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Development of Graphite-Polymer Composites as Electrode Materials

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Graphite powder was mixed to polyurethane, silicon rubber and Araldite® (epoxy) in order to prepare composite materials to be used in the preparation of electrodes. Results showed that voltammetric response could be obtained when at least 50% of graphite ($w.w^{-1}$) is present in the material. SEM and thermogravimetry were also used in the characterization of the composites.

Keywords: *composite electrodes, epoxy, polyurethane, silicon rubber*

1. Introduction

Due to its characteristics such as easiness of surface renewing and area reproducibility, the Hg electrode became very popular after its proposition by Kucera[1] and the conception of polarography by Heyrovsky in the earlier 1920's[2].

However, due to the limitations of using mercury electrodes in the anodic potential range, in which the metal is oxidized, nowadays the development of alternative electrode materials is a profitable and important branch of research in electrochemistry and electroanalytical sciences[3]. In addition the environmental problems caused by Hg allied to its toxicity is increasing concerning about its use.

Adams[4] proposed a dropping carbon paste as an electrode material intended to be used in the anodic potential range, for studies of organic substances with biological interest[5]. After that, the carbon paste became an important electrode material prepared by mixing graphite powder and an inner liquid agglutinant, such as mineral oil or melt paraffin, in a suitable proportion[6].

Alternatively a polymer can replace the liquid in order to prepare a rigid composite electrode material. The main advantages are the mechanical resistance and the enlargement of the possibilities of use in non-aqueous medium.

Tallman and Petersen[7] defined a composite electrode as "*a material consisting of at least one conducting phase commingled with at least one insulator phase*". These authors also classified disperse composites as materials in which the particles are randomly distributed by the material, such as in carbon pastes and polymer agglutinated materials, and consolidated composites in which the conductive particles occupy specific areas of the material.

Several examples of composite electrodes can be found in the literature. Regarding the use of polymers as agglutinants, many composite electrodes of graphite with epoxy[8,9], polyester[10,11], PVC[12,13], polypyrrole[14] have been proposed for amperometric and voltammetric determinations in the quantification of different analytes.

This work describes the characterization of composite electrodes prepared by graphite agglutinated by a castor oil derivative polyurethane (PU), silicon rubber (SR) and Araldite® (a commercial epoxy adhesive), which were proposed as electrode materials. Thermal analysis (TG/DTG and DSC), electron scanning microscopy (MEV) and cyclic voltammetry were used in order to characterize the composites.

2. Experimental

2.1. Reagents and solutions

Al the reagents were of analytical grade (PA) and used without further purification, unless when specified. Water used in the preparation of the solutions was distilled twice in a quartz stiller.

A 5 $mmol.L^{-1}$ $K_3[Fe(CN)_6]$ (Mallinckrodt) in 0.5 $mol.L^{-1}$ KCl (Mallinckrodt) solution was used to probe the electrodes, using cyclic voltammetry. Investigations were performed in five following mediuns: 1.0 $mol.L^{-1}$ H_2SO_4 (Mallinckrodt), 0.1 $mol.L^{-1}$ acetate buffer pH 4.0 prepared with sodium acetate and glacial acetic acid (both from Mallinckrodt), 70 $mmol.L^{-1}$ phosphate buffer pH 7.4 (prepared with dibasic and monobasic sodium phosphate, both from Mallinckrodt), 0.1 $mol.L^{-1}$ ammonium buffer pH 11.0 (prepared with ammonium chloride and ammonia, both from Mallinckrodt) and 0.1 $mol.L^{-1}$ NaOH (Mallinckrodt) solutions. For each solution the adequate potential window was evaluated.

2.2. Apparatus

Voltammetric experiments were performed using a BAS-CV 50 W potentiostat. A three-electrode cell (25.0 mL full capacity) was used with a saturated calomel electrode (SCE) and a platinum wire (ϕ = 1 mm and 1 cm longer) was used as the reference and auxiliary electrodes, respectively. All the measurements were taken at room temperature.

Scanning electron microscopy was performed in a Zeiss-DSM 940-A apparatus, operated at 5 kV, with different magnitudes. Ohmic resistance of the composite electrodes was estimated by means of a HP-3478A multimeter (Hewlett-Packard), by immersing the electrode in a mercury pool contact and using a platinum wire as the counter electrode.

Thermoanalytical data were obtained with a Q-600 modulus coupled with a Thermoanalyser Q-6000 controlled with the software

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Thermal Advantage for Q-Series (r. 4.2.1) both from TA-Instruments. Samples of c.a. 7 mg were placed in an alumina sample holder and heated up to 700 °C under nitrogen flow of 100 mL.min^{-1}, at a 10 °C.min^{-1} heating rate. Then the atmosphere was changed to dry air flowing at 100 mL.min^{-1} and the sample heated up to 900 at a 10 °C.min^{-1} heating rate.

2.3. Composite electrode preparation

A castor oil derivative polyurethane resin (POLIQUIL Brazil), was prepared by mixing 0.85 parts of the pre-polymer (A-249) and 1.0 part of the polyol (B-471) (w.w^{-1}), according to the manufacturers instructions. Silicon rubber (Dow-corning) was purchased in a local store and used directly from the package. Araldite® adhesive was also obtained in local market and used by mixing equal proportions (w.w^{-1}) of the resin and hardener as indicated by the manufacturer.

After taking appropriate amounts of the polymers, they were mixed with graphite powder, 1-2 μm (Aldrich, EUA) in order to obtain 30, 40, 50, 60 and 70% (w.w^{-1}) of graphite in the composite. Araldite was prepared only to be 50-70% (graphite, w.w^{-1}).

The uncured PU and Araldite composites were inserted in a hand press and extruded as rods with 3 mm diameter and cut in 1.5 cm long pieces. In order to establish electric contact, a 10 cm copper wire was attached to the composite rods with the help of a silver epoxy (EPO-TEK 410E, Epoxy Technology, USA) and let to cure for 24 hours. Then this set was inserted in a glass tube (5 mm i.d., 9.0 cm length) and filled with a SQ2004 epoxy resin (Silaex, Brazil) and stand 24 hours for cure. To assure a good assembly of all parts, any experiment was done with this assembly during this time.

The uncured SR composites were inserted in a glass tube (3 mm i.d., 9.0 cm length), a copper rod (ϕ = 3.0 mm, 10 cm longer) was inserted in the tube and the set was carefully pressed in a hydraulic press for 24 hours, at 5 kgf. Then the copper rod was attached to the composite with the help of a silver epoxy as described above.

All the electrodes were polished in a 600 grit sand paper and again with γ-Al_3O_3 (1 μm) suspension with an APL-2 polishing wheel (Arotec, Brazil), and sonicated in water followed by isopropyl alcohol for five minutes in each solvent.

3. Results and Discussion

The voltammetric response of the composite electrodes showed to be highly dependent on the graphite content and in lower extension of the nature of the agglutinant. An example of the voltammetric profile of the same 5 mmol.L^{-1} potassium ferricianyde in 0.5 mol.L^{-1} KCl at the PU composite in different compositions is presented in Figure 1a.

The 50, 60 and 70% (graphite, w.w^{-1}) PU composites presented good conductivity and an expected voltammetric profile, when compared with the glassy carbon electrode. Best results were obtained with the 60% (graphite, w.w^{-1}), composite. It is possible to observe that the 30 and 40% (graphite, w.w^{-1}) did not present any voltammetric response, probably due to the absence of graphite in amount enough to conduct current.

The SR (Figure 1b) and Araldite® (Figure 1c) composites presented similar results, but with best composition of 70% (graphite, w.w^{-1}). These results are in agreement with the findings of Trijueque et al[14,15] who described a composition of 62% as that which presents the best electroanalytical properties for graphite-epoxy electrodes based on the second threshold percolation theory. According to these authors the composite became conductor when the graphite particles can touch each other inside the material.

Due to the higher surface activity the 60 and 70% (graphite, w.w^{-1}) graphite-PU composite presented an ΔE_p smaller than that observed for the GC electrode. On the other hand the 50% (graphite, w.w^{-1}) Araldite® composite showed an ΔE_p higher than that observed for the GC electrode, suggesting a less active surface.

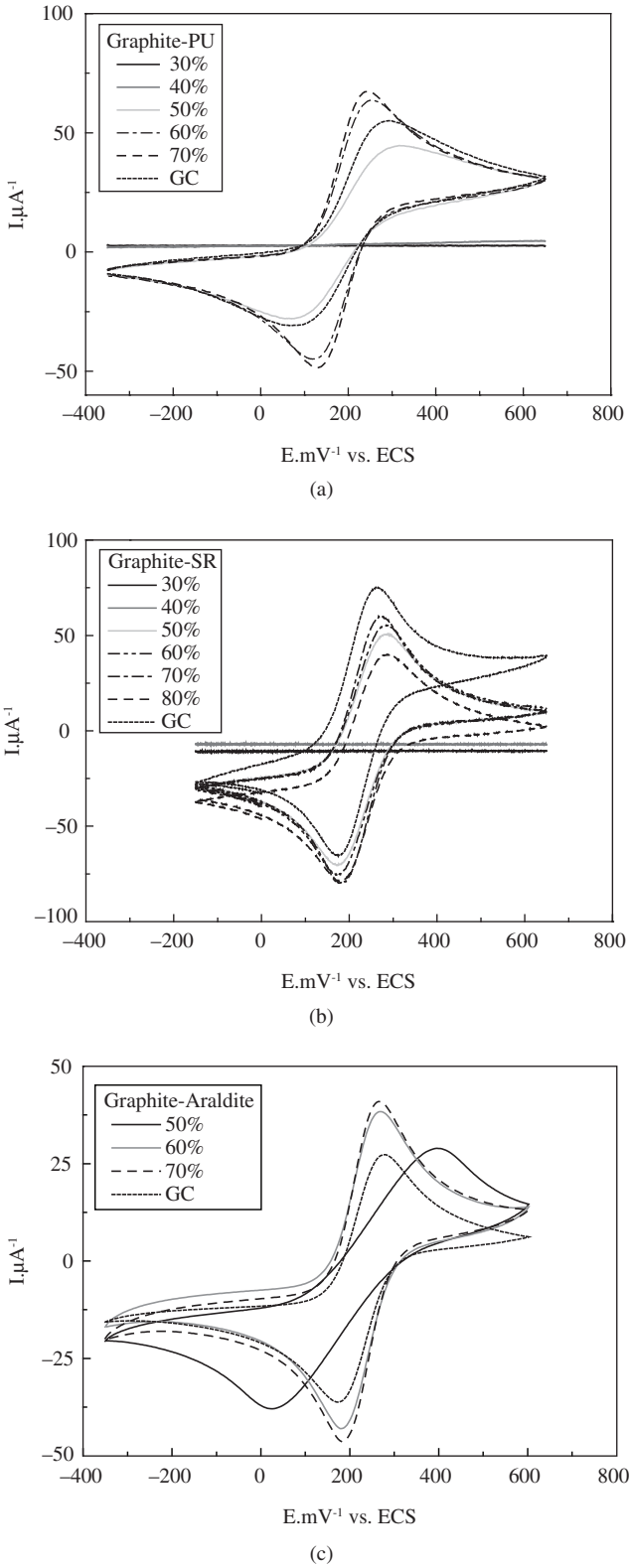

Figure 1. Cyclic voltammetric response obtained for composites: a) graphite-PU; b) graphite-SR; and c) graphite-Araldite® compared to the GC at 5.0 mmol.L^{-1} $K_4[Fe(CN)_6]$ in 0.5 mol.L^{-1} KCl, v = 100 mV.s^{-1}, pH = 3.0.

The ohmic resistance has also been determined for the composite electrodes. The results, presented in Table 1, agreed with the voltammetric results since only from 50% the resistance is almost 1000 times lower than that observed for 40% in the SR and PU composites and decreased even more for 60 and 70% (graphite, $w.w^{-1}$). In all cases the resistence was higher when compared with the glassy carbon, since in the GC only a conducting phase is present.

Table 2 describes the potential windows in which the composite electrodes can be used presenting maximum background currents of approximately 10 μA, in relation to the saturated calomel electrode. These experiments were performed in different supporting electrolytes such as 1.0 $mol.L^{-1}$ H_2SO_4, 0.1 $mol.L^{-1}$ acetate buffer pH 4.0, 70 $mmol.L^{-1}$ phosphate buffer pH 7.4, 0.1 $mol.L^{-1}$ ammonium buffer pH 11.0 and 0.1 $mol.L^{-1}$ NaOH solutions.

The highest potential windows were observed when the graphite-PU is used, however in the NaOH solution some unexpected signals were seen probably due to the instability of the polymer in such medium.

On the other hand the narrowest windows were found when the graphite-SR is used mainly in basic medium in which the electrode is limited in both anodic and cathodic ranges. Pungor had described this before, mainly in relation to severe limitation of this electrode material in the anodic range. However it still an alternative to mercury considering the anodic range in neutral or acidic medium.

Finally the graphite-Araldite® presented a potential window from –1000 to +900 mV in the acidic, neutral and slightly basic medium. In strong basic supporting electrolyte it was limited in the anodic range to +500 mV.

These limitations can be related to the presence of functional groups in the polymers that can be oxidized or reduced causing increase in the background current. Thus the nature of these functional groups is the responsible for the anodic or cathodic limitations of the resulting electrode materials.

One of the main problems that rise up when solid electrodes are used in voltammetric techniques is the reproducibility of the electrode surface. Much time is necessary to renew the surface by mechanical polishing since many analytes or their oxidation or reduction products use to adsorb at carbon surface.

In Table 3 the mean currents for 5.0 $mmol.L^{-1}$ $K_4[Fe(CN)_6]$ in 0.5 $mol.L^{-1}$ KCl obtained just after polishing of the composite electrodes are presented. The results are the mean of 5 successive determinations. The standard deviations suggest that a good reproducibility of the surface can be reached after successive polishing of the composite electrode surfaces at the investigated compositions.

The SEM images of the electrode surfaces before and after polishing are presented in Figure 2. Before polishing, all the composites presented homogeneous and rough surfaces. After treatment the graphite-PU composite presented a surface with some holes and smooth regions, while the SR and Araldite® presented a smooth regular surface.

The polyurethane composite presented the highest currents probably due to its rougher surface as demonstrated by SEM micrograph of polished surface of the composite.

Thermogravimetric data were used in order to determine the exact graphite content in each composite. The results are presented in Table 3. The unmodified resins and the composites were heated under nitrogen up to 700 °C, and thus the atmosphere was changed to air letting the carbon to burn. Typical curves for the resins and composites are presented in Figure 3.

The pure polymers burn in a single step resulting in no residue in the sample holder at 850 °C. Both the unmodified Araldite® and PU present a slight mass loss attributed to the carbon burning, which was considered in the calculations of the carbon content in the composites.

The composites presented a mass loss correspondent to that observed in the unmodified polymers in the same temperature range. A intense carbon burn can be observed at 700 °C, when the furnace atmosphere is changed to air. Details of such decompositions, such as mass losses and temperature ranges are described in Table 4.

The graphite contents were close to the expected showing that a good homogeneity of the material was reached, under the preparation mode.

Table 1. Ohmic resistance estimated for the composite electrodes by a mercury pool contact.

	Resistance[a]/Ω				
Electrodes/compositions[b]	30%	40%	50%	60%	70%
Graphite-PU	*	250000	98	25	7
Graphite-SR	290000	78000	75	11	6
Graphite-Araldite®	**	**	3500	86	61

[a]Glassy Carbon = 3 Ω; [b]graphite, $w.w^{-1}$; *not detected; and **not measured.

Table 2. Study of the useful potential window for the composites in different supporting electrolytes, limited to a background current of approximately 10 μA.

Supporting electrolytes	Potential window/mV (vs. ECS)		
	Graphite-PU	Graphite-SR	Graphite-Araldite®
H_2SO_4, 1.0 mol L^{-1}	–1750 - +1300	–500 - +1400	–900 - +1000
Acetate Buffer pH 4.0	–1750 - +1400	–500 - +1400	–1000 - +900
Phophate Buffer pH 7.4	–1500 - +1000	–300 - +1300	–1000 - +900
Ammonium Buffer pH 11.0	–1750 - +900	–300 - +900	–1000 - +900
NaOH, 0.1 $mol.L^{-1}$	–1600 - +900	–300 - +800	–1000 - +500

Table 3. Reproducibility of the composite electrodes response after 5 successive determinations and polishing between measurements.

Composites	$Ip_a/\mu A^*$	$Ip_c/\mu A^*$	$Ep_a/mV^{*,**}$	$Ep_c/mV^{*,**}$
Graphite-PU 60%	74.9 ± 0.0	–74.1 ± 0.0	259 ± 1	150 ± 1
Graphite-SR 70%	78 ± 1.0	–81 ± 2.0	275 ± 7	181 ± 4
Graphite-Araldite® 70%	29.3 ± 0.1	–33.4 ± 0.1	252 ± 0	176 ± 0

*a = anodic; c = cathodic; and ** - vs. SCE.

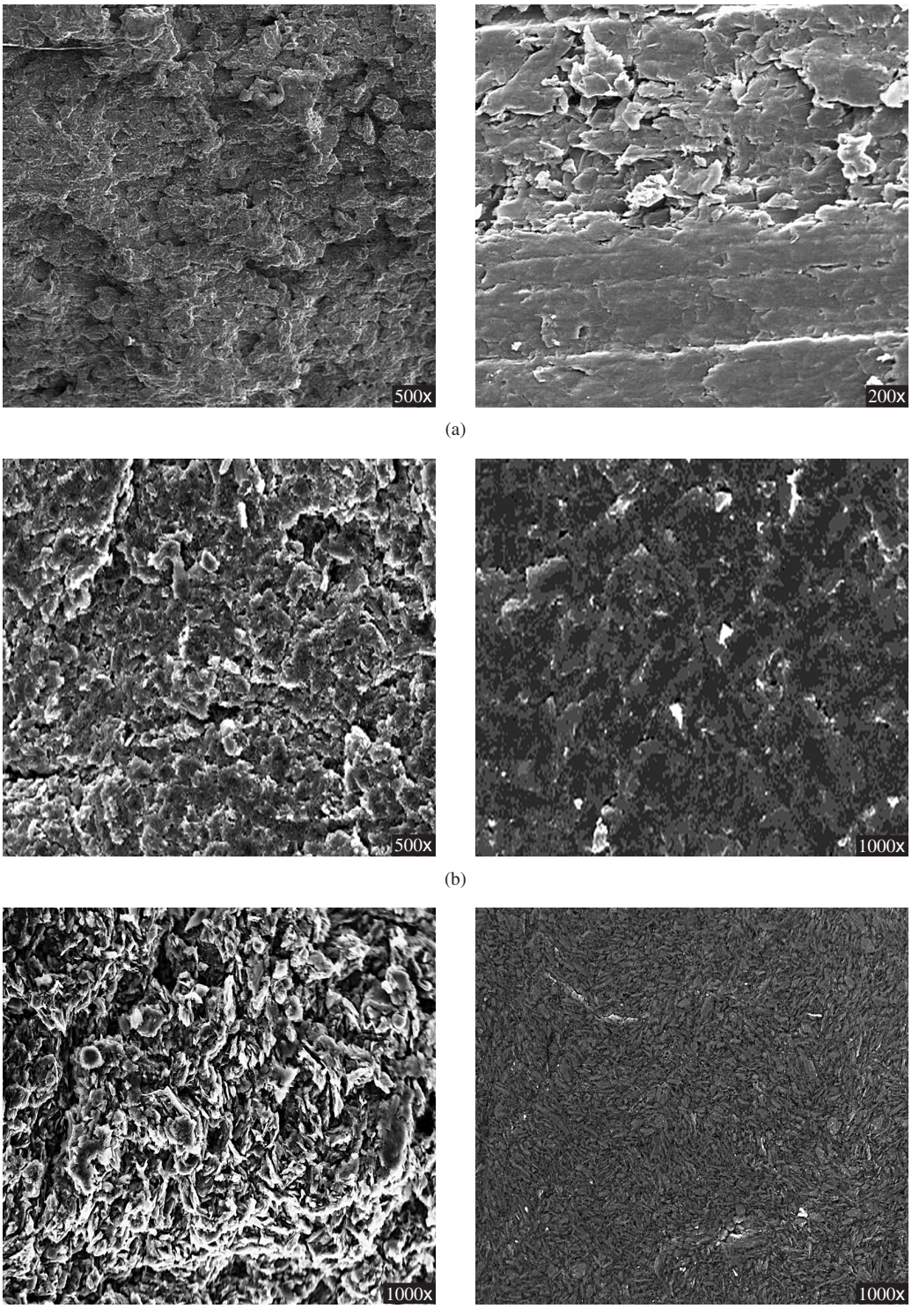

Figure 2. Scanning electron micrographs for a) graphite-PU 60% composite (graphite, w.w^{-1}); b) graphite-SR 70% composite (graphite, w.w^{-1}); and c) graphite-Araldite® 70% composite (graphite, w.w^{-1}) composites before treatment and after polishing, respectively.

4. Conclusions

All the polymers used lead to composites with capabilities to be used as electrode materials. The voltammetric response showed that at least 50% of graphite is necessary to reach current conduction.

The largest useful potential window was found for the PU, while the narrowest was observed in the SR case. The limitation of the last is in the cathodic range, while it can be used in the anodic region up to 1400 mV in neutral and acidic medium.

Thermogravimetric results permitted to determine the graphite content in the composites, after changing the furnace atmosphere from nitrogen to air. The results demonstrated that homogeneous materials can be obtained using the preparation procedure used here.

Table 4. Mass losses, temperature ranges and graphite content determined for the composites used to prepare the electrodes determined by TG.

Sample	Thermal event	Temperature interval (°C)	Mass loss or residue (%)	Graphite content (%)
PU	Resin decomposition	200-600	98	-
	CR burning	600-900	1	
	Residue	900	0	
Graphite-PU - Composite 60%*	Resin decomposition	200-600	37	
	Graphite burning	600-900	62	62
	Residue	900	0	
SR	Resin decomposition	338-600	88	-
	Residue	900	11	
Graphite-SR - Composite 70%*	Resin decomposition	300-586	23	73
	Graphite burning	633-871	73	
	Residue	900	4	
Araldite®	Resin decomposition	50-500	96	-
	CR burning	500-770	3	
	Residue	900	1	
Graphite-Araldite® - Composite 70%*	Resin decomposition	50-500	30	69
	Graphite burning	700-870	69	
	Residue	900	1	

* Graphite, w.w^{-1}.

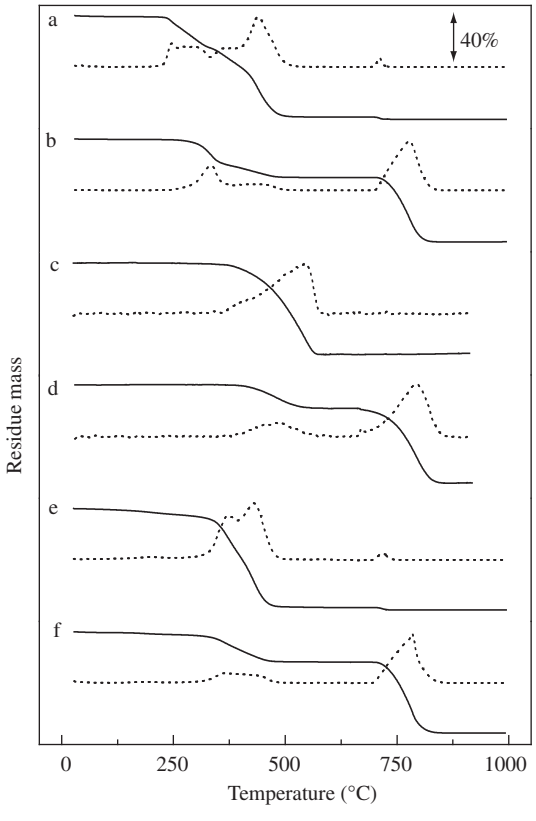

Figure 3. TG (solid) and DTG (dot) curves obtained for unmodifiede polymers and composites. a) PU; b) graphite-PU 60% composite (graphite, w.w^{-1}); c) SR; d) graphite-SR 70% composite (graphite, w.w^{-1}); e) Araldite®; and f) graphite-Araldite® 70% composite (graphite, w.w^{-1}).

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