Blends of Polyaniline with Nitrilic Rubber

M. R. VALLIM, M. I. FELISBERTI, M.-A. DE PAOLI

Laboratório de Polímeros Condutores, Instituto de Química, Unicamp, C. Postal 6154, 13083-970, Campinas, SP, Brazil

ABSTRACT: Nitrilic rubbers containing 29 or 45% of acrylonitrile were blended with polyaniline doped with different acids (chloridric, dodecylbenzenesulfonic, tetrapropylbenzenesulfonic, and *p*-toluenesulfonic acids). The blends were prepared by mechanical mixing in a roll-mill and vulcanized in a hot press. The volumetric conductivities and mechanical properties were evaluated. The results show that the polyaniline concentration strongly affects the behavior of the blends. Increasing the polyaniline content from 50 to 100 phr induces an increase in the electric conductivity from 10^{-10} to 10^{-8} S cm^{-1}; however, the blends become harder and more brittle than the crude rubber. Addition of polyaniline lowered the crosslinking degree, but produced a reinforcing effect in the elastomer. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 677–684, 2000

Key words: polyaniline; nitrilic rubber; blends; conductive elastomers; mechanical mixture

INTRODUCTION

Conductive vulcanized elastomers represent an important segment of the market for applications in the car industry. These materials are used for shielding the sources of electromagnetic radiation interference to protect electronic equipment in modern vehicles. Presently, they are produced by mixing conductive carbon black in the rubber compound prior to vulcanization. However, the percolation threshold for the conductivity is high and the conductivity values are not higher than 10^{-8} S cm^{-1}.[1] Doped conductive polymers present a much higher conductivity; unfortunately, their mechanical properties do not permit their use in substitution to vulcanized elastomers.[2]

Polyaniline (PAni) can be prepared from a low-cost raw material using low-cost reagents. The

process requires low temperatures and produces highly acid effluents; however, it is economically feasible.[3] PAni is highly conductive after doping with hydrochloric acid (100 S cm^{-1}), but loses this conductivity with time, due to the volatility of the acid dopant. Production of PAni with high molecular weight functionalized acids produces more stable products. Protonation with camphorsulfonic acid has proven to be a method to increase the conductivity and to impart the solubility of PAni.[4]

Nitrilic rubber is a copolymer of butadiene and acrylonitrile. It is produced with different relative concentrations of the comonomers and it is an insulating material in the crude or in the vulcanized form. Compounds of this rubber are largely used in the car industry for making brake fluid hoses due to its resistance to chemical attack, particularly from lubricants. Nitrilic rubber is also acid- and alkali-resistant and, in the vulcanized form, shows a low swelling degree with organic solvents.

The resistance of nitrilic rubbers to acid attack makes it a natural partner for blending with acid-doped PAni. This opens new perspectives for ap-

plications of electrically conductive elastomers. A blend of PAni with nitrilic rubber prepared by an electrochemical method was described in the literature.[5] Although this product shows outstanding mechanical, electrochemical, electrochromic, and conductive properties, the electrochemical method is not suited for large-scale production. More recently, a blend of PAni and a vulcanized terpolymer of ethylene, propylene, and a diene (EPDM rubber) was also described in the literature.[6] However, EPDM rubber does not show the same chemical resistance as that of nitrilic rubber.

In this work, we describe the preparation of blends of nitrilic rubber and PAni (NBR/Pani) by mechanical mixing in a roll-mill, aiming to obtain electrically conductive elastomers combining the mechanical properties of NBR and the electrical properties of PAni. Blends were characterized by their conductive, mechanical, and thermal properties.

EXPERIMENTAL

Materials

NBR

Two grades of NBR were used: N-206 and N-726 produced by Nitriflex, containing 45 and 29% (m/m) of acrylonitrile, respectively, and cited in this work as NBR45 and NBR29. The crude elastomers were purified by dissolution in $CHCl_3$ (Merck, p.a.), filtration, and coagulation by methanol (Ecibra, p.a.). They were subsequently dried to a constant weight.

PAni

PAni doped with dodecylbenzenesulfonic (DBSA), tetrapropylbenzenesulfonic (TBSA), p-toluenosulfonic (PTSA), and hydrochloric acids were milled in a ball mill (Ruhla MLW, Model KM1) and sieved to a maximum grain diameter of 74 μm. PAni doping conditions were described elsewhere.[6]

Blends Preparation

Blends were prepared by mechanical mixture in a roll-mill at 50°C according to the formulations indicated in Table I. The samples were vulcanized at 150°C and 3.75 MPa of pressure for 40 min using a Jasco hot press Model HP3 and according to the ASTM D3182 standard.

Table I   Blend Formulations Used in This Work

Formulation	Composition (phr)
NBR	100
ZnO	1.0
Stearic acid	0.5
Sulfur	0.4
PAni	50 (1) or 100 (2)
TMTD	3.0

phr, parts per hundred in weight; TMTD, bis(dimethylcarbamyl) disulfide.

Surface and Volumetric Conductivity Assays

Surface and volumetric conductivities were measured according to ASTM D257 using a Keithley Model 6105 resistivity accessory and a Keithley 617 electrometer, applying potentials between 10 and 100 V at 10 V steps.

Mechanical Properties

For stress–strain test measurements, we used an EMIC-MEM 500 instrument under a crosshead speed of 500 mm min^{-1} and with a cell of 50 N. Samples were cut as stripes of $50 \times 7 \times 1.6$ mm.

Dynamic Mechanical Analysis (DMA)

The DMA was done at a frequency of 1.0 Hz with a sinusoidal deformation of 0.15 mm using a TA 983 DMA instrument. For these measurements, the dimension of the samples were $16 \times 2 \times 6$ mm with a heating program from -100 to 100°C at 2°C min^{-1}.

Swelling Degree and Sol Fraction Measurements

The swelling degrees and soluble fraction in $CHCl_3$ were determined gravimetrically.

Scanning Electron Micrography

The morphology of the surface and of the fracture of the blends were studied by scanning electron microscopy using a JEOL TS-300 instrument and the samples were metalized in a Balzers MED 020 machine.

RESULTS AND DISCUSSION

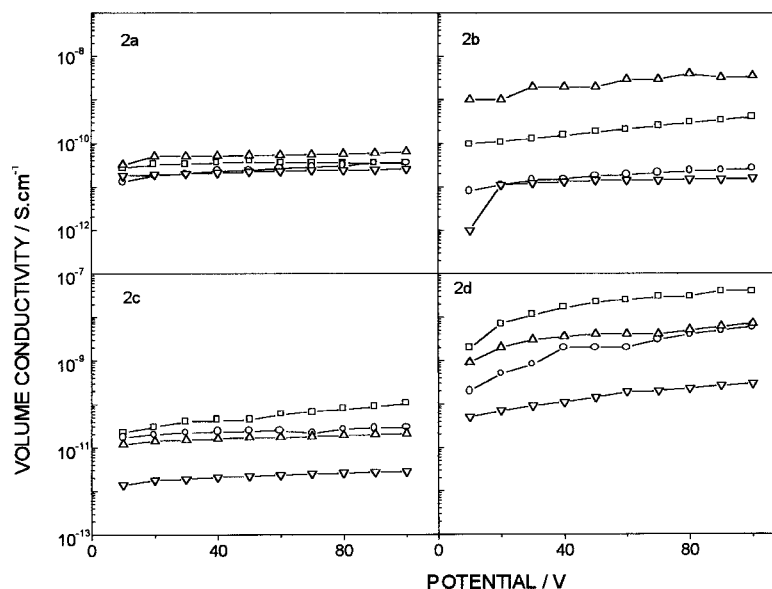### Surface and Volumetric Conductivity

The surface and volumetric conductivities of the samples are shown in Figures 1 and 2, respec-
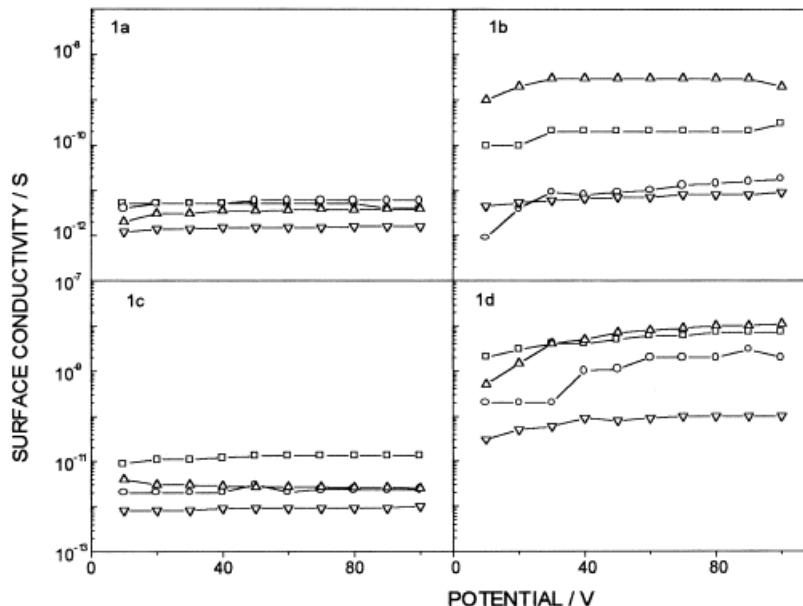
Figure 1 Surface conductivity as a function of applied potential. (a,b) NBR29; (c,d) and NBR45 containing (a,c) 50 phr or (b,d) 100 phr of PAni; ($\square$) NBR/PAni–TBSA; ($\bigcirc$) NBR/PAni–DBSA; ($\triangle$) NBR/PAni–PTSA; ($\triangledown$) NBR/PAni–HCl.

tively. These were measured in a range of potentials in order to confirm the ohmic behavior of the samples. Comparing the data in these figures, we observe that both the acrylonitrile content and the PAni doping acid affects the surface and the volumetric conductivities, presenting the same trend in both cases. The higher surface and volumetric conductivities for samples prepared with NBR29 occur when we use PAni doped with PTSA, and for NBR45, this occurs with TBSA. Also, blends with NBR29 present lower surface conductivities (10^{-12} and 10^{-10} S, 50 and 100 phr,

Figure 2 Volumetric conductivity as a function of applied potential. (a,b) NBR29 and (c,d) NBR45 containing (a,c) 50 phr or (b,d) 100 phr of PAni. ($\square$) NBR/PAni–TBSA; ($\bigcirc$) NBR/PAni–DBSA; ($\triangle$) NBR/PAni–PTSA; ($\triangledown$) NBR/PAni–HCl.

Table II   Mechanical Properties of the Crude Rubbers and Blends as a Function of PAni Concentration and Acid Dopant

% CN	PAni (phr)	Doping Acid	E (MPa)	σ_b (MPa)	ε_b (%)
29	0	Crude NBR	0.42 ± 0.06	8 ± 2	2100 ± 300
29	50	DBSA	2.61 ± 0.07	8 ± 2	547 ± 100
		TBSA	2.21 ± 0.04	14.5 ± 0.9	927 ± 60
		PTSA	2.0 ± 0.2	10.8 ± 0.9	605 ± 91
		HCl	1.9 ± 0.1	7.1 ± 0.5	738 ± 52
29	100	DBSA	2.1 ± 0.2	2 ± 1	243 ± 100
		TBSA	4.4 ± 0.1	11 ± 1	832 ± 100
		PTSA	4.1 ± 0.3	9 ± 1	547 ± 74
		HCl	4.2 ± 0.6	4 ± 2	221 ± 124
45	0	Crude NBR	0.8 ± 0.1	15 ± 13	770 ± 250
45	50	DBSA	4.1 ± 0.4	31 ± 8	1115 ± 188
		TBSA	4.9 ± 0.2	47 ± 2	1395 ± 53
		PTSA	4.5 ± 0.4	51 ± 3	1134 ± 68
		HCl	3.4 ± 0.4	28 ± 3	914 ± 62
45	100	DBSA	1.7 ± 0.2	1.2 ± 0.2	196 ± 42
		TBSA	1.7 ± 0.5	1.06 ± 0.09	210 ± 30
		PTSA	1.6 ± 0.4	1.4 ± 0.3	342 ± 74
		HCl	1.0 ± 0.4	1.4 ± 0.1	361 ± 7

E, Young's modulus; σ_b, stress at break; ε_b, elongation at break.

respectively) compared to NBR45 blends (10^{-11} and 10^{-9} S, 50 and 100 phr, respectively) with Pani doped with the same acid. The variation of the conductivity is caused by the effect of the doping acid on the dispersion of PAni in the rubber matrix. The content of acrylonitrile affects the
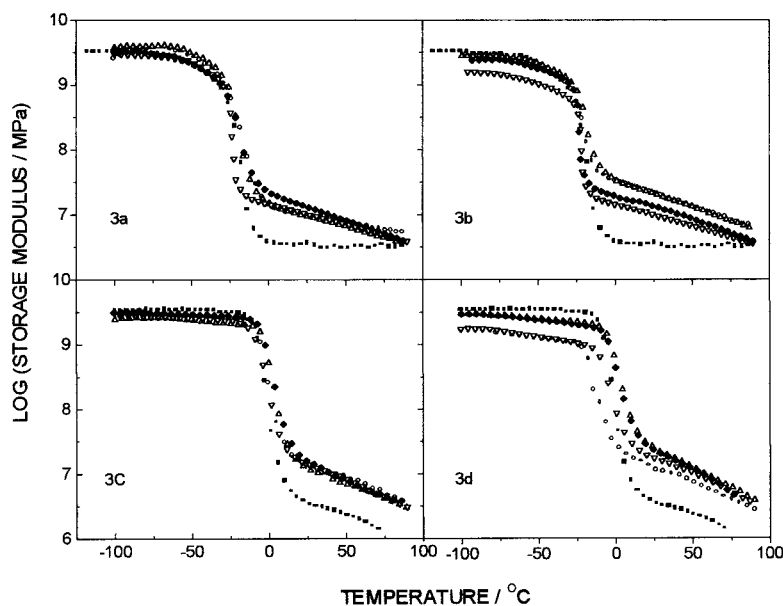
Figure 3   Storage modulus (log E' versus T) for (a) NBR29 + 50 phr of PAni, (b) NBR29 + 100 phr of PAni, (c) NBR45 + 50 phr of Pani, and (d) NBR45 + 100 phr of PAni. (●) crude NBR 29; (♦) PAni–HCl; (○) PAni–DBSA; (▽) PAni–TBSA; (△) PAni–PTSA.
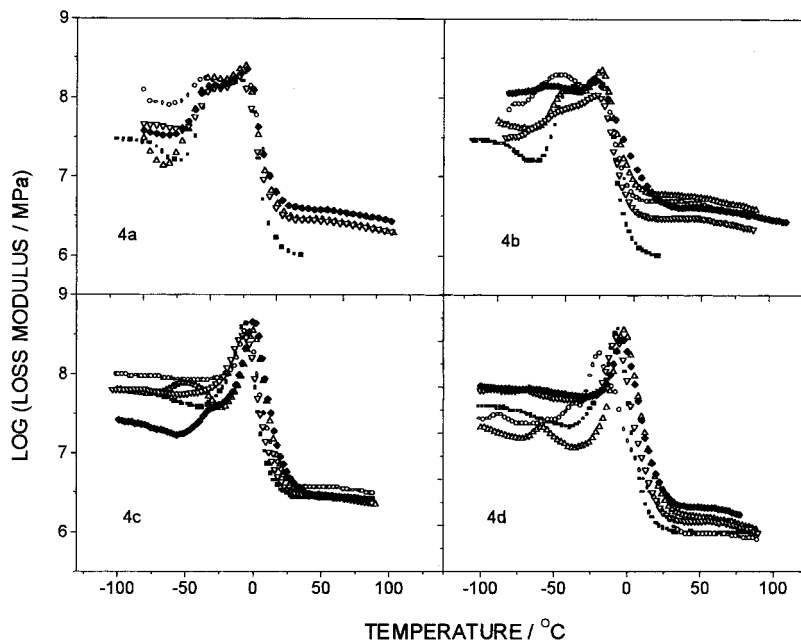
Figure 4 Loss modulus (log E'' versus T) for (a) NBR29 + 50 phr of PAni, (b) NBR29 + 100 phr of PAni, (c) NBR45 + 50 phr of Pani, and (d) NBR45 + 100 phr of PAni. (●) Pure NBR 29; (♦) PAni–HCl; (○) PAni–DBSA; (▽) PAni–TBSA; (△) PAni–PTSA.

polarity of the rubber, also increasing the compatibility with the polar-doped PAni.

In all cases, the samples prepared with PAni–HCl presented the lowest conductivity. This acid has the highest volatility and is lost during the processing in the roll-mill and vulcanization, similarly to what occurs when comparing the thermogravimetric curves of the different Pani's used in this work. Conductivity of the crude vulcanized NBR is 10^{-15} S cm^{-1}; thus, addition of PAni to its formulation increased the conductivity by three orders of magnitude, reaching the values obtained with conductive carbon black.[7]

Mechanical Properties

In Table II, we present the results obtained from the stress–strain tests for all blends in comparison to the crude NBR rubbers. All samples were formulated according to Table I and vulcanized. In comparing the crude rubbers, we observe that the increase of acrylonitrile content produces a material with a 100% higher modulus and strain at break and a lowering of 60% on the stress at break, thus making the material harder and stiffer. The acrylonitrile comonomer stiffens the polymer chains due to the dipole–dipole interactions between these repeating units.[8]

Compounding these rubbers with PAni produced different effects, depending on the acid dopant and on the concentration of PAni. For NBR29, there was, generally, an increase of the modulus and a lowering of the elongation at break for all acid dopants, while the stress at break increased only in the case of TBSA and PTSA, remaining constant for

Table III   Glass Transition Temperatures (°C) of the Crude Rubbers and Blends as a Function of PAni Concentration and Acid Dopant

PAni		TBSA		DBSA		PTSA		HCl	
% CN	NBR	50 phr	100 phr	50 phr	100 phr	50 phr	100 phr	50 phr	100 phr
29	−24	−28	−28	−15	−25	−24	−23	−24	−29
	−41	−47	−49	−52	−53	−49	−48	−47	−62
45	−6	−7	−8	−3	−18	−1	−1	−1	−3

Table IV   Swelling Degree of the Blends as a Function of PAni Concentration and Acid Dopant

% CN	NBR	PAni–TBSA		PAni–DBSA		PAni–PTSA		PAni–HCl	
		50 phr	100 phr	50 phr	100 phr	50 phr	100 phr	50 phr	100 phr
29	13.2	17.1	—	15.3	—	15.9	—	17.7	—
									—
45	40.3	25.8	—	24.7	—	20.7	—	32	

DBSA and HCl. The reduction of the elongation at break is much higher for 100 phr of PAni. For NBR45 containing 50 phr of PAni, we observed an increase in the modulus (400%), in the stress at break (ca. 100–200 %, depending on the acid dopant), and in the elongation at break. When we added 100 phr of PAni to NBR45, the modulus decreased twofold, the stress at break decreased by one order of magnitude, and the elongation at break decreased fivefold, in comparison to the sample containing 50 phr. The fragility of the material can be assigned to a different crosslinking degree and, perhaps, to degradation of the rubber compound.

Elastomers present a variation of the stress at break as a function of crosslinking density with a maximum followed by a sharp decrease, and the elongation at break is inversely proportional to the crosslinking density.[9] Besides, vulcanization is precluded by the presence of acids because these react with the sulfur compounds, competing with their radicalar degradation during the vulcanization process.[9] Thus, NBR29 should present a higher crosslinking density because it has a higher concentration of unsaturations in the polymer backbone. Also, the higher the concentration of PAni, the lower should be the crosslinking density due to the presence of the acid. This effect does not occur systematically along this work, probably because no rheologic control measurement was done during the vulcanization process.

DMA

Figures 3 and 4 show the variation of the storage and loss moduli as a function of temperature for all blends and for the crude rubbers. The DMA under constant frequency and variable temperature gives information on the molecular relaxation processes of the polymer chains, reflecting the miscibility, the composition, and the morphology of the blends. Observing the storage modulus curves (log E' versus T), we note a two orders of magnitude decrease of this variable with increase of the temperature. This decrease represents a transition from the vitreous to the elastic state and is associated with the glass transition.

Comparing NBR45 [Fig. 3(c,d)] and NBR29 [Fig. 3(a,b)], we observe that the curve for the first does not show a defined elastic plateau after the glass transition temperature, T_g, due to the flow of the chains. This can be assigned to a lower crosslinking efficiency, as expected for a lower butadiene content. For all blends containing PAni, we observe the same flow tendency in the elastic region, confirming the hypothesis that the acid is an additional barrier to the crosslinking process. Comparing the blends with the crude rubbers, we observe an increase in the modulus in the elastic region, confirming the reinforcing effect observed in the stress–strain measurements.

The temperatures of the maxima observed in the loss modulus curves (Fig. 4) can be correlated to the relaxation processes—in this case, related to the glass transition. The temperature of the maximum is assigned to the T_g. The crude rubbers present different loss modulus curves: NBR29 shows two transition peaks at −40 and −25°C and NBR45 presents only one peak at −3°C. The presence of two peaks for NBR29 can

Table V   Soluble Fraction (%) of the Blends as a Function of PAni Concentration and Acid Dopant

% CN	NBR	PAni–TBSA		PAni–DBSA		PAni–PTSA		PAni–HCl	
		50 phr	100 phr	50 phr	100 phr	50 phr	100 phr	50 phr	100 phr
29	11.4	19.4	55.6	23.1	37.3	28.1	61.4	29.9	52.7
45	60.7	42.6	55.8	33.5	70.5	36.5	69.0	66.2	99.8
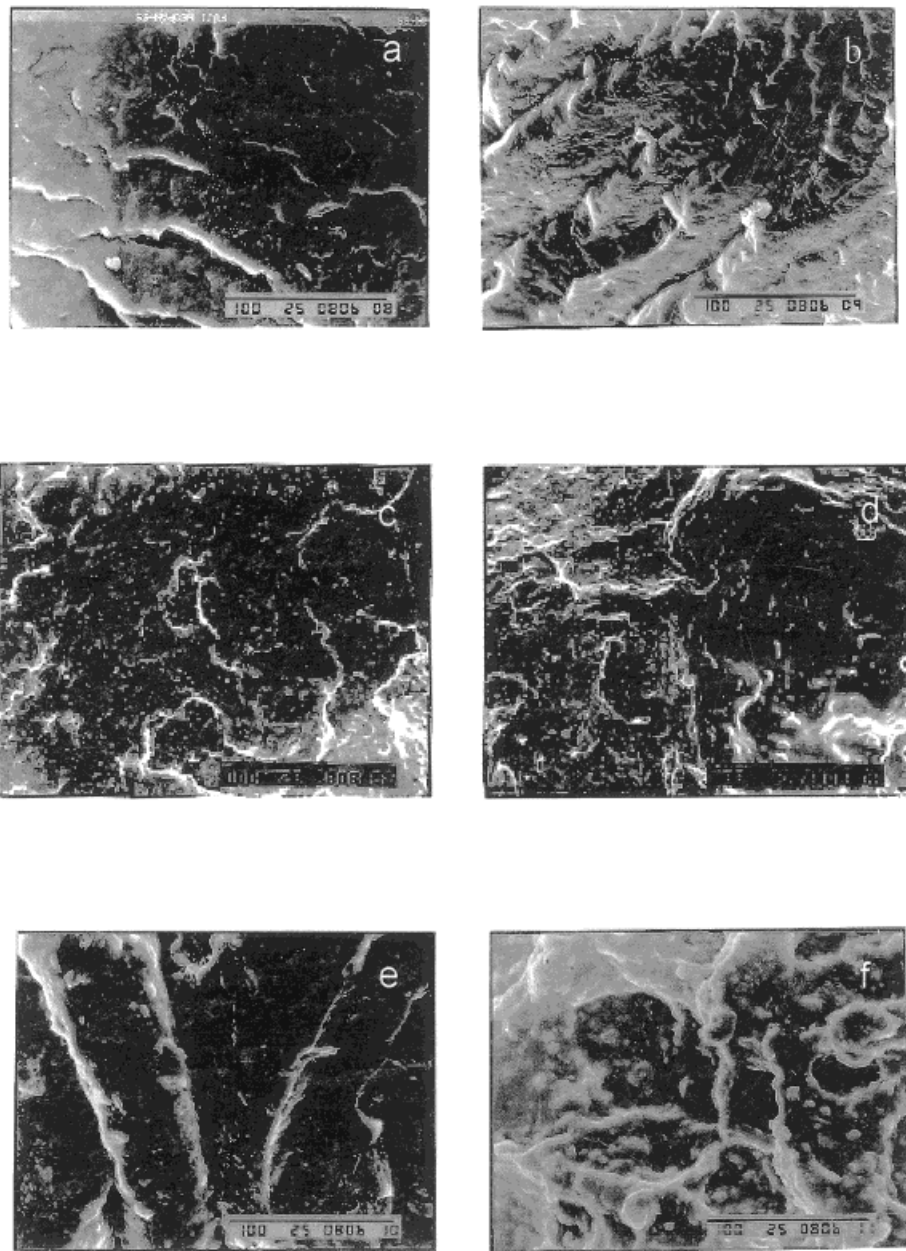
Figure 5 Scanning electron micrographs of the fracture of (a) crude NBR29 and (b) NBR45 samples compared with the blends of (c,d) NBR29 and (e,f) NBR45 containing (c,e) 50 phr or (d,f) 100 phr of PAni/HCl.

be assigned to different chain lengths for the acrylonitrile blocks in the block copolymer.[10] Table III shows the T_g values for the crude rubbers and blends. The higher acrylonitrile content of NBR45 produces a higher T_g due to the rigidity of the acrylonitrile blocks in the copolymer.[11] Addition of PAni produces a shift and a broadening of the peaks assigned to T_g, evidencing the low interaction of the polymers in the blends. Considering these results and

that PAni is vitreous at room temperature and the emeraldine base presents the T_g at about 220°C,[11] we conclude that the NBR/PAni blends are immiscible systems.

Some blends exhibit a T_g lower than that of the corresponding pure rubber. This effect can result from the low crosslinking density of the rubber in the blends and for blends containing PAni doped with high molar mass acids; they can act as a plasticizer, decreasing the T_g.

Swelling Degree and Soluble Fraction Measurements

Tables IV and V present the swelling degree and soluble fraction for the crude rubbers and the blends, respectively. Initially, we observe that NBR45 presents a higher swelling degree in comparison to NBR29. The opposite should be expected because NBR29 has a solubility parameter close to that of chloroform,[12] while the calculated solubility parameter for NBR45 is higher. This can be also associated to the lower crosslinking density of NBR45 in comparison to NBR29.

Addition of 50 phr of PAni to NBR29 caused an increase in both parameters, confirming the hypothesis of the decrease in the crosslinking efficiency with the presence of acid in the blend. For the blends with NBR45, however, there was a lowering of these parameters. This can be assigned to a badly controlled vulcanization process.

The sample prepared with 100 phr of PAni doped with HCl and NBR45 was soluble in chloroform. This confirms the hypothesis concerning the fact that the acid present in the conductive polymer precludes the vulcanization of the rubber blends, changing the mechanical properties measured in the stress–strain tests.[9] Comparing the storage modulus curves for the NBR45 blends and the swelling-degree measurements, we also confirm that the reinforcing effect observed in the DMA measurements is caused by the presence of PAni and not by crosslinking.

Scanning Electron Microscopy

Both NBR samples presented the same fracture propagation pattern, indicating that the acrylonitrile content does not affect the morphology of the rubber [Figs. 5(a,b)]. The same is observed after addition of PAni/HCl [Fig. 5(c–f)]. However, a phase segregation is observed in the NBR45 sample blended with 50 phr of PAni/HCl [Fig. 5(e)]. In this case, particles with an average diameter of 20 μm are observed.

For NBR45 rubbers blended with PAni/HCl, we observe a different fracture propagation pattern, indicating a different morphology [Figs. 5(e,f)]. In this case, a different morphology evidences phase segregation for NBR29 blended with 50 phr of PAni. These results corroborate the DMA results, which indicated phase segregation

for these blends. The same results were observed for the other samples blended with PAni doped with high molar mass acid.

CONCLUSIONS

High molar mass acid dopants increase the thermal stability of PAni and lower its electronic conductivity. The properties of the NBR/PAni blends depend strongly on its composition and are principally affected by the component in higher concentration. From this, the lower PAni concentration produces a lower conductivity (10^{-12} S cm^{-1}) and its mechanical properties are close to those of the crude rubber. High PAni content increases the conductivity by four orders of magnitude (10^{-8} S cm^{-1}); however, the mechanical properties are close to crude PAni, making the material hard and brittle. Addition of PAni lowers the crosslinking degree, but produces a reinforcing effect in the elastomer.

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