

## Characterization of graphite-polyurethane composites used as electrode materials

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### Abstract

Graphite powder was mixed with polyurethane in order to prepare composite materials in different proportions, such as 50, 60 and 70% (graphite *w/w*) intended to be used in voltammetric analysis. Results of thermogravimetry, differential scanning calorimetry and dynamical mechanical analysis were used in the characterization of the composites. Thermal and visco-elastic behaviors of pressed and non-pressed graphite-polyurethane composites used as electrode materials were investigated regarding the graphite content. TG curves revealed that thermal stability increases with the graphite content. DSC presented that the composites are completely cured after 24 h and DMA was used in the determination of glass transition of the composites, varying between approximately 56 - 59°C and 70 - 83°C for pressed at 4000 psi and non-pressed composites, respectively, showing that the pressing during the cure resulted in lower mobility of polymeric chains inside the composites.

**Keywords:** composite electrodes, polyurethane, thermogravimetry, dynamic-mechanical analysis.

### 1. Introduction

Polyurethanes (PU) are important class of engineering polymeric materials which are applied in a large variety of forms, such as foams, elastomers, adhesives, coatings, fibers, etc., in many different fields, e.g., insulation, packaging, medicine, electronics and many others [1]. They have also been proposed as agglutinants in the preparation of composites with graphite to be used as electrode materials [2].

According to Tallman and Petersen, a composite electrode is defined as "a material consisting of at least one conducting phase, commingled with at least one insulator phase [3]. In this case, the graphite is the conductor and the PU from vegetable source is the insulator phase.

In the electrode preparation, the main advantages of using a polymer instead of liquid agglutinants are the mechanical resistance, stability especially in non-aqueous medium and flow analysis applications. PU has the additional advantage of presenting lower swelling effects in relation to other polymeric agglutinants, even in aqueous medium [2].

Besides mechanical resistance, gain in sensitivity limits and relative simplicity in the preparation and surface renewing, possibility of incorporating modifiers, low cost and relative repeatability of active area are observed for graphite-polymer composites electrodes as described elsewhere [2,4].

Once graphite-PU composite electrodes are relatively new materials, few studies regarding their thermal and mechanical properties have already been presented. Some examples of thermal characterization of PU derivatives from vegetable sources include the differential scanning calorimetry (DSC) investigation of the reaction between castor oil and isophorone diisocyanate [5], as well as 1,4-butanediol with phenylisocyanate [6]. Such reports describe kinetic data determination and mechanical properties of these polymers from renewable natural source.

Liquid crystalline polyurethanes (LCPUs) from polybutadiene and commercial diisocyanates were also investigated by DSC and dynamical mechanical analysis (DMA) [7].

PU nanocomposites were studied by thermal analytical techniques as described by Chattopadhyay [8] and this subject was reviewed by Madbouly and Otaigbe [9].

Thermal analysis has been used as a tool in the characterization of graphite-polymer composite materials, used as working electrode in voltametric determination of environmental, inorganic and pharmaceutical samples [10-18].

Recently we have presented some results regarding the preparation and characterization of composites prepared with graphite as a conductive phase and epoxyde, polyurethane and silicone rubber as agglutinant phases, intended to be used as electrode materials. Results showed that voltammetric response could be obtained when at least 50% of graphite (*w/w*) is present in the material. Scanning electron microscopy (SEM) and thermogravimetry/derivative thermogravimetry (TG/DTG)

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were used in the characterization of the composites revealing relatively high homogeneity of the resulting material [19].

However, the investigation on thermal stability, composition, glass transition and structure of composites used in electrode construction with graphite agglutinated by castor oil PU, by TG/DTG, DSC, DMA and SEM still not investigated in detail.

Thus the objective of the present work is to investigate more deeply the thermal, mechanical and morphological features of this electrode material, regarding composition and pressure effect during curing process.

## 2. Experimental

### 2.1. Reagents and Materials

Graphite powder, < 20  $\mu\text{m}$  particle size (Aldrich, USA) and castor oil derivative polyurethane resin (CEQUIL, Brazil) were used in the preparation of the composites.

### 2.2. Composites preparation

The polyurethane resin was prepared by mixing 1.05 parts of the pre-polymer (hardener A-249) and 0.95 part of the polyol (adhesive B-471) (w/w), according to the manufacturer's instructions. After taking appropriate amounts of the PU, it was mixed with graphite powder in a glass mortar during 10 minutes, in order to obtain 50, 60 and 70% (w/w) of graphite in the resulting composite.

These uncured composites were inserted in stainless steel molds in order to prepare samples with  $35 \pm 1$  mm (length) x  $13 \pm 1$  mm (wide) x  $3.5 \pm 0.2$  mm (thickness) and submitted to DMA analysis.

DMA exploratory experiments were performed with the 60% (graphite, w/w) cured during 24 h under different pressures (2000, 4000 and 6500 psi) showing that above 4000 psi no changes were observed on the thermal behavior of the samples. Next 60% (graphite, w/w) samples were cured under 4000 psi, during 6, 12, 24, 48, 96 and 168 h, without significant changes for curing times longer than 24 h. Samples cured at atmospheric pressure were always used for comparison.

Thus 50, 60 and 70 % (graphite, w/w) were prepared under room pressure and 4000 psi and let to cure for 24 h. Small pieces of these samples ground in a glass mortar and slices were taken for TG/DTG-DTA and DSC analysis. DMA analyses were performed with species prepared under the optimized conditions in the dimensions described above.

### 2.3. Procedures

TG, DSC and DMA measurements were performed using pure PU and composites containing 50, 60 and 70% (graphite, w/w). The composites were designated according

to the content of graphite, so that PU50 refers to the material containing 50% of graphite (w/w), etc.

All the TG/DTG-DTA curves were obtained in a simultaneous TG-DTA SDT Q600 apparatus from TA Instruments, under  $\text{N}_2$  dynamic atmosphere (gas flow of  $50 \text{ mL min}^{-1}$ ) and at  $10 \text{ }^\circ\text{C min}^{-1}$  heating rate. The sample masses were about 5 mg ( $\pm 0.1 \mu\text{g}$ ).  $\alpha$ -alumina crucibles were used in the TG/DTG-DTA experiments. The TG-DTA curves were obtained for the composites in slices cut from the sample or powder from grinded sample.

DSC curves were recorded in a DSC Q10 modulus (TA Instruments), under  $\text{N}_2$  flow of  $50 \text{ mL min}^{-1}$ , at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ , as heat-cool-heat cycles between -60 and  $100 \text{ }^\circ\text{C}$ . The sample masses were about 3 mg ( $\pm 0.1 \text{ mg}$ ) and covered aluminum crucibles with a pin hole ( $f = 0.7 \text{ mm}$ ) in the center of the lid were employed during the analysis. The DSC apparatus was previously calibrated for temperature and enthalpy with indium metal (99.9%), according to the manufacturer instructions.

DMA measurements were obtained in a DMA Q800 modulus (TA Instruments), from different composites prepared as described above using a dual cantilever clamp, between -50 and  $120 \text{ }^\circ\text{C}$ , at a heating rate of  $5.0 \text{ }^\circ\text{C min}^{-1}$ . Data was collected at 1.1 Hz. A GCA (Gas Cooling Accessory – TA Instruments) was used in order to operate the DMA modulus under the room temperature, with liquid nitrogen.

SEM was performed in a Zeiss-DSM 940-A apparatus, operated at 5 kV, with different magnifications.

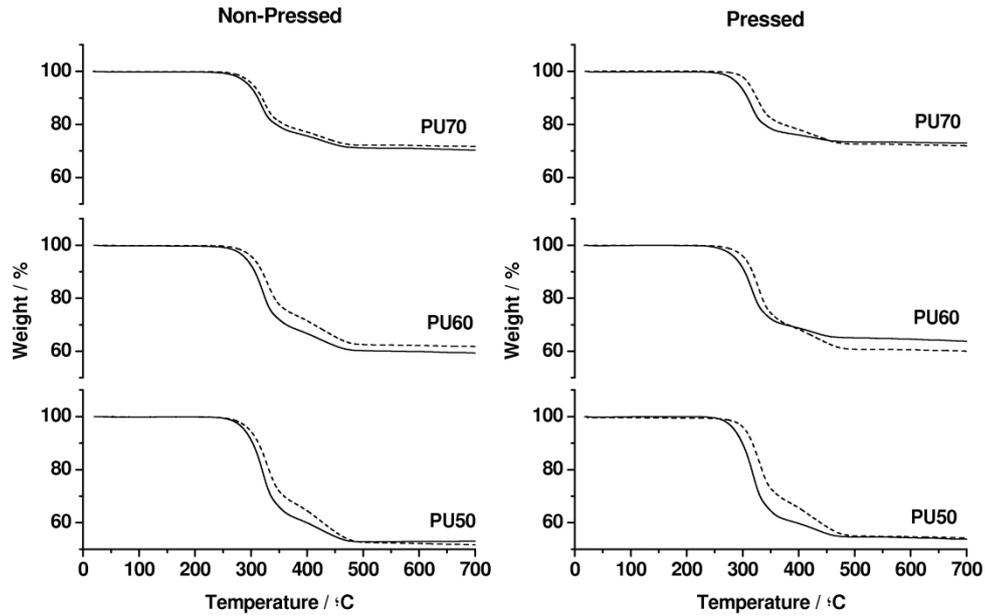
The resistance of the composite electrodes was measured with a digital bench multimeter Minipa MDM-8045 in relation to a platinum plate as counter electrode, both immersed in a mercury pool.

Cyclic voltammograms were recorded in a potentiostat/galvanostat AUTOLAB PG-STAT 30 (Ecochemie), at composites and a glassy carbon as working electrodes in a three electrode cell and a platinum wire as auxiliary and a saturated calomel electrode (SCE) as reference for  $5.0 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$  in  $0.50 \text{ mol L}^{-1}$  solutions at a  $50 \text{ mV s}^{-1}$  scan rate.

## 3. Results and Discussion

Thermogravimetric curves were taken under nitrogen atmosphere, from room temperature to  $700 \text{ }^\circ\text{C}$ , in order to obtain the actual percentage of graphite in each sample, since at this temperature it is assumed that the whole polymeric content is already decomposed, with a residue corresponding to carbon from graphite.

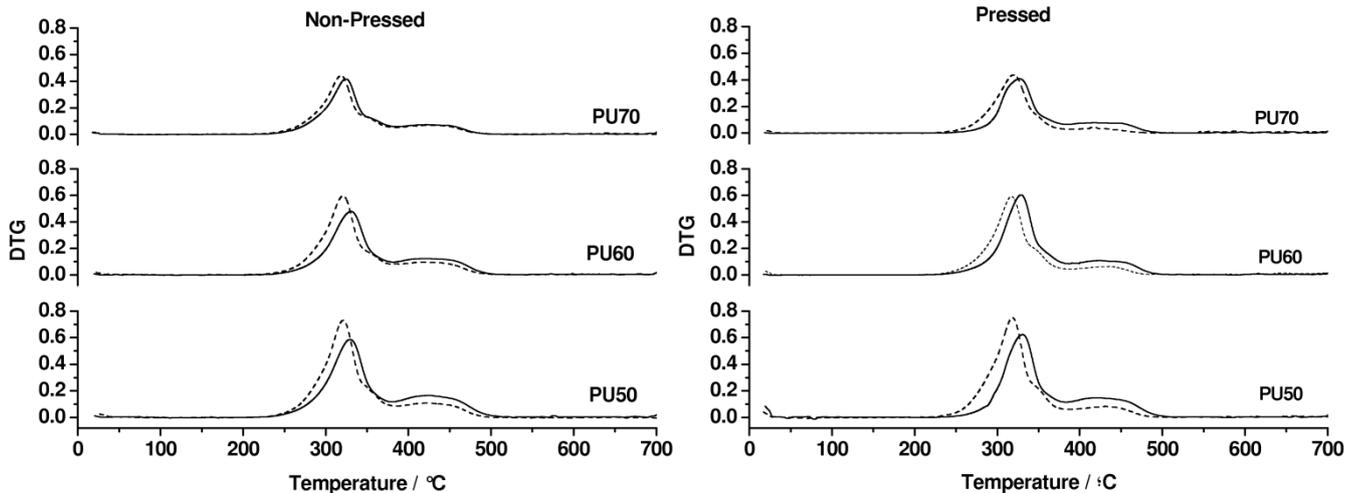
TG curves of graphite/PU composites (GPU) with different graphite contents are presented in Figure 1.



**Figure 1:** TG curves of non-pressed (left) and pressed GPU composites (4000 psi, right), in sliced (—) and powdered forms (---), with different graphite contents. Sample mass 5 mg ( $\pm 0.1 \mu\text{g}$ ), heating rate  $10 \text{ }^\circ\text{C min}^{-1}$ , and dynamic  $\text{N}_2$  atmosphere flowing at  $100 \text{ mL min}^{-1}$ .

It was observed that, in all cases and under the experimental conditions employed in this work, the thermal

decomposition of the composites takes place in two steps, as confirmed by DTG curves, in Figure 2.



**Figure 2:** DTG curves of non-pressed (left) and pressed (4000 psi, right) GPU composites, as sliced (—) and powdered (---) forms.

For powdered, sliced, pressed (4000 psi) and non-pressed (cured under atmospheric pressure) samples the residue values are very close to those expected, based on the amount of graphite used in the preparation of the materials,

allowing to conclude that they present a reasonable homogeneity. The results were calculated taking in account the residue obtained for the pure polymer, under the same conditions, which is 3.03 %, at  $700 \text{ }^\circ\text{C}$ , as presented in Table 1.

**Table 1:** Thermogravimetric residues and graphite contents of GPU composites

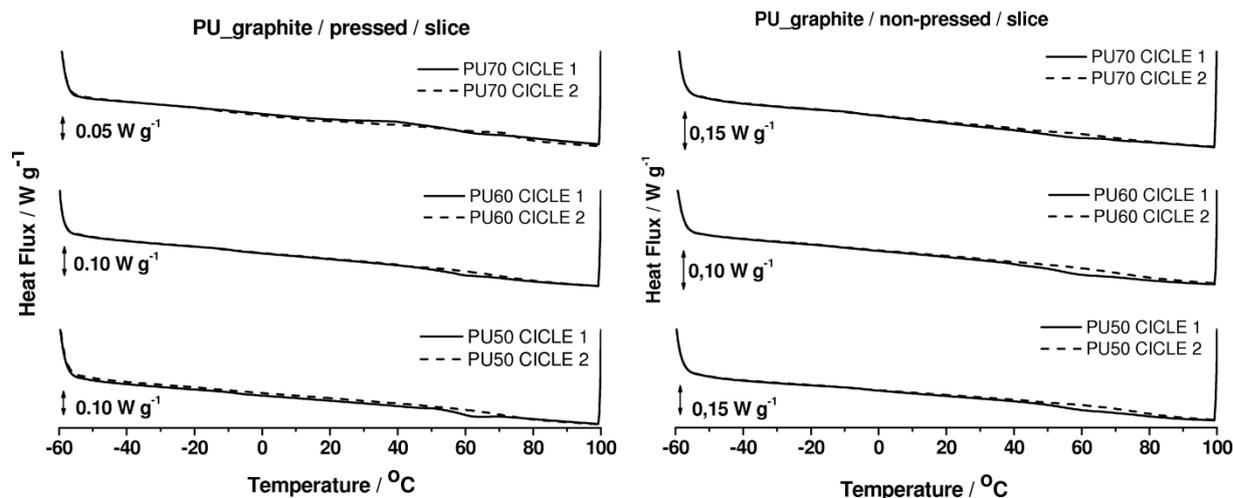
Composite	SLICES						POWDER					
	pressed			non-pressed			pressed			non-pressed		
	T <sub>dec.</sub> (°C)	Residue <sup>a</sup>	% graphite <sup>b</sup>	T <sub>dec.</sub> (°C)	Residue <sup>a</sup>	% graphite <sup>b</sup>	T <sub>dec.</sub> (°C)	Residue <sup>a</sup>	% graphite <sup>b</sup>	T <sub>dec.</sub> (°C)	Residue <sup>a</sup>	% graphite <sup>b</sup>
PU50	238.6	54.26	51.23	240.2	51.65	48.62	221.1	53.73	50.69	236.8	52.98	49.95
PU60	243.6	60.07	57.04	249.3	61.76	58.73	234.1	59.68	56.65	239.1	59.33	56.29
PU70	271.2	71.92	68.89	252.6	71.66	68.63	235.7	72.99	69.96	227.8	70.36	67.33

According to the TG curves (Fig. 1), it is possible to observe that the initial decomposition temperature increases with the increasing composite graphite content. The exception for this behavior is the non-pressed powdered PU70, which is stable up to 227.8 °C (Table 1).

Regarding the effect of pressure during curing of the samples, in all cases, it is possible to observe that, as a general trend, the non-pressed composites presented a higher thermal stability, when compared to the pressed ones.

However, the composites with larger graphite content did not follow this trend. In these cases, pressed slice or powdered PU70 are more thermally stable than the non-pressed samples. This could be related to the thermal insulating effect of graphite, which rises up with the particle contact when pressed, as discussed latter in this text.

Figure 3 depicts DSC curves from two consecutive heating cycles of pressed and non-pressed GPU composites, in sliced forms.



**Figure 3:** DSC curves of pressed (4000 psi) and non-pressed GPU composites, under N<sub>2</sub> flow of 50 mL min<sup>-1</sup>, heating rate of 10 °C min<sup>-1</sup>, sample masses were about 3 mg (± 0.1 mg), covered aluminum crucibles with a central pin hole ( $\phi = 0.7$  mm).

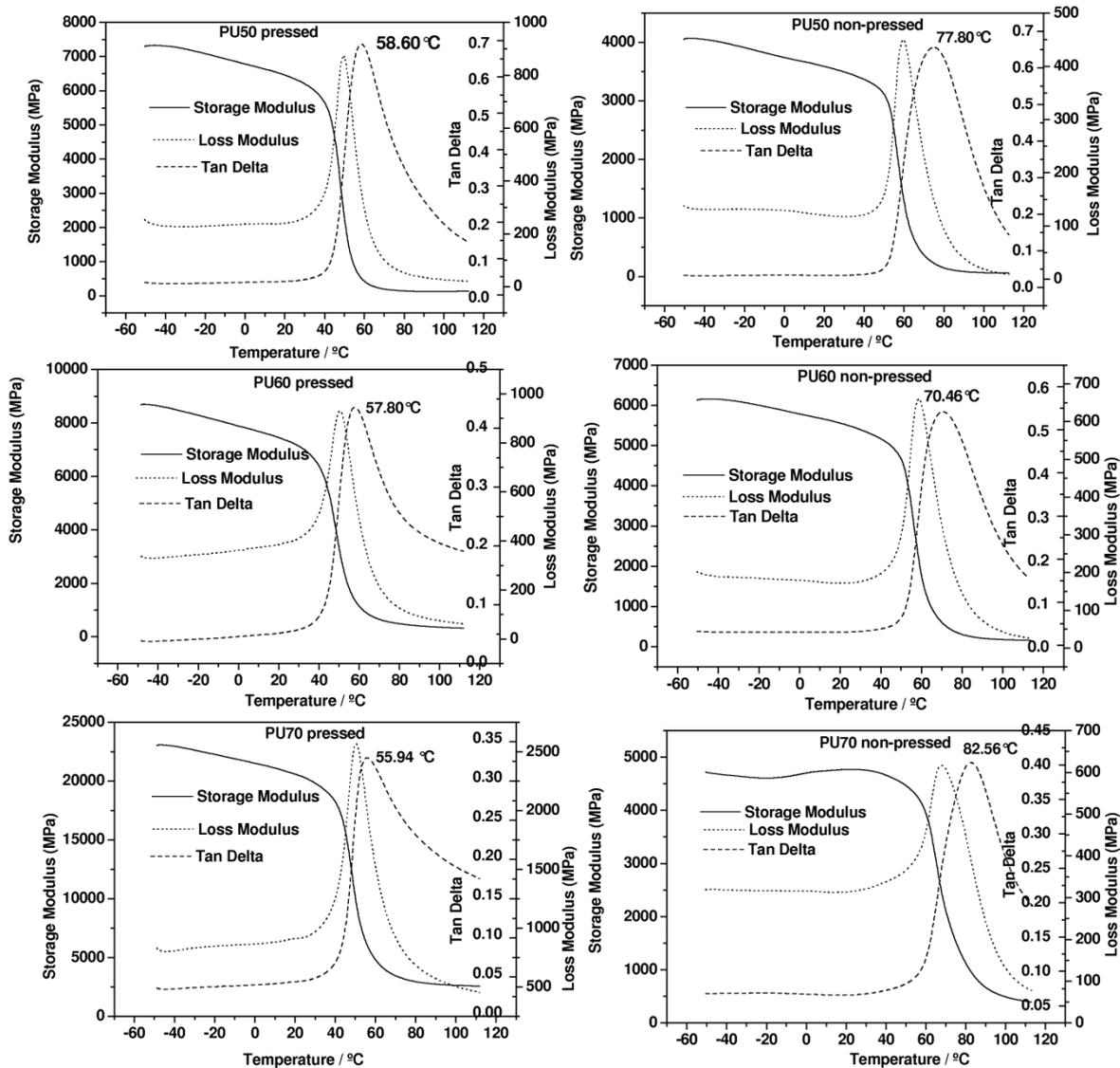
Although powdered samples were useful in TG/DTG in order to evaluate the homogeneity of the material, regarding graphite content, they did not show to be meaningful for DSC, once the particle size were not uniform and results will not be presented here.

Between -60 and 100 °C, it is possible to observe a shift in the baseline, corresponding to the glass transition of the polymeric phase present in the composite. However once the DSC is not as sensitive as DMA for such analysis the glass transitions were measured with the second and will be presented latter.

The baseline change observed during the first heating cycle in the DSC curves is a consequence of the relaxation of PU chains in the composites and it is certainly influenced by the graphite content. In all pressed composites the temperatures interval in which this relaxation appear are very close. These results lead to suppose that the slices are organized in a similar way, in terms of polymer chains and graphite distribution, once the glass transition occurs in the same range of temperature for pressed PU50, PU60 and PU70. From de DSC curves it was also possible to conclude that the polymers did not present additional thermal cure.

In the case of non-pressed slice samples, the transition interval is not so close, especially in the 1st cycle, suggesting that the composite organization is not as well defined as in the pressed ones.

Thus, DMA curves for non-pressed and pressed samples with 50, 60 and 70% (graphite, w/w) were taken and are presented in Figure 4.



**Figure 4:** DMA curves of GPU composites, using a dual cantilever clamp, between - 50 and 120 °C, heating rate of 5.0 °C min<sup>-1</sup>, frequency of 1.1 Hz and samples with 35 ± 1 mm (length) x 13 ± 1 mm (wide) x 3.5 ± 0.2 mm (thickness).

In a general manner it is possible to say that the pressed samples present only one tan δ peak in the investigated range, representing the glass transition temperature of the polymeric phase. This suggests that the pressed samples present a more rigid structure, without possibility of smaller segments motion or other secondary events, which would be represented by secondary transitions.

Meanwhile the non-pressed samples presented some secondary events that precede the glass transition, revealing that there is some freedom inside the material, allowing these secondary events to take place during heating of the composite. This is more evident in the composites with higher polymer contents and it can also be seen in the storage modulus curve.

Table 2 summarizes the glass transition temperatures determined from the tan δ peaks for the pressed and non-pressed samples with different graphite contents.

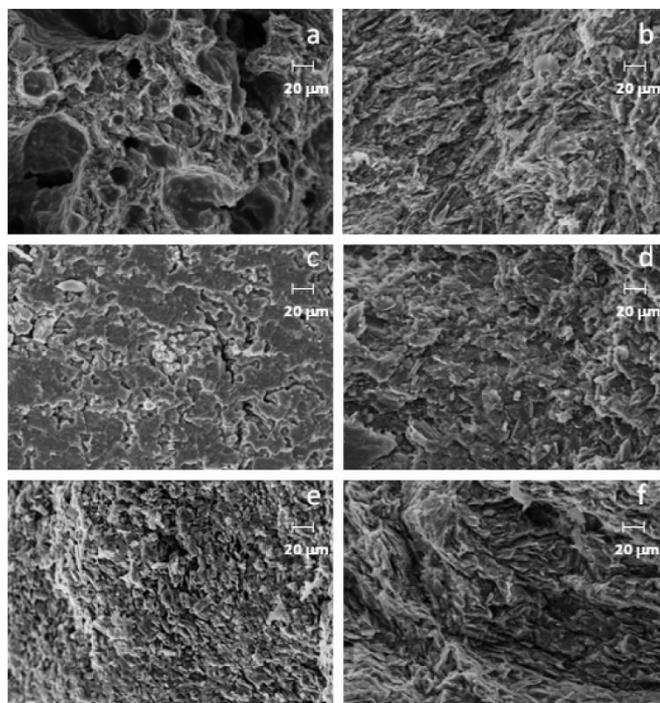
**Table 2:** Glass transition temperatures of GPU composites, obtained by DMA

Composite	Glass transition temperature / °C	
	pressed at 4000 psi	non-pressed
PU50	58.60	77.80
PU60	57.80	70.46
PU70	55.94	82.56

It is possible to notice that the pressed samples presented lower Tg temperatures similar for all the graphite contents, when compared to the non-pressed samples.

This may point to a higher degree of organization in the non-pressed composite, which could be justified by a higher freedom of the polymer chains during the curing process, resulting in a more organized system. The pressed samples seems to present a less organized state that could be the result of the pressure effect which seems to hindering the free organization of the chains imposing a structure without chance of a natural accommodation of the polymeric phase inside the composite.

SEM images presented in Figure 5 corroborate these ideas, as they showed that the fractured surface of the pressed GPU composite resulted in a more homogeneous material when compared to that prepared without pressure, in which a more porous material can be observed in the composites with lower graphite contents. As could be expected the pressed samples are more compact than those non-pressed, presenting much more defined structural profiles.



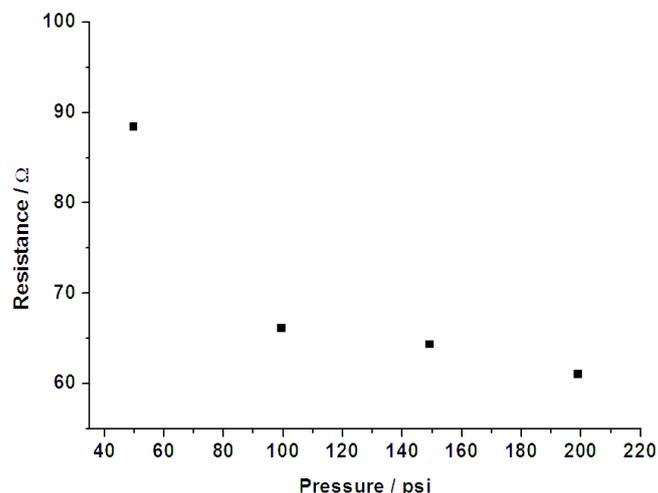
**Figure 5:** Scanning electronic micrographies of the fractured surfaces of the GPU composites non-pressed (a) 50%, (c) 60%, (e) 70% and pressed at 4000 psi (b) 50%, (d) 60%, (f) 70%. Magnification 1000 x.

These morphological features could be related with the TG/DTG data from which one see that non-pressed samples use to be more thermally stable than the pressed ones. This fact could be related with the porosity observed in the SEM micrographies of the composites, according to which the pressed material do not present internal pores. Such pores facilitate heat transfer inside the sample, once PU is a thermal and electrical insulating material. The effect of particle contact can be confirmed when one look at the electrical resistance that rises with the decrease in graphite

content as demonstrated for the 60% (graphite w/w) as example in Figure 6.

The organization of the composite structure under pressure can also be related with the DMA results in which there are any secondary transitions in the pressed samples.

It was performed an investigation about the effect of the pressure applied during the cure of the composites in their electrical resistance, once they use to be applied in the confection of electrodes for electroanalysis. The results are represented in Figure 6.

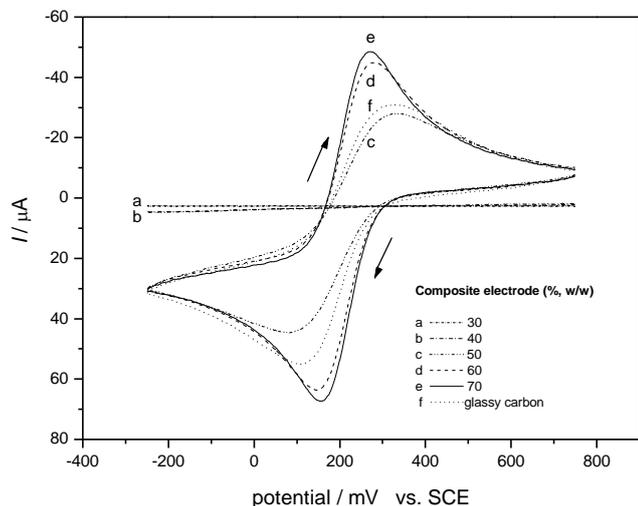


**Figure 6:** Resistance behavior against pressure, 60% graphite (w/w).

As expected, the ohmic resistance decreases as the pressure is raised up to a constant value, suggesting that the electrical contact was established. In other words, the current is increased, probably due to a more efficient contact among conductive particles present in the composites.

It is interesting to keep in mind that composites with less than 50% (graphite, w/w) do not act as conducting materials [2] and Navarro-Laboulais and coworkers found 62% as the best composition in epoxy-graphite composites, according to the percolation theory. It is explained that over this composition, the graphite particles are so close that electrical conduction starts.

This fact is also demonstrated by the voltammetric response of the composites. In Figure 7, the cyclic voltammograms obtained for 5 mmol L<sup>-1</sup> potassium ferricyanide in 0.5 mol L<sup>-1</sup> potassium chloride clearly demonstrate that the increase on graphite content from 40 to 50% (graphite, w/w) allows to reach the conductivity threshold that leads to the maximum response in 60% (graphite, w/w). In this figure is also included a cyclic voltammogram obtained with a glassy carbon electrode for comparison.



**Figure 7:** Cyclic voltammetric response of the composite electrodes (a) 30% (b) 40% (c) 50% (d) 60% (e) 70% (graphite, w/w) and (f) glassy carbon at  $5.0 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$  in  $0.5 \text{ mol L}^{-1} \text{ KCl}$  solution. Scan rate  $100 \text{ mV s}^{-1}$  and potential from  $-0.25 \text{ V}$  to  $+0.75 \text{ V}$  (vs. SCE).

#### 4. Conclusions

The results presented in this study revealed that the composites are relatively homogeneous regarding the graphite contents and that the polymer phase is completely cured after 24 h and properties do not change significantly when cured under pressure over than 4000 psi.

Regarding the effect of pressure on the composites curing one can conclude that pressure seems to better organize the system and result in a less porous material. As a consequence of this organization, it is possible to observe an increase in the thermal stability and electrical conductivity that rises up when more graphite is added to the sample due to the closest contact between the graphite particles.

The more precise determination of the glass transition was performed using DMA, which showed that pressure seems to play a remarkable role in the accommodation of the polymer chains, leading to a more compact structure with less mobility of chains during the curing process. The non-pressed samples presented secondary motions on chains and higher glass transition temperatures, suggesting higher mobility in the structure and a more stabilized accommodation of the chains.

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