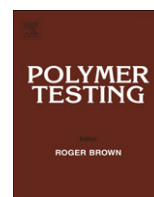




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Material Properties

Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid

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ARTICLE INFO

Article history:

Received 30 January 2011

Accepted 11 March 2011

Keywords:

Natural plasticizer

Rice fatty acid

PVC

Latex

ABSTRACT

The use of natural plasticizers with low toxicity and good compatibility in several polymer applications has become more attractive. In this study, a natural plasticizer was synthesized in the laboratory by esterification of rice fatty acids and polyols. The resulting product was added to PVC and natural rubber latex films (5% w/w). Mechanical properties of the films, as well as tests of migration and exudation of the plasticizer, were performed in order to evaluate the efficiency of plasticization. Optical microscopy (OM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to characterize the pristine and plasticized polymer. Mechanical tests indicated that the addition of the natural plasticizer resulted in an increase in the elongation at break and a consequent decrease in the tensile strength of the films. The plasticizing effect induced by the natural plasticizer was also confirmed by a glass transition temperature (T_g) shift towards lower temperatures in the plasticized films.

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1. Introduction

Plasticizers are an important class of low molecular weight non-volatile compounds that are widely used in polymer industries as additives [1]. The primary role of such substances is to improve the flexibility and processing of polymers by lowering the second order transition temperature, the glass transition temperature (T_g). The council of the IUPAC (International Union of Pure and Applied Chemistry) defined a plasticizer as “a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability or distensibility”. These substances reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time increasing the polymer chain

flexibility, resistance to fracture and dielectric constant [2]. Other properties are also affected, such as degree of crystallinity, optical clarity, electric conductivity, fire and biological degradation resistance [3].

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

The current market offers numerous choices of plasticizers with a range of attributes that can be selected for specific applications to meet critical material requirements. However, since the early 1980s, there have been concerns, and even controversy, regarding the use of phthalates and their effects on human health and the environment [4]. Thus, the use of plasticizers is being questioned due to their possible toxicity problems related to the migration of phthalates [5].

Nowadays, there is an increasing interest in the use of natural-based plasticizers that are characterized by low toxicity and low migration and have good compatibility with

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several plastics, resins, rubbers and elastomers in substitution of conventional plasticizers. Extensive research is going on to find alternative plasticizers for medical and other commodity plastic materials. This group includes epoxidized triglyceride vegetable oils from soybean oil, linseed oil, castor-oil, sunflower oil and fatty acid esters (FAEs) [6–8]. In addition, this search for natural-based plasticizers is also 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 [7–15].

The present study evaluated the performance of a natural plasticizer in polyvinylchloride (PVC) and natural rubber latex films. This natural plasticizer was synthesized in laboratory by esterification reaction of rice fatty acids and polyols.

2. Experimental

2.1. Materials

The natural plasticizer was obtained by an esterification reaction between rice fatty acid and polyols (octanol, diethylene glycol and monopropylene glycol) in the presence of a catalyst. 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-chemical characterization of the natural plasticizer is shown in Table 1.

Natural rubber latex, extracted from rubber trees (*Hevea brasiliensis*), purified and stabilized with ammonium (60%), and PVC K70 resin were kindly donated by Parabor (São Paulo, Brazil) and Braskem (São Paulo, Brazil), respectively.

2.2. Film preparation

2.2.1. Polyvinylchloride (PVC) films

PVC films were prepared by casting according to the procedure described in Lindström and Hakkarainen [16]. 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 and then the solution was cast into a clean glass Petri dish (diameter 14 cm). The films were dried at ambient temperature until complete solvent evaporation. Films without plasticizer addition were also prepared as control.

PVC films containing a mixture of natural plasticizer epoxidized with epichlorohydrin (Synth, Brazil) (2:1 mol/mol) at a concentration of 30 wt% (in relation to PVC resin), were also tested.

2.2.2. Natural rubber latex films

Latex films were also made by casting a prepared polymer solution. Latex (Parabor, Brazil) (10 g) was mixed with distilled water (6 mL) and 5% w/w of natural plasticizer (in relation to the mass of latex). The solution was poured into square Plexiglas® frames (225 cm²) and dried under ambient conditions for seven days. Films without plasticizer addition were also prepared as control.

2.3. Film characterization

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

2.3.2. 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 D882 [17]. Films were cut into strips (5.0 × 0.5 cm, for latex and 10 × 2.54 cm, for PVC) and mounted between the corrugated tensile grips of the instrument. For PVC film samples, the initial grip spacing and cross-head speed were set at 50 mm and 0.1 cm/s, respectively, while for latex films these parameters were set at 10 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.

2.3.3. 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.

2.3.4. Migration stability tests

Migration of the plasticizer from film samples were carried out in three different solvents: petroleum ether [4], gasoline and water at 25 °C. 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

Table 1
Physical-chemical characterization of natural plasticizer.

Characteristic	Natural plasticizer
Physical state (20 °C)	Liquid
Acidity index	8.8 mg KOH/g (0.88%)
Hydroxyl index	23.87 mg KOH/g of sample
Color	Dark amber
	Pattern: $L_0^* = 92.03$; $a_0^* = -0.88$; $b_0^* = 0.63$
	Sample: $L^* = 9.53$; $a^* = 0.03$; $b^* = 4.99$
	$\Delta E = 83.12$
Viscosity (20 °C)	$\mu = 31.5$ cP
Moisture (Karl Fischer)	$0.76 \pm 0.03\%$ (b.u)
Molar mass	$M_n = 385$ Da (383.5 g/mol); $M_w = 55.276$ Da; $M_w/M_n = 143.393$

determined. The percentage mass loss was calculated in relation to the initial plasticizer mass added to the sample.

2.3.5. Crystallinity

In order to observe modifications of crystallinity of the films induced by natural plasticizer addition, X-ray diffraction was performed on film samples with a Philips Analytical X'Pert PW 3050 diffractometer with Cu-K α radiation. The X-ray source was operated at 40 kV and 40 mA. Diffraction intensity was measured in reflection mode at a scanning rate of 0.6°/min for $2\theta = 5\text{--}35^\circ$.

2.3.6. Optical microscopy (MO)

Plasticized and pure latex films surfaces were examined by optical microscopy. Optical microscopy images were obtained with a Nikon Eclipse E200 (Nikon Corp., Japan). The films were photographed in normal light with a magnification of 40 \times .

2.3.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out in a Micro-meritics TGA (Micromeritics Instruments Corp., USA) in N₂ atmosphere (50 mL/min) at a heating rate of 10 °C/min. The samples were put into platinum pans and scanned from ambient temperature to 600 °C.

2.3.8. Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) was determined by differential scanning calorimetry using a Mettler Toledo 823e DSC (Mettler Toledo International Inc., USA). Samples of about 10 mg were conditioned in aluminum pans and heated at 10 °C/min under an inert atmosphere of N₂ (50 mL/min N₂) between -100 and 190 °C, with isothermal hold for 2 min at 190 °C. Then, samples were cooled again to -100 °C and finally heated to 100 °C at 5 °C/min. An empty pan was used as reference. Liquid nitrogen was used for sample cooling before the runs.

2.3.9. Fourier transform infrared spectrometry (FTIR)

The FTIR studies were carried out using a Bomem-MB102 spectrometer (ABB-Bomem, USA). The spectra were acquired in the range of 4000 to 650 cm⁻¹ at a resolution of 4 cm⁻¹.

2.4. Statistical analysis

Student's *t*-test was used to determine statistically significant differences ($p < 0.05$) between averages using Software Statistica V.11.5.

3. Results and discussion

3.1. Plasticized PVC and latex films

PVC and plasticized PVC (with natural plasticizer addition) films produced by casting showed a colorless, homogenous and transparent surface. Latex and plasticized latex films were also homogeneous and transparent but had a yellowish color. The average thickness of PVC and latex films with and without addition of the natural plasticizer is given in Table 2. For both polymeric matrices, a slightly increase in film thickness was observed with the addition of

Table 2

Average thickness, tensile strength and elongation at break of PVC and latex films with and without natural plasticizer addition.

Film	Thickness (μm)	TS (MPa)	E (%)
PVC	23 ± 1.0^a	45.39 ± 4.64^e	22.18 ± 2.53^a
Plasticized PVC	29 ± 1.0^b	26.97 ± 5.51^d	104.51 ± 17.04^b
Plasticized PVC (epi)	30 ± 1.0^b	22.30 ± 3.44^c	127.66 ± 17.87^c
Latex	443 ± 24^c	2.18 ± 0.18^b	1298.63 ± 55.08^d
Plasticized latex	459 ± 26^d	0.76 ± 0.12^a	1468.27 ± 115.54^e

Average \pm standard deviation of ten experimental determinations. Different letters in the same column indicate significant differences ($p < 0.05$).

the plasticizer. This increase in film thickness is probably related to the natural plasticizer penetration among polymer chains, spacing them and increasing their mobility.

The chemical modification of the natural plasticizer with epichlorohydrin did not show a significant influence in film thickness compared to the other plasticized PVC matrix.

3.2. Mechanical properties

The values of the mechanical properties of PVC and latex films are also shown in Table 2. From Table 2, it is possible to observe a significant influence of the addition of the natural plasticizer for both polymeric films. An increase of 371.2% (4.71 times higher for plasticized PVC) was observed for its elongation at break, and a consequent decrease in tensile strength of 40.58%. The addition of the plasticizer into latex caused a significant but relatively small increase of approximately 13% in the elongation at break, however, a decrease of 186% was also observed for the tensile strength of these films. As latex is an elastomer, it can be used in polymeric blends with its typically high elongation (above 1000%) acting in these systems as a "natural" plasticizer [4].

3.3. Exudation test

Average exudation of the natural plasticizer from latex films was $8.54 \pm 0.83\%$ in relation to the mass of plasticizer initially added to the film. On the other hand, plasticized PVC samples did not show any mass loss during the experimental period.

3.4. Migration stability tests

The results of the migration of the natural plasticizer from PVC and latex film matrix into the three solvents tested are shown in Table 3.

Table 3

Migration of natural plasticizer from PVC and latex films into different solvents.

Solvent	Migration (%)		
	PVC film	PVC film (epi)	Latex film
Water	–	–	7.55 ± 1.52^a
Petroleum ether	76.9 ± 6.9^a	33.5 ± 4.9^a	Dissolution of the film
Gasoline	54.9 ± 6.2^a	17.0 ± 5.8^a	Dissolution of the film

^a In relation to the mass of natural plasticizer initially added to the film.

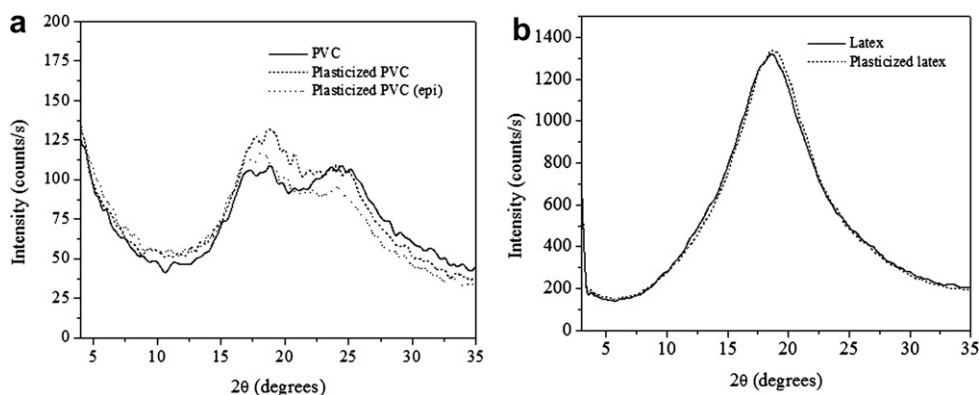


Fig. 1. X-Ray diffractograms of: (a) PVC and plasticized PVC films and (b) latex and plasticized latex films.

PVC films with natural plasticizer addition did not present water migration, indicating hydrophobic behavior of these films. However, when immersed in gasoline and petroleum ether, these plasticized samples presented a low migration resistance. It is interesting to observe that the migration of the modified natural plasticizer (with epichlorohydrin) was significantly lower into these two solvents, indicating that the epoxidation reaction was efficient in improving the plasticizer incorporation into the PVC matrix.

Latex samples immersed in gasoline and petroleum ether were partially dissolved by these solvents, making migration determination impossible. In water, 7.5% migration was observed.

3.5. Crystallinity

The X-ray diffraction patterns of pure and plasticized PVC and latex films are shown in Fig. 1 a and b, respectively. From the corresponding angle of the characteristic peaks and applying Bragg's Law ($n\lambda = 2d \cdot \sin \theta$), for λ of 1.542 Å, the interlamellar basal distance (d) can be calculated.

All three PVC samples presented two characteristics peaks at $2\theta \sim 17.7^\circ$ and 24.7° (Fig. 1a), corresponding to basal distances of 5.0 Å and 3.6 Å, respectively. The diffractograms of the latex and plasticized latex film revealed a more amorphous morphology with only one characteristic peak at $2\theta = 18.5^\circ$ (Fig. 1b), corresponding to a basal distance of 4.8 Å for both films. As observed in Fig. 1 a and b, the addition of the natural plasticizer did not affect the crystalline phase of either polymer.

3.6. Morphology of film surface

Optical microscopy was used to observe film surface morphology. Optical micrographs of PVC films (without plasticizer) revealed a smooth and homogenous surface (Fig. 2a). PVC films added with natural plasticizer presented some crystallites (Fig. 2b). However, PVC films containing the modified natural plasticizer (with epichlorohydrin) had a much smoother surface (Fig. 2c), similar to pure PVC films. This observation reinforces the hypothesis that the reaction between the double bonds of the natural plasticizer with the epoxy groups of the epichlorohydrin would improve the incorporation of plasticizer into the polymeric matrix.

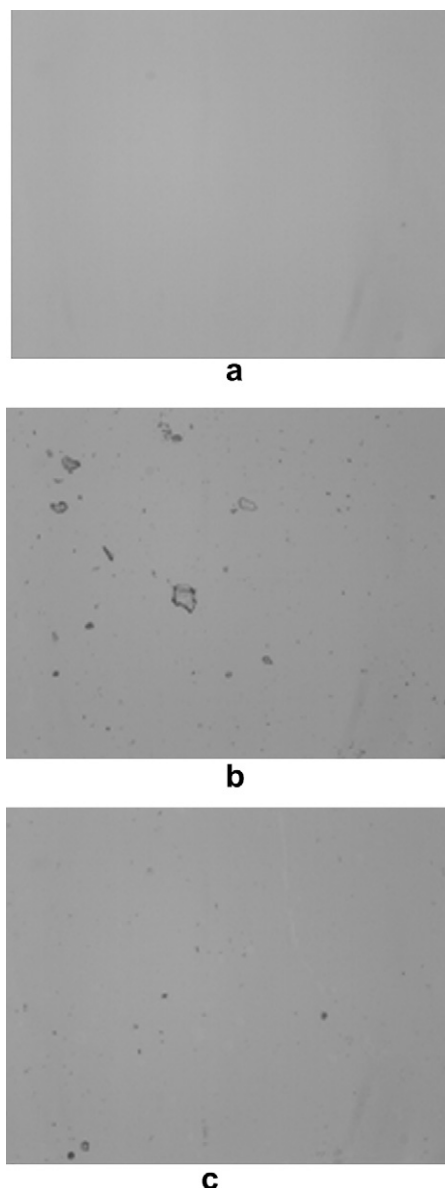


Fig. 2. Optical micrographs of the: (a) PVC films, (b) plasticized PVC films and (c) plasticized PVC films with epichlorohydrin (40x mag.).

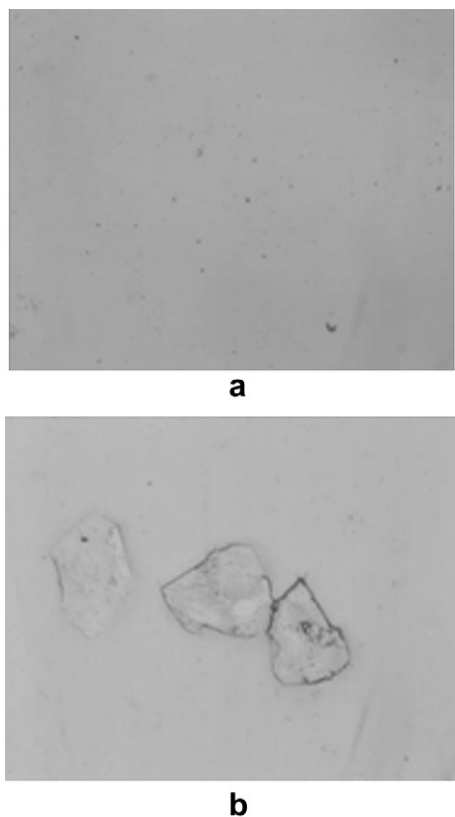


Fig. 3. Optical micrographs of the: (a) latex films and (b) plasticized latex films (40x mag.).

The optical micrographs of latex and plasticized latex films (Fig. 3a) confirm that the film surface was smooth and homogenous. However, as for PVC, plasticized latex films showed crystallites over the film surface (Fig. 3b).

3.7. Thermogravimetric analysis (TGA)

Thermogravimetric curves of pure PVC film (Fig. 4a) showed two degradation peaks at 287.7 °C and 453.8 °C, corresponding to losses of 62.85% and 18.84% of the initial mass, resulting in a total loss of 81.68%. The first plateau relates to the dechlorination of PVC, with formation and stoichiometric elimination of HCl, while the second is attributed to polymer crosslinking containing C=C bonds. Thermal degradation of polyenes involves cyclization and splitting of chains [18,19]. TG and DTG curves of plasticized PVC films (with and without epichlorohydrin) (Fig. 4 b and c) showed similar behavior to pure PVC films with two mass loss peaks at 285 °C and 466 °C for both samples, showing losses of 61.00% and 26.68% (without epichlorohydrin) and 63.41% and 27.19% (with epichlorohydrin) summing to a total mass loss of approximately 90% in both samples.

The TG and DTG curves of the latex and plasticized latex films are shown in Fig. 5a and b, respectively. Both films presented only one peak of mass loss at approximately 388 °C. This peak is related to natural rubber degradation [20]. The mass loss for latex and plasticized film samples,

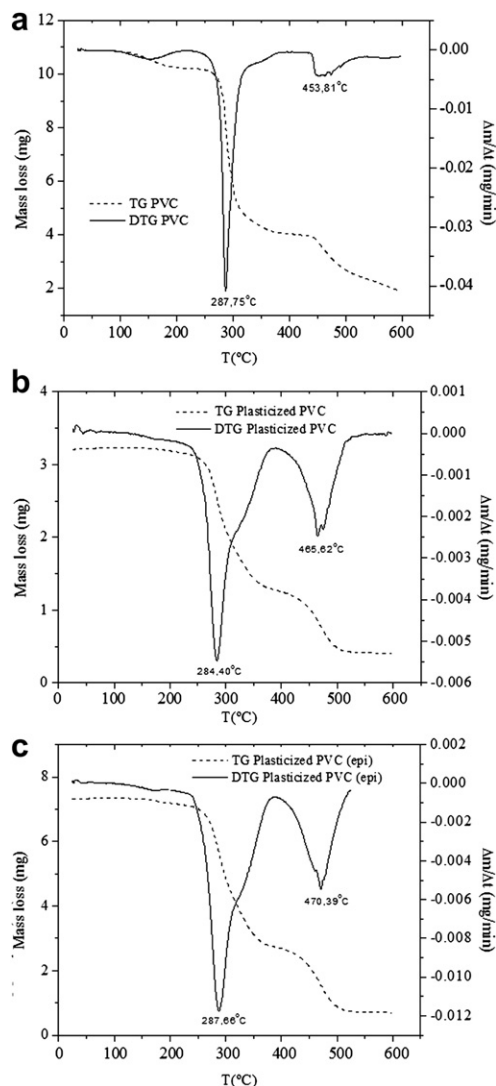


Fig. 4. Thermogravimetric curves of the (a) PVC films, (b) plasticized PVC films (without epichlorohydrin) and (c) plasticized PVC films (with epichlorohydrin).

in this temperature range, was 99.33% and 98.96% of the initial mass, respectively.

3.8. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed in order to determine the glass transition temperature (T_g) of polymeric matrix. This temperature is an important parameter in polymer characterization being able to evaluate the plasticizing effects of substances added to polymeric systems.

DSC curves of pure and plasticized PVC films are shown in Fig. 6. All three samples exhibit a single T_g characterized as an endothermic deviation from the baseline. For pure PVC, T_g was 93.5 °C, which is in the temperature range found in literature for this polymer [16,21,22]. Plasticized PVC films without and with epichlorohydrin showed lower T_g values,

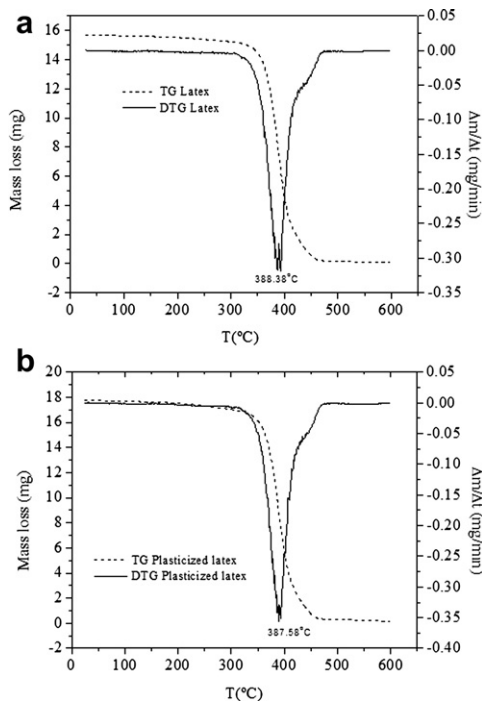


Fig. 5. Thermogravimetric curves of the (a) latex films and (b) plasticized latex films.

65.8 and 62.5 °C, respectively. This fact reinforces the plasticizing effect induced by the natural plasticizer addition, especially when it was epoxidized with epichlorohydrin.

The DSC curves for latex and plasticized latex films are given in Fig. 7. Both samples exhibited only one well defined glass transition. The addition of the natural plasticizer to the film shifted the T_g shift towards lower temperatures, from -63.6°C in the latex film to -67.7°C in the plasticized latex film. Similar T_g values are found in the literature for natural rubber latex [23,24].

3.9. Fourier transformed infrared spectrometry (FTIR)

Infrared spectroscopy is an important tool for the identification of polymeric chemical structures. The IR spectra vary according to material chemical composition and can

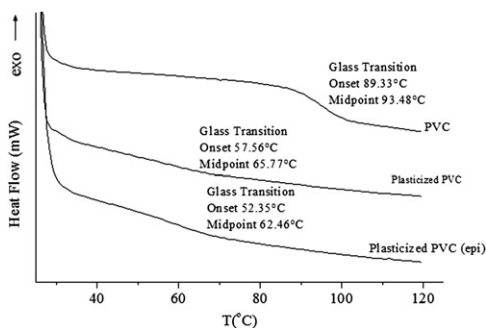


Fig. 6. DSC curves of PVC and plasticized PVC films.

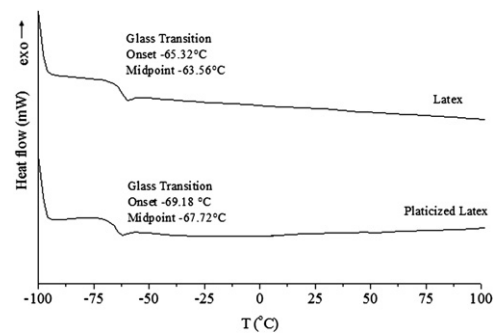


Fig. 7. DSC curves of latex and plasticized latex films.

indicate the complexation and interaction between its constituents [25].

The FTIR spectrum for pure PVC film showed characteristic peaks of this polymer (Fig. 8). C–H bond stretching is observed at 2911 cm^{-1} , CH_2 groups deformation (ρCH) at 1254 cm^{-1} , out of plane trans deformation (ωCH) at 959 cm^{-1} and C–Cl bond stretching at 836 cm^{-1} . These bands are in accordance with data found in literature for PVC [25]. Fig. 8 also shows the FTIR spectra for plasticized PVC films (with and without epichlorohydrin). Both spectra were very similar to that for pure PVC, but revealed, besides the characteristic peaks for the polymer, bands at 3375 cm^{-1} corresponding to the angular deformation of OH groups; at 2925 cm^{-1} , due to C–C and H–C–H ($\nu_{\text{as}}\text{CH}_2$) angular deformation; at 1734 cm^{-1} attributed to saturated aliphatic ester (C=O) and at 1458 cm^{-1} , related to asymmetric vibrations ($\nu_{\text{as}}\text{CH}_3$) or angular deformations ($\delta_s\text{CH}_2$).

The infrared spectra obtained for latex and plasticized latex films are shown in Fig. 9. The main characteristic peaks observed were at 836 , 1090 , 1128 , 1375 , 1450 , 1663 , 2915 , 2928 and 2961 cm^{-1} , which are related to the monomeric units of the cis-1,4-polyisoprene [26]. Latex and plasticized latex showed similar spectra, however a characteristic band at 1740 cm^{-1} , related to saturated aliphatic ester ($\nu_s\text{C}=\text{O}$), was observed for the plasticized film, indicating that the natural ester plasticizer was possibly incorporated in the film matrix.

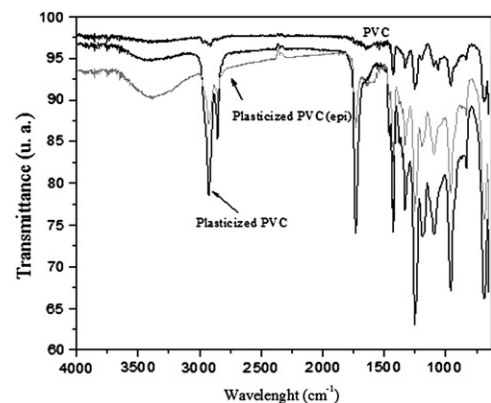


Fig. 8. FTIR spectra of PVC and plasticized PVC films.

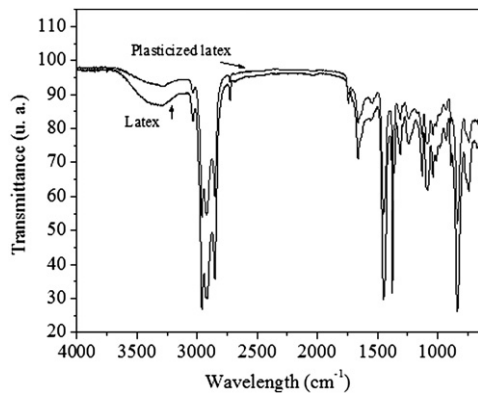


Fig. 9. FTIR spectra of latex and plasticized latex films.

4. Conclusions

The information gathered in the present study suggests that the natural plasticizer obtained by an esterification reaction of rice fatty acid was successfully incorporated into PVC and latex films prepared by casting, showing discrete exudation and migration into water. Mechanical tests showed that the addition of the natural plasticizer resulted in a significant increase in the elongation at break compared to pure polymer films, indicating the plasticization effect of this substance. No significant changes were observed in the pure and plasticizer films regarding thermal behavior by TGA and crystalline structure by X-Ray diffraction. FTIR spectra showed characteristic bands of the PVC and natural rubber and confirmed the presence of the plasticizer in the film matrix in the form of an ester functional group. The plasticizing effect induced by the natural plasticizer addition was also confirmed by a T_g shift towards lower temperatures in the plasticized films. The incorporation of the natural plasticizer in PVC and latex polymeric matrix showed promising results, indicating potential application that will be further investigated.

Acknowledgements

The authors would like to thank CAPES (Proc n. 1989/2008) and CNPq (Proc n. 50272/2009-0) for financial support.

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