Materials Research. 2014; 17(2): 386-391
DOI: http://dx.doi.org/10.1590/S1516-14392014005000017

Synthesis and Application of Natural Polymeric Plasticizer Obtained Through Polyesterification of Rice Fatty Acid

Melissa Gurgel Adeodato Vieira[a], Mariana Altenhofen da Silva[a], André Costa Gomes Maçumoto[a],

Lucielen Oliveira dos Santos[b], Marisa Masumi Beppu[a]*

[a]School of Chemical Engineering, University of Campinas – UNICAMP, Av. Albert Einstein, 500,
Cidade Universitária "Zeferino Vaz", CEP 13083-852, Campinas, SP, Brazil
[b]School of Chemistry and Food, Federal University of Rio Grande – FURG, CP 474,
CEP 96201-900, Rio Grande, RS, Brazil

Received: April 16, 2013; Revised: January 7, 2014

This study includes the synthesis of a new natural plasticizer obtained through esterification reaction of rice fatty acid and polyols, its physicochemical characterization and its preliminary application in polyvinyl chloride (PVC). Monopropylene glycol, octanol and diethylene glycol were used as polyols for esterification reaction. Catalyst Fascat® 4100, was also added. Viscosity, acidity and hydroxyl index, moisture content, molar mass, chemical composition (by FTIR) and color were determined to characterize the natural plasticizer synthesized. The results were compared with a commercial plasticizer (DOA: di-octyl adipate) derived from petrochemical source and synthesized in laboratory. According to the results, except from color, the natural plasticizer presented similar properties of commercially available plasticizers, such as DOA. Mechanical tests indicated that the addition of the natural plasticizer to PVC films resulted in a significant increase on its elongation at break (371.2%) compared to pure PVC film, indicating a possible application for this plasticizer.

Keywords: *esterification, fatty acid of rice, natural plasticizer*

1. Introduction

Rice bran is a by-product of the rice milling process to produce white rice. Rice bran oil (RBO 20-25 wt% in bran oil) is a mixture of esters of feluric acids with sterols and triterpene alcohols. The unsaponifiable content of RBO is approximately 4.0 to 5.0 %.

Plasticizers are an important class of non-volatile compounds of low molecular weight that are widely used as additives in the polymer industry[1]. They are necessary to maintain the film integrity, to avoid pores and cleavages[2], increase its flexibility, workability, or distensibility[3-6].

Plasticizers are substances that, once incorporated to the polymeric matrix, reduce the deformation tension, hardness, density, viscosity, glass transition temperature (Tg) and electrostatic charge of a polymer, increasing at the same time its flexibility, resistance to fracture and dielectric constant, among other properties[7]. Other properties are also affected, such as crystallinity degree, optical clarity, electrical conductivity, fire behavior, biodegradability, etc[8,9].

The efficiency of a plasticizer is dependent on its chemical structure, molecular weight and concentration. Its compatibility with the polymer is crucial for an effective plasticization, and is a function of molecules polarity and molecular configuration, i.e., the relative attraction between the polymer and plasticizer, as well as solubility parameters and dielectric constant[10].

Most plasticizers are usually prepared via esterification reaction between corresponding acids/anhydrides and alcohols in the presence of acid catalysts[1].

The use of natural plasticizers, characterized by low toxicity and good compatibility with several plastics, resins, rubbers and elastomers, in substitution to conventional plasticizers has become more and more attractive and has also motivated extensive research in the industrial and academic areas[2-4,11-16]. The application of phthalates as plasticizers is being questioned due to their toxicity induced by its migration. Indeed, the search for natural-based plasticizers is related to the increased interest of material researchers and industries in the development of new bio-based materials, made from renewable and biodegradable resources with the potential to reduce the use of conventional plastic goods.

In this context, the aim of this study is to develop a natural plasticizer through the esterification reaction of rice fatty acid followed by its physical and chemical characterization for potential application in polymers such as polyvinyl chloride (PVC). The concept of this natural plasticizer can be considered as an attempt to reuse agricultural by-products and to develop non-toxic polymer additives.

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*e-mail: beppu@feq.unicamp.br

2. Material and Methods

2.1. *Rice fatty acid*

The fatty acid of rice oil distillate was provided by Wells-Nuodex (Indústria Química Ltda, Brazil), with chromatographic average composition of 22% of palmitic acid, stearic acid 5%, oleic acid 33%, linoleic acid 36% and 4% linolenic acid. The physical characteristics of the rice fatty acid are presented in Table 1.

2.2. *Synthesis of natural plasticizer*

The natural plasticizer was prepared using a basis of 400 g of reaction mixture, containing octanol (5 wt%) diethylethylene glycol (10 wt%) monopropylene glycol (5 wt%), rice fatty acid (80 wt%) and Fascat® 4100 Catalyst (Butyl stannoic acid with 56.85% Sn) (0.004 wt%). Fascat® 4100 Catalyst is an amorphous white solid commonly used in the synthesis of saturated polyester resins and also used to produce polymeric plasticizers.

For the synthesis reaction the classical process was performed. The system was composed by a round bottom flask with 5 necks, an electric flask heating mantle, a distillation column (Vigroux 300 mm), a straight pipe condenser, a mechanical stirrer with glass stem and Teflon helix and a collection beaker. Nitrogen was used to promote an inert environment and a stirring level of 150 rpm was maintained throughout the process. Glass beads (3-5 mm) were added to the flask in order to promote turbulence during reaction. The esterification reaction was followed through hydroxyl and acidity index determination.

2.3. *Synthesis of commercial plasticizer*

A commercial plasticizer (DOA - dioctyl adipate) was synthesized in laboratory instead of using a standard grade from the market in order to validate the reaction system, as well as to compare the physico-chemical characteristics of the obtained products. The commercial plasticizer, synthesized from a derivative of the petrochemical chain (adipic acid), was produced using the same experimental system and conditions described for the natural plasticizer, taking a reaction time of 15 hours. The formulation (400g basis of reaction mixture) contained octanol, diethylethylene glycol, monopropylene glycol, adipic acid and Catalyst Fascat® 4100 (Butyl stannoic acid with 56.85% Sn).

Table 1. Physical characteristics of rice fatty acid.

Characteristic	Material
Aspect (25 °C)	Pasty yellow
Gardner Color	6 max.
Iodine index (cg I^2/g)	95-108
Saponification index (mg KOH/g)	196-206
Acidity index (mg KOH/g)	195-205
Moisture (%)	0.5 max.
Unsaponifiables (%)	3.0 max.
Title (°C)	27-34

2.4. *Natural plasticizer characterization*

2.4.1. Viscosity determination

The viscosity was determined using a Brookfield Rotatory Viscometer (Model LVDV II) with spindle number 18 (25 °C) at a rotation speed of 75 rpm.

2.4.2. Acidity index

Aliquots of approximately 1 g of plasticizer were diluted in 25 mL of a toluol/methanol solution (2:1) and titrated with alcoholic 0.1 M KOH solution, using phenolphthalein as indicator.

The acidity index (I_{ac}), expressed in mg KOH/g sample is obtained by Equation 1.

$$I_{ac} = \frac{(V_a - V_b) \cdot 56{,}1 \cdot M}{m} \tag{1}$$

where V_a is the volume of KOH solution used in the sample titration (mL), V_b is the volume of KOH solution used in blank titration (mL), M is the molarity of the KOH solution (M) and *m* is the sample mass (g).

2.4.3. Color

Color was determined in a colorimeter (Color Quest XE - Hunterlab, USA). Parameters L0* (luminosity), a0* (red-green) and b0* (yellow-blue) were determined for the pattern and compared with the plasticizer sample (L*, a* and b*). Equation 2 was used to calculate the color difference.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

where: ΔL* = L* - L0*; Δa* = a* - a0* and Δb* = b* - b0*.

2.4.4. Hydroxyl index

The hydroxyl index was determined according to ASTM standard method D4274-05[17]. Aliquots of plasticizers were transferred to Erlenmeyer flasks containing 20 mL of acetylating solution (acetic anhydride and pyridine solution). The flasks were maintained in a thermostatic bath at 98°C for two hours. When room temperature was reached, 20-30 mL of distilled water and 1 mL of phenolphthalein were added. Then samples were titrated with standardized NaOH solution (0.5 M). The hydroxyl number (N_{OH}), expressed in mg KOH (equivalent to hydroxyl groups) per g of sample is given by Equation 3.

$$N_{OH} = \frac{(V_b - V_a) \cdot 56{,}1 \cdot M}{m} \tag{3}$$

where V_a is the volume of the NaOH solution used in the sample titration (mL), V_b is the volume of the NaOH solution used in blank titration (mL), M is the molarity of the NaOH solution (M) and *m* is the sample mass (g).

2.4.5. Molar mass distribution

The molar mass and the polydispersity index of the natural plasticizer was determined by gel permeation chromatography (GPC) using a GPC Advanced System composed by a GPCmax - VE 2001 - Viscotek Module (bomb, degasser and automatic sampler) and a Viscotek Module TDA302 (oven for columns and detectors, refractometer, viscometer and light scattering 90°). Data was acquired using a Viscotek OmniSEC and control system v. 4.1.0.224 software.

The separation of sample components was achieved by using two Viscogel columns (7.8 x 300 mm) from Viscotek, with molar mass up to 10 million Daltons. The temperature of the columns was maintained at 30°C. Tetrahydrofuran was used as mobile phase (eluent) at a flow-rate of 1.0 ml/min. The volume injected was 100 µL. Detectors calibration was performed using PS170K and 400K patterns. The standard curve was obtained using THF solutions of known plasticizer concentration (1 to 7% m/m).

2.4.6. Infrared Spectroscopy by Fourier Transform (FTIR)

The chemical composition of the natural plasticizer was investigations through FTIR analysis using a Spectrum One – FT–IR spectrometer (Perkin Elmer, England). The absorption spectra was obtained using CaF_2 cell in the range of 4000 to 850 cm^{-1}.

2.4.7. Moisture content

The moisture content of natural plasticizer (%) was determined by Karl Fisher method (Metrohm, 758 KFD Titrino model) in triplicate.

2.5. *Preparation of pure and plasticized PVC films*

PVC films were prepared by casting, according to procedure described in Lindström and Hakkarainen[18]. In a glass beaker, 0.4 g of PVC K70 resin (Braskem, Brazil) was mixed with the natural plasticizer (30 wt% in relation to PVC resin) followed by the addition of 9 mL of tetrahydrofuran. The mixture was homogenized using a magnetic stirrer for 10 min at room temperature (25 °C) and then the solution was casted in a clean Petri dish (diameter 14 cm). The films were dried in ambient pressure and room temperature until complete solvent evaporation.

2.5.1. Mechanical properties

Tensile strength (*TS*) and percentage tensile elongation at break (*E*) of the PVC films were determined at room temperature using a TA.XT2 (Stable Microsystems SMD, England) according to ASTM standard method D882[19]. Films were cut into strips (10 x 2.54 cm) and mounted between the corrugated tensile grips of the instrument. The initial grip spacing and cross-head speed were set at 50 mm and 0.1 cm/s, respectively. The tensile strength was expressed as the maximum force at break divided by the initial cross-sectional area of the film strip and the elongation at break as a percentage of the original length.

Thickness of films was measured using a digital micrometer (Mitutoyo, MDC-25S, Japan). Measurements were taken at ten different positions of the film surface and the mean value was determined.

3. Results and Discussion

3.1. *Synthesis of natural plasticizer*

During reaction time, 3 samples were taken for acidity and hydroxyl index determination. Tests were performed in duplicate. It was necessary 17 hours of reaction (with temperature above 210 °C) until an adequate acidity index was achieved (below 1%). The amount of condensed liquid at the end of the reaction was 14 mL (11 mL water and 3 mL glycols).

3.2. *Synthesis of commercial plasticizer*

As for the natural plasticizer, 3 samples were taken for acidity and hydroxyl index determination during the esterification reaction for dioctyl adipate commercial plasticizer synthesis (DOA). Tests were performed in duplicate. It was necessary 29 hours of reaction (with temperature above 210 °C) until reaching an acidity index around 2.91%. The amount of condensed liquid at the end of the reaction was 44 mL (38 mL water and 6 mL glycols).

3.3. *Natural plasticizer characterization*

3.3.1. Physical characteristics of natural plasticizer

Physical characteristics of the natural plasticizer based on rice fatty acid compared to the commercial plasticizer (DOA) are shown in Table 2. The results are within the

Table 2. Physical characteristics of natural and commercial plasticizers.

Characteristic	Natural plasticizer	Commercial plasticizer (DOA)
Physical state (20 °C)	Liquid	Liquid
Acidity index	8.8 mg KOH/g (0.88%)	29.1 mg KOH/g (2.91%)
Hydroxyl index	23.87 mg KOH/g of sample	8.73 mg KOH/g of sample
Color	Dark amber Pattern: L_0*=92.03; a_0*= -0.88; b_0* = 0.63 Sample: L* = 9.53; a* = 0.03; b* = 4.99 ΔE = 83.12	Dark amber
Viscosity (20 °C)	µ = 31.5 cP	µ = 15 cP*
Moisture (Karl Fischer)	0.76 ± 0.03% (b. u.)	2.67 ± 0.44% (b. u.)
Molar mass	Mn = 385 Daltons (383.5 g/mol); Mw = 55.276 Daltons; Mw/Mn = 143.393	Mn = 370 g/mol *
Flash Point	-	190°C

*Averages values obtained from manufacturer.

typical values for both plasticizers, except from color, for which a light yellow color was expected. New tests, with addition of a natural antioxidant will be performed, in order to prevent darkening/oxidation of the final product.

It can observe that the hydroxyl and acidity index of natural plasticizer, measured after 17 hours of reaction, are close to the typical values of commercial plasticizers (hydroxyl index $\approx$ 20 mg KOH/g and acidity index $< 0.5\%$).

Both plasticizers can be considered "monomeric", showing molar masses lower than 500 g/mol. Low molar mass plasticizers can be more easily incorporated to polymers, however, they can also show low permanence, i.e., they are easily removed from polymeric matrix. The permanence of a plasticizer in a polymeric matrix is deeply related with volatility, resistance to migration and extraction by water, solvents and fuels.

Considering homologous chemical substances, the higher the plasticizer molar mass is, the higher is the flash point and, consequently, the lower is the volatility. The flash point of the natural plasticizer was not determined, but it is expected to be closer to the value of the commercial plasticizer (DOA).

3.3.2. Chemical composition analysis by FTIR

Fourier Transformed Infrared Spectroscopy was performed to identify organic groups present in the synthesized natural plasticizer. The natural plasticizer is resultant of polyesterification reaction between rice fatty acid and polyols in presence of a catalyst, and has as products, esters and water. The release of water during the synthesis process, the decreasing values of hydroxyl and acidity index, as well as the characteristic esters peaks in FTIR spectrum confirm the occurrence of the esterification reaction.

The FTIR spectrum of the natural plasticizer with its respective identified peaks is shown in Figure 1. The absorption bands with correspondent groups and/or bindings are found in Table 3.

The peaks observed in Figure 1, refer to alkanes, alkenes and saturated aliphatic esters. Alkanes only have absorptions due to C-H and C-C stretching vibrations; and C-C-C and H-C-H angular deformation vibrations. The weak band in 3007.73 cm^{-1} is related to C-H stretching binding of sp^2 carbon, and therefore to unsaturation content. It is found that the more intense this band, the richer is the compound in double bindings. In the 3000-2850 cm^{-1} range, two bands can be observed due to symmetric and asymmetric stretching of CH_3 and CH_2 bindings. In 1465 cm^{-1}, $\nu_{as}CH_3$ usually overlaps with the δ_sCH_2 band. In the absorption region of 1390-1370 cm^{-1}, only one peak attributed to symmetric angular deformation of $-CH_3$ group was observed[20].

Table 3. Absorption bands indentified in FTIR spectrum for the natural plasticizer.

Binding or Function	Absorption range (cm^{-1})	Attribution
Alkene	3007.73	ν=CH or νCH_2
Alkane	2924.88	$\nu_{as}CH_2$
Alkane	2853.82	ν_sCH_2
Saturated aliphatic ester	1739.88	$\nu_sC=O$
Alkane	1464.8	$\nu_{as}CH_3$ or δ_sCH_2
Alkane	1378.23	δ_sCH_3
Alkane	1349.38	ν_sCH
Saturated aliphatic ester	1243.58	νC-CO-O
Saturated aliphatic ester	1179.64	νC-CO-O
Saturated aliphatic ester	1137.61	νO-C-C

ν_s: Symmetric vibration, ν_{as} asymmetric vibration, δ_s: symmetric angular deformation in plan, ω: symmetric angular deformation out plan ("wagging"), τ: symmetric angular deformation out plan ("twisting").

The saturated aliphatic esters show a band related to C=O binding stretching in region of 1750-1725 cm^{-1}. There were also strong bands observed in 1275-1185 cm^{-1} and in 1160-1050 cm^{-1}. The first involves the stretching between oxygen and carbonyl carbon, attached to C-C binding stretching. The second is related to the stretching between oxygen atom and other carbon[20].

The FTIR analysis was able to confirm the presence of ester groups in the obtained natural plasticizer.

3.4. *Mechanical properties of PVC films*

The values of the mechanical properties of PVC films are given in Table 4. The tensile strength (TS) accounts for the film mechanical resistance due to the cohesion between the chains, while the elongation at break (E) measures its plasticity, which is the capacity of the film to extend before breaking.

By looking at Table 4 it is possible to observe a significant influence of the addition of the natural plasticizer to PVC films. An increase of 371.2% (4.71 times higher for plasticized PVC) was observed for its elongation at break,

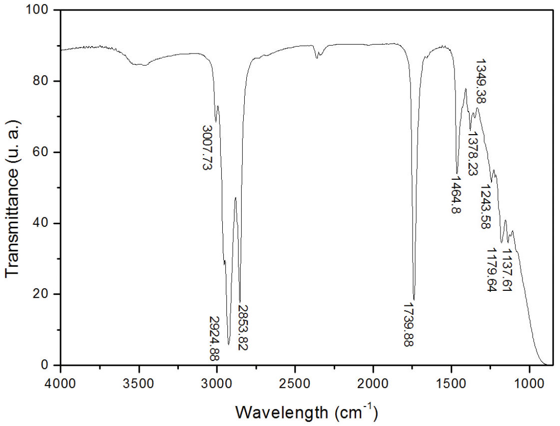

Figure 1. FTIR spectrum of natural plasticizer.

Table 4. Mechanical properties of pure PVC and plasticized PVC films.

Film	TS (MPa)	E (%)
PVC	45.39 ± 4.64[b]	22.18 ± 2.53[a]
Plasticized PVC	26.97 ± 5.51[a]	104.51 ± 17.04[b]

Average ± standard deviation of ten experimental determinations. Averages with the same letter in the same column indicates no significant difference ($p<0.05$) in Tukey test.

and a consequent decrease in tensile strength of 40.58%. These results indicate an expressive plasticization effect of the natural plasticizer synthesized. More experiments based on film impact strength, Young's modulus and flexural strength, for example, must be also conducted to better investigate this potential application.

4. Conclusions

The results showed that it is possible to obtain a natural plasticizer based on rice fatty acid, showing interesting properties compared to commercial plasticizer. The polyesterification reaction is essential in the synthesis process and several parameters influence in this stage.

The experimental set up used for this reaction showed satisfactory performance for both natural and commercial plasticizer synthesis. The natural plasticizer showed low molar mass, being therefore more easily incorporated into polymeric matrix. However, this characteristic can induce lower permanence and solvent extraction. The presence of ester groups in the natural plasticizer was confirmed by FTIR analysis.

The addition of the natural plasticizer resulted in a significant increase in the elongation at break compared to PVC pure film, indicating an expressive plasticization effect of this substance. The incorporation of the natural plasticizer in PVC polymeric matrix showed promising preliminary results, glimpsing a potential application that will be further investigated.

A better understanding of the interactions between the bio/polymers and the natural plasticizer as well as and the knowledge of the fundamental physicochemical and biochemical properties are still needed in order to enable the production of materials using compatible plasticizers.

Acknowledgements

The authors would like to thank CNPq (Proc n. 150272/2009-0) and CAPES (Proc n. 1989/2008) for financial support.

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