Novel Peroxide-Vulcanized NBR-PAni.DBSA Blends, Part 1: Preparation and Characterization

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ABSTRACT: Blends of poly(butadiene-*co*-acrylonitrile)-polyaniline dodecylbenzenesulfonate [NBR-PAni.DBSA] were successfully prepared using an internal mixer for the first time. Electrical conductivities of all the vulcanized blends (up to 10^{-2} S/cm with a conductivity percolation threshold 6.0 wt %/5.4 vol % of PAni.DBSA) were not affected with the addition of dicumyl peroxide (DCP) as the vulcanizing agent. The FTIR spectra of vulcanized NBR-PAni.DBSA blends resembled a superposition of the spectra of the raw materials, but with some notable peak shifts because of the changing intermolecular interactions between the polymers. Blends with ≤30 wt % of PAni.DBSA showed the best compatibility, i.e., with greatest peak shifts for their FTIR spectra and largest temperature shifts for their DSC recorded thermal events. The morphological studies (of both optical and transmission electron micrographs) showed that the thermomechanical mixing method had reduced the amounts of phase separation in all these NBR-PAni.DBSA blends. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3199–3208, 2009

Key words: polyaniline; conductive rubber blend; thermomechanical mixing

INTRODUCTION

NBR can be vulcanized either by sulfur, sulfur less, peroxide, or irradiation methods.[1] The irradiation method would be the most costly one, although it is the "cleanest" method, not involving any chemical additives. A nonsulfur system, i.e., the peroxide one, has some advantages over those involving sulfur. Peroxide-vulcanized nitrile rubber has excellent aging properties and is shiny, bloom-free, with a low compression set.[1] Because of the complete lack of sulfur, it neither stained silver nor discolored in the presence of lead, and peroxide could also vulcanize blends of NBR and other polymers that would not normally vulcanize with the same system.[1] The peroxide system could be much cheaper than irradiation, since only small amounts of peroxide vulcanizing agent [i.e., 2.4–4.1 phr of dicumyl peroxide (DCP)] are used for achieving the optimum vulcanizing level.[2] Hence, in this part of work, the peroxide-vulcanizing system (i.e., by using DCP) was selected.

Both basic- (using a two-roll mill, at temperature ≤60°C) and thermomechanical (using an internal mixer or extruder, at temperature ≥100°C) mixings are extremely popular types of method used for preparing electrical conductive elastomeric blends.[3–6] However, both nonvulcanized and vulcanized blends of NBR with PAni-based conductive filler have never been produced by thermomechanical mixing. Vallim et al.[5] prepared NBR-PAni.DBSA blends by using a two-roll mill (at 50°C) and vulcanized the blends with sulfur in a hot press (at 150°C), but all the blends showed poor electrical conductivities (ranging from about 10^{-8} to 10^{-12} S/cm).

The aim of this work was to establish a new method on preparing the electrically conductive DCP-vulcanized blends based on the NBR [48.2 wt % acrylonitrile (ACN) content] and different proportions of added PAni.DBSA. Characterization of the resulting blends is also reported here, using differential scanning calorimetry (DSC), infrared spectroscopy, determination of the electrical conductivity, and morphological study by both optical and electron microscopy. It was decided to produce the NBR-PAni.DBSA blends by thermomechanical mixing, i.e., by using a temperature-controllable internal mixer (Brabender Plasticorder, PL 2000E). In the view of the high conductivities observed for NBR-PAni.DBSA blends prepared by solution mixing,[7] it was hoped that good results could also be achieved by suitable condition of mixing, temperature, and vulcanization for the thermomechanically prepared blends, as described later in this article.

EXPERIMENTAL

Chemicals and raw materials

Aniline monomer (99 wt %, Sigma-Aldrich, UK), ammonium persulfate [APS] (98 wt %, Sigma-Aldrich), 36.5–38 wt % HCl solution (GPR), anhydrous ferric

Stage of mixing	Timing
1. Addition of raw NBR	0th minute
2. Addition of PAni.DBSA	1st minute
3. Sweeping	2nd minute
4. Dumping	10th minute (total time = 10 min)

chloride [FeCl$_3$] (98 wt %, Sigma-Aldrich), 33 wt % ammonia solution (GPR), 70 wt % DBSA solution in 2-propanol (GPR, Sigma-Aldrich), chloroform (GPR), and methanol (GPR) were used to synthesize the PAni.DBSA in house. PAni.DBSA with 42% protonation level was prepared by procedures as described in the literature.[7] Commercial-grade NBR [Krynac® 50.75 (Bayer, Germany)] was used. By ^{1}H NMR analysis of solutions in THF-d_8, the actual ACN content for NBR was identified as 48.2 ± 1.0 wt %. DCP (Peroximon DC40 supplied by Elf Atochem (UK) with 40 wt % of DCP, 55 wt % of calcium carbonate, and 5 wt % of silica gel) was used as the vulcanizing agent.

Preparation of NBR-PAni.DBSA blends and addition of peroxide

Nonvulcanized NBR-PAni.DBSA blend master batches with different compositions of NBR wt %: PAni.DBSA wt % (i.e., 99 : 1, 97.5 : 2.5, 95 : 5, 90 : 10, 80 : 20, 70 : 30, 60 : 40, 50 : 50) were first prepared by using an internal mixer (Brabender Plasticorder, PL 2000E). Only NBR with 48.2 wt % of acrylonitrile content was used here because of its best compatibility with the PAni.DBSA.[7] A fill factor of 0.75 was used here to perform the blending in the mixer (with free total volume, 320 mL). The starting temperature of each mixing was 140°C, and the mixer rotor speed was 100 rpm. Stages of each mixing are summarized in Table I.

Total DCP (2.5 phr) (density = 1030 kg/m^3) was added manually to each NBR-PAni.DBSA blend master batches (with different proportions of both blended polymers) on a slightly prewarmed (50°C) two-roll mill (with gap distance adjusted to about 3 mm). The master batch was removed from the two-roll mill in sheet form after about 3 min of mixing. The highest safe processing temperature of DCP is about 130°C according to the literature,[2] and this is to avoid the premature crosslinking of rubber.

Measurement of vulcanization behavior of peroxide-vulcanized NBR-PAni.DBSA blends

A Monsanto moving die-type rheometer (MDR 2000E) was used in this work. Frequency of the rheometer's rotary oscillation used was 1.7 Hz. Some of the vulcanization characteristics (as recommended by ISO 3417[8]) of the test compounds can be determined directly from the rheometer curve and they are as listed as follows: M_L, minimum torque; M_H, highest torque value attained where no constant or maximum value is obtained; $t_{s(x)}$, scorch time to (x) units of torque increase above minimum torque; $t_{c(x)}$ = cure time to (x) percent of maximum torque development.

The vulcanization behavior of DCP-vulcanized NBR-PAni.DBSA blends (with 2.5–50 wt % of added PAni.DBSA) was measured at a temperature of 150°C and duration of 60 min. Information obtained from this test was used as a guideline for the vulcanization of NBR-PAni.DBSA blend test pieces with hot-press molding.

Preparation of peroxide-vulcanized NBR-PAni.DBSA blends

The DCP-containing NBR-PAni.DBSA blend sheet as prepared by the two-roll mill was immediately used as it was still warm. Appropriate amounts of each blend were cut from the sheet and fed into a 2-mm-thick rectangle mold while it was still warm and soft. The mold together with the blend was sent for hot pressing (with a Bradley & Turton hot press) and curing (with temperature 150°C, pressure 0.42 MPa, and duration 38 min, as referred to the results gathered from "Measurement of vulcanization behavior of peroxide-vulcanized NBR-PAni.DBSA blends" section). Test pieces were also prepared from the raw-vulcanized NBR and pure PAni.DBSA for all testing for the control purposes.

Morphological studies (optical microscopy and TEM)

All peroxide-vulcanized NBR-PAni.DBSA blends prepared in this work were studied with a Nikon OPTIPHOT-2 optical microscope (magnification 200 times) and a TEM (Philips CM12 at accelerating voltage, 80 kV), respectively. All observed images were captured digitally. Films with thickness ∼ 6.0 μm for optical microscopy were prepared by further pressing the vulcanized blends in a Bradley & Turton hot press at 150°C for 5 min (pressure 0.42 MPa). Ultrathin samples (∼ 150 nm) for TEM were obtained by sectioning the vulcanized blends with a RMC MT7000 microtome. Samples for optical microscopy and TEM were collected on glass slides and standard copper grids, respectively.

FTIR spectroscopy

Infrared spectra of PAni.DBSA, peroxide-vulcanized NBR, and peroxide-vulcanized NBR-PAni.DBSA

blends were recorded on a Perkin-Elmer FTIR Spectrometer PARAGON 100. A small amount of each vulcanized sample was hot-pressed (with a Bradley & Turton hot press at 150°C, 5 min) to obtain a thin (6.0 μm), transparent film before it was put onto a KBr window (as the substrate) for characterization. Chloroform-based solution of pure PAni.DBSA (0.0167 g PAni.DBSA/mL solvent) was also prepared here. A small amount of the PAni.DBSA solution was later cast onto the KBr window to obtain a reasonably thin (∼ 6.0 μm) transparent film.

Thermal analysis

Pure PAni.DBSA, peroxide-vulcanized NBR, and peroxide-vulcanized NBR-PAni.DBSA blends were characterized by a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC). For above-ambient temperature (30–400°C), a heating rate of 20°C/min was used, and for subambient temperature (−60 to 0°C), the heating rate was 10°C/min. Each sample was sealed in a 40-μL aluminum pan and was analyzed under N_2 atmosphere. An empty pan was used as the reference. Each thermal analysis was repeated twice, and the error for all the results is ±1.5°C.

The onset temperature of the major exotherm was defined as the intersection of tangents drawn to the baseline and major exotherm slope at half height in the above-ambient temperature DSC thermograms. The onset temperature of the glass transition (T_g) was defined as the intersection of tangents drawn to the baseline and major "endotherm" slope at half height in the subambient temperature DSC thermograms.

Electrical conductivity determination

The dc electrical conductivity values for pure PAni.DBSA, peroxide-vulcanized NBR 48.2 ACN wt %, and peroxide-vulcanized NBR-PAni.DBSA blends were calculated from electrical "resistance" (voltage/current) values measured by 2- or 4-probe techniques. The dc electrical conductivity values for both nonvulcanized NBR 48.2 ACN wt % and NBR-PAni.DBSA blends were calculated here to make comparison with the peroxide-vulcanized ones. The nonvulcanized blends were prepared by using an internal mixer with the same procedures described in Table I. The effect of the addition of the vulcanizing agent (i.e., DCP) on the electrical conductivities of NBR-PAni.DBSA blends was studied here by comparing the measured values for the nonvulcanized and vulcanized materials.

A Keithley 617 programmable electrometer and a Keithley 224 programmable current source were used for this purpose. Hot-press molded samples (Bradley & Turton hot press at 150°C, 0.42 MPa, and 38 min) of all materials with dimensions, 25 mm (length) × 25 mm (width) × 2 mm (thickness) were used in this work. The van der Pauw 4-probe method[9] and the 2-probe method were used to measure all samples with electrical conductivities $\geq 10^{-7}$ S/cm and $< 10^{-7}$ S/cm, respectively. All measurement setups were exactly the same as those used for cast-film samples (see Ref. 7), except that no microscope slides were used here as all prepared test pieces were thick enough to support themselves. For the samples measured by the 4-probe technique, the van der Pauw equation [eq. (1)] configuration was used.

$$\sigma = \frac{2ln2}{(R_1 + R_2)\pi df} \qquad (1)$$

where σ is the electrical conductivity (S/cm), R_1 and R_2 are the mean values of apparent resistance for a pressed sample in its two perpendicular contact configurations, d is the thickness of the pressed sample, and f is a geometric factor (close to unity for symmetrical contacts on circular pellets or square plaques).

Electrical conductivities were calculated from the eq. (2) configuration for the samples measured by the 2-probe method.

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{L}{A}\right) \qquad (2)$$

where σ is the electrical conductivity, R is the mean value of apparent resistance (voltage/current ratio) for the pressed sample, L is the measured electrode spacing distance, and A is the cross-sectional area of pressed sample between the current-carrying electrodes.

RESULTS AND DISCUSSION

Measurement of vulcanization behavior of peroxide-vulcanized NBR-PAni.DBSA blends

Results of three rheometer curve examples are summarized in Table II. The slowest cure time (t_{c95}) was identified as about 38 min for the blend with 2.5 wt % of added PAni.DBSA. A 38-min vulcanization time was therefore used for all blends as a reference to achieve a vulcanizing level of 95% or above (based on the t_{c95} value). It was observed that the vulcanizing times of all blends slightly decreased with increasing the proportion of PAni.DBSA. This is likely that there were some extra crosslinkings on the NBR, which contributed to the free radicals released by the PAni.DBSA itself (apart from the peroxide-vulcanizing agent) during the high-temperature heating process (150°C).

TABLE II
TABLE II
Vulcanization Behavior of Dicumyl Peroxide-Vulcanized NBR-PAni.DBSA Blends

Rheometer curve value	Blend with 2.5 wt % PAni.DBSA	Blend with 20 wt % PAni.DBSA	Blend with 50 wt % PAni.DBSA
Minimum torque (M_L) (dN/m)	0.81	0.83	0.80
Maximum torque (M_H) dN/m	8.96	8.99	8.97
Scorch time (t_{S2}) (min)	5	4	4
Cure time (t_{c95}) (min)	38	37	35

It was found that all the rheometer curves (see Fig. 1 for one of the example curves) showed a constant value after its maximum torque. It is suggested that all blends reached their maximum vulcanization level within the chosen test period, i.e., 60 min.

Morphological studies (optical microscopy and TEM)

Optical microscopy was used to study all the peroxide-vulcanized NBR-PAni.DBSA blends, but only images of blends containing 5, 20, 30, and 40 wt % of PAni.DBSA are shown here (Fig. 2). For all the micrographs, two distinct colored regions were observed, i.e., the pale (pale green in actual)-ones and the dark (dark green in actual)-ones. The dark-colored regions (rich in PAni.DBSA) showed some large conductive particles and their agglomerates, which related to some degree of phase separation. The well-blended regions of PAni.DBSA and NBR were shown as pale-colored regions (rich in NBR); they became denser in color (more greenish in actual) when the concentration of PAni.DBSA was increased. According to the literature,[7] by increasing the proportion of PAni.DBSA, the total area of the dark-colored region will increase. For all the optical micrographs, some large, isolated particles could be observed (see Fig. 2). However, it is strongly believed that the two blended polymers are significantly compatible, based on the results obtained from the FTIR spectroscopy and DSC thermal analysis.

Preparation of NBR-PAni.DBSA blends by using the internal mixer at high temperature produced numerous well-blended regions of NBR and PAni. DBSA (pale-colored regions in Fig. 2). It is likely that most of the electrical conductivity of these thermo-mechanically mixed blends was contributed by the conducting polymers in these well-blended regions [see Fig. 2(a,b)]. This is in contrast with the same type of blend prepared by solution mixing at room temperature, where it was suggested that the built-up networks or pathways of large phase-separated PAni.DBSA particles had played important role in the overall conductivity.[7,10]

Figure 3 shows the examples of TEM micrographs of blends with 5 wt % (generally below the percolation threshold) and 10 wt % (generally above the percolation threshold) of added PAni.DBSA. The dark regions in both TEM micrographs relate to the large conductive PAni.DBSA particles in a lighter NBR matrix. The TEM also successfully revealed some small particles of PAni.DBSA (of colloidal dimensions, 50–1000 nm). It was reported[7] that all these small PAni.DBSA particles had also contributed to the electrical conductivity of blends prepared in this part of work, especially the ones that were below the main percolation threshold. Some bright white-colored spots were also found in Figure 3(a,b). They are actually small holes (left over from air bubbles trapped inside the material) that were created during the process of preparing (using microtome) these ultrathin microscopy specimens.

Thermal analysis

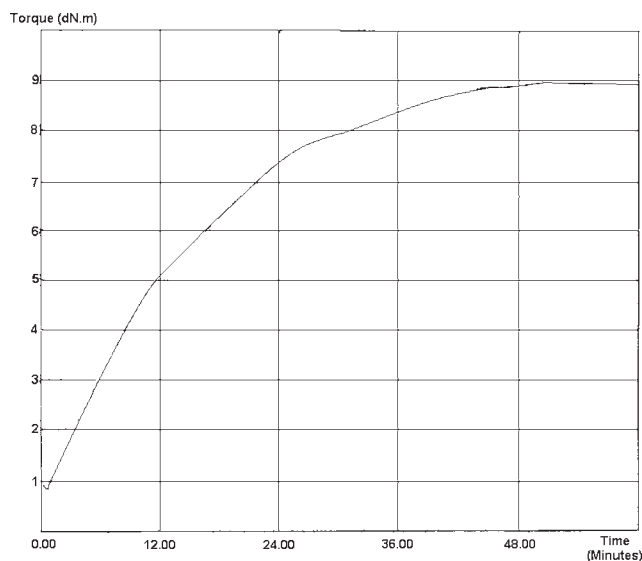Examples of the subambient temperature DSC thermograms for peroxide-vulcanized NBR and

Figure 1 Rheometer curve of peroxide-vulcanized NBR-PAni.DBSA blends (97.5 wt % NBR : 2.5 wt % PAni. DBSA).
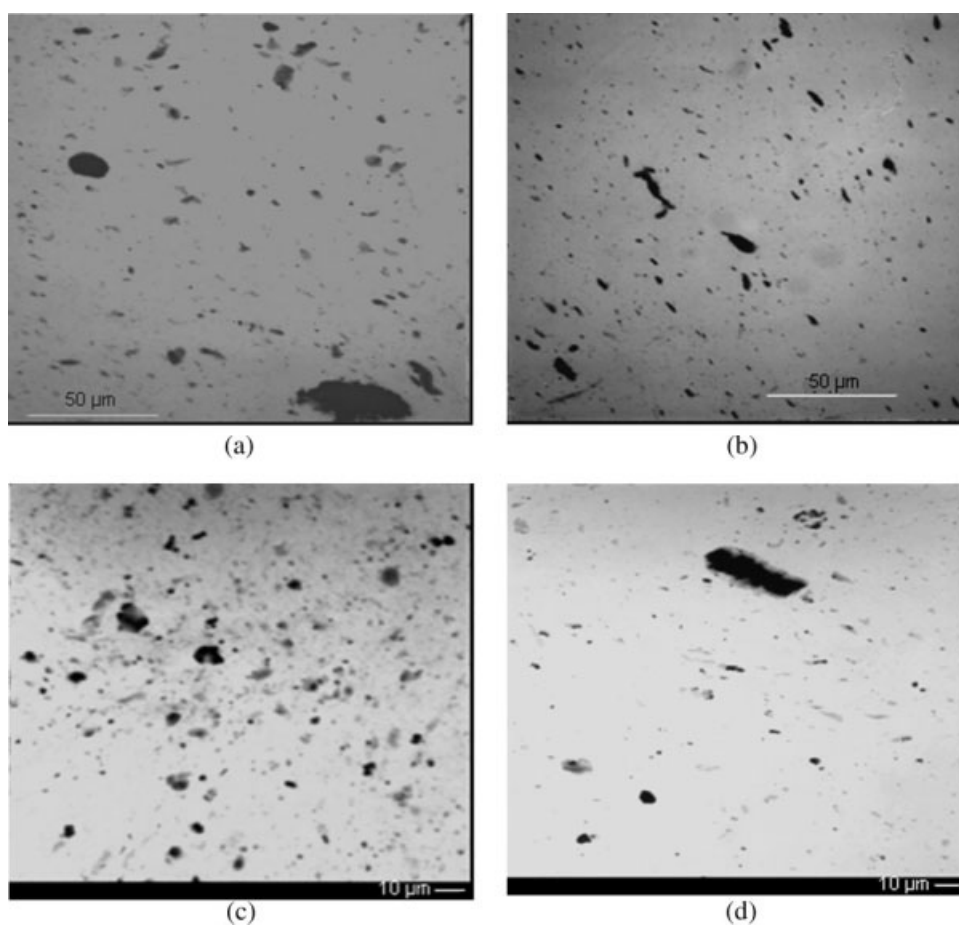
Figure 2 Optical micrographs (×200 magnification) for the peroxide-vulcanized blends of NBR-PAni.DBSA prepared by thermomechanical mixing. Blends contain (a) 60 : 40, (b) 70 : 30, (c) 80 : 20, and (d) 95 : 5 wt % NBR : wt % PAni.DBSA.

peroxide-vulcanized NBR-PAni.DBSA blends with 10–50 wt % of PAni.DBSA are shown in Figure 4. (A DSC thermogram for pure PAni.DBSA is not shown because there were no obvious thermal processes in the low-temperature region.) Figure 5 shows the examples of above-ambient temperature DSC
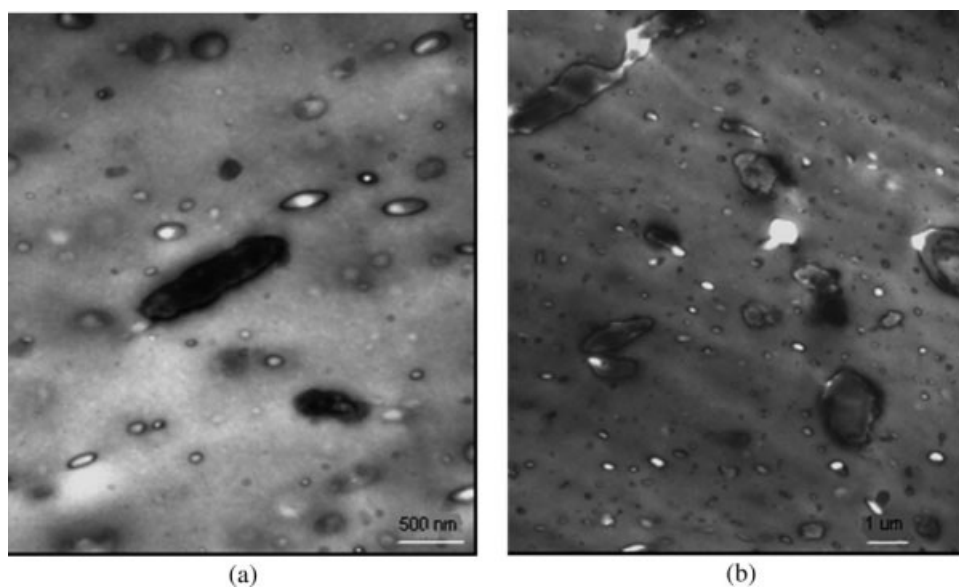

Figure 3 Transmission electron micrographs of the peroxide-vulcanized NBR-PAni.DBSA blends prepared by thermomechanical mixing. Blends contain (a) 5 wt % of PAni.DBSA and (b) 10 wt % of PAni.DBSA.
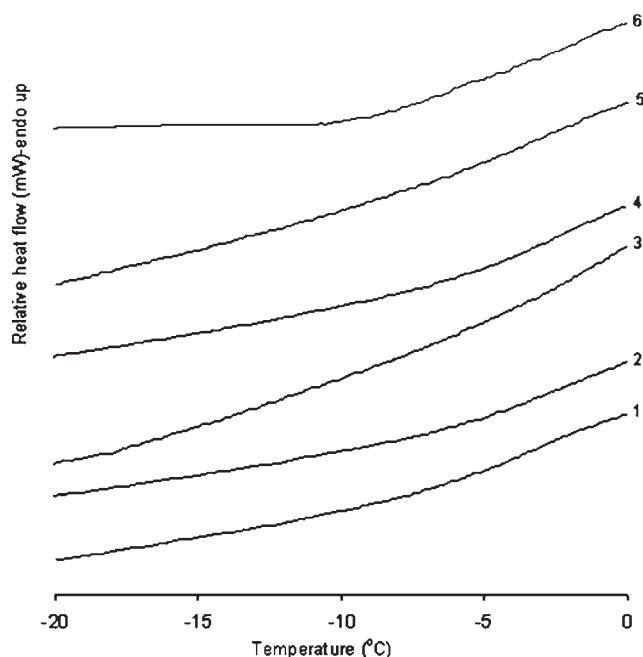
Figure 4 Subambient temperature DSC thermograms for peroxide-vulcanized NBR-PAni.DBSA blends of different composition (wt % NBR : wt % PAni.DBSA*). Line 1, blend (50 wt % NBR : 50 wt % PAni.DBSA); line 2, blend (60 wt % NBR : 40 wt % PAni.DBSA); line 3, blend (70 wt % NBR : 30 wt % PAni.DBSA); line 4, blend (80 wt % NBR : 20 wt % PAni.DBSA); line 5, blend (90 wt % NBR : 10 wt % PAni.DBSA); line 6, vulcanized NBR.
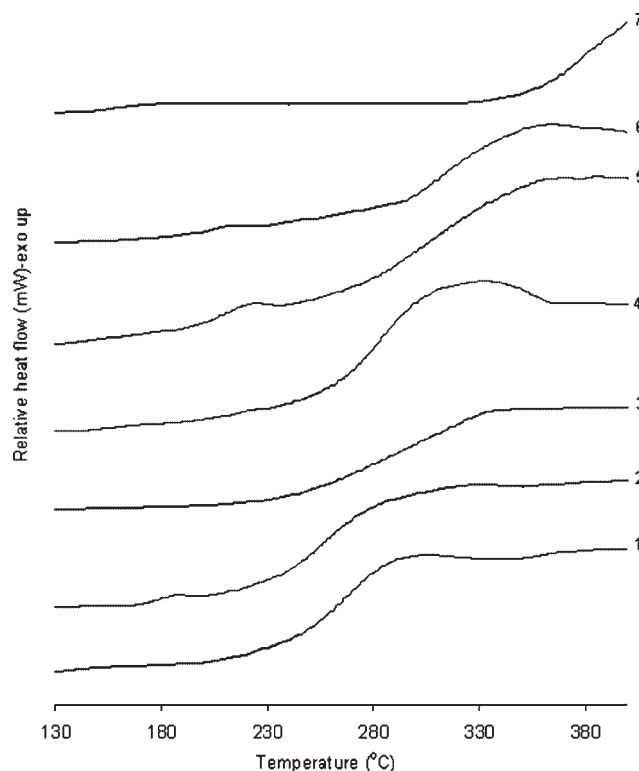

Figure 5 Above-ambient temperature DSC thermograms for PAni.DBSA, peroxide-vulcanized NBR, and different compositions (wt % NBR : wt % PAni.DBSA*) of peroxide-vulcanized NBR-PAni.DBSA blends. Line 1, PAni.DBSA; line 2, blend (50 wt % NBR : 50 wt % PAni.DBSA); line 3, blend (60 wt % NBR : 40 wt % PAni.DBSA); line 4, blend (70 wt % NBR : 30 wt % PAni.DBSA); line 5, blend (80 wt % NBR : 20 wt % PAni.DBSA); line 6, blend (90 wt % NBR : 10 wt % PAni.DBSA); line 7, vulcanized NBR.

thermograms for the PAni.DBSA, peroxide-vulcanized NBR, and their peroxide-vulcanized blends with 10–50 wt % of PAni.DBSA.

The calculated mean T_g values for the peroxide-vulcanized NBR and NBR-PAni.DBSA blends are shown in Table III. The subambient temperature DSC thermograms of the blends have positive T_g shifts for the NBR component, which increase with the proportion of PAni.DBSA. Blends with up to 30 wt % of PAni.DBSA content showed the greatest T_g shifts because of the best compatibility level that was achieved by them. Less dark, big particles would be seen from the optical micrographs for these blends (w.r.t. Fig. 2) because of a better dispersion level of the PAni.DBSA particles. For blends with ≥40 wt % of PAni.DBSA, their T_g values were shifted back to the T_g value of raw NBR, and this was due to the more serious phase separation problem that had occurred in these blends. At the same time, bigger agglomerated PAni.DBSA particles could also be found from the optical micrographs of these blends (see Fig. 2).

The vulcanized NBR was found (see Table IV) to be thermally stable up to about 354°C (which is 23°C higher than the nonvulcanized one discussed in literature[7] because of its more rigid crosslinked structure[11]). The PAni.DBSA had good thermal stability up

to about 233°C (same value as found in literature[7]). The thermal processes that were combinations of events recorded for the two raw materials could be observed from all the above-ambient temperature DSC thermograms. However, the detailed examination successfully revealed that the events also showed some degrees of temperature shift related to the corresponding processes in the raw materials.

TABLE III
The Mean Glass Transition Temperature (T_g) Values for Peroxide-Vulcanized NBR and Peroxide-Vulcanized NBR-PAni.DBSA Blends

Composition (wt % NBR : wt % PAni.DBSA*)	Glass transition temperature (T_g) (°C)
Vulcanized NBR (48.2 wt % ACN)	−10
Vulcanized blend	
90 : 10*	−7
80 : 20*	−7
70 : 30*	−5
60 : 40*	−8
50 : 50*	−8

TABLE IV
The Mean Onset Temperature Values of Major Exotherms for the Above-Ambient Temperature DSC Thermograms of PAni.DBSA, Peroxide-Vulcanized NBR, and Peroxide-Vulcanized NBR-PAni.DBSA Blends

Composition (wt % NBR : wt % PAni.DBSA*)	Onset temperature of major exotherm (°C)
Vulcanized NBR (48.2 wt % ACN)	354
Vulcanized blend	
90 : 10*	297
80 : 20*	276
70 : 30*	252
60 : 40*	239
50 : 50*	229
PAni.DBSA	233

For the above-ambient temperature DSC analysis, the larger the onset temperature shifts of the blend from the constituent materials, the better is the compatibility between the two blended polymers using this high-temperature mixing method. From Table IV, it was found that the blends containing low to moderate amounts of PAni.DBSA ($\leq$30 wt %) showed larger shifts in the onset temperature of the major exotherm (with respect to the pure PAni. DBSA). However, only smaller shifts in the onset temperature of the major exotherm were observed for the blends with high contents of PAni.DBSA ($\geq$40 wt %). This is again in agreement with the results obtained from "Morphological studies (optical microscopy and TEM)" section, where more phase-separated (dark green) regions could be found for the blends with $\geq$40 wt % of PAni.DBSA attributed to the lower level of compatibility between the two constituent polymers.

FTIR spectroscopy

Examples of FTIR spectra for PAni.DBSA, peroxide-vulcanized NBR, and their peroxide-vulcanized blends (i.e., with 30 and 40 wt % of PAni.DBSA) are shown in Figure 6. FTIR spectrum for the hot-pressed film of peroxide-vulcanized NBR shows its
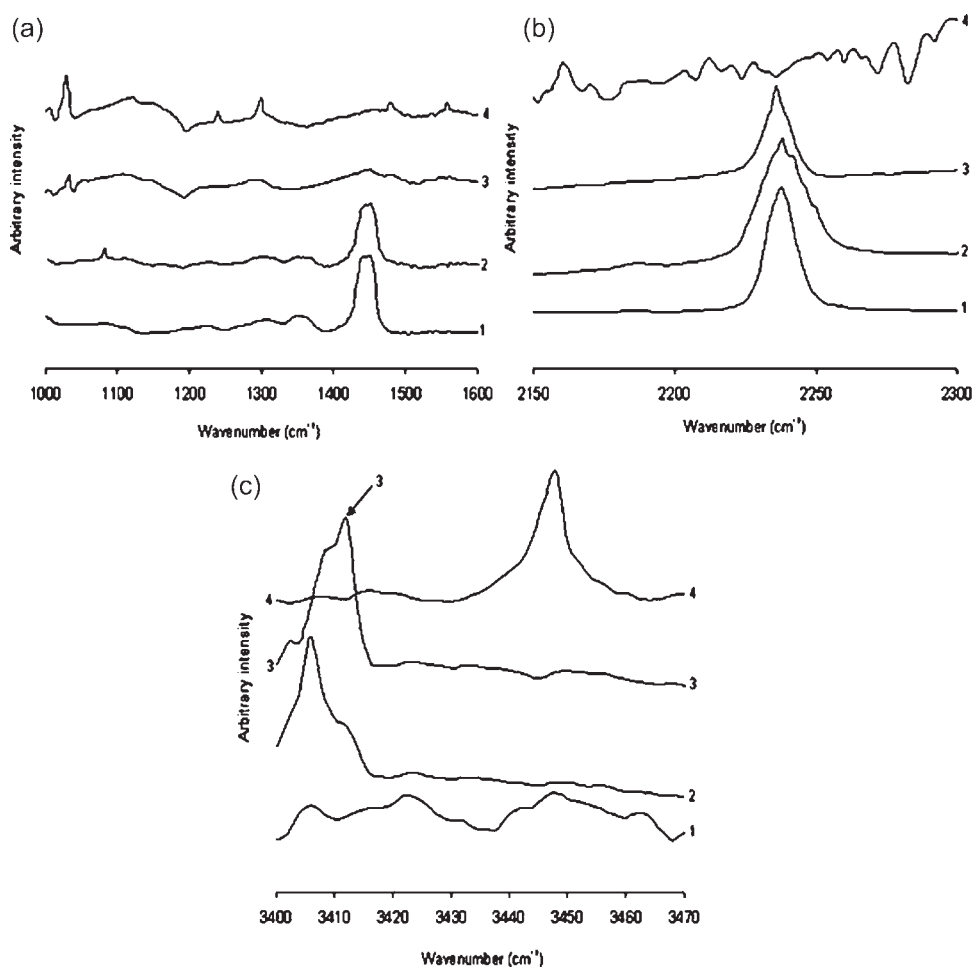

Figure 6 FTIR spectra of PAni.DBSA, peroxide-vulcanized NBR, and peroxide-vulcanized NBR-PAni.DBSA blends: (a) 1000–1650 cm^{-1}, (b) 2150–2300 cm^{-1}, and (c) 3400–3470 cm^{-1}. Line 1, vulcanized NBR; line 2, vulcanized blend 10 wt % of PAni.DBSA; line 3, vulcanized blend 40 wt % of PAni.DBSA; line 4, PAni.DBSA.

TABLE V
Characteristic Infrared Absorption Peaks for PAni.DBSA, Peroxide-Vulcanized NBR,
and Peroxide-Vulcanized NBR-PAni.DBSA Blends

Pure material or blend (wt % NBR : wt % PAni.DBSA*)	Peak assignment (cm^{-1})		
	=N—H stretching	S=O stretching	—C≡N stretching
PAni.DBSA	3448W	1030M	–
Vulcanized NBR	–	–	2238M
Vulcanized blend			
90 : 10*	3406W	1081W	2238W
80 : 20*	3406W	1081W	2237W
70 : 30*	3406W	1081W	2236W
60 : 40*	3412W	1033W	2236W
50 : 50*	3430W	1032W	2236W

Indication of peak intensity: W, weak; M, medium.

characteristic absorptions at 2238 cm^{-1} (—C≡N stretching), 1630 cm^{-1} (C=C stretch), and 1440–1445 cm^{-1} (out of plane C—H wagging). The spectrum of PAni.DBSA has characteristic absorptions at 3448 cm^{-1} (=N—H stretching), 1559 cm^{-1} (N=quinoid =N), 1478 cm^{-1} (N—benzoid—N), 1295 cm^{-1} (quinoid=N—benzoid), 1240 cm^{-1} (C aromatic—N stretching), and 1030 cm^{-1} (S=O stretching).

For all the peroxide-vulcanized blends with low contents of PAni.DBSA (i.e., ≤30 wt %), their infrared spectra showed a predominance of NBR absorption bands. There was a predominance of PAni.DBSA absorption bands in all the infrared spectra of peroxide-vulcanized blends with higher levels of PAni.DBSA (i.e., ≥40 wt %). However, some significant shifts of certain characteristic peaks were successfully found through some detailed examination, and the mixing efficiency of the two blended polymers was assessed by studying some of these infrared peak shifts (see Table V).

The bands at 3448 cm^{-1} (N—H stretching) and 1030 cm^{-1} (S=O stretching) are solely attributed to the PAni.DBSA, whereas that at 2238 cm^{-1} is derived from the peroxide-vulcanized NBR. From the spectra of all peroxide-vulcanized blends, all these bands were found to have intensities when compared with those for the raw material ones. However, two large peak shifts were successfully found, i.e., a decrease to 3406 cm^{-1} for the N—H stretch and an increase to 1081 cm^{-1} for the S=O stretch, attributed to the changes of intermolecular interactions. The peak positions for all the dilute blends largely revert to those of the pure conducting polymer at higher concentrations (≥40 wt % PAni. DBSA). According to Yong et al.,[7] the positively charged N—H hydrogens of pure PAni.DBSA would have a strong propensity for hydrogen bonding with the negative sulfonate oxygens, and the infrared frequency changes (i.e., decrease in wave number) suggest that this bonding is disrupted by greater polar interactions with the rubber matrix especially in the well-dispersed blends (with ≤30 wt % PAni.DBSA). The larger and more aggregated particles in the concentrated blends [see Morphological studies (optical microscopy and TEM) section] are likely to have much smaller specific surface areas. As a result, the H-bonding characteristic of pure PAni.DBSA is again detected in the IR spectra.

Electrical conductivity determination

Figure 7 shows the electrical conductivities of nonvulcanized NBR and nonvulcanized NBR-PAni. DBSA blends. The calculated electrical conductivity values for the peroxide-vulcanized NBR and peroxide-vulcanized NBR-PAni.DBSA blends are shown in Figure 8.

Both nonvulcanized and peroxide-vulcanized NBR showed conductivities of the order of 10^{-14} S/cm and they are considered as good electrical insulators. Pure PAni.DBSA had a high electrical conductivity
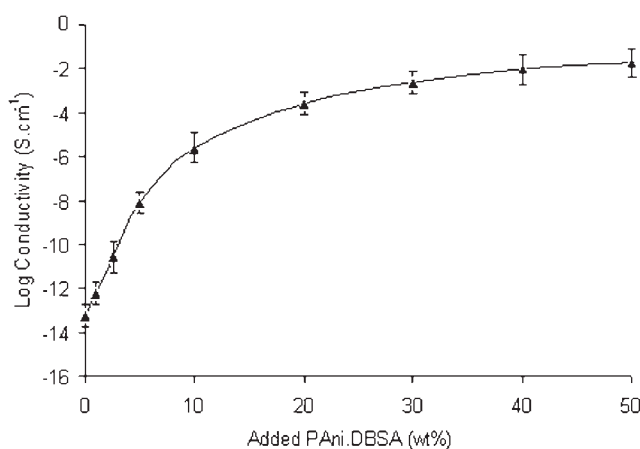

Figure 7 Electrical conductivities for the nonvulcanized NBR-PAni.DBSA blends as a function of PAni.DBSA content (wt %).
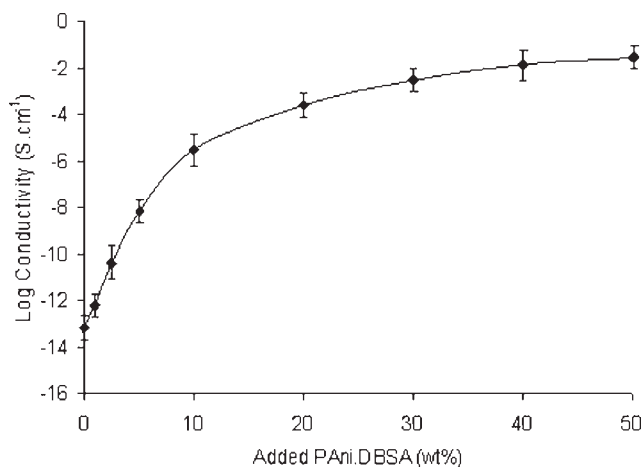
Figure 8 Electrical conductivities for peroxide-vulcanized NBR-PAni.DBSA blends as a function of PAni.DBSA content (wt %).

of 1.4 ± 0.5 S/cm when compared with literature ones for pressed pellet samples.[7,12] The electrical conductivity of all blends (both vulcanized and non-vulcanized) increased with the proportion of PAni.DBSA, as observed in several studies of different PAni.DBSA blends.[5,7,13] Both vulcanized and non-vulcanized blends reached plateau electrical conductivity of the order of 10^{-2} S/cm with about 40 wt % PAni.DBSA loading.

The data from Figure 7 were fitted to a simple percolation model as defined by eq. (3)[14,15] to estimate the conductivity percolation threshold for the nonvulcanized blends. The data were fitted to a plot of log electrical conductivity (σ) versus log (f (f_p) to estimate the values of critical exponent (t) and correlation coefficient (R). The estimated electrical conductivity percolation threshold for the nonvulcanized blends is 6.0 wt % (or 5.4 vol %) of PAni.DBSA (with $t = 3.8$ and $R = 0.99$).

The conductivity percolation threshold for peroxide-vulcanized NBR-PAni.DBSA blends was also estimated by fitting the data from Figure 8 to the simple percolation model as defined by eq. (3).[14,15] Again, it was possible to estimate the values of t and R by fitting the data to a plot of log electrical conductivity (σ) versus log ($f - f_p$). The estimated electrical conductivity percolation threshold for the peroxide-vulcanized NBR-PAni.DBSA blends is 6.0 wt % (or 5.4 vol %) of PAni.DBSA (with $t = 3.7$ and $R = 0.99$).

$$\sigma_f = c(f - f_p)^t \qquad (3)$$

where c is a constant, t is the critical exponent, f is the volume fraction of the conductive medium, and f_p is the volume fraction at the percolation threshold. All the weight fractions referred to above were converted into volume fractions for this analysis.

The values of t for both the nonvulcanized and vulcanized blends are in the range between 2 and 4, which can be explained by a single-percolation model. There was no evidence for a second stage of percolation for these high-temperature prepared blends. It is likely due to the more homogeneous mixings obtained from the thermomechanical method if compared with the solution mixed ones.[7] So, the contact between the large particles makes very little contribution to the changing of electrical conductivities.

Kathirgamanathan[16] compared the volume conductivities (measured with 4-probe method) of epoxy systems loaded with PAni.p-TSA (p-toluene sulfonic acid-doped polyaniline), carbon black, and silver-coated nickel flakes. It was reported that carbon black percolated at a low volume loading of about 5 vol %, PAni.p-TSA at about 10 vol % and silver-coated nickel flakes at about 26 vol %. It was observed that while the percolation curves for carbon black and silver-coated nickel flakes were steep, the percolation curve for PAni.p-TSA was very shallow and the transition was gradual. This phenomenon could be explained on the basis of molecular level interaction of the intrinsic electrical conductive filler, i.e., PAni.p-TSA with the epoxy resin host.[16]

It was also found that electrical conductivities of the NBR-PAni.DBSA blends were not much affected by the presence of DCP as vulcanizing agent since both the nonvulcanized and vulcanized blends had very close conductivity values at the same levels of PAni.DBSA content. As explained in the literature,[1] only carbon–carbon bonds are formed among the NBR chains in the peroxide vulcanizing system and this has the same effect as using the chemical-free irradiation method.[1,11] As a result, this will minimize the disruption on the PAni.DBSA molecular structure and will also help to retain its good electrical properties.

CONCLUSION

NBR-PAni.DBSA blends with useful electrical conductivities (up to 10^{-2} S/cm) were successfully prepared by thermomechanical mixing. The effect of crosslinking with DCP as vulcanizing agent was proved to not affect the electrical properties of NBR-PAni.DBSA blends. Results from the FTIR spectroscopy and DSC thermal analysis studies were consistent with those obtained from the morphological studies (optical and electron microscopy); where the best compatibilities were found for the blends with ≤30 wt % of PAni.DBSA. The morphological studies also showed that the thermomechanical mixing method (with high temperature and high shearing

conditions) had reduced the amounts of phase separation in the NBR-PAni.DBSA blends. It was likely that the high mixing efficiency of this method could help to reduce the particle size of the PAni.DBSA and subsequently created some better dispersed region of this conductive filler within the NBR host matrix.

In the literature,[17–20] it was reported that some conventional conductive filler (e.g., carbon blacks) could also reinforce their polymer host by enhancing the resulted blends' mechanical properties up to an optimum level of loading. Study of the effect of PAni.DBSA content on the mechanical properties of its NBR blends will be the subject of focus in the second part of this work.

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