Electrically Conductive Poly(butadiene-co-acrylonitrile)-Polyaniline Dodecylbenzenesulphonate [NBR-PAni.DBSA] Blends with Hydroquinone as Compatibiliser

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Blends of poly(butadiene-co-acrylonitrile) [NBR] and polyaniline dodecylbenzenesulphonate [PAni.DBSA] with electrical conductivities up to 10^{-1} S.cm^{-1}, have been successfully prepared using the technique of solution mixing and casting. Compatibility of both NBR and PAni.DBSA was found to be maximised by the introduction of hydroquinone as a compatibiliser. Blends prepared with added hydroquinone exhibited the lowest electrical conductivity percolation threshold and were more conductive than the ones without any compatibiliser. Transmission electron micrographs of blends with added compatibiliser showed the lowest level of phase separation. FT-IR spectra and DSC thermal of blends with added compatibiliser also showed the largest peak and temperature shifts, respectively. These phenomenons occured due to the higher intermolecular interactions between the two blended polymers in the presence of hydroquinone.

Keywords: conductive rubber; nitrile rubber; polyaniline; hydroquinone; electrical conductivity

Novel electrically conductive rubber blends are non-carbon black and non-metallic particle filled polymer blends. They should ideally be blends of elastomeric host with intrinsic electrically conductive polymer (ICP) filler[1–12]. The blends' constituent polymers should also have good compatibility with each other in order to enhance its processability[7–13], electrical conductivities[7–13] and also mechanical properties[9–13].

ICPs may have poor stability[14], poor mechanical properties[15], higher cost than commodity polymers[16] and insolubility in organic solvents[14]. An effective method to overcome these problems is by preparing composite materials containing the ICPs as fillers dispersed in elastomeric matrices. Solution mixing[7–8,17] is one of the most common and efficient techniques that can be used for the novel electrically conductive rubber blends preparation. In this technique, the ICPs may be doped with sulphonic acid in order to enhance their solubility in various organic solvents[18].

Special interest has been focused on polyaniline dodecylbenzenesulphonate (PAni.

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DBSA) due to its low toxicity, high thermal stability and well established synthesis method[7,18]. The author's earlier work[7] reported the preparation of poly(butadiene-co-acrylonitrile) (NBR)-PAni.DBSA blends without addition of any compatibilising agents by solution mixing. Blends with reasonably good electrical conductivities in the magnitude order of 10^{-2} S.cm^{-1} were successfully produced. However, phase separations of the two constituent polymers were able to be observed for blends with PAni. DBSA content as low as 5.0 weight percentage (wt %). It was also suggested the compatibility between the two constituent polymers could be further enhanced *via* the introduction of a compatibiliser such as hydroquinone[17].

This work aimed to study the novel electrically conductive rubber blends prepared by mixing of NBR with different proportions of PAni.DBSA in the presence of hydroquinone as compatibiliser. It was decided to prepare the blends by solution mixing, which required both constituent polymers to be soluble in a shared solvent, *i.e.* chloroform. Some common characterisation techniques (*i.e.* Fourier-transform infrared spectroscopy, differential scanning calorimetry, electrical conductivity determination of pure polymers and their blends and morphological study by transmission electron microscopy) were performed in order to assess the effects of added hydroquinone.

EXPERIMENTAL

Chemicals and Raw Materials

The chemicals and raw materials were aniline monomer (99 wt %, Sigma-Aldrich), ammonium persulphate [APS] (98 wt %, Sigma-Aldrich), 36.5-38 wt % hydrochloric acid [HCl] solution (GPR), anhydrous ferric chloride [FeCl$_3$] (98 wt %, Sigma-Aldrich), 33 wt % ammonia solution (GPR), 70 wt % dodecylbenzene sulphonic acid [DBSA] solution in 2-propanol (GPR, Sigma-Aldrich), chloroform (GPR) and methanol (GPR). Commercial grade NBR [Krynac® 50.75, manufactured by Bayer] was chosen as the elastomeric host. The NBR was washed with methanol for 24 h using Soxhlet extraction in order to remove chemical additives. By ^{1}H NMR analysis of solutions in THF-d8, the actual ACN content for this grade of NBR was identified as 48.2±1.0 wt %. Pure PAni. DBSA, NBR Krynac® 50.75 and chloroform were reported to have the solubility parameter values of 20.8, 20.7 and 19.0 (MJ m^{-3})$^{0.5}$ respectively[7]. As a result, both NBR and PAni. DBSA were highly soluble in chloroform. Hydroquinone (benzene 1, 4-diol) was used as received (ReagentPlus®, ≥99 wt %, Sigma-Aldrich).

Synthesis of PAni.DBSA

Conductive emeraldine salt PAni.HCl was synthesised by the oxidative chemical polymerisation technique based on an oxidant (APS)/monomer (aniline) initial mole ratio of 1.0. 50 mL of aniline and 125.2 g of APS were dissolved in 375 mL and 276 mL of 2 M HCl respectively, which had been pre-cooled to 1ºC. The aniline solution was placed in an ice bath with an overhead stirrer. After the addition of FeCl$_3$ solution (about 1 mL) as a catalyst, the APS solution was added gradually over a period of 20 min, with constant stirring to ensure thorough mixing. The temperature of the polymerisation mixture was maintained at ≤2ºC while the pH was adjusted to be ≤1.0 by the addition of concentrated HCl. The mixture was left for 6 h to complete the polymerisation and the precipitate was allowed to settle before decanting and final washing with distilled water until the filtrate was colourless. PAni emeraldine base (EB) was prepared by deprotonating the wet PAni.

HCl in 33% aqueous ammonia solution (about 5000 mL) with 24 h stirring, followed by washing and reprotonation in 1M aqueous DBSA at a molar ratio EB:DBSA of 1:1. Filtration was performed with a sintered glass funnel of grade 3 porosity (16 - 40 microns). All products were washed with large quantities of distilled water until the filtrates were colourless and no odour of ammonia could be detected. Final drying of the powdered filter cake was done in a vacuum oven at 50ºC for 24 hours. A sample of PAni.DBSA synthesised here was submitted for elemental analysis at the Malaysian Rubber Board Characterisation Laboratory and was estimated thereby to have a 42% protonation level on the basis of the S:N atomic ratio.

Blend Preparation

Masterbatch solutions of pure NBR (50 mg NBR/mL solvent) and PAni.DBSA (16.5 mg PAni.DBSA/mL solvent) in chloroform were prepared and filtered. The pure NBR solution was added to the PAni.DBSA solution in appropriate amounts in order to obtain the following compositions (wt % NBR : wt % PAni.DBSA), 50:50, 60:40, 70:30, 80:20, 90:10, 95:5, 97.5:2.5 and 99:1 respectively. Hydroquinone of 1 wt % (dosage as recommended by literature[17]) was added to each blend solution as the compatibiliser. A comparable set of blend solutions without the addition of hydroquinone was also prepared as the control sample. Each of the above blend solutions was magnetically stirred for 24 h at room temperature prior to casting.

Fourier-Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra of PAni.DBSA, pure NBR and all NBR-PAni.DBSA blends were recorded on a Nicolet Magna-IR 560 infrared spectrometer. A small amount of each sample solution was cast onto a KBr window in order to obtain a reasonably thin (~3.0 μm), transparent film.

Thermal Analysis by using Differential Scanning Calorimetry (DSC)

The PAni.DBSA powder, pure NBR and NBR-PAni.DBSA blends cast films were characterised by using the DSC technique (Mettler Toledo DSC822e). For above ambient temperature (30 to 400ºC), a heating rate of 20ºC/min was used and for sub-ambient temperature (–60 to 0ºC), the heating rate was 10ºC/min. Each sample was sealed in a 40 μL aluminium pan and was analysed under nitrogen. An empty pan was used as reference. Each thermal analysis was repeated three times and error for all the results was ±1.5ºC.

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 sub-ambient temperature DSC thermograms.

Electrical Conductivity Determination

The dc electrical conductivities for PAni.DBSA, pure NBR and NBR-PAni.DBSA blends were calculated from electrical resistances measured by guarded 2-probe techniques. The equipment employed was a Keithley 6517A Electrometer with built in voltage source up to 1kV. A pressed pellet of pure PAni.DBSA, diameter 13 mm, thickness 1.5 mm, was placed in a holder with two spring loaded metallic contacts in order to measure

its electrical resistance. Samples of pure NBR and NBR-PAni.DBSA blend were cast respectively from their solution onto square microscope slides, 625 mm^2 and the solvent was allowed to evaporate for 24 hours.

Electrical conductivities were calculated from the mean resistance values based on a set of five samples obtained by the 2-probe method using *Equation 1*[7].

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

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

Morphological Study (Transmission Electron Microscope)

All NBR-PAni.DBSA blends were studied by using a transmission electron microscope, Philips CM12 microscope, at accelerating voltage 80 kV. Ultrathin, *ca*. 150 nm sample of each blend frozen with liquid nitrogen was obtained for this study by sectioning with a microtome.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

Examples of FT-IR spectra for PAni.DBSA, pure NBR and their blends are shown in *Figures 1*, without hydroquinone and *2*, with hydroquinone.

FT-IR spectrum for cast film of pure NBR shows the characteristic absorptions at 2237 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 cast film also exhibits characteristic absorptions at 3447 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).

Detailed examination of FT-IR spectra of the blend films reveal significant shifts of certain key bands. The compatibility level of the two constituent polymers may be assessed by studying some of these shifts (*Table 1*). It is proposed that the larger the peak shift, the higher the intermolecular interaction or compatibility of the two constituent polymers. The bands at 3447 cm^{-1} (N-H stretching) and 1030 cm^{-1} (S=O stretching) solely corresponded to PAni.DBSA, while that at 2237 cm^{-1} derives from NBR.

In the spectra of all blends, these bands have intensities comparable to those for the pure polymers. However, for the blends with added hydroquinone, two larger, opposing peak shifts can be observed (*i.e.* a decrease to 3405 cm^{-1} for the N-H stretch and an increase to 1080 cm^{-1} for the S=O stretch) if compared to the ones without hydroquinone. This phenomenon was attributable to changes in the intermolecular interactions as a result of the introduction of compatibiliser. The peak positions of blends with added hydroquinone only revert to those of the pure PAni.DBSA at a higher level of concentration, *i.e.* 50 wt % of PAni.DBSA if compared to the blends without hydroquinone, *i.e.* ≥40 wt % of PAni. DBSA. In other words, larger amounts of PAni.DBSA could be introduced into a blend with compatibiliser before encountering a more serious phase separation problem.

It is proposed that the high polarity diol functional group of hydroquinone enhanced the interaction of both NBR and PAni.DBSA
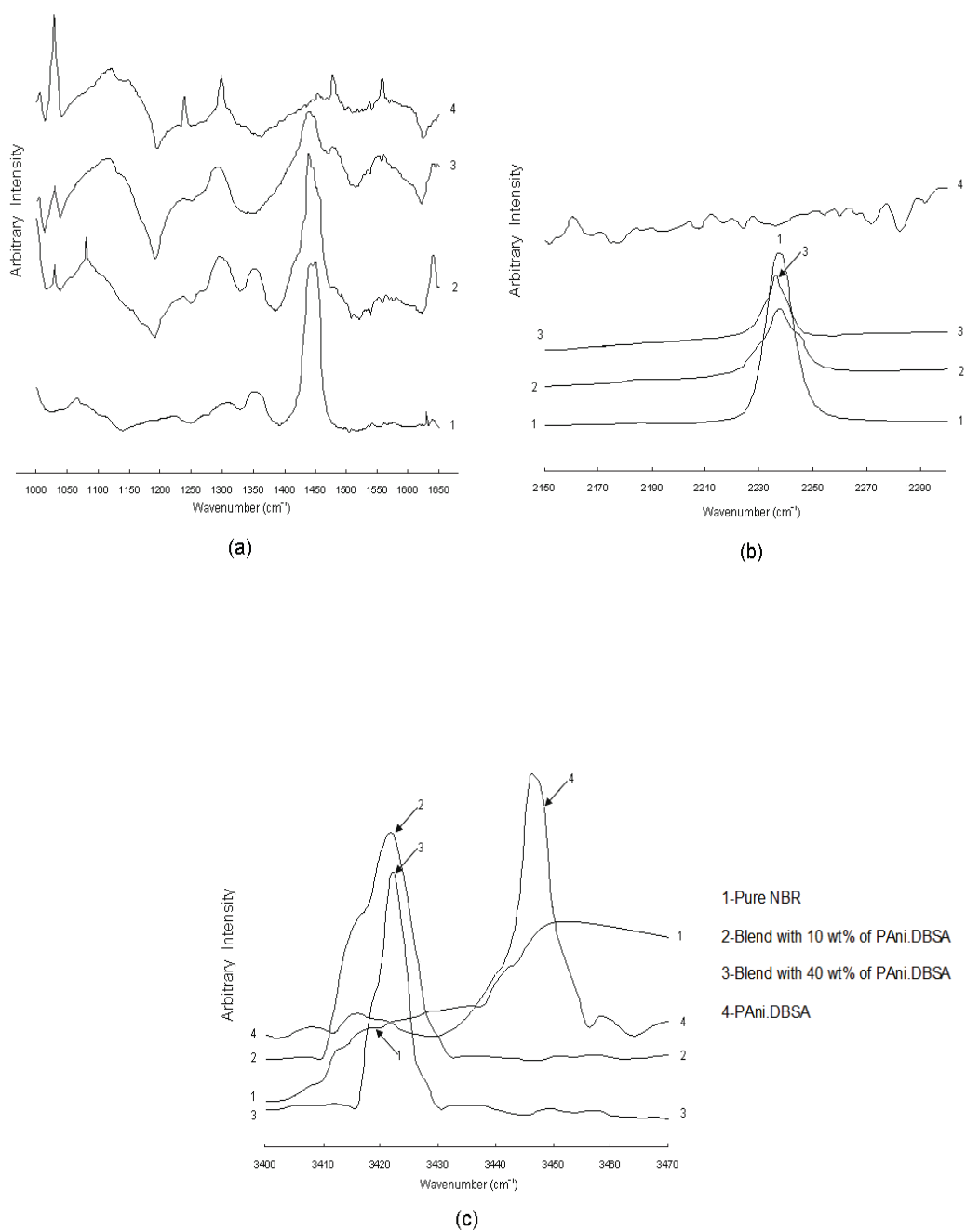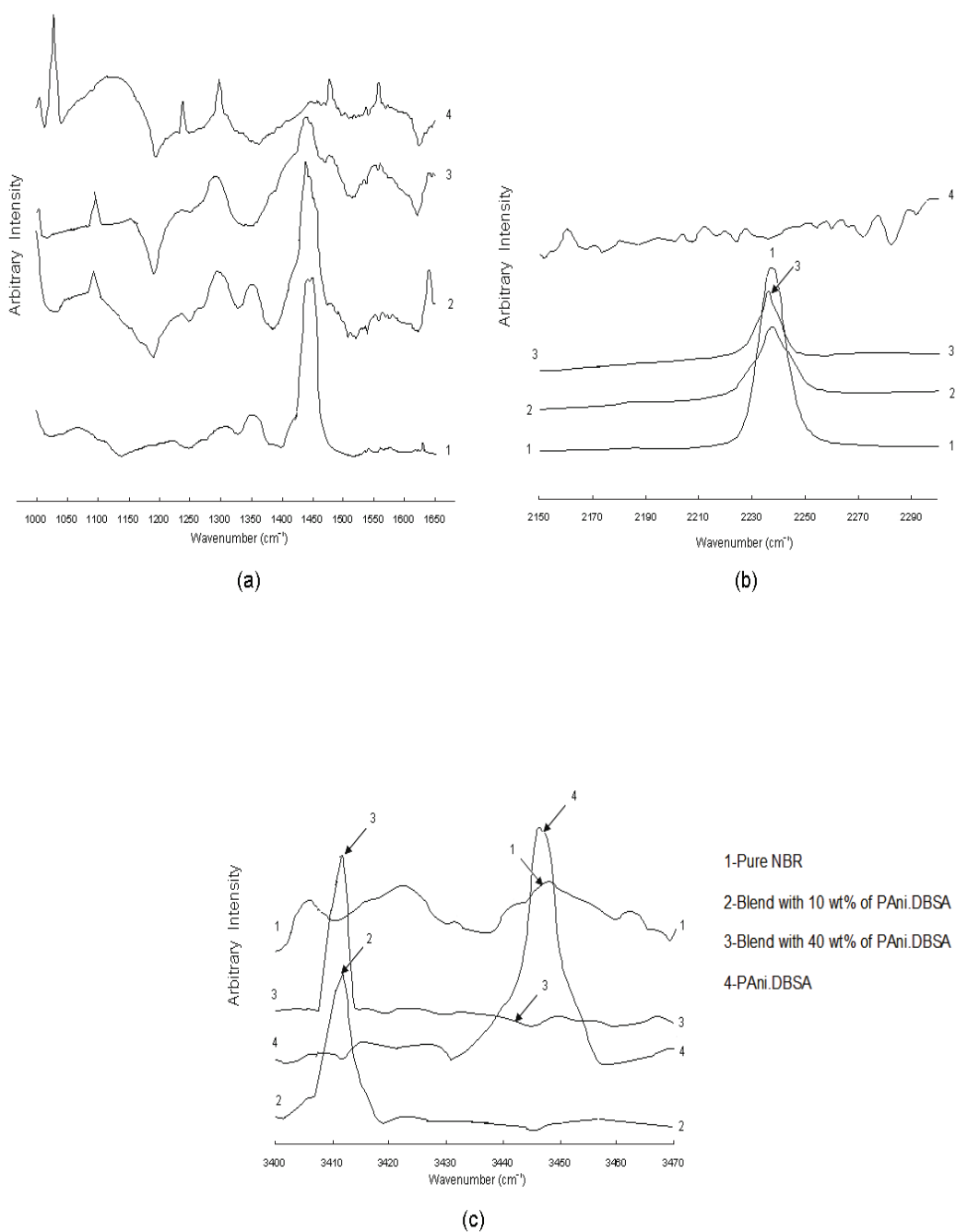
Figure 1. FT-IR spectra of PAni.DBSA, pure NBR and their blends without hydroquinone.
(a) region 1000 cm^{-1} to 1650 cm^{-1}, (b) region 2150 cm^{-1} to 2300 cm^{-1} and
(c) region 3400 cm^{-1} to 3470 cm^{-1}.

Figure 2. FT-IR spectra of PAni.DBSA, pure NBR and their blends with hydroquinone.
(a) region 1000 cm^{-1} to 1650 cm^{-1}, (b) region 2150 cm^{-1} to 2300 cm^{-1} and
(c) region 3400 cm^{-1} to 3470 cm^{-1}.

at their molecular level while being solution mixed. Parkhutik *et al*.[19] reported that the hydroquinone molecules played a double role in determining the structure and properties of a polyaniline salt. They could produce protonation of the imine bonds of the polymer, similar to the mechanism of acid anion doping and at the same time, operated as agents which caused the reorientation of conformational planes in polymeric chains *via* bridging and their mutual ordering. According to literature[7], the positively charged N-H hydrogens of PAni.DBSA would have a strong propensity for hydrogen-bonding with the negative sulphonate oxygens and hence the FT-IR frequency changes suggest that this bonding was disrupted by polar interactions with the hydroquinone added NBR matrix. Blends without compatibiliser featured larger, more aggregated PAni.DBSA particles. As a result, the strong H-bonding characteristic of bulk PAni.DBSA could be detected again by the FT-IR spectrometer for these blends as shown by the peak positioned at 1030 cm^{-1}.

Thermal Analysis by using DSC

Figures 3 and *4* show examples of the sub-ambient temperature DSC thermograms for pure NBR and its blends with and without added hydroquinone. DSC thermogram of the pure PAni.DBSA is not shown here because there were no obvious thermal processes in the sub-ambient temperature region. *Figures 5–6* show examples of the above ambient temperature DSC thermograms for PAni. DBSA, pure NBR and their blends with and without added hydroquinone.

The calculated mean T_g values for the pure NBR and all NBR-PAni.DBSA blends are shown in *Table 2*. The sub-ambient temperature DSC thermograms of the blends with added hydroquinone show larger T_g shifts compared with the ones without compatibiliser. For

blends with added compatibiliser, phase separation had only started to occur at a very high level of PAni.DBSA content, *i.e*. 50 wt %, as indicated by higher T_g value which is comparable with the blends without addition of compatibiliser.

All the above-ambient temperature DSC thermograms for the blends show thermal processes that are combinations of events recorded for pure NBR and PAni.DBSA, but the events show some degree of temperature shift relative to the effect of hydroquinone addition. As shown by the data in *Table 3*, pure NBR and PAni.DBSA are thermally stable up to about 332ºC and 230ºC, respectively.

Some indication of the level of compatibility of PAni.DBSA with NBR may also be assessed from the onset temperatures as shown in *Table 3* (with the caveat that the polymers are approaching the onset of thermal decomposition). For blends without hydroquinone, only small shifts in the onset temperature of the major exotherm, w.r.t. that for pure polymers, are observed. Larger shifts in the onset temperature of the major exotherm were being observed for blends with hydroquinone, echoing the evidence for better compatibility in these blends. It was also likely that the incorporated hydroquinone had promoted degradation of the NBR-PAni. DBSA blends at such high temperatures.

Electrical Conductivity Determination

The calculated mean electrical conductivity values for PAni.DBSA, pure NBR and their blends with and without addition of hydroquinone are shown in *Figure 7*. Pure NBR is a very good electrical insulator, with conductivity in the region of 10^{-14} S.cm^{-1}. The in house synthesised PAni.DBSA showed a high electrical conductivity of 1.3 ± 0.5
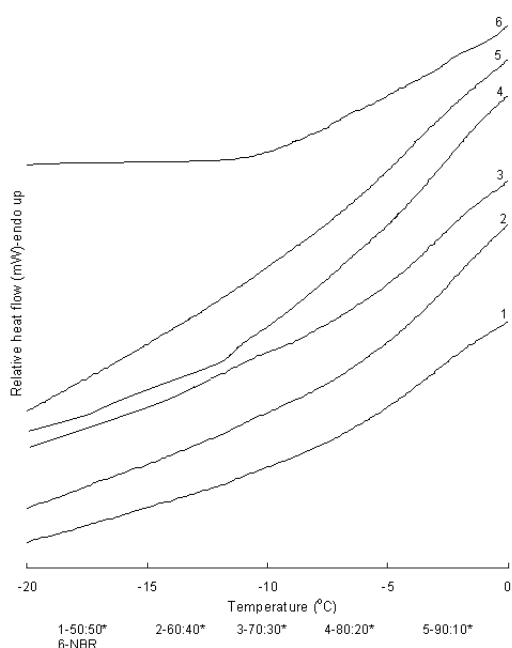
Figure 3. Sub-ambient temperature DSC thermograms for pure NBR and NBR-PAni.DBSA blends (*wt % NBR : wt % PAni.DBSA) without hydroquinone.
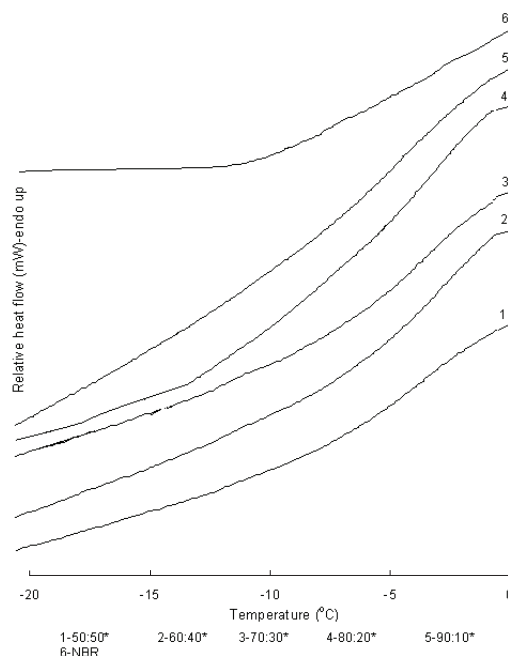

Figure 4. Sub-ambient temperature DSC thermograms for pure NBR and NBR-PAni.DBSA blends (*wt % NBR : wt % PAni.DBSA) with hydroquinone.

S.cm^{-1}, comparable with literature values for pressed pellet samples[7,18].

The electrical conductivities of all blends generally increased with the content of PAni.DBSA, as observed in several studies of PAni.DBSA based blends[7–12]. However, the compatibility of the blended polymers in the present work, especially for those with added compatibiliser was greater and showed more distinctive properties.

Blends prepared with added compatibiliser exhibited higher electrical conductivities, up to about 10^{-1} S.cm^{-1} than those prepared without compatibiliser, up to about 10^{-2}

S.cm^{-1}. Literatures[9,10,20] reported the blends of NBR-PAni.DBSA prepared *via* high temperature mechanical mixing with less phase separation were found to have higher electrical conductivities. This suggests that the more compatible constituent polymers favour the formation of higher level of microscopic conductive pathways (*Figure 8*).

The conductivity percolation threshold for each set of blends with and without hydroquinone addition was estimated by fitting the data from *Figure 7* to a simple percolation model as defined by *Equation 2*[21].

$$\sigma_f = c(f - f_p)^t \qquad \qquad \dots 2$$

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. By fitting the data to a plot of log electrical conductivity (σ) versus log (f-f_p), it was possible to estimate the values of t and correlation coefficient (R) for each set of data. The estimated electrical conductivity percolation thresholds (in wt % and volume % of PAni. DBSA) are summarised in *Table 4*. The lower electrical conductivity percolation threshold can evidently be achieved with the introduction of hydroquinone due to the higher level of compatibility between the two blended polymers.
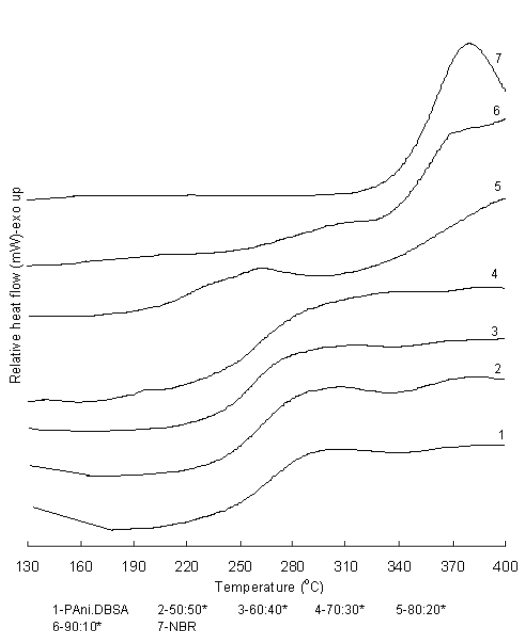
Morphological Study using Transmission Electron Microscope

All NBR-PAni.DBSA blends were studied by using a transmission electron microscope, but only examples of transmission electron micrographs of blends with 40 wt % PAni. DBSA are shown in *Figure 8*. The darker coloured regions (rich in PAni.DBSA) are large conductive particles and their agglomerates, resulting from some degree of phase separation. The lighter coloured regions (rich in NBR) are related to well-blended PAni.DBSA and NBR. Some bright white spots were also found from the micrographs and they were actually related to small holes created on the test specimens during the microtome process.

Figure 5. Above ambient temperature DSC thermograms for PAni.DBSA, pure NBR and NBR-PAni.DBSA blends (*wt % NBR : wt % PAni. DBSA) without hydroquinone.
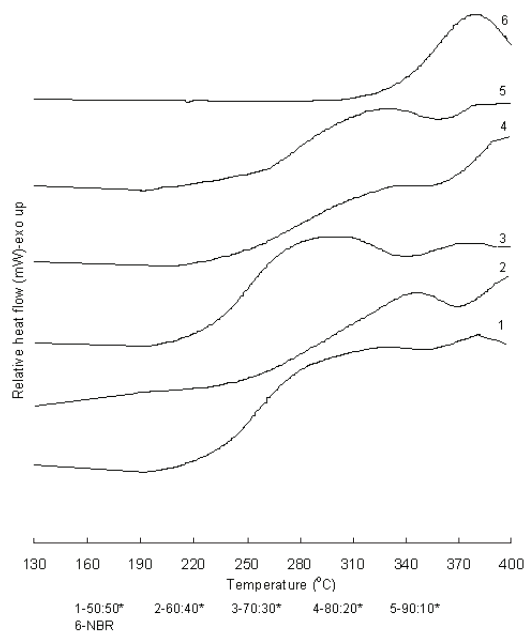

Figure 6. Above ambient temperature DSC thermograms for pure NBR and NBR-PAni.DBSA blends (*wt % NBR : wt % PAni.DBSA) with hydroquinone.

TABLE 1. REPRESENTATIVE FT-IR SPECTROSCOPY PEAKS FOR PAni.DBSA, PURE NBR AND NBR-PAni.DBSA BLENDS WITH AND WITHOUT HYDROQUINONE

Pure material/ Blend (wt% NBR: wt% PAni.DBSA)*	Peak assignment, cm⁻¹ Indication of peak intensity: W=weak; M=medium		
	=N-H stretching	S=O stretching	-C≡N stretching
PAni.DBSA	3447W	1030M	-
Pure NBR	-	-	2237M
Blends without hydroquinone			
90:10*	3422W	1030W,1080W	2237W
80:20*	3423W	1030W,1080W	2237W
70:30*	3419W	1030W,1080W	2237W
60:40*	3423W	1030W	2236W
50:50*	3443W	1030W	2236W
Blends with hydroquinone			
90:10*	3413W	1080W	2237W
80:20*	3412W	1080W	2237W
70:30*	3405W	1080W	2236W
60:40*	3412W	1080W	2236W
50:50*	3436W	1030W	2236W

TABLE 2. THE MEAN GLASS TRANSITION TEMPERATURE (T_g) VALUES FOR PURE NBR AND NBR-PAni.DBSA BLENDS WITH AND WITHOUT HYDROQUINONE

Raw polymer/ Blend (wt % NBR: wt % PAni.DBSA)*	Glass transition temperature, ºC
Pure NBR	-11
Blends without hydroquinone	
90:10*	-8
80:20*	-8
70:30*	-7
60:40*	-8
50:50*	-8
Blends with hydroquinone	
90:10*	-5
80:20*	-5
70:30*	-5
60:40*	-5
50:50*	-7

TABLE 3. THE MEAN ONSET TEMPERATURE VALUES OF MAJOR EXOTHERMS OF THE ABOVE AMBIENT TEMPERATURE DSC THERMOGRAMS FOR PAni.DBSA, PURE NBR AND NBR-PAni. DBSA BLENDS WITH AND WITHOUT HYDROQUINONE

Raw polymer/ Blend (wt % NBR: wt % PAni.DBSA)*	Onset temperature of major exotherm, ºC
PAni.DBSA	230
Pure NBR	332
Blends without hydroquinone	
90:10*	330
80:20*	320
70:30*	229
60:40*	227
50:50*	233
Blends with hydroquinone	
90:10*	260
80:20*	237
70:30*	219
60:40*	243
50:50*	226

TABLE 4. ELECTRICAL CONDUCTIVITY PERCOLATION THRESHOLDS FOR NBR-PAni.DBSA BLENDS WITH AND WITHOUT ADDED HYDROQUINONE

NBR-PAni.DBSA blend	Estimated percolation threshold (wt %/volume % of PAni.DBSA content)	Critical component, t	Correlation coefficient, R
Blends without hydroquinone	6.9/6.0	3.9	0.99
Blends with hydroquinone	6.2/5.5	3.7	0.99

Blends without addition of any compatibiliser, *Figure 8a* for example showed more obvious phase separation than those with added compatibiliser, *Figure 8b* for example. In both figures, the PAni.DBSA particles are starting to cluster or to form conductive pathways, which is consistent with the much higher conductivity for the 40 wt % PAni. DBSA-blend. Numerous small particles of PAni.DBSA were also revealed by the micrographs; most of these were of colloidal dimensions *i.e*. 50-1000 nm and they might also be expected to make a contribution to the electrical conductivity.

CONCLUSION

NBR-PAni.DBSA blends with useful levels of electrical conductivity up to 10^{-1} S.cm^{-1} were successfully prepared by the solution mixing technique. Their compatibility level was also successfully enhanced by addition of 1 wt % compatibiliser *i.e.* hydroquinone.
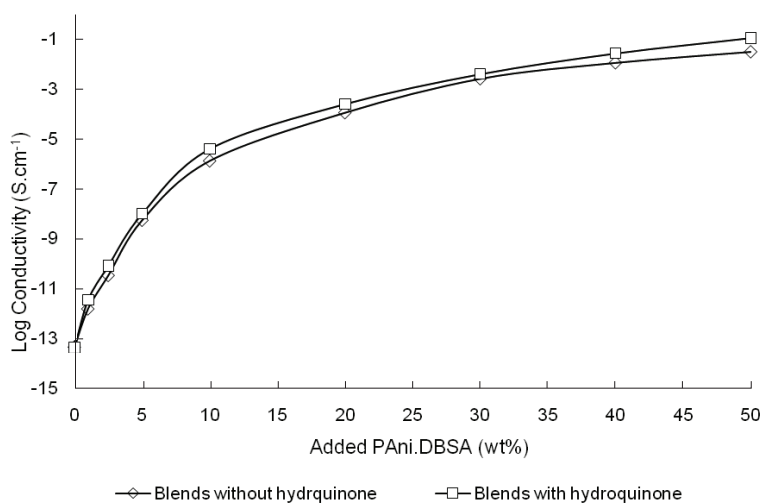
Figure 7. Electrical conductivities for NBR-PAni.DBSA blends with and without hydroquinone as a function of PAni.DBSA content (wt %).
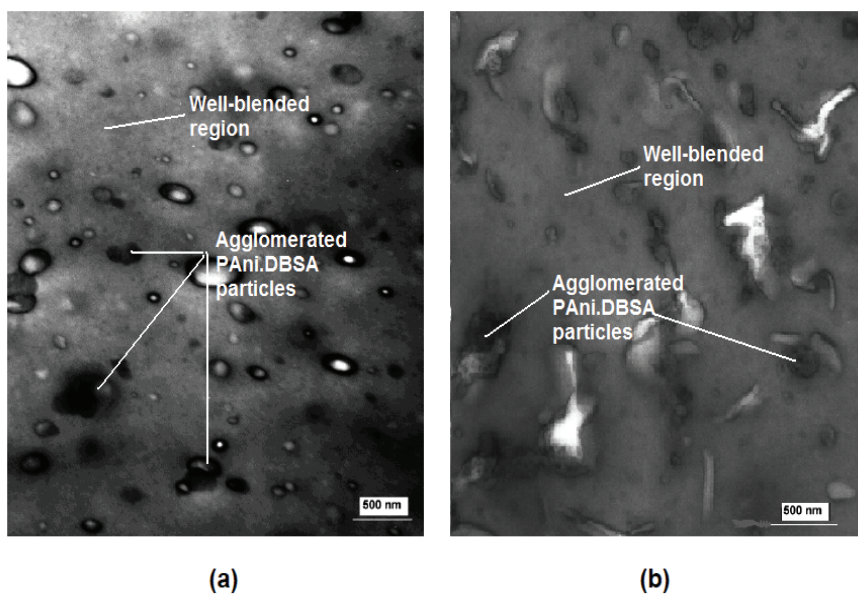

Figure 8. Transmission electron micrographs of NBR-PAni.DBSA blend with 40 wt % of PAni.DBSA. (a) blend without hydroquinone and (b) blend with added hydroquinone.

This phenomenon was evidently supported by the larger FT-IR peak shifts and temperature shifts for DSC thermal events, both ambient and sub-ambient temperature regions of blends with added hydroquinone. These blends were also the ones with the lowest phase separation as indicated by transmission electron micrographs. A lower conductivity percolation threshold was also observed for the hydroquinone added blends which corresponded to the higher formation level of conductive PAni.DBSA networks due to its better compatibility with the NBR host matrix.

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