

NANOSTRUCTURED COMPOSITES BASED ON EXPANDED GRAPHITE AND POLYMERS FOR FLEXIBLE HEATERS

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ABSTRACT

Flexible heaters, such as body heating devices for thermal comfort and health improvement for poor blood circulation are increasingly necessary and desired devices. The high cost of these devices nowadays prevents their use for low-income classes. This work proposes the construction of a low cost flexible expanded graphite sheet with excellent properties of electrical and thermal conductivity in addition to good mechanical properties. The preliminary results obtained with development of nanocomposites based on graphite nanoplatelets with acrylic polymer, show good results with thermal conductivity of 40,6 W/mK and resistivity of $1,2.10^{-2} \Omega.cm$, which makes this material possible to be applied as proposed.

Keywords: graphene, graphite, flexible conductivity plate, polymer nanocomposite, heaters.

INTRODUCTION

The search for flexible conductive graphene/nanographite films has been carried out by the scientific and technological community in recent years. Due to their resilience, fluid impermeability, chemical inertness, high temperature resistance, high electrical and thermal conductivity, and low thermal expansion, flexible graphite sheets have many applications already reported in the literature [1,2,3,4,5,6].

Currently, the most common process for producing flexible graphite sheets, consist in compressing the powder material [7, 8, 9] under a high pressure, preferably in the absence of a binder [10,11,12]. A high complexity of working with dry particulate materials becomes a limiting factor for a large-scale production due to associated occupational risks [8].

To overcome these drawbacks, polymer composites with modified graphite have been extensively explored. Several works can be cited on conductive materials, using carbon in its various allotropic and granular forms, mixed with some insulating organic polymers such as PVC [13], Teflon [14], polyethylene [15], polystyrene [16], cellulose acetate [17], epoxy adhesive [18], silicone rubber [19] among others [20]. The advantages of these composites over pure graphitic compounds are ease of handling and preparation of the material, high mechanical strength, better flexibility, durability, relatively low cost of production.

Among various applications for these materials [21,22,23,24], we can mention flexible heaters, such as body heating devices intended for thermal comfort, during recreational, sport, and other daily activities in particular at low ambient temperatures. In addition, these heaters can be used to minimize the effects of poor blood circulation in patients with diabetes mellitus and peripheral arterial disease. Other applications of flexible, low-cost, highly conductive

(electrically and thermally) graphite based composites with biopolymers can also include wearable sensors, RFID antennas, thermal interface materials, protective layers among others.

Here we show preliminary results in development of nanostructured composites based on expanded graphite with polymeric materials, looking for flexible heaters applications. The material is biocompatible thus allowing for biomedical and cosmetics applications.

MATERIALS AND METHODS

Flexible nanostructured graphite films were prepared by mixing expanded graphite (supplied by Nacional de Grafite Ltda) with polymers (~10% m/m) and water until formation of a paste. The expanded graphite is composed by graphitic sheets of irregular shape, with lateral dimensions around 10 µm and thicknesses in the range of a few tens of nm. The material was stirred continuously for 10 minutes at room temperature, and using a doctor blade technique spread on a paper for drying, see Figure 1. Samples were dried for 4 hours at 90 ° C and after calendered to provide better uniformity, alignment of graphitic flakes and reduced porosity of the material. For electrical conductivity measurements, a four probe method was used, and mechanical properties were tested using an Instron Universal Tester. Thermal conductivity evaluation tests were performed with samples cut into a rectangular shape with known dimensions in a vacuum chamber (100-500 mbar). A simple setup was built up where one side of the sample was kept at a constant elevated temperature during 3-4 h using and external Joule effect heater, after this time the heat flow was stabilized on the opposite side of the sample (a heat sink). After this the difference of temperatures between the heater (T_0) and the sink (T_1) was stabilized ($\Delta T = T_0 - T_1 = \text{const}$) and didn't change anymore. A heater was a flat resistance that provides a constant power of ~3W and the temperature was monitored using a thermocouple and it was maintained at 100°C through a NOVUS temperature control. A second thermocouple was fixed on the suspended opposite side of the sample using a little mass clamp, two other thermocouples $(T_3 = T_4)$ were used for monitoring the temperature in the heater supports to check the energy loss through them. From the known values of the power flux, ΔT and sample dimensions, the material thermal conductivity was estimated using the Fourier equation for heat conduction.



Figure 1. Expanded graphite/polymer nanocomposite paste

RESULTS AND DISCUSSION

Figure 2 shows graphite nanocomposite sheets obtained for acrylic and polyelectrolyte polymers used as binders. It is possible to verify the good formation of flexible graphite films, with dimensions of 18x30 cm, obtained with both polymers. These dimensions are limited due to the equipment used and can be increased if necessary.

The SEM images, shown in Figure 3, show a better exfoliation of the graphite sheets when the acrylic polymer was used to prepare the nanocomposite, but a better compaction when the polyelectrolyte was used.



Figure 2. Expanded graphite/polymer nanocomposite sheets (A) acrylic polymer and (B) polyelectrolyte polymer.



Figure 3. Expanded graphite/polymer nanocomposite, SEM micrograph of at the magnification of 6000x, (A) acrylic polymer and (B) polyelectrolyte polymer.

The DC electrical resistivity measurements of the thin films were conducted for the inplane direction using the Van der Pauw's (or the four-probe) method, with application of a current (I) and voltage measurements (U) employing the Agilent® B2912A Series Low Noise Power Source equipment. From the results of measurements, using the Van der Pauw factor f, for a specific sample geometry, it was possible to calculate the resistivity of the material. The results are summarized in Table I. The results show a small improvement (~25%) in conductivity with the use of polyelectrolyte polymer instead of acrylic polymer probably due to the better compaction of the sheets as seen in Figure 3.

Sample	Composition	Thickness (mm)	Resistence (Ω)	Resistivity (Ω.cm)
GAP	Graphite, Acrilic Polymer, water	0,229	0,1181	1,2. 10 ⁻²
GPP	Graphite, Polyelectrolyte Polymer, water	0,25	0,083	9,4. 10 ⁻³

Table 1 - Electrical test results

The results obtained for resistivity, $1,2.10^{-2} \Omega$.cm are superior compared with those reported in literature for various polymeric composites with carbon nanotubes with best results in the range of $7.10^{-2} \Omega$.cm [25], for buckypaper of multi-walled carbon nanotubes with values close to 1.4 Ω .cm [26] and with exfoliated graphite in cellulose solution of $4.10^{-2} \Omega$.cm [27].

The results on thermal conductivity of polymer nanocomposites are summarized in Table II, shows that no significant gain (within 10%) was observed with the use of the polyelectrolyte polymer. The reports in literature show results considerably smaller: 0,25W/mK for carbon nanotubes/epoxy polymer composites [28] and 0,85W/mK for paraffin/expanded graphite composite [29], so the composites prepared here have superior thermal properties.

Sample	Composition	Thickness (mm)	K (W/m.K)
GAP	Graphite, Acrilic Polymer, water	0,26	40,5
GPP	Graphite, Polyelectrolyte Polymer, water	0,21	44,8

Table 2 - Thermal conductivity test results

The tensile tests were performed in a Universal Testing Machine (MTS, Alliance RT/5, 1000 N), according to ASTM D 882-02 Standard [30], using a 10 mm/min test speed. The dog bone tensile specimens were produced with length, width and thickness of 100 mm, 25,0 mm and 0,30 mm, respectively. Five specimens were analyzed. The results of the Young modulus and tensile strength, for the polymer nanocomposites, are summarized in Table III.

Table 3 - Tensile test results

	Mechanical Properties		
Sample	Young modulus (MPa)	Tensile strength (MPa)	
GAP	668,1	1,57	
GPP	76,6	0,09	

Comparing the Young modulus results above for the GPP sample (76,6MPa) and for GAP sample (668,1 MPa), it can be concluded that the structure of the nanocomposite with acrylic polymer is much more resistant than that for that produced with polyelectrolyte polymer. Values found in literature for Young's module for composites are again considerably smaller, for example 220 MPa for composites of 20% expanded graphite in polyethylene [31].

The flexural strength was performed in a Universal Testing Machine (MTS, Alliance RT/5, 100N), according to ASTM D 790 Standard [32], using a 2 mm/min test speed, for specimens with dimensions of 50,8 mm /12,7 mm / 0,30 mm (length / width / thickness), respectively. Five specimens were analyzed. The results of the flexural strength of polymer nanocomposites are summarized in Table IV.

Table 4 - Flexural test results

Sample	Mechanical Properties	
Sample	Flexural strength (GPa)	
GPA	9,944	
GPP	7,247	

In the 3-point bending tests, no strain at break was observed as the material did not break within the 5% strain limit. The maximum flexural stress sustained by the test specimen during a bending test was 9,94GPa, see Table IV, for GPP sample. These results show that the sample produced with acrylic polymer (GPA) presents greater resistance to rupture by flexion than that produced with polyelectrolyte polymer (GPP).

CONCLUSIONS

Preliminary results obtained in development of nanocomposites based on expanded graphite with two kinds of polymers, acrylic polymer and polyelectrolyte polymer, show in general superior performance for the acrylic polymer based composite. It is important to emphasize that the content of expanded graphite in the composite (90%) used here is higher compared with values reported in literature. In summary, the acrylic based composite with expanded graphite developed in the present study, with thermal conductivity of 40,6 W/mK, electrical resistivity of 1,2 $\cdot 10^{-2} \Omega$.cm, tensile strength of 1,57 MPa, and flexural strength of 9,944 GPa, is a material of choice for the proposed application in low-cost flexible heaters using highly abundant natural resources.

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REFERENCES

[1] NASSAR, A. S.; ALKELANI, A. A. Clamp Load loss due to elastic interaction and gasket creep relaxation in bolted joints. J. Pressure Vessel Technol, v. 128, n. 3, p. 394–401, 2006.

[2] LUO, X.,; CHUNG, D. D. L. Vibration damping using flexible graphite. Carbon, v. 38, n. 10, p. 1510–2, 2000.

[3] LEE, S.; SEO, S.; JIN, Y.; SHIM, H.; KIM; D. A graphite foil electrode covered with electrochemically exfoliated graphene nanosheets. Electrochemistry Communications, v 12, n. 10, p. 1419–22, 2010.

[4] FU, Y.; HOU, M.; LIANG, D.; YAN, X.; FU, Y.; SHAO, Z. The electrical resistance of flexible graphite as flow field plate in proton exchange membrane fuel cells. Carbon, v. 46, p. 19–23, 2008.

[5] YAZICIA, M. S.; KRASSOWSKIA, D.; PRAKASH, J. Flexible graphite as battery anode and current collector. J Power Sources, v. 141, p.171–6, 2005.

[6] HU, K.; CHUNG, D. D. L. Flexible graphite modified by carbon black paste for use as a thermal interface material. Carbon, v. 49, p. 1075–86, 2011.

[7] SHANE, J. H.; RUSSELL, R. J.; BOCHMAN, R. A. Flexible graphene material of expanded particles compressed together. Patent:US3404061A, 68-10-01

[8] KONDO, T.; ISHIGURO, J.; WATANABE, N. Process for producing flexible graphite product. Patent: US4244934A, 1981-01-13.

[9] MERCURI, R. A.; GETZ, G.; GREINKE, R. A.; HOWARD, R. A. Ultra-thin pure flexible graphite calendered sheet and method of manufacture, Patent: US5149518A, 1992-09-22.

[10] MERCURI, R. A.; CAPP, J. P.; GOUGH, J. J. Flexible Graphite Composite. Patent: US5902762, 1999-05-11.

[11] MERCURI, R. A.; CAPP, J. P.; WARDDRIP, M. L.; WEBER, T. W. Flexible Graphite Articles and Method of Manufacture. Patent: US6432336 B1, 2002-08-13.

[12] MERCURI, R. A.; KLUG, J.; GETZ, M.G.; WEBER, T. W. Method for preparing composite flexible graphite material. Patent: US7232601 B2, 2007-07-19.

[13] ALBERTUS, F.; LLERENA, A.; ALPIZAR, J.; CERDA, V.; LUQUE, M.; RIOS, A.; VALCARCEL, M. A PVC–graphitecompositeelectrode for electroanalytical use. Preparation and some applications. Anal. Chim. Acta, v. 355, p. 23, 1997.

[14] KLATT, L. N.; CONNELL, D. R.; ADAMS, R. E.; HONIGBERG, I. L.; PRICE, J. C. Voltammetric characterization of a graphite-teflon electrode. Anal. Chem., v. 47, p. 2470, 1975. [15] ARMENTROUT, D. N.; MCLEAN, J. D.; LONG, M.W. Trace determination of phenolic compounds in water by reversed phase liquid chromatography with electrochemical detection using a carbon-polyethylene tubular anode. Anal. Chem., v. 51, p. 1039, 1979.

[16] TAPAN, K. D.; SMITA, P. Graphene-Based Polymer Composites and Their Applications. Polymer-Plastics Technology and Engineering, v. 52, n. 4, p. 319, 2013.

[17] JEON, G. W.; YOUNG, J. A.; JEONG, J. High performance cellulose acetate propionate composites reinforced with exfoliated graphene. Composites Part B: Engineering, v. 43, n. 8, p. 3412, 2012.

[18] MARTIN-GALLEGO, M.; VERDEJOA, R.; LOPEZ-MANCHADO, M. A.; SANGERMANO, M. Epoxy-Graphene UV-cured nanocomposites. Polymer, v. 52, n. 21, p. 4664, 2011.

[19] SHI, G.; ZHAO, Z.; PAI, J.; LEE, I.; ZHANG, L.; STEVERSON, C.; ISHARA, K.; ZHANG, R.; ZHU, H.; MA, J. Highly Sensitive, Wearable, Durable Strain Sensors and Stretchable Conductors Using Graphene/Silicon Rubber Composites. Adv. Funct. Mater., v. 26, p. 7614, 2016.

[20] BEZERRA DA SILVA, R. A; RABELO, A. C.; BOTTECHIA, O. L.; MUÑOZ, R. A. A.; RICHTER, E. M. Desenvolvimento, Caracterização e Aplicação Eletroanalítica de um compósito fluido de adesivo epóxi, grafite e ciclo-hexano. Quim. Nova, v. 33, n. 6, p. 1398, 2010.

[21] FU, Y.; HOU, M.; LIANG, D.; YAN, X.; FU, Y.; SHAO, Z. The electrical resistance of flexible graphite as flow field plate in proton exchange membrane fuel cells. Carbon, v. 46, p. 19, 2008.

[22] HU, K.; CHUNG, D. D. L. Flexible graphite modified by carbon black paste for use as a thermal interface material. Carbon, v. 49, p. 1075, 2011.

[23] LEE, S.; SEO, S.; JIN, Y.; SHIM, H.; KIM, D. A graphite foil electrode covered with electrochemically exfoliated graphene nanosheets. Electrochemistry Communications, v. 12, n. 10, p. 1419, 2010.

[24] YAZICIA, M. S.; KRASSOWSKIA, D.; PRAKASH, J. Flexible graphite as battery anode and current collector. J Power Sources, v. 141, p. 171, 2005.

[25] WU, M.; SHAW, L. L. A novel concept of carbon-filled polymer blends for applications in PEM fuel cell bipolar plates. International Journal of Hydrogen Energy, v. 30, p. 373, 2005.

[26] ROSCA, D.; HOA, S. V. Highly conductive multiwall carbon nanotube and epoxy composites produced by three-roll milling. Carbon, v. 47, n. 8, p. 1958, 2009.

[27] GALEMBECK, F.; FERREIRA, E. S.; DA SILVA, D. S.; BURGO, T. A. L.; BATISTA, B. C. Graphite exfoliation in cellulose solutions, Nanoscale, v. 9, p. 10219, 2017.

[28] GOJNY, F.H.; WICHMANN M. H. G.; FIEDLER B.; KINLOCH, I. A.; BAUHOFER, W. ; WINDLE, A.H.; SCHULTE, K. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. Polymer, v. 47, n. 6, p. 2036, 2006.

[29] SAR, A.; KARAIPEKLI, A. Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. Applied Thermal Engineering, v. 27, p. 1271, 2007.

[30] D882-02, Standard Test Method for Tensile Properties of Thin Plastic Sheeting, in: Annual Book of ASTM American Society for Testing and Materials, Philadelphia, PA, 2002.

[31] LI, Y.; CHEN, G. HDPE/Expanded Graphite Nanocomposites Prepared Via Masterbatch Process. Polym. Eng. Sci., v. 47, p. 882, 2007.

[32] D790-17 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials, in: Annual Book of ASTM American Society for Testing and Materials, West Conshohocken, PA, 2017.