

An elastomeric conductor based on polyaniline prepared by mechanical mixing

Roselena Faez, Wilson A. Gazotti, Marco-A. De Paoli*

Laboratório de Polímeros Condutores e Reciclagem — Instituto de Química — Universidade Estadual de Campinas, C. Postal 6154, 13083-970, Campinas-SP, Brazil

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Abstract

In this work we describe the conditions of preparation and the electrical, mechanical, thermal and morphological characteristics of a conductive blend prepared by combining the elastomer poly(ethylene-*co*-propylene-*co*-diene-monomer) and polyaniline doped with *p*-toluene sulfonic acid. Polymer mixtures were prepared in a mixer chamber (cam rotors) coupled to a rheometer. A higher mixing temperature improves the homogeneity of the mixtures, as seen by an increase in conductivity and in crosslinking efficiency. In spite of the good homogeneity, the mixtures are immiscible. Therefore, the formation of bonds between the high molar mass chains of polyaniline and the oligomers explain the increase of the conductivity with an increase in polyaniline content. The modulus values also increase by adding polyaniline to the rubber suggesting a reinforcement effect. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Intrinsically conducting polymers are an extensively studied class of materials due to their interesting properties, including electrical conductivity, electrochromism and electroactivity [1]. However, their mechanical properties preclude their utilisation in the polymer industry. Since their first preparation in 1984 [2,3], conductive polymer blends became the most used way to improve the mechanical properties of conductive polymers [4].

The use of blends in the rubber industry is important because it allows tailoring of the characteristics of a material by using two or more polymers with different properties in the composition. EPDM rubber was chosen in this work because its highly saturated structure affords a material having good resistance to attack by heat, light, oxygen, acid and ozone. On the other hand polyaniline (PAni) is one of the most studied conducting polymers due to its high electrical conductivity associated to good stability, facility of preparation and low cost of monomer.

In previous work the initial particle size of the components of the mixture was shown to affect the final conductivity of blends. Blends of poly(vinyl chloride), PVC, and PAni-HCl, were prepared by casting from tetrahydrofuran

solutions [5]. A low percolation threshold was observed (volume fraction of PAni = 4×10^{-4}) with a conductivity of $10^{-1} \text{ S cm}^{-1}$ using 8% (w/w) of nanosized polyaniline particles. Shackleton and Han [6] prepared blends of Versicon® (PAni doped with *p*-toluene sulfonic acid, PAni-TSA) with PVC and Nylon by melt mixing and observed a good dispersivity of micrometer sized PAni particles. According to these authors, the percolation threshold depends on the particle size of the conducting polymer. Blends of conducting polymers and EPDM have also been previously studied. Zoppi and De Paoli [7] prepared blends of polypyrrole and EPDM by the sorption of pyrrole (vapour phase) in an EPDM matrix containing CuCl_2 . Elastomeric blends with conductivity in the order of $10^{-7} \text{ S cm}^{-1}$ were obtained. In other work, the same authors prepared semi-IPNs by swelling the vulcanised EPDM rubber with a tetrahydrofuran solution of FeCl_3 , followed by exposure to pyrrole vapours. The highest conductivity obtained by this method was ca. $10^{-5} \text{ S cm}^{-1}$ [8].

In this work we prepared blends of EPDM rubber and PAni-TSA using a double screw conrotatory mixer coupled to a Haake rheometer. To vulcanise the rubber, we used dicumyl peroxide in the mixture. Different concentrations of PAni [from 0.5 to 50 parts per hundred (phr)] with controlled granulometry and of the peroxide were mixed with the rubber and the mixture was subsequently vulcanised.

* Corresponding author.

Table 1

Rheometric parameters: minimum torque (ML), maximum torque (MH) and time for 90% of complete reaction (t_{90}), gel fraction (GF) and mechanical properties: (strain at break, σ_b and elongation at break, ϵ_b)

Properties	PA尼/peroxide relative concentrations in blends (phr)			
	15/1.5	30/1.5	15/3.5	30/3.5
ML (N.m)	25	26	20	24
MH (N.m)	57	33	58	42
t_{90} (min)	8	12	8	9
GF	0.82	0.42	0.92	0.88
σ_b (MPa)	6.4	3.3	7.2	3.9
ϵ_b (%)	436	316	513	368

2. Experimental

2.1. Polyaniline preparation:

HCl doped PANi was prepared according to a published route [9]. The product was neutralised with NH_4OH and doped with *p*-toluene sulfonic acid (Hoechst, used as purchased) by stirring for 24 h in a 1.0 mol l^{-1} solution of the acid.

2.2. Blends preparation:

The following sequence was used to prepare the mixtures in the mixing accessory of the Haake Rheocord 90 equipment:

- Loading of the mixer with EPDM at 150°C and 30 rpm.
- Two minutes after temperature stabilisation, loading with PANi-TSA, followed by 4 min mixing in the same conditions.
- Discharge of the mixing chamber and cooling to 120°C .
- Loading with the mixture EPDM/PANi-TSA, addition of stabilisers (Irganox 1076® and Tinuvin 327®, used as obtained from Ciba-Geigy) and dicumyl peroxide. The concentrations of stabilisers for EPDM were previously determined by Guzzo and De Paoli [10].
- Closure of the mixing chamber, mixing and recording of the torque as a function of time until reaching a constant value.

Mixing time was 12 min for 0.5–10 phr of PANi, 16 min for 20–30 phr and 20 min for 40–50 phr. The samples were vulcanised at 175°C and 5 MPa of pressure for 15 min using

Table 2

Gel fraction (GF) variation and conductivity for EPDM/PANi-TSA blends (30 phr) as a function of mixing temperature

Temperature($^\circ\text{C}$)	GF	σ (S cm^{-1})
60	0.70	10^{-8}
80	0.77	10^{-8}
120	0.88	10^{-6}
150	0.97	10^{-6}

a Jasco Hot Press model HP3 and according to ASTM D3182 standard.

Cure parameters were determined at 175°C and 3° arc using a Monsanto oscillating disk rheometer. Thermal stability of mixtures and pure components was studied by thermogravimetric analysis (TGA) using a DuPont 951 thermal analyser from 25°C to 800°C ($10^\circ\text{C min}^{-1}$) under air. Dynamical mechanical analysis was carried out using TA 983 DMA equipment at 1.0 Hz of frequency with a sinusoidal deformation. The fracture morphology was studied by scanning electron microscopy (SEM) in a Jeol JSM-T3000 microscope operating at 20 kV using samples metalised in a Balzers MED 020 machine. Optical microscopy (OM) was carried out using Olympus-CBA-K equipment with $200\times$ magnification. Stress–strain tests were done using EMIC DL 2000 equipment, according to ASTM D412-92 standard using a crosshead speed of 500 mm min^{-1} and a cell of 50 N. Electrical conductivity of blends was measured by an adaptation of the Coleman method [11], using a Keithley 617 programmable electrometer and a four-probe sensor with gold contacts. Infrared spectra were recorded using a Perkin-Elmer FT-IR 1600 spectrophotometer. The degree of swelling determinations were carried out at room temperature in cyclohexane.

3. Results and Discussion

The use of rubber products always involves vulcanised materials because crosslinked elastomers present better mechanical properties. Thus, to prepare EPDM–PANi blends it is necessary to study the effect of the conductive polymer on the crosslinking process of the rubber. This effect was studied by changing PANi and dicumyl peroxide (crosslinking agent) relative contents, according to statistical factorial planing [12]. Table 1 presents the characteristic of vulcanised mixtures studied by using a curemeter. Minimum torque, ML, represents the effective viscosity of the mixtures before vulcanisation. ML does not change with the PANi and/or the peroxide contents.

Maximum torque value after vulcanisation, MH, is an index of the extent of crosslinking reactions and represents the elastic modulus of the fully vulcanised rubbers. For the EPDM–PANi blend containing 15 phr of conducting polymer we observed no changes in the MH values when increasing the crosslinking agent content. For these conditions, the low concentration of dicumyl peroxide is already sufficient to induce a good extent of crosslinking. However, comparing these results with those obtained for blends containing 30 phr of PANi it is observed that the MH values decreases, indicating that the conducting polymer inhibits the crosslinking process in the elastomer. This effect is partially counterbalanced by using a higher concentration of crosslinking agent. PANi has an intrinsic acid content and increasing the mass fraction of PANi in the blend induces degradation processes of the crosslinking agent by

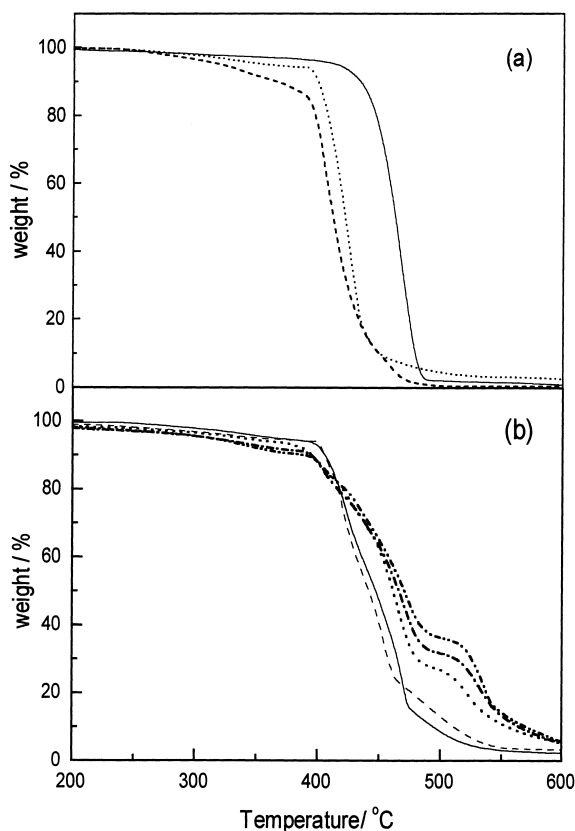


Fig. 1. Thermogravimetric curves ($10^{\circ}\text{C min}^{-1}$, air) for blends: 1a: (—) EPDM; (---) 1 and (.....) 5 phr of PANi-TSA and 1b: (—) 10, (---) 20, (.....) 30, (-.-.-) 40 and (-.-.-.-) 50 phr of PANi-TSA.

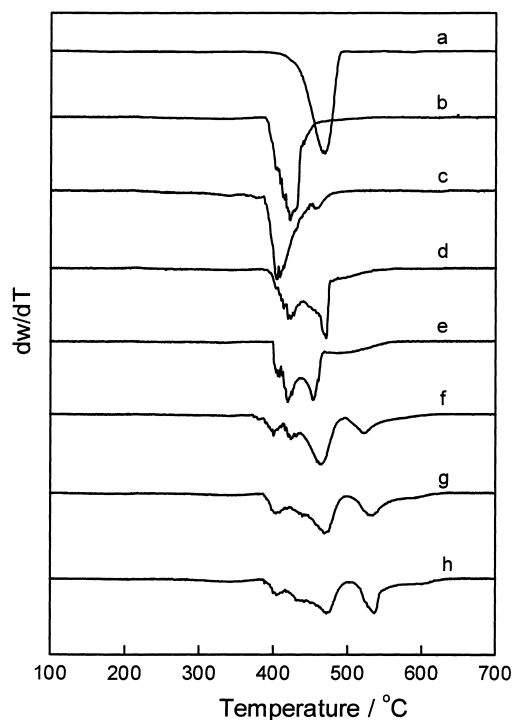


Fig. 2. DTG curves for (a) EPDM and for blends containing: (b) 1, (c) 5, (d) 10, (e) 20, (f) 30, (g) 40 and (h) 50 phr of Pani-TSA.

heterolytic decomposition inhibiting the formation of the free radicals necessary for the vulcanisation reaction [13, 14].

Mixing temperature is also an important factor to be considered in the preparation of blends. The interaction between PANi and EPDM has an influence in the crosslinking process of the blend. Keeping all other variables constant ($[\text{PANi}]/[\text{peroxide}] = 10$ and cam rotors speed = 50 rpm) and changing the temperature we observe pronounced effects in gel fractions, GF, and conductivity, Table 2. We observed an increase in GF when increasing the mixing temperature. This effect is assigned to a good interaction between PANi and EPDM. The electrical conductivity results are also an evidence for the effect of the mixing temperature. There is an increase in conductivity of two orders of magnitude for blends prepared at higher temperature. For blends prepared at 80°C and 150°C the conductivity are 10^{-8} and $10^{-6} \text{ S cm}^{-1}$, respectively, suggesting a better dispersion of the conductive polymer in the elastomeric matrix at the higher the temperature.

Using these results we prepared samples varying the concentrations of PANi-TSA, using 150°C as the mixing temperature and 3.5 phr of peroxide. Particle sizes between 100 and 200 mesh were used to improve the dispersibility of PANi in the matrix. We studied the thermal, morphological, mechanical and mechanic-dynamical properties and the electrical conductivity of the mixtures.

From TG curves, Fig. 1, we observe different weight losses depending on the blend compositions. Pure EPDM and the mixtures containing 1 and 5 phr of PANi-TSA showed only one visible weight loss. Blends with higher contents of the conducting polymer present complex thermo-decomposition processes and the several weight losses observed can be related to the degradation of the elastomer and of the conducting polymer.

Dependence of degradation of blend composition is better visualised in DTG curves, Fig. 2. Pure EPDM presents its maximum of weight loss at 470°C , assigned to the liberation of volatile hydrocarbons. These oligomers are initially formed by free radicals occurring in the main chain during the heating [15]. Blends containing 1 and 5 phr of PANi-TSA (curves b and c) show the same weight loss process, but at lower temperatures (ca. 420°C). This means that, for these mixtures, the conducting polymer acts as pro-degrading for the elastomer. Probably, free radicals formed in the PANi accelerate the formation of volatile oligomers in the EPDM chains.

Other processes are observed by increasing PANi contents in the blend. Weight losses at 420°C and 470°C (related to EPDM degradation when pure and mixed to PANi, respectively) are still observed but their relative intensities change with the PANi contents in the mixtures. By increasing PANi content the degradation of EPDM occurs preferentially at 470°C (as observed for pure EPDM) and other weight losses are observed at approximately 400°C and 535°C . These last processes can be assigned to TSA and dedoped PANi

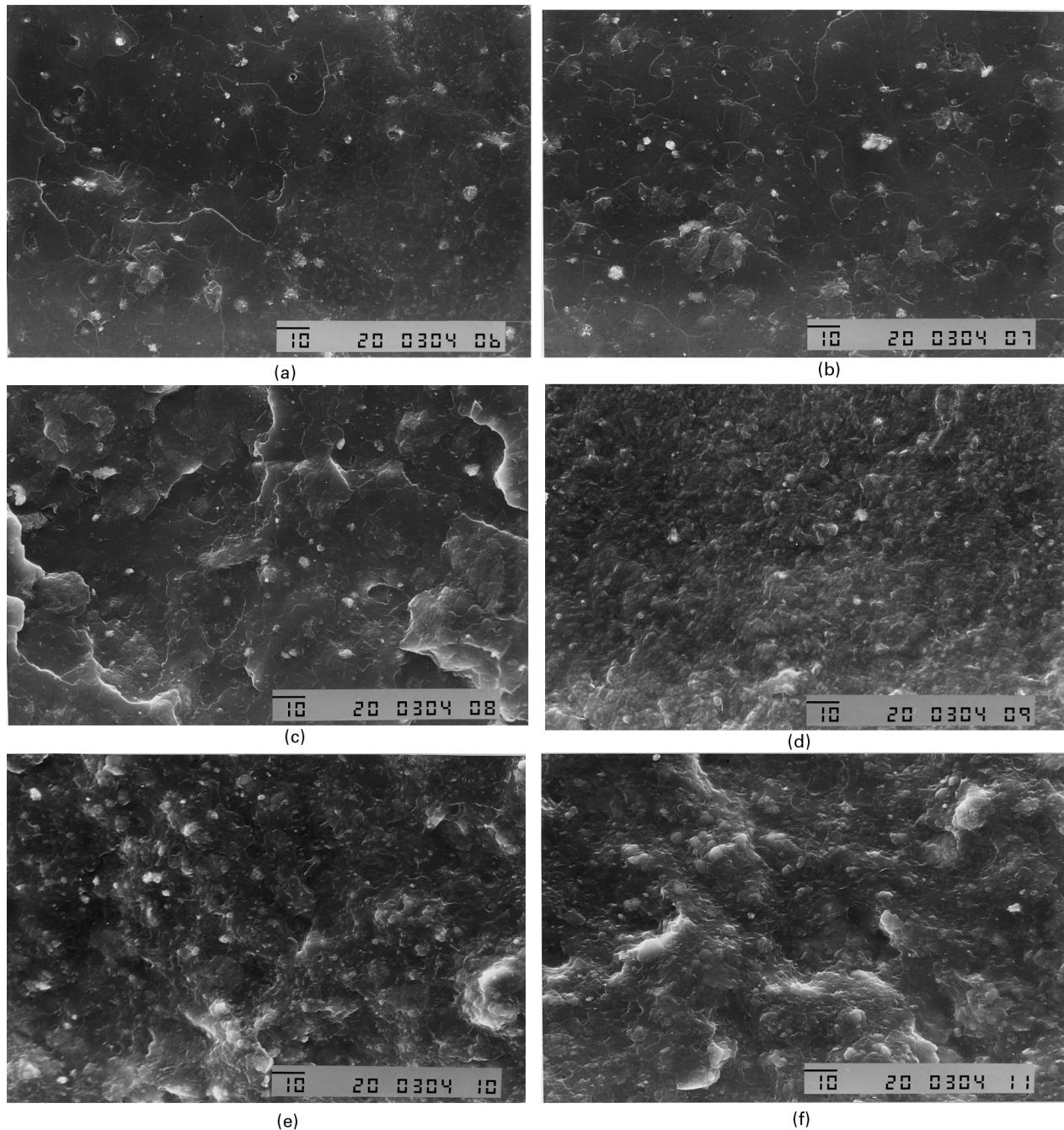


Fig. 3. Scanning electron micrographies of blends fracture with: (a) 5; (b) 10; (c) 20; (d) 30; (e) 40; and (f) 50 phr of PANi-TSA. Magnification of $700\times$. Bar in the bottom represents $10\ \mu\text{m}$.

degradations, respectively. The relative increase of the degradation of EPDM at 470°C and the new weight losses observed, suggest that the pro-degrading effect produced by the conducting polymer is less pronounced for mixtures with higher contents of PANi than for those mixtures with smaller amount of PANi. This probably means that a higher PANi content in the mixtures induce a higher phase separation between the components.

The effect of PANi in the blend can be also observed in the SEM, Fig. 3. There is no change in the lamellar structure of

the rubber for low concentrations of PANi. By increasing the concentration we observe a change in the morphology of the fracture, from regular to a very rough. At low concentrations we observe the dispersion of the conductive polymer in the rubber matrix, white dots in Fig. 3b, showing a low interaction between the materials. For higher concentrations this is not observed. The changes of the morphology may possibly suggest a compatibilization of the blend constituents. In the optical micrographies the dispersion of PANi is better observed, Fig. 4. Powder distribution and formation of a

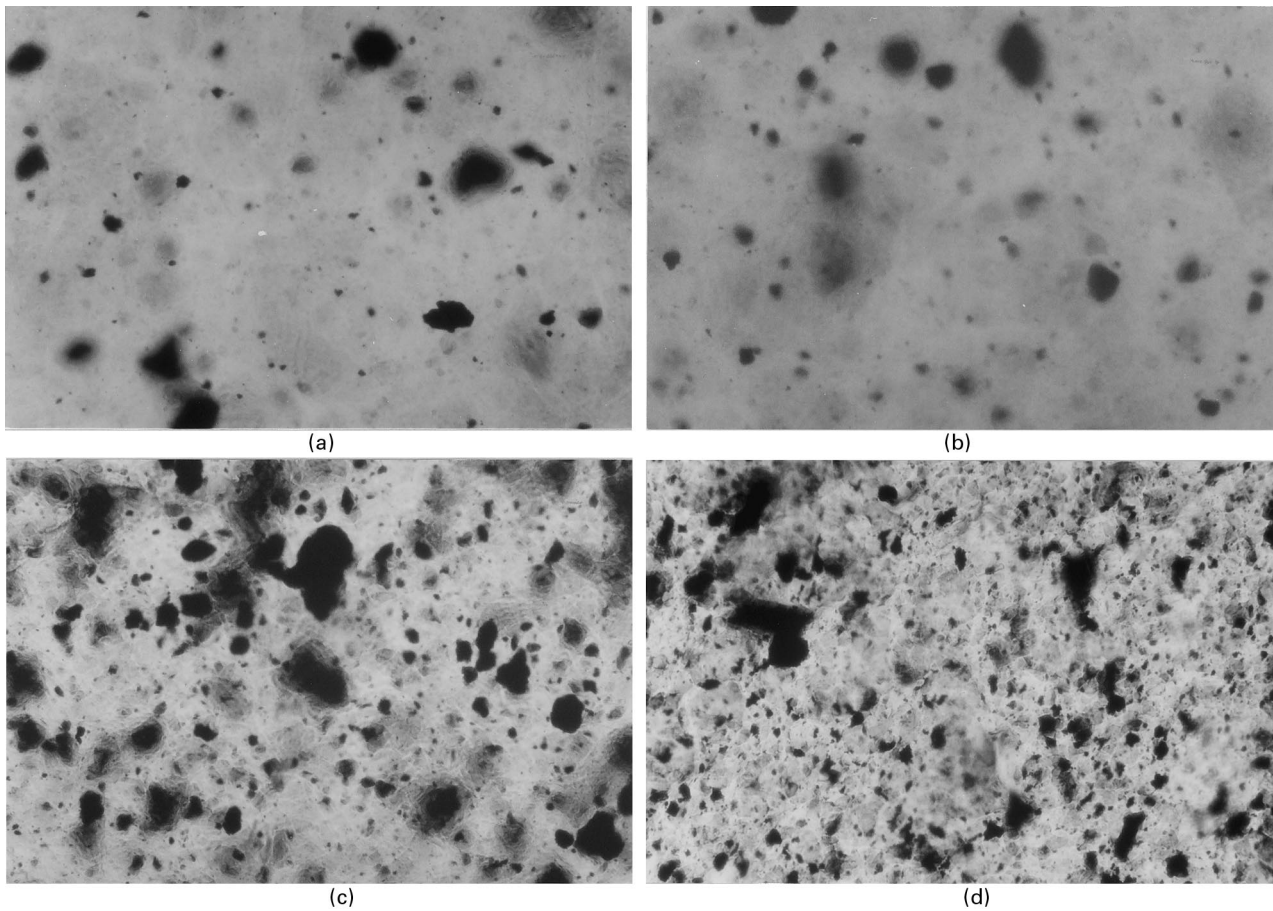


Fig. 4. Optical microographies for blends with: (a) 1; (b) 5; (c) 10; and (d) 30 phr of PANi-TSA. Magnification of $200\times$ times.

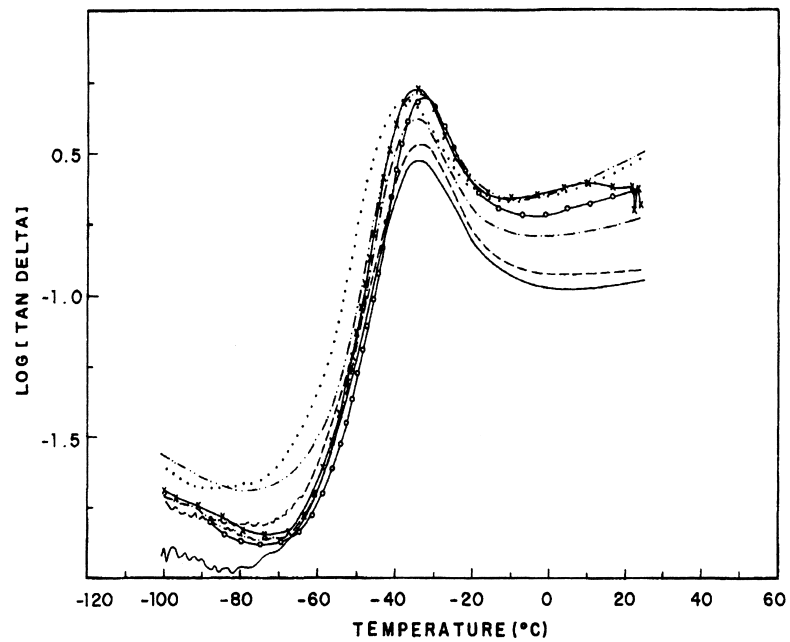


Fig. 5. Log $\tan\delta$ as function of temperature for blends with: (-x-x-) 0; (-.-.-) 1, (.....) 10, (-.-.-) 20, (-o-o-) 30, (----) 40 and (—) 50 phr of PANi-TSA.

Table 3

Mechanical properties and gel fraction of pure rubber and blends as a function of polyaniline concentration in phr: Young modulus (E), strain at break (σ_b), elongation at break (ϵ_b) and gel fraction (GF)

PAni conc. (phr)	E (MPa)	σ_b (MPa)	$\epsilon_b \times 10^{-2}$ (%)	GF
0	3.0 ± 0.2	5.4 ± 0.4	6.0 ± 0.3	0.94
5	3.0 ± 0.1	7.6 ± 0.9	9.4 ± 0.8	0.96
10	5.0 ± 0.1	6.6 ± 0.8	6.4 ± 0.7	0.96
20	9.0 ± 0.7	6.0 ± 0.5	3.5 ± 0.3	0.96
30	14.0 ± 0.5	6.5 ± 0.3	2.8 ± 0.2	0.97
40	13.0 ± 0.7	8.0 ± 0.4	2.0 ± 0.1	0.99
50	26.0 ± 1.8	7.9 ± 0.6	1.0 ± 0.1	0.99

green layer (grey in the black and white print) is assigned to PAni dispersion. The green phase is due to the low molar mass oligomers of PAni connecting the high molar mass spots. These links may be responsible for formation of a network. Increasing PAni concentrations results in a larger density of high molar mass spots improving the reinforcement effect.

By comparing the FT-IR spectra of pure EPDM and the blends we observe that the absorption at 1200 cm^{-1} becomes more pronounced with the increase in PAni concentration. This absorption is characteristic for out-of-plane and in-plane bending of the C–H bonds of the aromatic rings present in PAni [16]. The absorption of the rubber conceals the other absorptions of PAni.

Table 3 shows the variation of the modulus, strain at break and elongation at break as a function of PAni-TSA concentration. There is an initial increase of the elongation at break for 5 phr, followed by a pronounced decrease to 20 phr and a further decrease for mixtures with concentrations higher than 20 phr. The modulus shows an increase between 5 and 30 phr and there is an abrupt increase for mixtures with concentrations higher than 30 phr. This effect is assigned to the rigidity of PAni, acting as a reinforcing filler and changing the viscoelastic behaviour of the rubber to a rigid material. PAni contributes also to increase the rubber crosslinking density as determined in the swelling measurements (gel fraction, GF, increase in Table 3).

Dynamical mechanical analyses (DMA) gives information about storage modulus (E'), loss modulus (E'') and $\tan\delta$. Fig. 5 shows the $\tan\delta$ curves as function of temperature for all mixtures. There is no variation in the glass transition temperature (T_g) of the EPDM phases suggesting that the mixtures are immiscible. The region between -10°C and 30°C shows a decrease in the plateau of the elastic region with an increase of PAni concentration confirming the reinforcing effect observed in the stress–strain measurements. The correct value for the glass transition temperature of PAni has not yet been established although there are some papers that try to explain the molecular relaxation processes of the chains [17].

Fig. 6 shows a plot of the logarithm of the electrical conductivity as function of PAni concentration in the

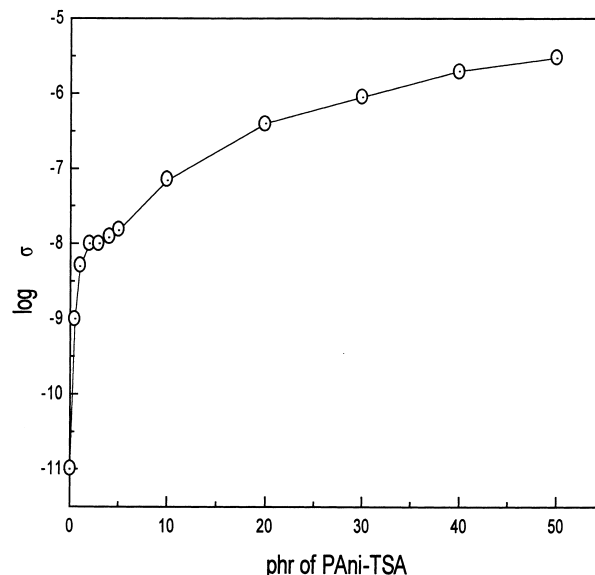


Fig. 6. Variation of the logarithm of the electrical conductivity ($\log\sigma$) as function of PAni-TSA concentrations.

mixtures. Percolation threshold is defined as the minimum amount of conductive filler that must be added to an insulator matrix to cause the onset of electrical conductivity. Theoretical studies for inorganic fillers show that the percolation threshold occurs when the filler represent 16% (v/v) in the mixtures [18]. According to Fig. 6 the onset of conductivity increase is reached with only 1 phr of PAni-TSA [$d_{\text{PAni-TSA}} = 1.07 \text{ g cm}^{-3}$, $d_{\text{EPDM}} = 0.86 \text{ g cm}^{-3}$, thus 1 phr = 0.99% (w/w) = 1.24% (v/v)]. This means that the percolation threshold is about 13 times smaller than the calculated by the theory. Other blends using conducting polymers also presented low percolation threshold [19], and this is explained by the formation of interpenetrating networks between the components of the mixture, which was observed by SEM measurements [20]. The conductivity increases continuously with PAni-TSA content and seems to reach a plateau at 50 phr ($10^{-6} \text{ S cm}^{-1}$).

4. Conclusion

In this work we prepared vulcanised elastomeric conductive blends of EPDM and PAni-TSA and observed that for a fixed composition the temperature of mixing affects the conductivity of the blend. The formation of links between high molar mass and oligomers of PAni-TSA is related to the continuous increase of conductivity of the blends when increasing PAni concentration. By changing the concentration of PAni-TSA and controlling the mixing parameters it is possible to produce vulcanised conductive (10^{-9} – $10^{-6} \text{ S cm}^{-1}$) materials with elastomeric properties.

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