

## Epoxidation of Modified Natural Plasticizer Obtained from Rice Fatty Acids and Application on Polyvinylchloride Films

Adelia Ferreira Faria-Machado,\* Mariana Altenhofen da Silva, Melissa Gurgel Adeodato Vieira, Marisa Masumi Beppu

School of Chemical Engineering, University of Campinas (UNICAMP), Cidade Universitária "Zeferino Vaz", Campinas, SP 13083-852, Brazil

\*Present address: Embrapa Food Technology, Av. das Américas 29501, Rio de Janeiro, RJ 23020-470, Brazil

Correspondence to: M. M. Beppu (E-mail: beppu@feq.unicamp.br)

**ABSTRACT:** In recent years, much research effort has been driven to develop alternative plasticizers for medical and commodity plastic materials. In this study, a modified natural plasticizer, synthesized by esterification of rice fatty acids, was modified by epoxidation with peroxy acid generated *in situ*. Two natural epoxidized plasticizers were obtained, using peracetic acid (NP-Ac) and peroctanoic acid (NP-Oc) as reagent. PVC films after addition of these natural epoxidized plasticizers presented fairly good incorporation and plasticizing performance, as demonstrated by results of mechanical properties,  $T_g$  values (as shown by DSC), optical microscopy, exudation, and migration tests, FTIR and X-ray diffraction obtained for plasticized PVC films. NP-Ac plasticizer presented enhanced plasticizing performance compared with NP-Oc, probably due to a higher epoxidation degree obtained in the reaction with peracetic acid. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** modified natural plasticizer; epoxidation; rice fatty acid; PVC

Received 21 July 2011; revised 12 September 2011; accepted 8 March 2012; published online 00 Month 2012

DOI: 10.1002/app.37671

### INTRODUCTION

A plasticizer is a material that when added to another substance, makes the material softer and more flexible.<sup>1</sup> According to the International Union of Pure and Applied Chemistry (IUPAC), a plasticizer may be defined as “a substance incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility. In addition, a plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition (glass transition temperature,  $T_g$ ), or lower the elastic modulus of the product”.

To be effective, a plasticizer must distribute itself between the polymer chains and interact with functional groups, thereby reducing the interactions between the polymer chains and softening the matrix.<sup>2</sup> The composition, size, and shape of a plasticizer as well as its compatibility with the polymer could affect the interactions between the plasticizer and the polymer.<sup>3</sup> The selection of a plasticizer for a specified system is normally based on the compatibility and permanence of the plasticizer, the amount necessary for plasticization, and the desired physical properties of the films.<sup>3,4</sup> Plasticizers are required for nearly all polymers used in film coating to reduce the polymers brittle-

ness, improve flow, import flexibility, and increase toughness, strength, as well as shear resistance.<sup>2</sup>

Some of the most common plasticizers are phthalate<sup>5,6</sup> and adipate<sup>7,8</sup> esters. Esters, phosphates, and epoxides are the most suitable plasticizers for poly(vinyl chloride) (PVC). Since PVC is polar in nature, most ester type plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate are used for its compounds. Fatty epoxides are used directly as plasticizers that are PVC compatible and as stabilizers for PVC resins to improve their thermal stability.<sup>2,9</sup>

Despite the innumerable advantages on using phthalate plasticizers, several controversies have arisen in recent years regarding possible toxicity of these compounds. In addition, DOP can migrate from the polymer matrix to the medium, making the use of this plasticizer unfeasible in packagings that have direct contact with food.<sup>10</sup> Although there is no consensus concerning the wide use of DOP in PVC, manufacturers and consumers are increasingly worried about this issue, considering the perspectives for expanding plasticized PVC applications. Extensive research is going on to find alternative plasticizers which are able to replace conventional plasticizers for medical and other

© 2012 Wiley Periodicals, Inc.

commodity plastic materials.<sup>11</sup> These additives should be non-toxic and biodegradable, and also, when applied in a polymer matrix, they should improve the appearance and mechanical properties of the film.<sup>12</sup>

In recent years, vegetable oil modification technology (e.g., production of epoxidized oil, biodiesel synthesis, among others), has attracted the interest of manufacturers and researchers since these products are obtained from natural renewable sources and can be used as raw material in chemical industries.<sup>13,14</sup> Epoxidized soybean oil (ESBO) and other epoxidized vegetable oils are extensively used in the industry as stabilizers and plasticizers into PVC matrices.<sup>15–17</sup>

Among the possible technologies for vegetable oils epoxidation, the most widely used in the industry is carried out using organic peracids with mineral acids or enzymes as catalysts.<sup>14–17</sup> The reaction between an organic peracid and unsaturated fatty acids results in the addition of an oxygen atom into the double bonds (C=C), forming epoxide groups (or oxirane rings) in the fatty acid molecular structure.<sup>18–21</sup>

In this work, two epoxidant agents were used for modification of a modified natural plasticizer obtained from rice oil distillate. The plasticizing performance of both natural epoxidized products added to PVC films was then evaluated.

## EXPERIMENTAL

### Materials

The fatty acid of rice oil distillate was provided by Wells-Nuodex (Indústria Química, Brazil). Boron trifluoride (BF<sub>3</sub>) was purchased from Merck (Darmstadt, Germany), octanoic acid (98% purity) was purchased from Fluka (Steinheim, Germany). All other solvents and reagents were of analytical grade. A pool containing 36 fatty acid methyl esters (Supelco FAME Mix, Bellefonte, USA) was used for fatty acid identification and the tridecanoic acid methyl ester (purity > 99%, GC) from Sigma-Aldrich (Chemie, Germany) was used as internal standard for fatty acid quantification. PVC K70 resin was kindly donated by Braskem (São Paulo, Brazil).

### Fatty Acid Analysis

The fatty acid from both the rice oil distillate (raw material used for the producing the modified natural plasticizer) and the modified natural plasticizer (before epoxidation reaction) were analyzed by gas chromatography (GC) according to the official method of AOCS.<sup>22</sup> The fatty acid methyl esters (FAME) were analyzed in a GC Shimadzu (model GC2010, Kyoto, Japan), equipped with a flame ionization detector at 260°C, split injector (1/50) at 250°C, a CP-SIL 88 column (100 m, 0.25 mm i.d., 0.20 μm; Chromopack, Middleburg, Netherlands) and a workstation (GCSolution, Shimadzu). The chromatographic conditions were as follows: H<sub>2</sub> as carrier gas at 34 cm/s; N<sub>2</sub> as make up gas at 30 mL/min; column temperature – 120°C for 8 min, increase to 160°C at 20°C/min, at 160°C for 4 min, increase to 195°C at 3°C/min, at 195°C for 10 min, increase to 220°C at 35°C/min, at 220°C for 3 min, increase to 240°C at 20°C/min, at 240°C for 5 min. The injection volume was 2 μL by the hot needle technique for 5 s.

The fatty acids were identified based on the retention times of 36 FAME standards: C8:0, C10:0 to C24:0, C14:1n9, C15:1n5, C16:1n7, C17:1n7, C18:1n9 (*cis* and *trans* isomers), C18:2n6 (*cis* and *trans*), C18:3n6 and n3, C20:1n9, C20:2n6, C20:3n6 and n3, C20:4n6, C20:5n3, C22:1n9, C22:2n6, C22:6, C24:1n9, and were quantified using C13:0 as internal standard.

### Epoxidation of the Modified Natural Plasticizer

The modified natural plasticizer, obtained by esterification reaction between rice fatty acids and polyols as previously reported,<sup>23</sup> was modified by epoxidation with peroxy acid generated *in situ*. Thus, two epoxidized-modified natural plasticizers were obtained, using peracetic acid (NP-Ac) and peroctanoic acid (NP-Oc) for the reaction, respectively.

The modified natural plasticizer was dissolved in toluene (2:1). Then sulfuric acid, in a concentration of 2% (in relation to the mass of plasticizer), and acetic or octanoic acid were added. The system was kept under agitation by a magnetic stirrer and hydrogen peroxide (30% v/v) was slowly dropped into the solution. The amounts of acid (acetic or octanoic) and hydrogen peroxide were calculated in order to obtain a molar proportion of 1:0.5:1.5 (C=C: acid: hydrogen peroxide). After the addition of hydrogen peroxide, the system was heated until 60 ± 2°C and stirred for 6 h. The mixture was then cooled to room temperature and the natural epoxidized plasticizer was recovered by liquid–liquid extraction with ethyl ether. The residual moisture was removed by using anhydrous sodium sulfate and the organic solvents (toluene and ethyl ether) were evaporated in a rotary evaporator (at 40°C) followed by freeze-drying.

### FTIR Analysis of Epoxidized-Modified Natural Plasticizers

Fourier transform infrared spectroscopy (FTIR) analyses were carried out using a Spectrum One—FTIR spectrometer (Perkin Elmer, Waltham, USA). The spectra were acquired in the range of 4000–600 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The modified natural plasticizer was analyzed as a liquid supported on NaCl pellets.

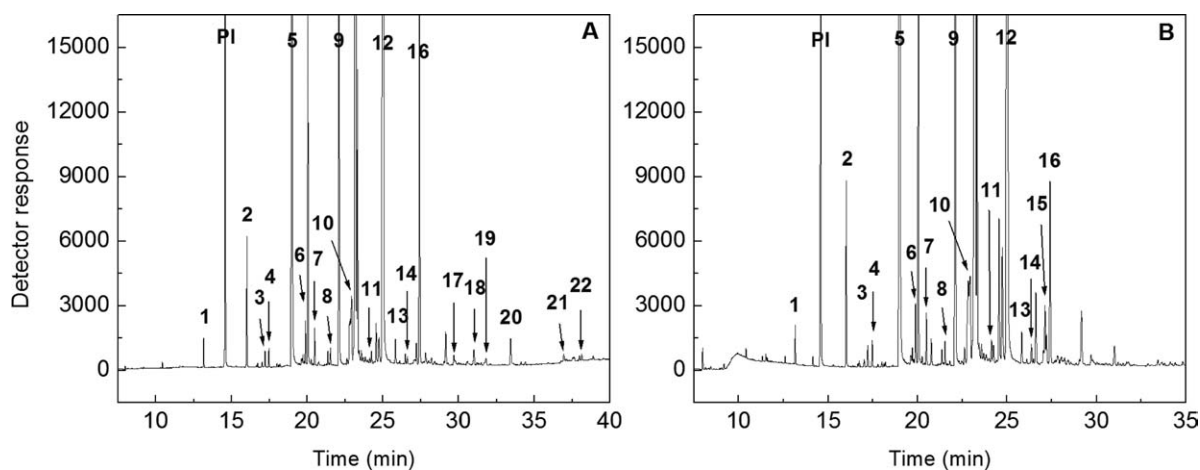
### Film Preparation

The epoxidized-modified natural plasticizers (NP-Ac and NP-Oc) were incorporated into PVC films in order to evaluate their plasticizing performance.

Polyvinylchloride (PVC) films were prepared by casting, according to procedure described in Lindström and Hakkarainen.<sup>8</sup> In a glass beaker, 0.4 g of PVC K70 resin (Braskem, Brazil) was mixed with the epoxidized-modified natural plasticizers (30%<sub>w/w</sub> 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 and then the solution was casted in a clean glass Petri dish (diameter 14 cm). The films were dried at ambient temperature until complete solvent evaporation.

### Film Characterization

**Thickness.** Film thickness was controlled by pouring a constant mass of solution over the support. At the end of the drying process, films were detached from the support and conditioned at room temperature and 52% RH for 3 days inside desiccators before characterization. Thickness of the conditioned films was



**Figure 1.** Chromatograms, obtained by GC-FID, of fatty acids from the rice oil distillate (A) and from the modified natural plasticizer (B). Peak identification: (1) C12:0; (2) C14:0; (3) C15:1; (4) C15:0; (5) C16:0; (6) C17:0; (7) C17:1; (8) C18:1n9t; (9) C18:0; (10) C18:1n9c; (11) C18:2n6t; (12) C18:2n6c; (13) C20:0; (14) C18:3n6; (15) C20:1; (16) C18:3n3; (17) C20:2n6; (18) C22:0; (19) C20:3n6; (20) C20:4n6; (21) C24:0; (22) C24:1; (IS) internal standard (C13:0).

measured using a digital micrometer (Mitutoyo, MDC-25S, Japan). Measurements were taken at 10 different positions of the film surface and the mean value is reported.

**Mechanical Properties.** Tensile strength (TS) and percentage tensile elongation at break ( $E$ ) of the films were determined at room temperature using a TA.XT2 (Stable Microsystems SMD, England) according to ASTM standard method D882.<sup>24</sup> Films were cut into strips ( $10 \times 2.54 \text{ cm}^2$ ) 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.

**Exudation Test.** Exudation of the plasticizer was evaluated by placing a sample of film between two pieces of vegetable paper. The system (sample + paper) was then placed in a drying oven at 40°C for 48 h. After this period, the weight increment of the paper was determined and the extent of plasticizer exudation was calculated.

**Migration Stability Tests.** To appraise critical conditions of plasticizers application, migration of the plasticizer from film samples were carried out in three different solvents (petroleum ether, gasoline, and water) at 25°C.<sup>25</sup> Samples were weighed (in triplicate) and kept in 100 mL of each solvent. The samples were taken out after 72 h, dried in a drying oven at 30°C for 24 h and the weights of the dried samples were determined. The percentage of mass loss was calculated in relation to the initial plasticizer mass added to the sample.

**Crystallinity.** To observe modifications on crystallinity of the films induced by modified natural plasticizer addition, X-ray diffraction was performed on film samples with a Philips Analytical X'Pert PW 3050 diffractometer with Cu-K $\alpha$  radiation. The X-ray source was operated at 40 kV and 40 mA. Diffraction

intensity was measured as reflection mode at scanning rate of 0.6°/min for  $2\theta = 5\text{--}35^\circ$ .

**Differential Scanning Calorimetry.** Glass transition temperature was determined by differential scanning calorimetry using a Mettler Toledo 823e DSC (Mettler Toledo International, USA). Samples of about 10 mg were conditioned in aluminum pans and heated at 10°C/min, under inert atmosphere of N<sub>2</sub> (50 mL/min N<sub>2</sub>), from ambient temperature ( $24 \pm 1^\circ\text{C}$ ) to 120°C. Then samples were cooled again to ambient temperature and finally heated to 120°C at 10°C/min. An empty pan was used as reference. Liquid nitrogen was used for sample cooling before the runs.

**Fourier Transform Infrared Spectroscopy.** The FTIR analyses were carried out using a Bomem-MB102 spectrometer (ABB-Bomem, USA). The spectra were acquired in the range of 4000–650  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , measuring directly the polymer films and recording the IR absorption

## RESULTS AND DISCUSSION

### Fatty Acid Profile of Rice Oil Distillate and Modified Natural Plasticizer

The esterification reaction used to obtain of the modified natural plasticizer did not change the relative proportion of fatty acids present in the raw material, since similar fatty acid profiles were observed as shown by the chromatograms in Figure 1. However, the esterification reaction reduced the major fatty acids content (Table I). These results were expected since the reaction was carried out at high temperatures ( $T > 210^\circ\text{C}$ ) favoring isomerization and degradation of fatty acids.<sup>26</sup> The major fatty acids contents found in the rice oil distillate were in agreement with the values reported by the raw material supplier (36% of linoleic acid (C18:2), 33% of oleic acid (C18:1), 22% of palmitic acid (C16:0), 5% of stearic acid (C18:0), and 4% of linolenic acid (C18:3)).

**Table I.** Major Fatty Acids Contents from Rice Oil Distillate and Modified Natural Plasticizer

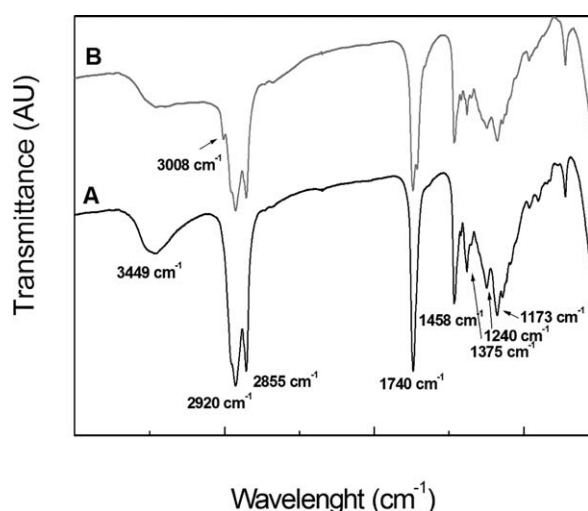
Fatty acid	$t_R$ (min)	Content (g/100 g) <sup>a</sup>	
		Rice oil distillate	Modified natural plasticizer
C16:0	19.0	21.89 ± 0.45	17.58 ± 1.30
C18:1n9t	21.5	5.18 ± 0.14	4.14 ± 0.44
C18:1n9c	22.8	25.38 ± 0.54	20.20 ± 2.11
C18:2n6c	25.0	33.58 ± 0.80	20.79 ± 2.18
C18:3n3	27.4	2.53 ± 0.07	0.67 ± 0.06

<sup>a</sup>Mean ± standard deviation (SD) of triplicate analysis.

### Epoxidized-Modified Natural Plasticizers

The results obtained in a previous study<sup>23</sup> denoted that it was necessary to modify the modified natural plasticizer obtained from the rice oil distillate in order to reach an improved plasticizing performance. Epoxidation reactions have been widely applied for modifying vegetable oils to obtain natural PVC plasticizers and some oleochemical intermediate products.<sup>2,16</sup> So the modified natural plasticizer from rice oil distillate was epoxidized with two different peracids (peracetic and peroctanoic acids) by *in situ* peracid generation, resulting in two modified natural plasticizers (NP-Ac and NP-Oc).

These modified plasticizers were analyzed by FTIR spectroscopy to check the organic functional groups, specially the presence of oxirane ring (epoxide group). The absorption bands in the FTIR spectra of NP-Ac and NP-Oc (Figure 2, spectra A and B, respectively) refer mainly to alkanes (2920  $\text{cm}^{-1}$  –  $\nu_{\text{as}}\text{CH}_2$ , 2855  $\text{cm}^{-1}$  –  $\nu_{\text{s}}\text{CH}_2$ , 1458  $\text{cm}^{-1}$  –  $\delta_{\text{as}}\text{CH}_3$  or  $\delta_{\text{s}}\text{CH}_2$ , 1375  $\text{cm}^{-1}$  –  $\delta_{\text{s}}\text{CH}_3$ ), alkenes (3008  $\text{cm}^{-1}$  –  $\nu=\text{CH}$  or  $\nu\text{CH}_2$ , only for NP-Oc), saturated aliphatic esters (1740  $\text{cm}^{-1}$  –  $\nu_{\text{s}}\text{C}=\text{O}$ , 1240  $\text{cm}^{-1}$  –  $\nu\text{C}-\text{CO}-\text{O}$ , 1173  $\text{cm}^{-1}$  –  $\nu\text{C}-\text{CO}-\text{O}$ , 1137  $\text{cm}^{-1}$ ) and alcohol (3449  $\text{cm}^{-1}$  –  $\nu\text{O}-\text{H}$ ).

**Figure 2.** FTIR spectra from (A) NP-Ac and (B) NP-Oc plasticizers.**Table II.** Tensile Strength and Elongation at Break of Plasticized PVC Films

Film	TS (MPa) <sup>a</sup>	E (%) <sup>a</sup>
PVC+NP-Ac	19.6 ± 1.5	146.4 ± 22.8
PVC+NP-Oc	21.5 ± 1.8	104.0 ± 34.0

<sup>a</sup>Mean ± SD from 15 experimental determinations.

When an epoxide group (or oxirane ring) is present in a compound structure, characteristic absorption bands occur at 1270–1230  $\text{cm}^{-1}$  ( $\nu_{\text{s}}\text{C}-\text{O}-\text{C}$ ) and at 880–805  $\text{cm}^{-1}$  ( $\nu_{\text{as}}\text{C}-\text{O}-\text{C}$ ).<sup>27</sup> Epoxidized-modified natural plasticizers produced (NP-Ac and NP-Oc) did not show absorption bands at 880–805  $\text{cm}^{-1}$ , and the absorption at 1270–1230  $\text{cm}^{-1}$  was not clear possibly due to overlap of the ester characteristic peak at 1240  $\text{cm}^{-1}$  (Figure 2). In addition, the absorption band at 3449  $\text{cm}^{-1}$  in both spectra denotes the presence of hydroxyl groups in both NP-Ac and NP-Oc plasticizers. These results indicate that oxirane rings could have been broken during the epoxidation reaction, since this is a common secondary reaction in the epoxidation process.<sup>18–21,28</sup>

Another interesting feature concerning IR-spectra of the epoxidized-modified natural plasticizers, was the fact that NP-Oc [Figure 2(B)] showed a weak absorption band at 3008  $\text{cm}^{-1}$  which did not appear in the NP-Ac spectrum. The absorption band is related to C–H bond stretching for  $\text{sp}^2$  carbon atom and, thus, denotes the presence of double bonds in the molecule. The more intense this absorption band, the greater the amount of double bonds in the compound structure.<sup>27</sup> These results indicate that the epoxidation by peracetic acid was more efficient and consumed all (or almost all) double bonds (C=C) present in the plasticizer molecular structure, which did not happen in the epoxidation by peroctanoic acid.

### Plasticized PVC Films

Plasticized PVC films produced by casting exhibit colorless, homogenous, smooth, and transparent surfaces with average thicknesses of  $28 \pm 0.7 \mu\text{m}$  and  $30 \pm 0.8 \mu\text{m}$  for films added with NP-Ac and NP-Oc, respectively. No signs of plasticizer exudation were observed for both films. These values were 1.3 times higher compared with the thickness of PVC films obtained in a previous study,<sup>23</sup> but in the same range of PVC films prepared with natural nonmodified plasticizer and natural plasticizer modified by epichloridrine.<sup>23</sup> As expected, plasticizer addition increased PVC films the thickness; however, the plasticizer epoxidation as well as the type of epoxidation agent did not affect the final thickness of the plasticized PVC film.

**Mechanical Properties.** The mechanical properties of PVC films are shown in Table II. 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.

Compared with PVC film plasticized with NP-OC, PVC film added with NP-Ac was more flexible and showed an increase of

**Table III.** Migration of Epoxidized Modified Natural Plasticizers from PVC Films into Different Solvents

Solvents	Film	
	PVC + NP-Ac (%) <sup>a</sup>	PVC + NP-Oc (%) <sup>a</sup>
Water	0.47 ± 0.04	2.09 ± 0.51
Gasoline	8.62 ± 0.66	8.57 ± 0.57
Petroleum ether	8.46 ± 0.18	17.90 ± 0.95

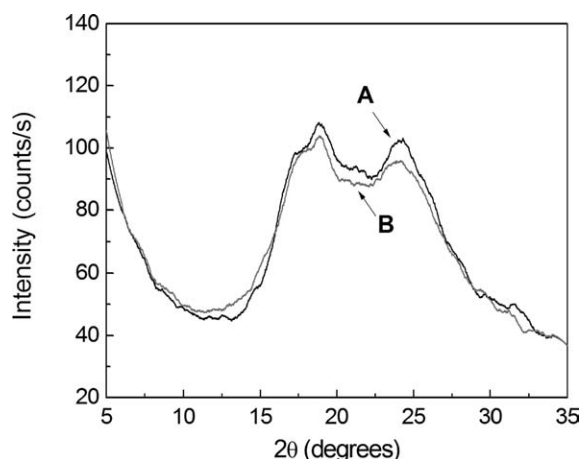
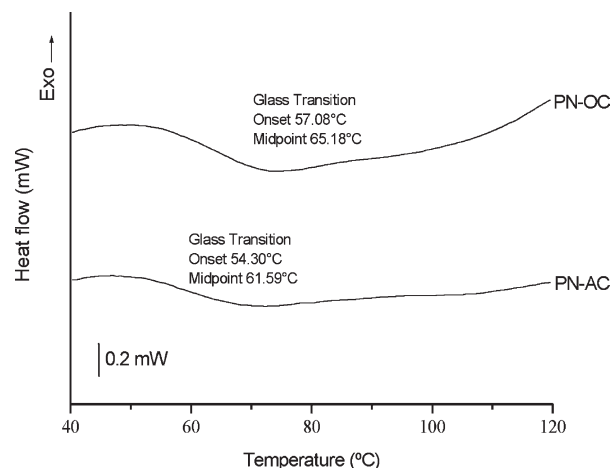
<sup>a</sup>Mean ± SD obtained from mass losses shown by samples of plasticized PVC films.

41% in the elongation at break. FTIR data suggests that epoxidation reaction with peracetic acid was more efficient than with peroctanoic acid, agreeing with the enhanced plasticizing effect observed for NP-Ac.

Besides, both epoxidized-modified natural plasticizers (NP-Ac and NP-Oc) improved PVC films elasticity when the values in Table II are compared with previous results for pure PVC film ( $TS = 45.4$  MPa,  $E = 22.8\%$ ) and PVC films plasticized by natural nonmodified plasticizer ( $TR = 27.0$  MPa,  $E = 104.5\%$ ),<sup>23</sup> reinforcing the idea that epoxidation degree was responsible for increasing the plasticizing performance of the modified natural plasticizers.

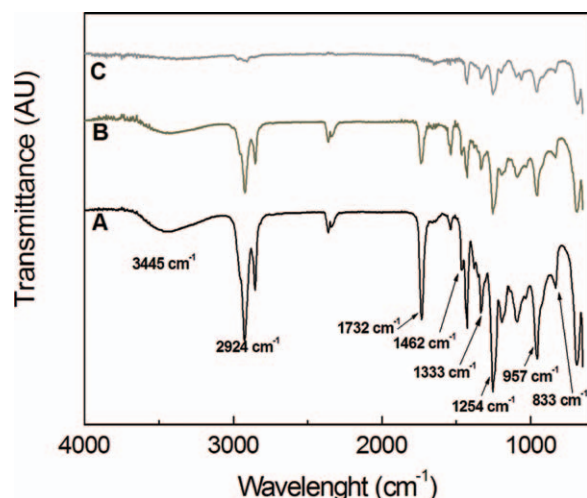
**Exudation and Migration Stability Tests.** In the exudation test, plasticized PVC films (NP-Ac and NP-Oc) did not present any significant mass loss during the experimental period (48 h, 40°C).

If a polymeric material comes into contact with liquids (water, solvents, oil) the probability of plasticizer extraction increases. To have increased resistance to extraction, the plasticizer should have limited compatibility with the extractant and good compatibility with the polymer. Epoxidized-modified natural plasticizers showed lower migration rates into water compared with nonpolar solvents (Table III), which is in agreement with the hydrophobic character of these plasticizers.

**Figure 3.** X-ray diffractograms from PVC films plasticized by (A) NP-Ac and (B) NP-Oc.**Figure 4.** DSC curves from PVC films plasticized by NP-Ac and NP-Oc.

Another interesting feature from migration stability tests is that NP-Ac migration rates from PVC films into water and petroleum ether were, respectively, two and four times lower than for NP-Oc. In addition, when the results from Table III are compared with previous reported results for natural nonmodified plasticizer,<sup>23</sup> the epoxidation of natural plasticizer by *in situ*-generated peracids decreased the migration rates into nonpolar solvents by 77–89%, for gasoline and petroleum ether, respectively.

**Crystallinity.** The X-ray diffraction patterns of PVC films incorporated with NP-Ac and NP-Oc (Figure 3) showed two characteristic peaks at  $2\theta \sim 18.8^\circ$  and  $24.1^\circ$ , which correspond to interlamellar basal distances of 4.8 Å and 3.8 Å, respectively (as calculated by Bragg's Law:  $\lambda = 2d \cdot \sin \theta$ , for  $\lambda = 1.542$  Å). According to the obtained diffractograms, no differences in the crystalline phase of PVC films were observed with the incorporation of the epoxidized-modified natural plasticizers (NP-Ac or NP-Oc). In addition, comparing these diffractograms to that reported in a previous study for pure PVC film,<sup>23</sup> neither NP-Ac nor NP-Oc changed the polymer crystallinity.

**Figure 5.** FTIR spectra from PVC films plasticized by (A) NP-Ac and (B) NP-Oc, as well as (C) pure PVC film.

**Morphology of Film Surface.** Optical micrographs of PVC films plasticized by NP-Ac and NP-Oc (data not shown) show smooth and homogeneous film surfaces, being comparable to pure PVC film surface.<sup>23</sup> These results denote good plasticizer incorporation into the PVC polymeric matrix for both NP-Ac and NP-Oc plasticizers.

**DSC Analyses.** Differential scanning calorimetry was performed in order to determine the glass transition temperature ( $T_g$ ) of polymeric matrix. DSC curves for PVC films plasticized with NP-Ac and NP-Oc are shown in Figure 4. All two samples exhibit a single  $T_g$  characterized as an endothermic deviation on the baseline. The analyzed plasticized PVC films showed  $T_g$  values of 61.6°C and 65.2°C for NP-Ac and NP-Oc, respectively. The presence of these plasticizers (NP-Ac and NP-Oc) into the PVC polymeric matrix decreased its  $T_g$  value, since pure PVC film showed a  $T_g$  value of 93.5°C.<sup>23</sup> Although the decrease in  $T_g$  was not so intense as in some cases reported in the literature,<sup>29,30</sup> these results still reinforce the plasticizing effect promoted by the natural epoxidized plasticizer addition.

**FTIR Analyses.** The IR spectra vary according to material chemical composition and can indicate the complexation and interaction between its constituents.<sup>31</sup> In this way, FTIR spectra may help to identify possible changes that occurred after plasticizer addition, as well as possible modifications resulting from the epoxidation reaction of natural plasticizer. In general, the FTIR spectra from PVC films plasticized with NP-Ac and NP-Oc (Figure 5, spectra A and B, respectively) showed similar absorption peaks. In addition, the obtained spectra were similar to those reported for pure PVC [Figure 5(C)] film and PVC film plasticized by natural nonmodified plasticizer.<sup>23</sup>

As shown in Figure 5, the obtained spectra presented the characteristic PVC absorption bands:  $\text{CH}_2$  deformation at 1333  $\text{cm}^{-1}$ , angular deformation out of plan ( $\rho\text{CH}$ ) at 1254  $\text{cm}^{-1}$ , *trans* deformation out of plan ( $\omega\text{CH}$ ) at 957  $\text{cm}^{-1}$ , and C—Cl stretching at 833  $\text{cm}^{-1}$  (see Ref. 31). Besides the characteristic peaks for the polymer, the plasticized PVC films spectra (Figure 5) also showed the following bands: OH angular deformation at 3445  $\text{cm}^{-1}$ ; alkane angular deformation ( $\nu_{\text{as}}\text{CH}_2$ ) at 2924  $\text{cm}^{-1}$ ; at 1732  $\text{cm}^{-1}$  attributed to saturated aliphatic ester (C=O); and asymmetric vibration ( $\nu_{\text{as}}\text{CH}_3$ ) or angular deformation ( $\delta_s\text{CH}_2$ ) at 1462  $\text{cm}^{-1}$ .

As discussed for FTIR results of epoxidized-modified natural plasticizers, the absorption band regarding OH angular deformation (3445  $\text{cm}^{-1}$ ) can possibly be related to the presence of hydroxyl groups in the chemical structure of epoxidized-modified natural plasticizers (maybe due to oxirane ring opening) or also due to partial substitution of chlorine atoms by hydroxyl groups in the PVC chain.

The FTIR results of plasticized PVC films denote that no significant change in the PVC chemical structure has been occurred after plasticizer addition.

## CONCLUSIONS

Both epoxidant agents, peracetic and peroctanoic acids, were able to epoxidize the natural plasticizer obtained from rice oil distillate, peracetic acid being more efficient in this issue than

peroctanoic acid. On the other hand, whatever the epoxidant agent, there was oxirane ring opening in the chemical structures of epoxidized-modified natural plasticizers, indicating necessity of optimizing epoxidation conditions in the next studies.

The epoxidized-modified natural plasticizers obtained in this study showed good incorporation and plasticizing performance into the PVC polymeric matrixes, as demonstrated by results of mechanical properties,  $T_g$  values (DSC), optical microscopy, exudation, and migration tests, FTIR and X-ray diffraction obtained for plasticized PVC films. In addition, the plasticizer NP-Ac showed enhanced plasticizing performance compared with NP-Oc and natural nonmodified plasticizer, probably due to a higher epoxidation degree obtained for the plasticizer modified by peracetic acid.

## ACKNOWLEDGMENTS

The authors thank the Brazilian Funding Agency CAPES (Proc n. 1989/2008) for financial support.

## REFERENCES

- Godwin, A. D. In: *Applied Polymer Science: 21st Century*, Craver, C. D., Carraher, C. E., Eds.; Elsevier: Oxford, **2000**, Chapter 9.
- Bouchareb, B.; Benaniba, M. T. *J. Appl. Polym. Sci.* **2008**, *107*, 3442.
- Cao, N.; Yang, X.; Fu, Y. *Food Hydrocolloid* **2009**, *23*, 729.
- Cheng, L. H.; Karim, A. A.; Seow, C. C. J. *Food. Sci.* **2006**, *71*, E62.
- Nalli, S.; Cooper, D. G.; Niceii, J. A. *Biodegradation* **2002**, *13*, 343.
- Pielichowski, K.; Swierz-Motysia, B. *J Therm Anal Calorim* **2006**, *83*, 207.
- Cano, J. M.; Marín, M. L.; Sánchez, A.; Hernandis, V. J. *Chromatogr. A* **2002**, *963*, 401.
- Lindström, A.; Hakkarainen, M. J. *Appl. Polym. Sci.* **2006**, *100*, 2180.
- Bueno-Ferrer, C.; Jiménez, A.; Garrigós, M. C. *Food Addit. Contam.* **2010**, *27*, 1469.
- Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. *Polym. Test.* **2008**, *27*, 221.
- Choi, J. S.; Park, W. H. *Polym. Test.* **2004**, *23*, 455.
- Vieira, M.G. A.; da Silva, M. A.; dos Santos, L. O.; Beppu, M. M. *Eur. Polym. J.* **2011**, *47*, 254.
- Gupta, A. P.; Ahmad, S.; Dev, A. *Polym. Eng. Sci.* **2011**, *51*, 1091.
- Lee, K.-W.; Hailan, C.; Yinhu, J.; Kim, Y.-W.; Chung, K.-W. *Korean J. Chem. Eng.* **2008**, *25*, 474.
- Cai, C.; Dai, H.; Chen, R.; Su, C.; Xu, X.; Zhang, S.; Yang, L. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 341.
- Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Klaas, M. R.; Schäfer, H. J.; Schneider, M. P. *Angew. Chem. Int. Ed.* **2000**, *39*, 2206.
- Metzger, J. O.; Bornscheuer, U. *Appl. Microbiol. Biotechnol.* **2006**, *71*, 13.

18. Campanella, A.; Fontanini, C.; Baltanás, M. A. *Chem. Eng. J.* **2008**, *144*, 466.
19. Klaas, M. R.; Warwel, S. *Ind Crop. Prod.* **1999**, *9*, 125.
20. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. *Bioresour. Technol.* **2008**, *99*, 7333.
21. Smith, P. C.; Ngothai, Y.; Nguyen, Q. D.; O'Neill, B. K. *Fuel* **2009**, *88*, 605.
22. AOCS. Official Methods and Recommended Practices of the AOCS; American Oil Chemist's Society: Urbana, **1998**.
23. da Silva, M. A.; Vieira, M.G. A.; Maçumoto, A.C. G.; Beppu, M. M. *Polym Test* **2011**, *30*, 478.
24. ASTM. Annual Book of ASTM Standards: Standard D882; American Society for Testing and Materials: Philadelphia, **1995**.
25. Sunny, M. C.; Ramesh, P.; George, K. E. *J. Elastomer. Plast.* **2004**, *36*, 19.
26. McClements, D. J.; Decker, E. A. In: Food Chemistry, Damodaran, S., Parkin, K. L., Fennema, O. R., Eds., CRC Press: Boca Raton, **2008**.
27. Silverstein, R. M.; Webster, F. X.; Kiemle, D. Spectrometric Identification of Organic Compounds Wiley: New York, **2005**.
28. Swern, D. *Chem. Rev.* **1949**, *45*, 1.
29. Robeson, L. M. Polymers Blends: A Comprehensive Review; Carl Hanser Verlag: Munich, **2007**.
30. Madaleno, E.; Rosa, D. S.; Zawadzki, S. F.; Pedrozo, T. H.; Ramos, L. P. *Polímeros* **2009**, *19*, 263.
31. Ramesh, S.; Leen, K. H.; Kumutha, K.; Arof, A. K. *Spectrochim. Acta Part A* **2007**, *66*, 1237.