

Dependence of the Electrical Conductivity and Elastomeric Properties on Sample Preparation of Blends of Polyaniline and Natural Rubber

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Received 30 May 2003; accepted 13 January 2005

DOI 10.1002/app.21899

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

ABSTRACT: Blend films (free-standing) containing 20% in volume of polyaniline (PANI) in 80% of natural rubber (NR) were fabricated by casting in three different ways: (1) adding PANI-EB (emeraldine base) dissolved in *N*-methyl-2-pyrrolidone (NMP) to the latex (NRL), (2) adding PANI-EB dissolved in *m*-cresol to NR dissolved in xylol (NRD), (3) overlaying the surface of a pure NR cast film with a PANI layer grown by *in situ* polymerization (NRO). All the films were immersed into HCl solution to achieve the primary doping (protonation) of PANI before the characterization. The main goal here was to investigate the elastomeric and electrical conductivity properties for each blend, which may be applied as pressure and deformation sensors in the future. The characterization was carried out by optical mi-

croscopy, *dc* conductivity, vibrational spectroscopy (infrared absorption and Raman scattering), thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and tensile stress-strain curves. The results suggest that the NRL blend is the most suitable in terms of mechanical and electrical properties required for applications in pressure and deformation sensors: a gain of conductivity without losing the elastomeric property of the rubber. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1498–1503, 2005

Key words: conducting polymer; natural rubber; thermal analysis; blend film; polyaniline

INTRODUCTION

The electrical and optical properties of conducting polymers make them potential candidates for applications in batteries, electrochromic displays, field effect transistors, electrochemical sensors, and solar cells.^{1,2} To achieve such applications, processibility and the mechanical properties of the conducting polymers must be improved, and this is the reason blends and composites have been extensively investigated. The aim is to combine mechanical properties and ease of processibility of other polymers with the electrical properties of the conducting polymers. In this context, blends and composites were obtained in the form of films and fibers, with a variety of polymers such as acrylonitrile-butadiene-styrene (ABS), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), styrene-ethylene/butylene-styrene (SEBS), and styrene-butylene-styrene (SBS) copolymers, nylons, poly(ethylene terephthalate) (PET), poly(vinyl chloride) (PVC), and conducting polymers.^{3,4}

The rubber EPDM is the most used elastomeric material to make blends with conducting polymers such as polypyrrol and polyaniline doped with toluene sulfonic acid (PANI-TSA). The conductivity in the blends of vulcanized EPDM-PANI ranges from 10^{-9} to 10^{-6} S cm⁻¹⁵ and depends on parameters of the mixture and PANI concentration. Alternatively, in this work we used PANI as the conducting polymer and natural rubber (NR) to produce conductive elastomeric blends. We investigated preparation conditions to optimize both the electrical conductivity and the elastomeric performance of blend films containing both materials with the purpose of applying the blend in pressure and deformation sensors. The blends were characterized by optical microscopy, vibrational spectroscopy, *dc* conductivity, thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), thermal dynamic mechanical analysis (DMTA), and stress-strain measurements.

EXPERIMENTAL

Blend preparation

PANI was synthesized as described elsewhere to have a molecular weight (MW) of $\sim 50,000$ g mol⁻¹.⁶ NR lattices of RRIM 600 clone from the town of Indiana, in the region of Presidente Prudente, São Paulo State,

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Contract grant sponsor: FAPESP.

Contract grant sponsor: CNP.

Contract grant sponsor: CAPES.

Brazil, were collected from different trees. The stabilization of the latex was made by using a commercial solution of NH_4OH (4.7 mL NH_4OH for 100 mL latex). The characterization for both latex and NR followed standard procedures described by the Brazilian Association of Standard Methods-ABNT⁷ (NBR/11597/1997), which are consistent with those from ISO 2859-1:1989 and ISO/DIS 3951:1989. All reagents were grade for analysis and were used as received.

NRL blend

Stock solutions ($\approx 1\%$) of PANI were prepared by dissolving the emeraldine base (insulating form) in *N*-methyl-pyrrolidone (NMP). Blends of NR-PANI were prepared by mixing PANI stock solution and NR latex in the desired 80–20 proportion for 5 min and then casting it in a Petri dish. Flexible, free-standing films were obtained after solvent evaporation (60°C for 10 h). Doping was carried out by immersion in HCl 1 mol L⁻¹ solution for 12 h. After doping, the films were dried in a desiccator for 12 h.

NRD blend

NR films fabricated by using the latex heated at 60°C for 6 h were dissolved into xylol. Considering that the percentage of NR in the latex is 40%, blend films containing 20% in mass of PANI in NR were fabricated. For the latter, PANI dissolved into *m*-cresol was slowly added into the NR films dissolved into xylol under permanent stirring and the mixture deposited into a Petri dish was kept drying at room temperature in a hood. Doping was carried out by immersion in HCl 1 mol L⁻¹ solution for 12 h. After doping, the films were dried in a desiccator for 12 h. The NRD blend did not present a strong green color as presented by NRL blend, which is the characteristic of the doped state of PANI, and sulfur was not used to avoid interference on the conductivity.

NRO blend

A film of NR fabricated as described previously was immersed in a medium where PANI was polymerized *in situ* right on the NR film surfaces by using the conventional chemical synthesis.^{6,8} The NR film can be kept inside the reactional media from 6 min to 2 h depending on the thickness of the PANI overlayer desired. During this time, the solution color changes from colorless to green, characteristic of the PANI emeraldine salt (conducting form). The film was then washed with 1 mol L⁻¹ HCl solution, dried in air for 1 h, and left in a desiccator for 72 h to minimize the moisture.

It must be mentioned that coagulation occurs if PANI dissolved in NMP is added to NR dissolved in

xylol or if PANI dissolved in *m*-cresol is added to the latex, which impairs the fabrication of blend films.

Characterization

The thermal analysis was carried out by using TGA, DSC, and DMTA in Netzsch equipment, models 209, 204 and 242C, respectively. The TGA and DSC measurements were carried out in triplicate by using 5 mg of each sample and by using purified N_2 gas (10 mL/min) at a heating rate of 10°C/min. The DMTA results were prepared by using samples in triplicate 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 of -120 to 180°C and a frequency of 10 Hz. The FTIR spectra were recorded by using a Bruker spectrograph model Vector 22, resolution of 4 cm⁻¹, 32 scans, and in transmission mode for pellets and in the ATR mode for films. Electrical conductivity (*dc*) experiments were carried out by using the two-point method in which bulk conductivity is measured. Tensile stress-strain curves using an EMIC model DL-2000 were collected following ASMT D412-A for each sample. The four measurements whose samples (films) did not break near the holders were considered. To minimize breaking the samples, spring pressure holders were used. The force used was between 1 and 5 Kgf, speed of 50 mm per minute and at room temperature ($\sim 25^\circ\text{C}$). The Raman spectra were recorded with the 633-nm laser line (He-Ne laser, Spectra Physics, 4.5 mW maximum power) using a micro-Raman Renishaw 2000 equipped with a Leica microscope, a CCD detector, and a spectrograph with a 2400 g/mm grating (2 cm⁻¹ spectral resolution).

RESULTS AND DISCUSSION

Figure 1 shows optical images of NRL, NRD, and NRO blend films and pure NR cast film. Because doped PANI is greenish, one can infer qualitatively that the conducting polymer is more homogeneously distributed in NRL followed by NRO and NRD. Therefore, the compatibility of the components appears to depend on the blend preparation method. The *dc* electrical conductivity shown in Figure 2 increases in the order NR < NRD < NRO < NRL. This dependence is consistent with the optical microscopy analysis and is probably associated with the compatibility between the conducting polymer and the rubber. In the case of PANI, components are more segregated (phase separation), and the charge carriers become spatially localized, thus leading to a conductivity decrease because the conducting polymer formed dispersed aggregates.⁹ Accordingly, the conductivity results also suggest a diffusion of PANI through NR for the NR cast film overlaid with PANI (NRO), which is supported by morphology studies using scanning

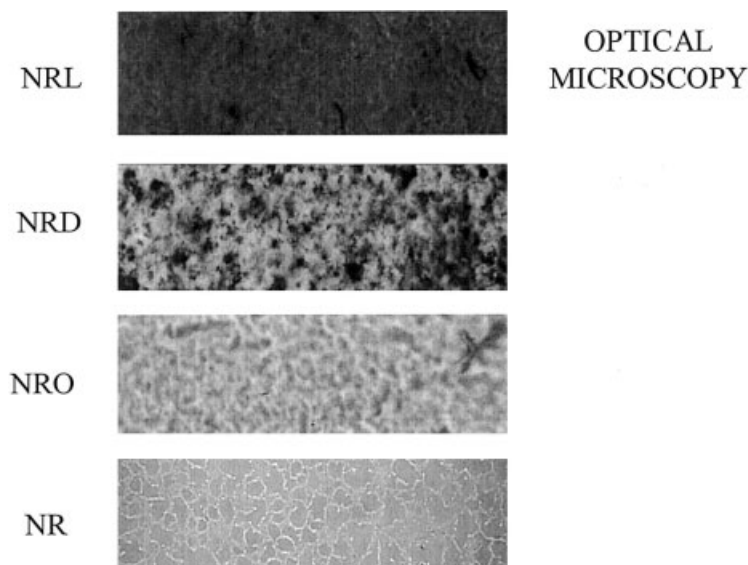


Figure 1 Optical microscopy recorded for NRL, NRD, NRO blend cast films, and pure NR cast film (magnification, $\times 50$).

electron microscopy where pores were observed in NR cast films (results not shown). Such pores could work as channels for PANI diffusion.

The conductivity results found for the blends can be also related with the doping level of the PANI within the blend. A detailed Raman study of the influence of NR on the doping of PANI and for blends prepared in the same way as NRL can be found in ref. ¹⁰. In the latter article, NR itself was found to dope PANI either by protonation (primary doping) or by an effect similar to *m*-cresol on the chain conformations (secondary doping).¹¹ This effect can be further enhanced by using other procedures such as exposure to HCl. Figure 3 contains the Raman spectra for NRL, NRD, NRO blend films, and pure NR cast film where it can be

seen that the band at $\sim 1332\text{ cm}^{-1}$ (C-N⁺ stretching—polaron) is stronger for the NRL than for the other samples, which can be explained by the fact that NR itself in the latex form is able to dope PANI.¹⁰ This shows that the NRL sample reaches a more effective doping (either by NR itself or by HCl), which is in agreement with the conductivity measurements. Besides, from the NRL spectrum it is possible to observe a greater number of bands of the NR itself such as 995, 1040, 1431, 1451, and 1663 cm^{-1} than from the other blends, which suggests that such vibrations in NR molecules are more localized in the NRL blend. The infrared spectra for all the samples were also recorded. However, NR dominates the spectra as it comprises 80% of the blend. Useful information from the

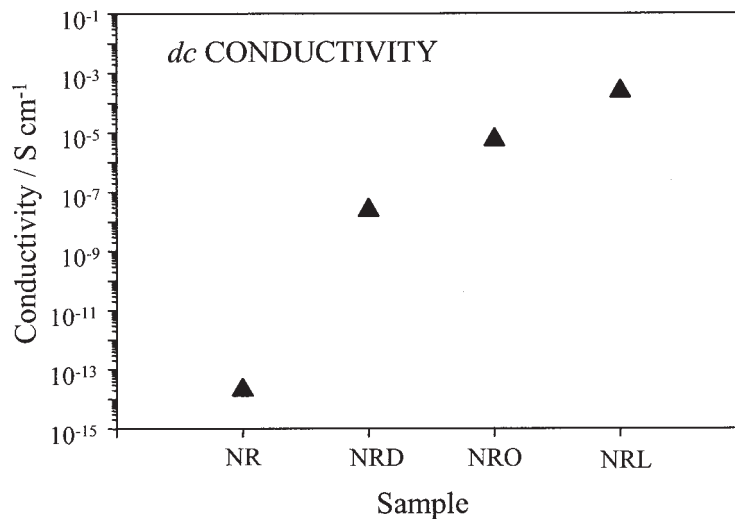


Figure 2 *dc* electrical conductivity for NRL, NRD, NRO blend cast films, and pure NR cast film.

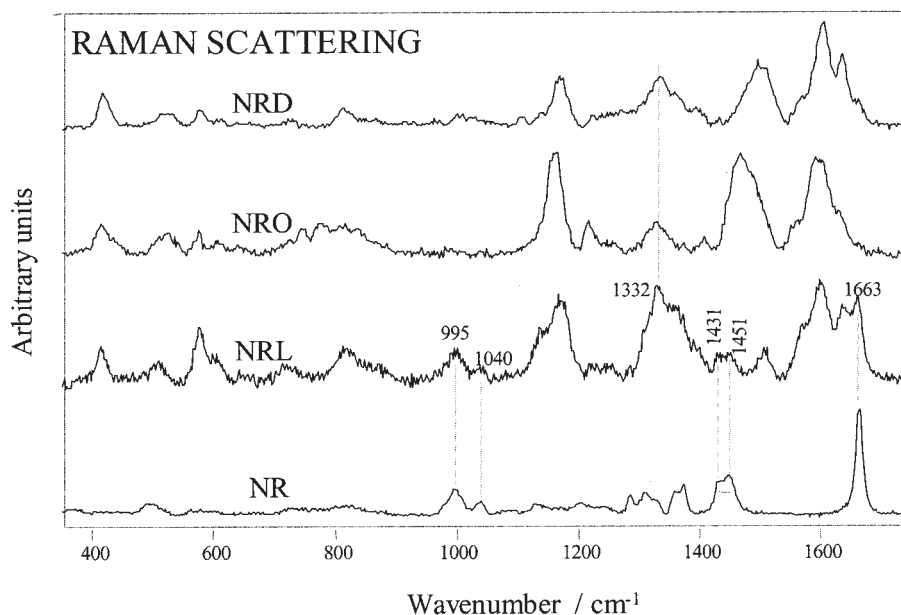


Figure 3 Raman spectra for NRL, NRD, NRO blend cast films, and pure NR cast film.

slight differences among the spectra could not be extracted because of the complexity of the NR spectrum. Only the band at $\sim 1240 \text{ cm}^{-1}$ assigned to the polaron structure of PANI¹² is observed in the blend spectra, showing that the doped feature of PANI is kept in the blend in agreement with the Raman data.

The thermal and mechanical analyses of the blends were carried out through TGA, DSC, and DMTA as shown in Figures 4, 5, and 6, respectively. The TGA

data show that no mass loss is observed for NRL and NRO up to 250°C , indicating that these blends are stable in the temperature range they are used. Above 250°C , a mass loss starts probably because of the evaporation of the dopant (HCl). On the other hand, for NR and NRD, mass loss starts below 100°C , which could be attributed to water evaporation. In all cases $\sim 85\%$ of the mass is lost before $\sim 370^\circ\text{C}$, owing to a degradation process, regardless of the preparation method.

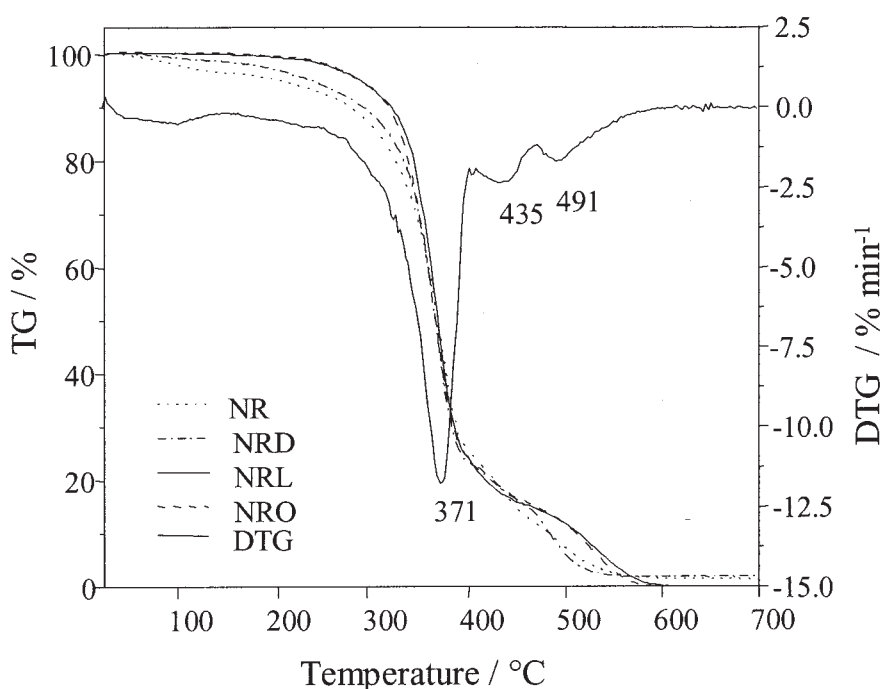


Figure 4 TGA for NRL, NRD, NRO blend cast films, and pure NR cast film.

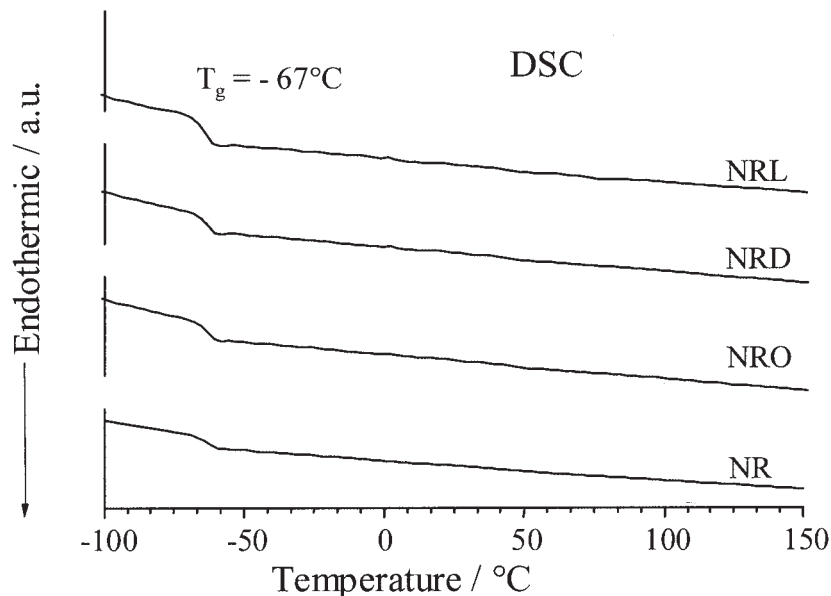


Figure 5 DSC for NRL, NRD, NRO blend cast films, and pure NR cast film.

Besides, the glass transition temperature (T_g) of NR observed at -67°C appears to be unaffected by the conducting polymer as observed by DSC measurements in Figure 5. However, the DMTA results in Figure 6 present distinctive features. The $\tan \delta$ values, associated with the T_g of the rubber, are shifted to lower temperatures for the blends in such a way that $T_{g_{NR}} > T_{g_{NRL}} > T_{g_{NRD}} > T_{g_{NRO}}$. This indicates that the preparation method for the blends must play an important role leading to a higher mobility of the rubber

chains. The trend in E' values (i.e., $E'_{NR} > E'_{NRL} > E'_{NRD} > E'_{NRO}$) corroborates the results for $\tan \delta$ as higher E' indicates a stiffer material. However, an opposite result would be expected because the conducting polymer is stiffer than the natural rubber. Therefore, the differences in stiffness found here may be related with some degradation that might be occurring because of the preparation method used rather than with the conducting polymer itself. The difference in stiffness may be also responsible for the better

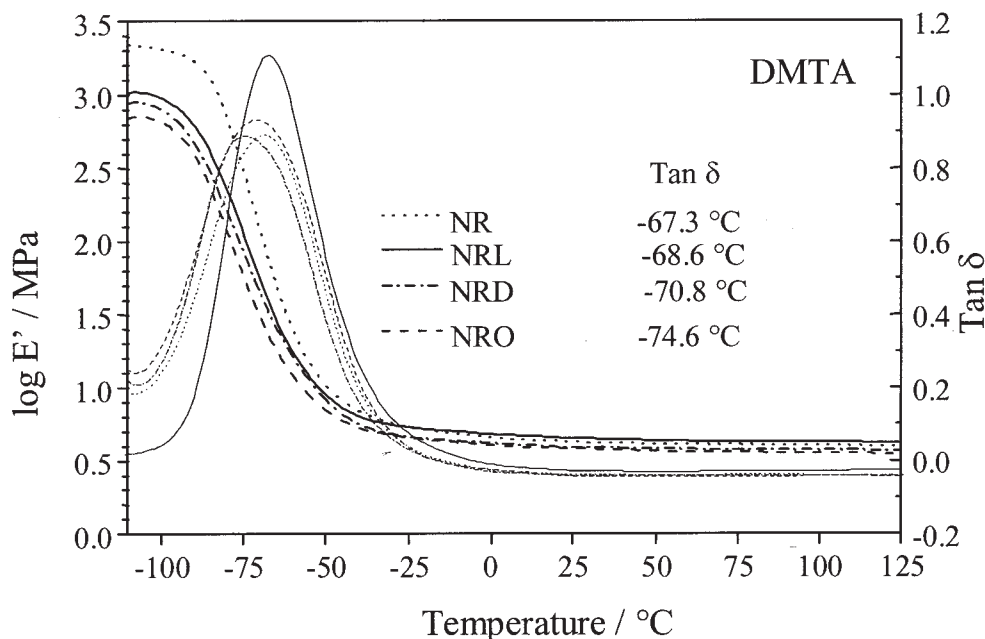


Figure 6 DMTA for NRL, NRD, NRO blend cast films, and pure NR cast film.

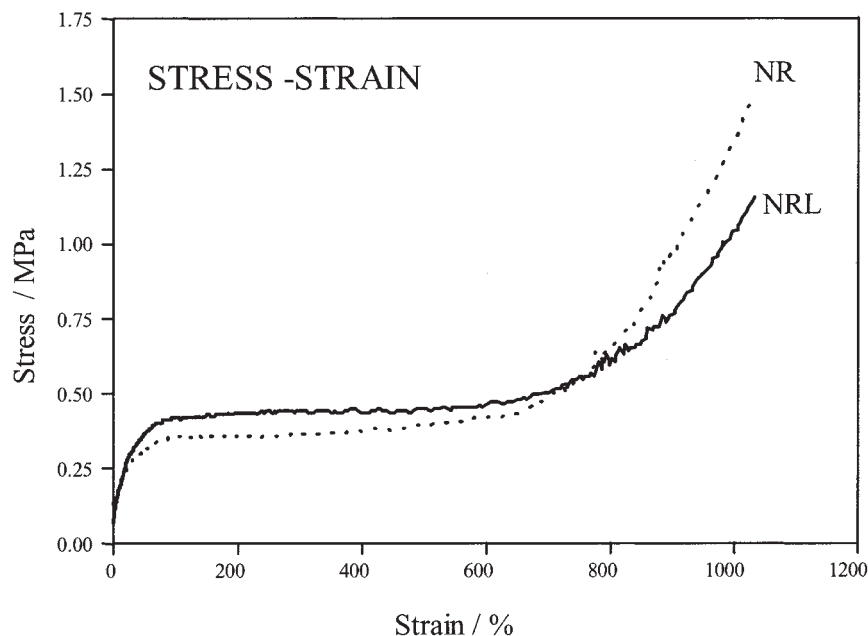


Figure 7 Tensile stress–strain curves for NRL, NRD, NRO blend cast films, and pure NR cast film.

Raman scattering of the light observed for the NRL in relation to the other blends (Fig. 3).

Because the NRL blend film seems to be the most suitable for this work, a tensile stress–strain test was carried out for both NRL and NR cast films whose curves are shown in Figure 7. In the region where it increases under a constant tensile stress (σ), the elongation (ε) is practically the same for NRL and NR up to 700%. The rupture point for NR is 1.4 ± 0.5 MPa, whereas for NRL it is 1.1 ± 0.5 MPa. This difference suggests that the polyisoprene chains responsible for the elastomeric properties of NR were only slightly affected by the film preparation method. From the stress–strain tests, it is possible to identify NR and the NRL blend as soft, tough with low tensile modulus, low yield point, and low-to-moderate tensile strength.¹³

CONCLUSION

Blend films of NR and PANI (80:20 v:v) were fabricated in different ways [adding PANI dissolved in NMP to the latex, NRL; adding PANI dissolved in *m*-cresol to NR (dried film) dissolved in xylol, NRD; overlaying the surfaces of pure NR cast film with a PANI layer grown by *in situ* polymerization, NRO]. The electrical conductivity increases because of the lower phase separation between the polymer and the rubber, where NRL displayed the highest conductivity. The T_g of the rubber is slightly shifted to lower temperatures because of possible rubber degradation during the blend preparation, which is corroborated by E' and tensile properties. No mass loss is observed

for the NRL and NRO blends up to 250°C, indicating that these materials are stable in the operational temperature range. Finally, the NRL blend film has presented the most desirable combination between electrical conductivity and elastomeric property for future applications in pressure and deformation sensors.

The financial support from FAPESP, CNPq, and CAPES is gratefully acknowledged. We also thank Dr. Ricardo Zanatta from IFSC/USP for the Raman facilities.

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