Synthesis and Characterization of Polymeric Materials from Vegetable Oils

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Summary: Although the petrochemical polymers have revolutionized the technological development, the intensive use of these materials have contributed to the global pollution. In this context, researches involving ecofriendliness materials are growing up, as well as, a current interest in developing materials from inexpensive and renewable resources, such as vegetable oils. In this work, is described the synthesis of polymeric materials by thermal polymerization from linseed oil (*Linum usitatissimum* L.) and passion fruit oil (*Passiflora edulis*) and their characterization by gas chromatographic (GC), Fourier transform infrared (FTIR) spectroscopy, solubility in organic solvents, thermogravimetry (TG), differential scanning calorimetry (DSC) and Raman spectroscopy. The TG curve shows that those polymeric materials present two stages of decomposition. DSC plots of the vegetable oils showed some endothermic and exothermic transitions which are not present in the DSC curves corresponding to oil-based polymers. The Raman spectra of the polymers indicate declining of absorbance in the region of C=C stretching ($\sim$1600 cm^{-1}). This absorption was used to estimate the degree of polymerization (79% and 67.5% for linseed and passion fruit oils, respectively).

Keywords: materials; thermal analysis; vegetable oils

Introduction

Vegetable oils are one of the most readily available alternative renewable resources and have several applications in the preparation of many types of materials, mainly the industrial use, which has become extremely important in recent years due to the environmental protection. These new materials can replace petroleum-based polymers with additional advantages related to low cost, thermal stability, flexibility, resistance to chemicals, biocompatibility, biodegradability, adhesion to metallic substances, gas permeability, electrical conductivity and non-flammability.[1–4]

Triglycerides are triesters of glycerol mostly composed of mixtures of fatty acids, have been used since 19th century in paint formulations.[2,3] Triglyceride resins are an attractive alternative to petroleum resins because they are inexpensive, have good properties, are derived from renewable resources and are abundant.[3,5] In the last decade, investigations on oil-based polymers have been focused on different purposes, depending in their usage area.[4]

Among the several known vegetable oils, linseed (*Linum usitatissimum* L.) is used for synthesis of oil-modified polymers. Compared to common other oils, linseed oil have better performances, due the high content of linolenic acid.[6,7] The passion fruit (*Passiflora edulis*) it is original of the tropical America. The juice is a product with an aroma and acidity accentuated and the oil is rich in unsaturated fatty acids,

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mainly linoleic acid (70%). Based on this percentage, the passion fruit oil is considered a drying oil.[8,9] The percentage of unsaturated fatty acids is the base of the chemistry of these materials due the your tendency to polymerization.[10] These and other oils harden on exposure to oxygen through the oxidation of double bonds to hydroperoxides followed by decomposition to free radicals and radical combination.[11]

The present work focus on the preparation of polymeric materials from linseed and passion fruit oils through thermal polymerization and their characterization by gas chromatographic (GC), FTIR spectroscopy, solubility in organic solvents, thermogravimetry (TG), derivative thermogravimetric curves (DTG), differential scanning calorimetry (DSC) and Raman spectroscopy.

Experimental Part

Materials

Linseed oil was obtained from Pindorama™ (Brazil) and passion fruit oil from Naturais da Amazônia™, both with purity of 99%. The benzoyl peroxide was purchased from Aldrich Co.

Polymer Preparation

Polymeric materials were prepared by thermal polymerization (92 °C), in the same conditions. The polymerization time was ten hours and benzoyl peroxide (BPO) was used as initiator, the reaction happened at inert atmosphere (N_2). After the reaction in thermal bath, the mixtures were put in oven at 80 °C for 30 days until complete polymerization.

Characterization

GC analysis of vegetable oils was performed on a Varian CP 3800 gas chromatograph equipped with a flame ionization detector and a capillary column (CPwax 52 CB, 30 m ×0.32 mm ×0,25 μm film). Helium was the carrier gas to a flow of 2 mL min^{-1}. The column temperature was programmed it began in 80 °C and it stayed for 1 minute, following by a ramp of 10 °C min^{-1} up to 250 °C, staying in this temperature for more 7 minutes. Each analysis happened in 25 minutes. Esters of the sample were identified by retention times and by comparing them with authentic standards analyzed under the same conditions. The quantification was measured in agreement in the relative area of each constituent peak of the chromatogram, considering that the total area was of 100%.

FTIR spectra were acquired on Bomem MB-100 FT-IR spectrometer by transmission through NaCl tablets using with vibration frequency of cm^{-1}.

The solubility test in organic solvents was realized in test tube with approximately 3.4 mg of sample and 10 mL of organic solvents (chloroform, water, methanol, ethanol, ethyl acetate, toluene, carbon tetrachloride, tetrahydrofuran and acetone), in two different conditions (room temperature and at 50 °C). The qualitative fusibility test was realized observing the comportment of the sample after heated directly in test tube (~200 °C).

TG curves were obtained in a thermobalance Shimadzu TGA-50, using a platinum crucible under atmospheric air. The temperature was scanned up to 650 °C, heating rate of 10 °C min^{-1}. Sample mass varied between 6.0 ± 0.5 mg. The temperature of decomposition (T_d) was ascertained by DTG.

DSC curves were obtained in DSC-50/Shimadzu, from –100 up to 200 °C at 10 °C min^{-1}, using aluminum crucible closed in inert atmosphere (He). Two scans were obtained for each sample and the second scan's resulting curve was used for analysis. The temperature at the midpoint of the change in slope of the DSC heat-capacity change was taken as the glass transition temperature (T_g).

The Raman spectra were acquired in a module FRA 106/S coupled to a spectrometer Equinox 55 both of the Brüker with a mirror in the direction of the dispersal (128 scanning and resolution of 4 cm^{-1}). The excitement laser (Nd:YAG) and potency of the laser of 1064 nm and 250 mW, respectively, the sign was detected by a detector of Ge freezing by N_2 liquid.

Results and Discussion

The natural oils are triglycerides that comprise three fatty acids linked by a glycerol center, this molecule triglyceride oil can have from 94–96% of weight of fatty acids. [4,12] Larger part of the common oils contains fatty acids that vary from 14 to 22 carbons in length, with 1–3 double bonds.[12] Fatty acids composition of the studied oils is shown in Table 1.

Through the table, it is observed that the studied oils present high unsaturated index, with predominance of the linoleic acid in the passion fruit oil and linolenic acid in the linseed oil. The unsaturated degree is an important parameter in the choice of oil because plays an important role on polymer properties, the average degree of unsaturation is measured by iodine value.[4] Due to that, triglyceride oils are divided into three groups depending on their iodine values, such as, drying (iodine value is higher than 130), semi-drying (iodine value is between 90 and 130) and nondrying oils (iodine value is smaller than 90).[4] In that study, it was verified that the linseed and passion fruit oils are drying because present iodine values of 180,5 and 139,4 cg I_2/100g, respectively. For that reason, those oils tend to the process of autoxidative curing with initiation, propagation and termination steps.[12] It is observed that in the initiation, the oxidation happen in the presence of double bonds, that it consists on the formation of hydroperoxides or cyclic peroxides decompose to form free radicals. These radicals react with natural antoxidants and after consuming the antioxidants, react with the fatty acid chains of the drying oil. The propagation continues by the abstraction of the hydrogen atoms present between double bonds of the methylene groups, resulting in the free radical that is resonance stabilized. Then it follows the termination, cross-linking proceeds.[7,12]

FTIR spectroscopy can also be used for the structural analysis of oils e to verify the authenticity of edible oils, due to its simplicity, rapidity and ease of sample preparation.[4,13] In this work that technique was used mainly to elucidate the unsaturation area of vegetable oils. In Figure 1 are shown the spectra of vegetable oils. At the same, in Table 2 the main bands absorptions and their function groups are assigned.[4,7,13] Usually, it is observed that the vegetable oils that present high unsaturation index present similarities when characterized by IR.[7]

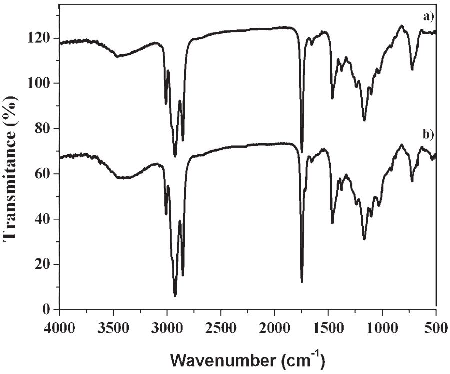

Figure 1.
FT-IR spectra of the vegetable oils (a) linseed oil and (b) passion fruit oil.

Table 1.
Fatty acid composition of vegetable oils.

Fatty acid	Linseed oil (%)	Passion fruit oil (%)
Palmitic acid $C_{16:0}$	6,7	10,5
Palmitoleic acid $C_{16:1}$	0,1	–
Stearic acid $C_{18:0}$	4,7	1,6
Oleic acid $C_{18:1}$	25,1	13,9
Linoleic acid $C_{18:2}$	4,7	72,8
Linolenic acid $C_{18:3}$	57,6	0,5

Table 2.
IR absorption band values for linseed and passion fruit oil.[4,7,13]

Absorption bands (cm^{-1})	Funcionality
3500	−OH functions corresponding to free glycerol and/or residual moisture
3011	(C−H)=CH stretching
2930–2850	$-CH_2-$ groups (with an additional weak shoulder around 2960 cm^{-1} reflecting the presence of terminal methyl groups)
1745	−COOH groups
1160	C−O−C functions of the ester group
720	$-(CH_2)_n-$ sequences of the aliphatic chains of the fatty acids
1650, 3010	(C=C) Non-conjugated unsaturation

Recently, thermoanalytical methods are more commonly used for characterization of fats, oils and materials, as well as for investigation of thermal auto-oxidation process. [15] The thermal stability of linseed and passion fruit oils and also polymers was investigated by TG and DTG analysis. In the thermo-oxidative curves of the vegetable oils (Figure 2a) two regions of decomposition can be observed. The first decomposition stage of linseed oil begins at 233 and ends at 347 °C and for passion fruit oil happens between 300 e 376 °C. This stage is referred in the literature to the oxidation of unsaturated fatty acids. The second mass loss step occurs at a fast rate for linseed oil, between 384 and 466 °C and for passion fruit oil between 402 and 449 °C, associated to carbon chain oxidative decomposition. Although both oils have two degradation steps, it was verified that the linseed oil shows less thermal stability than passion fruit oil, as a consequence of its higher unsaturation index.

DTG curves of linseed oil polymer (LOP) and passion fruit oil polymer (PFP) (Figure 2b) present two decomposition stages. The first degradation stage observed occur between 300 and 400 °C, and is probably due to the degradation of the cross-linked polymer network. The second decomposition step comes out over 400 °C, corresponding to the thermo-oxidative degradation of carbon chains.[9] It is also observed that in the second stage PFP is more thermally stable than the LOP (Table 3). From the analysis of the thermo-oxidative curves we can conclude that the materials synthesized show degradation steps relatively near to the corresponding oils (Table 3). As the first degradation step of the oils corresponds to the unsaturated fatty acids decomposition, in the materials this step will correspond to the cross-linked polymer network degradation, indicating that polymerization reac-

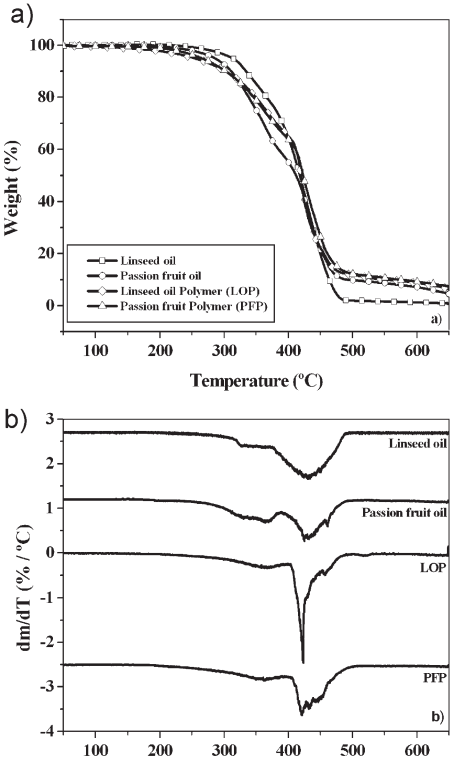

Figure 2.
(a) TG curves of vegetable oils and materials, (b) DTG curves of vegetable oils and materials.

Table 3.
TG measures of oils and polymeric samples.

Oils/Materials	T_{onset} (°C)	T_d (°C)	T_{endset} (°C)
Linseed oil	387	431	468
Passion fruit oil	403	424	463
LOP	407	413	415
PFP	409	421	428

tion occurred. When antioxidants are used in the thermopolymerization process and also smaller temperatures than 50 °C, it is observed that the materials present an increase in the thermal stability when compared to materials synthesized without the presence of antioxidants.[15,16] Polymeric materials obtained by thermal polymerization present aspect rubbery. At the same time, solubility and fusibility qualitative tests showed that the materials are not soluble neither melting, demonstrating that the polymers are thermoset.[16]

Vegetable oils and polymeric materials DSC curves are shown in Figure 3. Linseed oil curve presents an exothermic transition at −74 °C, probably due to a higher double-bond density. Additionally, linseed oil curve shows two endothermic peaks near to −40 and −30 °C, related to the phase transition of fatty acids constituents of the oil. Passion fruit oil DSC curves present some thermodynamic transitions between −100 and 0 °C. At 80 °C an endothermic transition can be observed, due to some transition order-disorder in solid state, and at −72 °C an exothermic, related with the crystallization of the fatty acids with high density of double bonds present in the oil. This same region of transition is observed in the linseed oil,[12] although the remaining transition regions are assigned to the different oil unsaturation levels. Two other endothermic transitions were observed at −41 and −30 °C, both related to the solid-liquid transition of fatty acids constituents of the oil.[9] DSC curves of the corresponding polymeric materials didn't reveal transitions up to 0 °C, indicating that the polymerization reaction occurred. However, a new transition between 14 and 23 °C, assigned to glass transition became visible, indicating the formation of the elastomer.

Usually, Raman spectroscopy is used to identify the unsaturation of fatty acids, the spectra obtained present predominantly bands from vibrations of hydro-carbon chains, with some contributions from those of polar groups.[17,18] In the Figure 4 are presented FT-Raman spectra of the vegetable oils used in this study and the corresponding polymeric materials. The passion fruit oil spectrum present peaks with intensities similar to soybean oil spectrum.[18] At the same time, spectrum of linseed oil presents peaks with the highest intensities and the passion fruit oil spectrum has the lowest intensities. However, the bands are in the same area

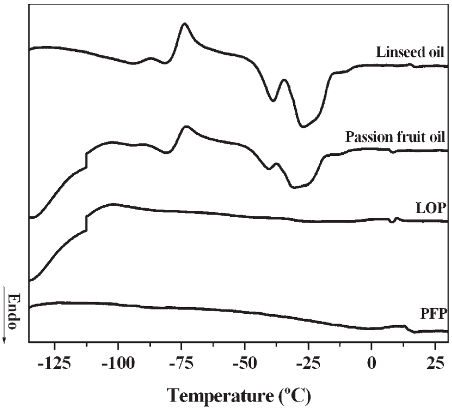

Figure 3.
DSC curves of vegetable oils and materials.

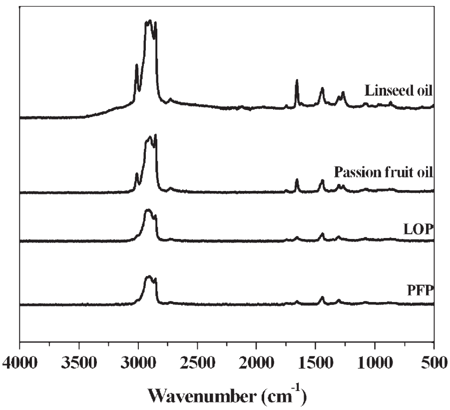

Figure 4.
Raman spectra of vegetable oils and materials.

due high unsaturation index present in the oils. It is possible to observe bands such as asymmetric aliphatic C$-$H at 2926 cm^{-1}, symmetric aliphatic C$-$H at 2855 cm^{-1}, C$=$O stretching at 1661 cm^{-1} and in an ester at 1743 cm^{-1}, CH_2 scissoring deformation at 1439 cm^{-1}, in-phase methylene twisting motion at 1304 cm^{-1} and in plane $=$C$-$H deformation in an unconjugated *cis*-double bond at 1268 cm^{-1}.[17,18]

The main differences observed between the oils and materials spectra are located at 1268 ($\delta_{=C-H}$), 1655 ($\nu_{C=C}$) and 3014 cm^{-1} ($\nu_{=C-H}$). The spectra of vegetable oils showed that the region of unsaturations is located at $\sim$1650 cm^{-1} and that in the spectra of materials these regions decrease, confirming that the polymerization reaction occurred. The FT-Raman absorption at 1655 cm^{-1} (C$=$C stretching) was used to estimate the polymerization degree of the samples. This measured was accomplished by the normalized area of spectroscopic data that was done to compensate for gross differences in the spectral response that were caused by physical effects. Compared to vegetable oils, relative intensities of unsaturation degree obtained were 79.0% and 67.5% for LOP and PFP, respectively. Indicating that the polymerization process is satisfactory, also associated to the high unsaturation degree of vegetable oils.

Conclusion

This study demonstrated that thermal polymerization it is an appropriate technique for preparation of polymeric materials from linseed and passion fruit oils. Moreover, the polymeric materials synthesized exhibit similar characteristics such as thermoset, present aspect rubbery high thermal stability. GC analysis showed that the linseed and passion fruit oils present high unsaturation degree. IR e Raman spectroscopy techniques was used for quantitative and qualitative measurement of edible oils. The evolution of the polymerization reaction was monitored by Raman analysis, and observed by the gradual decrease of peaks intensities assigned to double bonds at 1600 cm^{-1}. The absorption at this frequency was used to estimate the materials degree of polymerization. On the other hand, the characterization by DSC showed that the polymeric materials presented glass transition temperature close to 20 °C.

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