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# Characterization of Polyurethanes from Vegetable Oils by TG/DTG, DMA and FT-IR

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**Summary:** Given the demand for renewable resources by industries and the promising potential of vegetable oils for this purpose, the current study aims to evaluate the properties of polyurethanes (PUs) obtained from linseed (*Linum usitatissimun* L.) oil (PULO) and passion fruit (*Passiflora edulis* Sims *f. flavicarpa Degener*) oil (PUPFO), by thermogravimetry (TG), derivative thermogravimetry (DTG), dynamic mechanical analysis (DMA) and Fourier transform infrared (FT-IR). The results showed that PULO is more thermally stable than PUPFO, suggesting that the first presents more urethane linkages. The DMA analysis showed that both prepared PUs have uneven porosity, causing the loss of the elastic plateau. It was found as well that PUPFO exhibits a higher value of glass transition temperature ($T_g$), signifying that it seems to be more crosslinked than PULO. The analysis by FT-IR showed that the curing reaction of PUs was successful.

**Keywords:** thermal analysis; polyurethanes; vegetable oils

## Introduction

The demand for renewable resources to polymeric materials has increased remarkably over recent years. In the socio-economic context is very important to search for alternatives that minimize environmental impacts caused by the lack of management of waste arising from the use polymers based on fossil fuels. In this sense, vegetable oils are potentially promising materials for the preparation of polymeric materials, due to its numerous advantages such as wide availability, low cost, easy processing, low toxicity and rate of generation of waste during the production and, above all, the possibility of being biodegradable, resulting in a lower generation of waste in the environment.[1]

Linseed oil (LO) is obtained from the seed of *Linum usitatissimun* L. and its composition is mostly about 53% linolenic acid.[2] The passion fruit oil (PFO) is a triglyceride obtained from the seeds of passion fruit (*Passiflora edulis* Sims f. *flavicarpa* Degener) rich in unsaturated fatty acids, where as linoleic acid represents about 70% of their composition.[3]

Among various polymeric materials prepared with vegetable oils, polyurethanes (PUs) are classified into one of the most important subclasses of the family of thermoplastic elastomers. These materials are originated from reactions of polyols with isocyanates by policondensation. Besides urethane linkages, the main polymeric chain of the PUs may also contain other functional groups, such as ester, ether, urea and amide. The polymeric chains consist of alternating short sequence of hard (rigid) isocyanate segments and soft (flexible) polyol that providing high elasticity to PU. In fact, physical, mechanical, adhesive e thermal properties of PUs depend strongly on the composition and chemical structure of hard and soft segments.[4–6] PUs are members of a class of versatile polymers with broad application, considered one of the most important groups of plastics.[7] Therefore, these

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materials have been subject of industrial and academic researches, being able widely to be used as flexible and rigid foams, and also employed as elastomers, fibers, lacquers and adhesives.[8,9]

In the present study it was evaluated the thermal properties of PULO and PUPFO, PUs obtained respectively by polymerization of LO and PFO, applying thermogravimetry, derivative thermogravimetry (TG/DTG) and dynamic mechanical analysis (DMA).

## Procedures

### Materials

Linseed oil (LO) was obtained from Olvepin™ (Industry of Vegetable Oils Pindorama), Passion fruit oil (PFO) was purchased from Naturais da Amazônia™, both with 99% purity. It was still used formic acid (85%) from Isofar, hydrogen peroxide (30%) from Dinâmica, as well as sodium bisulphite, ethyl ether, sodium carbonate and anhydrous sodium sulphate purchased from Vetec, all in analytical grade.

### Polyols Synthesis

LO and PFO presented average molar mass of 863 and 869 g mol$^{-1}$, respectively, that represents the molecular weight of all oligomer chains, considering the number of chains.[10] The functionality of theses oils was 4.0 and 3.8 double bonds per mole and they were hydroxylated according to procedure adapted from the literature.[11] Then, 21.74 mmol of double bonds (LO); 65.24 mmol of formic acid and 32.62 mmol of hydrogen peroxide was slowly added to the mixture at room temperature for 30 minutes under strong mechanical stirring. After addition of hydrogen peroxide, the resultant mixture was heated to 65 °C for 5 hours. Then, the heating was removed and 10% wt/vol sodium bisulphate solution was added. The isolated organic layer was washed with 10% wt/vol sodium carbonate solution until neutralization. The neutral solution was dried with sodium sulfate and the solvent was removed under vacuum. The same experimental methodology was used to obtain the polyol of PFO according to the following molar ratios: 20.82 mmol of double bonds; 62.46 mmol of formic acid and 31.23 mmol of hydrogen peroxide. Hydroxyl index was determined by ASTM D 1957-86.[12]

### Preparation of PUs

The preparation of PUs was carried out in a glass bottle, by means of the addition of polyol into the amount of diphenylmethane diisocyanate (MDI, molar ratio [NCO]/[OH] = 0.8). Then the mixture was poured into Teflon molds and remained in the oven at 100 °C for 24 h. The content of free isocyanate (NCO) present in the MDI (was performed by titration according to ASTM D 5155-96.[13]

### Characterization of PUs

The thermogravimetric analyses (TG) and derivative thermogravimetry (DTG) were performed in a thermobalance Shimadzu TGA-50, using a platinum crucible. The temperature was scanned up to 650 °C, heating rate of 10 °C min$^{-1}$ under helium atmosphere (50 mL min$^{-1}$). Sample mass varied between $6.0 \pm 0.5$ mg. The temperature of decomposition ($T_d$) was ascertained by DTG. Analysis by DMA was performed in a DMTA V Rheometric Scientific mode of traction, in the temperature range of -140 to 300 °C with a heating rate of 5 °C min$^{-1}$, frequency of 1 Hz and 0, 20 mm wide. Sample sizes were $6.0 \times 4.5 \times 1.4$ mm, approximately. Infrared spectra were acquired on Michelson Bomem Hartmann & Braun, Serial B, MB-100 FT-IR spectrometer. The samples of LO, PFO and their polyols were analyzed in NaCl tablets. FT-IR spectra were obtained between 4000 and 400 cm$^{-1}$.

## Results and Discussion

Hydroxyl index obtained for polyols from LO (125,40 mg KOH/g) and PFO (122,40 mg KOH/g) were satisfactory compared with literature data for other vegetable oils, such as: soybean oil (179,30 mg KOH/g), corn oil (179,0 mg KOH/g), cottonseed oil (76,80 mg KOH/g), canola oil (173,60 mg KOH/g), sunflower oil (177,80 mg KOH/g).[14,15]

The free isocyanate content was determined by titration described in the standard which is an indirect titration method. Furthermore, the content of free isocyanate is the amount of NCO groups which are available for cross-linking.[16-18] In the present work, the NCO index was 30.82%, similar to values found in literature.[19,20] In this work, we chose the molar ratio [NCO]/[OH] = 0.8 in order to obtain a flexible foam.

TG/DTG curves of PULO and PUPFO are shown in Figure 1. The curves profile shows that the process of thermal decomposition of PUs occurred apparently in three steps (Figure 1a). However, for analysis, it were considered the two most obvious steps (Figure 1b), being the second more pronounced, for the two PUs.

The $T_d$ values obtained for these two steps and their respective mass losses are listed in Table 1.

**Table 1.**
$T_d$ and mass loss values for the PUs.

| PUs | $T_d1$ (°C) | Mass loss (%) | $T_d2$ (°C) | Mass loss (%) |
|---|---|---|---|---|
| PULO | 410 | 72 | 473 | 19 |
| PUPFO | 393 | 78 | 476 | 13 |

The results also showed that PULO is more thermally stable, because the first stage of the decomposition reaction began at 235 °C, with $T_d$ at around 410 °C, in contrast to PUPFO which first stage of thermal decomposition started at 155 °C and $T_d$ at around 393 °C. It was observed that the mass loss of the first stage of decomposition of PULO (72%) was lower than that of PUPFO (Table 1), indicating that in addition to the thermal decomposition of the rigid segments in the first stage may have occurred, probably. The literature shows the mechanism of thermal decomposition which involves three routes for cleavage of PU linkages 200–400 °C. They are summarized as: dissociation into isocyanate and alcohol, dissociation into carbamic acid and olefin, dissociation of carbamic acid into $CO_2$ and secondary amine.[21–24] The more closely peak of the first stage of PUPFO decomposition in the DTG curve (Figure 1b) suggests that its urethane bonds decompose more rapidly than those from PULO.

Figure 2 shows the DMA curves of the PULO and PUPFO. In the Log É *versus* temperature curves (Figure 2a), it was observed that É decreased with increasing temperature for both PUs. For PULO, the decline occurred gradually to −32 °C and then the modulus decreased rapidly to near 25 °C, with loss of signal from 100 °C, showing consequent absence of the elastic *plateau* and response at higher temperatures. PUPFO featured a gradual decrease of Log É to −13 °C. After 0 °C,

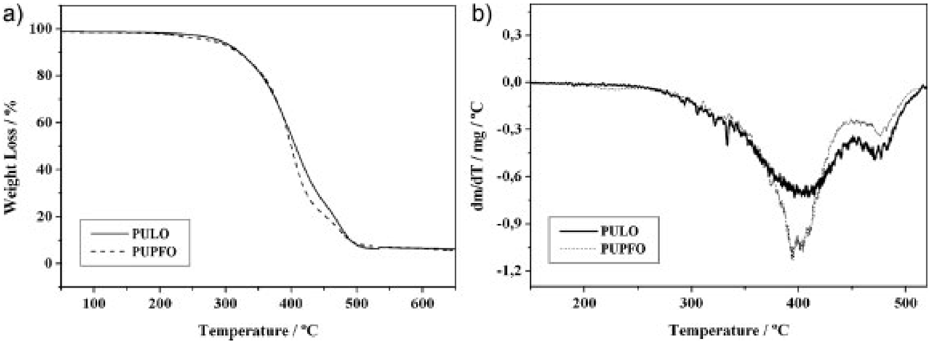

**Figure 1.**
(a) TG and (b) DTG curves of PUs. Heating rate: 10 °C min$^{-1}$.

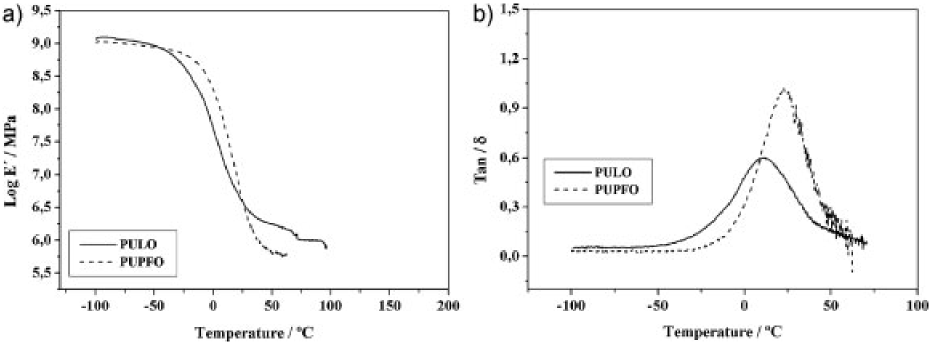

**Figure 2.**
(a) Variation of storage modulus (Log *E*′) *versus* temperature; (b) variation of tan δ *versus* temperature for PULO and PUPFO.

there was a very sharp fall of the module until approximately 60 °C with loss of signal near 70 °C. The signal loss observed by Log *E*′ *versus* temperature curves for the PUs, probably occurred as a result of the material fragility and uneven pores. Glass transition temperature ($T_g$) of the PUs were determined by tan δ *versus* temperature curves (Figure 2b). $T_g$ values determined for PULO and PUPFO were respectively, about 11 and 23 °C, suggesting that PUPFO is more crosslinked than PULO. Evaluating the degree of mechanical damping in Figure 2b, the values of 0.6 for PULO and 1.2 for PUPFO suggest that the latter is less ductile (flexible) than PULO.

The curing reaction of PUs was monitored by FT-IR. For this, the FT-IR spectrum performed at the initial time of the synthesis reaction was compared with the FT-IR spectrum obtained after 24 h, when the reaction was accomplished, in order to check the decrease of the bands related to absorptions of the isocyanate and hydroxyl groups. FT-IR spectra of curing reaction of PUs are showed in Figure 3.

The monitoring by FT-IR showed mainly the disappearance of the band at 3380 cm$^{-1}$ corresponding to the stretching of the OH group, and the appearance of bands at approximately 3300 and 1530 cm$^{-1}$, respectively, correlated to the stretching and deformation of the NH bonds, resulting from the reaction between OH groups of polyols with NCO of MDI.[25–28] After 24 h of reaction, the

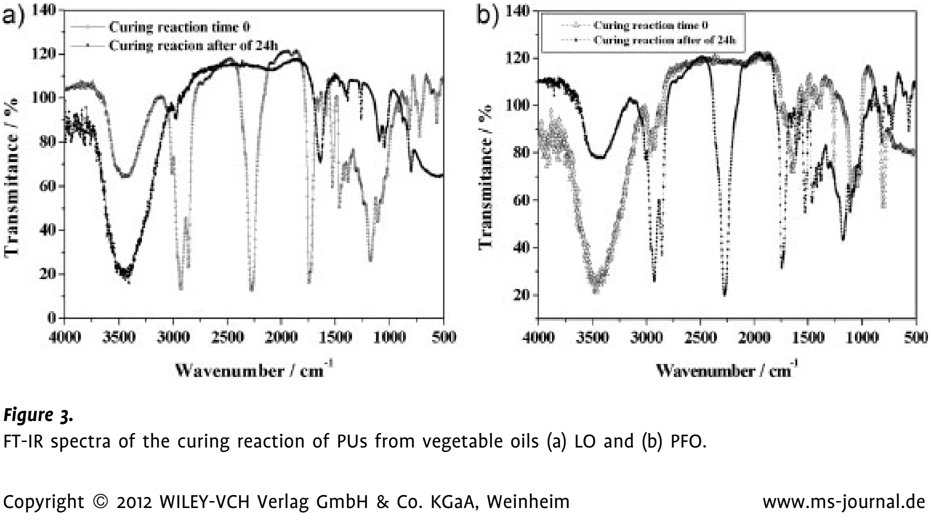

**Figure 3.**
FT-IR spectra of the curing reaction of PUs from vegetable oils (a) LO and (b) PFO.

spectrum showed a reduction of the band at 2700 $cm^{-1}$ characteristic NCO, indicating that the MDI was completely consumed. The broad band near 3340 $cm^{-1}$, characteristic of NH stretching, was identified in all spectra, implying the presence of hydrogen bonds in the PUs chains.[25,26] The band related to the urethane linkage (amide) at 1646 $cm^{-1}$ was also identified. The band characteristic of the CO-O bond occurred in 1242 $cm^{-1}$ and is characteristic of polyester.[27,28] FT-IR spectra for the 24 h time of reaction also showed the occurrence of stretch in the region of 1084 and 1064 $cm^{-1}$, characteristic of the group N-CO-O of urethane.[28,29]

## Conclusion

The analyses of the PUs by TG/DTG showed that PULO is more thermally stable than PUPFO. The first stage of thermal decomposition of PUPFO began at 80 °C before the corresponding step regarding to PULO. These results suggest that PULO has a higher amount of urethane linkages, compared to PUPFO. DMA analyses suggested loss of the elastic *plateau* for both materials tested, presumably because their pores are uneven and flawed. These facts deserve further experimental investigation. It was also verified by $T_g$ values that PUPFO is probably more crosslinked than the PULO. By degree of mechanical damping the PUPFO is less flexible than PULO. The monitoring by FT-IR showed that the curing reaction was accomplished in 24 h.

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