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Soy Ink Vehicles from Waste Frying Oils for Green Printing Technology

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Abstract: The objectives of this study were to synthesis printing ink vehicles via thermal polymerization from waste frying soybean oil. Properties of products with a variety of Waste frying oil (W) to Virgin oil (V) weight ratios (W:V ratios) were determined. We found that both viscosities and molecular weights of the obtained printing ink vehicles increased as the W:V ratios increased. Therefore, different types of eco-friendly printing inks for various printing applications can be produced. In addition, the cost and polymerization time of ink vehicle production could be reduced by using the waste frying oil.

Key words: Waste frying oil, soy ink vehicle, green printing technology, products, ratio

INTRODUCTION

In recent years, much attention has been paid on the problem of waste frying oils from households and food industries. These oils usually contain a large number of harmful decomposition products occurring from hydrolysis, oxidation and polymerization(Cvengros and Cvengrosova, 2004; Kulkarni and Dalai, 2006; Choe and Min, 2007; Ng *et al*., 2014). Normally, they are poured down to the drain or spilled onto ground which causes many environmental problems. Sometimes, they are integrated into the food chains through animal meat that bring potential negative effects on human health. Various approaches have been studied utilizing these residues in any way that is not harmful to human beings, for example, biodiesel production (Kulkarni and Dalai, 2006). Vegetable oil based-printing inks, the nonpetroleum-based printing inks produced from vegetable oils have received more attention since the petroleum crisis in 1970's. Due to the environmental benefits such as sustainable raw materials and few Volatile Organic Compounds (VOCs), vegetable oil based-printing inks play an essential role for green printing technology. Several studies have demonstrated the possibility of producing vegetable oil based-printing inks via thermal polymerization from various vegetable oils such as soybean, canola, cottonseed, safflower and sunflower oil (Erhan and Bagby, 1991, 1994, 1995; Erhan *et al*., 1992). Results show that these printing inks had physical properties that met the industry standards for lithographic and letterpress newsprint applications and soybean oil-based ink vehicles were proved to degrade faster than the commercial petroleum-based vehicles (Erhan, 1995). Recently, many manufacturers have made extensive efforts to develop products from soybean oil-based formulations. Therefore, soy inks are applied nowadays in many printing applications. For synthesis via thermal polymerization, the vegetable oil is heated at elevated temperature in which the unsaturated bonds of triglycerides are thermolytic to form radical species and undergo polymerization to form high molecular weight polymers (Erhan *et al*., 1992). However, the crucial hindrance in the commercialization of vegetable oil based-printing ink is the greater price of virgin vegetable oils and also the high energy consumption during the manu-facturing process.

Waste frying oils which are priced 2-3 times lower than virgin vegetable oils could be promising alter-native raw materials for the manufacture of printing inks. Additionally, the structural transformation of oil during frying is in a similar manner to that of vegetable oil based-ink vehicles produced via thermal poly-merization (Cvengros and Cvengrosova, 2004; Choe and Min, 2007; Mehta and Swinburn, 2001; Zhang *et al*., 2012). Thus, by using these waste frying oils, it is not only prevents serious environmental pollution but also provides the positively influences on the reduction of the final cost of printing inks. In this research we attempted to prepare eco-friendly printing ink vehicles from waste frying soybean oil blending with virgin oil at different weight ratios. The effect of waste frying oil composition on

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properties of the soy ink vehicles was studied. The printing inks based on the obtained ink vehicles were also prepared to evaluate the potential use of the obtained vehicles.

MATERIALS AND METHODS

Waste frying soybean oil was collected after being used several times for frying purposes at small shops within Chulalongkorn University, Thailand. Virgin soybean oil was purchased from Thai Vegetable Oil Public Company Limited, Thailand and used as received. Activated bleaching earth (Wonder Earth NK 309) was a gift from Bornnet Corporation Co., LTD., Thailand. Carbon black was purchased from Chemical Village Co., Ltd., Thailand.

Synthesis of ink vehicles and printing inks: Prior to synthesis, waste frying soybean oil was filtered to eliminate discernible impurities. The filtrated oil was then gently stirred for 2 h in the presence of 5% w/w of activated bleaching clay at 80°C under nitrogen atmosphere for decolorization. After that, the mixture was centrifuged and filtered to remove the as-absorbed clay. To synthesis the soy ink vehicles, the waste frying soybean oil was blended with virgin oil at various weight ratios and placed in a 2000 mL three-necked reaction flask equipped with a mechanical stirrer. The weight ratios of waste oil to virgin oil were varied from 0:100, 30:70, 50:50, 70:30 and 100:0. The blending oil was pre-treated with nitrogen gas for 10 min to eliminate oxygen gas in the mixture and then heated at 300°C for 4 h under nitrogen atmosphere. After which time, the obtained vehicle was allowed to cool to room temperature, degassed and kept in a vacuum bottle until further investigation.To evaluate the possible use of the obtained ink vehicle as printing ink binder, black printing inks were prepared by mixing the asprepared vehicles with carbon black (10 %w/w). The mixtures were vigorously stirred at 70°C for 12 h. The viscosity, ink tack and rub resistance of the obtained printing inks were also determined.

Characterization and property measurements: The physical properties of raw materials as well as the asprepared vehicles were examined with regard to Iodine Value (IV), Acid Value (AV), Molecular weight (M_w), viscosity and color. The iodine value was determined with modified method based on ASTM D1959. The acid value was calculated based on ASTM D1980. The weight average molecular weight was determined by means of a GPC system (Shimadzu class-VP, Shimadzu Scientific Instruments, Columbia, MD, USA). The viscosities of both prepared ink vehicles and printing inks were measured using a Brookfield DV-III programmable viscometer (Brookfield Engineering Labs, Stoughton, MA USA). The color was determined by comparison with the color of standard Gardner solutions. The chemical structures were characterized using a Nicolet FTIR spectrophotometer (Model Thermo Nicolet NEXUS 670; Nicolet Instrument Inc., Madison, WI, USA). Ink Tack was measured by Tack Tester (Model IGT Tack Tester 450; IGT Testing System Inc., USA) based on ASTM D4361. Ink rub resistance was measured by an Ink rub tester (Model Digital Ink rub Tester 10-18-01-0001; TMI Group of Companies, USA) based on ASTM D526

RESULTS AND DISCUSSION

Properties of waste frying soybean oil: Table 1 illustrates the properties of waste frying oil in comparison with those of virgin oil. The iodine value which measures the degree of unsaturation of oil decreased from 123 for virgin oil to 91 g I_2 100 g^{-1} for waste frying oil. The waste frying oil had a molecular weight of 2,206 g mol^{-1} which is higher than that of virgin oil (1,663 g mol^{-1}). In addition, the oil was darker and its acid value increased after frying. In order to study the chemical transformation of waste frying oil, FTIR spectrum was analyzed. Figure 1 illustrates the FTIR spectrum of the waste frying oil in comparison with that of the virgin soybean oil. The characteristic absorption peaks of the virgin oi coincided with the general evidence of triglyceride structures, presenting absorption peaks at 3009 cm^{-1} (C = C-H stretching), 2926 cm^{-1} and 2855 cm^{-1} (C-C-H stretching), 1746 cm^{-1} (C=O stretching of esters) and1650 cm^{-1} (C=C stretching). For waste frying oil, its FTIR spectrum is identical with that of virgin soybean oil except the decrease in absorption

Table 1: Properties of virgin and waste frying soybean oils

Types of oils	M_w g mol^{-1}	IV (g I_2 100 g^{-1})	AV (mg KOH g^{-1})	Color (Gardner)
Virgin oil	1.663	123	0.22	1.5
Waste oil	2.206	91	0.48	4.0

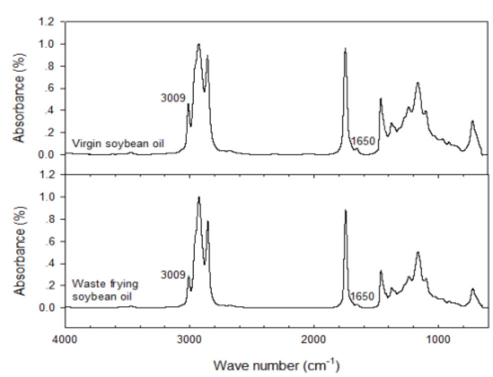

Fig. 1: FTIR spectra of waste oil and virgin soybean oil

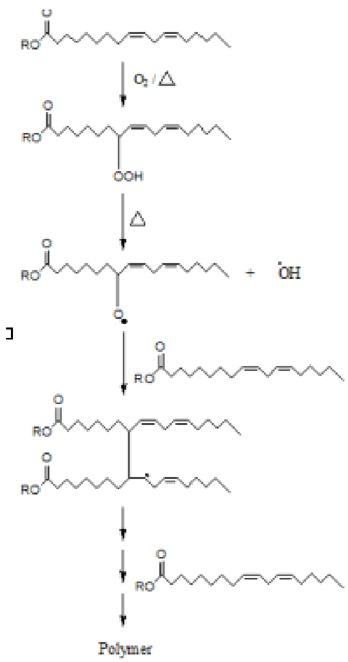

Fig. 2: Thermal oxidation mechanism of unsaturated oil during frying

peaks of unsaturated structures at 3009 cm^{-1} and 1650 cm^{-1} which confirms the chemical alteration of the unsaturated structures after frying. This is owing to the reduction of unsaturated structures of oil during frying at high temperature in the presence of air and moisture (Cvengros and Cvengrosova, 2004; Kulkarni and Dalai, 2006; Choe and Min, 2007; Zhang *et al*., 2012). The proposed thermal oxidation mechanism of unsaturated oil during heating is depicted in Fig. 2. As shown in Fig. 1, the carbon carbon double bonds can undergo oxidation when in contact with oxygen at elevated temperature to form alkyl hydroperoxides (ROOH) which then decompose to produce alkoxy radicals (RO) that are capable of further polymerization. Dialkyl peroxides (ROOR) are also produced and readily decomposed to peroxy radicals (ROO·) leading to dimer and polymer formation (Choe and Min, 2007). This corresponds to an increase in the molecular weight and a decrease in the iodine value of the oil after frying. Additionally, an increase in the acid value is possibly due to hydrolysis of the oil after frying that produces free fatty acids (Choe and Min, 2007) while the color of the waste frying oil is darker due to the presence of nonvolatile substances resulted from oxidation reaction after frying. Another reason for frying oil darkening is maillard's compound (Mehta and Swinburn, 2001).

Properties of soy ink vehicles: Soy ink vehicles were prepared by heat polymerization of the oils under nitrogen blanket. Table 2 shows the effect of waste frying oil to virgin oil (w:v) weight ratios on the physical properties of the as-prepared ink vehicles. It is clearly seen that the molecular weight, viscosity and acid value of the vehicles increase whereas the iodine value decrease with the increase in the amount of waste frying oil. In inert atmosphere, the radical chain reaction is initiated by allylic radicals which are formed by the abstraction of hydrogen atoms at methylene carbons alpha to double bonds as shown in Fig. 3. Dimerization or polymerization is achieved by linkage of carbon-carbon double bonds to form dimers or polymers without oxygen atom (Mehta and Swinburn, 2001)

Table 2: Properties of as-prepared soy ink vehicles with various waste frying oil to virgin oil (W:V) weight ratios

W:V ratio	Mw ($gmol^{-1}$)	Viscosity (cP)	IV (g I_2/100 g)	AV (mg KOH/g)
0:100	3.600	333.0	81	0.79
30:70	3.687	358.0	78	0.82
50:50	3.814	392.0	73	0.87
70:30	4.135	410.0	69	0.95
100:0	5.237	1.038	56	1.98

However, when the waste frying oil was presented in the mixtures, the polymerization was accelerated by peroxide products obtained during frying that easily decomposed into reactive radicals at elevated temperature (Mehta and Swinburn, 2001). Not only peroxide products presenting in waste frying oil acted as initiating species in the thermal polymerization but also the poly-merization of oil took place during frying process. Thus, the reaction time to produce ink vehicle could be shortened by using waste frying oil. As a result, the molecular weight and viscosity of the obtained ink vehicles increased with increasing waste frying oil content. The alteration of vehicles' chemical structures was investigated using FTIR spectra. As shown in Fig. 4 the FTIR spectra of the as-prepared vehicles exhibit similar characteristic absorption peaks to those of virgin and waste frying oils (Fig. 1), except for the remarkable decrease in absorption peaks of unsaturated bonds at 3009 cm^{-1} and 1650 cm^{-1}. However, for the vehicle produced from100% waste oil (W:V ratio = 100:0), the board absorption peak of carboxylic groups (-COOH) at 3000-2500 cm^{-1} was observed. This observation indicates that the tri-glycerides decomposed into carboxylic acids during the thermal polymerization. These results are related to the physical properties of the as-prepared vehicles as well.

Properties of as-prepared black printing inks: To investigate the potential use as printing ink binder, the properties such as ink viscosity, ink tack and rub-off resistance of the black printing inks formulated with the obtained soy ink vehicles were measured and the results

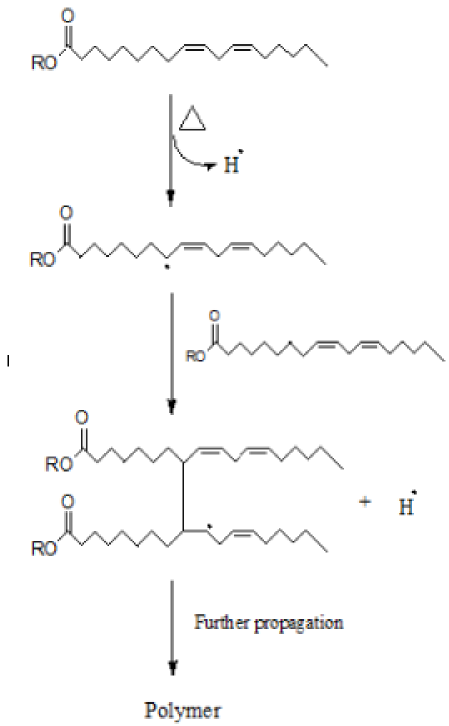

Fig. 3: Thermal polymerization mechanism of ink vehicles in inert atmosphere (Choe and Min, 2007)

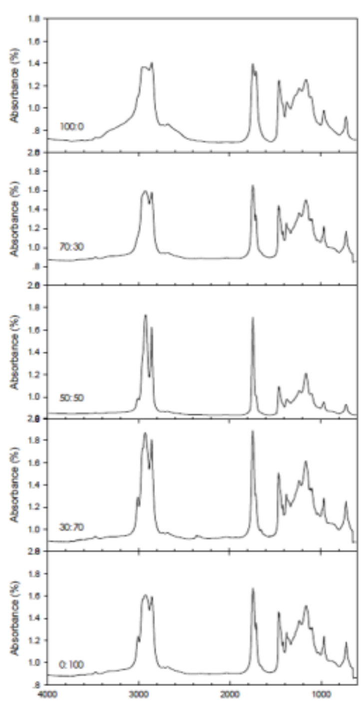

Fig. 4: FTIR spectra of the as-prepared printing ink vehicles with various Waste oil to Virgin oil (W:V) weight ratio

Table 3: The properties of black printing inks prepared from soy ink vehicles with various Waste frying oil to Virgin oil (W:V) weight ratio

w:v ratio	Ink viscosity (poise)	Ink tack (gm)	Rub resistance (%)
0:10050:50	66.25	1.571	82.3820
100:0	23.30	3.37	54.0000

are presented in Table 3. The obtained printing inks are characterized by viscosities from 6-23.3 poises, tack values from 1.57-3.37 gm andrub resistance from 54- 82.3%. The typical viscosities of a black letterpress new ink and black lithographic news ink are in the range of about 5-12 and 13-24 poises, respectively while the tack values for letterpress inks are about 2.6-3.4 gm and about 3.5-4.8 gm for lithographic inks (Erhan *et al*., 1992). The printing ink based on 100% waste frying oil (W:V = 100:0) had the highest tack value probably due to its highest viscosity (Izdebska and Thomas, 2015). Tack values of these inks were lower than the typical values. However, better tack value of the formulated inks can be achieved by adding appropriate additives. The data shown in Table 3 suggest that the 100% waste frying soybean oil-based ink is suitable for lithographic application, while the other two are suitable for making letterpress inks.

For rub resistance, the result was analyzed in term of the amount of transfer ink from the tested printed sample to white paper. As shown in Table 3, the obtained ink from 100% waste frying soybean oil had the lowest rub resistance. This may be due to its highest viscosity affecting in decreased absorption of ink into the printed sample surface. However, further investigation on printing ink formulations based on waste frying oil will be continued and we expect that waste soybean frying oil could be a promising alternative raw material for the manufacture of green printing inks.

CONCLUSION

Waste frying soybean oil-based printing ink vehicles were successfully prepared via heat polymerization. A good relationship was found between the molecular weights and their viscosities of the as-prepared soy ink vehicles. With increasing content of waste frying oil, the polymerization was accelerated leading to the increase in molecular weight and viscosity of the synthesized vehicles. The obtained formulated inks are suitable for making lithographic and letterpress inks. This vehicle system can be easily modified to give products with a range of properties that suitable for making inks with a variety of printing applications. Results suggest that this approach can be used to produce environmental friendly and lower-cost ink vehicles from waste products such as used frying soybean oil.

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