with consequent reduction in the absorption at 3008 cm<sup>-1</sup> (CH stretching) and double in *cis* conformation at 722 cm<sup>-1</sup> (out of plane deformation of the *cis* double bond). At 1708 cm<sup>-1</sup>, a small increase of the carboxyl group of carboxylic acids (axial stretching) was observed, corroborating the results obtained in acid values. Thermogravimetric analysis showed that for both refined and used oils, the decomposition in inert atmosphere (N<sub>2</sub>) occurred near to 350 °C. In oxidative stability experiments using the Rancimat method, the induction time drastically reduced from 5.9 to 1.1 h after the frying process (Figure 1). This result strongly suggests that the oxidative process of soybean oil has already started during the frying process, as well established in the literature.<sup>18</sup>

#### Thermal polymerization

Initially, the polymerization of UFO was compared to refined oils with different amounts of unsaturation in their alkyd chains. Indeed, the unsaturation degree of the oils increased in the order canola < corn < sunflower < soybean. Through the results seen in Figure 2a, it is clear that all oils showed an increase in their kinematic viscosity throughout the reaction period. Plotting the natural logarithm of kinematic viscosity vs. time leads to the graph presented in Figure 2b. The apparent kinematic viscosity constants

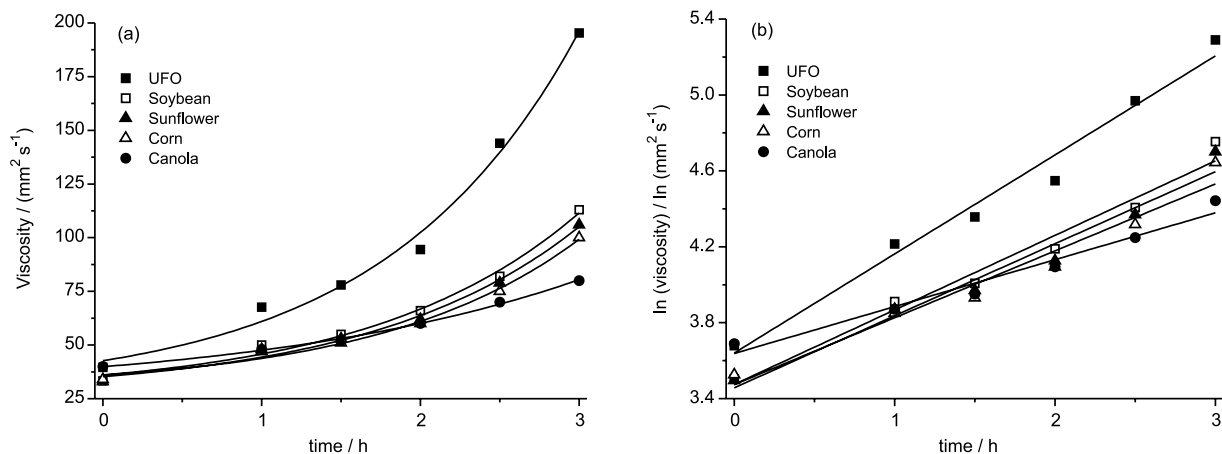


**Figure 1.** Oxidative stability of refined soybean oil and used frying oil (UFO).

were obtained through the slope of the line and their values are shown in Table 1. Thus, it can be stated from the viscosity and the apparent kinematic viscosity constant observed for the refined oils that the polymerization rate increased in the order canola < corn < sunflower < soybean, in perfect agreement with the amount of double bonds present in the alkyd chains. On the other hand, using UFO, it was observed an apparent kinematic viscosity constant up to 1.3 times greater than those observed for refined soybean oils, as well as an increase in the viscosity of the polymer up to 80%. This result is particularly interesting because UFO presented lower iodine value than refined soybean oil, suggesting that the oxidation reactions started during the frying process increases the reactivity of the oil during the thermal polymerization.

In the sequence, the final polymers were analyzed by acid value and the results are shown in Figure 3 and Table 1. As can be observed, a linear increase in the acid values throughout the reaction occurred. The increment order followed the same sequence as observed for viscosity. However, in the case of UFO, the final acid was only 25% higher than that obtained with refined soybean oil, although the viscosity was 75% higher. Comparing the acid value of polymers with similar viscosity (ca. 80 cSt), it can be observed that when using UFO as starting material, the acid value was lower than that using refined vegetable oils.

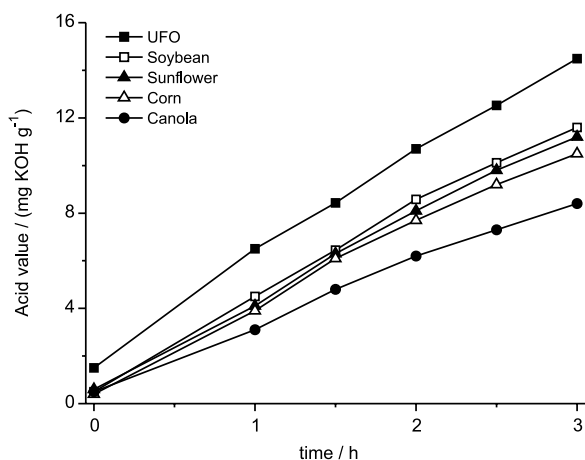
The FTIR analysis of the polymers corroborates the previous results and showed new information. As can be depicted in Figure 4, the diminishing of the absorption characteristic of double bonds at 3008 cm<sup>-1</sup> during the reaction was observed. A reduction in the absorption characteristic of the ester group at 1747 cm<sup>-1</sup> and subsequent increase at 1708 cm<sup>-1</sup> related to carbonyl of carboxylic acid was also observed. This result indicated that the increase of the acid values occurred because of the decomposition of the ester groups into carboxylic acids.



**Figure 2.** Thermal polymerization of UFO (■), soybean oil (□), sunflower (▲), corn (△) and canola (●) oils: (a) viscosity (mm<sup>2</sup> s<sup>-1</sup>) and (b) ln (viscosity).

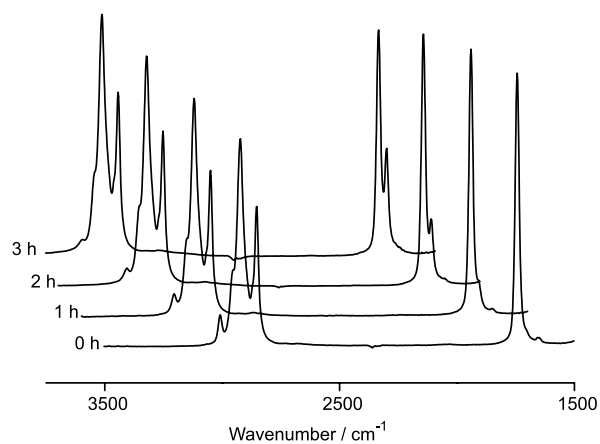
**Table 1.** Apparent kinematic viscosity constant, initial and final viscosities and acid value after 3 h of thermal polymerization of different oils at 300 °C

entry	Vegetable oil	$k \times 10 /$ (ln (mm <sup>2</sup> s <sup>-1</sup> ) h <sup>-1</sup> )	Initial viscosity / (mm <sup>2</sup> s <sup>-1</sup> )	Final viscosity / (mm <sup>2</sup> s <sup>-1</sup> )	Final acid value / (mg KOH g <sup>-1</sup> )
1	UFO	5.1	40	198	14.5
2	Soybean	3.9	33	110	11.6
3	Sunflower	3.7	33	105	11.2
4	Corn	3.5	34	100	10.5
5	Canola	2.3	40	81	8.4



**Figure 3.** Acid value obtained in thermal polymerization using as raw material: UFO (■), soybean (□), sunflower (▲), corn (△) and canola (●) oils.

In sequence, the effect of temperature in the polymerization of UFO was evaluated and the results are shown in Table 2. Because of its high activity when compared to other refined oils, soybean oil was chosen to perform a comparative study. It was possible to observe in Table 2 that the increase in the viscosity and acid values of the polymers were strongly dependent on the temperature. For the temperature range studied, a higher viscosity



**Figure 4.** Infrared spectra obtained during thermal polymerization of UFO.

was obtained using UFO, demonstrating once again its advantages as starting material when compared to refined soybean oil.

#### Catalyst evaluation

The catalytic activity of divalent metal ion complexes with general formula M(Carboxilate)<sub>2</sub> (M = Ni<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> and Sn<sup>2+</sup>) in the polymerization of UFO was evaluated and the main results are presented in Figure 5 and

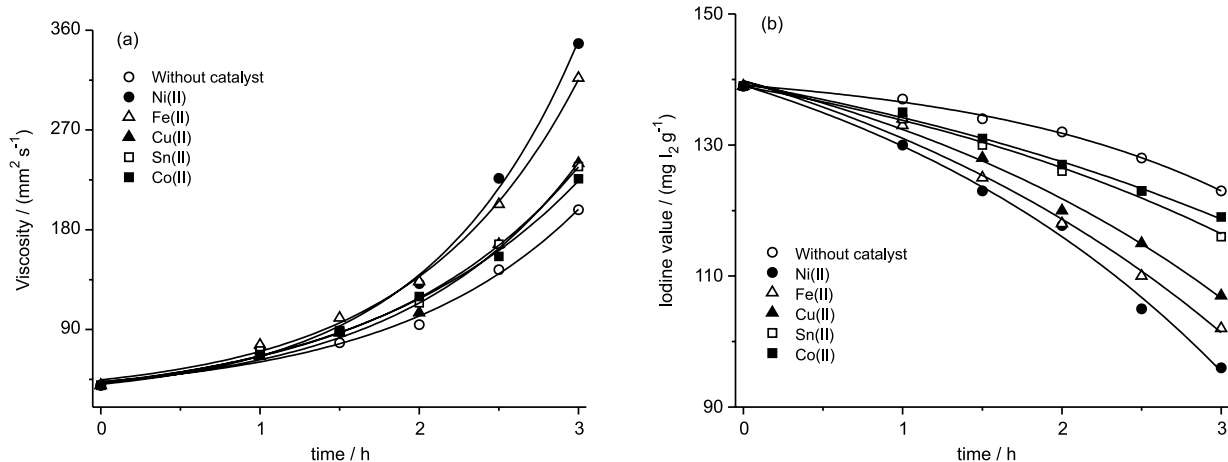
**Table 2.** Apparent kinematic constant, viscosity and acid value of thermal polymerization using soybean and UFO at different temperatures

entry	Vegetable oil	Temperature / °C	$k \times 10 / (\ln (\text{mm}^2 \text{s}^{-1}) \text{h}^{-1})$	Final viscosity / ( $\text{mm}^2 \text{s}^{-1}$ )	Final acid value / ( $\text{mg KOH g}^{-1}$ )
6	UFO	280	2.5	87	4.8
1	UFO	300	5.1	198	14.5
7	UFO	310	10.8	840	25.5
8	Soybean	280	1.9	60	3.2
2	Soybean	300	3.9	110	11.6
9	Soybean	310	8.5	554	20.2

Table 3. As can be depicted in Figure 5a and Table 3, for all complexes, a decrease in the reaction time to achieve similar viscosity than when in the absence of catalyst was observed, evidencing that all complexes presented a catalytic activity and that crescent order in their activity was  $\text{Sn}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Fe}^{2+} < \text{Ni}^{2+}$ . Note that this catalytic activity order was almost the same observed in a previous work for refined soybean oil ( $\text{Co}^{2+} < \text{Sn}^{2+} < \text{Cu}^{2+} < \text{Fe}^{2+} < \text{Ni}^{2+}$ ).<sup>16</sup> When comparing the reaction in the absence of catalyst and in the presence of  $\text{Ni}^{2+}$ , it become clear that the polymerization assisted by the complex increased its apparent kinematic viscosity constant 1.4 times and the final product presented a viscosity 75% higher. It is important to

mention that metal ions with high activity in Diels Alder processes, such as Ni and Fe, were the ones that showed the best performance. On the other hand, the low catalytic activity of Co, usually related to radical formation when in contact with oils and fats,<sup>19</sup> suggested a limited contribution of the radical polymerization in the process.

In Figure 5, it is possible to compare the viscosity (Figure 5a) and the iodine value (Figure 5b) of the polymers for the reactions in the absence and presence of different bivalent metal ions. It may be observed that there is an exponential decay of iodine value in all situations. Using the metal ions, it was possible to observe a higher decay, especially for metals that had promoted greater

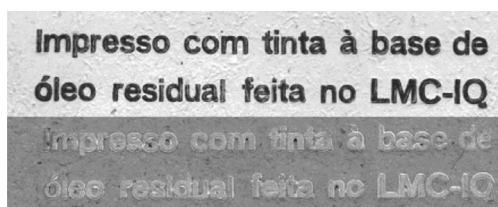
**Figure 5.** Thermal polymerization using UFO in thermal polymerization: in the absence of catalyst (○) and in the presence of  $\text{M}(\text{carboxylate})_2$  (Ni(II) (●), Fe(II) (△), Cu(II) (▲), Sn(II) (□) and Co(II) (■)): (a) viscosity and (b) iodine value.**Table 3.** Apparent kinematic viscosity constant, viscosity and acid value in thermal polymerization at 300 °C using UFO and different catalysts

entry	Vegetable oil	$k \times 10 / (\ln (\text{mm}^2 \text{s}^{-1}) \text{h}^{-1})$	Final viscosity / ( $\text{mm}^2 \text{s}^{-1}$ )	Final acid value / ( $\text{mg KOH g}^{-1}$ )
1	-	5.1	198	14.5
10	Ni(II)	7.2	348	25.3
11	Fe(II)	6.8	317	24.2
12	Cu(II)	5.9	240	20.3
13	Co(II)	5.8	236	18.2
14	Sn(II)	5.7	226	17.4

increases in the viscosity of the polymer. On the other hand, the variation of the acid value followed a linear increase with greater inclination for catalysts with higher catalytic activity. These results corroborate the proposed mechanisms that better explained the polymerization in terms of double-bond reaction than by carboxyl groups.

#### Ink formulation

Finally, a preliminary test was carried out in order to evaluate the possibility of using the UFO based resin to produce printing inks. The polymer obtained using Ni as catalyst in 3 h was mixed with carbon black and titanium oxide to prepare black and white printing ink, respectively. The composition was approximately 80% resin and 20% of pigments. Thus, the inks formulated using the biobased resin were used in a typographic printer and the prints can be seen in Figure 6. It is worth to mention that the performance of these inks in the typographic printer was similar than those petroleum based inks obtained from commercial sources. As can be depicted in Figure 6, the use of UFO based resin did not compromise the final color of the ink, even when using white pigment. Of course, more studies are needed to optimize the production of inks, but this preliminary test highlighted the high potential of UFO as starting material to produce printing inks.



**Figure 6.** Prints on a handmade paper obtained in a typographic printer using black and white inks formulated with UFO based resin (80%, polymer obtained using Ni as catalyst in 3 h) and pigment (20%, carbon black for black ink or titanium oxide for white ink).

#### Conclusion

In summary, it was demonstrated that UFO may become an important source of raw material for the thermal polymerization process to obtain biobased resins suitable to be used as binders in printing inks. Indeed, besides its lower cost, UFO presented a higher reactivity compared to refined oils (soybean, sunflower, corn and canola oils), leading to a polymer with higher viscosity (up to 80%) under similar conditions. Independent of the feedstock, it was also observed that during the polymerization, the decomposition of the ester groups to produce carboxylic acids occurred. Using metal ions ( $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and

$\text{Sn}^{2+}$ ), it was possible to reduce the polymerization time and that the  $\text{Ni}^{2+}$  complex presented the higher catalytic activity.

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