*Polymer* Vol. 37 No. 10, pp. 1999–2009, 1996

0032-3861/96/$15.00+0.00

# Chemical preparation of conductive elastomeric blends: polypyrrole/EPDM—II. Utilization of matrices containing crosslinking agents, reinforcement fillers and stabilizers

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*(Received 23 June 1995)*

Semi-interpenetrating networks (semi-IPN) of polypyrrole and ethylene-propylene-5-ethylidene-2-norbornene rubber, EPDM, were prepared by chemical oxidation of the monomer using two different methods of synthesis. In the first method, EPDM rubber samples containing $CuCl_2$ (powder with granulometry $<105\,\mu m$) and dicumyl peroxide were obtained by mechanical mixing, crosslinked by heating and exposed to pyrrole vapours. In the second route, EPDM rubber crosslinked with dicumyl peroxide was swollen in an $FeCl_3$/THF solution and exposed to pyrrole vapours. Both methods provided semi-IPN of polypyrrole/EPDM rubber, but the electrical conductivities of the materials obtained by the second route ($\sigma \approx 10^{-5}$ S cm$^{-1}$) are higher than for the first route ($\sigma \approx 10^{-10}$ S cm$^{-1}$). Further, the second method allowed the prior incorporation of silica and kaolin fillers into the rubber, producing a semi-IPN with mechanical properties similar to a crosslinked rubber containing the same amount of fillers. The incorporation of antioxidant agents was also studied using the second route. Thermal ageing showed that the electrical conductivity decreases as a function of the heating time, independent of the presence of an antioxidant agent. However, the thermal stability of the rubber phase in the semi-IPN was improved. Copyright © 1996 Published by Elsevier Science Ltd.

**(Keywords: polypyrrole/vulcanized EPDM blend; conductive rubber; reinforcement fillers)**

## INTRODUCTION

The chemical preparation of polypyrrole in an insulating matrix was initially reported by Bjorklund *et al.*[1]. Cellulose paper was swollen in an aqueous $FeCl_3$ solution and exposed to pyrrole vapours. The electrical conductivity of paper impregnated with polypyrrole was 2 S cm$^{-1}$ and its properties were similar to polymer–carbon black composites which are used for antistatic protection or electromagnetic shielding.

Blends constituted by intrinsically conducting polymers present some advantage in comparison to extrinsically conducting polymers. In the latter case, it is necessary to control the rate of conductive filler addition and the particle aggregation phenomena. The electrical conductivity is a function of inter-particle electronic transfer. It is also necessary to have large amounts of conducting filler (15–30%) to arrive at moderate levels of conductivity. This increases the cost and the density of the final products[2].

The chemistry of intrinsically conducting polymers offers a great diversity of synthetic methods which allows their incorporation in different kinds of insulating matrices. Under determined synthesis conditions, it is possible to have inter- and intra-particle electronic transfer. In some cases, 2% (w/w) of intrinsically conducting polymers provide blends with electrical conductivity of 1 S cm$^{-1}$, without a percolation threshold[2].

Blends of polypyrrole and insulating polymers can be chemically prepared by different methods. The most reported routes include:

(1) Dissolution of the insulating polymer in a solution of an oxidizing agent. Stabilized polypyrrole colloidal solutions are obtained by adding pyrrole under stirring[3,4]. Powder composites are prepared by evaporation of the colloidal solutions[5–7].

(2) Covering of polymeric films or textiles by polypyrrole. The insulating matrix is immersed in a mixture of oxidizing agent and pyrrole[8–12].

(3) Interfacial polymerization. The insulating polymer separates a monomer solution and a solution of an oxidizing agent. The monomer and oxidant diffuse across the matrix and the polymerization occurs[13–16].

(4) Preparation of blends by swelling of insulating matrices in a solution of an oxidizing agent, followed by exposure to pyrrole vapours[17–21].

(5) Preparation of blends by mixing the insulating polymer and oxidizing agent solutions, followed by film casting by solvent evaporation. The matrices containing oxidant are subsequently exposed to monomer vapours[22,23].

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In a previous paper, we reported a method of synthesis of polypyrrole/EPDM rubber blends based on the mechanical mixing of $CuCl_2$ into EPDM rubber. The effect of the oxidizing agent particle-size on electrical conductivity and mechanical properties of polypyrrole/EPDM rubber blends was evaluated[24]. In this work we have prepared a semi-interpenetrating network (semi-IPN) by polymerizing pyrrole into crosslinked EPDM matrices. Our aim was to improve the mechanical properties of the polypyrrole/EPDM products. Two synthetic routes were investigated. In the first method, we take advantage of the procedure previously described[24]. $CuCl_2$ and dicumyl peroxide were mechanically incorporated into EPDM rubber. These samples were crosslinked and exposed to pyrrole vapours. In the second method, crosslinked EPDM was swollen in a solution of an oxidizing agent, followed by exposition to pyrrole vapours. Using the second method, we verified that the semi-IPN electrical conductivity does not depend on the degree of rubber crosslinking or the oxidant solution concentration. The second method presents interesting advantages, such as it is possible to use vulcanized rubber matrices and, most importantly, it is possible to incorporate reinforcements or inert fillers which improve the mechanical properties.

The second method was also used to incorporate stabilizing agents. The chemical synthesis of polypyrrole into insulating matrices presents a disadvantage: the need of an oxidizing agent. This can affect the long-term stability of the rubber blend. It has been shown that iron oxide can act as a catalyst for the elastomer degradation[25]. Armes *et al.* verified that Fe(III) promotes the chemical decomposition of chemically prepared polypyrrole[26]. We also studied the thermal stability of polypyrrole/EPDM semi-IPN containing, or not, stabilizing agents. Further, we investigated the effect of silica and kaolin addition into the EPDM rubber which was used in the synthesis of the polypyrrole/EPDM semi-IPN. In this case, we determined the ideal filler concentration by using chemometric planning. The electrical conductivity and mechanical properties of the final products prepared by using the above-described methods are presented and discussed.

## EXPERIMENTAL

### *Polypyrrole/EPDM semi-IPN obtained by mechanical mixing of oxidizing and crosslinking agents with the rubber*

EPDM matrices containing the oxidizing agent and dicumyl peroxide were prepared by mechanical mixture of $CuCl_2{\cdot}2H_2O$ (particle size $<105\,\mu m$) and dicumyl peroxide (Dicup 40) by calendering at 50°C. The rotation speeds on the two cylinders were 19 and 23 rev $min^{-1}$, respectively. Samples containing 9 or 33% (w/w) of $CuCl_2$ and 0.8 or 3.8% (w/w) of dicumyl peroxide were crosslinked in a Jasco HP-3 heating system at 180°C and 9 MPa of pressure, for 10 min. Semi-IPN were obtained by exposing the crosslinked matrices to pyrrole vapours for different times at room temperature.

### *Polypyrrole/EPDM semi-IPN obtained by swelling of crosslinked rubber in an oxidant solution*

*Crosslinking of EPDM rubber.* EPDM matrices containing 2.9, 4.8 or 6.5% (w/w) of dicumyl peroxide were prepared by calendering at 50°C (using the same conditions as above). The samples were crosslinked for 10, 20 or 30 min (180°C, 9 MPa). The crosslinking density and sol–gel fractions of the samples were determined by swelling tests in cyclohexane as described by Billmeyer *et al.*[27].

*Polypyrrole/EPDM semi-IPN preparation.* Crosslinked EPDM samples were immersed in a solution of $FeCl_3$ in tetrahydrofuran (0.67, 1.64, 3.22, 4.76 or 9.09% w/w). The swelling kinetics was gravimetrically followed. The samples were dried under vacuum to determine the $FeCl_3$ concentration by energy dispersive X-ray fluorescence (Tracor EDXRF spectrace 5000). Standard samples were prepared by mechanical incorporation of $FeCl_3$ in EPDM rubber. The samples swollen in $FeCl_3$/THF were exposed to pyrrole vapours for 26 h at room temperature and dried under vacuum for 48 h.

### *Effect of silica and kaolin addition*

As shown in *Table 1*, EPDM rubber samples containing dicumyl peroxide, silica and kaolin were prepared by calendering at 50°C and crosslinked (180°C, 20 min, 9 MPa). The crosslinked EPDM rubber samples were swollen in an $FeCl_3$/THF solution (4.76% w/w) for 24 h and subsequently exposed to pyrrole vapours for 26 h. Silica (Rhodia S/A) and kaolin (Satintone SP-33) were used without previous treatment.

### *Effect of stabilizing agents addition*

EPDM rubber containing 3.5% dicumyl peroxide, 14% silica, 14% kaolin, 0.07% Irganox 1076® and 0.55% Tinuvin 327®, were prepared by calendering and crosslinked as described above. The stabilizing agents were furnished by Ciba Geigy. EPDM samples were swollen in an $FeCl_3$/THF solution (4.76% w/w) for 24 h and subsequently exposed to pyrrole vapours.

**Table 1** Variable values used for the chemometric plan and respective levels* $xP'$, $xS'$ and $xC'$ of the dicumyl peroxide, $P$, silica, $S$, and kaolin, $K$, concentrations

| Test number | $P$ (%) | $S$ (%) | $K$ (%) | $xP'$ | $xS'$ | $xK'$ |
|---|---|---|---|---|---|---|
| 1 | 4.2 | 20 | 20 | +1 | +1 | +1 |
| 2 | 2.8 | 20 | 20 | −1 | +1 | +1 |
| 3 | 4.2 | 8 | 20 | +1 | −1 | +1 |
| 4 | 2.8 | 8 | 20 | −1 | −1 | +1 |
| 5 | 4.2 | 20 | 8 | +1 | +1 | −1 |
| 6 | 2.8 | 20 | 8 | −1 | +1 | −1 |
| 7 | 4.2 | 8 | 8 | +1 | −1 | −1 |
| 8 | 2.8 | 8 | 8 | −1 | −1 | −1 |
| 9 | 3.5 | 14 | 14 | 0 | 0 | 0 |
| 10 | 3.5 | 14 | 14 | 0 | 0 | 0 |
| 11 | 3.5 | 14 | 14 | 0 | 0 | 0 |
| 12 | 3.5 | 14 | 14 | 0 | 0 | 0 |
| 13 | 3.5 | 14 | 14 | 0 | 0 | 0 |
| 14 | 4.7 | 14 | 14 | 1.732 | 00 | 0 |
| 15 | 2.3 | 14 | 14 | −1.732 | 0 | 0 |
| 16 | 3.5 | 24 | 14 | 0 | 1.732 | 0 |
| 17 | 3.5 | 3.6 | 14 | 0 | −1.732 | 0 |
| 18 | 3.5 | 14 | 24 | 0 | 0 | 1.732 |
| 19 | 3.5 | 14 | 3.6 | 0 | 0 | −1.732 |

$P$, $S$ and $K$ concentrations were calculated by using the equations: $xP' = (P - 3.5)/0.7$; $xS' = (S - 14)/6$; $xK' = (K - 14)/6$ and the minimum and maximum amounts for each variable were determined as: $2.0 < P < 6.5$; $0 < S < 25$; and $0 < K < 25\%$

Polypyrrole/EPDM semi-IPN containing, or not, the stabilizing agents, were thermally aged at 80°C for 24 h under ambient atmosphere. Electrical conductivity was measured at intervals of 1 h, for the first 8 h, using the method described by Coleman[28].

*Physical measurements*

Stress–strain measurements were carried out in an EMIC MEM500 equipment by using a 20 N load cell, and a cross-head speed of 50 or 500 mm min$^{-1}$. The sample dimensions were 10 × 50 mm with thickness between 0.50 and 0.70 mm. Elemental analyses were carried out on a Perkin Elmer CHN 2400 elemental analyzer. Transmission electron microscopy was done with a Zeiss CEM 902 transmission electron microscope, by using films (thickness = 60 nm) which were obtained by cutting in a Leica Reichert & Jung F4E ultramicrotome at liquid $N_2$ temperature. Thermal analysis were carried out on a Du Pont 990 thermal analyzer, with Ar or synthetic air flows. Infrared reflectance spectroscopy was carried out in a Perkin Elmer 1600 FT-IR spectrophotometer, by using an ATR-6 Jasco accessory.

## RESULTS AND DISCUSSION

### *Polypyrrole/EPDM semi-IPN obtained by mechanical mixing of $CuCl_2$ and dicumyl peroxide into the rubber*

*Figure 1* shows the polypyrrole weight fraction variation, Xpolypyrrole, as a function of polymerization time for EPDM matrices containing 9 or 33% $CuCl_2$ (particle size <105 μm) crosslinked by using 0.8 or 3.8% dicumyl peroxide. Independent of the polymerization time, Xpolypyrrole values for matrices crosslinked with 3.8% dicumyl peroxide are lower than for matrices without dicumyl peroxide (denominated polypyrrole/EPDM blends) or matrices obtained using 0.8% crosslinking agent. This behaviour has been ascribed to the limited sorption of pyrrole vapour on crosslinked matrices.

The electrical conductivity of the semi-IPN was *ca* $10^{-10}$ S cm$^{-1}$, independent of $CuCl_2$ or dicumyl peroxide concentrations or polymerization time. *Table 2* shows the electrical conductivity values for semi-IPN which were obtained after 24 h of polymerization. The electrical conductivity for semi-IPN prepared by using 9% $CuCl_2$ is similar to the material prepared using the non-crosslinked matrix (*ca* $10^{-10}$ S cm$^{-1}$). We observe that, for samples prepared using 33% $CuCl_2$ and 0.8% dicumyl peroxide, the electrical conductivity of the semi-IPN is three orders of magnitude lower than for the blend, although Xpolypyrrole values in both materials are very close[24]. Using transmission electron microscopy we observe some porous structures on the semi-IPN (*Figure 2*).

By using differential scanning calorimetry we verified that the thermograms of EPDM containing $CuCl_2$ and polypyrrole/EPDM blends present an endothermic peak between 100 and 140°C (samples without crosslinking agent). This peak disappears after a second temperature scan. Thermogravimetry shows that the mass loss percentage in this temperature range (6–7%) is close to the amount of water present in the matrix ($CuCl_2 \cdot 2H_2O$ incorporation). The porous structure can be due to water evaporation during crosslinking. By transmission electron microscopy we also verified that the edges of the pores are dark and there are some dark particles in the interior of the pores. In an immiscible system like this, we

**Table 2** Electrical conductivity values for semi-IPN as a function of $CuCl_2$ (<105 μm) and dicumyl peroxide concentrations; 24 h polymerization time

| % $CuCl_2$ <105 μm | % Dicumyl peroxide | Xpolypyrrole (%) | σ (S cm$^{-1}$) |
|---|---|---|---|
| 9 | zero | 5.6 ± 0.4 | $4 \times 10^{-10}$ |
| 9 | 0.8 | 5.8 | $5 \times 10^{-10}$ |
| 9 | 3.8 | 3.4 | $5 \times 10^{-10}$ |
| 33 | zero | 16.9 ± 0.3 | $2 \times 10^{-7}$ |
| 33 | 0.8 | 18.4 | $3 \times 10^{-10}$ |
| 33 | 3.8 | 12.8 | $1 \times 10^{-10}$ |

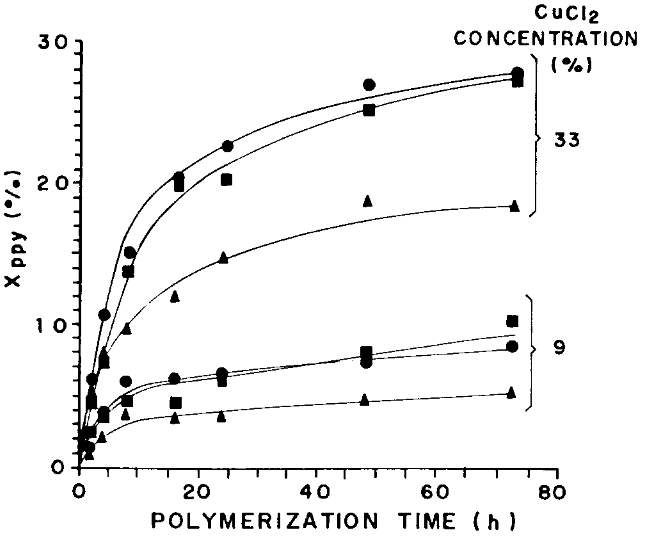

**Figure 1** Polypyrrole weight fraction on polypyrrole/EPDM semi-IPN as a function of polymerization time. The matrices contain 9 or 33% $CuCl_2$ (granulometry <105 μm) and 0.8 (●) or 3.8% (▲) dicumyl peroxide. For comparison, we show the curves for samples without dicumyl peroxide (■)

**Figure 2** Transmission electron micrographs of polypyrrole/EPDM semi-IPN prepared using 33% $CuCl_2$ (<105 μm) and 0.8% dicumyl peroxide (24 h polymerization time). Magnification = 12000

imagine that the pores present in the matrix can induce a localized polymerization of pyrrole. Under these conditions, the contact between polypyrrole islands is precluded and the electrical conductivity is compromised.

With respect to mechanical properties, the elasticity modulus values for a semi-IPN containing 9 or 33% of $CuCl_2$ and 0.8 or 3.8% of dicumyl peroxide, were similar to the respective blends (obtained using non-crosslinked matrices). The tenacity values, however, depend on the dicumyl peroxide concentration. *Figure 3* shows the tenacity values as a function of polymerization time for polypyrrole/EPDM semi-IPN and blends. For materials containing 9% $CuCl_2$ the behavior is similar to *Figure 3*. Up to 48 h polymerization, the semi-IPN prepared using 3.8% dicumyl peroxide show higher tenacity values than blends. After this, their tenacity is similar to the blends. It is interesting to note that the materials present maximum tenacity values at the initial polymerization times. This behaviour has been attributed to the polypyrrole oligomers which may act as plasticizers. The semi-IPN obtained using 0.8% dicumyl peroxide present lower tenacity values than the blends, independent of the polymerization time. We were surprised with this behaviour, because we expected that the semi-IPN tenacity would always be higher than (or equal to) the values for the blends. We suppose that the free radical concentration used to promote matrix crosslinking is inferior to the $O_2$ concentration present in the matrix, producing a thermo-oxidative degradation instead of crosslinking. We tried to verify this degradation occurrence by using *FT*i.r. spectroscopy. EPDM matrices containing 9% $CuCl_2$ (particle-size <105 $\mu$m) and 0.8 or 3.8% dicumyl peroxide were crosslinked for different times at 180°C. Independent of the heating time used (10, 20 or 30 min), of the dicumyl peroxide concentration (0.8 or 3.8%) and the $CuCl_2$ presence, we observed no changes on the infrared spectra. We believe that either the probability of degradation occurrence is very low or the degradation is not detected by infrared spectroscopy. We were not able to explain this behaviour.

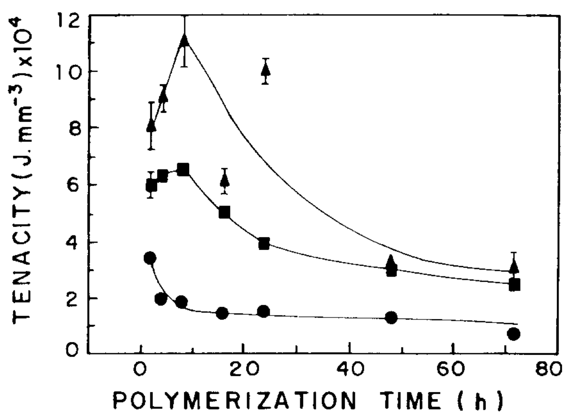

**Figure 3** Tenacity values for polypyrrole/EPDM semi-IPN as a function of polymerization time. (■) Non-vulcanized polypyrrole/EPDM; vulcanized polypyrrole/EPDM using 0.8 (●) or 3.8% (▲) dicumyl peroxide

*Polypyrrole/EPDM semi-IPN obtained by swelling of crosslinked rubber in a solution of an oxidizing agent*

The method used to obtain polypyrrole/EPDM semi-IPN by mechanical incorporation of $CuCl_2$ and dicumyl peroxide produces materials which have low electrical conductivity. We solved this problem by using an alternative method. Crosslinked EPDM matrices were swollen in an $FeCl_3$ or $CuCl_2$/THF solution, and exposed to pyrrole vapours at room temperature. The pyrrole polymerization was very slow (taking nearly a week) and was non-uniform when the matrices were swollen in $CuCl_2$/THF solution. More homogeneous semi-IPN were obtained by using an $FeCl_3$/THF solution with a polymerization time of 20–26 h. Similar results have been reported for polypyrrole polymerization in an aqueous $CuCl_2$ or $FeCl_3$ solution[29]. In the case of the polymerization in THF and into EPDM matrices, we verified that an uniform polymerization occurs if the matrices are partially swollen. The polymerization is inhibited for dry matrices or excessively swollen matrices. Using Fe(III) to control the experimental conditions, we were able to avoid the solvent interference and to obtain reproducible results. The same experimental conditions were adopted for $CuCl_2$/THF swollen samples, but the polymerization was still inhibited. We therefore used $FeCl_3$/THF solutions for the syntheses.

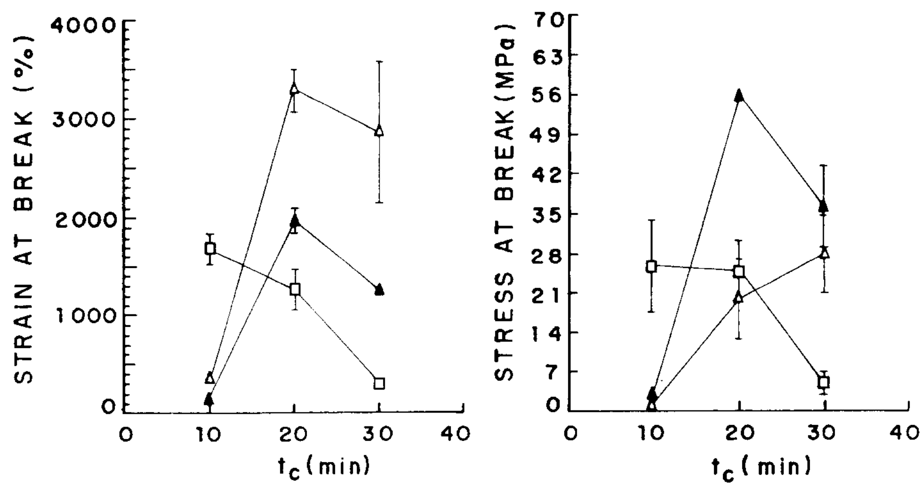

**Figure 4** Mechanical properties of EPDM matrices containing 2.9 (△), 4.8 (▲) or 6.5% (□) dicumyl peroxide, as a function of crosslinking time

*Crosslinking of EPDM matrices.* *Figure 4* shows the behaviour of the stress and strain at break as a function of crosslinking time for EPDM matrices crosslinked using 2.9, 4.8 or 6.5% of dicumyl peroxide. The elasticity moduli do not depend on the crosslinking time and were: 0.68 ± 0.09, 1.0 ± 0.1 and 1.3 ± 0.3 MPa for crosslinked matrices using 2.9, 4.8 and 6.5% dicumyl peroxide, respectively. *Figure 4* shows that the stress and strain at break for matrices crosslinked with 2.9% dicumyl peroxide increase when the crosslinking time increases from 10 to 20 min. If the crosslinking time was increased to 30 min the stress and strain at break remained nearly constant. For samples which were crosslinked with 4.8% dicumyl peroxide, the stress and strain at break present maximum values at 20 min of crosslinking time. For samples crosslinked with 6.5% dicumyl peroxide, the stress and strain at break are nearly constant when the crosslinking time changes from 10 to 20 min. Increasing the time to 30 min, we observe a decrease of the stress and strain at break. These results show that the best crosslinking time is 20 min, and the dicumyl peroxide concentration should be between 2.9 and 6.5%. By this method, we obtained EPDM crosslinked matrices with optimized mechanical properties. These results show a good agreement with those described by other authors[30,31]. The strain at break of elastomers decreases when the crosslinking degree increases. The stress at break reaches maximum values for low degree of crosslinking and decreases when the degree of crosslinking increases. The undesirable effects caused by the increase in degree of crosslinking have been attributed to the heterogeneity in the number average molecular weight of the polymer between crosslinks ($M_x$) or the spacing between crosslinks, which places most of the stress on relatively few of the network chains. These highly stressed chains break first and give rise to some defects that accelerate the overall material break[31].

Crosslinking densities ($\nu$) were determined by swelling tests in cyclohexane for EPDM samples containing 2.9, 4.8 or 6.5% of dicumyl peroxide and crosslinked for 10, 20 or 30 min. The swelling kinetics were followed gravimetrically. $M_x$ and $\nu$ were calculated by considering $k_1 = 0.35$ (polymer–solvent interaction parameter) and $\rho_2 = 0.865\ \mathrm{g\,cm^{-3}}$ (polymer density)[32–34]. *Table 3* shows $M_x$ and $\nu$ values obtained by considering Flory's theory for swelling of network structures[35]. Independent of the dicumyl peroxide concentration, the crosslinking density of the samples increases when the crosslinking time increases. For 10 min of crosslinking time, $\nu$ increases from $(0.11 \pm 0.01) \times 10^{-4}$ to $(0.22 \pm 0.01) \times 10^{-4}\ \mathrm{mol\,cm^{-3}}$, when the dicumyl peroxide concentration changes from 2.9 to 6.5%. Similar behaviour has been observed by Crespi *et al.*[36]. For 20 and 30 min of crosslinking time, the crosslinking density presents maximum values for samples containing 4.8% of dicumyl peroxide. These results show that dicumyl peroxide concentrations excessively higher than (or lower than) 4.8% are not adequate and can promote an inefficient crosslinking. For samples containing 2.9% of dicumyl peroxide, the crosslinking agent concentration can be insufficient to promote an efficient crosslinking. For samples containing 6.5% of dicumyl peroxide, we can have some chain scission parallel to crosslinking. This proposition is understood when we observe the gel fractions of the samples (*Table 4*). For 20 and 30 min of crosslinking time, the gel fraction of samples containing 4.8% dicumyl peroxide is higher than for samples containing 2.9 or 6.5%. In these cases, there are more polymer chains that dissolve in cyclohexane during swelling. These polymer chains originate from an inefficient crosslinking or from chain scissions.

*Swelling of crosslinked EPDM in THF containing $FeCl_3$.* *Figure 5* shows the swelling ratio for EPDM samples crosslinked with 2.9, 4.8 or 6.5% dicumyl peroxide as a function of $FeCl_3$/THF solution concentration. The swelling ratio was calculated by considering Flory's theory[35]. For concentrations of $FeCl_3$ in THF lower than 0.67%, the pyrrole polymerization does not take place. For concentrations higher than 9.09%, we obtained super-saturated $FeCl_3$/THF solutions. Independent of the dicumyl peroxide concentration, the swelling ratio decreases when the $FeCl_3$ concentration increases and reaches a constant value (*Figure 5*). This behaviour is expected because $FeCl_3$ reduces EPDM solubility in THF.

*Table 5* shows the concentration of $FeCl_3$ in EPDM samples after swelling. These concentrations were measured by X-ray fluorescence. Independent of the dicumyl peroxide concentration used to crosslink the rubber, the amount of $FeCl_3$ incorporated increases when the $FeCl_3$/THF solution concentration increases from 0.67 to 1.64%. For $FeCl_3$/THF solutions with concentrations higher than 1.64%, the $FeCl_3$ amount incorporated depends on the EPDM crosslinking degree. For samples crosslinked with 2.9% dicumyl peroxide, the $FeCl_3$ amount is nearly constant (~7%). For samples which were crosslinked using 4.8% dicumyl peroxide, the amount of $FeCl_3$ incorporated increases when the $FeCl_3$/THF solution concentration changes from 3.22 to 4.76%, and is nearly constant for higher concentrations. For samples crosslinked with 6.5% dicumyl peroxide, the amount of $FeCl_3$ incorporated increases when the concentration of the $FeCl_3$/THF solution increases. It is interesting to note that, in the case of the more diluted

**Table 3** Crosslinking density ($\mathrm{mol\,cm^{-3}} \times 10^4$), $\nu$, and number average molecular weight of the polymer between crosslinks ($\mathrm{g\,mol^{-1}} \times 10^{-4}$), $M_x$, for EPDM samples as a function of dicumyl peroxide concentration and crosslinking time, $t_c$

| % Dicumyl peroxide | Property | $t_c = 10$ min | $t_c = 20$ min | $t_c = 30$ min |
|---|---|---|---|---|
| 2.9 | $\nu$ | 0.11 ± 0.01 | 0.11 ± 0.01 | 0.36 ± 0.03 |
| 4.8 | $\nu$ | 0.07 ± 0.02 | 1.0 ± 0.7 | 1.0 ± 0.1 |
| 6.5 | $\nu$ | 0.22 ± 0.01 | 0.5 ± 0.1 | 0.59 ± 0.08 |
| 2.9 | $M_x$ | 8 ± 1 | 8.3 ± 0.8 | 2.4 ± 0.2 |
| 4.8 | $M_x$ | 13 ± 4 | 1.4 ± 0.9 | 0.9 ± 0.1 |
| 6.5 | $M_x$ | 4.0 ± 0.3 | 2.0 ± 0.5 | 1.5 ± 0.2 |

**Table 4** Gel fraction of EPDM crosslinked samples as a function of dicumyl peroxide concentration and crosslinking time, $t_c$

| % Dicumyl peroxide | Gel fraction | | |
|---|---|---|---|
| | $t_c = 10$ min | $t_c = 20$ min | $t_c = 30$ min |
| 2.9 | 0.59 ± 0.05 | 0.81 ± 0.09 | 0.82 ± 0.02 |
| 4.8 | 0.67 ± 0.06 | 0.94 ± 0.06 | 0.95 ± 0.05 |
| 6.5 | 0.87 ± 0.02 | 0.875 ± 0.005 | 0.83 ± 0.02 |

$FeCl_3$/THF solutions (0.67, 1.64 and 3.22%), the amount of $FeCl_3$ incorporated for samples containing 2.9% dicumyl peroxide is higher. This anomalous behaviour is difficult to explain by considering only the swelling ratio differences. Further, the $FeCl_3$ amount present in crosslinked samples of EPDM is lower than the amount that could be mechanically incorporated.

*Polypyrrole/EPDM semi-IPN preparations. Table 6* shows the electrical conductivity, Xpolypyrrole and mechanical properties for semi-IPN which were obtained by exposure of swollen crosslinked EPDM samples to pyrrole vapours. The $FeCl_3$/THF solution concentrations were 3.22 and 4.76% (w/w). We verified that the polymerization is not effective by using $FeCl_3$/THF solutions whose concentrations are lower than 1.64 or higher than 4.76%. We note, however, that the electrical conductivity and the mechanical properties are practically independent of dicumyl peroxide and $FeCl_3$/THF solution concentrations. Xpolypyrrole is slightly higher for semi-IPN obtained from matrices initially containing 2.9 or 4.8% of dicumyl peroxide and immersed in a 4.76% $FeCl_3$/THF solution. In these cases, the electrical conductivity is practically equal to the semi-IPN prepared by using different dicumyl peroxide and $FeCl_3$/THF solution concentrations.

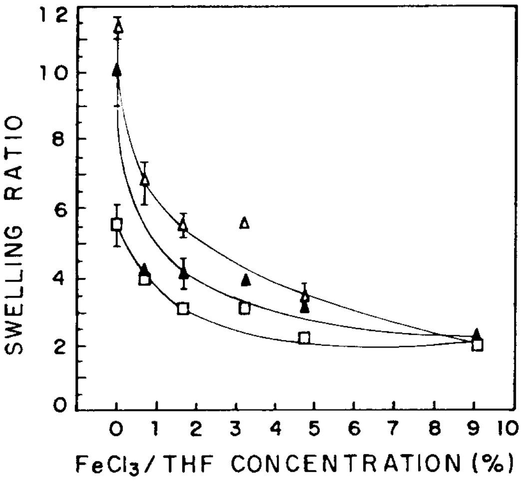

**Figure 5** Swelling ratio of EPDM matrices crosslinked containing 2.9 (△), 4.8 (▲) or 6.5% (□) of dicumyl peroxide as a function of the concentration of $FeCl_3$/THF solution used during the sample swelling

**Table 5** $FeCl_3$ percentage incorporated in crosslinked samples of EPDM after swelling in $FeCl_3$/THF solutions, as a function of dicumyl peroxide concentration, $P_c$

| $FeCl_3$ in THF (%) | $FeCl_3$ concentration for (%) $P_c = 2.9\%$ | $P_c = 4.8\%$ | $P_c = 6.5\%$ |
|---|---|---|---|
| 0.67 | 3.8 ± 0.6 | 1.1 | 0.92 |
| 1.64 | 7.1 | 3.2 ± 0.8 | 2.1 ± 0.1 |
| 3.22 | 7.4 | 4.0 ± 0.2 | 3.9 ± 0.6 |
| 4.76 | 6.1 | 6.8 ± 0.2 | 3.2 ± 0.3 |
| 9.09 | 7.5 | 6 ± 1 | 7 ± 1 |

*Table 7* shows the elasticity modulus, stress and strain at break, and tenacity values for polypyrrole/EPDM semi-IPN and crosslinked EPDM rubber. Compared to crosslinked EPDM rubber, the semi-IPN present lower tenacity, and lower stress and strain at break values. These results have been observed for other systems which are constituted from insulating and conducting polymers. The conducting polymer makes the final products more fragile and hard[37,38].

By comparing semi-IPN obtained by the mechanical mixture of the oxidizing agent and by swelling in an oxidant solution, it is important to note that the second method produces polypyrrole/EPDM semi-IPN with electrical conductivity values ($\sim 10^{-5}\,S\,cm^{-1}$) five orders of magnitude higher than those obtained by the first method ($\sim 10^{-10}\,S\,cm^{-1}$). It is also higher than for blends ($\sim 10^{-7}\,S\,cm^{-1}$). The mechanical properties were also improved. By the first route, the semi-IPN tenacity values reach $1 \times 10^{-3}\,J\,mm^{-3}$. By the second route, the semi-IPN tenacity values are two or three times higher. Another important difference is the Xpolypyrrole value. Xpolypyrrole for semi-IPN obtained by the second route does not reach 5% and is significantly lower than Xpolypyrrole for semi-IPN prepared by the first method. We attributed these differences mainly to the morphology of the semi-IPN. In the swelling method, the oxidizing agent is homogeneously distributed into the matrix and there is no particle agglomeration (as was observed in the mechanical incorporation method). By the second method, the polypyrrole formation is more uniform and the conducting polymer is homogenously distributed in the matrix, as shown in *Figure 6*. We have a continuous conducting phase formation, and, with a small amount of conducting polymer, it is possible to obtain final products with higher conductivities.

### *Effect of silica and kaolin*

Mathematical and statistical methods have been used in chemistry to select optimal conditions to reduce the

**Table 6** Composition and properties of polypyrrole/EPDM semi-IPN which were obtained by swelling of crosslinked EPDM, as a function of dicumyl peroxide and $FeCl_3$/THF solution concentrations; $\epsilon$ = elasticity modulus

| % Dicumyl peroxide | $FeCl_3$ in THF (%) | $\sigma$ ($S\,cm^{-1}$) $\times 10^5$ | $\epsilon$ (MPa) | Stress at break (MPa) | Strain at break $\times 10^2$ | Tenacity ($J\,mm^{-3}$) $\times 10^3$ | Xpolypyrrole (%) |
|---|---|---|---|---|---|---|---|
| 2.9 | 3.22 | 1 | 1.6 ± 0.4 | 4.9 ± 0.9 | 2.7 ± 0.4 | 2.4 ± 0.6 | 3.2 ± 0.4 |
| 2.9 | 4.76 | 0.7 | 1.7 ± 0.1 | 5 ± 1 | 3.1 ± 0.9 | 2.5 ± 0.7 | 5 ± 1 |
| 4.8 | 3.22 | 5 | 1.2 ± 0.4 | 5 ± 1 | 2.4 ± 0.3 | 2.2 ± 0.4 | 2.5 ± 0.1 |
| 4.8 | 4.76 | 3 | 1.7 ± 0.5 | 5 ± 2 | 2.6 ± 0.2 | 2.6 ± 0.8 | 5.0 ± 0.5 |
| 6.5 | 3.22 | 0.1 | 1.6 ± 0.7 | 6 ± 2 | 3.0 ± 1.0 | 3 ± 1 | 3.0 ± 0.1 |
| 6.5 | 4.76 | 0.1 | 1.2 ± 0.3 | 7 ± 4 | 3.0 ± 1.0 | 3 ± 1 | 2.4 ± 0.3 |

**Table 7** Mechanical properties of polypyrrole/EPDM semi-IPN and crosslinked EPDM rubber as a function of dicumyl peroxide concentration; $\epsilon$ = elasticity modulus; $FeCl_3$/THF solution concentration = 3.22%

| Material | % Dicumyl peroxide | $\epsilon$ (MPa) | Stress at break (MPa) | Strain at break (%) $\times 10^3$ | Tenacity (J $mm^{-3}$) $\times 10^3$ |
|---|---|---|---|---|---|
| Semi-IPN | 2.9 | $1.6 \pm 0.4$ | $4.9 \pm 0.9$ | $0.27 \pm 0.04$ | $2.4 \pm 0.6$ |
| Semi-IPN | 4.8 | $1.2 \pm 0.4$ | $5 \pm 1$ | $0.24 \pm 0.03$ | $2.2 \pm 0.4$ |
| Smi-IPN | 6.5 | $1.6 \pm 0.7$ | $6 \pm 2$ | $0.30 \pm 0.10$ | $3 \pm 1$ |
| EPDM | 2.9 | $0.59 \pm 0.03$ | $20 \pm 7$ | $3.30 \pm 0.20$ | $14 \pm 3$ |
| EPDM | 4.8 | $0.79 \pm 0.06$ | $56 \pm 1$ | $2.00 \pm 0.10$ | $21 \pm 2$ |
| EPDM | 6.5 | $0.92 \pm 0.04$ | $25 \pm 5$ | $1.30 \pm 0.20$ | $13 \pm 3$ |

number of experiments and to obtain a maximum amount of information about an investigated system[39–41]. In the case of polypyrrole/EPDM semi-IPN preparation, the aim was to optimize the electrical conductivity as a function of composition and mechanical property variation when silica and kaolin were present. *Table 8* shows the electrical conductivity, elasticity modulus, tenacity, and Xpolypyrrole for semi-IPN which were obtained by using matrices containing fillers corresponding to *Table 1* (1–19 tests).

The relationship between the three variables (dicumyl peroxide, *P*, silica, *S*, and kaolin, *K*) and the responses (electrical conductivity, elasticity modulus, tenacity and composition) were calculated by using Fatorial and Modreg software*. The relationships show that the elasticity modulus of the polypyrrole/EPDM semi-IPN samples changes linearly with silica concentration. By considering the experimental deviation, which was determined by replicate tests (tests 9–13), the electrical conductivity, tenacity and composition are practically not affected by dicumyl peroxide, silica or kaolin concentrations. These considerations are valid for the concentration range established in the Experimental part.

By using the Modreg software, we verified that the elasticity modulus of the semi-IPN depends on the silica concentration as shown in equation (1). The significance level for this relationship was 99.5% and it is possible to say that secondary or tertiary effects of interaction between *P*, *S* and *K* can be neglected. In this case, $xS'$ is related to $S$ by $xS' = (S\text{-}14)/6$.

$$\text{Modulus} = 3.9(\pm 0.6) + 1.4(\pm 0.6)xS' \qquad (1)$$

For crosslinked EPDM rubber, the same treatment showed that the elasticity modulus also depended on the silica concentration, equation (2). In this case, the significance level was 99%.

$$\text{Modulus} = 2.2(\pm 0.6) + 0.8(\pm 0.6)xS' \qquad (2)$$

In *Figure 7* we compare the stress–strain curves for crosslinked EPDM and for polypyrrole/EPDM semi-IPN samples which contain, or not, silica and kaolin. We observe (comparing with *Table 8*) that determined concentrations of dicumyl peroxide, silica and kaolin make possible the preparation of polypyrrole/EPDM semi-IPN, which present tenacity similar to EPDM, elasticity modulus higher than EPDM, and electrical conductivity in the range of $10^{-5}$ S $cm^{-1}$, several orders of magnitude higher than EPDM. For samples without fillers, the mechanical properties are very different, although the electrical conductivity is also $10^{-5}$ S $cm^{-1}$. The semi-IPN is more fragile than the EPDM rubber. By adding fillers, it was possible to maintain the electrical conductivity and to increase the tenacity of polypyrrole/EPDM semi-IPN. Further, no differences were observed in the semi-IPN morphology. For semi-IPN containing fillers polypyrrole forms a continuous phase, as was verified for polypyrrole/EPDM semi-IPN without silica and kaolin.

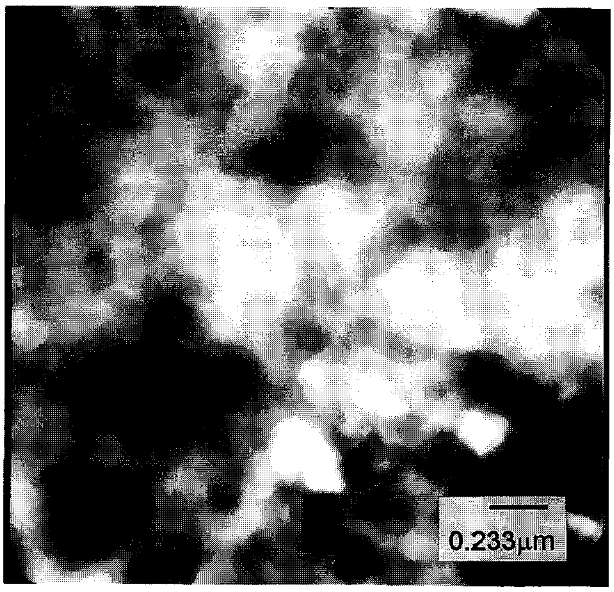

**Figure 6** Transmission electron micrographs of polypyrrole/EPDM semi-IPN obtained by swelling of crosslinked EPDM rubber in 4.76% $FeCl_3$/THF solution (4.8% dicumyl peroxide). Magnification = 30000

### *Effect of stabilizing agents*

Tinuvin 327® and Irganox 1076® are efficient stabilizing agents for EPDM rubber. The stabilizer concentrations used in this work correspond to the optimal percentages which were previously determined by De Paoli *et al.*[42,43]. Tinuvin 327®, 2(2′-hydroxy-3′,5′-diterbutylphenyl)-5-chlorobenzotriazole, protects against u.v. irradiation. Irganox 1076®, octadecyl-3-(3′,5′-diterbutyl-4′-hydroxyphenyl) propionate, is an antioxidant which reacts with peroxy radicals.

With respect to the semi-IPN electrical conductivity, there is a one order of magnitude decrease in the initial

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*The Fatorial and Modreg software can be obtained from IQ-UNICAMP, Departamento de Fisico-Química

**Table 8** Composition and properties for polypyrrole/EPDM semi-IPN prepared using crosslinked EPDM matrices containing silica and kaolin. $\epsilon$ = Elasticity modulus

| | Semi-IPN | | | | EPDM | |
|---|---|---|---|---|---|---|
| Test number | $\sigma \times 10^7$ (S cm$^{-1}$) | $\epsilon$ (MPa) | Tenacity $\times 10^3$ (J mm$^{-3}$) | Xpolypyrrole (%) | $\epsilon$ (MPa) | Tenacity $\times 10^3$ (J mm$^{-3}$) |
| 1 | 400 | 4.2 ± 0.8 | 6.4 ± 0.8 | 1.91 ± 0.09 | 3.7 ± 0.1 | 7.3 ± 0.6 |
| 2 | 200 | 4.1 ± 0.8 | 6 ± 4 | 3.4 ± 0.4 | 1.9 ± 0.3 | 17 ± 8 |
| 3 | 300 | 3.6 ± 0.3 | 10.2 ± 0.7 | 2.3 ± 0.1 | 2.3 ± 0.4 | 13 ± 4 |
| 4 | 400 | 3.2 ± 0.5 | 9 ± 5 | 3.0 ± 0.2 | 1.6 ± 0.2 | 10 ± 4 |
| 5 | 200 | 4 ± 2 | 13 ± 6 | 2.14 ± 0.04 | 2.9 ± 0.6 | 10.5 ± 0.6 |
| 6 | 200 | 6.3 ± 0.6 | 9 ± 1 | 3.2 ± 0.2 | 3.9 ± 0.3 | 13 ± 3 |
| 7 | 70 | 1.5 ± 0.2 | 30 ± 10 | 1.1 ± 0.2 | 0.71 ± 0.04 | 9 ± 3 |
| 8 | 20 | 2.7 ± 0.6 | 2.3 ± 0.3 | 3.30 ± 0.05 | 0.8 ± 0.1 | 4 ± 1 |
| 9 | 400 | 4.1 ± 0.6 | 11 ± 5 | 2.62 ± 0.07 | 2.1 ± 0.2 | 8 ± 3 |
| 10 | 500 | 3.3 ± 0.7 | 7 ± 4 | 3.9 ± 0.7 | 2.5 ± 0.3 | 10 ± 2 |
| 11 | 100 | 3.9 ± 0.3 | 9 ± 1 | 3.1 ± 0.4 | 2.90 ± 0.02 | 10 ± 3 |
| 12 | 300 | 4.2 ± 0.6 | 8 ± 4 | 2.6 ± 0.2 | 2.9 ± 0.5 | 9 ± 4 |
| 13 | 200 | 4.1 ± 0.4 | 13 ± 1 | 2.5 ± 0.2 | 1.4 ± 0.4 | 13 ± 5 |
| 14 | 300 | 5.0 ± 0.3 | 8 ± 1 | 2.4 ± 0.2 | 3.0 ± 0.7 | 8 ± 2 |
| 15 | 30 | 3.4 ± 0.3 | 15 ± 3 | 3.0 ± 0.2 | 1.5 ± 0.2 | 21 ± 7 |
| 16 | 100 | 8 ± 1 | 4 ± 3 | 3.5 ± 0.4 | 3.3 ± 0.3 | 21 ± 5 |
| 17 | 1 | 1.2 ± 0.6 | 3 ± 2 | 3.9 ± 0.2 | 1.3 ± 0.2 | 10 ± 6 |
| 18 | 200 | 4.1 ± 0.5 | 5 ± 1 | 3.4 ± 0.2 | 1.4 ± 0.2 | 12 ± 6 |
| 19 | 70 | 2.3 ± 0.4 | 10 ± 5 | 1.4 ± 0.1 | 1.7 ± 0.2 | 22 ± 5 |

period (1–2 h) of the thermal ageing at 80°C, independent of stabilizing agent presence. After 6 h, the electrical conductivity has a tendency to stabilize (near $10^{-8}$ S cm$^{-1}$).

*Figure 8* shows $\ln(\sigma/\sigma_0)$ for polypyrrole/EPDM semi-IPN as a function of thermal ageing time. In this case, $\sigma$ is the electrical conductivity at time $t$, and $\sigma_0$ is the initial conductivity. We observe that $\ln(\sigma/\sigma_0)$ changes linearly with respect to thermal ageing time only at the initial times. This behaviour was observed by Truong for electrochemically prepared polypyrrole doped with *p*-toluenesulfonate[44,45]. The polypyrrole degradation under air atmosphere has been associated with oxidation by $O_2$ or $H_2O$ and it can be limited by oxygen diffusion in the material. The electrical conductivity decrease, $\Delta\sigma = \sigma_0 - \sigma$, can be expressed as a function of $t^{1/2}$ (*Figure 9*). Linear curves for $\Delta\sigma/\sigma_0$ vs $t^{1/2}$, were obtained by Truong[44,45] and Thiéblemont *et al.*[46], who proposed that the electrical conductivity decrease is proportional to the amount of oxygen absorbed by the film. They related the $\Delta\sigma/\sigma_0$ vs $t^{1/2}$ curves to the $M_t/M_\infty$ vs $t^{1/2}$ curve, where $M_t$ is the $O_2$ mass absorbed at time $t$ and $M_\infty$ is the $O_2$ mass absorbed at equilibrium. Then, $\Delta\sigma = cM_t$, where $c$ is a constant. At equilibrium, equation (3) is valid[44,45]:

$$\sigma_0 - \sigma_\infty = cM_\infty \qquad (3)$$

By considering $\sigma_0 \gg \sigma_\infty$, equation (3) becomes:

$$\sigma_0 \approx cM_\infty \qquad (4)$$

Then,

$$\Delta\sigma/\sigma_0 \approx M_t/M_\infty = \alpha(Dt)^{1/2} \qquad (5)$$

where $\alpha = 4/\iota\pi^{1/2}$, $\iota$ is the thickness of the film and $D$ the $O_2$ diffusion coefficient into the film[47]. By using $t_{0.5}$ as the time needed to reduce the electrical conductivity to $\sigma_0/2$, or $\Delta\sigma/\sigma_0 = 0.5$, $D$ can be calculated from equation (6):

$$D = 0.04919\iota^2/t_{0.5} \qquad (6)$$

Oxygen diffusion coefficient values were calculated for polypyrrole/EPDM semi-IPN. We obtained $(1.8 \pm 0.3) \times 10^{-7}$ and $(1.8 \pm 0.7) \times 10^{-7}$ cm$^2$ s$^{-1}$ for samples containing, or not, stabilizers, respectively. These values are comparable to $O_2$ diffusion coefficients in insulating

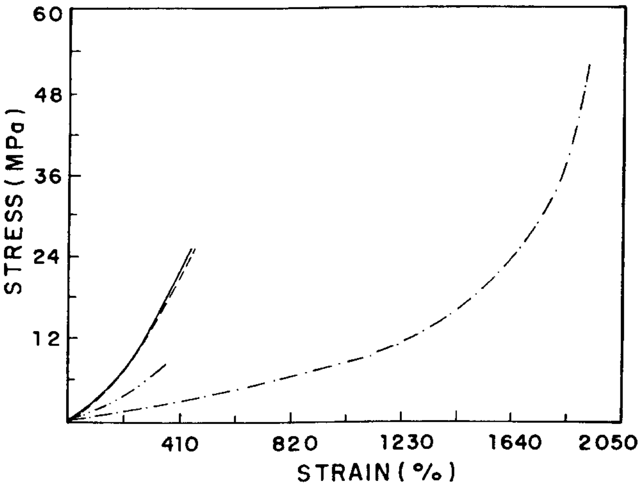

**Figure 7** Stress–strain curves for polypyrrole/EPDM semi-IPN and EPDM rubber, for samples containing dicumyl peroxide, silica and kaolin. Concentrations are 3.5, 14 and 14%, respectively. For samples without fillers, the dicumyl peroxide concentration is 4.8%. (——) EPDM with fillers, (----) semi-IPN with fillers, (-·-·-·-) semi-IPN without fillers and (-··-··-) EPDM without fillers

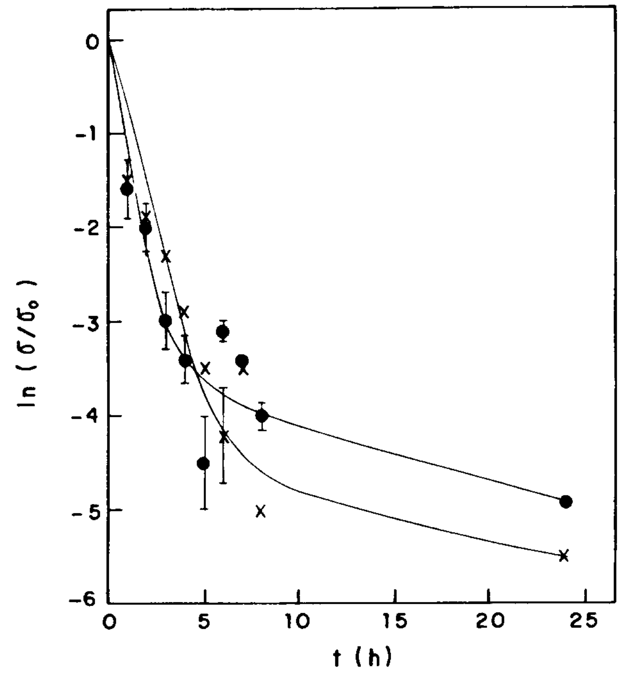

**Figure 8** Variation of $\ln(\sigma/\sigma_0)$, where $\sigma$ is the conductivity after time $t$ and $\sigma_0$ is the conductivity at $t = 0$, as a function of ageing time under ambient atmosphere at 80°C; (×) stabilized and (●) non stabilized semi-IPN samples

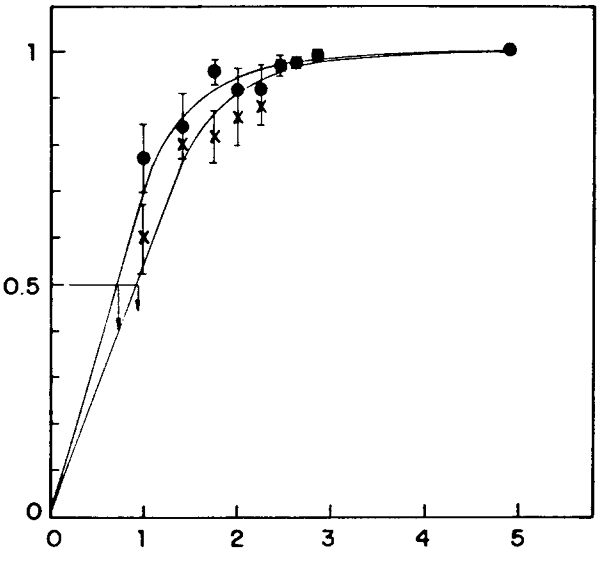

**Figure 9** Variation of $\Delta\sigma/\sigma_0$ as a function of $t^{1/2}$, where $t$ = ageing time under ambient atmosphere at 80°C; (×) stabilized and (●) non stabilized semi-IPN samples

polymers ($10^{-9}$–$10^{-6}\,cm^2\,s^{-1}$, 25°C[48]). Although $D$ values are very close, it is interesting to note that $t_{0.5}$ for samples containing stabilizers (0.90 h) is higher than $t_{0.5}$ for samples without stabilizers (0.56 h). A similar effect was observed for polypyrrole/crosslinked polystyrene composites which contained stabilizers such as acetamide, 3-hydroxybenzoic acid and phthalic acid[49].

The $t_{0.5}$ values for polypyrrole/EPDM semi-IPN are very low compared to $t_{0.5}$ values obtained for textiles covered by polypyrrole chemically prepared with $FeCl_3$. In these cases, $t_{0.5}$ at 80°C is higher than 100 h[46]. For *p*-toluenesulfonate doped polypyrrole obtained electrochemically, $t_{0.5} \geqslant 70$ h at 80°C and depends on film thickness[44,45]. The higher stability of these materials has been assigned to the organic dopants, like *p*-toluenesulfonate (and arylsulfonates for textiles covered by polypyrrole).

With respect to mechanical properties, *Table 9* shows the elasticity modulus, $\epsilon$, stress and strain at break and tenacity values, for polypyrrole/EPDM semi-IPM containing, or not, stabilizing agents and thermally aged, or not, at 80°C under air. After thermal ageing the elasticity modulus for samples containing, or not, stabilizing agents slowly increases. It is interesting to note that the tenacity values for samples without stabilizers are lower than for samples containing it. This tenacity decrease can indicate a fragilization of the material without Tinuvin 327® and Irganox 1076®, in accordance with thermogravimetric analysis results.

*Figures 10* and *11* show the thermograms for polypyrrole, EPDM and polypyrrole/EPDM semi-IPN which were carried out with Ar or synthetic air flows. We observe that the thermal stability of the samples containing Tinuvin 327® and Irganox 1076® are improved. Pure polypyrrole and EPDM decompose at lower temperatures using synthetic air as purge gas as compared to thermograms carried out with Ar flow. With synthetic air flow, the maximum mass loss occurs at 378°C for EPDM and 423°C for polypyrrole. In these cases, there is no residue for pure EPDM, and a 10% residue for polypyrrole. With Ar flow, the maximum mass loss temperature for polypyrrole was 466°C and for pure EPDM, 470°C. With synthetic air flow, for all polypyrrole/EPDM semi-IPN we observe a 30% residue, which is related to the silica and kaolin concentrations present in the matrices. The occurrence of the polypyrrole and EPDM degradation process for samples analysed with synthetic air flow is very clear. For non-aged polypyrrole/EPDM semi-IPN, the maximum mass loss temperatures were 370 and 383°C for samples without and with stabilizers, respectively. For thermally aged samples, these temperatures were 326 and 332°C for semi-IPN without or with stabilizers, respectively. These results show that the presence of Tinuvin 327® and Irganox 1076® can improve the thermal stability of the rubber matrix.

For non-aged samples without stabilizers, analysed with Ar or synthetic air flows, we verified that the polypyrrole presence (or indirectly, the matrix treatment with an oxidizing agent) produces a small decrease of the maximum mass loss temperature which is related to EPDM decomposition. With Ar flow, these temperatures were 466 and 470°C for semi-IPN and pure EPDM,

**Table 9** Mechanical properties for polypyrrole/EPDM semi-IPN containing, or not, stabilizers and thermally aged, or not, at 80°C under air

| Polypyrrole/EPDM | Elasticity modulus (MPa) | Stress at break (MPa) | Strain at break | Tenacity ($J\,mm^{-3}$) $\times 10^2$ |
|---|---|---|---|---|
| Without stabilizer | 3.3 ± 0.6 | 33 ± 4 | 480 ± 60 | 1.5 ± 0.4 |
| Without stabilizer[a] | 5 ± 1 | 26 ± 3 | 320 ± 40 | 1.1 ± 0.2 |
| Stabilized | 4 ± 1 | 38 ± 7 | 560 ± 100 | 1.8 ± 0.6 |
| Stabilized[a] | 5.5 ± 0.7 | 36 ± 7 | 420 ± 90 | 1.7 ± 0.5 |

[a] Samples thermally aged at 80°C for 24 h

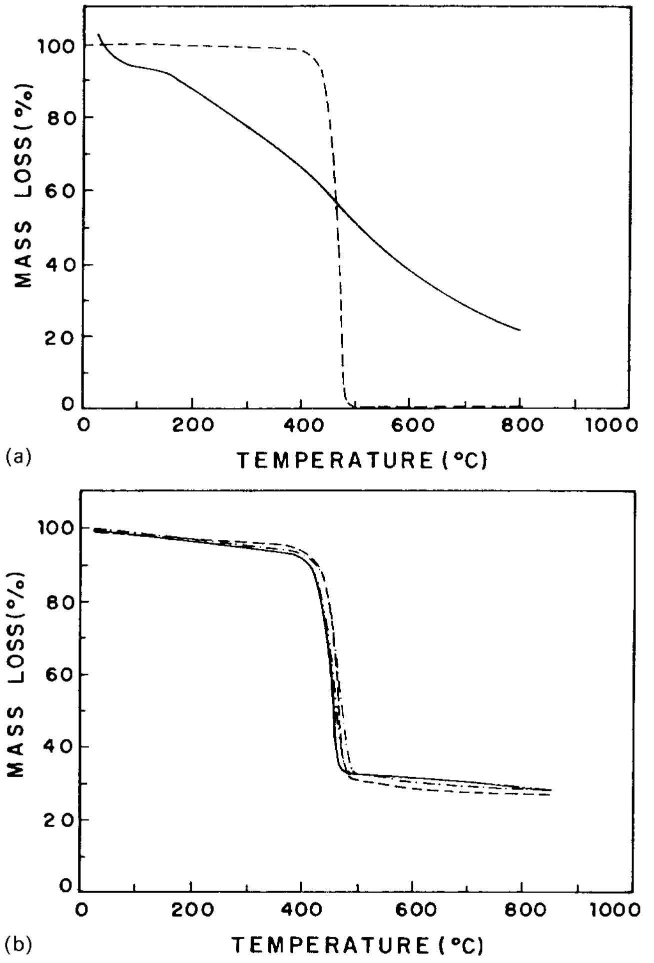

**Figure 10** (a) Thermograms (10°C min$^{-1}$, Ar) for pure polypyrrole (—) and EPDM rubber (----). (b) Thermograms for polypyrrole/EPDM semi-IPN (----) without stabilizers and before thermal ageing, (—) without stabilizers and after thermal ageing, (-·-·-) containing stabilizers and before thermal ageing, and (·······) containing stabilizers and after thermal ageing

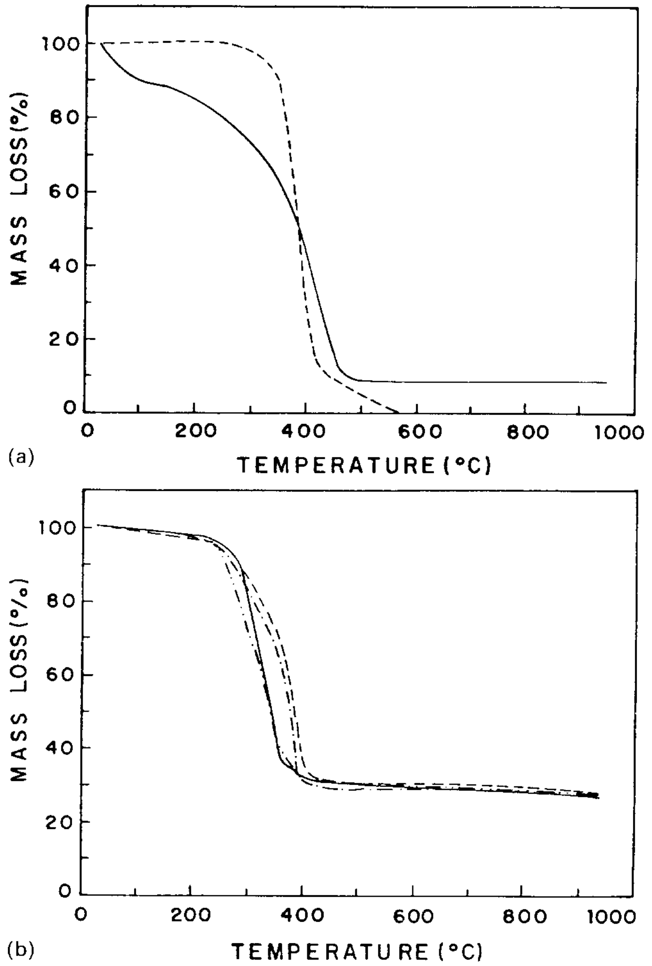

**Figure 11** (a) Thermograms (10°C min$^{-1}$, synthetic air) for pure polypyrrole (—) and EPDM rubber (----). (b) Thermograms for polypyrrole/EPDM semi-IPN (----) without stabilizers and before thermal ageing, (—) without stabilizers and after thermal ageing, (-·-·-) containing stabilizers and before thermal ageing, and (·······) containing stabilizers and after thermal ageing

respectively. With synthetic air flow, we obtained 370 and 378°C for semi-IPN and pure EPDM, respectively. This temperature decrease does not occur in the case of non-aged samples containing stabilizers. In these cases, the maximum mass loss temperature was practically the same as for pure EPDM and polypyrrole/EPDM semi-IPN (Ar flow = 470°C for EPDM and semi-IPN; synthetic air flow = 378 and 383°C for EPDM and semi-IPN, respectively).

## CONCLUSIONS

Polypyrrole/EPDM rubber semi-IPN were obtained by two different methods. With the first route, the oxidant and crosslinking agent were mechanically incorporated into the rubber by calendering. These samples were crosslinked and exposed to pyrrole vapours. In this case, the electrical conductivity of the semi-IPN was nearly equal to that of the pure rubber.

An alternative synthetic route was investigated in order to obtain final products with higher conductivity. In this second route, EPDM crosslinked samples were swollen in an FeCl$_3$/THF solution. The swollen rubber was exposed to pyrrole vapours to originate polypyrrole/EPDM semi-IPN. In this case, the final material presents electrical conductivity of the order of $10^{-5}$ S cm$^{-1}$. It was also possible to incorporate some reinforcement fillers that improved the mechanical properties of semi-IPN.

The elasticity modulus increases when the silica concentration increases. By using nearly 30% of fillers (14% silica and 14% kaolin), it was possible to obtain polypyrrole/EPDM semi-IPN with mechanical properties similar to crosslinked EPDM rubber and electrical conductivity in the range of $10^{-5}$ S cm$^{-1}$. It was possible to improve the thermal stability of the elastomeric phase of the semi-IPN by incorporating stabilizing agents into the matrices.

The second route may allow the large scale preparation of semi-IPN which present unique properties and can be used as antistatic protection or microwave absorption coatings. Polypyrrole/EPDM semi-IPN ($\sigma = 10^{-5}$ S cm$^{-1}$) presented microwave absorption of 85% in the range of 10–13 GHz. For defence applications these materials should absorb *ca.* 80% of radiation over a wider range of frequencies (5–15 GHz). However, they have the advantage of low density (0.8 g cm$^{-3}$) in comparison to metallic shields.

## ACKNOWLEDGEMENTS

We thank M. L. Gregório (IPQM, Rio de Janeiro, Brazil) for the microwave absorption measurements. R. A. Zoppi thanks FAPESP (Proc. 91/3650-5) for a fellowship. The authors also thank FINEP for financial support.

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