

Thermally Stable Conducting Composites Based on a Carbon Black-Filled Polyoxadiazole Matrix

Fernando G. Souza, Jr.,¹ Maria E. Sena,² Bluma G. Soares¹

¹Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bl. J, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brasil

²Universidade Estadual Norte Fluminense, Centro de Ciência e Tecnologia, Av. Alberto Lamego, 2000, Campos dos Goytacazes, 28015-620, Rio de Janeiro, RJ, Brasil

Received 28 December 2003; accepted 8 March 2004

DOI 10.1002/app.20601

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: New thermally stable conducting materials can be obtained by dispersing conducting carbon black into poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD–DPE) solution in NMP. The blend preparation process resulted in quite good dispersed composite and a relatively low percolation threshold (around 5 wt % of CB). The effect of the compressive stress on the resistivity of composite has been evaluated. The resistivity decreases continuously as the applied pressure is increased. In addition to the electrical conductivity, the presence of carbon black resulted in higher thermally stable materials. The thermal stability, electrical

conductivity, and pressure-sensible characteristics make this conducting material a good candidate for application in manufacture of pressure sensors for high temperature ambient. This material shows a typical semiconductor behavior, characterized by an increase of conductivity with the temperature. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1631–1637, 2004

Key words: high performance polymers; conducting polymers; nanocomposites

INTRODUCTION

Oxadiazole-based polymers form a class of high-performance polymers with great thermal and chemical stability, excellent mechanical strength, and stiffness. The outstanding thermal stability was ascribed to the fact that the oxadiazole ring is electronically equivalent to the phenylene ring structure.¹ The ability of π -electrons delocalization along their polymer chains increases the mobility of charge carriers, and consequently, their tendency to transport electrons.² This characteristic makes them good candidate for application in electronic devices like sensors, light emitting diode, etc.³ Some poly(1,3,4-oxadiazole)s with substituted aromatic ring, such as poly(2,5-diphenyl-1,3,4-oxadiazole), show intense photoluminescence and electroluminescence when combined with an additional layer of electron transporter.⁴ Quantum chemical bond length calculation of poly(p-phenylene-1,3,4-oxadiazole) has shown that the alternated phenylene-oxadiazole rings along the chain promote the π -electrons delocalization in an isolated polymer chain.⁵

The applicability of these polymers is, however, limited because of their insolubility in common or-

ganic solvent and their difficult processability.^{6,7} The introduction of certain substituent on the aromatic rings, flexible bridge in the chain, or some specific units pendant to the chain has shown to be a good approach to improve solubility, provided that the conjugation is not disturbed.⁸ For example, Sena and Andrade have introduced ether groups in the polymer chain of poly(1,3,4-oxadiazole) by reacting 4,4'-diphenylether dicarboxylic acid and hydrazine sulphate in poly(phosphoric acid) medium.⁹ The resulting poly(4,4'-diphenylether-1,3,4-oxadiazole) (POD–DPE) presented good solubility in formic acid and *N*-methyl pyrrolidone (NMP) and excellent film formation ability. These features open new possibilities of applications of these materials when good environmental and thermal stability must be associated to appropriate electrical properties.

The aim of this work is to develop new conducting polymer composites with outstanding thermal stability by dispersing conducting carbon black inside the POD–DPE matrix. As it will be discussed later, the POD–DPE matrix presents some conductivity, and the combination with carbon black should give rise to materials with interesting electrical properties.

EXPERIMENTAL

Materials

4,4-Diphenyl dicarboxylic acid (DPE) (Amoco Chemical Co., USA), poly(phosphoric acid) (PPA) (Fluka

Correspondence to: F. G. Souza, Jr. (fgsj@ima.ufrj.br).

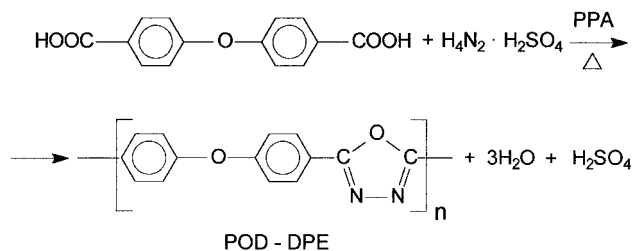


Figure 1 Synthesis of POD-DPE.

A.G., Germany), Hydrazine sulphate (HS) (Janssen Chimica, Holland), and *N*-methyl pyrrolidone (NMP) Aldrich Chemical Co., St. Louis, MO) were used as received. Conductive carbon black (Conductex 975) (CB) (average particle size = 21 nm; DBP absorption index = 169 cm³/100 g) was generously supplied by Columbian Chemicals, USA.

Synthesis of POD-DPE

The synthesis of POD-DPE, illustrated in Figure 1, was performed according to the literature.⁹ In a typical procedure, 5 g (38.4 mmol) of HS were mixed to 250 g PPA at 150°C under stirring. Then, 10 g (38.7 mmol) of DPE were added and the medium was kept at 150°C for 4 h under stirring, in nitrogen atmosphere. The resulting polymeric material was poured into water, treated with NaOH aqueous solution, filtered, and dried under vacuum at 80°C. At this condition, a POD-DPE sample was obtained with intrinsic viscosity $[\eta] = 0.90$, which corresponds to a molecular weight of $\bar{M}_w = 130,000$, as determined by size-exclusion chromatography.¹⁰ This sample also presented good film formation ability.

The characterization of the polymer was performed by Fourier Transform Infrared (FTIR) analysis on a Shimadzu FTIR 8300. The polymer was analyzed as a film casted from a NMP solution.

Blend preparation

According to the literature,⁹ the glass transition temperature of the POD-DPE matrix is too high (around 300–360°C) to be processed by the usual melt blending. Therefore, the conducting mixtures studied in this work have been prepared by dispersing carbon black in a POD-DPE solution in NMP at 140°C. The dispersion was performed under stirring for 15 min. Then, the solvent was evaporated in an oven at 150°C for 48 h and the resulting composites were pressed at 100°C for 10 min under 30 MPa pressure.

Characterization of the composites

Volume resistivity of disk-shaped samples, 1.3 cm in diameter, was measured using a typical cell connected

to a regulated voltage/current generator through which voltage was applied and resistance was measured with a multimeter. Silver paste was used to ensure good contact between samples and electrodes, namely, to eliminate the contact resistance. All values of resistivity reported in this work are values of DC resistivity, and were obtained from measurements performed in three to five samples taken from the pressed film. For measurements at different temperatures, the entire electrode system was placed in an oven, where the temperature could be monitored and controlled. The experiments have been performed in the range of 50–100°C.

The volume resistivity of the composites under pressure was measured using disk-shaped molded samples (30 mm diameter and 0.50 mm thickness). The specimen was placed between two electrodes of a typical home-made cell, where variable pressure on the specimen could be applied by varying the weight on the cell (Fig. 2). The measurement of conductivity was done on the compressed sample, 1 min after the application of pressure.

Thermogravimetric analyses of the matrix and composites were performed on a SDT2960 analyzer from TA Instruments, operating under nitrogen flow, in the temperature range of 25 to 600°C and at a heating rate of 10°C/min.

Scanning electron microscopy (SEM) was performed on Zeiss DSM 962 equipment. The films were cryogenically fractured and the surface was coated with a thin layer of gold.

Transmission electron microscopy (TEM) was performed on Zeiss DTM 962 equipment, using a voltage of 120 kV. The film was embedded in epoxy resin containing the curing agent. The material was cured and cryoultramicrotomed.

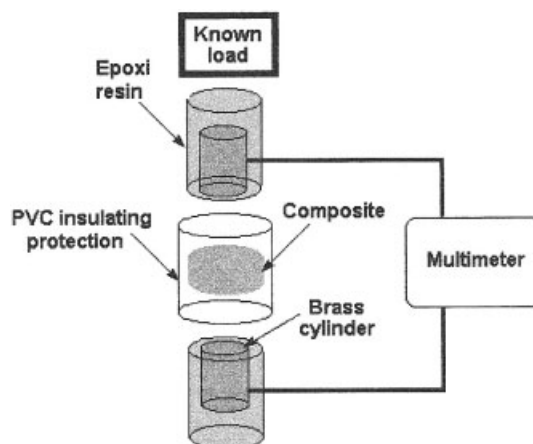


Figure 2 Homemade cell for resistivity measurement as a function of pressure.

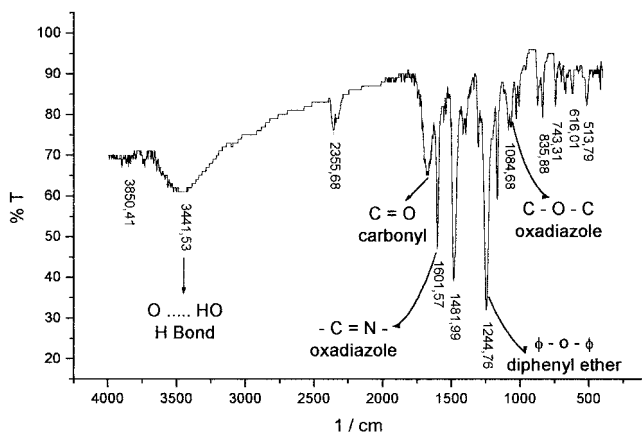


Figure 3 FTIR spectrum of POD-DPE film obtained from a NMP solution.

RESULTS AND DISCUSSION

Characterization of POD-DPE sample

Figure 3 presents the FTIR spectrum of POD-DPE film obtained from a NMP solution. The strong absorptions at 1600 and 1080 cm^{-1} are related to the C=N and C—O vibrations, respectively, corresponding to the oxadiazole ring. The diphenyl ether group is characterized by the absorption at 1244 cm^{-1} . Besides these characteristic peaks, another one at 1680–1650 cm^{-1} can also be observed, which is attributed to the carbonyl group of the residual hydrazine moiety. This group is normally formed as the intermediary, during the synthesis of polyoxadiazole.⁹ The amount of hydrazine in the POD-DPE sample synthesized in this work was in the range of 5–8%, as determined by TGA analysis.¹⁰

The volume resistivity value of the pure POD-DPE sample was found to be $3.3 \times 10^7 \Omega \cdot \text{cm}$, which corresponds to the resistivity of a semiconducting material.

The electrical conductivity of the carbon black-based composites

The effect of the CB concentration on the volume resistivity of POD-DPE-based composites is illustrated in Figure 4. The presence of CB in a concentration up to approximately 5% resulted in composites with resistivity values similar to that of the pure matrix. After this concentration, known as the percolation threshold point, the resistivity decreases continuously until approaching a plateau close to the CB resistivity. This plateau is reached at a CB concentration in the range of 40–50 wt %.

The percolation threshold at around 5% is considered low for polar hosts, compared to other systems related in the literature.^{11,12} This behavior can be attributed to the procedure employed to prepare the

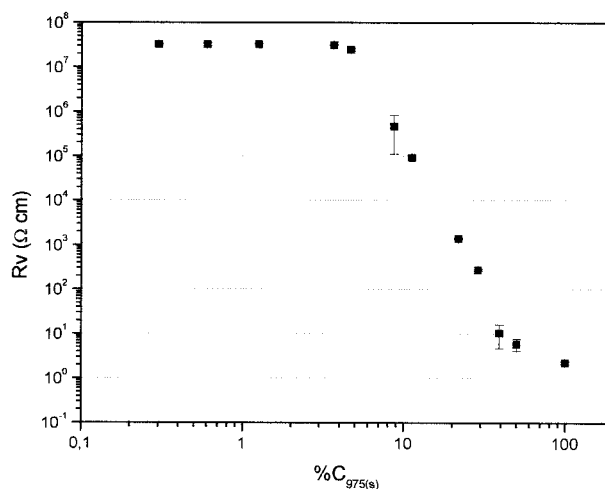


Figure 4 Effect of the CB concentration on the volume resistivity of POD-DPE-based composites.

composites, that is, the dispersion process results in lower shear stress, which decreases the possibility for reducing the highly structured CB aggregates to primary particles. The structured CB aggregates favor the contact each other at lower CB concentration.

As mentioned in the Experimental part, the resistivity of each composite was taken from measurements of three to five samples from the same film. Table I presents the error found for each composite, which was very small compared to the magnitude of the resistivity values. This result indicates that the process used to disperse CB aggregates inside the POD-DPE solution resulted in very homogeneous conducting composite films.

The SEM micrographs of the composites with 11 and 40 wt % of CB are presented in Figure 5. The micrograph of the composite containing 11 wt % of CB [Fig. 5(a)] displays quite a good CB dispersion, with several white particles and agglomerates uniformly

TABLE I
Volume Resistivity of the Composites as a Function of the Volume Fraction of Carbon Black

% CB	Rv ($\Omega \text{ cm}$)
0	$(3.3 \pm 0.2) \times 10^7$
0.3	$(3.2 \pm 0.1) \times 10^7$
0.6	$(3.2 \pm 0.3) \times 10^7$
1.25	$(3.2 \pm 0.1) \times 10^7$
3.66	$(3.10 \pm 0.05) \times 10^7$
4.67	$(2.4 \pm 0.1) \times 10^7$
8.65	$(5.0 \pm 1) \times 10^5$
11.18	$(9.0 \pm 1) \times 10^4$
21.84	$(1.37 \pm 0.05) \times 10^3$
28.84	$(2.7 \pm 0.1) \times 10^2$
39.22	$(1.0 \pm 0.6) \times 10^1$
50.08	$(6.0 \pm 2) \times 10^0$
100	$(2.2 \pm 0.1) \times 10^0$

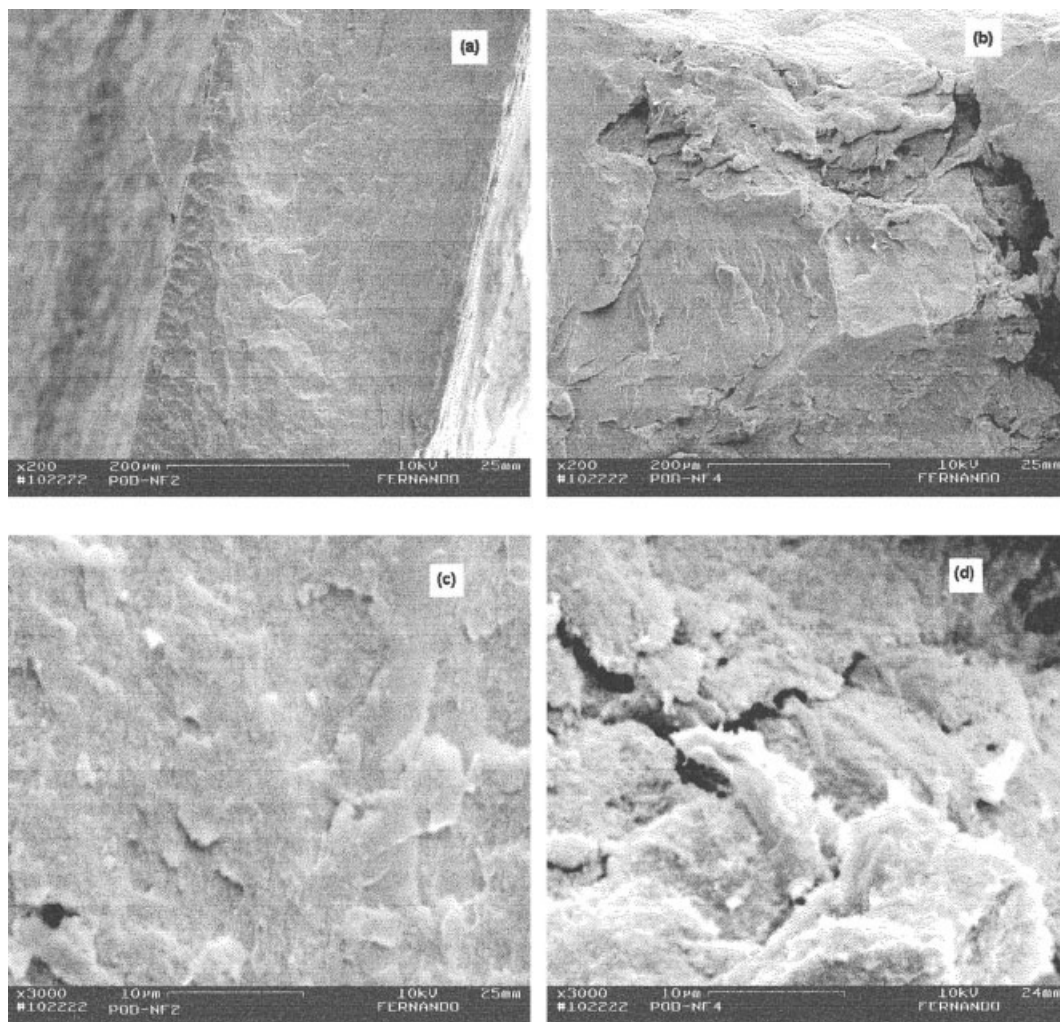


Figure 5 SEM micrographs of the composites containing 11 wt % (a = 200 \times ; b = 3000 \times) and 40 wt % (c = 200 \times ; d = 3000 \times) of CB.

dispersed inside the matrix. Composite with a higher amount of CB resulted in a more heterogeneous morphology with an irregular fracture. This morphological aspect suggests that the dispersion process used in this work was not efficient for high loaded composites. The heterogeneity was not observed in electrical resistivity measurements, but has strongly affected the film stability. Indeed, films with CB concentration higher than 40 wt % were very difficult to handle due to their brittle characteristic.

The good dispersion of CB in the composite containing 11 wt % of the CB was also observed from TEM. The corresponding micrograph is illustrated in Figure 6, where it is possible to observe two distinct regions: the light one constituted by the POD–DPE matrix, and the dark region that corresponds to the carbon black. The CB is in the form of well-connected agglomerates, forming the conducting network, which is responsible for the electron transport inside the material.

The dependence of the resistivity with temperature

The volume resistivity of the POD–DPE composites as a function of the temperature was studied in the range of 50 to 100°C. Figure 7 illustrates this behavior for different carbon black content. The resistivity decreases with the temperature increase. This behavior is more significant in composites containing low amount of CB (1.25 to 4.7%), and suggest a typical semiconductor behavior. It is important to observe that the decrease of electric resistance is not sharp, being useful for temperature sensors application.

The natural logarithm of the conductivity against the inverse absolute temperature for the pure POD–DPE and the corresponding composites is shown in Figure 8. From this relationship, the activation energy related to the conduction process was calculated, whose values are summarized in Table II. Below the percolation threshold point, the activation energy increases as filler concentration increases, indicating that

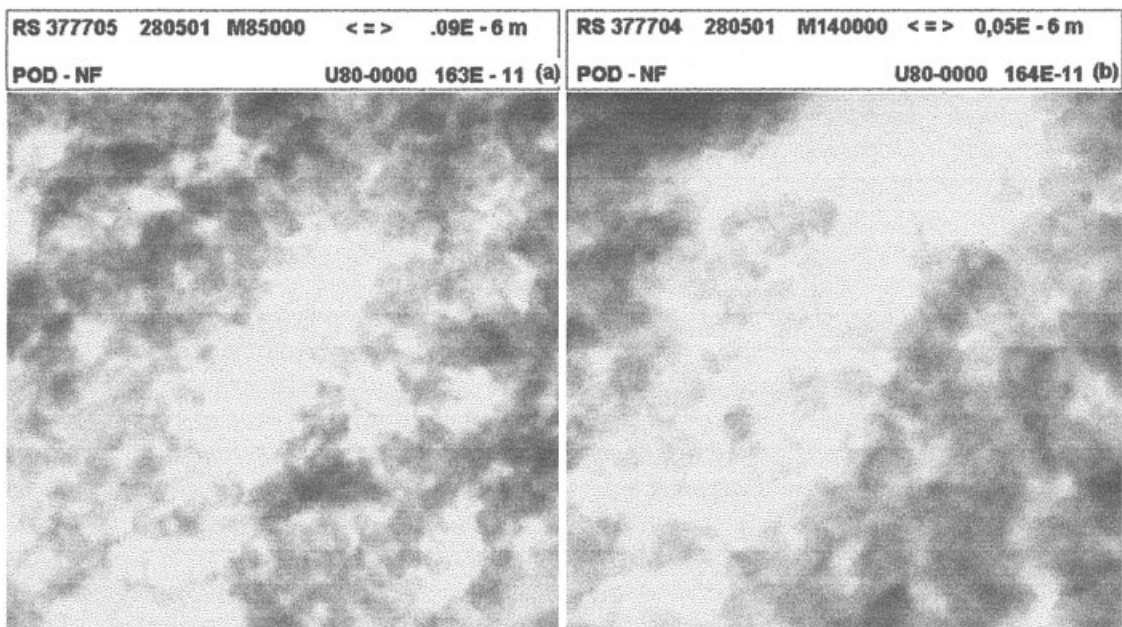


Figure 6 SEM micrographs of the composite containing 11 wt % of CB. (a) 85,000x and (b) 140,000x.

the conduction process is more difficult before the percolation threshold. After this point, the conduction process becomes easier, indicating by the continuous decrease on the activation energy.

Probably, the carbon black particles acts as impurities that modify the polymer chains distances, resulting in minicapacitors that, when charged, hold back the electron flow, driving an electric conduction activation energy rise. This initial behavior is making up for the carbon black content rise that allows the electron conductor pathway formation, decreasing the activation energy and the electric resistivity.

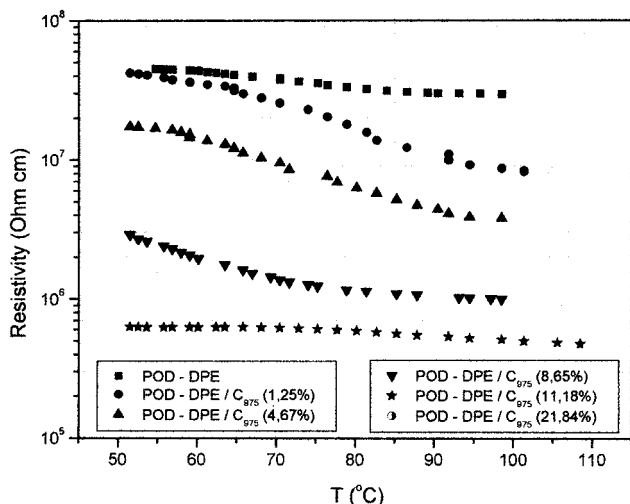


Figure 7 Electrical resistivity as a function of temperature for pure POD-DPE and its composites.

The dependence of resistivity with applied pressure

The pressure has a significant effect on the conductivity of conducting rubber composites. Depending upon the degree of applied pressure and the nature of dispersed conducting additive, the conductivity of such composites may change by several orders of magnitude.¹³ The nature of the insulating polymer matrix also exerts great influence on the pressure-resistivity dependence. Sau et al.¹⁴ reported that for rubber-based matrices, the conductivity of the composite might increase or decrease with the increase of pres-

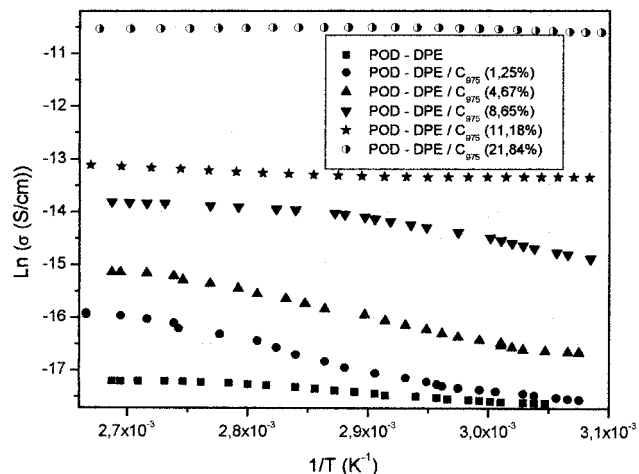


Figure 8 Natural logarithm of the conductivity against the inverse absolute temperature for the pure POD-DPE and its composites.

TABLE II
Activation Energy of POD–DPE and Some
of the Carbon Black-Based Composites

CB (%)	E_{at} (eV)	Correlation
0	$(2.31 \pm 0.08) \times 10^{-1}$	0.987
1.25	$(7.6 \pm 0.2) \times 10^{-1}$	0.991
4.67	$(7.6 \pm 0.1) \times 10^{-1}$	0.996
8.65	$(4.8 \pm 0.3) \times 10^{-1}$	0.962
11.18	$(1.04 \pm 0.04) \times 10^{-1}$	0.983
21.84	$(2.6 \pm 0.1) \times 10^{-2}$	0.965

sure, depending upon the viscosity and stiffness of the matrix.

The POD–DPE matrix used in this work constitutes a rigid matrix with very high glass transition temperature. The variation of electric resistance with applied pressure (KPa) is shown in Figure 9. These studies were performed with the composite containing 25 wt % of CB, which presents a resistivity of $152.4 \Omega \cdot \text{cm}$ and also good mechanical stability. The resistivity decreases continuously as the applied pressure is increased. This behavior is contrary to that reported by Sau et al.,¹⁴ who have suggested that rigid matrices result on an increase of resistivity with an increase in pressure as a consequence of a breakdown of existing conductive networks.

The results found in our system may be attributed to the presence of large CB agglomerates as a consequence of the procedure used to prepare the composite. With applied pressure, the agglomerates touch each other, raising the electric conductivity. This reduction in electric resistivity follows a linear behavior, eq. (1), where R is the electric resistance and P is the pressure applied. This linear model shows a correlation equal to 0.9987.

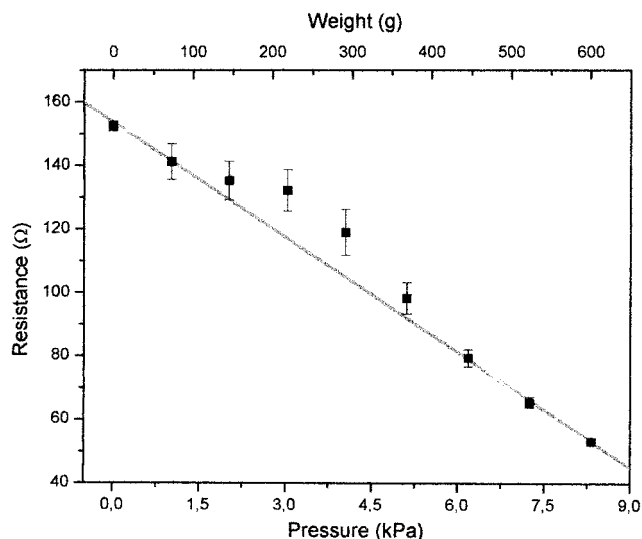


Figure 9 Electrical resistance (Ohm) as a function of the applied pressure (kPa).

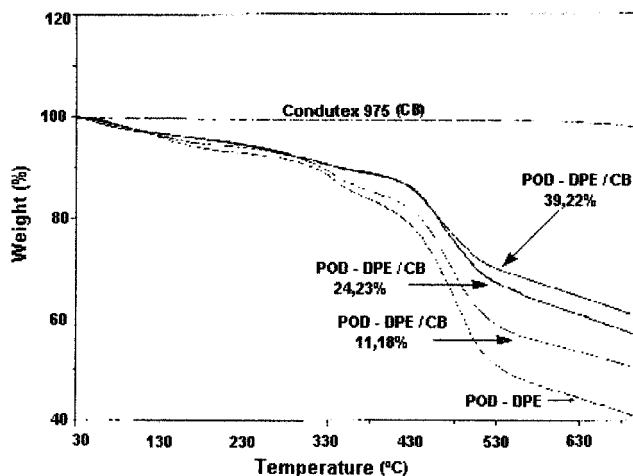


Figure 10 Thermogravimetric decomposition curve of POD–DPE matrix and its corresponding composites.

$$R = (154 \pm 2) - (12,1 \pm 0,2) \times P \quad (1)$$

In the case of rubber-based systems reported by Sau, the mixtures were done in a higher shear stress condition, in a Brabender Plasticorder, which favor the breakdown of the CB agglomerates into highly structured CB aggregates and also into primary particles. The additional forces promoted by the applied pressure would favor the breakdown of these aggregates in smaller CB particles, destroying the conducting network.

Thermal stability

One of the important applications of polyoxadiazole-based conducting composites is on the development of thermal stable materials. Therefore, it is useful to determine the influence of carbon black on thermal stability of these composites. Figure 10 compares the thermogravimetric decomposition curve of the POD–DPE matrix with those of the corresponding composites. The first weight loss occurs around 130–190°C for all samples, and is related to the water normally present in the samples. The second step of decomposition is related to the elimination of water as a consequence of the cyclization process of residual hydrazine moiety into oxadiazole.¹⁰ The third step (between 400–500°C) is related to the polyoxadiazole chain. There is no influence of the CB on the onset of this decomposition step. However, the decomposition step related to the hydrazine cyclization is significantly affected by the presence of CB. This degradation process decreases as the amount of CB in the composite increases, and completely disappears at a high amount of CB. This behavior may be related to the decrease of the POD–DPE proportion in the composite and, con-

sequently, the proportion of the residual hydrazine moiety.

CONCLUSION

New thermally stable conducting materials can be obtained by dispersing conducting carbon black into polyoxadiazole solution in NMP. The blend preparation process resulted in quite good dispersion of CB inside the POD–DPE matrix and a relatively low percolation threshold (around 5 wt % of CB). The dispersion of CB was more difficult in composites containing higher filler concentration.

The effect of the compressive stress on the resistivity of composite has been evaluated. The resistivity decreases continuously as the applied pressure is increased. This behavior is not expected for a rigid matrix, and can be explained as follows: despite the good dispersion achieved in these composites, the procedure used to prepare the blend involves low shear stress conditions, favoring the presence of agglomerates, together with high-structured aggregates. With applied pressure, the agglomerates break into aggregates that have more chance to touch each other, thus forming additional conducting network, which is responsible for the increase of conductivity.

In addition to the electrical conductivity, the presence of carbon black resulted in higher thermally sta-

ble materials. The thermal stability, electrical conductivity, and pressure-sensible characteristics make this conducting material a good candidate for application in manufacture of pressure sensors for high temperature ambient.

References

1. Cotter, R. J.; Matzner, M. I.; Blomquist, A. F.; Wasserman, H., Eds. Ring-Forming Polymerizations. Heterocyclic Rings, 13B; Academic Press: New York, 1972; Part B1.
2. Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *J. Science* 1995, 267, 1969.
3. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymer*; Marcel Dekker: New York, 1998.
4. Kamminorz, Y.; Schulz, B.; Brehmer, L. *Synthetic Metals* 2000, 111–112, 75.
5. Kamminorz, Y.; Schulz, B.; Scharader, S.; Brehmer, L. *Synthetic Metals* 2001, 122, 115.
6. Janietz, S.; Anlauf, S.; Wedel, S. *Synthetic Metals* 2001, 122, 11.
7. Song, S. Y.; Ahn, T.; Shim, H. K.; Song, I. S.; Kim, W. H. *Polymer* 2001, 42, 4803.
8. Iosip, M. D.; Bruma, M.; Ronova, I.; Szesztay, M.; Muller, P. *Eur Polym J* 2003, 39, 2011.
9. Sena, M. E.; Andrade, C. T. *Polym Bull* 1994, 33, 439.
10. Gomes, D.; Pinto, J. C.; Borges, C. *Polymer* 2001, 42, 851.
11. Wessling, B. *Synthetic Metals* 1991, 45, 119.
12. Miyasaka, K.; Watanabe, K.; Jojima, E.; Ainda, H.; Sumita, M.; Ishikawa, K. *J Mater Sci* 1982, 17, 610.
13. Kanamoni, K. *Int Polym Sci Technol* 1986, 13, 2.
14. Sau, K. P.; Chaki, T. K.; Khastgir, D. *Rubber Chem Technol* 2000, 73, 310.