

SBS/Pani · DBSA mixture plasticized with DOP and NCLS – Effect of the plasticizers on the probability density of volume resistivity measurements

Fernando G. Souza Jr. ^{a,b}, José C. Pinto ^{a,*}, Bluma G. Soares ^b

^a *Programa de Engenharia Química COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária,
CP: 68502, Rio de Janeiro, 21945-970 RJ, Brazil*

^b *Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Cidade Universitária, Centro de Tecnologia,
Bl. J, Rio de Janeiro, 21945-970 RJ, Brazil*

Received 25 September 2006; received in revised form 30 January 2007; accepted 22 February 2007
Available online 2 March 2007

Abstract

Plasticized mixtures of styrene–butadiene–styrene block copolymer (SBS) and Polyaniline (Pani) were prepared in a Haake internal mixer. Two different plasticizers were used: dioctyl phthalate (DOP) and cashew nut shell liquid (CNSL). Pani and plasticizers were characterized by FTIR and the resistive behavior of plasticized mixtures was investigated along the electrification time. It is shown that obtained experimental data are subject to deterministic dynamic fluctuations that cannot be described by single normal probability distribution functions (PDF) along the time. The PDF analysis shows that obtained PDFs must be described as sums of at least three distinct Gaussian distributions with different areas. It is also shown that the Gaussian component with larger area may provide better representation of the measured volume resistivity values.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Polyaniline; Conducting composite; CNSL; Modeling; Probability distribution function

1. Introduction

Preparation of conducting composites that use styrene–butadiene–styrene (SBS) triblock copolymers as insulating matrixes may be very interesting because these materials allow for development of conducting and/or semi-conducting resins with good flexibility and elasticity without vulcanization [1–3].

The use of polyaniline (Pani) as an intrinsic conductive polymer was proposed by MacDiarmid in 1985. Since then, polyaniline has attracted the interest of many researchers due to its high conductivity, easiness of preparation, good stability to the heat and to the air and low production costs [4–7]. The main disadvantage of this conducting polymer, however, is its poor processibility both in the melt and in solutions of common organic solvents, because of the stiffness of its backbone [8]. This disadvantage can be minimized if Pani is doped with functional protonic acids, such as dodecylbenzene-sulfonic acid (DBSA) [9].

* Corresponding author. Tel.: +55 21 2562 8337; fax: +55 21 2562 8300.

E-mail address: pinto@peq.coppe.ufrj.br (J.C. Pinto).

Cashew nut shell liquid (CNSL) is an important by-product of the cashew nut industry. The potential annual availability of this material, which accounts for about 32 wt% of the cashew shell, is enormous. Industrial application of CNSL-based products are numerous, including brake linings, paints and primers, foundry chemicals, lacquers, cements, coatings and transformed cardanol for gasoline stabilization [10]. The main component of CNSL is cardanol, a phenol derivative that presents a C15 unsaturated hydrocarbon chain with 1–3 double bonds in the meta position [11,12]. Because of its structure, cardanol can also be used as a stabilizer of liquid–liquid dispersions and/or a plasticizer. As a matter of fact, it was shown in a previous paper that CNSL can be used to improve the melt processing of conductive mixtures of Pani and SBS [13].

Probability distribution functions (PDF) are used to describe the spread of noisy experimental data around an average value. Probability distributions are generally represented in terms of integrals (continuous variables) or histograms (discrete variables). The commonest PDF is the normal distribution, normally used for computation of confidence limits of experimental data.

PDFs must satisfy the following conditions:

1. PDFs must be non-negative everywhere;
2. The area bounded by PDFs must be equal to 1 [14];
3. The probability for a random value to be within the interval (α, β) must be equal to the area bounded by the PDF within this interval (Fig. 1).

Most investigations assume that the spread of experimental fluctuations can be appropriately represented by a normal distribution. This approach is very useful for a large number of reasons, including

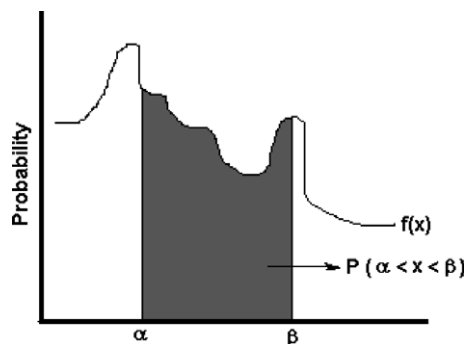


Fig. 1. Illustrative example of a PDF.

the simplicity of the normal representation, as described by Bard [15]. However, experimental fluctuations can follow rather different distribution patterns. Analysis of distributions of experimental fluctuations can allow for improved interpretation of the experimental technique and of the obtained experimental data.

In this work, commercial plasticizers were mixed with SBS and Pani. The effects of the increasing plasticizer concentrations on the electrical behavior of conductive SBS/Pani mixtures were analyzed with the help of empirical statistical models. This constitutes a very interesting experimental system for this sort of investigation because it combines the analyses of well-known conductive (polyaniline) and non-conductive (SBS) materials with the analyses of a broad range of semi-conductive composites (plasticized and non-plasticized SBS/Pani mixtures). The PDFs that describe the scattering of available experimental volume resistivity data were then determined and analyzed. Obtained results show that volume resistivity may be strongly correlated with time, which means that measurement of volume resistivities may be subject to long deterministic dynamic effects, which has been largely overlooked in the literature. Based on the PDF analysis, two distinct numerical procedures are proposed for definition of the most representative volume resistivity values among obtained experimental data.

2. Experimental

2.1. Materials

SBS (TR-1061; PBD content = 70 wt%; M_w = 120,000 g/mol, density = 0.98 g/cm³) was kindly supplied by Petroflex S.A. (Rio de Janeiro, Brazil). Aniline (analytical grade from Vetec, Brazil), ammonium peroxydisulfate (APS) (analytical grade from Vetec, Brazil), dodecylbenzenesulfonic acid (DBSA; commercial grade from Solquim LTDA, Brazil), DOP (commercial grade from Vulcan Ltda, Brazil) and CNSL (commercial grade kindly supplied by RESIBRAS Ltda, Brazil) were used without further purification.

2.2. Synthesis of Pani · DBSA

Polyaniline doped with DBSA (Pani · DBSA) was synthesized with the one-step route in toluene, as described in the literature [16]. In a typical run,

4.7 mL (0.051 mol) of aniline and 16.7 g (0.051 mol) of DBSA are dissolved into 250 mL of toluene under constant stirring. The medium is kept at 0 °C and an aqueous solution containing 11.36 g (0.051 mol) of APS in 40 mL of water is slowly added over a period of 20 min. After 6 h, the reaction medium is poured into methanol, filtered, washed several times with

methanol and dried. Pani · DBSA prepared with this procedure presents a surface conductivity of 2.1 S/cm. The experimental setup included a Keithley 6517A electrometer; a Minipa ET2907 multimeter and a home-made four-probe device, with average probe distance of 0.17 ± 0.03 cm. The electrical resistivity measurements were performed with the

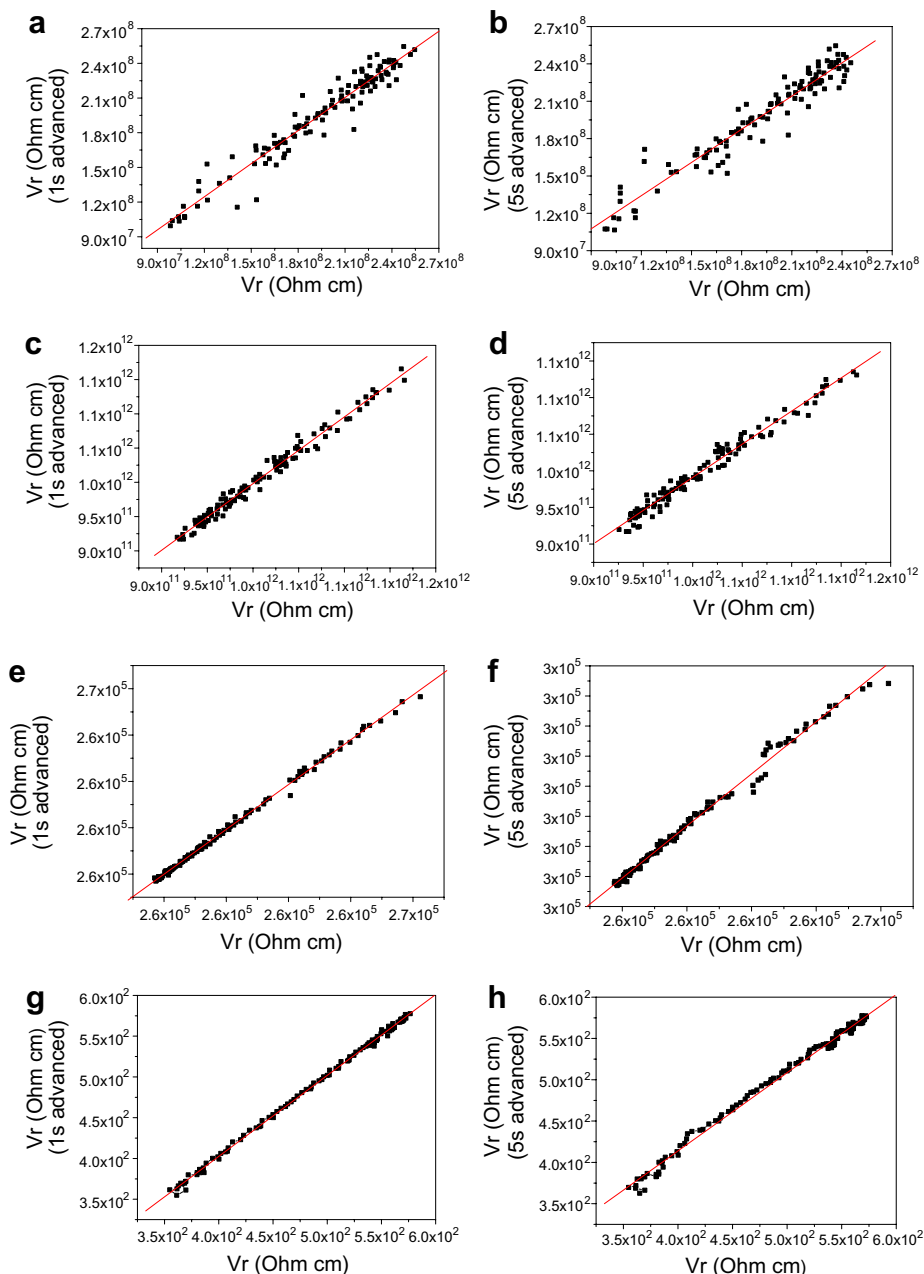


Fig. 2. Time series correlations of SBS/Pani mixtures displaced (a) 1 s and (b) 5 s; mixtures containing 20 phr of DOP, displaced (c) 1 s and (d) 5 s; mixtures containing 20 phr of CNSL displaced (e) 1 s and (f) 5 s; and Pani · DBSA displaced (g) 1 s and (h) 5 s.

conventional four point method [17,18], using pressed pellets of composite particles prepared at room temperature.

2.3. Preparation of mixtures

First, a specified amount of SBS copolymer is introduced into a Haake Rheocord 9000 internal mixer operating with a Cam rotor at 60 rpm and 100 °C. After 2 min, proper amounts of conductive filler and plasticizer are added to the mixture and mixing is performed for 8 min. The total amount of used materials never exceeded 60 g.

2.4. Volume resistivity and PDF determination

The composites and the pure Pani · DBSA were pressed in disk molds with 38 mm of diameter, at 100 °C, for 3 min, using a force of 4.5 ton. All resistivity measurements were performed with a Keithley 6517A electrometer and resistivity data were taken during 120 s with intervals of 1 s. Obtained data were recorded for further analyses. An ASTM D257 sample holder was used for determination of the volume resistivity (V_r). Empirical modeling

was performed with the help of the public R software and with routines written in Python.

3. Results and discussion

3.1. Exponential modeling and PDF determination

In a previous paper [19], it was observed that the reproducibility of measured volume resistivity depends on the experimental conditions and on measured volume resistivity values. For this reason, the detailed analysis of experimental errors during volume resistivity tests is analyzed here.

Volume resistivity tests can supply an expressive large number of experimental data, given the fast measuring procedure. This allows for analysis of time-dependence of experimental measurements. Figs. 2 and 3 show how volume resistivities change along the time. Fig. 2 shows that volume resistivities measured at different times are strongly correlated, while Fig. 3 shows very clearly that volume resistivities experience some sort of long-lasting dynamic effect during the measurement procedure. Fig. 2 shows that obtained experimental data seem to follow a well defined trend along the time, while Fig. 3 shows very clearly the dynamic trajectory of mea-

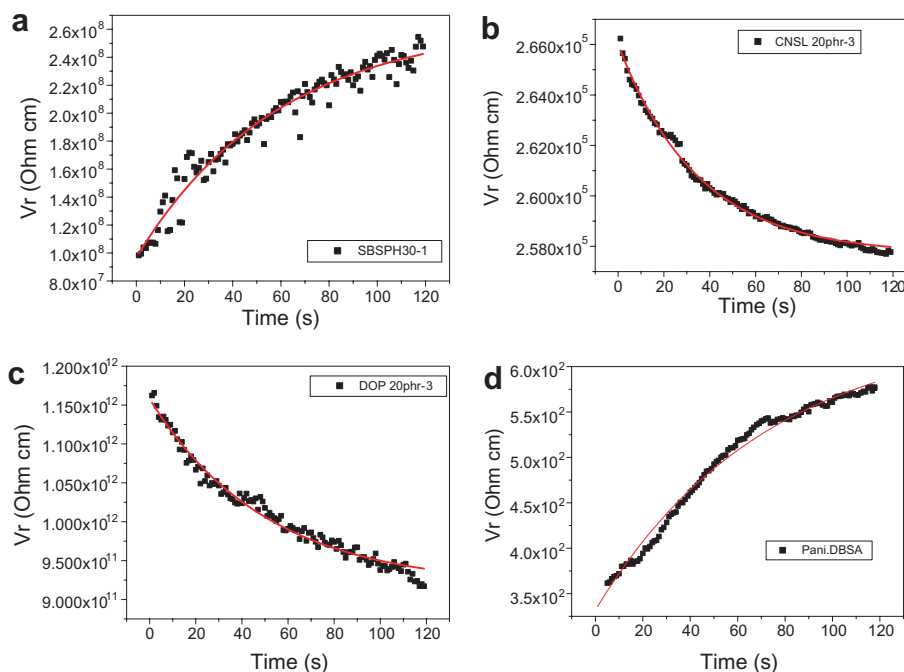


Fig. 3. Volume resistivity as a function of time for (a) SBS/Pani mixtures; (b) mixtures containing 20 phr of DOP; (c) mixtures containing 20 phr of CNSL and (d) Pani · DBSA.

sured volume resistivities. These results indicate that fluctuations of measured resistivity values are also subject to deterministic dynamic effects, which cannot be explained only in terms of random fluctuations. This point has been completely overlooked and has not been discussed in the literature yet.

Auto-correlation analyses of measured resistivities for different samples are shown in Table 1. Volume resistivity measurements of SBS do not present significant auto-correlation, indicating that the observed phenomenon is related to Pani. Volume resistivity measurements of SBS–Pani mixtures, plasticized SBS–Pani mixtures and pure Pani·DBSA show very strong correlations when results are displaced 1–5 s. These results indicate that time-dependence of measured data may be related to polarization effects, induced by the electrical field on the conductive Pani chains. The observed behavior is believed to be caused by morphological arrangements of the conductive filler inside the insulating matrix that constitutes the composite. Similar

effects may occur in pure Pani·DBSA materials, as it is well known that conductive Pani islands may be surrounded by less conductive polyaniline matrixes [20,21]. As the pure SBS does not contain Pani, this dynamic effect is absent for analyzed SBS samples. This is a very interesting result because it indicates that variances of observed values can indeed depend on the analyzed sample (as observed previously) and that volume resistivity tests should be adjusted for different measuring conditions. More interesting, this indicates that the composite components are subject to some sort of internal organization during measurement, possibly due to the high mobility and polar nature of the constituents of the polymer materials, which may eventually lead to significant changes of the electrical resistivity along time. Therefore, understanding of these dynamic effects may be very useful for interpretation of the conductive mechanism and for design of electrical and electronic components, when the electrical characteristics of the material must be precisely controlled.

Obtained volume resistivity measurements suggest a first-order exponential dynamics, as illustrated in Fig. 3. This can probably be attributed to existence of some sort of charge and discharge mechanism. For this reason, the empirical model presented in Eq. (1) was used for analyses of obtained experimental data. It is important to emphasize that measurements were performed with continuous electrical current, so that capacitive, inductive and resistive contributions of the overall volume resistivity values cannot be discriminated from each other. Thus, future investigations should be focused on this particular issue.

$$V_r = V_{r0} + A_1 \times e^{-t/A_2} \quad (1)$$

In Eq. (1), V_r is the volume resistivity, in Ω cm; V_{r0} is the final volume resistivity, in Ω cm; A_1 and A_2 are empirical model parameters and t is the time in s. If V_{r0} increases, the entire curve is shifted towards higher resistivity values. If A_1 increases, larger differences are observed between the initial and final measured values. A_2 is related to the sluggishness of the experimental responses. If A_2 is large, then dynamic effects last for longer times.

Parameter values obtained from empirical exponential modeling are shown in Table 2. When obtained correlations among experimental and calculated values were smaller than 0.90, model results were rejected. Model results were rejected for all SBS samples (which are not subject to the observed

Table 1
Time series correlation

Pani (w%)	Plasticizer/phr	Time advanced (s)	R^2
0	–/–	1	–0.00837
		2	–0.01391
		3	–0.00993
		4	–0.00872
		5	–0.00849
30	–/–	1	0.96923
		2	0.95041
		3	0.94621
		4	0.95129
		5	0.96279
	DOP/20	1	0.99151
		2	0.98931
		3	0.98888
		4	0.98979
		5	0.98706
	CNSL/20	1	0.99882
		2	0.99812
		3	0.99715
		4	0.99647
		5	0.99567
100	–/–	1	0.99926
		2	0.99854
		3	0.99795
		4	0.99749
		5	0.99583

Table 2
Parameter estimates for the exponential models

Pani (w%)	Plasticizer/phr	Sample	Parameters			R^2
			V_{r0}	A_1	A_2	
0	–/–	1	$-(2.44 \pm 0.00) \times 10^{16}$	$(2.47 \pm 0.07) \times 10^{16}$	$(3 \pm 35) \times 10^4$	0.0000
		2	$(2.04 \pm 0.00) \times 10^{16}$	$-(2.08 \pm 0.04) \times 10^{16}$	$-(0 \pm 5) \times 10^{11}$	–0.1270
		3	$(4.42 \pm 0.00) \times 10^{17}$	$-(4.41 \pm 0.08) \times 10^{17}$	$-(0 \pm 7) \times 10^{54}$	–0.0047
30	–/–	1	$(2.65 \pm 0.06) \times 10^8$	$-(1.68 \pm 0.05) \times 10^8$	$(5.9 \pm 0.5) \times 10^1$	0.9589
		2	$(3.59 \pm 0.08) \times 10^9$	$-(2.09 \pm 0.08) \times 10^9$	$(2.3 \pm 0.1) \times 10^2$	0.9987
		3	$(7.4 \pm 0.5) \times 10^9$	$-(5.4 \pm 0.5) \times 10^9$	$(4.8 \pm 0.5) \times 10^2$	0.9986
	DOP/5	1	$(5.95 \pm 0.08) \times 10^9$	$-(2.09 \pm 0.08) \times 10^9$	$(2.0 \pm 0.1) \times 10^2$	0.9980
		2	$(4.78 \pm 0.05) \times 10^9$	$-(1.45 \pm 0.05) \times 10^9$	$(2.08 \pm 0.09) \times 10^2$	0.9988
		3	$(5.6 \pm 0.1) \times 10^9$	$-(2.0 \pm 0.1) \times 10^9$	$(2.7 \pm 0.2) \times 10^2$	0.9985
	DOP/10	1	$(4.99 \pm 0.01) \times 10^{10}$	$(1.39 \pm 0.01) \times 10^{10}$	$(3.80 \pm 0.09) \times 10^1$	0.9922
		2	$(3.15 \pm 0.01) \times 10^{11}$	$(1.65 \pm 0.01) \times 10^{11}$	$(4.8 \pm 0.1) \times 10^1$	0.9946
		3	$(1.386 \pm 0.008) \times 10^{11}$	$(3.8 \pm 0.1) \times 10^{10}$	$(3.3 \pm 0.3) \times 10^1$	0.9198
	DOP/15	1	$(3.42 \pm 0.02) \times 10^{11}$	$(2.46 \pm 0.02) \times 10^{11}$	$(5.4 \pm 0.1) \times 10^1$	0.9968
		2	$(4.08 \pm 0.03) \times 10^{11}$	$(2.84 \pm 0.03) \times 10^{11}$	$(5.9 \pm 0.2) \times 10^1$	0.9953
		3	$(2.93 \pm 0.02) \times 10^{11}$	$(2.06 \pm 0.04) \times 10^{11}$	$(2.6 \pm 0.1) \times 10^1$	0.9697
	DOP/20	1	$(1.320 \pm 0.003) \times 10^{12}$	$(1.28 \pm 0.04) \times 10^{11}$	$(3.4 \pm 0.3) \times 10^1$	0.8952
		2	$(7.2 \pm 0.3) \times 10^{11}$	$(2.2 \pm 0.3) \times 10^{11}$	$(1.1 \pm 0.2) \times 10^2$	0.9019
		3	$(8.96 \pm 0.06) \times 10^{11}$	$(2.55 \pm 0.05) \times 10^{11}$	$(6.1 \pm 0.3) \times 10^1$	0.9809
	CNSL/5	1	$(1.195 \pm 0.005) \times 10^9$	$-(8.90 \pm 0.04) \times 10^8$	$(1.29 \pm 0.01) \times 10^2$	0.9999
		2	$(1.440 \pm 0.007) \times 10^9$	$-(1.06 \pm 0.01) \times 10^9$	$(8.3 \pm 0.1) \times 10^1$	0.9994
		3	$(2.23 \pm 0.01) \times 10^9$	$-(1.38 \pm 0.01) \times 10^9$	$(6.6 \pm 0.1) \times 10^1$	0.9981
	CNSL/10	1	$(1.439 \pm 0.008) \times 10^9$	$-(1.06 \pm 0.01) \times 10^9$	$(5.6 \pm 0.1) \times 10^1$	0.9974
		2	$(1.79 \pm 0.01) \times 10^9$	$-(1.24 \pm 0.01) \times 10^9$	$(5.1 \pm 0.1) \times 10^1$	0.9962
		3	$(9 \pm 30) \times 10^9$	$-(9 \pm 30) \times 10^9$	$(0.9 \pm 3.3) \times 10^3$	0.7214
	CNSL/15	1	$(2.73 \pm 0.03) \times 10^8$	$-(2.32 \pm 0.02) \times 10^8$	$(4.9 \pm 0.1) \times 10^1$	0.9920
		2	$(1.42 \pm 0.01) \times 10^8$	$-(1.10 \pm 0.01) \times 10^8$	$(6.6 \pm 0.1) \times 10^1$	0.9974
		3	$(7.44 \pm 0.05) \times 10^7$	$-(4.96 \pm 0.04) \times 10^7$	$(1.03 \pm 0.02) \times 10^2$	0.9993
	CNSL/20	1	$(7.054 \pm 0.001) \times 10^4$	$(3.99 \pm 0.07) \times 10^2$	$(5.3 \pm 0.3) \times 10^1$	0.9772
		2	$(1.4218 \pm 0.0001) \times 10^5$	$(6.09 \pm 0.05) \times 10^3$	$(3.9 \pm 0.1) \times 10^1$	0.9916
		3	$(2.5761 \pm 0.0001) \times 10^5$	$(8.39 \pm 0.05) \times 10^3$	$(3.83 \pm 0.07) \times 10^1$	0.9953
100	–/–	1	$(6.43 \pm 0.08) \times 10^2$	$-(3.12 \pm 0.07) \times 10^2$	$(7.2 \pm 0.4) \times 10^1$	0.9856
		2	$(6.39 \pm 0.06) \times 10^2$	$-(2.86 \pm 0.05) \times 10^2$	$(7.5 \pm 0.3) \times 10^1$	0.9934
		3	$(6.36 \pm 0.06) \times 10^2$	$-(2.63 \pm 0.05) \times 10^2$	$(7.9 \pm 0.3) \times 10^1$	0.9933

dynamic effect, as already explained) and for one plasticized sample containing 10 phr of CNSL (which presented very high resistivity, probably related to low conductive contribution Pani inclusions).

It may be observed in Table 2 that rising of the DOP content shifts V_{r0} towards higher values, which means that the conductivity of the mixture is worsened. On the other hand, increasing of the CNSL content causes a substantial reduction of the V_{r0} values, especially for samples containing 20 phr of CNSL. This clearly indicates that the initial states of DOP and CNSL mixtures are very different and that the use of CNSL may be very useful for preparation of conductive materials.

The analysis of parameter A_1 in Table 2 indicates that volume resistivity may either increase or decrease along the time, depending on the plasticizer and preparation conditions. For most CNSL samples and for pure polyaniline, the volume resistivity increases along the time (A_1 is negative). This may indicate that important capacitive effects take place in these samples, probably due to intrinsic morphological characteristics. Polarization of conductive filler particles may occur along the time in the composites, giving birth to the observed capacitive effect. Similar effects may occur in pure Pani, due to the existence of conductive islands, as discussed above.

For some plasticized SBS/Pani composites the volume resistivity decreases significantly along the time (A_1 is positive). This means that the mixture is reorganized to produce improved conductive materials. Therefore, electrical conditioning may be used to improve the electrical properties of these mixtures, which has not been discussed in the literature yet. The presence of high amounts of plasticizer in these composites probably indicates that the mobility of conductive inclusions is fundamental for development of this sort of behavior. Improved mobility of conductive inclusions may also be supported by the reduction of percolation thresholds in plasticized composites, as observed previously [19].

The analysis of parameter A_2 in Table 2 indicates that, in comparison with DOP mixtures and even pure Pani·DBSA, dynamic transitions are much faster in CNSL mixtures, which can probably be related to the enhanced electrical properties and improved plasticizing characteristics of these materials. These results can be supported by the EPR analyses, presented in a previous paper [19].

Obtained results show very clearly that the available experimental volume resistivity data collected during measurements are not replicates and that the experimental noise is indeed much lower than suggested by the preliminary analysis of the raw values (see Fig. 3). Therefore one may wonder how the obtained resistivity values should be stored and reported for future analyses. One possible solution to this question is to provide the experimental data as reported in Table 2. This means that one would have to describe initial resistivity values, final resistivity values and the characteristic response time for dynamic transitions. It is not clear yet which of these values are the most representative for characterization of the final polymer mixture. Based on the previous discussions, it seems clear that the usual sample mean should be used with caution to characterize the performance of the final material. This may be true even for the very well known Pani samples.

In order to provide a single resistivity value for characterization of the performance of the material, an alternative numerical procedure is proposed here. Fig. 4 shows the spread of experimental data during a typical experiment performed with the SBS–Pani mixture. This figure shows that the spread of volume resistivities cannot be described by a single normal distribution. Actually, as observed through many examples (see Figs. 4–7), at least three distinct weighted Gaussian curves should be used for proper representation of the available data. As the area (weight) of a specific Gaussian curve increases, its central value becomes more important for description of the full set of available experimental data. Thus, it is proposed here that the central point of the Gaussian curve that presents the larger area (weight) be used to represent the performance of the mixture.

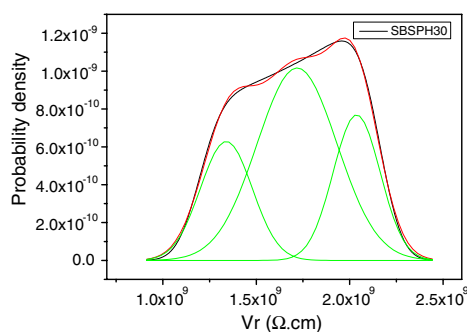


Fig. 4. Probability density to SBS–Pani mixture.

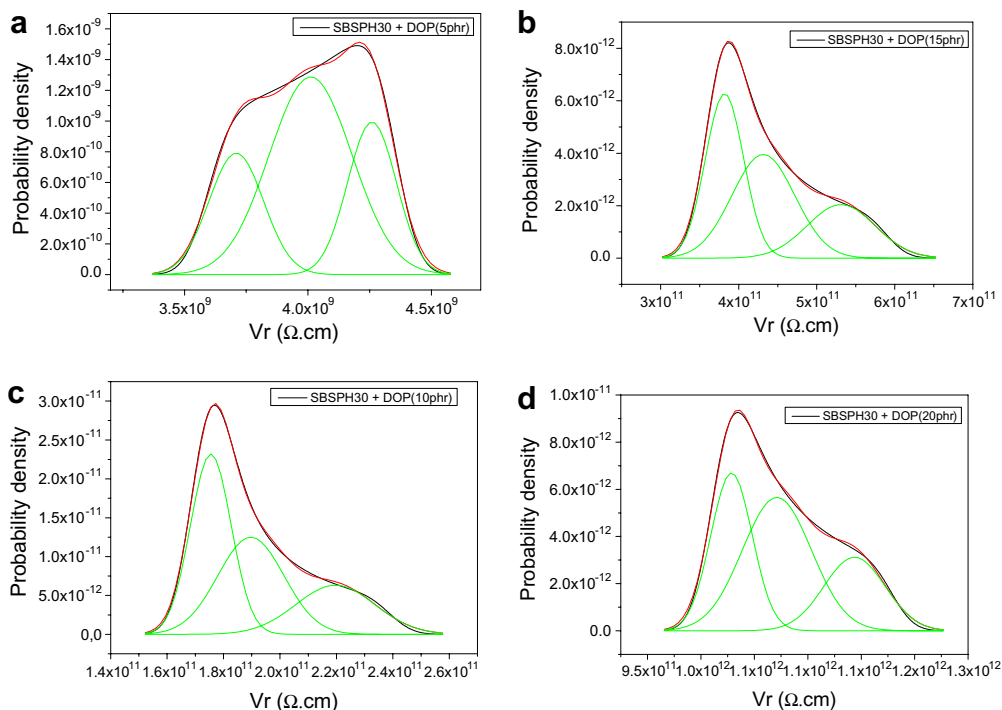


Fig. 5. Probability density functions of SBS–Pani mixtures plasticized with 5 (a), 10 (b), 15 (c) and 20 (d) phr of DOP.

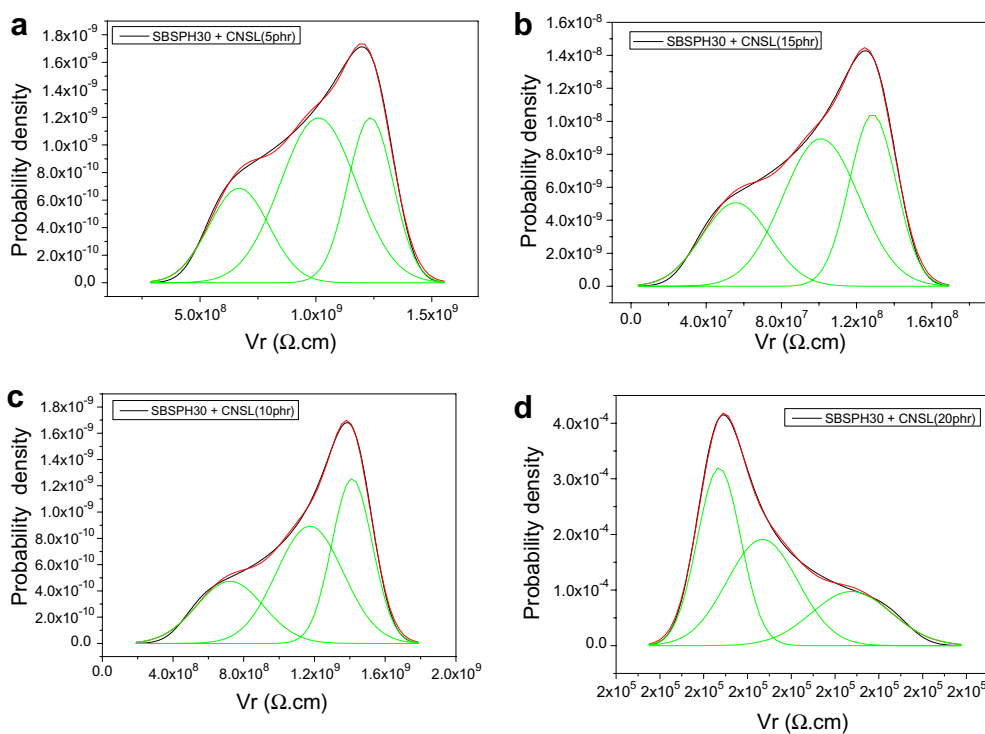


Fig. 6. Probability density functions of SBS–Pani mixtures plasticized with 5 (a), 10 (b), 15 (c) and 20 (d) phr of CNSL.

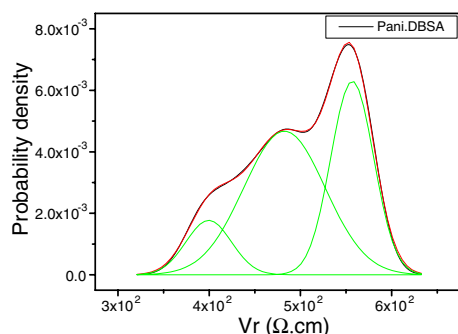


Fig. 7. Probability density functions of Pani · DBSA.

Results obtained after Gaussian deconvolution are presented in Table 3. Correlation values (R^2) in Table 3 show that three Gaussian curves can always be used to describe the density distribution of the analyzed experimental data sets. The larger areas are usually obtained for the central Gaussian

Table 3
Gaussian deconvolution of SBS/Pani data

Pani (w%)	Plasticizer/ phr	Peak	Parameters			R^2
			Area	Center	Time (s)	
30	—/—	1	0.2187	1.34×10^9	15	0.9987
		2	0.5451	1.72×10^9	59	
		3	0.2425	2.04×10^9	102	
	DOP/5	1	0.2190	3.71×10^9	15	0.9988
		2	0.5414	4.01×10^9	59	
		3	0.2460	4.26×10^9	102	
	DOP/10	1	0.4191	1.76×10^{11}	88	0.9992
		2	0.3658	1.90×10^{11}	47	
		3	0.2220	2.20×10^{11}	13	
	DOP/15	1	0.3855	3.82×10^{11}	91	0.9991
		2	0.3985	4.32×10^{11}	50	
		3	0.2229	5.31×10^{11}	14	
	DOP/20	1	0.3255	1.03×10^{12}	96	0.9989
		2	0.4576	1.07×10^{12}	54	
		3	0.2236	1.14×10^{12}	14	
	CNSL/5	1	0.2217	6.68×10^8	14	0.9988
		2	0.4922	1.01×10^9	55	
		3	0.2928	1.24×10^9	98	
	CNSL/10	1	0.2238	7.22×10^8	14	0.9990
		2	0.4232	1.17×10^9	51	
		3	0.3599	1.41×10^9	93	
	CNSL/15	1	0.2270	5.57×10^7	14	0.9989
		2	0.4554	1.01×10^8	54	
		3	0.3243	1.29×10^8	96	
	CNSL/20	1	0.3966	1.57×10^5	90	0.9991
		2	0.3882	1.58×10^5	49	
		3	0.2221	1.60×10^5	13	
100	—/—	1	0.11044	3.99×10^2	6	0.99963
		2	0.52278	4.83×10^2	43	
		3	0.37107	5.57×10^2	91	

curve (peak 2). Therefore, it seems that the data set is best represented by these central modes. However, the important peak is shifted towards smaller values (peak 1) when the plasticizer concentration increases, as shown in Figs. 5 and 6. This effect is related to the faster responses obtained when larger amounts of plasticizer are added to the mixture. It is also important to notice that in all cases the most representative values are observed after 50 s of experimentation, which shows the importance of the electrification time in this type of measurement.

4. Conclusions

An interesting dynamic resistivity effect was observed when conductive mixtures containing SBS, Pani and two different plasticizers were prepared. While addition of CNSL causes the decrease of the volume resistivity of the mixtures, DOP causes the inverse effect. It was shown that volume resistivity measurements change along the time exponentially. This dynamic effect seems to be related to the polar nature of the constituents, as no significant effect was observed for SBS materials. In order to represent the performance of the prepared mixtures, two techniques were proposed. The first technique is based on the exponential fitting of the experimental responses. This indicated that DOP and CNSL cause different responses on the volume resistivity of the prepared materials and that addition of plasticizer leads to faster experimental responses. The second technique is based on the Gaussian deconvolution of experimental data. It was shown that the central deconvoluted mode is normally the most representative value of the experimental data set, although the smallest mode becomes more representative when the amount of plasticizer is large.

Acknowledgments

The authors thank CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico, for the financial support and the scholarships (CNPq – PDJ – 151616/2006-0), and FAPERJ – Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro, for supporting our work.

References

- [1] Souza Jr FG, Soares BG, Pinto JCC. Macromol Mater Eng 2006;291:463–9.

- [2] Leyva ME, Barra GMO, Gorelova MM, Soares BG, Sens M. *J Appl Polym Sci* 2001;80:626–33.
- [3] Souza Jr FG, Soares BG, Mantovani GL, Manjunath A, Somashekarappa H, Somashekar R, et al. *Polymer* 2006; 47:2163–71.
- [4] Anand J, Palaniappan S, Sathyanarayana DN. *Prog Polym Sci* 1998;23:993.
- [5] Gazotti Jr WA, De Paoli M-A. *Synthetic Met* 1996;80:263.
- [6] Jia W, Tchoudakov R, Segal E, Joseph R, Narkis M, Siegmann A. *Synthetic Met* 2003;132:269.
- [7] Souza Jr FG, Michel RC, Soares BG. *Polym Test* 2005; 24(8):998–1004.
- [8] Moon Gyu Han, Seok Ki Cho, Seong Geun Oh, Seung Soon Im. *Synthetic Met* 2002;126:53.
- [9] Han D, Chu Y, Yang L, Liu Y, Zhongxian L. *Colloid Surface A* 2005;259:179.
- [10] Trevisan MTS, Pfundstein B, Haubner R, Würtele G, Spiegelhalder B, Bartsch H, et al. *Food Chem Toxicol* 2006;44:188.
- [11] Ikeda R, Tanaka H, Uyama H, Kobayashi S. *Polymer* 2002; 43:3475.
- [12] Aziz SH, Ansell MP. *Compos Sci Technol* 2004;64:1231.
- [13] Souza Jr FG, Soares BG, Siddaramaiah, Barra GMO, Herbst MH. *Polymer* 2006;47(21):7548–53.
- [14] O'Hagan A, Luce BR. A primer on BAYESIAN STATISTICS in Health Economics and Outcomes Research. Bayesian Initiative in Health Economics & Outcomes Research Centre for Bayesian Statistics in Health Economics; 2003, p. 57.
- [15] Bard Y. Nonlinear parameter estimation. New York: Pergamon Press; 1974.
- [16] Ho Ko-Shan. *Synthetic Met* 2002;126:151.
- [17] MacDiarmid AG, Epstein AJ. *Synthetic Met* 1995;69:85.
- [18] Min Y, Xia Y, MacDiarmid AG, Epstein AJ. *Synthetic Met* 1995;69:159.
- [19] Souza Jr FG, Pinto JC, Herbst MH, Oliveira GE, Soares BG. *Polym Test*, submitted for publication.
- [20] Lu X, Tan CY, Xu Je, He C. *Synthetic Met* 2003; 138:429–40.
- [21] Huang HG, Zheng ZX, Luo J, Zhang HP, Wu LL, Lin ZH. *Synthetic Met* 2001;123:321–5.