Study of the Thermomechanical and Electrical Properties of Conducting Composites Containing Natural Rubber and Carbon Black

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ABSTRACT: This work describes the preparation and characterization of composite materials obtained by the combination of natural rubber (NR) and carbon black (CB) in different percentages, aiming to improve their mechanical properties, processability, and electrical conductivity, aiming future applications as transducer in pressure sensors. The composites NR/CB were characterized through optical microscopy (OM), DC conductivity, thermal analysis using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMA), thermogravimetry (TGA), and stress–strain test. The electrical conductivity varied between 10^{-9} and 10 S m^{-1}, depending on the percentage of CB in the composite. Furthermore, a linear (and reversible) dependence of the conductivity on the applied pressure between 0 and 1.6 MPa was observed for the sample with containing 80 wt % of NR and 20% of CB. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1001–1006, 2007

Key words: natural rubber; thermal properties; conducting polymers; composite film; piezoresistive sensor

INTRODUCTION

Electrically conducting polymers such as polyaniline have been subject of intense studies due to the great interest in their potential technological applications. However, the low electrical stability widely restricts their practical applications to a few cases. Alternatively, electrical conducting composites have been successfully prepared by adding conducting filler to polymeric materials. For instance, conducting rubbery composites with carbon black (CB) are interesting due to their successful applications in electromagnetic shielding, electrostatic charge dissipation,[1] sensor of vehicle weight to collect tolls in the highways,[2] pressure sensor,[3,4] and selective gas sensor.[5] The electrical conductivity of polymeric composites depends on the nature of the polymeric matrix and particles, such as its size, geometrical structure, surface, and their dispersion of the particles as well as the test conditions such as temperature and pressure.[6] Different physical processes are proposed to explain the mechanism of transport of electrons, and the dominant process is dependent on the composition of the mixture and on the conditions of the sample preparation.[7] Basically, three physical processes govern the transport of the electrons: percolation, tunneling, and thermal expansion.[8]

Pressure sensors based on polymeric materials as thick or thin films are advantageous due to their low cost and easier fabrication process. They have been employed for medical, industrial, sports applications, and more recently as wearable sensors.[9–11] Piezoelectric polymeric and ceramic materials have been used as host for sensor applications[12] and piezoresistive materials are often used as transducer material in sensors.[13–15] In the latter, the variation of the electric conductivity with an applied pressure is the principle for its utilization as sensors and they have been produced from a large variety of materials such as the conductive polymers, electrical conductive composites, blends, and foams.[3,16,17]

In this work, we have complemented our previous work on the electrical conductivity of composite films of natural rubber and carbon black[4] with thermomechanical and electrical properties as the first step aiming to explore theses materials as transducers in pressure sensors.

EXPERIMENTAL

Composite preparation

The latex of *Hevea brasiliensis*, clones RRIM-600 (RRIM-Rubber Research Institute of Malaysia), was collected from different trees from Presidente Prudente, São Paulo State, Brazil. The stabilization of

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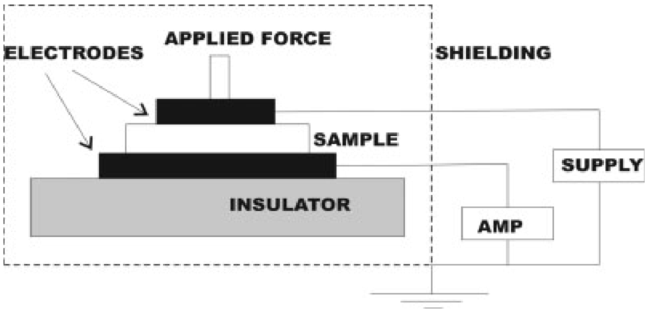

Figure 1 Schematic representation of the setup and the circuit used to determine the electrical conductivity dependence on the pressure.

the latex was made adding 2 vol % of ammonium hydroxide solution (NH_4OH). The solid percentage of rubber in the latex is ~ 40% as determined by thermogravimetry measurements. The CB (lampblack type) from Degussa AG Company was used as received. The size and specific surface area of CB particles are between 60 and 200 nm and 16 and 24 m^2/g, respectively.

A dispersion of CB and 25 mL of NH_4OH solution (concentration) was prepared by stirring for 15 min. Afterwards, 10 mL of the stabilized latex was mixed with the previous CB solution and mixed for 10 min. Finally, composites were prepared by casting the NR/CB solution onto a glass substrate and heating it at 65°C during 6 h to evaporate the volatile components. Free-standing films with thickness, *L*, of the order of 0.5 mm were obtained for composites with proportions of 95/5, 90/10, 85/15, 80/20, and 75/25 wt % (NR/CB wt %).

Techniques of characterization

Electrical conductivity (DC) measurements were carried out using the two electrodes method. A homemade system, schematically shown in Figure 1, with two metallic electrodes was built allowing application of the voltage and the mechanical pressure to the composite film with a planar geometry. Samples were placed between the electrodes in allowing simultaneous voltage supply and the mechanical pressure to the sample. The electrodes were connected to a programmable Keithley electrometer/supply model 617 and the electrical current was measured for different values of the applied pressure. The electrical conductivity of the sample, σ, was determined according to the equation, $\sigma = \frac{L}{A}\frac{I}{V}$, where V is the applied voltage, I is the electrical current, and L and A are the sample thickness and electrode area, respectively, being the $A = 0.78$ cm^2. A steady force was applied to the sample using a hydraulic press as depicted schematically in Figure 1, and a pressure gauge was used to read the mechanical force value. The applied pressure was varied between 0 (ambient pressure) and 2.4 MPa and the sample voltage bias to determine the sample conductivity was 100 mV. Conductivity measurements showed, during the first 15 min, a rather fast decay and afterwards a tendency to constant value. It is worth mentioning that the time required to reach the constant value did not present significant change for different samples. To ensure that the complete equilibrium was reached each conductivity measurement as function of pressure was carried out only after 30 min.

The thermal analysis was collected using thermogravimetry (TGA), differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMA) Netzsch equipments, models 209, 204, and 242C, respectively. The TGA measurements were carried out in N_2 atmosphere (10 mL/min) and heating rate of 10°C/min from 25 to 700°C. The DSC measurements were obtained using a heating rate of 10°C/min from −100 to 300°C and purified N_2 gas (10 mL/min). All measurements were made using 5 mg of each sample. The DMA results were made using a sample with dimensions of 0.5 mm thickness, 5 mm width, and 12 mm length, with a heating rate of 5°C/min in the range between –100 and +100°C for a frequency of 10 Hz.

The stress–strain tests were recorded following the ASTM 417 standard using a DL2000 Emic testing machine, operated at the speed of 500 mm/min. Four specimens were tested for each composition at room temperature (25°C) and in air at relative humidity of ~ 55%. The measured parameters are the elongation (ε%), rupture stress (MPa), and rupture strain (%). The results shown correspond to the average values of the four specimens. Optical microscopy (MO) was carried out using a microscope, Leica model DMRX with a 100X lens coupled with a digital camera Sony model SSC-DC54A.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the electrical conductivity on the CB content in composites at the atmospheric pressure (9.5×10^4 Pa, ~ 710 mmHg). The addition of CB up to 20 wt % promoted an increase of nine orders of magnitude on the conductivity, ranging from 10^{-9} to 10 S/m. Above this CB percentage, the conductivity tends to a constant value as found in other composites.[18] It is worth mentioning that usually the electrical conductivity of the polymeric material is insensitive to small content of conducting particles and an abrupt increase is noticed only when the amount of particles, about 30–40% in wt %, is enough to reach the percolation

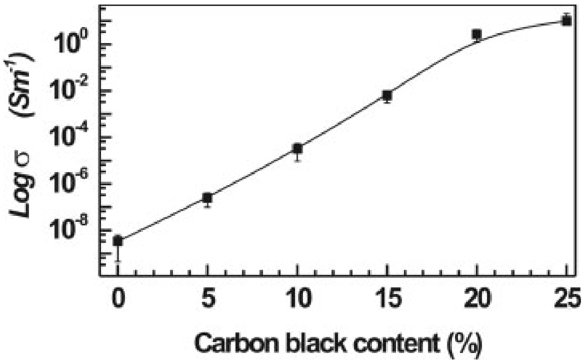

Figure 2 Electrical conductivity as a function of CB content in composites with NR at the atmospheric pressure.

threshold (samples were prepared according to ASTM N472 standard).[8,19,20]

It is believed that for higher percentage of CB, the particles of the filler maintain contact with each other creating a continuous conductive pathway. However, some studies of electronic microscopy involving CB/poly(vinyl chloride) composite revealed the absence of this continuous pathway between CB particles.[21] This observation took to the study of the transport process by tunneling, which happens through the insulating gaps of the polymer (size of the order of some nanometers), which separate the conductive particles forming a potential barrier between them.[7,8] Besides, the property of the polymeric ones of expanding thermally creates a dependence of the conductivity on the temperature due to changes in the separation distance between the conductive particles.

The electrical conductivity dependence on the applied pressure for composites with (a) 95/5, (b) 90/10, (c) 85/15, (d) 80/20, and (e) 75/25 wt % (NR/CB wt %) is shown in Figure 3. For the 95/5 sample [Fig. 3(a)], despite the linear dependence, σ has a low value in the range from 0.4×10^{-6} to 10^{-6} S m^{-1}, which is not suitable for sensor applications. For 90/10 and 85/15 samples [Fig. 3(b,c)], a sudden increase of σ is observed around the pressure of 1.2 MPa, which is also not adequate for sensor applications as well where a linear dependence is required. This abrupt increase might be related either to nonhomogeneity of the filler or to the percolation threshold reached when the pressure is increased. For the 80/20 sample [Fig. 3(d)], the dependence of σ on the pressure is linear in the range from 0 to 1.6 MPa with σ varying from 1 to 4 S m^{-1}. Besides, the behavior of the σ on the pressure is reversible, which makes the sample containing 20 wt % of CB the most suitable for potential application as pressure sensors. For samples with 25 wt % of CB in the composite [Fig. 3(e)], the value of σ as function of the pressure has a low reproducibility, which must be related to the fact that the sample becomes more brittle, losing its elasticity, thus, not suitable for pressure sensors.

Optical microscopy images of the composite film NR/CB were used to analyze the morphology for the different percentages of the CB filler. Figure 4 shows the images of samples with different percentages of CB in NR. The dark coloration is characteristic of the CB particles (the sample side which was in contact with the Petri plate presents a smoother and more brilliant surface when compared with the bare sample surface). For the samples with 95/5 and 90/10 wt %, the CB particles tend to accumulate at the

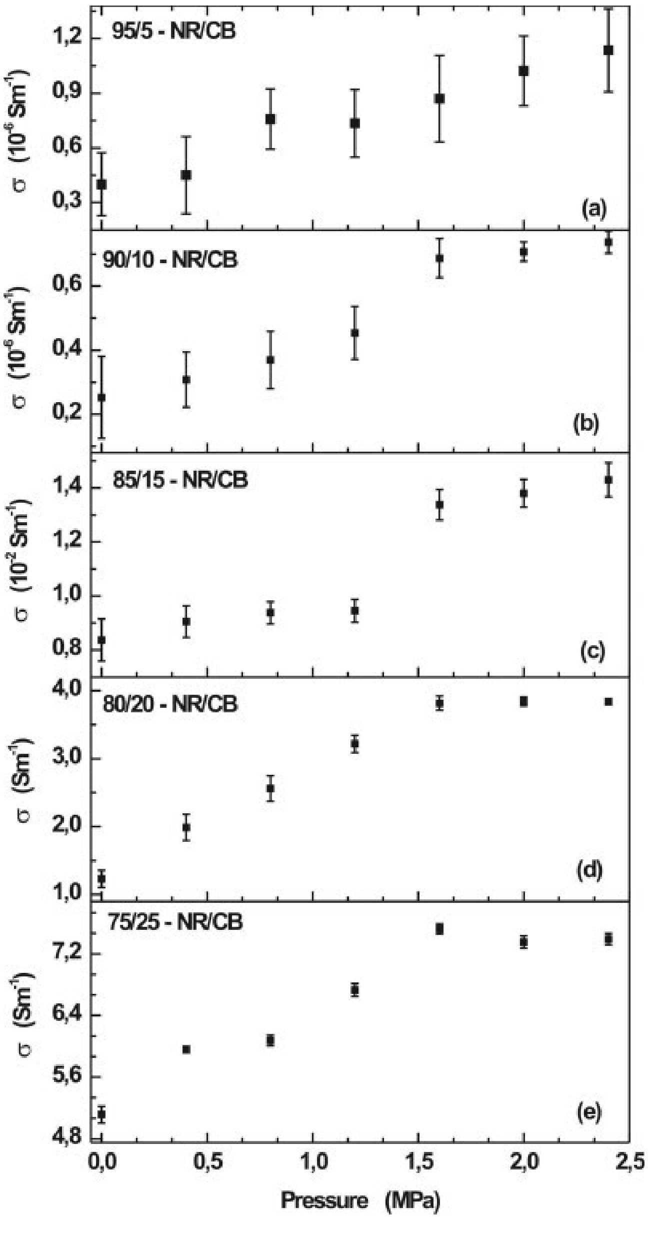

Figure 3 Dependence of the electrical conductivity, sigma, on the applied pressure for sample with contents of CB (a) 95/5, (b) 90/10, (c) 85/15, (d) 80/20, and (e) 75/25 (NR/CB wt %).

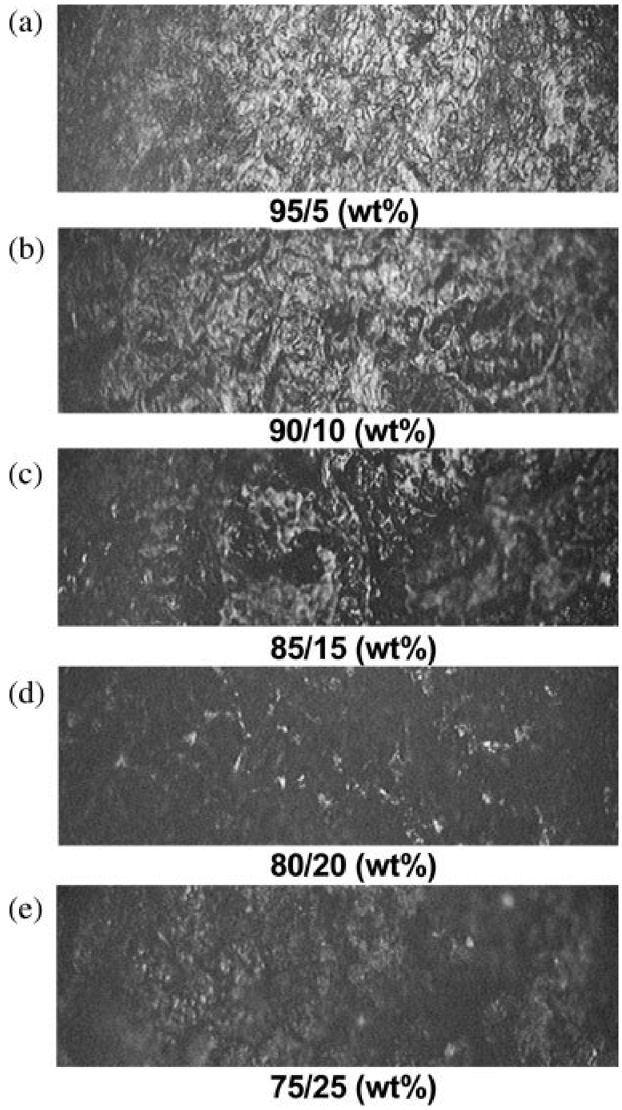

Figure 4 Optical microscopy of the samples NR/CB with percentages of (a) 95/5, (b) 90/10, (c) 85/15, (d) 80/20, and (e) 75/25 (NR/CB wt %).

top of the film, since the density of the carbon is lower than the latex. Increasing the CB content, the dispersion of the CB particles improves significantly, resulting in a clear surface with lower roughness. Besides, the sample with 80/20 wt % was obtained with the desired electrical properties and a good dispersion of the CB into the NR matrix. It reveals the efficiency of the casting method used here for preparing the films, which is different from the traditional methods of homogenization latex and CB. The methods used more often are the open mixer (mill/cylinder) or the closed mixer (banbury).

To evaluate the mechanical properties of the composite NR/CB film, tensile stress–strain tests were carried out. Table I contains the average values of the stress rupture (MPa) and strain rupture, i.e., the specific deformation (%) and the elongation (ε%) (also known as work area). It is observed that the samples have different rupture points. For instance, for the samples with 95/05 and 90/10 wt %, the specific deformation is 515 and 435%, respectively, and the elongation between 100 and 450% and 100 and 350%, respectively. These results show a significant loss of the elasticity compared with that of NR. At these percentages, there is a decrease of 52 and 63% in the stress module, respectively, compared with that of NR, which is of 1.5 ± 0.5 MPa. It is worthwhile to point out that in these two proportions, the CB particles are at the film surface. The samples with 85/15 and 80/20 wt % present a higher mechanical resistance with specific deformations around 480 and 535% and stress rupture at 4.2 ± 0.5 MPa and 3.0 ± 0.4 MPa, respectively. In these cases, the stress modules have an increase of about 280 and 206%, respectively, with a decreasing of the work area between 80 and 350% for both. Therefore, taking into account both electrical and mechanical analyses, it can be concluded that samples with the composition of 80/20 wt % present both elastomeric and conducting properties desired for application in pressure sensors. The composites that contain higher amount of 20% of CB are excellent conductive materials; however, they are brittle, which leads to poor elastomeric properties.

Subsequently, the thermal analysis of the composites was carried out through DSC, DMA, and TGA techniques, whose results are shown in Figures 5–7, respectively. The DSC curves show that the glass transition temperature (T_g), the little unevenness of the baseline, maintains the same value for all samples (−67 ± 2°C), which is the same value found for the NR itself. This uncertainty of ±2°C is associated with the inherent properties of the equipment, which might make this technique not sensitive enough to detect T_g changes in this type of material. Therefore, DMA was used as an attempt to better characterize this system.

Figure 6 presents the DMA results emphasizing the behavior of the storage module E' and tan δ. The E' results in Figure 6(a) show that it increases with

TABLE I
Mechanical Properties of Natural Rubber (NR) and Composites of NR with 5, 10, 15, 20, and 25 wt % of carbon black (CB)

Sample (NR/CB wt %)	Elongation (ε%)	Rupture Stress (MPa)	Rupture Strain (%)
100/0	50–700	1.5 ± 0.4	1029 ± 70
95/5	100–450	0.8 ± 0.6	515 ± 70
90/10	100–350	0.9 ± 0.2	435 ± 70
85/15	80–350	4.2 ± 0.5	534 ± 70
80/20	80–350	3.0 ± 0.4	477 ± 70
75/25	50–400	1.7 ± 0.2	461 ± 70

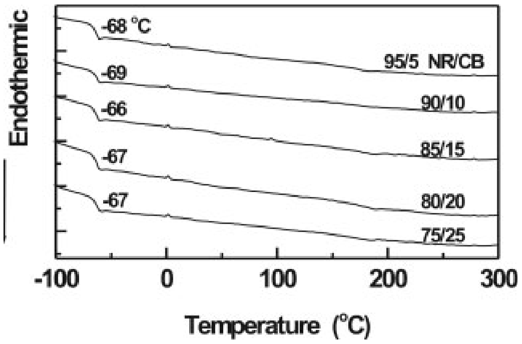

Figure 5 DSC curves for NR/CB composites films with different contents of CB 95/5, 90/10, 85/15, 80/20, 75/25 (NR/CB wt %).

the CB content. Since the increase of E' is directly related to the elastic properties of the samples, the higher the percentage of CB the stiffer are the films. Figure 6(b) shows the tan δ dependence on temperature, whose peak indicates the T_g values. A reduction in the amortization intensity and an increase in the T_g for higher percentage of CB is observed: $T_{g(95/5)} = –83°C < T_{g(90/10)} = –73°C < T_{g(85/15)} = –63°C < T_{g(80/20)} = –62°C < T_{g(75/25)} = -61°C$. This trend indicates a decrease in the mobility of the segments and/or functional groups of the chains due to the incorporation of CB. Note that the $T_{g(95/5)}$ and $T_{g(90/10)}$ are below that of $T_{g\text{NR}} = –67°C$. This can be explained by looking at the optical microscopy images where the CB particles are placed mainly on the surface of the film or close to it. This behavior is compatible with the results obtained in the stress–strain test, whose module for the same samples presented lower values compared to the NR.

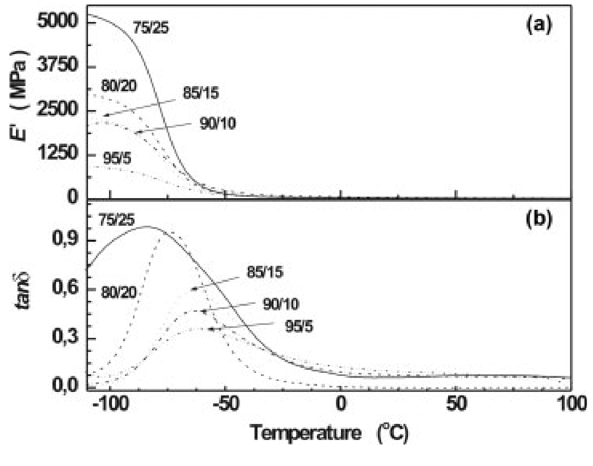

Figure 6 DMA curves with heating rate of 5°C/min and frequency 10 Hz: (a) showing the behavior of the elastic module, E', for the composites prepared in the proportions 95/5, 90/10, 85/15, 80/20, 75/25 (NR/CB wt %); (b) corresponding tan δ curves.

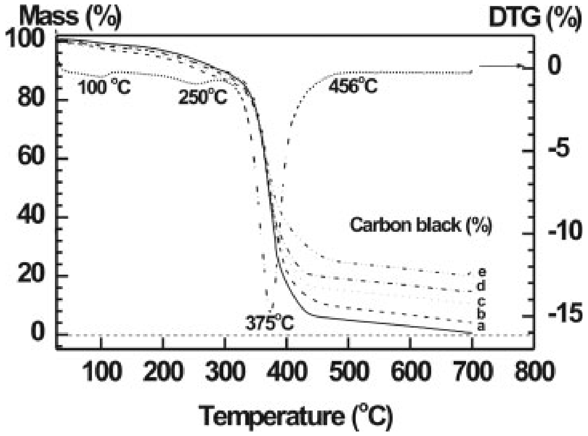

Figure 7 Thermogravimetry measurements of the samples with different contents of CB 95/5, 90/10, 85/15, 80/20, 75/25 (NR/CB wt %).

Figure 7 shows the TGA results for all samples. The first derivative (DTG) is shown only for the composition with 90/10 wt %, since the results are quite similar for all samples. A mass loss of about 5% for all samples between 100 and 250°C was observed. This mass loss is related to the water evaporation as well as to the release of subproducts of the proteins such as amino acids, carbohydrates, lipids, nucleic acid, and others present in the latex.[22] The third mass loss happens at ~ 375°C and it is attributed to the thermal decomposition of the organics quoted above those present in the NR, corresponding to approximately 84% of the total mass of the material. The fourth mass loss of 6% of the total mass occurs at about 456°C, which is related to the thermal decomposition of the lateral organic groups present in the structure of the NR. Above 456°C, only the CB remains. It is important to note that the mass values at this temperature are proportional to the amount of CB in the sample, showing that the sample preparation method is suitable. The degradation of the CB happens slowly with the increase of the temperature and the DTA measurements show that the structural degradation of the CB occurs at 900°C (not shown).

CONCLUSIONS

The thermal analysis using DMA showed that the mechanical resistance and the T_g of the composites films increase with contents (wt %) of the CB particles as well as the electrical conductivity for the composites of NR/CB. However, it was found that composites having greater percentage of CB are more suitable for pressure sensor applications due to the larger variation of the conductivity as a function of the pressure. The linear and reversible dependence of the conductivity on the pressure for samples with 80/20 wt % in the range from 0 to 1.6 MPa ensure that these composites can be applied as pressure sensors in orthopedic applications for this range. Further investigation will be necessary to elucidate the sudden increase of the conductivity of the 90/10 and 85/15 samples around the pressure of 1.2 MPa.

References

1. Stephen, R.; Ranganathaiah, C.; Varghese, S.; Joseph, K. Polymer 2006, 47, 858.
2. Sau, K. P.; Chaki, T. K.; Khastgir, D. Compos A 1998, 29, 363.
3. Souza, F. G.; Michel, R. C.; Soares, B. G. Polym Test 2005, 24, 998.
4. Job, A. E.; Oliveira, F. A.; Alves, N.; Giacometti, J. A.; Mattoso, L. H. C. Synth Met 2003, 135/136, 99.
5. Gouma, P. I.; Prasad, A. K.; Iyer, K. K. Nanotechnology 2006, 17, 48.
6. Ali, M. H.; Abo-Hashem, A. J Mater Process Technol 1997, 68, 163.
7. Tang, H.; Chen, X.; Tang, A.; Luo, Y. J Appl Polym Sci 1996, 59, 383.
8. Skotheim, T. A. Handbook of Conducting Polymers; Marcel Dekker: New York, 1986.
9. Pramanik, C.; Saha, H. Sens Actuators A 2006, 128, 317.
10. Pvalin, M.; Belavic, D.; Mozek, M. Informacije Miden J Microelectron Electron Component Mater 2003, 33, 49.
11. Choi, S.; Jiang, Z. Sens Actuators A 2006, 128, 317.
12. Luck, R.; Agba, E. I. ISA Trans 1998, 37, 65.
13. Harsnayi, G.; Hahn, E. Mechatronics 1993, 3, 167.
14. Ausanio, G.; Barone, A. C.; Campana, C.; Iannotti, V.; Luponio, C.; Pepe, G. P; Lanotte, L. Sens Actuators A 2006, 127, 56.
15. Clark, A. C.; Ho, P. S.; LaBerge, M. Tribology Int 2006, 39, 1327.
16. Brady, S.; Lau, K. T.; Megill, W.; Wallace, C. G.; Diamond, D. Synth Met 2005, 154, 25.
17. Knite, M.; Teteris, V.; Polyakov, B.; Erts, D. Mater Sci Eng C Biomimet Supramol Syst 2002, 19, 15.
18. Ishigure, Y.; Ijima, S.; Ito, H.; Ota, T.; Unuma, H.; Takahashi, M.; Hikichi, Y.; Suzuki, H. J Mater Sci 1999, 34, 2978.
19. ASTM N472 standard: NBR, 1159, 1997.
20. Ruschau, G. R.; Newnham, R. E. J Compos Mater 1992, 26, 2727.
21. Sichel, E. K. Carbon Black-Polymer Composites; Marcel Dekker: New York, 1982.
22. Subramaniam, A. Immunol Allergy Clin North Am 1995, 15, 1.