Conductivity and Mechanical Properties of Composites Based on MWCNTs and Styrene-Butadiene-Styrene Block™ Copolymers

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ABSTRACT: Composites based on multiwall carbon nanotubes (MWCNTs) and the block copolymer styrene-butadiene-styrene with two different contents of styrene have been investigated and their electrical conductivity and mechanical properties have been evaluated. The composites were prepared by a solution casting procedure, using a dispersant agent for the MWCNTs. Conductivity values of 10^{-4} and 1.6 S cm^{-1} have been obtained for samples containing 1 and 12 wt % of MWCNTs, respectively. The percolation threshold achieved for these systems was ~0.25 wt %.

According to dynamic mechanical analysis, the MWCNTs interact with both phases of the copolymers, acting as a reinforcement filler, whereas the dispersant agent acts as a plasticizer. However, it was shown that the reinforcing effect of the MWCNTs overcomes the latter, resulting in an overall improvement of mechanical properties of the composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3241–3248, 2009

Key words: nanocomposites; block copolymers; elastomers

INTRODUCTION

Polymeric composites based on carbon nanotubes (CNTs) are of great interest in both academic and technological areas due to their ability to combine the remarkable properties of CNTs, such as extremely high electrical and thermal conductivity, low density, high tensile strength, and Young's modulus, etc., with the versatility, processability, and mechanical properties of polymers.[1–9] As polymeric composites are multiphase systems, their properties can be tailored by modification of the nature of the polymer and the ratio of components, allowing for customization of these materials to suit desired applications.[3–8]

CNTs are amazing materials that can be understood as graphene layers rolled up to form either single-walled (SWCNTs) (one graphene layer) or multi-walled nanotubes (MWCNTs) (several graphene layers). They have some extremely high mechanical properties (elastic modulus of 0.3–1 TPa, tensile strength of 10–60 TPa),[10] thermal and electrical conductivities (3000 W m^{-1} K^{-1} and 1.85 × 10^3 S cm^{-1},

respectively),[10,11] and interesting optical and magnetic properties.[10–17] Their geometry, with an exceptionally high aspect ratio (the ratio between length and diameter), and their nanometric dimensions, allied with these remarkable properties, make these materials ideal for use as fillers in polymers to obtain high performance materials with excellent mechanical and electrical properties and extremely low percolation thresholds.[4,16,18]

The outstanding properties displayed by composites of polymers and CNTs allow their application in electrostatic charge dissipation (ESD), electromagnetic interference (EMI) shielding, field emission devices, pressure and chemical sensors, aerospace applications, etc.[2,9–15,18–24] Although there are several studies on conductive elastomers in the literature, only a small number relate the use of CNTs as fillers. Most of the polymer composites containing CNTs use thermoplastic matrices, such as polyethylene, poly(ethylene terephthalate), polypropylene, polystyrene, polycarbonate,[15,17,22,25–27] or thermosetting polymers,[28–30] especially epoxy resins.[13,16] Reports regarding CNT/elastomer composites are more concerned with the mechanical properties, whereas the electrical properties of these systems have scarcely been investigated.

The use of elastomers in electroconductive materials allows the fabrication of flexible materials with outstanding mechanical and electrical properties.

Conductive elastomers can be applied as artificial muscles, electromechanical actuators, touch control switches, and shape-memory polymers, etc.[5,9,23,31–37] Several elastomers have been used to prepare conductive rubbers, such as natural, nitrile, silicone and butyl rubbers, ethylene propylene diene monomer rubber, etc. However, these matrices pass through a vulcanization process to achieve good mechanical properties and elasticity. This process can negatively affect the final electrical conductivity of the material[38] and, more importantly, prevent reprocessing and recycling. The styrene-butadiene-styrene (SBS) block copolymer is a thermoplastic elastomer that can be used without being vulcanized. It has the mechanical properties of a vulcanized rubber and the processability of a thermoplastic. Furthermore, the nonpolar nature of the copolymer plus the presence of double bonds and aromatic rings in the chains are expected to improve the interaction of the polymer with the CNTs, increasing the dispersion of these materials in the polymer matrix.

Although polymer composites based on CNTs have great potential and may possess remarkable properties, as discussed above, there are still some critical issues in the production of these materials. Besides the large scale production of CNTs, dispersion of CNTs in the matrix and the adhesion between filler and polymer are two important issues that need to be considered. Indeed, these issues are those that most affect the properties and performance of these composites. The extended π electron system and their nonpolar nature make CNT materials subject to intense van der Waals forces, causing aggregation of the nanotubes and, as a consequence, a weak interaction with the polymer matrix.

In this work, composites of the SBS block copolymer and MWCNTs were prepared and characterized. The use of a nonpolar matrix with double bonds and aromatic rings was intentionally chosen in an attempt to improve the interaction between filler and polymer. Two grades of SBS with different contents of styrene were used and the effects of MWCNT loading on the electrical conductivity and on the thermodynamic and mechanical properties of these matrices were evaluated and compared.

EXPERIMENTAL SECTION

Two different grades of SBS block copolymer were used, Kraton-D® 1102 BT, with 29.5 wt % of styrene and Kraton-D® 4274 BT, with 48.0 wt % of styrene. The samples were supplied by Kraton Polymers do Brasil S/A, and named as KD-30 and KD-50, respectively. Table I presents some physical properties of these matrices. A polymeric dispersing agent, Polyvell 3900, supplied by Polystell do Brasil, was used to improve dispersion of the CNTs. According to the supplier, Polyvell 3900 is a polyurethane derivative.

TABLE I
Some of the Physical Properties of the SBS Block Copolymers Used in This Work

	Kraton-D® 1102 BT (KD-30)	Kraton-D® 4274 BT (KD-50)
Bound styrene (neat polymer)	28.5–30.5 wt %	47–51 wt %
Specific gravity	0.94 g/m³	0.94 g/m³
Bulk density	0.4 g/m³	0.4 g/m³
Melt Flow, 200°C, 5 kg	6 g/10 min	14–26 g/10 min

The MWCNTs were supplied by CNT Co., Ltd., Seoul, Korea and, according to the supplier, have 95 wt % of purity, typical lengths of 10–20 μm, and diameters of ~100 nm. Figure 1 shows the field-emission scanning (FESEM) and the high-resolution transmission (HRTEM) electron microscopic images of these MWCNTs, obtained to confirm the supplier's technical information. The FESEM and HRTEM images were obtained using FEG-SEM JSM 6330F and HRTEM-JEM 3010 URP microscopes, respectively, at the National Synchroton Light Laboratory (LNLS), Campinas, Brazil. According to the images, MWCNT bundles have a variable diameter ranging from 10 up to 100 nm. HRTEM images confirm the high purity of the samples. Scanning electron microscopic (SEM) images of the composites were obtained with a JEOL JSM 6360LV.

The composites were prepared by a casting solution technique. First, a chloroform (Aldrich) solution of the SBS copolymers KD-30 or KD-50 was stirred for 24 h. In a separate vessel, a dispersion of the MWCNTs in xylene (Aldrich) was prepared in the presence of 1 wt % of the polymeric dispersant agent and placed in an ultrasonic bath for 2 h. The mass fractions of the dispersant and of the MWCNTs were calculated considering the final mass of the composites. The MWCNT dispersion was mixed into the polymeric solution and stirred for 24 h. This mixture was heated under stirring to reduce the solvent volume until it become a gel, and then allowed to return to room temperature under stirring. The composite films were obtained after drying this final mixture in vacuum at 70°C for 6 h. Control samples with conductive carbon black (XC 72 Vulcan, Cabot) were prepared using the same procedure. Table II summarizes the composition of the samples prepared.

For the evaluation of the dispersant agent on the mechanical properties of the composites, samples containing only the elastomers and the dispersant were prepared adding it directly to the polymer solution at concentrations of 1 and 3 wt %.

Electrical conductivity of the samples was measured by Coleman's method using a Keithley 617 programmable electrometer, a digital multimeter
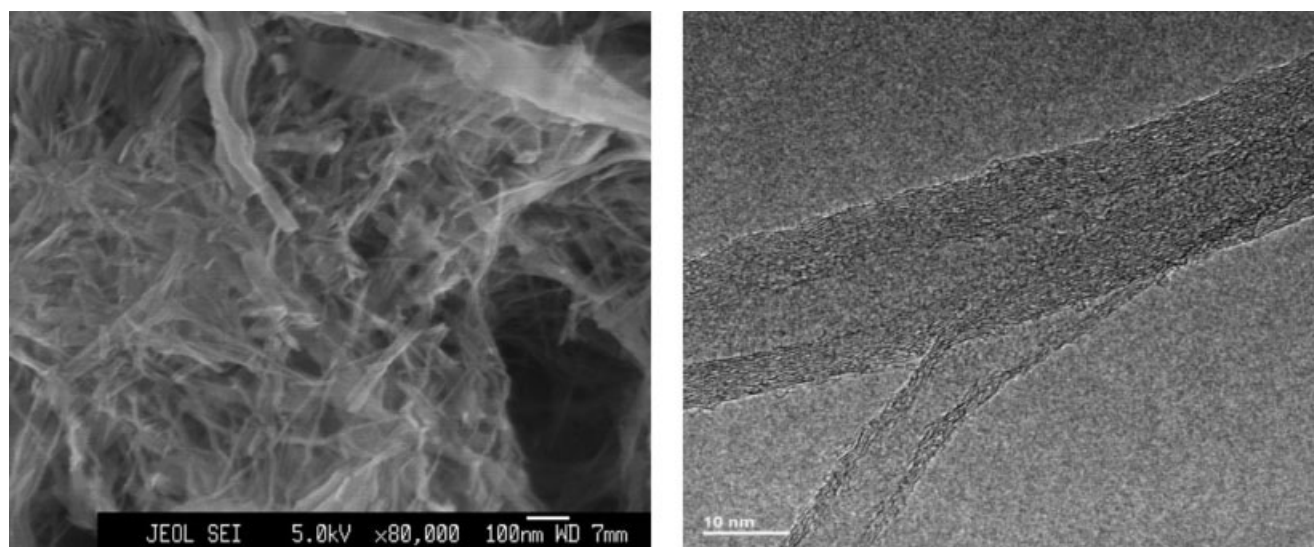
Figure 1 Field emission scanning and high resolution transmission electron microscopies of the MWCNT sample furnished by CNT Co., Ltd.

Minipa ET-2500, and a four-probe sensor with gold contacts.[39–41] Coleman's method consists of an adaptation of the 4-probe method for flexible samples.

The dynamic mechanical properties were evaluated in a DMTA V Rheometrics-Scientific analyzer, using specimens with dimensions of $6.0 \times 5.0 \times 0.4$ mm at a deformation of 0.10 mm and frequency of 1 Hz. The samples were heating from $-120°C$ to $150°C$ at a rate of $2°C \ min^{-1}$.

TABLE II
Composition of the MWCNTs and SBS Composite Samples Investigated in This Work

MWCNTs	
Wt % MWCNTs	Wt % SBS
0.25	98.75
0.5	98.5
1	98
1.5	97.5
2	97
3	96
5	94
7	92
9	90
12	87
Carbon black	
Wt % carbon black	Wt % SBS
6	93
9	90
12	87
15	84
18	81

The amount of Polyvell dispersant agent was kept constant in all samples at 1 wt %

RESULTS AND DISCUSSION

Electrical conductivity

The chemical structure of the block copolymer SBS is shown in Figure 2. Figure 3 displays the electrical conductivity as a function of MWCNT loading for the composites containing KD-30 or KD-50 as polymer matrices. The data were analyzed according to the percolation power law[5,13,16,42]:

$$\sigma \propto (\phi - \phi_c)^{\beta}$$

where σ is the electrical conductivity of the samples, ϕ is the volumetric fraction of MWCNTs, ϕ_c is the percolation threshold, and β is the power law exponent. Because the density of the CNTs depends of the conditions of their synthesis, it is not easily identified, complicating the determination of the volumetric fraction on the composites. Hence, the mass
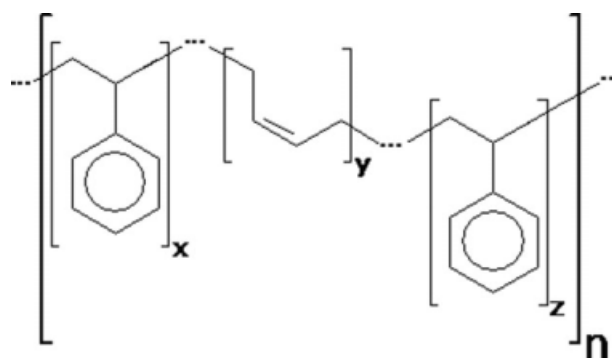

Figure 2 Chemical structure of the block copolymer SBS where x and z indicate the styrene units and y indicates the butadiene units.
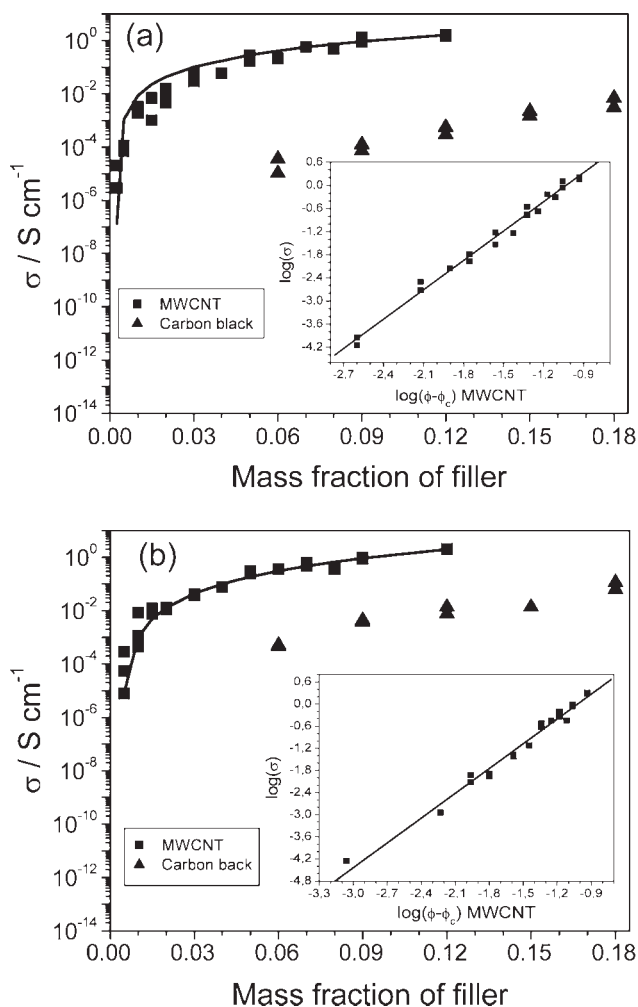
Figure 3 Percolation threshold determination for the composites of MWCNTs and SBS and comparison of their electrical conductivities with samples containing carbon black: (a) KD-30 and (b) KD-50. The inset plots represent the linear form of the power law used.

fraction is preferred instead of the volumetric fraction, because this property is much easier to determine and is also a better way to express the results.[43,44] The inset plots in Figure 3 represent a linearization of the above expression, obtained by applying logarithms to the both sides of the equation. These plots are used to verify the agreement of data with calculated values of β and ϕ_c by using a linear regression fitting.[5,28,45]

According to the data displayed in Figure 3, the electrical conductivity behavior as a function of MWCNT content is very similar for both the systems. The percolation threshold found for both lies between 0.25 and 0.50 wt %. The use of MWCNTs causes a drastic increase in the electrical conductivity. With only 1 wt % of MWCNT, the conductivity of the samples reaches 10^{-4} S cm^{-1}. This represents an increase of about 10 orders of magnitude when compared with the pure polymer.[46] With 12 wt %, the highest concen-

tration investigated in this work, the electrical conductivity is close to 2 S cm^{-1}.

These results suggest that the MWCNTs are randomly dispersed throughout the samples, independent of the composition of the polymer matrix, indicating that the MWCNTs interact similarly with the polybutadiene and the polystyrene phases, probably being uniformly distributed in both. This hypothesis is reinforced by the dynamic-mechanical results discussed below.

For comparison, samples containing conductive carbon black, a common industrial filler used to provide electrical conductivity, were prepared and characterized in the same fashion as the composites based on MWCNTs for both polymer matrices. Figure 3 also displays the conductivity behavior obtained for these samples. Because of the very high aspect ratio and electrical conductivity of the MWCNTs, the concentration of MWCNTs needed to achieve the same electrical conductivity obtained using carbon black is substantially lower.[4,16,18] In the range of filler content
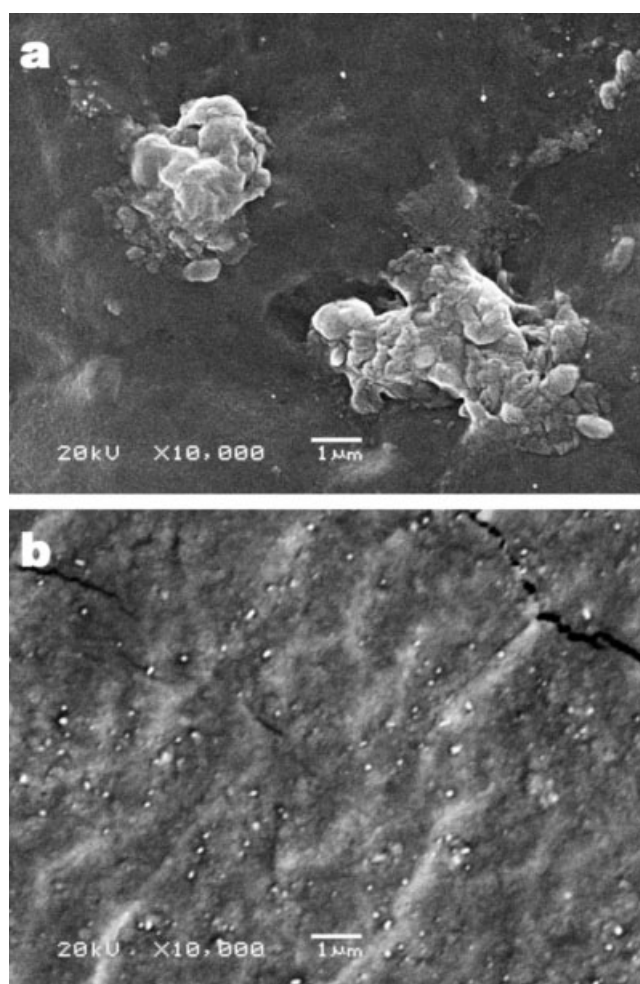

Figure 4 SEM images of composites based on SBS and 4 wt % of MWCNTs: (a) in the absence of the dispersant agent and (b) with 1 wt % of the dispersant.

investigated (where the conductivity lies between 10^{-4} and $10^{-3} \, S \, cm^{-1}$), the necessary MWCNT concentration is 6–12 times lower than the carbon black concentration. It was not possible to determine the percolation threshold for the carbon black composites because the conductivity of the samples containing small amounts of carbon black lies below the measurement range of the equipment. However, as the transition of conductivity occurs between 3 and 6 wt % of carbon black, it can be conclude that the percolation threshold for this system lies in this range of filler content.

Mechanical properties

The thermomechanical properties of the composites composed of block copolymer SBS and MWCNTs were investigated by dynamic mechanical analysis (DMA) as a function of the polymeric dispersant (Polyvell 3900) and MWCNT content.

As the CNTs tend to aggregate, a dispersant agent can be useful to assist in the dispersing of the nanotubes in the polymer matrix. According to the SEM images obtained for these systems (Fig. 4), the dispersant agent improved the homogeneity of the samples and the distribution of the fillers within the matrix. Although aggregates of MWCNTs of about 3–5 μm uniformly dispersed through the polymer matrix can be observed in the samples without the polymeric dispersant [Fig. 4(a)], a rather fine dispersion of the nanotubes is observed for composites containing Polyvell 3900 [Fig. 4(b)].

Figure 5 exhibits the dynamic mechanical curves (storage and loss moduli and loss factor) for pure KD-30 and KD-50 samples and also for the samples containing 1 and 3 wt % of the dispersant agent. The storage modulus curves for both systems present a
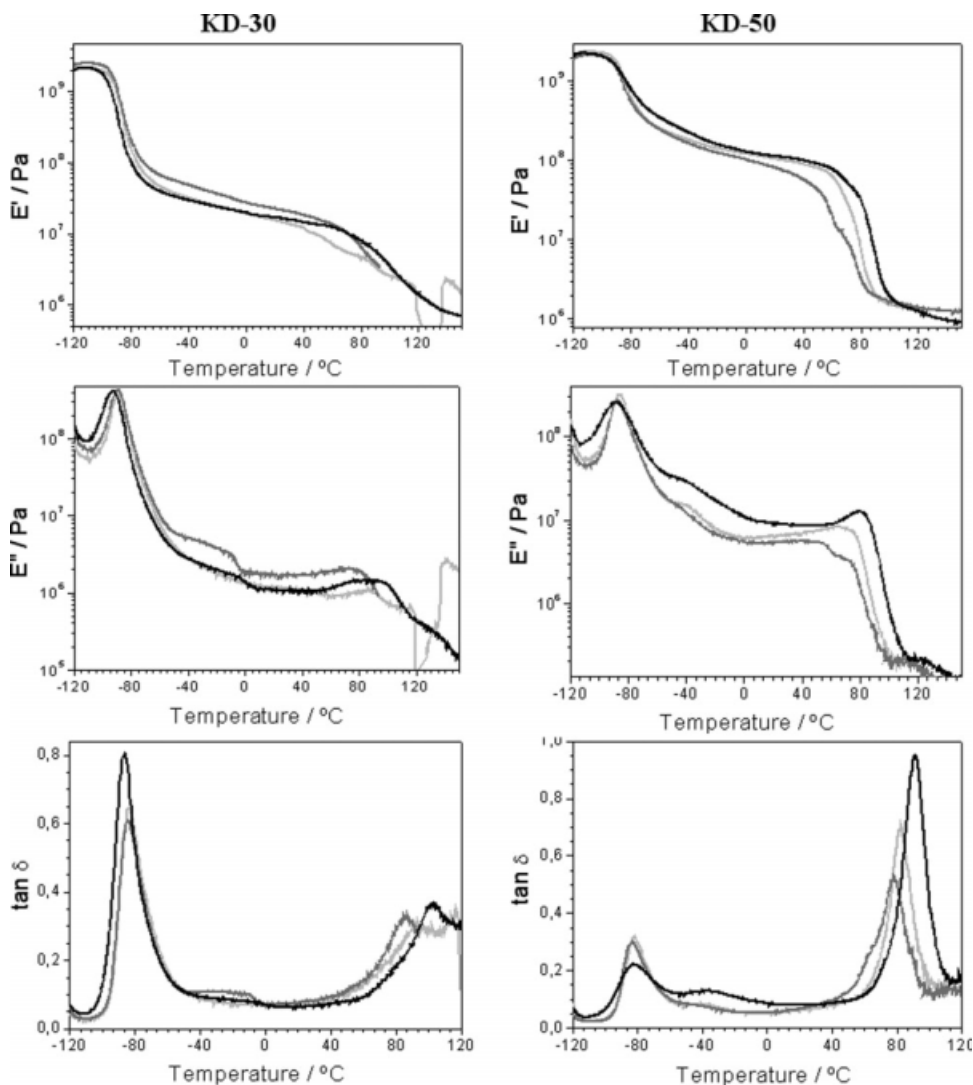

Figure 5 KD-30 and KD-50 storage moduli, loss moduli, and loss factors with different contents of dispersant. (━━━) without dispersant, (━━━) with 1 wt %, and (━━━) 3 wt % of dispersant.

drop at about $-80°C$, which is attributed to the glass transition (T_g) of the polybutadiene phase of SBS, and another drop at ~$100°C$, attributed to the glass transition of the styrene phase. The differences in the storage modulus observed between the glass transition temperatures of both SBS copolymer phases reflect the composition and the morphology. The typical morphology of KD-30 triblock copolymer has been reported as a polybutadiene matrix with spherical domains of polystyrene randomly distributed inside. On the other hand, the morphology of KD-50 was reported to be cocontinuous.[47,48]

As the dispersant is added to the SBS, the storage modulus at $0°C$, for example, decreases. The peaks of the loss modulus curves ($E'' \times T$) and the loss factor curves (tan $\delta \times T$) at around $-80°C$ do not shift, although a slight decrease in their intensities can be observed. However, the peak of $E'' \times T$ and tan $\delta \times T$ corresponding to the glass transition of the polystyrene phase shifts to lower temperatures as the amount of dispersant increases, independent of the SBS composition. These results indicate that the dispersant is acting as a plasticizer and that, apparently, the polystyrene phase is more affected by the presence of the dispersant.

Figure 6 shows the storage modulus (E') and the loss modulus (E'') curves for the composites at different MWCNT loadings for the KD-30 and KD-50 matrices, respectively. The glass transition tempera-

tures (T_g) were assumed to be the temperatures corresponding to the maximum of the peaks in the $E'' \times T$ curves. The T_g as functions of the composite compositions are shown in Table III.

There is no significant difference in the T_g values when comparing both phases for all composites. In contrast, the storage modulus at temperatures higher than the T_g of the polybutadiene phase increases as the amount of MWCNTs increases. The storage modulus at $25°C$ is displayed in Table III for composites of KD-30 and KD-50. The modulus increases from 16.3 MPa for pure KD-30 to 94.1 MPa for the composites of KD-30 with 12 wt % of MWCNTs. This means an increase of about 480%. On the other hand, at the same temperature the storage modulus of the samples prepared with KD-50 increases about 60% with the addition of 12 wt % of MWCNTs. These results reflect the difference in the constitution of the two SBS copolymers. As KD-50 possesses more PS (rigid) phase, it presents an initial modulus higher than KD-30 and less improvement. The softer KD-30 is more easily reinforced, reaching greater increase of toughness.

Above the glass transition of the polystyrene, the storage modulus presents the same behavior: it increases as the amount of MWCNTs increases. In this case, the modulus increases one order of magnitude when 12 wt % of MWCNTs are incorporated in the SBS matrix, independent of the SBS composition.
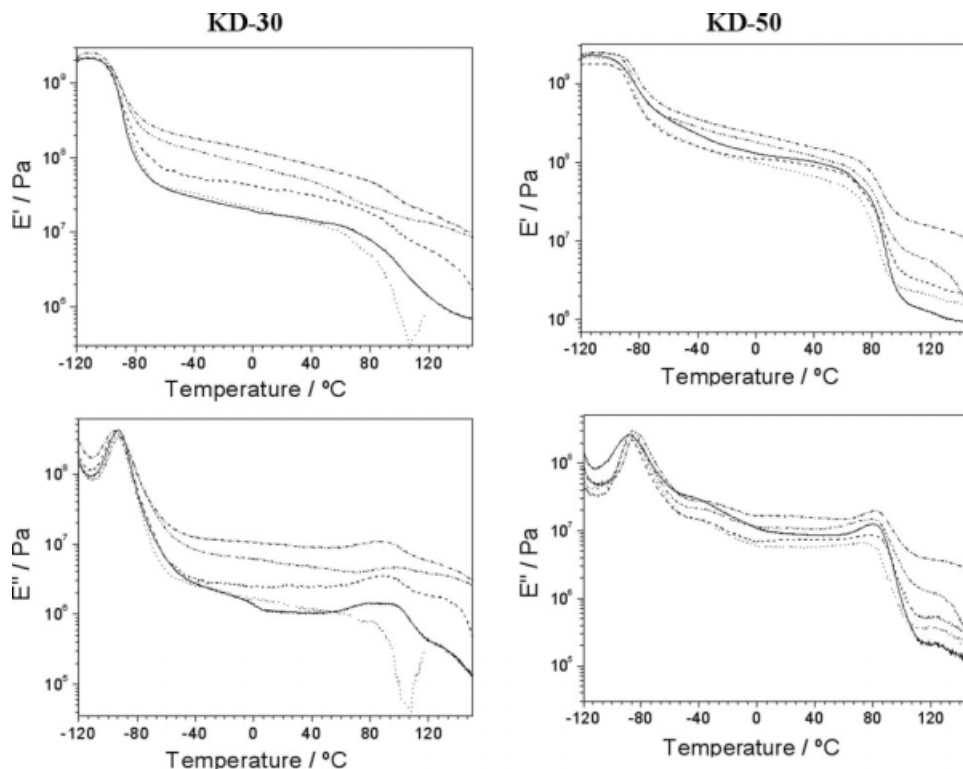

Figure 6 KD-30 and KD-50 storage and loss moduli at different loadings of MWCNTs. (——) KD-30, (·······) 3 wt % MWCNTs, (– – –) 5 wt % MWCNTs, (–··–··–) 9 wt % MWCNTs, and (–·–·–·) 12 wt % MWCNTs.

Wt % MWCNTs	KD-30			KD-50		
	E' $(T = 25°C)/Pa$	T_g PB/°C	T_g PS/°C	E' $(T = 25°C)/Pa$	T_g PB/°C	T_g PS/°C
0	1.63×10^7	-87	102	1.11×10^8	-83	91
3	1.59×10^7	-88	103	7.74×10^7	-83	86
5	3.56×10^7	-88	100	9.94×10^7	-84	90
9	5.79×10^7	-87	103	1.39×10^8	-83	89
12	9.41×10^7	-90	99	1.77×10^8	-80	89

PB and PS indicate polybutadiene and polystyrene phases, respectively.

Because the modulus of both phases of SBS is increased in the composites, a dispersion of the filler in the butadiene phase as well in the polystyrene phase is expected to occur. In conclusion, although the dispersant agent acts as a plasticizer for the SBS matrix, this effect is overcome by the reinforcing effect of the MWCNTs on the polymeric matrix.

CONCLUSIONS

Conducting elastomeric composites based on MWCNTs and SBS block copolymers have been prepared and characterized. The electrical conductivity was greatly increased by the addition of the MWCNTs, producing conductive elastomers with the lowest percolation threshold reported so far (the percolation threshold found for both systems lies between 0.25 and 0.50 wt %). With only 1 wt % of MWCNTs content, the conductivity of the samples reached 10^{-4} S cm^{-1}. These results imply that these materials have a great potential and could be used as charge dissipators in electronic equipment and EMI shielding.

The results have also shown that MWCNTs act as a reinforcing agent, this effect overcomes the plasticizer effect observed for the polymeric dispersant agent, leading to an overall improvement in the mechanical properties.

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