

Electrically conductive nanocomposites produced by in situ polymerization of pyrrole in pre-vulcanized natural rubber latex

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Abstract

Flexible conductive polymeric nanocomposites were produced by in situ polymerization of polypyrrole (PPy) in a natural rubber (NR) latex medium. Pre-vulcanized and non-pre-vulcanized NR latex, with varying NR/pyrrole (Py) monomer ratio was studied. The resulting nanocomposites were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy, DC electrical conductivity, and mechanical properties. The electrical conductivity increased as the NR/Py ratio decreased reaching a maximum of 1.0×10^{-2} S/cm for a vulcanized nanocomposite with NR/PY = 4 mass ratio. In terms of mechanical properties, it was observed that tensile strength at break ($\sigma_{atbreak}$) also increased with decreasing of NR/Py mass ratio, and for the same proportion of Py, the nanocomposites obtained from vulcanized latex presented higher strength. SEM analysis revealed that unlike non-pre-vulcanized latex, PPy nanoparticles tend to be distributed in the pre-vulcanized matrix in circumferential patterns, with an average diameter of 1 micron, indicating that the rubber microparticles have been encapsulated by the conductive polymer. This engineered morphological structure has been shown to significantly influence the final properties of the nanocomposites, compared to those prepared from non-vulcanized latex, changing not only the distribution of PPy in the matrix, but also changing the coalescence behavior of NR particles, as well as influencing the percolation threshold.

KEYWORDS

conductive elastomers, in situ polymerization, natural rubber latex, polypyrrole

1 | INTRODUCTION

Natural rubber is a critical raw material used for engineered materials for over a century, yet today is gaining in importance in modern green economies.^[1,2] This high-molecular weight biopolymer, extracted from a renewable source, is formed into long chains of isoprene

units linked in the *cis*-1,4 conformation.^[3] The physical and chemical properties of NR are engineered through chemical and/or physical processes, such as by vulcanization and filler addition.^[4–7] In terms of the electrical characteristics, NR is considered, and used as, an insulating material. The introduction of conductive fillers like carbon based materials (such as: carbon black, graphite, carbon

nanofiber, carbon nanotubes); metal fillers (nickel, iron, and silver) and also intrinsically conductive polymers (ICPs) such as polypyrrole (PPy), PEDOT, and polyaniline (PANi), can increase the electrical conductivity of the NR matrix and expand its application range.^[8–15] However, incorporation of high-modulus fillers and thermoplastics often reduces the attractive softness and flexibility of NR. Therefore, new solutions are sought for flexible elastic materials that provide sufficient conductivity for wearables, electronics, and military applications.

Among the most significant and studied conducting polymers is PPy, mainly due its high-chemical stability, non-toxicity, low cost, and variable electrical conductivity (between 10^{-10} and 10^3 S/cm) which can be controlled by synthesis and/or doping.^[16–18] Such properties make it possible for PPy to be used as a conductive filler in polymeric matrices to engineer conductive polymer composites (CPCs).^[19–21] There are many different methods to produce CPCs such as electrochemical, casting, in situ polymerization, and melting-mixing, among others.^[20–25] The in situ polymerization methods, that is, polymerization of Py in a NR latex medium, deserve to be highlighted because this approach overcomes the PPy low solubility, allowing improved PPy dispersion, thereby creating electrically conductive PPy/NR composites. The main difficulty encountered in this type of polymerization is the coagulation of latex during the synthesis process due to the low pH required for the reaction medium. One way to mitigate this problem is to do the synthesis in latex with low-NR concentrations and large amounts of surfactants. Hong-Quan Xie et al.,^[26] reported the formation of PPy/NR composites by in situ polymerization of pyrrole in the latex medium. In their experiments, the natural rubber latex (NRL) was diluted to 20% solid content and a suitable amount of nonionic surfactant was added to allow the Py polymerization to take place at pH less than 3. Ferric chloride (FeCl_3) was used as the oxidant. According to their work the optimum molar ratio of oxidant/monomer was 2.50 and a maximum conductivity over 2 S/cm. Polypyrrole-coated NR latex particles, by admicellar polymerization, was synthesized by Bunsomsit et al.^[27] The NRL was purified by centrifugation and diluted to 14%. Sodium dodecyl sulfate (SDS) and ammonium persulfate were used as surfactant and oxidant. According to their work, the surfactant adsorption, and pyrrole adsolubilization was enhanced when salt (sodium chloride) was added. The highest electrical conductivity achieved was around $1.5 \mu\text{S}/\text{cm}$. Ghalib et al.^[28] prepared NR/polystyrene/polypyrrole (NR/PS/PPy) conductive blends by the emulsion polymerization of an organic solution of Py dispersed in the emulsion of 40/60 NR/PS as the continuous phase. The electrical conductivity was in the range of 8.9×10^{-8} – 2.89×10^{-4} S/cm. Devi et al.,^[29]

reported the production of composites of NR/PPy and NR/PPy/PPy-coated short nylon fiber by in situ polymerization method. The latex was diluted to 20% solids and stabilized by a non-ionic surfactant, before use. It was verified that the PPy and fiber formed a homogeneous dispersion in the NR matrix. The maximum electrical conductivity was 8.3×10^{-4} and 6.25×10^{-2} S/cm, for NR/PPy and NR/PPy incorporated with short nylon fibers, respectively.

In this work, for the first time, nanocomposites of NR/polypyrrole were produced by the polymerization of Py into the pre-vulcanized natural rubber latex (NRV) for different NR/Py monomer ratios. The Py synthesis was also done in non-pre-vulcanized latex for comparison in both cases resulting in electrically conductive soft, flexible materials. The effect of the synthesis conditions on the morphology, structure, mechanical and electrical properties of the resulting nanocomposites was evaluated. Surprisingly, for a given synthesis condition, PPy nanoparticles were distributed circumferentially, indicating that the rubber microparticles have been encapsulated by the conductive polymer, thus promoting an attractive combination of electrical and mechanical properties.

2 | MATERIALS AND METHODS

2.1 | Materials

Pyrrole (Py) (99.98%) and sodium dodecylsulphate (SDS) (98.5%) were purchased from Sigma-Aldrich. Ammonium peroxydisulfate (APS) (99.8%) was obtained from Merck. Acetone (99.5%) and methyl alcohol (99.8%) was purchased from Dinâmica—Brazil. The Py was distilled before in situ polymerization. The NR latex was collected from the *Hevea brasiliensis* tree (RRIM600 clones) localized in the UNESP's experimental farm (São Paulo State University), campus of Ilha Solteira-SP, Brazil. Concentrated ammonium hydroxide solution (1.0 M) was used to stabilize the pH of the NR latex at approximately 10.2 and stored at 5°C (refrigerator). The total solids content, obtained by the standard methods ISO 124:2014, was 42.0%.

2.2 | Pre-vulcanization of NR latex

The pre-vulcanization of NR latex was carried out following the conventional vulcanization system (CV) according to the reagents/quantities described in Table 1 [30]. A dispersion containing the sulfur, zinc oxide (ZnO) and zinc diethyldithiocarbamate (ZDEC) was prepared using a ball mill with 16 alumina balls (half of them with a mass of

TABLE 1 Formulation used for pre-vulcanization of NR latex in phr (parts per hundred rubber)

Reagents	Conventional system (CV) (phr)
Total solids	100
ZnO—50%	1.50
Sulfur—50%	2.80
ZDEC—50%	0.80

7.53 g and the other eight with a mass of 3.36 g) at constant rotation.

The dispersion of Sulfur, ZnO and ZDEC was added to the latex, stabilized at pH between 10.2 and 10.3. The Sulfur, ZnO and ZDEC dispersions were added to the latex under stirring and keep under stirring for at least 15 min at room temperature. Then the dispersion was heated in a bain-marie shaking water bath, at 70°C for 2 h, under 80 cycles per minute. After that, the dispersion was cooled down to room temperature (25°C) under stirring and then, the pre-vulcanized latex was stored at 5°C until used.

2.3 | Preparation of NR/PPy nanocomposites

The non-vulcanized and vulcanized cast films were prepared by casting each latex samples onto a glass substrate and dried in a conventional oven at 40°C for 48 h. NR/PPy nanocomposites were obtained from the in situ polymerization of Py in NR latex. The monomer/oxidant/dopant molar ratio (Py/APS/SDS) was maintained at 1.0:1.0:0.5, for all syntheses, varying only the NR/Py mass ratio. The synthesis of Py was performed in NR latex without any previous treatment and in pre-vulcanized NR latex. No organic solvent was used to stabilize the synthesis. The procedure is summarized in Figure 1. Initially 2 ml of Py was added to the SDS aqueous solution (51.6 ml at 8% m/V) and stirred for 1 h (solution 1). Then, the solution 1 was added to an appropriate amount of NR latex, under mechanical stirring (solution 2). After 10 min, an aqueous solution of 6.57 g of APS in 20 ml of H₂O was added to solution 2 under mechanical stirring, and after 5 min the stirring was stopped and the final solution was refrigerated to around 5°C while polymerization was allowed to proceed for 14 h. Next, the NR/PPy emulsion was destabilized by adding acetone. The precipitate was filtered and washed several times with acetone and deionized water until the washing became colorless. Then, the nanocomposite was dried in an oven at 60°C for 48 h. The same procedure was adopted to obtain

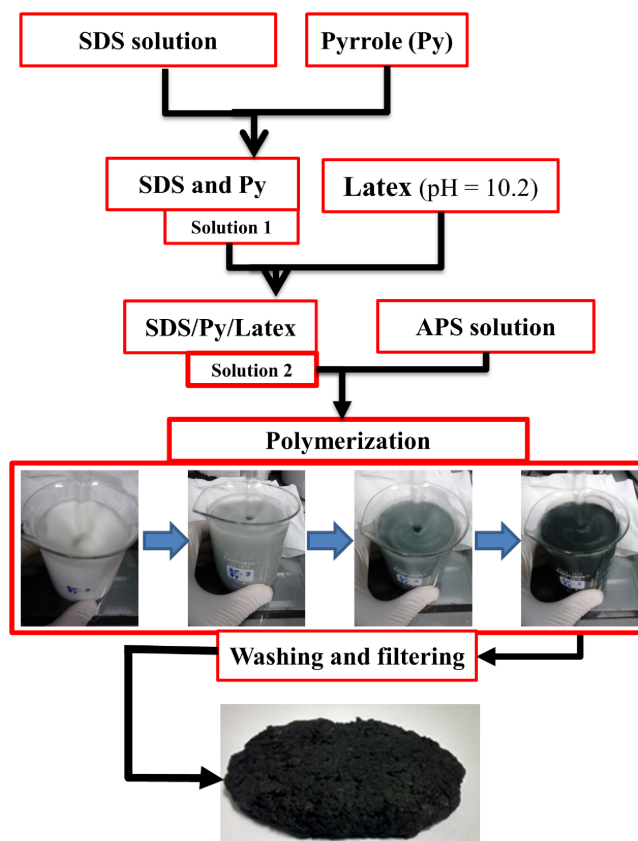


FIGURE 1 Synthesis route for preparation of NRPPy and NRVPPy nanocomposites with varying NR/Py ratio. NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole; Py, pyrrole

nanocomposites using pre-vulcanized latex. We designed the nomenclature NRPPy and NRVPPy for the samples obtained from latex non-vulcanized and pre-vulcanized, respectively. For example, NRVPPy4, means that the nanocomposite sample was obtained from pre-vulcanized latex using NR/Py ratio of 4. Table 2 show the samples names and the ratios used in this study.

After drying, the samples were formed into films by pressing the nanocomposites with a heated hydraulic press (Marconi model MA-098). The NRPPy and NRVPPy nanocomposites were placed between Kapton sheets and then pressed at 110 and 150°C, respectively, by applying a 3 t load for 15 min. Following, the heating was turned off and the load was maintained until the plate cooled to a temperature of 30°C. The highest pressing temperature for NRVPPy samples was adopted to obtain uniform flat samples with smooth surfaces. The temperature of 150°C is below the threshold for PPy degradation.^[31]

The polypyrrole control material was also synthesized in the same molar ratios/condition of the nanocomposites, that is, via microemulsion using Py monomer, APS as oxidant and SDS as surfactant/dopant with the molar ratio 1.0:1.0:0.5 (Py/APS/SDS), only latex was not added.

TABLE 2 NR/Py mass ratio used to obtain of NRPPy and NRVPPy nanocomposites

Samples	NR/Py ratio (m/m)	Samples	NRV/Py ratio (m/m)
NRPPy4	4	NRVPPy4	4
NRPPy8	8	NRVPPy8	8
NRPPy12	12	NRVPPy12	12

Abbreviations: NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole; Py, pyrrole.

2.4 | Characterization

Fourier transform infrared (FTIR) analysis was performed using an Agilent Technologies spectrophotometer, Cary 600 model in ATR mode (attenuated total reflectance). The FTIR analyses were carried out between the 4000 and 600 cm^{-1} range, with 2 cm^{-1} resolutions in 128 scans.

The cryofractured surface morphology of the nanocomposites was examined by scanning electron microscopy (SEM) (ZEISS, EVO LS15 model). The samples were cooled with liquid nitrogen and then cleaved. Subsequently, the cryofractured samples were dipped in toluol for 100 min, dried at 28°C for 10 h in oven. The toluol promotes the NR swelling making the distribution of conductive polymers in the matrix more evident.

The tensile tests were performed on five specimens (D1708-2010) of each sample using a universal tensile testing machine (Instron model 3369) under ambient conditions. Before each tensile test, the samples were stored for 24 h in a desiccator with silica gel, which was previously subjected to vacuum for 20 min in order to standardize the relative humidity. The test followed the ASTM-D412 standard, with a 500 N load cell and deformation speed of 500 mm min^{-1} .

The DC volume conductivity measurements were carried out using a two-probe method. Gold electrodes were evaporated onto both faces of the all samples by evaporation using HHV Ltd. Metallizer, model AUTO 306. Electrical conductivity was determined using the equation:

$$\sigma = \frac{Id}{AV}, \quad (1)$$

where A is the metallized area, d the sample thickness, V the electrical potential applied to the sample and I the ohmic current through the sample.

3 | RESULTS AND DISCUSSION

3.1 | Morphology

Figure 2 shows the SEM images of the neat PPy, NRPPy, and NRVPPy nanocomposites. In Figure 2A,B we observed that the particles showed spherical morphology and average

diameter around 35 nm. There are several studies in the literature that present the possible nanostructures of PPy (granular, nanofibers, nanotubes, nanospheres and other morphologies) by varying the polymerization conditions and/or reagents used.^[31–34] Our results are similar to that found by other researchers.^[32–34]

Figure 2C–F shows the SEM images of the cryofractured surface for NRPPy and NRVPPy nanocomposites films after pressing. Significant changes in morphology were observed when the synthesis of PPy was made in the pre-vulcanized latex compared to the non-vulcanized latex. Note that the PPy nanoparticles were distributed circumferentially. As reported in the literature,^[35,36] *Hevea brasiliensis* produces rubber particles encapsulated with phospholipid monolayer membranes consisting of species-specific fatty acids, proteins and phospholipids. These particles have a diameter in the range of approximately 3–3000 nm with the majority being around 1000 nm. More detailed analysis of Figure 2D, showed the PPy circumferences distribution was around 1 μm indicating that the rubber particles have been encapsulated by the conductive polymer. This morphology was less evident for higher NR/Py ratios (Figure 2F) due to the lower amount of PPy in the nanocomposite. For nanocomposites produced from non-vulcanized latex, the circumferential distribution of PPy nanoparticles was not evident. With the addition of APS, it was observed that the viscosity of the non-vulcanized latex emulsion increases faster than vulcanized emulsion, indicating that the vulcanized system is more stable. The higher stability of the particles in the vulcanized latex emulsion essentially solved the problem of coalescence under the initial (~ 5 min) mixing of APS into the system. Note: to prevent the complete coagulation of the latex, once APS was incorporated, the polymerization was performed without stirring. The lower stability of the latex allows the coalescence of rubber particles with a decrease in pH, preventing the existence of the circumferential pattern as observed for the vulcanized samples.

3.2 | FTIR analysis

Figure 3A,B shows the FTIR spectra of neat PPy, NR, NRV, and nanocomposites, respectively. The bands

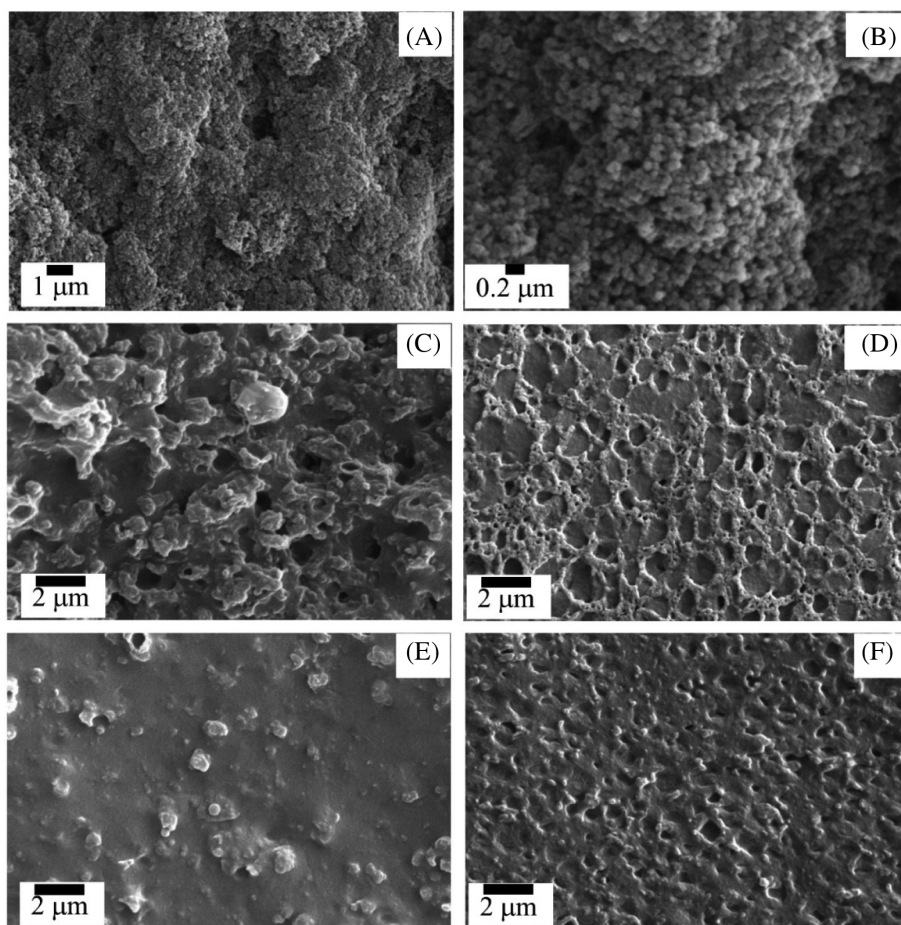


FIGURE 2 SEM images of the neat PPy (A) and (B). For CPC samples: (C) NRPPy4, (D) NRVPy4, (E) NRPPy12 and (F) NRVPy12. CPC, conductive polymer composite; NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole; SEM, scanning electron microscopy

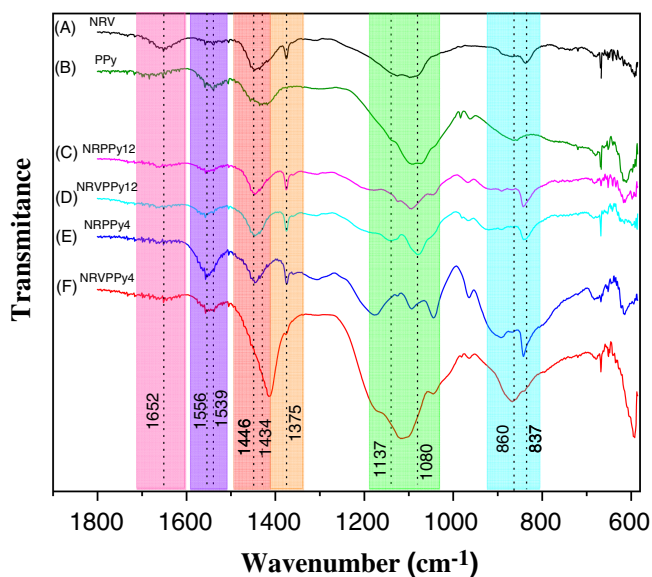


FIGURE 3 FTIR spectra of (A) NRV, (B) PPy, (C) NRPPy12, (D) NRVPy12, (E) NRPPy4, and (F) NRVPy4 samples. The colored rectangles highlight the region of the main absorption bands. FTIR, Fourier transform infrared; NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole

assignments are summarized in Table 3. Neat NR and NRV FTIR spectra show the principal polyisoprene bands at 837, 1375, 1446, and 1652 cm^{-1} .^[37,38] For pristine PPy, the bands at 860 and 1080 cm^{-1} correspond to the vibration of =C–H out and in plane, respectively while 1137 cm^{-1} band can be attributed to the breathing vibration of the pyrrole ring.^[39] The bands at 1434 and 1539 cm^{-1} may be assigned to typical polypyrrole ring vibrations and indicate the polymerization of PPy in its doped state.^[39–43]

The spectra of FTIR nanocomposites, in both cases studied, showed superpositions of the pristine polymer bands. A reduction of the band intensity in 1556 cm^{-1} was observed with the increase of the NR/Py fraction in the NRPPy nanocomposites, corroborating with the reduction of PPy fraction and indicating a possible reduction of the longer conjugation length and the ordered arrangement of the macromolecule chains of PPy.^[40] On the other hand, this was not verified in the NRVPy nanocomposites, in which the intensity of the 1556 cm^{-1} band remained almost unchanged, indicating that the degree of conjunction for the nanocomposite remains.

TABLE 3 Wavenumber (κ) characteristic and assignments of the main bands in the FTIR spectra of neat NR, NRV, PPy, and nanocomposites

$\kappa \text{ cm}^{-1}$	Band assignment	Samples					
		NR/NRV	PPy	NRPPy4	NRVPPy4	NRPPy12	NRVPPy12
837	=C–H wagging	√		√	√	√	√
860	=C–H out of plane vibration		√	√	√	√	√
1080	=C–H band in plane vibration		√	√	√	√	√
1137	Breathing vibration of pyrrole ring		√	√	√	√	√
1300	=C–H band in plane vibration		√	√	√	√	√
1375	CH ₃ symmetrical deformation	√		√	√	√	√
1446	CH ₂ deformation	√		√	√	√	√
1434	C–C and C–N stretching mode		√	√	√	√	√
1539	C=C/C–C stretching mode		√	√	√	√	√
1652	C=C stretching	√		√	√	√	√

Abbreviations: NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole; Py, pyrrole.

3.3 | DC electrical conductivity

NR is known as insulating material.^[44] In this work, the σ_{dc} value for the NR film was determined to be 4.5×10^{-16} S/cm. The neat PPy sample, obtained in its doped state, showed $\sigma_{dc} = 8.2 \times 10^{-2}$ S/cm. Figure 4 shows the σ_{dc} values for the NRPPy and NRVPPy nanocomposites as function of NR/Py mass ratio. Electrical conductivity increased as the NR/Py ratio decreased reaching a value of 1.0×10^{-2} S/cm for NRVPPy4. However, σ_{dc} value for NRVPPy samples is higher than NRPPy samples, at NR/Py 4–8. This finding was attributed to the encapsulation of insulating NR particles by the conductive polymer, thus facilitating the physical and electrical percolation of PPy, reflecting in a higher conductivity.

3.4 | Mechanical properties

The tensile strength ($\sigma_{atbreak}$), elongation at break ($\epsilon_{atbreak}$), and elastic modulus at 100% of strain ($\sigma_{100\%}$) of the nanocomposites are presented in Table 4. An increase of approximately 414% of tensile strength at break, in relation to pristine rubber, was observed for the NRPPy4 nanocomposite, due to mechanical load transfer from the matrix to the PPy particles. As the NR/Py ratio increased, there was no significant change in the $\sigma_{atbreak}$ values, demonstrating a good dispersion of PPy in the matrix. On the other hand, $\epsilon_{atbreak}$ increased with NR/Py ratio, and attributed to the higher fraction of NR in the nanocomposite.

The NRV sample had a substantially higher tensile strength, as expected, compared to the unvulcanized NR, owed to cross-links formation. The nanocomposites

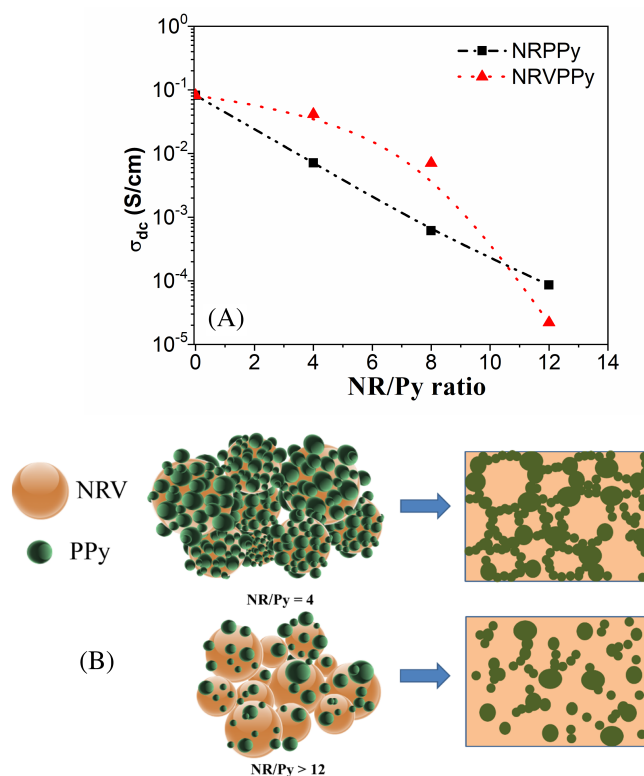


FIGURE 4 (A) DC electrical conductivity of NRPPy and NRVPPy nanocomposite samples in relation to NR/monomer mass ratio. (B) Representative scheme exemplifying the NRV particles coating process and the formation of the percolative system in the nanocomposites on a two-dimensional scale. NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole, Py, pyrrole

showed lower tensile strength and elongation at break; for example, a decrease of approximately 44% in the $\epsilon_{atbreak}$, in relation to NRV, was observed for the

Samples	NR/Py ratio	$\sigma_{atbreak}$ (MPa)	$\epsilon_{atbreak}$ (%) $\times 10^2$	$\sigma_{100\%}$ (MPa)
NR	100	1.36 \pm 0.04	7.7 \pm 0.1	0.68 \pm 0.05
NRV	100	18 \pm 3	8.7 \pm 1	1.37 \pm 0.03
NRPPy	4	7 \pm 1	0.90 \pm 0.04	–
	8	7.3 \pm 0.6	1.0 \pm 0.2	6.9 \pm 0.3
	12	6 \pm 1	3.5 \pm 0.4	1.3 \pm 0.1
NRVPPy	4	10.2 \pm 0.1	0.26 \pm 0.02	–
	8	6.2 \pm 0.5	1.8 \pm 0.2	4.4 \pm 0.3
	12	6.4 \pm 0.3	2.6 \pm 0.5	2.2 \pm 0.1

TABLE 4 Values obtained from stress–strain tests of tensile strength ($\sigma_{atbreak}$) and elongation ($\epsilon_{atbreak}$) at break, and elastic modulus at 100% of strain ($\sigma_{100\%}$) of all samples

Abbreviations: NR, natural rubber; NRV, pre-vulcanized natural rubber latex; PPy, polypyrrole; Py, pyrrole.

NRVPPy4 sample. This behavior was attributed to the encapsulation of the rubber particles, which hindered their coalescence. The reduction observed in $\sigma_{atbreak}$ for the NRVPPy8 and NRVPPy12 samples in relation to the NRVPPy4 sample basically correlates with the interruption of the percolative paths in the system and the consequent reduction of the mechanical load transfer process originated by the three-dimensional network structure formed by the PPy. The $\sigma_{100\%}$ value decreases with the increase of NR content in both nanocomposites, due to the samples becoming less rigid and more elastic.^[26]

4 | CONCLUSION

We have successfully synthesized NR/polypyrrole nanocomposites from the in situ polymerization of pyrrole in a NRV medium. The use of pre-vulcanized latex was demonstrated for the first time, showing unique nanocomposite morphology leading to attractive physical properties. For nanocomposites obtained from pre-vulcanized latex, the PPy nanoparticles were distributed around the border of latex particle circumferences, encapsulating the rubber microparticles by the conductive polymer. The resulting nanocomposites showed higher conductivity than those obtained with non-pre-vulcanized latex. We attribute this to the greater stability of rubber particles of vulcanized latex, allowing PPy to be synthesized around particles' borders, improving the physical and electrical percolation. Increasing nanocomposite conductivity was observed with a decrease in the NR/Py ratio. Thus, the mechanical and electrical properties of the nanocomposites could be readily tuned by selection of NR/Py ratios. Therefore, these synthesized materials could be used in many applications, including piezoresistive, wearables and electromagnetic shielding.

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