Synthesis and characterization of the polyols by air oxidation of soybean oil and its effect on the morphology and dynamic mechanical properties of poly(vinyl chloride) blends

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ABSTRACT: The use of natural additives, with low toxicity and good compatibility, for PVC is becoming increasingly attractive. In this study, soybean oil additives were prepared by air oxidation reactions and blending with PVC. The oxidation reaction produced a significant increase in the number of hydroxyl groups in soybean oil; however, this kind of reaction results in the formation of a heterogeneous structure due to free radical reactions in the medium. The oxidized soybean oil improved the compatibility with PVC due to an increase in the number of polar groups, such as hydroxyls, and thus a reduction in the amount of atactic polymer was observed. Furthermore, an increase in the molecular weight of the oxidized oil, as well as large amounts of polar groups contributes to reducing the migration of oil in the PVC. Regarding the crystallinity of PVC, the use of pure and oxidized soybean oil causes small changes in the crystalline phase of the polymer. Oxidized soybean oil has great potential for usage as a secondary plasticizer for PVC. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42102.

INTRODUCTION

Poly(vinyl chloride), commonly abbreviated to PVC, is employed for a wide range of applications and is the third most widely produced polymer. It can be rigid or flexible and requires the addition of additives for further processing into products. Several additives are used such as plasticizers, stabilizers, lubricants, anti-oxidants, processing aids, fillers, flame retardants, smoke suppressors, agents to improve tenacity and heat-and-form stability, optional pigments, and others. These additives facilitate the processing and determine the properties of the final products, allowing PVC to be used for a wide range of applications including rigid profiles, pipes and fittings, roofing membranes, rigid films and sheets, soft films for packaging, electrical cable insulations, imitation leather, signs, and inflatable products.[1,2] Among the additives, plasticizers and lubricants have received special attention in recent years.[3]

Numerous efforts have been made to find a viable substitute for phthalates as a plasticizer for PVC.[1,2,4,5] The toxicity of low-molecular weight plasticizers, such as bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) and benzyl butyl phthalate (BBP), is now well established. The European Union and the United States of America banned their use for some applications, e.g., toys and childcare articles,[6,7] in 2005 and 2009, respectively. Manufacturers have increasingly been replacing low-molecular weight plasticizers with less toxic high-molecular weight plasticizers, such as diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP), and certain plasticizers have become important economically. Nontoxic plasticizers which could be used as alternatives to phthalates with similar effectiveness, compatibility and cost include polymer plasticizers based on polyol, adipic acid, adipates, terephthalates and 2,5-furandicarboxylic acid (FDCA).[2,8–10] Plasticizers obtained from renewable sources represent a good substitute due to their lower toxicity. Many studies have been focused on plasticizers originating from vegetable oils.[11–15] The use of derivatives from corn oil, which is a widespread product, has been quite successful in such applications.[16] The literature shows that the mechanical properties and the thermal stability of plasticized PVC can been improved with the use of epoxidized oils.[17–19] The oil-based plasticizer diffusion can be controlled through selective reactions involving the polymer chain with the formation of covalent

bonds, or using chemical substances with good interaction levels.[20–22] Another alternative is the use of oil-based plasticizers with higher molecular weight, however these may induce a phase separation phenomenon.[23,24] The technology available for the modification of vegetable oils, e.g., the production of epoxidized oil, biodiesel, and polyol, has attracted the interest of manufacturers and researchers, both motivated to obtain substitutes for phthalates from renewable sources or use as secondary plasticizer.[3,12,25–27] Soybean oil has been widely used in the chemical industry, due to its availability and low cost, to produce numerous substances through chemical reactions, e.g., the formation of epoxy and hydroxyl groups, aldehyde and maleic anhydride. The agriculture-based triglycerides are considered to be "green" raw materials.[27–34]

Air oxidation without a catalyst is a simple method for the synthesis of monomer and feedstock additives. The air oxidation process involves free radical intermediates due to the abstraction of allylic hydrogen and the subsequent formation of a delocalized free radical. These free radicals react with other triglycerides and oxygen to generate polyols, among a variety of other products.[25,35] Fornof et al.[35] reported that this process shows three regimes: (i) initially the consumption of the natural antioxidants occurs (ii) followed by rapid oxidation with the formation of highly hydroxylated soybean polyols (under this regime the polydispersity index is increased due to the radical-radical coupling reactions) and, finally, (iii) crosslinking and termination.[35]

The aim of this study was to synthesize and characterize an oil-based additive for PVC obtained from natural renewable sources by air oxidation at elevated temperature, in the search of a viable alternative to secondary plasticizers to in terms of material and processing costs. The main aspects of this research are the obtainment of a soybean oil-based additive, and the morphological and viscoelastic characterization of PVC blends produced with this plasticizer.

MATERIALS

The commercial soybean oil (Primor, Bunge Alimentos S.A, Brazil) had an acid number of 1.16 mg KOH g^{-1} and 4.50 mol of the double bond per mol of triacylglyceride molecules, according to ^{1}H NMR determinations.[36] Polyvinyl chloride was purchased from China General Plastic Co. (CGPC H-58), with a density of 1.52−1.59 g cm^{-3}, weight-average molecular weight (M_w) of 78,000 g mol^{-1} and a polydispersity index (M_w/M_n) of 3.3 based on GPC experiments in THF using polystyrene standards.

METHODS

Synthesis of Soybean Additive
The soybean additive was prepared in a round-bottomed flask (1L), which was mechanically stirred at 250 rpm and maintained at 120°C ± 1°C for different time periods: 24, 48, 60, and 84 h. The induced air oxidation of the soybean oil was carried out using ambient air at a constant flow rate of 25 L min^{-1}.

Characterizations
Spectroscopy Measurements. Fourier transformed infrared spectroscopy (FTIR) was performed on a Perkin-Elmer Impact

400 spectrometer in the attenuated total reflection (ATR) mode. The spectra were obtained over the 4000 to 500 cm^{-1} region employing 62 scans with a resolution of 4 cm^{-1}.

The nuclear magnetic resonance (NMR) spectra for the soy additive were obtained on a Varian Inova 300 spectrometer. The quantitative ^{1}H NMR spectra were acquired from a chloroform-d solution with a sample concentration of 3 wt % at 22°C, operating at 299.95 MHz, using a spectral width of 10 ppm, acquisition time of 2.049 s, relaxation delay of 1 s and 128 scans.

Gel Permeation Chromatography (GPC). The GPC experiments were performed on a Viscotek TDAmax chromatograph, using a tetrahydrofuran (THF) solution with a sample concentration of 10 mg mL^{-1}, flow rate of 1 mL min^{-1} and volume of 150 μL. The samples in solution were filtered through a 0.2 mm-pore size PTFE membrane prior to analysis. The column (Waters HR 4E, HR 4, HR 3, and HR 2) temperature was set at 45°C. Polystyrene standards were used to construct the calibration curve.

Hydroxyl Number Determination. The hydroxyl number (HN) was measured by titration according to ASTM 4274 with the use of eq. (1):

$$HN = \frac{(B-A)56.1}{M_a} \qquad (1)$$

where A is the volume (mL) of NaOH solution used for the titration, B is the volume (mL) of NaOH used for the reference titration, N is the normality of the NaOH solution, and M_a is the sample weight (g).

Acid Index (AI). A solution of 0.1 mol L^{-1} KOH was standardized with potassium biphthalate and used to titrate the reaction products. For each sample of soybean oil, 1 g was dissolved in 50 mL of a diethyl ether solution: neutral ethanol at 40°C. The sample was stirred for 30 min and 1 mL of phenolphthalein indicator solution (1% alcohol) was added. The solution was titrated with 0.1 mol L^{-1} alcoholic KOH solution until a pink color appeared and persisted for 30 s. The acid value (expressed in mg of KOH per gram of sample) was determined according to the relationship:

$$AI = \frac{V_t.N.56.1}{M_a} \qquad (2)$$

where V is the volume titrated (mL), N is the normality of the KOH solution, and M is the sample weight (g).

Differential Scanning Calorimetry (DSC). DSC analysis was performed using a Shimadzu DSC 50 using 9−10 mg of sample under nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The melting temperature and enthalpy were calibrated with indium and zinc. The samples were analyzed from −100 to 100°C applying a heating rate of 20°C min^{-1}.

Rheological Measurements. The rheological behavior of the plasticizers was investigated on an Anton Parr Physica MCR502 oscillatory rheometer with cone and plate geometry (50 mm of diameter). The gap between the cone and plate was set at

Table I. Mixing Protocols

	Pure PVC	Pure Oil/PVC		Oxidized Oil 24 h/PVC	
Wt. oil (%)	0	20	50	20	50
Wt. PVC (g)	5	4	2.5	4	2.5
Wt. oil (g)	0	1	2.5	1	2.5

0.05 mm. The measurements were taken at 120°C over a shear rate (γ) range of 5 to 1000 s^{-1}.

PVC/Soy Plasticizer Blends

Preparation. The PVC/soybean oil additive blend samples were prepared by solution mixing of the PVC powder and soybean oil using THF as the solvent. The blends were stirred at room temperature until the total dissolution of the PVC powder (∼1 h). Table I shows the mixing protocols used in this study.

Migration Tests. The migration of the soybean additive from film samples was analyzed in hexane at room temperature. The samples were taken out after 168 h, dried in a drying oven at 30°C for 24 h and the weights of the dried samples were determined. The percentage mass loss was calculated in relation to the initial additive mass added to the sample according to the method proposed by Altenhofen da Silva et al.[14]

Wide Angle X-ray Diffraction (WAXD). The WAXD analysis of neat PVC and PVC/soy plasticizer blends was performed in a Shimadzu XRD-600 diffractometer, with Cu Kα radiation ($\lambda = 1.5418$ Å). The data were collected within a 2θ angle range of 3−40° at a scanning rate of 2° min^{-1}.

Dynamic Mechanical Thermal Analysis (DMTA). Dynamic mechanical experiments were performed on a Netzsch DMA 242C using tension geometry. Rectangular bars (10 × 4 × 0.5 mm^3) were cut from PVC films and used as samples. The experiments were conducted within the linear viscoelastic region using small amplitude (30 μm) in the temperature range of −150 to 100°C, at a heating rate of 3°C min^{-1} and frequency of 1 Hz.

RESULTS AND DISCUSSION

Soybean Additive

The FTIR spectra for the pure and oxidized soybean oils are shown in Figure 1(a). The spectra show the presence of the characteristic transmittance bands of triglycerides [3, 26] for both samples, i.e., the absorption bands of the ester carbonyl group at around 1740 cm^{-1} and aliphatic hydrocarbons groups at 854 and 2923 cm^{-1}. However, the oxidized soybean oil spectra showed a new absorption band in the region between 3600 and 3300 cm^{-1}, characteristic of hydroxyl groups.[31] The oxidation reaction results in the formation of polyol molecules.[31] Also, for higher oxidation times there was: (i) higher absorption band intensity in the region of hydroxyl groups, which corresponds to the increased number of hydroxyls in the polyol;[31] and (ii) lower absorption band intensity at 3010 cm^{-1}, which, according to Godoy et al.,[37] is directly related to the degree of oxidation of the (C=)C—H bonds in the chain. The lower
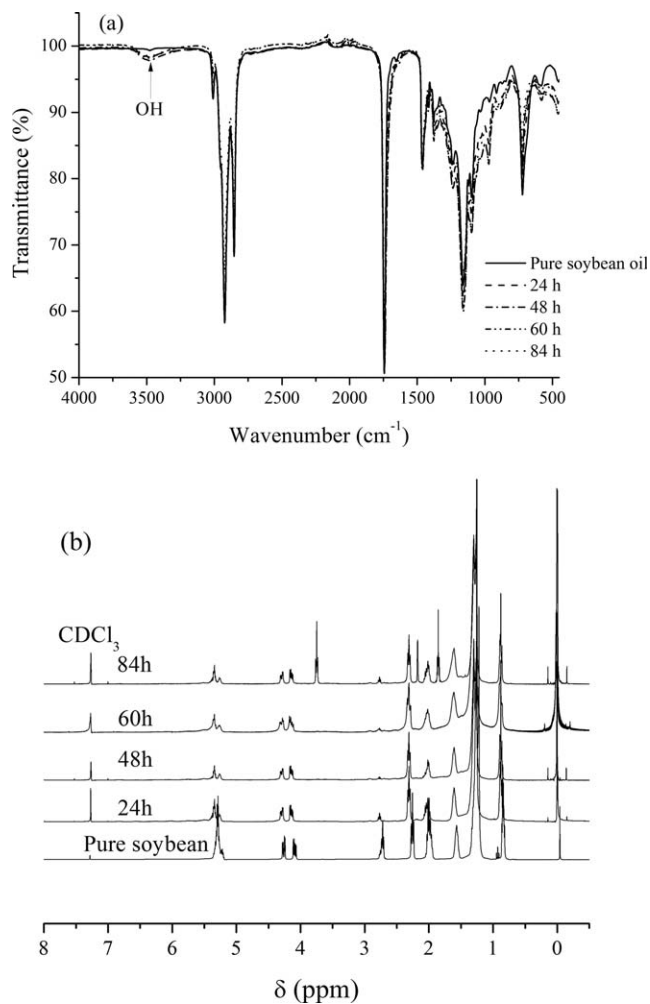

Figure 1. FTIR spectra (a) and (b) NMR H^1 spectra of the pure and oxidized soybean oil.

intensity in this region indicates that more double bonds were oxidized. These results confirm the efficiency of the oxidation method applied in this study.

The ^{1}H NMR spectra for the pure and oxidized soybean oils are shown in Figure 1(b). As can be observed the spectra present the following resonance signals: singlets at 0.9 and 1.3 ppm, corresponding to CH$_3$ and CH$_2$ protons, singlet at 1.7 ppm corresponding to protons in double bond β position, and doublet centered at 4.15 ppm corresponding to the protons of the triglyceride groups. Two resonance signals are also present at 2.8 ppm and 5.25 ppm and these are more intense for the pure soybean oil than the oxidized samples. The signal at 5.25 ppm corresponds to the protons of the alkene group. The intense signal at 2.3 ppm corresponds to the protons of the allyl group present in triglycerides.[27,31] The reduction in the intensity of these signals with an increase in the oxidation time supports that double bonds are consumed during the oxidation process.[27,35] Reports in the literature indicate that the oxidation of vegetable oils at high temperature is controlled by Diels-Alder reactions.[38,39] However, reactions involving free radicals predominate at higher temperatures when compared with other groups
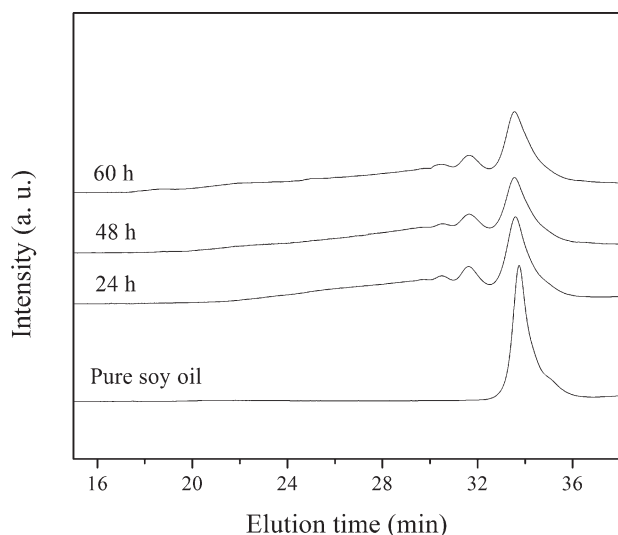
Figure 2. GPC chromatograms for the pure and oxidized soybean oil samples.

formed in lower amounts, such as acetone, alcohol, aldehyde, and ether groups.[38,40] The free radical species generated in the reaction medium can recombine, resulting in the formation of the peroxyl groups, which increases the molecular weight.[38,41] The sample oxidized for 84 h also showed a resonance signal at 3.75 ppm relative to the mid chain ─CH─OH.[31]

The chromatographs obtained by GPC are shown in Figure 2. Although the maximum elution time for all samples was around 33.5 min, it is possible to observe differences between pure and oxidized soybean oils in terms of the elution time behavior. The chromatogram for the pure soybean oil shows a single peak with a maximum at around 33.5 min. The synthesized plasticizers obtained by the air oxidation showed elution in a wider multi peak range of between around 18 and 36 min, and a maximum at around 33.5 min. Similar results were obtained by John *et al.*[31]

The number-average molecular weight (M_n) and the polydispersity index (PDI) obtained for the species are shown in Table II. The M_n values for the oxidized samples were higher than those for pure soybean oil, although these values were similar. The PDI increased with the oxidation time due to the increase in the fractions of larger molecule. Furthermore, the pure soybean oil is almost monodispersed (PDI = 1.1). These differences observed in the M_n and PDI values are related to the radical recombination reactions that occur during the oxidation process.[38,41] The samples oxidized for 84 h could not be completely dissolved for the GPC experiments.

Table II. Number-Average Molecular Weight and Polydispersity Index

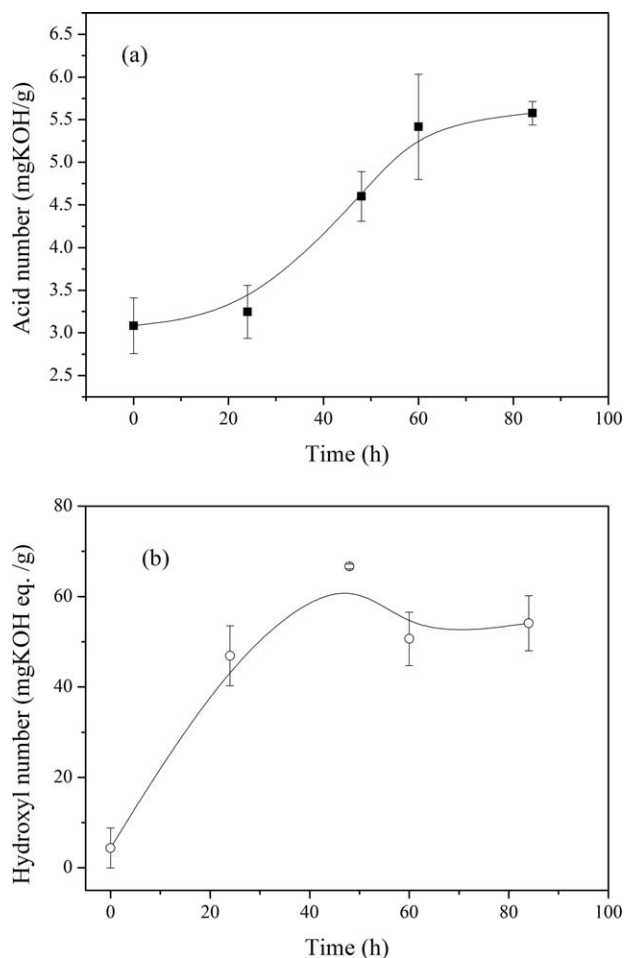| Sample	M_n (g mol^{-1})	PDI (M_w/M_n)
Pure soy oil	1389	1.1
24 h	1517	4.3
48 h	1512	6.9
60 h	1512	16.2

Figure 3. Acid number (a) and hydroxyl number (b) as a function of oxidation time of the soybean oil.

The air oxidation reactions increase the acid number [Figure 3(a)]. The acid number increases until 60 h of air oxidation and after this reaction period the high viscosity of the medium limited the molecular diffusion of the chemical species and thus there was a reduction in the oxidation rate with the subsequent generation of new functional groups.[35] The acidity index provides information on the degree of deterioration of a vegetable oil. A high acid value indicates breakage of the oil chains, which may occur through the action of the temperature and radical species generated by the air intake of the system, releasing fatty acids.[31]

The values for the acidity index obtained for the pure soybean oil are in the range of 3─5.5 mg KOH g^{-1}, which indicates the potential of this raw material for uses such as in the preparation of polyurethanes (>8 mg KOH g^{-1}).[42] The number of hydroxyls showed an increasing trend, as observed for the acid index (Figure 3). After 48 h of reaction it was noted that the number of hydroxyls remained almost constant (around 60 mg KOH g^{-1}), but the polydispersity (M_w/M_n) of the oil increased significantly. This is also due to the recombination of macro radicals generated in the reaction. These results indicate that hydroxyl groups were introduced into the soybean oil chains, as suggested previously by the spectroscopy analysis.
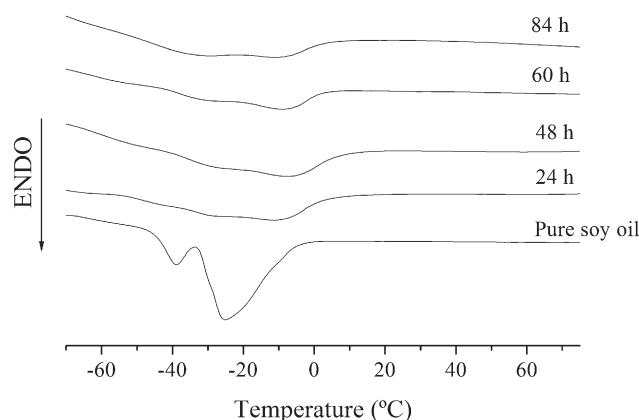
Figure 4. DSC of pure and oxidized soybean oils.

Figure 6. Average values for the atactic fractions.

Figure 4 shows the thermographs obtained in the DSC analysis. The pure soybean oil presented two endothermic peaks at $-39°C$ and $-25°C$, related to the melting temperatures of the components of the soybean oil.[43] The multiple peaks observed for the pure oil sample are due to the polymorphism of mixed lipids. Most vegetable oils are polymorphic and can be found in at least three crystalline forms, designated as α, β', and β.[43,44] All oxidized samples exhibit a broadened melting peak with maximum intensity at around $-12°C$ for 24 h, $-7.5°C$ for 48 h, $-8°C$ for 60 h, and $-10.5°C$ for 84 h of oxidation. The free radical reactions promoted by the air oxidation generate lipids of different sizes, resulting in a higher molecular heterogeneity and therefore a broadening of the range of melting temperatures. The increased molecular heterogeneity can also be seen in the GPC curves (Figure 2).

The flow curves for the pure and oxidized soybean oil are shown in Figure 5. The samples oxidized for 48 h show a New-tonian rheological behavior. At a shear rate of less than 10^2 s^{-1} the oils behaved as Newtonian fluids, as shown by the linear relationship between shear rates. With oxidation for 60 h devia-tion from Newtonian behavior was observed at shear rates above 10 s^{-1}. Geller *et al.*[45] reported that the viscosity of
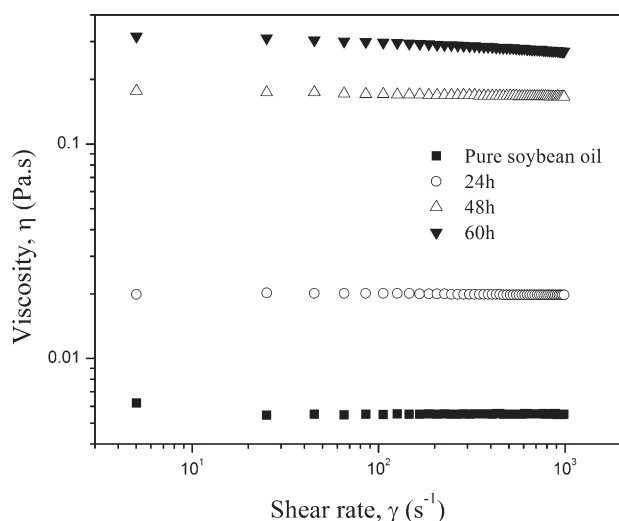

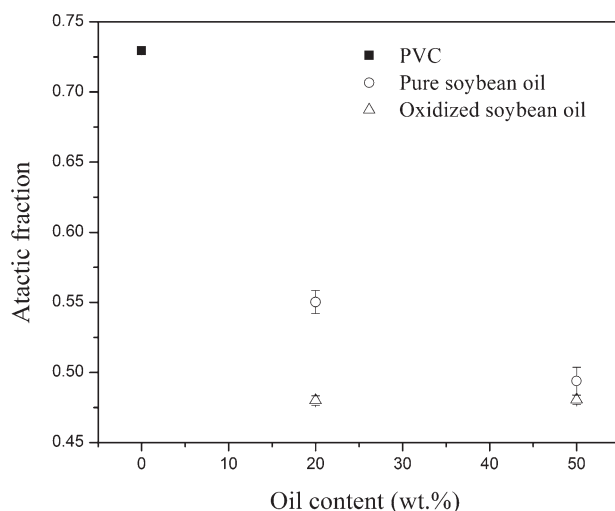**Figure 5.** Viscosity of pure and oxidized soybean oils.

vegetable oils was shear-dependent below a shear rate of 7 s^{-1}, indicating a non-Newtonian flow behavior at very low shear rates. However, when the rate was >7 s^{-1} the oil behaved as a Newtonian fluid. Using the different rheological models, Güler *et al.*[41] studied the rheological behavior of the oxypolymerized linseed oil at higher temperatures. In the same study the authors demonstrated the rheological behavior of linseed oil with a power index very close to unity.[41] However, the oxypoly-merized oils behaved as non-Newtonian fluids, because the polymer chains became longer and a crosslinked structure was formed during the reaction, exhibiting a plastic liquid flow behavior. Thus, for oxidized soybean oil there is a range of Newtonian behavior and another of non-Newtonian behavior.

PVC/Soy Additive Blends
PVC/soy additive blends with concentrations of 20 and 50 wt % of soybean oil (pure and oxidized) were prepared by solution casting using THF. The addition of oil additives to the polymer modifies the thermal, mechanical and other properties, for example, it reduces the atactic fraction of the PVC.[46,47] Apply-ing the methodology described by Gonzales,[46,47] it was possible to determine the atactic fraction of PVC and the influence of the addition of oxidized soybean oil. To quantify the extent of interaction between the soybean oil additive and the PVC, we calculated the atactic fractions for experimental FTIR spectra according to eq. (3). The atactic fraction is defined by the ratio between the band area at 615 cm^{-1} and the global area of the two configurational bands, in the absorption region of C—Cl bonds.[46]

$$f_{\text{atactic}} = \frac{\text{area } 615}{\text{area } 615 + \text{area } 635} \qquad (3)$$

The values for the atactic fractions (Figure 6) were obtained using the calculated areas, which were applied in eq. (3). The areas were estimated using Gaussian functions and the corre-lation coefficient was 0.99.

According to Gonzales, the addition of a plasticizer, such as dioctyl adipate (DOA) or diisodecyl phthalate (DIDP), results in a decrease in the PVC atactic fraction with a low content of
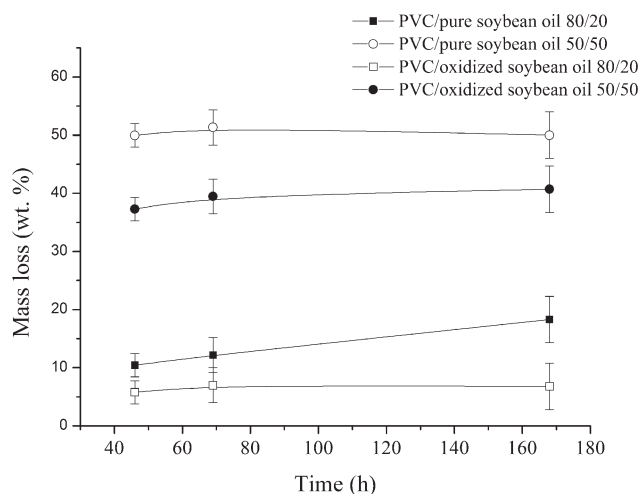
Figure 7. Association between mass loss and migration time.

Figure 8. WAXD of neat PVC and PVC blends with (a) 20 wt %, and (b) 50 wt % pure or oxidized soybean oil.

plasticizer.[46,47] This behavior corroborates our results and in addition, in this study, the samples with oxidized oil showed a lower atactic fraction for a low weight percentage of plasticizer. The compatibility between the plasticizer and the polymer changes according to the polymer tacticity.[30] Greater changes in the values for the atactic fraction indicate higher degrees of compatibility. A more abrupt change in the atactic fraction values was observed for the samples with the oxidized oil (Figure 6) when compared with the neat PVC, suggesting an increased compatibility with the PVC after the insertion of new functional groups, such as hydroxyls.

An important aspect when additives are added to polymers is their migration from the polymer interior to the surface, which affects many properties.[48] Figure 7 shows the dependence of the mass loss on the migration time. The mass loss is almost constant over the whole time period tested for all of the samples except the PVC/pure soybean oil 80/20 sample. Furthermore, it was observed that the migration time of the oxidized oil is lower than that of the pure oil, since the atactic fraction was lower for the oxidized soybean oil. These results corroborate those obtained for the FTIR and GPC analysis. Thus, the high degree of compatibility and the high molecular weight of the oxidized soybean oil improve the migration time when compared to the pure oil.

The wide-angle X-ray diffraction (WAXD) patterns for the neat PVC and the 80/20 wt % PVC/soybean oil samples are shown in Figure 8(a). All samples presented two characteristic peaks at 1.3 Å^{-1} and 1.7 Å^{-1}, which correspond to basal distances, estimated according Bragg's law as 5.0 Å and 3.7 Å, respectively. Similar results were also found in the literature for PVC plasticized with polyesterified rice oil.[14] PVC shows small crystallite sizes and the presence of a mesomorphic phase.[49] For all samples the first peak was at $s = 1.3$ Å^{-1} relative to the (2 0 0) reflection, which is equal to or greater than the (1 1 0) reflection in terms of apparent intensity, and the second peak was at $s = 1.7$ Å^{-1} relative to the (2 1 0), (2 0 1), and (1 1 1) reflections.[49] The addition of 20 wt % of pure and oxidized soybean oils did not affect the crystalline phase of the polymer.
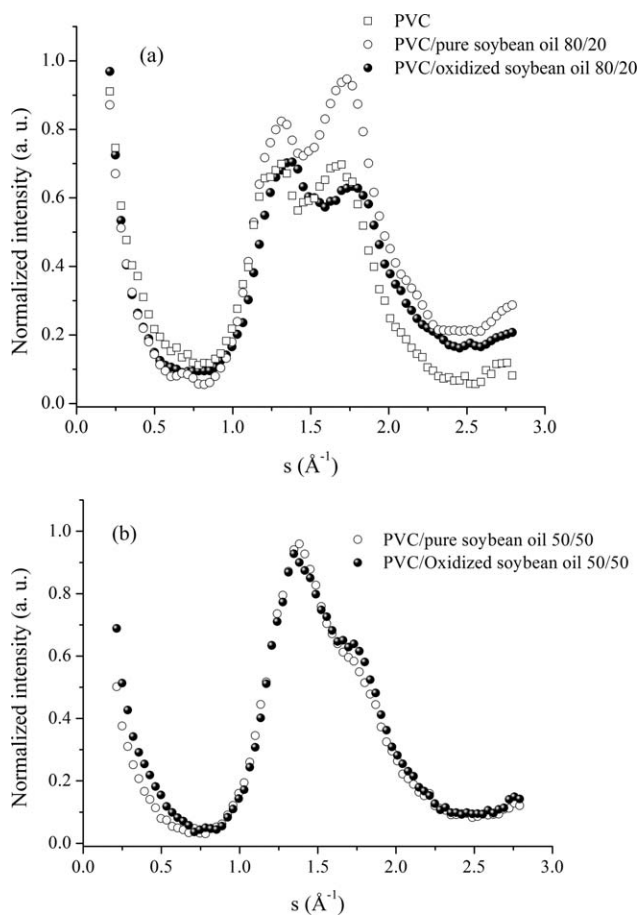
Figure 8(b) shows the WAXD diffractograms for the samples with 50/50 wt % of PVC/soybean oil. An increase in the oil content (from 20 to 50 wt %) decreased the intensity of the second peak at $s = 1.7$ Å^{-1}. The plasticizers interact preferentially with the polar portion of polymer chains, while the nonpolar section has less possibilities for interactions,[50] and these interactions are considered to be weak, e.g., dipole–dipole type. Thus, the hydroxyl and other polar groups from the oil plasticizers interact with the PVC chains and decrease the interaction between them. Therefore, the non-interaction between the chlorine atoms contributes to reducing the second peak intensity, as shown by the atactic fraction results.

Figure 9(a) shows the dependence of the tan δ curves on the temperature. For all samples, over the entire temperature range studied, solid-like behavior prevailed. The pure PVC has a glass transition temperature (T_g) of around 90°C.[14] The use of oil-based plasticizers alters the T_g of PVC.[17] However, the oxidized soybean oil slightly changes the T_g value. For the sample with 50 wt % of oxidized oil, a new transition at −14°C was detected. This result suggests that there are oil-rich regions, indicating heterogeneity for this material. This transition is related to the melt transition of the oil, as observed in the DSC results. A similar behavior was observed for the sample with 50 wt % of pure oil at lower temperatures ($T < −50$°C). The
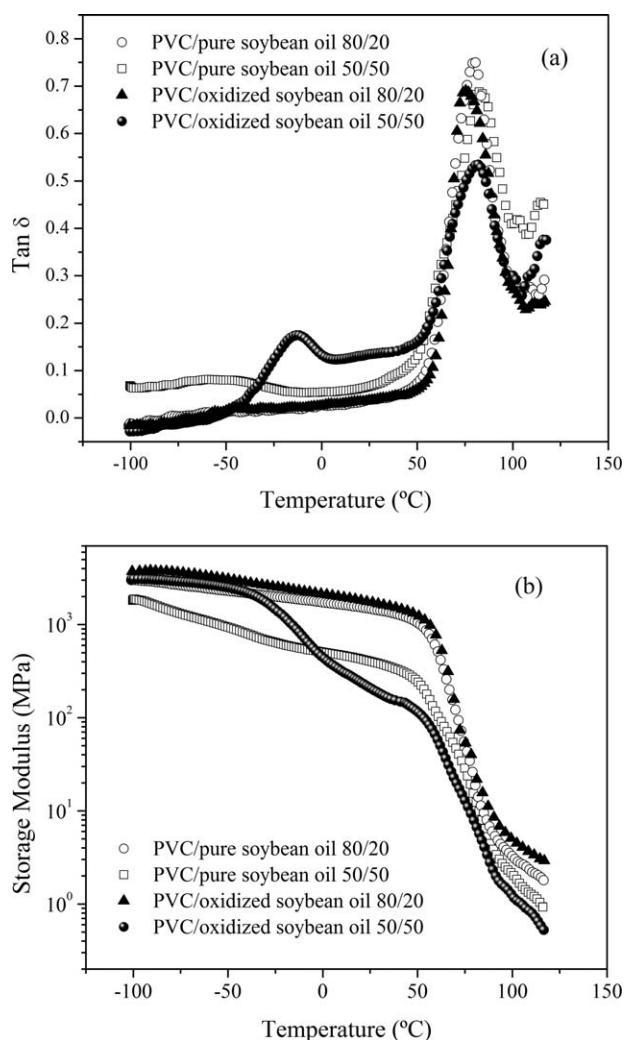
Figure 9. DMTA results for the PVC blend samples at 1 Hz. (a) Tan δ, and (b) storage modulus as a function of temperature.

pure and oxidized soybean oils have molecules with higher molecular weight than common plasticizers used in PVC compounds, such as DOP. So higher molecular weight molecules can lead to phase separation. The same behavior was not observed for molecules with lower molecular weight, such as esterified triglycerides.[14]

Figure 9(b) shows the storage modulus (E') as a function of temperature. At temperatures above 50°C, an abrupt reduction in the E' values due to the higher mobility of the chains was observed. The samples with 20 wt % of pure, and oxidized oil show a similar E' behavior on the entire temperature range under study. For samples with 50 wt % a different behavior was observed. The pure oil act as an external lubricant causing a reduction on the E' values. Nevertheless, no significant changes on the glass transition temperature or on the global E' behavior was observed when compared to the 20 wt % samples. On the other hand, the oxidized oil notably changes the E' behavior throughout the temperature range, owing to the higher interaction caused by the new functional groups from the oxidation reaction. All samples have E' values of around 10^3 MPa in the glassy state.

CONCLUSIONS

In this study, soybean oil additives were prepared by air oxidation at elevated temperature and this approach represents a viable alternative to the use of secondary plasticizers, in terms of material and processing costs, for application in PVC. The soybean additives were characterized by spectroscopic, titrimetric, chromatographic, thermal, and rheological measurements. The PVC/soybean additive blends were prepared by solution casting using 20 and 50 wt %. The morphology and viscoelastic properties of the blends were evaluated.

The oxidation reaction of the soybean oil resulted in new absorption bands in the region of 3600 to 3300 cm^{-1}, characteristic of hydroxyl groups, which corroborated the ^{1}H NMR results, through the intense signals at 5.25 and 2.3 ppm, showing that the consumption of double bonds occurs during the oxidation process. The M_n value for the oxidized samples is higher than those for the pure soybean oil, due to the macroradical recombination reactions which occur during the oxidation process. The acid index and hydroxyl number show a tendency to increase with increasing oxidation time. The free radical reactions, which occurred during the air oxidation, resulted in higher molecular heterogeneity and therefore a broadening of the range of melting temperatures. Oxidized oil has greater compatibility with PVC through the insertion of new functional groups when compared with pure soybean oil, which does not result in significant changes in the crystallinity or glass transition of the PVC.

ACKNOWLEDGMENTS

REFERENCES

1. Chiellini, F.; Ferri, M.; Morelli, A.; Dipaola, L.; Latini, G. *Prog. Polym. Sci.* **2013**, *38*, 1067.

2. Coltro, L.; Pitta, J. B.; da Costa, P. A.; Fávaro Perez, M. Â.; de Araújo, V. A.; Rodrigues, R. *Food Control* **2014**, *44*, 118.

3. Adhvaryu, A.; Erhan, S. Z. *Ind. Crops Products* **2002**, *15*, 247.

4. Fenollar, O.; Garcia-Sanoguera, D.; Sánchez-Nácher, L.; López, J.; Balart, R. *J. Appl. Polym. Sci.* **2012**, *124*, 2550.

5. Earla, A.; Braslau, R. *Macromol. Rapid Commun.* **2014**, *35*, 666.

6. Abb, M.; Heinrich, T.; Sorkau, E.; Lorenz, W. *Environ. Int.* **2009**, *35*, 965.

7. Bernard, L.; Décaudin, B.; Lecoeur, M.; Richard, D.; Bourdeaux, D.; Cueff, R.; Sautou, V. *Talanta* **2014**, *129*, 39.

8. Yu, Z.; Zhou, J.; Zhang, J.; Huang, K.; Cao, F.; Wei, P. *J. Appl. Polym. Sci.* **2014**, *131*, 40938.

9. Schossler, P.; Schripp, T.; Salthammer, T.; Bahadir, M. *Sci. Total Environ.* **2011**, *409*, 4031.

10. Oriol-Hemmerlin, C.; Pham, Q. T. *Polymer* **2000**, *41*, 4401.

11. Nihul, P.; Mhaske, S.; Shertukde, V. *Iran Polym. J.* **2014**, *23*, 599.

12. Bueno-Ferrer, C.; Garrigós, M. C.; Jiménez, A. *Polym. Degrad. Stabil.* **2010**, *95*, 2207.

13. Vieira, M. G. A.; da Silva, M. A.; dos Santos, L. O.; Beppu, M. M. *Eur. Polym. J.* **2011**, *47*, 254.

14. Altenhofen da Silva, M.; Adeodato Vieira, M. G.; Gomes Maçumoto, A. C.; Beppu, M. M. *Polym. Test.* **2011**, *30*, 478.

15. Vijayarajan, S.; Selke, S. E. M.; Matuana, L. M. *Macromol. Mater. Eng.* **2014**, *299*, 622.

16. Peng, Y.; Lin, H. *Adv. Mat. Res.* **2014**, *852*, 256.

17. Bouchareb, B.; Benaniba, M. T. *J. Appl. Polym. Sci.* **2008**, *107*, 3442.

18. Baltacioğlu, H.; Balköse, D. M. *J. Appl. Polym. Sci.* **1999**, *74*, 2488.

19. Semsarzadeh, M. A.; Mehrabzadeh, M.; Arabshahi, S. S. *Eur. Polym. J.* **2002**, *38*, 351.

20. Stuart, A.; LeCaptain, D. J.; Lee, C. Y.; Mohanty, D. K. *Eur. Polym. J.* **2013**, *49*, 2785.

21. Yu, B. Y.; Lee, A. R.; Kwak, S.-Y. *Eur. Polym. J.* **2012**, *48*, 885.

22. Navarro, R.; Pérez Perrino, M. N.; Gómez Tardajos, M.; Reinecke, H. *Macromolecules* **2010**, *43*, 2377.

23. Stark, T. D.; Choi, H.; Diebel, P. W. *Geosynthetics Int.* **2005**, *12*, 99.

24. Boo, H.-K.; Shaw, M. T. *J. Vinyl Technol.* **1989**, *11*, 176.

25. Köckritz, A.; Martin, A. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 812.

26. Karmalm, P.; Hjertberg, T.; Jansson, A.; Dahl, R. *Polym. Degrad. Stabil.* **2009**, *94*, 2275.

27. Karmalm, P.; Hjertberg, T.; Jansson, A.; Dahl, R.; Ankner, K. *Polym. Degrad. Stabil.* **2009**, *94*, 1986.

28. Wang, R.; Schuman, T. P. *eXPRESS Polym. Lett.* **2013**, *7*, 272.

29. Vlček, T.; Petrović, Z. *J. Am. Oil Chem. Soc.* **2006**, *83*, 247.

30. Niedermann, P.; Szebényi, G.; Toldy, A. *J. Polym. Environ.* **2014**, 1.

31. John, J.; Bhattacharya, M.; Turner, R. B. *J. Appl. Polym. Sci.* **2002**, *86*, 3097.

32. Uyama, H.; Kuwabara, M.; Tsujimoto, T.; Nakano, M.; Usuki, A.; Kobayashi, S. *Chem. Mater.* **2003**, *15*, 2492.

33. Guo, A.; Cho, Y.; Petrović, Z. S. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3900.

34. Kandanarachchi, P.; Guo, A.; Petrovic, Z. *J. Mol. Catal. A: Chem.* **2002**, *184*, 65.

35. Fornof, A. R.; Onah, E.; Ghosh, S.; Frazier, C. E.; Sohn, S.; Wilkes, G. L.; Long, T. E. *J. Appl. Polym. Sci.* **2006**, *102*, 690.

36. Miyake, Y.; Yokomizo, K.; Matsuzaki, N. *J. Am. Oil Chem. Soc.* **1998**, *75*, 15.

37. Godoy, S.; Ferrão, M.; Gerbase, A. *J. Am. Oil Chem. Soc.* **2007**, *84*, 503.

38. Choe, E.; Min, D. B. *J. Food Sci.* **2007**, *72*, R77.

39. Gertz, C.; Klostermann, S.; Kochhar, S. P. *Eur. J. Lipid Sci. Technol.* **2000**, *102*, 543.

40. Mallégol, J.; Lemaire, J.; Gardette, J.-L. *Prog. Organ. Coat.* **2000**, *39*, 107.

41. Güler, Ö. K.; Güner, F. S.; Erciyes, A. T. *Prog. Organ. Coat.* **2004**, *51*, 365.

42. Kiatsimkul, P.-P.; Suppes, G. J.; Sutterlin, W. R. *Indust. Crops Products* **2007**, *25*, 202.

43. Wang, T.; Briggs, J. *J. Am. Oil Chem. Soc.* **2002**, *79*, 831.

44. O'Brien, R. D. Fats and Oils: Formulating and Processing for Applications, 3rd ed.; Taylor & Francis: Boca Raton, **2008**.

45. Geller, D.; Goodrum, J. *J. Am. Oil Chem. Soc.* **2000**, *77*, 111.

46. González, N.; Fernández-Berridi, M. J. *J. Appl. Polym. Sci.* **2008**, *107*, 1294.

47. González, N.; Fernández-Berridi, M. J. *J. Appl. Polym. Sci.* **2006**, *101*, 1731.

48. Marcilla, A.; Garcia, S.; Garcia-Quesada, J. C. *Polym. Test.* **2008**, *27*, 221.

49. Elicegui, A.; del Val, J. J.; Bellenger, V.; Verdu, J. *Polymer* **1997**, *38*, 1647.

50. Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley: New York, **1982**.