

## COMPARATIVE ANALYSIS BETWEEN SUGARCANE BAGASSE-REINFORCED COMPOSITES PRODUCED FROM COMMERCIAL EPOXIDIZED SOYBEAN OIL AND SOYBEAN OIL FROM FRYING

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## ABSTRACT

Commercial epoxy is produced from petroleum derivatives and is widely used as a matrix in the production of composites due to its simple processing. Epoxidized soybean oil makes it possible to produce a more sustainable matrix. With a view to sustainability, the present work aims to produce composite materials produced from commercial epoxidized soybean oil and epoxidized residual frying soybean oil. The characterization of the epoxidized oils was carried out by determining the oxirane oxygen content (OOe), infrared spectroscopy by Fourier transform and tensile test. As epoxidized soybean oils are less resistant to tensile than commercial epoxy derived from petroleum, it is necessary to add fibers to improve the mechanical characteristics of the material. Natural sugarcane bagasse fibers were chosen as reinforcement material. The materials were produced with the two types of epoxidized soybean oil, the mechanical evaluation was carried out by means of tensile tests with the addition of 0%, 5% and 7% fibers. The tensile strength limit was significantly improved for both materials, mainly with the addition of 5% reinforcement in commercial epoxidized soybean oil, reaching 133% higher than the resin without reinforcement. As for the oxirane oxygen content, the epoxy of residual oil presented a percentage of 4.55% m/m and the commercial 6.53% m/m, the residual oil presents a lower number of unsaturations, therefore lower content of OOe.

Keywords: Composites. Epoxidized Soybean Oil. Sugarcane Bagasse.

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## INTRODUCTION

Currently, the great challenge of materials engineering is the development of sustainable alternatives. This discussion is necessary because there is a concern about how to keep evolving technologically without affecting the availability of resources for future generations. In this sense, the development of efficient and sustainable products that do not cause an environmental impact from their production to their disposal is of increasing importance (Graduation in Materials Engineering, 2023).

Vegetable oils are presented as a renewable raw material with a great diversity of sources and are used in the food industry in a high volume in fried foods, and with this arose the concern about their final destination. Incorrect disposal can cause major environmental impacts, such as water and soil contamination, and when the oil degrades, methane gas is formed, which is highly polluting. In view of this, ways were developed to recycle this residual oil, which is more used in the production of biodiesel and in saponification, in addition to a small percentage that is destined for the manufacture of paints and putty. Epoxidation is another sustainable alternative to have the reuse of these oils, with potential for high added value (SILVA, 2013).

Another challenge is the search for the reuse of agricultural waste, in which Brazil currently leads the world ranking in sugarcane production. In the sugarcane industry, the main solid waste generated is sugarcane bagasse due to its guantity, since it is a fibrous by-product resulting from the sugarcane milling process. The amount produced of this byproduct varies according to the fiber content of the processed sugarcane. According to EMBRAPA (2022), sugarcane contains an average of 46% fiber and 50% moisture, which results in approximately 280 kilograms of bagasse per ton of processed sugarcane. The main use of bagasse is in energy cogeneration, and it is estimated that the plants in the sector use 60 to 90% as a source of energy through burning. Another option is the production of lignocellulosic ethanol, in addition to this option, there are other purposes for non-energy use, such as cattle feed, use in fertilizers, such as industrial agglomerates, in the pulp and paper industry. However, there is a surplus that is not used, which causes storage problems and environmental pollution. The main components of the bagasse cell wall are approximately 40% cellulose, 35% hemicellulose and 15% lignin, making it an excellent lignocellulosic material, which confers an improvement in the mechanical properties to which it will be used. (EMBRAPA, 2022).

In this way, the possibility of materials with optimized properties that can be applied in the most different ways and are called composites arises. Generally speaking, a composite is defined as any multiphase material that has a significant proportion of



properties of both constituent phases in order to have a better combination of properties. According to Callister (2020), the constituent phases must be of different chemical compositions and be separated by a distinct interface. This combination results in improved mechanical properties such as stiffness, toughness and strengths at elevated temperatures. Generally, composite materials are made up of two phases, one called matrix and the other dispersed phase and such phases will define the mechanical properties of this material, other factors that will influence these properties are the relative amount of each phase and the geometry of the dispersed phase. The geometry of the dispersed phase is understood as distribution, shape, size, and orientation. Composites are classified into structural composites, fiber-reinforced composites, particle-reinforced composites, and nanocomposites (CALLISTER, 2020).

In fiber-reinforced composites, the matrix phase performs numerous functions and must have a ductile characteristic. At first, it has the action of joining the fibers to each other and works as a means to transmit and distribute tensions to the fibers, being a small portion of tension supported by the matrix. Another function of the matrix is to protect the fibers against external damage, such as mechanical abrasion or chemical reactions with the environment that can cause cracks and consequently compromise the mechanical efficiency of the material. Polymer matrix composites consist of a polymer resin as the matrix phase filled with fibers as the reinforcing medium. This type of composite has a wide applicability due to its properties, ease of manufacture and costs. There are several options for polymeric resins that can be used as a matrix, one of these options is epoxies, widely used in structural applications. Its advantages are easy to handle, have good chemical resistance and have high resistance and modulus of elasticity. Another advantage is that they have low viscosity in the liquid state, which facilitates the preparation of composites, they are cured at high temperatures and have good resistance to corrosive environments. They also have better mechanical properties and moisture resistance than polyester and vinyl resins. These factors contribute to its employability in numerous applications, especially in fiber composites. The fibers most used in polymeric matrices are aramids, carbon, and glass fibers, but these fibers have some disadvantages such as high cost and complexity of production, low resistance to chemical attack, and limitation of service temperature (CALLISTER, 2020). The replacement of synthetic fibers with vegetable fibers becomes a great attraction to be used in various applications, as they come from renewable sources, biodegradable, have a low cost, are less abrasive, have low specific weight and great availability. Brazil has a large amount of agricultural waste,



so the use of natural fibers becomes quite interesting in the production of lignocellulosic composites (CAVALCANTI, 2022).

Thus, the possibility of developing lignocellulosic composite materials is an environmentally sustainable alternative applicable to the industry, making it possible to develop new materials with optimized physical-mechanical characteristics. In this context, the present work describes the study on the development, production and characterization by tensile test and infrared spectroscopy of composites made from epoxidized residual soybean oil resin reinforced with lignocellulosic residues from pre-treated sugarcane bagasse in order to compare it with a composite from commercial epoxidized soybean oil. According to data in the literature, lignocellulosic composites showed interesting values regarding the modulus of elasticity in tensile, bending, stiffness, and reduction of toughness under impact (CAVALCANTI, 2022). The results obtained from the researched materials showed that the developed process is economically viable and sustainable for the manufacture of new composites made from epoxidized vegetable oil reinforced with lignocellulosic residues vegetable oil reinforced with lignocellulosic residues and sustainable for the manufacture of new composites made from epoxidized vegetable oil reinforced with lignocellulosic residues exhibited superior or similar mechanical properties to several materials used in variable areas.

#### MATERIALS AND METHODS

#### MATERIALS

The materials used from the epoxidation process of the residual soybean oil to the production of the specimens were: residual soybean oil from frying purchased in an industrial kitchen in Belo Horizonte, commercial epoxidized soybean oil (Inbra Indústrias Químicas), sugarcane bagasse supplied by the Garapão establishment (Belo Horizonte), and the sugarcane bagasse would be discarded after the extraction of the sugarcane juice. The following reagents were also used: glacial acetic acid 99.7% w/w, potassium biphthalate, hydrobromic acid and gentian violet, all from the Synth brand, hydrogen peroxide 35% w/w from Química Moderna, chloroform 99.08% w/w from Neon and ethyl ether 98% w/w from the Qhemis brand, the ion exchange resin Amberlite IR-

120 H (Sigma Aldrich), the hardener ARADUR HY 2918-1 BR from Huntsman, with a chemical composition of methyl-tetrahydrophthalic anhydride (MTHPA, 166.176 g/mol) and the AL2024 curing accelerator (Polipox).

## METHODS

## **Epoxidation process**

For the production of epoxidized soybean oil, frying soybean oil was used. In addition to the reagents glacial acetic acid, hydrogen peroxide 35% w/w, Amberlite ion exchange resin IR-120 H and ethyl ether.

The preparation of soybean oil from epoxidized frying was based on the work of ESPINOSA PÉREZ (2009) and LAGE (2015), with some changes. Two hundred grams of used soybean oil, 29.2 mL of glacial acetic acid and 42.24 g of Amberlite IR-120 H ion exchange resin were added to a beaker on a heating plate (Fisaton), together with a mechanical stirrer (Fisaton). They were kept under agitation (500 rpm) and heating for approximately 1 h, until the temperature of 70°C was reached. Soon after, 224 mL of hydrogen peroxide 35% m/m was gradually added, at the end of the addition the reaction continued for another 5 h.

Subsequently, the reaction product underwent vacuum filtration to remove the ion exchange resin. Then, the final product was washed with distilled water at 50°C until the neutral pH was reached. After washing, the epoxidized soybean oil was extracted with ethyl ether (GOUD, 2006 apud LAGE, 2015), part of the solvent was extracted with the aid of a rotary evaporator (Fisaton), to remove the remaining ether the epoxidized oil was placed for 4 h in an oven at 50°C and for 48 h in a desiccant.

### Determination of oxirane oxygen mass content

The AOCS Cd 9-57 method (AOCS, 2009) was used to determine the mass oxirane oxygen content of epoxidized frying soybean oil and commercial epoxidized soybean oil. Approximately 0.4 g of epoxidized oils dissolved in chloroform were weighed. The samples were titrated with 0.1 mol/L hydrobromic acid, previously standardized, with an indicator solution of 0.1% methyl violet in acetic acid. The titration turning indicator is violet to bluish-green.

### Healing cross-linking

Curing cross-linking was performed for commercial epoxidized soybean oil and for previously produced epoxidized frying soybean oil. The curing process was carried out using methyl tetrahydrophthalic anhydride as a hardener, as well as Lage (2021), as it is a potential hardener for biocomposites. To determine the PHR value (hardener parts per 100 parts resin), equation 1, described by Mallick in 1997, was used.

AEW is the equivalent weight of methyl tetrahydrophthalic anhydride (166.17g/eq) and EEW is the equivalent weight in epoxy, calculated by equation 2, where OOe is the experimental value of oxyrane oxygen.

*PHR*=100 × <u>*AEW*</u>

EEW

$$EEW = \frac{1600}{OO_e} \tag{2}$$

Tabela 1- V	<u>'alores obtidos de EEW e P</u>	HR
Tipo de óleo	EEW (g/eq)	PHR (g/100g)
Óleo de soja comercial epoxidado	245,02	67,82
Óleo de soja de frituras epoxidado	351,65	47,25

Fonte: elaborado pelos autores, 2023.

#### **Chemical treatment of bagasse**

Sugarcane bagasse was cleaned in running water to remove impurities. Based on the work SANCHEZ (2010), the sampling was dried in an oven for 8 hours at a temperature of 100°C, defragmentation was performed with a blender and returned to the oven for another 2h30 at a temperature of 100°C. After drying the sampling, another defragmentation was performed again using a blender. Sampling was submitted to particle size classification using a vibrating sieve, 50g of the 40 mesh retained grain size was separated.

The extractives were removed based on the work of LAGE (2021) using ethanol as a solvent, adapting a round-bottomed flask with 3 outlets and a ball condenser. A volume of 500 mL of ethanol and 25g of bagasse was added to each glass flask, and the heating blanket was programmed so that the temperature did not exceed 70°C for a time of 3 hours. After extraction, vacuum filtration and washing with distilled water of the sampling was carried out until the neutral pH was reached, then the sampling was directed to the oven for drying at a temperature of 100°C for a time of 6 hours.

After drying, the alkaline pretreatment was carried out based on the work of SANCHEZ (2010), the sampling was immersed in a 10% mass/mass sodium hydroxide



solution for 24h (1 fiber/5 m/m solution). After this immersion, the fibers were washed with distilled water and filtered at a vacuum until the residual water reached neutral pH. Subsequently, the sampling was dried in an oven at 100°C for 6 hours.

## Preparation of specimens for tensile testing

For the production of the specimens, pre-treated sugarcane bagasse was used as reinforcement material together with epoxidized oils. Based on Lage (2021) with some modifications, the reinforcement material with a 200 mesh through-grain size was used, in order to achieve greater homogeneity of the material. Specimens were made for epoxidized frying soybean oil and commercial soybean oil, both with 0, 5 and 7% reinforcement. The Aradur HY 2918 hardener was used, the epoxidized oils, according to the proportions described in table 1, which together with the reinforcement were kept under vigorous mechanical agitation (500 rpm) for 30 minutes, then 5g of AL2024 accelerator was added for each 100g of epoxidized soybean oil. To perform the heat treatment, the materials were arranged in tensile test molds made of silicone for high temperatures, then kept in an oven at 100°C for about 2 hours and the next day 5 hours at 150°C. They are removed from the oven after cooling, to prevent cracks in the composite.

# **RESULTS AND DISCUSSION**

# MEASUREMENT OF OXIRANE OXYGEN MASS CONTENT

Table 2 describes the results obtained in the hydrobromic acid titrations to determine the oxirane oxygen mass content of the epoxidized oils.

Tabela 2- Resultados para determinação do teor mássico de oxigênio oxirano							
Tipo de óleo	00e (%)	EEW (g/eq)	PHR (g/100g)				
Óleo de soja comercial epoxidado	6,53	245,02	67,82				
Óleo de soja de frituras epoxidado	4,55	351,65	47,25				

Fonte: elaborado pelos autores. 2023.

The commercial epoxidized soybean oil had an oxirane oxygen mass content of 6.53%, approaching that described by Lage (2015), where the acetic acid epoxidized soybean oil (figure 1) had an oxirane oxygen content of 7.0%. On the other hand, soybean oil from frying presented a content of 4.55%, which was expected, since soybean oil at high temperatures undergoes oxidative and chemical changes, reducing the number of unsaturations (RIOS, 2013), which are responsible for the formation of the oxirane ring (figure 2).



# FOURIER TRANSFORM INFRARED SPECTROSCOPY

The characterization of the samples by infrared spectroscopy was performed using the PerkinElmer Spectrum Two spectrometer, with a resolution of 0.5 <sup>cm-1</sup> in the spectral range of 350-8300 <sup>cm-1</sup>. The residual soybean oil was characterized before and after the epoxidation and curing processes, as well as the commercial epoxidized soybean oil before and after curing.





One of the main characteristics to evidence the epoxidation of soybean oil is the disappearance of the band close to 3010 <sup>cm-1</sup> (=C-H) and the formation of the epoxy group (C-0-C), with bands in the range of 823 cm-1 (Leite, 2017). In figure 3, we have the spectra of the residual oil before and after epoxidation, where point A indicates the unsaturation of the oil and B the formation of the epoxy group, confirming the presence of oxirane oxygen (4.55%), previously calculated by means of titration with hydrobromic acid.



In figure 4, we can see the similarity between epoxidized soybean oil produced from frying oil and commercial epoxidized soybean oil. Points A and B show the epoxy group at 823cm-1 in both epoxidized oils.



Figure 5- FTIR spectra for epoxidized soybean oil from frying before and after the curing process

Source: prepared by the authors, 2023.



Figure 6- FTIR spectra for commercial epoxidized soybean oil before and after the curing process.

The curing cross-linking was performed using anhydride as a curing agent, anhydrides require higher temperatures than amines, and form thermosetting resins with good chemical, mechanical and electrical properties (THEREE BOND, 1990 apud LAGE, 2015). In figures 5 and 6, we can observe that after curing crosslinking, it is no longer possible to observe the peak at 823 <sup>cm-1</sup> (A), which indicates the efficiency of the cure, since the epoxy group is no longer present, as expected.

## TRILEE TEST

The tensile tests were carried out with specimens suitable for the tests. The two epoxidized oils were used with the reinforcement percentages of 0, 5 and 7%. With the data obtained in the tests, the modulus of elasticity (MPa) was calculated by means of the inclination of the elastic line; the tensile strength limit (MPa) and the percentage of elongation.

Table 3 shows the data from the tensile test for commercial epoxidized soybean oil with different percentages of natural reinforcement of treated sugarcane bagasse.

remorcement.						
Material	% Reinforce ment	Modulus of Elasticity e (MPa)	Tensile Strength Limit (MPa)	% Elongation (Ductility)		
Petroleum	0	187,27	3,15	3,23		
soy Commercial Epoxide	5 7	269,77 49,127	7,34 4,71	10,03 13,36		

 Table 3 - Results of the tensile tests for commercial epoxidized soybean oil varying the percentage of reinforcement.

Source: prepared by the authors, 2023.







From the analysis of the data in table 3 and figure 7, it is possible to observe that the addition of sugarcane bagasse as a reinforcement material caused the material to increase its ductility, that is, its rupture is delayed.

The tensile strength limit increases significantly with the addition of 5% reinforcement, it was expected that this behavior would be linear, since the reinforcement acting on the matrix results in the transfer of the applied stress from the matrix to the fibers. But with 7% reinforcement, the tensile strength limit decreases, according to Barbosa (2014) due to the microvoids that appear in the composite during the interaction of the epoxidized oil with the hardener, the higher the percentage of reinforcement, the greater the tendency to create microvoids and weaken the material.

The modulus of elasticity is related to the ability of the material not to break as it is subjected to deformations, so it was also predicted that it would increase with the increase in the addition of reinforcement. It is possible to observe that with 5% reinforcement there was a significant increase of approximately 44% in the modulus of elasticity in relation to the material without reinforcement, while with 7% reinforcement there was a reduction of around 26%, which is also explained by the formation of microvoids, which increase the concentration of tension.

As for the tests for the materials produced with epoxidized residual soybean oil, the tests resulted in materials with high ductility. The percentages of elongation (ductility) were 76.35; 50.18 and 69.63% for the 0, 5 and 7% booster additions, respectively. As the resin produced had high ductility, it is understandable that the addition of fibers will reduce this ductility, leaving the material a little more fragile. With the addition of 7% reinforcement, the material comes closer to the characteristics of the unreinforced material, this is due to the nature of the epoxidized oil produced, which has high flexibility. The tensile strength limit maintained the standard of the test with commercial epoxide oil, with the highest value

for the addition of 5% reinforcement. Because it is a very ductile material, the force exerted during the tests was not high and remained constant for a long time, resulting in low and approximate tensile strength limits, 3.36; 3.67 and 3.54 (Mpa) for the 0, 5 and 7% reinforcement additions, respectively.

## CONCLUSIONS

Treated sugarcane bagasse was presented as a potential reinforcing fiber of composites produced with resins of vegetable origin, as it has a significant improvement in the tensile strength of the materials, which is the main deficiency of vegetable epoxidized oils, in relation to commercial epoxy from petroleum derivatives.

The production of epoxy from residual frying oil proved to be feasible by the analyses made by Fourier transform infrared spectroscopy (FTIR), since the same characteristics present for commercial epoxidized soybean oil are observed. Such as the presence of the epoxy group and its total removal with the curing process. Soybean oil is residual from frying and is a potential raw material for the production of composite materials.

Analyzing the elongation percentages of each material, obtained by the tensile test, it is observed that these values are approximately 6 times higher for the residual oil resin in relation to the maximum percentage obtained for the epoxidized commercial oil resin. However, the tensile strength limit is more efficient for the resin of the epoxidized commercial oil.

For future work, it would be possible to make a mixture of different percentages of the epoxidized oils and reinforcement material, in order to obtain a material that has both good tensile strength and good ductility.



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