The Thermodynamic Method of Vitrification of Copaíba Oil-Resin (*Copaifera Langsdorffii*)

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Abstract: *The development of the method of vitrification of copaiba oil resin (COR) consisted of three protocols named by Hp-1, Hp-2 and Hp-3. The vitrified heteropolymers were analyzed using photographs, optical microscopy, scanning electron microscopy, thermogravimetric analysis and differential thermal analysis. The results showed that there was the formation of vitrification and, therefore, the vitrification of the COR. The image results showed that the surfaces have rough and orderly microregions. Thermal analyzes showed that among the heteropolymers made with the Hp-1 and Hp-2 protocols are similar by TGA and DTA. Suggesting greater thermal stability than Hp-3.*

Keywords: Copaiba, Oil-Resin, Heterotermopolymer, Thermodynamic Protocol

1. Introduction

This method consists of disintegration, volatilization, vaporization and rearranging coherent or random copaiba oil-resin molecules for the formation of heterotermpolymer induced by heating-cooling. The method is based on the application of localized heat in a volume of COR to cause the hemolysis of the double bond of several types of monomers, volatization of other molecules and consequently the heteropolymerization of the material leading to the vitrification. The methods generally applied in the polymer industry such as bulk polymerization, solution, emulsion and suspension have advantages and disadvantages in the production of polymers with few monomer types [1], [2]. It usually works for the production of petroleum-based polymer and it is possible to obtain a large quantity of specific monomers [3]. However, to obtain heteropolymers using COR, the use of chemical contaminants for the development of biocompatible drugs may not be recommended. In this case, a thermodynamic process will be cleaner and more suitable. At molecular copolymerization of COR. COR is used *in natura* without any chemical treatment. The COR is extracted from the trunk of the *Copaifera Langsdorffii* tree (composed of several species and native to the Amazon and Central Africa) whose oil consists of two classes of organic molecules, namely diterpenes (resin) and sesquiterpenes (essential oil) [4]-[6]. The diterpenes ($C_{(16-22)}H_{(15-28)}O_{(1-9)}$) COR are constituted by cauran, clerodane and labdanum skeletons in a total of 27 different molecules [5]. Molecular weights range from 239.37g/mol to 498.34g/mol [6]. All the molecules present polar surface area with donor points and binding acceptors in their structures [6]. The group of molecules sesquiterpenes (essential oil) ($C_{15}H_{24}$), which are composed of hydrocarbons in a total of 72 molecules in which the amount of carbon and hydrogen does not change only for the molecules of the bergamonten, cadinol, cedrol, cyperene, phenohenol, humulene, guaiol, multifugenol, muurol, muurolene, caryophyllene oxide, veridiflorol containing the basic skeleton preserved, but with oxygen atoms in their structures having polar surface area with donor points and hydrogen bonding acceptors. The molecular weight of the sesquiterpenes ranges from 198.31g/mol to 222.37g/mol. In this way they can facilitate heterotermopolymerization of the various molecules of the COR [4]-[6].

The polymers obtained from oils are biopolymers in the sense that they are generated from renewable natural sources; they are often biodegradable as well as non-toxic. Some biopolymers obtained from vegetable oils are flexible and elastic. Generally, they are prepared as cross-linked copolymers [7]-[9]. However, vegetable oil biopolymers can be heteropolymer when the oil has a large number of different molecules such as molecular weight, *n* possibilities for molecular interactions with each other presenting complex thermodynamic principles. The possible vitrification occurs when the system is subjected to temperature variation T_i at a temperature T_f, where $T_f \gg T_i$ in the heating regime to volatilize the essential oil molecules present in the resin oil composition [10]-[13] and then the cooling natural in an aqueous medium of $\pm 10°C$ where $T_i \gg T_f$.

This work consists in developing and applying three methodological protocols using heating and cooling to obtain the vitrification of the copaiba resin oil. With the results to evaluate which route will present better technical conditions and quality of the manufactured heterotermopolymer.

2. Materials and Methods

2.1 Materials

In this work protocols were developed for application in three systems of resin oil heating: in the first protocol the heating was done using a magnetic stirrer of the FARSTOM model 752A with heating capacity up to 350ºC, with maximum magnetic rotation of 1000 rpm. The second using a 2895 JUNG muffle furnace with internal volume of 2L for maximum temperature of 1700°C with temperature programming and heating time at constant pressure. The third one was the heating using system with refractory plate with Bunsen nozzle. The average flame temperature can reach 1540°C (mixture of butane and propane). Optical

measurements made with Coleman bifocal microscope model 120N, halogen lamp of 6V/20W and with CCD camera. Measurements with Scanning Electron Microscope (SEM), Jeol, JSM-6610, equipped with EDS, Thermo scientific NSS Spectral Imaging laboratory LABIMIC-UFG-BR.

The resin oil was extracted in environmental reserve area (latitude -10.74852879 and longitude -61.54753355) in the region of Ji-Paraná state of Rondônia-Brazil. The resin oil was extracted from the *Copaifera Langsdorffii* tree by means of 2 cm diameter holes and connected to a sterilized glass tube and connected to the closed 20 liter vessel. The drum was deposited in the Nanomaterials and Nanobiomagnetism-LNBIOMAG laboratory of the Federal University of Rondônia-Brazil.

2.2 Method Description

2.2.1 Protocol-1 (Hp-1): Heating the COR with Magnetic Stirrer Application

A quantity of 100 mL of COR placed in the 150 mL capacity cast aluminum sample holder. Then the sample holder was placed on the magnetic stirrer, which was set at a temperature of 340°C. The frequency rotation of the magnetic bar was adjusted to 400 rpm. The temperature of the system was measured by an analogue mercury thermometer with a minimum scale of 0.5°C inserted half-way into the tripod-mounted sample. A second digital thermometer with 0.001s accuracy thermocouple was inserted at half height separated by 1cm. All procedures were carried out inside an exhaust hood. The heating of the COR was carried out from 0 to 30 minutes to avoid carbonization of the material in formation. Vitrification of the heterotermpolymer was achieved by cooling in water at $\pm$ 10°C to equilibrium temperature. The procedure was repeated six times. After each cooling the mass of the sample was measured. In this process, the mass and volume of the COR reduces to less than half of the initial values by vaporizing and exhausting the more volatile molecular components. The process diagram is shown in figure 1.
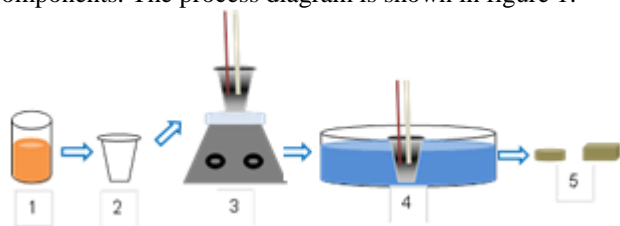

Figure 1: Warming scheme of COR applying magnetic stirring plate. Cooling process of COR in water at 10°C. (1-COR, 2-Sample holder, 3-Cooking, 4-Cooling at 10°C, 5-Sample Ready).

The heterotermpolymer obtained by this protocol was thermally controlled by the thermostat. It was set to maintain the heating temperature in the sample without destroying its molecular structures without carbonization. Were performed around six heating stages Δt_H(0 a 30min) and cooling Δt_C(30 a 120min) of the sample as shown in the experimental data curve of figure 2. The temperature range measured directly on the sample was from ambient temperature $\pm$27°C to $\pm$

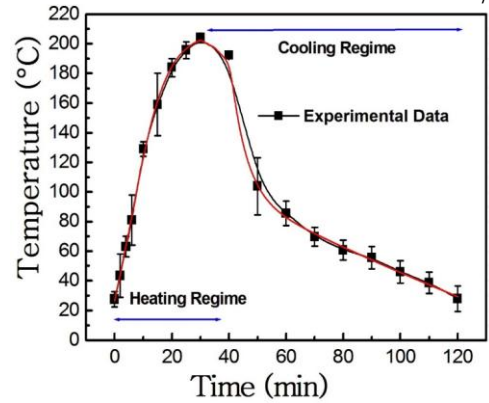204°C achieved with continuous external heat flow $\phi\,(x,y,z,t)$

Figure 2: Heating curves Δt_H(0 to 30 min) and cooling Δt_C(30 to 120 min) in the vitrification process of the copaiba resin oil heteropolymer (COR). The red curve represents the adjustment of the experimental data using the combination of two functions a Boltzmann distribution (heating region) and another sum of three exponential functions of decay (cooling region).

Around de $\pm$350°C. In this sample heating temperature range, the heat gradient showed an increasing behavior whose adjustment of the experimental data was obtained using software origin 8.1 and then applying the Boltzmann function (heating interval) in the regression analysis of the data as shown in equation 1:

$$T(t) = \frac{\Delta A}{1 + e^{\Delta t / \tau}} + A_2 \tag{1}$$

where A_1, A_2, t_0 and τ are constants, $\Delta A = (A_1 - A_2)$ determined in the adjustment of the experimental data. The region of the sample cooling curve was adjusted using the third-order exponential model in the form equation 2.

$$T(t) = T_0 + A_3 e^{-t/T1} + A_4 e^{-t/T2} + A_5 e^{-t/T3} \tag{2}$$

here T_0, A_3, A_4, A_5 and T_1, T_2, T_3 are constants of the cooling curve fitting. Table 1 shows the constants obtained using equation 1 and Table 2 shows the constants obtained by applying equation 2.

Table 1: Ratio of curve fitting parameters in the heating region shown in figure 2.

Boltzmann distribution (heating)			
A_1(°C)	A_2 (°C)	t_0 (°C/s)	τ(s/°C)
(5.78±2.05)	(205.83±2.54)	(5.88±1.06)	(5.96±0.55)
χ^2=9.39098 R^2=0.99872			

Table 2: Ratio of the curve fitting parameters in the cooling region shown in figure 2.

Exponential decay (cooling)		
A_1(°C)	(388.24±2.47)	
A_2(°C)	(1513±24.04)	χ^2=7.19211 R^2=0.99938
A_3(°C)	(50.54±2.80)	
T_0(°C)	(-36.20±2.86)	
T_1(s/°C)	(1.651±0.58)	
T_2(s/°C)	(5.419±0.98)	
T_3(s/°C)	(4.867±3.41)	

2.2.2 Protocol-2 (Hp-2): Heating of the COR with the Bunsen Nozzle Application

The use of the Bunsen nozzle for the heating and heteropolymerization of the COR was done using a closed aluminum sample port with a maximum volume of 150 mL. The container is placed on a tripod with a refractory exhaust hood. The container is placed on a tripod inside of a refractory exhaust hood. Baking was carried out for up to 30 minutes at maximum temperature around (250 ± 9)ºC. Each time the material is subjected to the cooling of ± 10°C to the equilibrium temperature (ambient temperature 27°C) it presents opaque, refractive and increasing hardening physical characteristics. The process can be repeated several times until the hardening thereof has vitreous properties (was performed around 6 heating and cooling repetitions). On the other hand, the significant loss of mass and volume of COR was observed until COR vitrification. The scheme of the process is shown in figure 3.
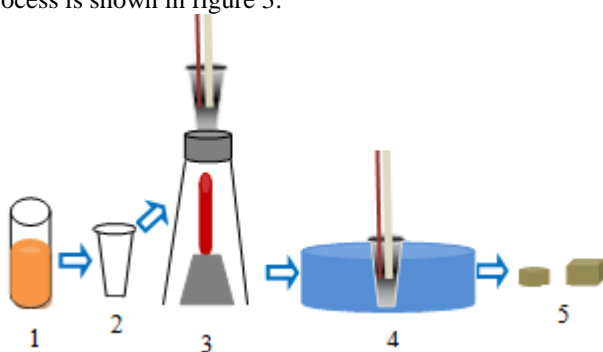

Figure 3: COR heating scheme using Bunsen nozzle refractory plate system. Cooling process of COR in water at 10 °C. (1-Copaiba Oil Resin, 2- Sample Holder, 3-Cooking, 4-Cooling at 10°C, 5-Sample Ready).

In this protocol the vitrified heterotermopolymer had the temperature measured by an analogue thermometer with precision of 0.1 °C inserted at half height of the sample volume. Another digital thermometer with accuracy of 0.01°C was inserted next to the analog thermometer in the heating process and in the cooling process. Heating were carried out in the range of Δt_F(0 a 40 min) and cooling Δt_C(40 a 120 min) of the sample as shown in figure 4. The temperature range measured directly in the sample was from the ambient temperature ± 27°C to ± 268°C achieved with continuous external heat flow ϕ (x,y,z,t) (x, y, z, t) around 1350°C. In this temperature range the heat gradient in the sample presented an increasing behavior whose adjustment of the experimental data was obtained using the Boltzmann function (see Equation 1). In the region of the sample cooling curve was adjusted applying the exponential model of third order in the form of equation 2. The results of the adjustments in the two regions are presented in Table 3 and Table 4.

Table 3: Ratio of curve fitting parameters in the heating region shown in figure 4.

Boltzmann distribution (heating)			
$A_1(°C)$	A_2 $(ºC)$	t_0 $(°C/s)$	$\tau(s/°C)$
(81.74±3.37)	(268.17±3.76)	(4.47±1.10)	(5.49±0.55)
$\chi^2=13.42223$ $R^2=0.9991$			

Table 4: Ratio of the curve fitting parameters in the cooling region shown in figure 4.

Exponential decay (cooling)		
$A_1(°C)$	(218.66±6.38)	
$A_2(°C)$	(89.36±13.68)	
$A_3(°C)$	(88.19±12.73)	$\chi^2=10.0163$
$T_0(°C)$	(28.04±6.37)	$R^2=0.99711$
$T_1(s/°C)$	(7.96±1.57)	
$T_2(s/°C)$	(8.54±1.76)	
$T_3(s/°C)$	(8.54±1.42)	

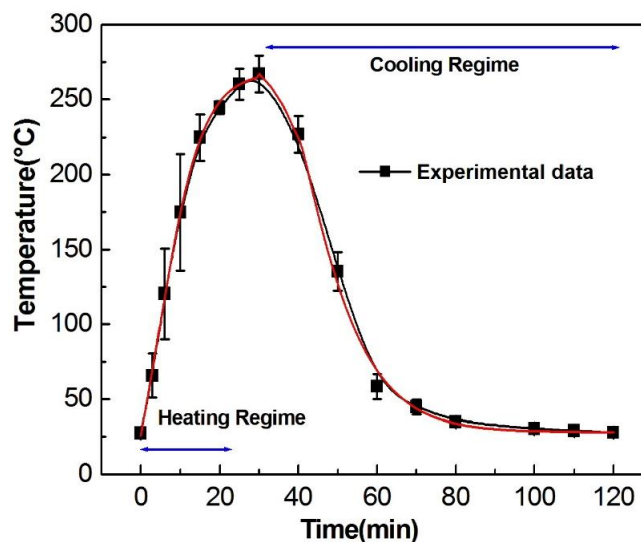**Figure 4**: Heating curves Δt_H(0 to 40 min) and cooling Δt_C(40 to 120 min) in the vitrification process of the copaiba resin oil heteropolymer (COR). The red curve represents the adjustment of the experimental data using the combination of two functions a Boltzmann distribution (heating region) and another sum of three exponential functions of decay (cooling region).

2.2.3 Protocol-3 (Hp-3): Heating of the COR with the Application of the muffle furnace

To carry out the heating of the COR in the muffle furnace was constructed a sample holder of molten aluminum with a maximum capacity of 150 ml with wall thickness of the 5 mm container. For the heating of the ORC a volume of 100 mL introduced in the sample holder was measured and then taken to the oven. The oven was programmed for heating the ORC at fixed temperature, fixed time and heating rate of 5°C/min. After reaching the programmed temperature (range 150 to 220°C) the cooking remains for the programmed time and at the end of the period the oven is switched off and the sample port is subjected to cooling in water at ± 10°C temperature.

This procedure may be repeated n times until a desired texture of the material, whether malleable or hard, is obtained. In this work the procedure was repeated twenty times. Experiment with cooling in liquid nitrogen flow was carried out and favors the instantaneous freezing of the networks of ORC molecules giving the characteristic material brittle and hard. Significant loss of mass and volume of the material after the vitrification process was observed. The process diagram is shown in figure 5.
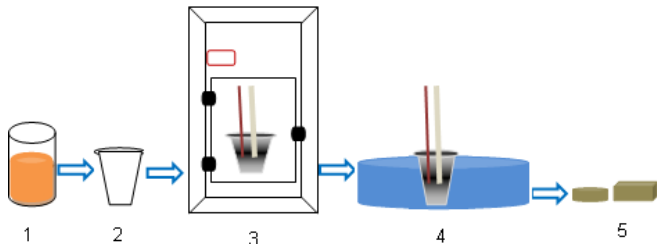
Figure 5: Heating scheme of the COR in a muffle furnace. Process of cooling the COR in water at 10ºC. (1- Copaiba Oil-Resin, 2- Sample Port, 3-Cooking, 4-Cooling at 10°C, 5-Sample Ready).
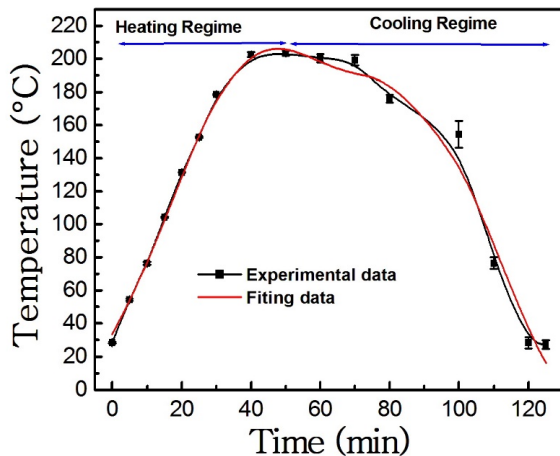

Figure 6: Heating curves Δt_H (0 to 60 min) and cooling Δt_C (60 to 120 min) of the vitrification process of the copaiba oil-resin (COR) heterotermopolymer. The red curve represents the adjustment of the experimental data obtained using the two Gauss distribution functions.

Table 5: Ratio of adjustment parameters of the heating versus cooling curve shown in figure 6.

Gauss distribution (heating) and (cooling)		
A_1(°C)	(141.96±31.81)	
A_2(°C)	(79.04±21.98)	
T_0(°C)	(22.16±2.57)	
t_1(s^2)	(42.44±3.56)	$\chi^2=85.943$
t_2(s^2)	(91.43±3.95)	$R^2=0.98877$
W_1(s/°C)^2	(50.94±6.70)	
W_2(s/°C)^2	(39.25±6.09)	

$$T(t) = T_0 + \frac{A}{W\sqrt{\pi/2}}e^{-2\frac{(t-t_i)^2}{W^2}} \qquad (3)$$

The data measured in the heating and cooling process of the temperature and time were adjusted using the coupling of two Gaussian functions equation 3 as shown in figure 6. The results of the adjustments in the two regions are shown in Table 6.

3. Results and Discussion

The results showed that the heterotermopolymeric vitrification obtained by the three thermodynamic heating-cooling protocols, that it was possible to obtain a complex polymeric material constituted by molecules arranged in a random and distinct manner [12-18]. The measurements of the samples obtained by the three protocols are presented in the results below in this section.

3.1 Heterotermopolymer obtained by protocol-1

Samples generated by this protocol are identified by Hp-1. Figure 7 shows the photo of a heterotermopolymer piece glazed applying the protocol-1 in copaiba oil-resin.
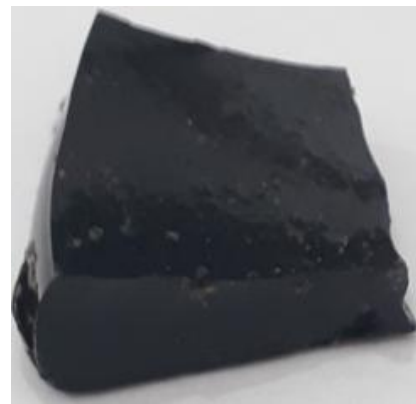

Figure7: Sample photo Hp-1 heterotermopolymer synthesized from the copaiba oil-resin (COR) using the first protocol.

It is observed in the micrographs shown in figure 8a obtained by optical microscope (400x) and using a red filter where it is possible to identify approximately "crests" and "valleys" on the rough surface of the heterotermopolymer. The dark regions are due to empty spaces in the sample.
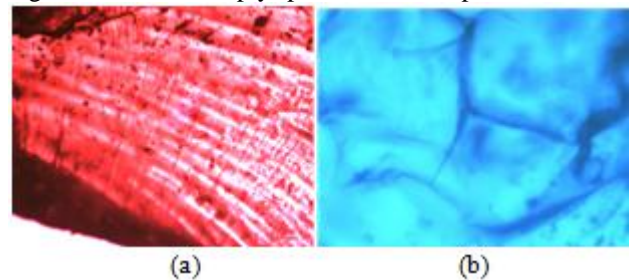

Figure 8: Optical micrograph 400X ((a) red filter and (b) blue filter) COR vitrified using optical microscope Coleman model 120N.

The scanning electron micrographs of figure 9 show details of the heterotermopolymer surface with resolution of 5 μm and 50 μm. The thermodynamic heating and cooling process influences considerably the molecular arrangement of the heterotermopolymer such that the surface is not fully regular. The random rearrangement due to entropy variation influences surface roughness growth [12;13].
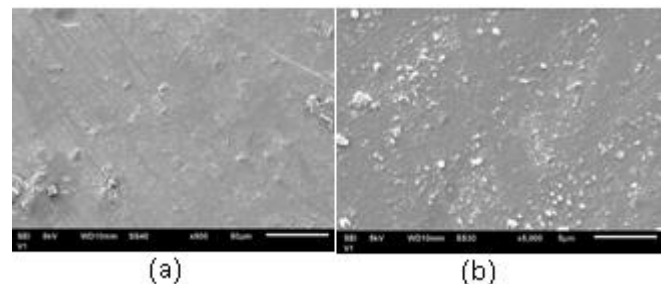

Figure 9: Scanning electron micrograph, (a) x500 (50μm) and (b) x5000 (5μm) vitrified COR using Jeol JSM – 6610, 5 kV, scanning microscope.

3.2 Heterotermopolymer obtained by protocol-2

Samples generated by this protocol are identified by Hp-2. Figure 10 shows the photo of a vitrified heterotermopolymer piece applying the protocol-2 in copaiba oil-resin.

Figure 10: Sample Hp-2 fragment photo of the vitrified heterotermopolymer of copaiba oil-resin (COR) using the vitrification protocol 2.

It is observed that the material has a reflective surface. The micrograph of figure 11 was obtained by optical microscope (400x) using red filter sample fragment. The surface of some regular grooved channels to "crests" and "valleys". The dark regions are due voids in the sample developed in the process of heating and cooling the material with molecular rearrangement in random heterotermopolymeric networks.
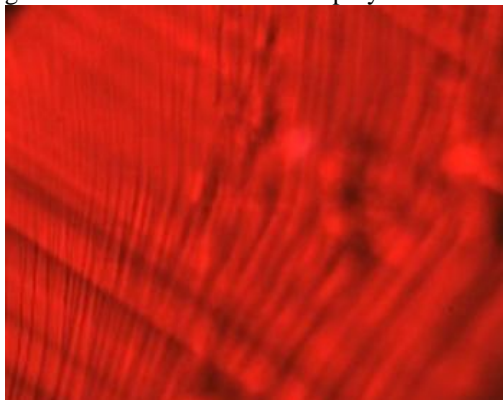

Figure 11: Optical microscopy 400x (red filter) of vitrified COR using Coleman optical microscope model 120N.
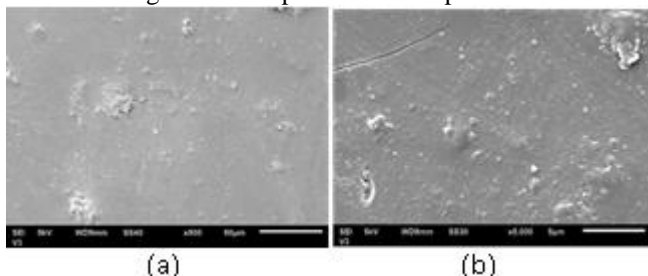

Figure 12: Scanning electron micrograph, sample Hp-2 (a) x500 (50μm) and (b) x5000 (5μm) vitrified COR using Jeol JSM – 6610, 5 kV, scanning microscope.

The scanning electron micrographs of figure 12 show details of the heteropolymer surface with a resolution of 5 μm and 50 μm. The thermodynamic heating and cooling process influences considerably the molecular arrangement of the heterotermopolymer such that the surface is not fully regular. The random rearrangement due to entropy variation influences surface roughness growth [12;14].

3.3 Heterotermopolymer obtained by protocol-3

Samples generated by this protocol are identified by Hp-3. Figure 13 shows the photo of a vitrified heteropolymer piece applying the protocol-3 in copaiba oil-resin.

Figure 13: Sample Hp-3 fragment photo of the vitrified heteropolymer of copaiba oil-resin (COR) using the vitrification protocol 3.

Observed in the micrographs shown in figure 14a obtained by light microscopy (400x) using red filter and where it is possible to identify the surface "irregular" of the heteropolymer of clear dark regions. The dark regions are due to empty spaces in the sample. In figure 14b obtained from the same fragment of figure 13, with green filter (400x) regions in darker blue are observed.
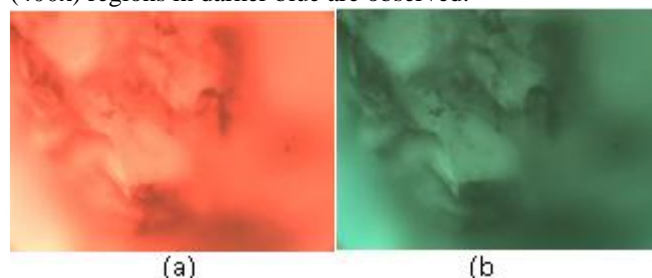

Figure 14: Optical microscopy 400x ((a) red filter and (b) green filter) of COR glazed using Coleman optical microscope model 120N.

Refers to empty spaces developed in the heating and cooling process of the material with molecular rearrangement in random heterotermopolymer networks [12].
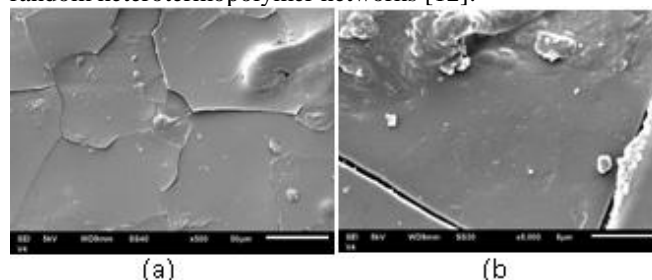

Figure 15: Scanning electron micrograph, sample Hp-3 (a) x500 (50μm) and (b) x5000 (5μm) vitrified COR using Jeol JSM – 6610, 5 kV, scanning microscope.

The scanning electron micrographs of figure 15 show details of the surface of the heterotermopolymer with a resolution of

5 μm and 50 μm. The thermodynamic heating and cooling process influences considerably the molecular arrangement of the heterotermopolymer such that the surface is not fully regular. The random rearrangement due to entropy variation influences surface roughness growth [12;13].

3.4 Thermogravimetric Analysis-TG and Differential Thermal Analysis-DTA

Thermogravimetric analysis and differential thermal analysis were performed using samples of copaiba oil-resin, the heterotermopolymer synthesized by protocol-1 (Hp-1), protocol-2 (Hp-2) and protocol-3 (Hp-3). Figure 16 shows the TGA curves of COR, Hp-1, Hp-2 and Hp-3.
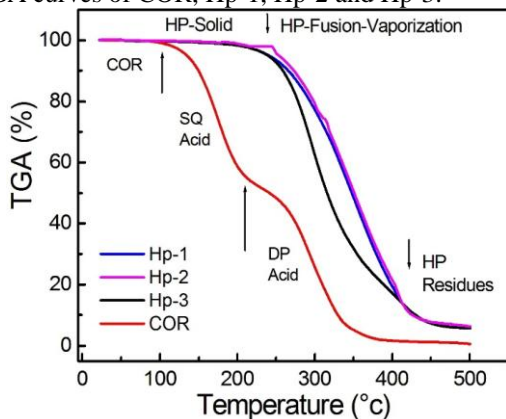

Figure16: TGA curves (%) as a function of temperature (°C) from 27 ° C to 500 ° C. Red curve represents the behavior of the Copaíba (COR) resin oil mass where it presents the region of fusion and volatilization of sesquiterpene acids SQ Acid, the melting and volatilization region of diterpene acids DP Acid and waste region. The blue curve represents the heteropolymer obtained by applying the protocol-1 (Hp-1) containing the heterotermopolymer region (HP-Solid), the melting-vaporization region (HP-Fusion-Vaporization) for all other TGA curves of the heterotermopolymers. The magenta curve represents the heterotermopolymer obtained by applying protocol-2 (Hp-2) and the black curve represents the heterotermopolymer obtained by applying protocol-3 (Hp-3). The COR curve shows the copaiba oil-resin without changing its molecular properties up to approximately 97°C with 100% of its mass. In the region between 97°C and 212°C the mass of the COR reduces to approximately 54% the hypothesis is that there was loss by volatization of essential oils represented by sesquiterpene (SQ) acid molecules. In the temperature range of 212°C-350°C the mass of the COR reduces to 0.26% the region represented by the resinous part of the COR by molecules of diterpenoic acids (DP).

The Hp-1 curve shows that the heterotermopolymer (HP) is in the solid state up to 270ºC. From 270°C the material goes into melting and vaporization process up to 417°C with loss of 92.5% of mass and retaining 7.5% of waste.

The Hp-2 curve shows that the heterotermopolymer (HP) is in the solid state up to 274°C. From 274°C the material enters the process of melting and vaporization up to 424°C with loss of 92.25% of mass and conserving 7.75% of residues.

The Hp-3 curve shows that the heterotermopolymer (HP) is in the solid state up to 253°C. From 253°C the material goes into melting and vaporization process up to 445°C with loss of 94% of mass and conserving 6% of residues.
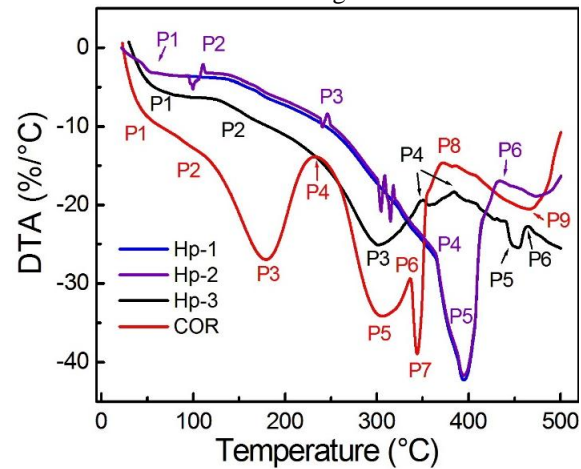

Figure 17: DTA curves (%/°C) as a function of temperature (°C) from 27°C to 500°C. The red curve represents the behavior of the mass of Copaíba oil-resin (COR). The blue curve represents the heteropolymer obtained by applying protocol-1 (Hp-1). The violet curve represents the heteropolymer obtained by applying protocol-2 (Hp-2) and the black curve represents the heteropolymer obtained by applying protocol-3 (Hp-3).

The figure 17 shows the thermograms of 27°C to 500°C for COR, Hp-1, Hp-2 and Hp-3 and highlighted in Table 4. Table 4 presents the quantitative data of the heat of reaction (endothermic and exothermic) obtained through the area bounded by the baseline of each peak of the curves of figure 17. The theory of differential thermal analysis states that the area of the DTA curve bounded by the baseline is directly proportional to the heat of transformation of the material [18]. Thus, according to the specialized literature, area in each region of the DTA curve is numerically equal to endothermic or exothermic enthalpy. Such that $A = \frac{m}{k}\Delta H$, where m is the mass loss of the sample and k the thermal conductivity of the material. So in Tabela.4 is presented only the value of the area without considering the weight variation of the sample (the data will be considered in future work).

Table 4: Reaction heat obtained from the thermograms results of samples of heterotermopolymer COR, Hp-1, Hp-2 and Hp-3 [19].

Enthalpy (a.u.)	Sample			
	COR	Hp-1	Hp-2	Hp-3
(ΔH_{P1})	-948.70 ±9.52	-1337.97 ±11.23	-1337.97 ±11.23	-641.45 ±5.32
(ΔH_{P2})	922.01 ±7.56	973.92 ±7.98	988.19 ±8.42	443.34 ±3.18
(ΔH_{P3})	-753.55 ±3.13	2072.37 ±17.12	2318.27 ±18.97	-494.46 ±5.4
(ΔH_{P4})	1004.59 ±10.45	1025.66 ±9.39	1008.31 ±6.89	142.68 ±2.23
(ΔH_{P5})	-395.62±5.41	-453.43 ±7.61	-453.43 ±7.61	-126.09 ±3.96

(ΔH_{P6})	284.93±4.12	446.22 ±6.83	446.22 ±6.83	76.11 ±1.45
(ΔH_{P7})	-42.87±1.89			
(ΔH_{P8})	9941.79±41.89			
(ΔH_{P9})	-1915.73±16.31			

The negative values refer to the region where the physical-chemical process was endothermic and the positive signal the region where the process was exothermic. The enthalpy values for COR show higher modulus compared to DTA results for heterotermopolymers. The lowest and highest values occurred at peaks 9 and 8 in the region of decomposition and vaporization of sample residues. The HP-1 and HP-2 heteropolymers showed similar enthalpy. With the exception of the Hp-2 heteropolymer in the P2 and P3 region, there were small endothermic and exothermic transitions located at three points on T1 (93.9 and 114.2°C), T2 (237.62 and 251.17°C) and T3 (301.9 and 351.5°C). The heterotermopolymer Hp-3 showed an intermediate behavior between the heteropolymers Hp-1, Hp-2 and COR.

4. Conclusion

The vitrification methods presented in this work showed that there are significant differences between the method presented in protocol 1 and 2 in relation to the method presented in protocol-3. The heteropolymers Hp-1 and Hp-2 presented texture, molecular rearrangement in the physical-chemical process in their similar randomized accommodation and greater thermal stability, characteristic of hard material, whose decomposition process starts at 400°C. While the heterotermopolymer Hp-3 the texture, differentiated random molecular rearrangement and lower thermal stability and start of the decomposition process at 300°C. In this case the synthesized material has more flexible and moldable physical characteristics.

5. Acknowledgment

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