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Electrically Conductive Epoxidised Natural Rubber-polyaniline dodecylbenzenesulfonate Blends Prepared by Solution Mixing

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Epoxidised natural rubber (ENR) and polyaniline dodecylbenzenesulfonate (PAni.DBSA) were predicted to be miscible, on the basis of simple solubility parameter calculations. Blends with electrical conductivities up to 10^{-3}*S.cm*$^{-1}$ *were prepared for the first time by solution mixing. The lowest estimated electrical conductivity percolation threshold for these blends was 2.9 wt% or 2.5 volume% of added PAni.DBSA. NMR spectroscopy showed that the epoxide level of the host, ENR decreased with increasing PAni.DBSA loading (due to the sensitive nature of ENR to acidic conditions). This decrease was a direct sign of ring opening in the ENR molecular structure. The ring opening of ENR was also identified indirectly through the increasing absorption value of FT-IR peaks in the region of 3390 cm*$^{-1}$ *and through the trends observed by differential scanning calorimetry (DSC). Electrical conductivity measurement and morphology studies [by optical microscopy and transmission electron microscopy (TEM)] revealed that the ring opening did not affect the electrical properties of the blends.*

Key words: epoxidised natural rubber (ENR); polyaniline; conductive blend; epoxide level; solution mixing; electrical conductivity; ring opening

Numerous types of electrically conductive rubber blends (based on a carbon[1–16] or non-carbon[17–31] conductive filler) have been prepared either through mechanical mixing[1–16,18–20,30], solution mixing[17,19,21–26,32,33], electrochemical intergrowth[27–28,31] or in situ polymerisation[29]. However, studies[1,18–29] involving synthetic rubbers, *e.g.* nitrile rubber, polychloroprene, poly(ethylene-co-propylene-co-diene) (EPDM), poly(butadiene-co-styrene) (SBS) copolymer and others have become major interests. Literature on conductive elastomeric blends based on natural rubbers and intrinsically electrically conductive polymers is limited.

Blends of Standard Malaysian Rubber (SMR-20 grade) with polyaniline were prepared as in previous work by Helaly and co-workers[30], using a two-roll mill in order to study

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the efficiency of polyaniline as an antioxidant against thermal ageing for SMR-20. Some blends of SMR-polythiophene have also been prepared by the electrochemical method[31] and reached a high electrical conductivity (of the order of 10^{-1}S.cm^{-1}), but only with 80 wt% of polythiophene loading.

In this work, ENR was selected for the blending studies because of its good mechanical properties[34] and good predicted compatibility with intrinsically conductive polymers (based on values of solubility parameters found in the literature[26,34]). Special interest has been focused on PAni, since the monomer (aniline) is relatively inexpensive, the polymerisation process is straightforward and it proceeds with a high yield[35,36]. When PAni is doped with sulfonated organic acids containing large alkyl groups (long flexible chains), *e.g.* dodecylbenzenesulfonic acid (DBSA) or p-toluenesulfonic acid (p-TSA), it becomes highly electrically conductive and soluble in many organic solvents[37].

The aim of the present work was to study ENR-intrinsically conductive polymer blends made by combining a commercially available grade of ENR with different amounts of PAni.DBSA. It was decided to produce all of the blends from solution, which required both components to be soluble in a common shared solvent. This method has been successfully applied to the synthetic rubber-intrinsically conductive polymer blends[26], but it had not previously been used for natural rubber-based ones. Characterisation of the resulting blends is reported here, using Fourier-transform infrared (FT-IR) and proton NMR spectroscopy as well as differential scanning calorimetry (DSC). The electrical conductivities of all the pure polymers and blends were determined, and their morphologies were studied by optical and electron microscopy.

EXPERIMENTAL

Chemicals and Raw Materials

Aniline monomer (99 wt%, Sigma-Aldrich), ammonium persulphate [APS] (98 wt%, Sigma-Aldrich), 36.5-38 wt% HCl solution (GPR), anhydrous ferric chloride [$FeCl_3$] (98 wt%, Sigma-Aldrich), 33 wt% ammonia solution (GPR), 70 wt% DBSA solution in 2-propanol (GPR, Sigma-Aldrich), chloroform (GPR), methanol (GPR), and ENR (grade ENR 50 with 50 mole% of epoxide level, manufactured by the Malaysian Rubber Board). The raw ENR was washed with methanol for 24h using Soxhlet extraction in order to remove chemical contaminants.

Solubility Parameter Value Calculations for Main Materials

Equation 1 and the values of functional group molar attraction constants F_i calculated by Hoy[38] were used to estimate the solubility parameters (δ_p) for pure ENR 50 and PAni.DBSA.

$$\delta_p = \frac{\rho \times \Sigma F_i}{M_0} \qquad \ldots 1$$

where,

ρ = the density of the polymer (kg.m^{-3}),

M_0 = the formula weight of the polymer repeat unit (kg.mol^{-1})

ΣF_i = the sum of the group molar attraction constants in the polymer repeat unit [(J.m^3)$^{0.5}$.mol^{-1}].

Synthesis of PAni.DBSA

Conductive emeraldine salt PAni.HCl was synthesised by an oxidative chemical polymerisation based on an oxidant (APS)/ monomer (aniline) initial mole ratio of 1.0.

50mL of aniline and 125.2 g of APS were dissolved in 375 mL and 276 mL of 2M 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 a few drops of $FeCl_3$ solution as a catalyst, the APS solution was added gradually over a period of 20 min, with constant stirring to ensure thorough mixing. The pH of the polymerisation mixture was adjusted to 0 – 0.5 with concentrated HCl, while the temperature was maintained between 0 – 2ºC. In order to complete the polymerisation, the mixture was left for 6 h. 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 de-protonating the wet PAni.HCl in 33% aqueous ammonia solution (3000 – 5000 mL) with 24 h stirring, followed by washing and re-protonation in 1M aqueous DBSA at a molar ratio EB:DBSA of 1:1. Filtration was done 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 carried out in a vacuum oven at 50ºC for 24 h. A sample of PAni.DBSA prepared here was submitted for elemental analysis[26,37] (at Medac Ltd., U.K.) and was estimated to have a 42% protonation level on the basis of the S:N atomic ratio.

Preparation of Blend

Masterbatch solutions of pure ENR 50 (0.02 g ENR/mL $CHCl_3$) and PAni.DBSA (0.0167 g PAni.DBSA/mL $CHCl_3$) were prepared and filtered. The pure rubber solution was added to portions of the PAni.DBSA solution in appropriate amounts to obtain the following compositions (ENR wt%: PAni.DBSA wt%), 50:50, 60:40, 70:30, 80:20, 90:10, 95:5, 96:4, 97.5:2.5, 98:2 and 99:1 respectively. Each of these blend solutions was magnetically stirred for 24 h at room temperature prior to casting.

NMR Spectroscopy

Samples of pure ENR 50 and ENR-PAni.DBSA blends were studied using a H^1 NMR (Bruker AC300 with processor WIN NMR) in order to investigate the extent of possible ring-opening of the ENR as a result of adding PAni.DBSA. About 0.005 g of each sample was dissolved in d-chloroform before being examined by NMR (with 30º pulse and 6 sec pulse delay). In each case, 4 to 6 portions of the sample were examined.

Morphological Studies (Optical Microscopy and TEM)

The ENR-PAni.DBSA blends were studied with a Nikon OPTIPHOT-2 optical microscope (200 x magnification) linked to a computer by a video converter (LINKAM VTO 232) for digital image capture. A small drop of each sample blend solution was put onto a microscope cover-glass (2 cm × 2 cm) and allowed to evaporate to form a thin (~3.0 µm) transparent film.

Blends with 2.5 wt% (generally below the conductivity threshold) and 5 wt% (generally above the conductivity threshold) of PAni.DBSA were also studied by TEM (with a Philips CM12 microscope at accelerating voltage, 80 kV). Ultra-thin samples (*ca*. 150 nm) of each blend were obtained for this purpose by sectioning with an RMC MT7000 microtome.

FT-IR Spectroscopy

Infra-red spectra of pure ENR 50, PAni.DBSA and ENR-PAni.DBSA blends were recorded on a Perkin-Elmer FT-IR PARAGON 100 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

DSC was used to characterise PAni.DBSA powder, pure ENR 50 and all the ENR-PAni.DBSA blend films. Above-ambient temperatures (30 to 300ºC), a Mettler Toledo DSC 822e (heating rate 20ºC/minute) was used while sub-ambient temperature scans (–60 to 0ºC) were obtained using a Perkin-Elmer Pyris Diamond DSC (heating rate 50ºC/minute). Each sample was sealed in a 40 µL aluminium pan and analysed under N_2 atmosphere, with an empty pan as the reference. Each thermal analysis was repeated twice, and the error for all of the results was about ± 1.5ºC.

Electrical Conductivity Measurement

The dc electrical conductivities of PAni.DBSA, pure ENR 50 and ENR-PAni.DBSA blends were calculated from electrical resistance values measured by 2- or 4-probe techniques. A Keithley 617 programmable electrometer and a Keithley 224 programmable current source (both under computer control) were used for this purpose. A pressed pellet of pure PAni.DBSA (diameter 13 mm, thickness 1.5 mm; prepared in a KBr press at 10 tonnes load) was placed in a holder with four spring-loaded metallic contacts in order to measure its electrical resistance.

For the 4-probe van der Pauw technique[39], samples of each ENR-PAni.DBSA blend were cast from solution onto square microscope slides (625 mm^2), and the solvent was allowed to evaporate for 24 h. Fine copper wires 50 mm long were attached to the four corners of the cast films using small silver paint contacts (Acheson Electrodag 915). Guarded 2-probe electrical resistance measurements[26] were performed for less conductive cast films (conductivity < 10^{-7}S.cm^{-1}).

For the samples measured by the 4-probe technique, electrical conductivities were calculated from the mean resistance values using the van der Pauw equation (*Equation 2*).

$$\sigma = \frac{2\ln 2}{(R_1 + R_2)\pi d f} \qquad \ldots 2$$

where σ is the electrical conductivity [S.cm^{-1}], R_1 and R_2 are the mean values of apparent resistance (voltage/current ratio) for a cast blend in its two perpendicular contact configurations, *d* is the thickness of the sample and f is a geometric factor (close to unity for symmetrical contacts on circular pellets or square plaques).

Electrical conductivities were also calculated from the mean resistance values obtained by the 2-probe method using *Equation 3*.

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{L}{A}\right) \qquad \ldots 3$$

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

The dc electrical conductivities of PAni.DBSA, pure ENR 50 and ENR-PAni.DBSA blends were calculated from electrical “resistance” (voltage/current) values measured by 2- or 4-probe techniques.

RESULTS AND DISCUSSION

Solubility Parameter Value Calculations for Main Materials

Chloroform has a solubility parameter of 19.0(MJ.m^{-3})$^{1/2}$ [37], and pure ENR 50 was soluble in it. The PAni.DBSA prepared in this work was highly soluble in chloroform, giving dark green solutions. The calculated solubility parameters for the PAni.DBSA and pure ENR 50 used here are 20.8 and 18.4(MJ.m^{-3})$^{1/2}$ respectively. All of these calculated values agreed with those reported in the literature[26,28,34]. It is predicted that the miscibility between ENR and PAni.DBSA could be enhanced by increasing the epoxidation level of ENR.

NMR Spectroscopy

The calculated results of epoxide level and ring-opening (mole%) for pure ENR 50 and ENR 50-PAni.DBSA blends are summarised in *Table 1*. Examples of the blends NMR spectra are shown in *Figures 1* to *3*. Results from *Table 1* show a decreasing epoxide content and increasing total of ring-opening. There is quite a lot of variability for the furan group analysis due to the difficulty of inaccurate integration as a result of background noise. It is worth noting the type of ring-opening observed here. When the epoxide ring in ENR opens, it can result in two alternative structures: (1) Ring-opening to form furan groups by adjoining the next monomer unit[40,41], which will result in peaks assigned to CH-O (in the region of 3.9-3.7p.p.m.). (2) Ring-opening to form 'diol' groups[42] with CH-OH moieties (assigned to peaks in the region of 3.5 – 3.3 p.p.m.).

Often, both types occur together, with furan tending to predominate when the host rubber has a high epoxide content. In these samples there is a predominance of furan formation in both 95:5 and 90:10 blends but in the other cases of higher PAni.DBSA levels (*i.e.* 20–50 wt%), there appears to be a predominance of peaks in the 3.5–3.3p.p.m. region and hence greater evidence of 'diol' formation.

TABLE 1. THE MEAN PROPORTIONS OF EPOXIDE CONVERSION AND RING-OPENING (MOLE%) FOR PURE ENR 50 AND ENR 50-PAni.DBSA BLENDS (UNCERTAINTY= ±1.5 wt%)

Pure material/blend (wt% ENR 50:wt% PAni.DBSA)	Mole % Epoxidised Isoprene Unit	Furan Group (3.9–3.7 p.p.m.)	'Diol' Group (3.5–3.3 p.p.m.)	Total of Ring Opened (Furan + 'Diol')
Pure ENR 50	47.2	2.1	0.4	2.5
Blends				
95:05	46.4	2.0	1.0	3.0
90:10	43.1	3.5	2.0	5.5
80:20	40.9	1.6	6.1	7.7
70:30	26.3	9.1	14.0	23.1
60:40	24.6	2.2	21.5	23.7
50:50	21.5	10.6	17.0	27.6

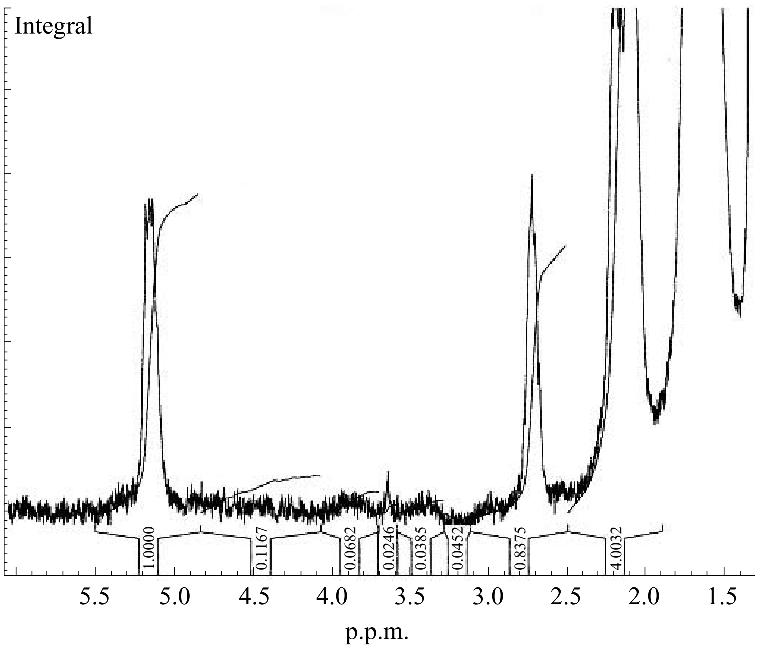


Figure 1. NMR spectrum of ENR-PAni.DBSA blend (90 wt%:10 wt%).

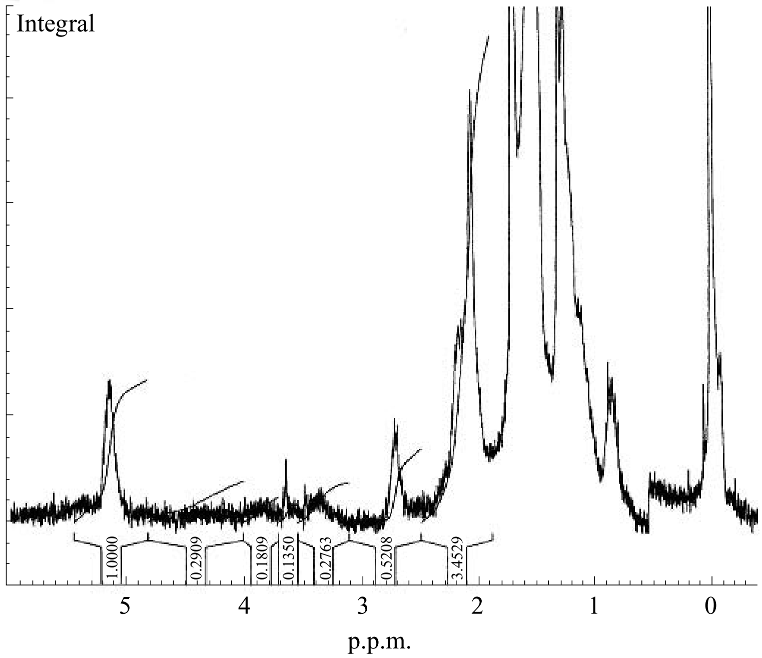


Figure 2. NMR spectrum of ENR-PAni.DBSA blend (70 wt%:30 wt%).

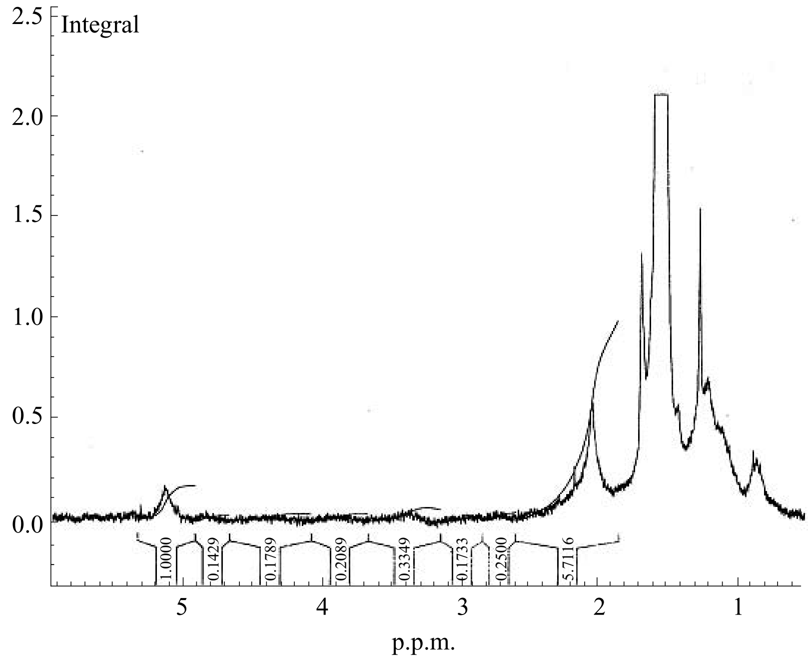


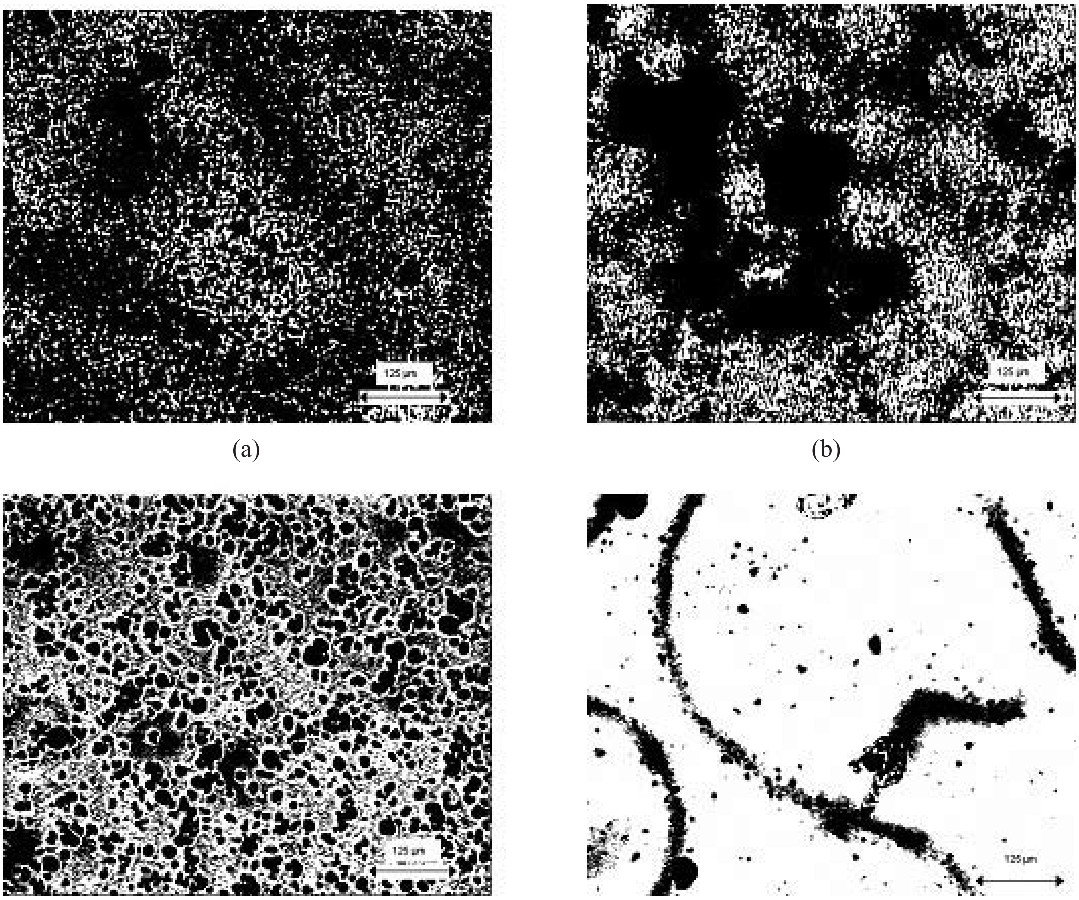
Figure 3. NMR spectrum of ENR-PAni.DBSA blend (50 wt%:50 wt%).

Morphological Studies (Optical Microscopy and TEM)

All the ENR 50-PAni.DBSA cast films were studied by optical microscopy, but only images of blends containing 5, 20, 30 and 40 wt% of PAni.DBSA are shown in *Figure 4*.

As for the synthetic rubber based blends[26], two different regions were observed, *i.e.* the regions rich in ENR (in pale colour or pale green in actual) and the regions rich in PAni.DBSA (in dark colour or dark green in actual). The dark-coloured regions consisted of large conductive particles and their agglomerates, as a result of some degree of phase separation. The pale-coloured regions were the regions of well-blended PAni.DBSA and ENR. The ENR-PAni.DBSA blends were similar to those in previously-studied NBR-PAni.DBSA blends[26] in that the total area of the dark-coloured region increased with increasing content of PAni.DBSA. For the blend containing ≥30 wt% of PAni.DBSA, some large particles could be found.

Figure 5 shows the TEM micrographs of blends with 2.5 and 5 wt% of added PAni.DBSA. PAni.DBSA particles in the rubber matrix were again observed as the darker regions in both TEM micrographs. Some large isolated PAni.DBSA particles could be found from *Figure 5(a)* for the ENR blend with 2.5 wt% PAni.DBSA, which also had the relatively low electrical conductivity (*Figure 12*). Some conductive networks were also formed when the PAni.DBSA particles were getting closer to each other [*Figure 5(b)*] and this was attributed to the higher loading and better dispersion of PAni.DBSA particles



(a) (b)

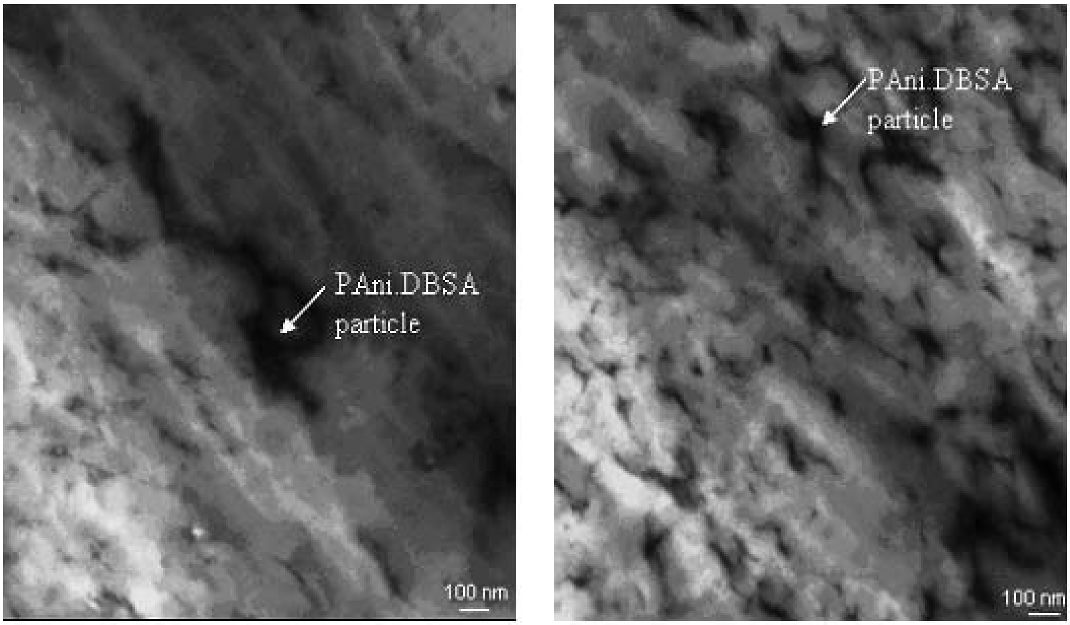
(c) (d)

Figure 4. Optical micrographs (200 × magnification) for the blends of ENR 50-PAni.DBSA. Blends contain (a) 60:40 (b) 70:30 (c) 80:20 and (d) 95:5 wt% ENR50:wt% PAni.DBSA.

within the ENR host matrix. This is why the 5 wt% PAni.DBSA blend had relatively much higher electrical conductivity (*Figure 12*). Both the TEM micrographs show some very small particles of PAni.DBSA (in colloidal dimensions, ~20 – 100 nm). These small particles had contributed to the electrical conductivity of the blends since they could also form some small conductive networks as described in the literature[26].

FT-IR Spectroscopy

Selected regions of the FT-IR spectra for pure PAni.DBSA, pure ENR 50 and their blends with 5 to 50 wt% of PAni.DBSA are shown in *Figure 6*. The FT-IR spectra of pure ENR 50 and all the blends show the characteristic absorptions at 1250 cm^{-1} (epoxy ring bond stretching), 875 cm^{-1} (C-C of epoxy ring stretching), 796 cm^{-1} and 837 cm^{-1} (ring



(a)

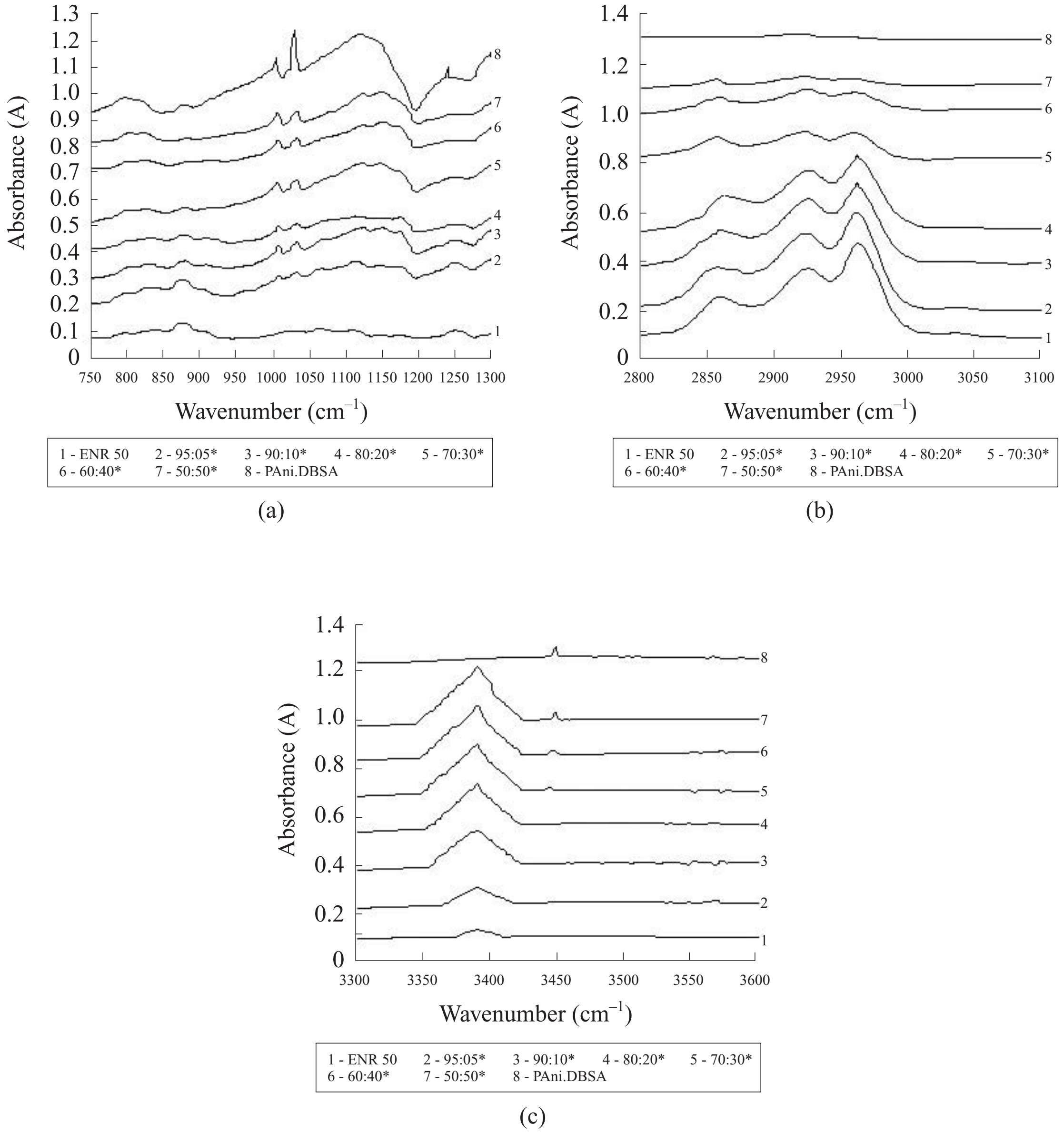
(b)

Figure 5. Transmission electron micrographs (40,000 × magnification) of the ENR 50-PAni.DBSA blends. Blends contain, (a) 2.5 wt% of PAni.DBSA and (b) 5 wt% of PAni.DBSA.

deformation), 2859 cm^{-1} (C-H stretching vibration of epoxy ring) and 3390 cm^{-1} (-OH stretching vibration of 'diol' ring-opening). Some very weak absorptions at 1112 cm^{-1} (aliphatic ethers, C-O-C for furan group) were also observed in the FT-IR spectra of pure ENR 50 and all blends.

For the blends with low levels of PAni.DBSA (*i.e.* ≤20 wt%), there was a predominance of ENR absorption bands in their FT-IR spectra. Meanwhile for the blends with high levels of PAni.DBSA (i.e. ≥30 wt%), their FT-IR spectra exhibited a predominance of PAni.DBSA absorption bands. However through some detailed examination, the intensity of absorptions at 3390 cm^{-1} (solely corresponding to the 'diol' ring-opening) for all the blends increased with the amount of added PAni.DBSA. At the same time, the intensity of absorptions at 2859 cm^{-1} (solely corresponding to the epoxide ring) decreased with the proportion of PAni.DBSA. The absorbance intensity for each of these peaks is directly related to the changing level of each assigned functional group (since the cast films of all blends had the same thickness). It is proposed that the higher the peak absorbance intensity, the higher the level of each assigned functional group content. All values of absorbance intensity were based on the local baseline position.

Results from this section are in agreement with those from NMR spectroscopy, where both of them are showing that the proportion of the 'diol' ring opening increased and the proportion of the epoxide ring decreased with



(a) (b)

(c)

Figure 6. FT-IR spectra of PAni.DBSA, pure ENR 50 and their blends (wt% ENR:wt% PAni.DBSA). (a) 750–1300 cm^{-1}, (b) 2800–3100 cm^{-1} and (c) 3300–3600 cm^{-1}.*

Line 1-ENR 50, Line 2-Blend (95 wt% ENR:5 wt% PAni.DBSA), Line 3-Blend (90 wt% ENR:10 wt% PAni.DBSA), Line 4- Blend (80 wt% ENR:20 wt% PAni.DBSA), Line 5- Blend (70 wt% ENR:30 wt% PAni.DBSA), Line 6- Blend (60 wt% ENR:40 wt% PAni.DBSA), Line 7- Blend (50 wt% ENR:50 wt% PAni.DBSA), Line 8-PAni.DBSA.

the PAni.DBSA loading. Graphs (*Figures 7* and *8*) were plotted for these two characteristic peak absorbance intensities *versus* the proportion of PAni.DBSA in order to make the comparison quantitatively.

Thermal Analysis

Figure 9 shows the sub-ambient temperature DSC thermograms for pure ENR 50 and its blends with 10 to 50 wt% of PAni.DBSA. (A DSC thermogram for pure PAni.DBSA is again not shown here because there were no obvious thermal events in the low-temperature region). *Figure 10* shows the above-ambient temperature DSC thermograms for PAni.DBSA, pure ENR 50 and its blends with 10 to 50 wt% of the conducting polymer.

The mean T_g values for the pure ENR 50 and ENR-PAni.DBSA blends are given in *Table 2*. The results show a significant and progressive rise in the T_g values with the proportion of PAni.DBSA. While this may partly be an effect of some phase mixing between the polymers, it also very likely to be the result of ENR ring opening. Ring opened and furanised ENR also has a raised T_g depending on the extent of the ring opening[34]. A log T_g (Kelvin) *versus* log ring-opening (mole%) chart was plotted in order to compare these two parameters quantitatively (*Figure 11*). It was found that the log values of these two parameters were linearly related with a slope of 0.0457 and intercept of 2.378 as shown in *Figure 11*.

From *Table 3*, pure ENR was thermally stable up to about 206ºC. PAni.DBSA also had good thermal stability up to about 233ºC. All the above-ambient temperature DSC thermograms for the blends showed thermal processes that were combinations of events observed for pure ENR 50 and PAni.DBSA, but the events showed some temperature shifts relative to the corresponding processes in the pure polymers (*Table 3*). The blends with ≤40 wt% of PAni.DBSA showed the largest temperature shifts due to reasonably good compatibility between the two polymers (as shown by the optical micrographs: *Figure 4*). As shown in *Figure 10*, the endothermic event before the major exotherm (corresponding to the total absorbed energy for the ring opening process) increased with increasing loading of PAni.DBSA. It is believed that this was corresponded to the further ring opening (catalysed by the higher concentration of PAni.DBSA) occurred before the major exothermic process (*i.e.* degradation) of the blend.

Electrical Conductivity Measurement

The calculated electrical conductivity values for the PAni.DBSA, pure ENR 50 and ENR-PAni.DBSA blends are shown by *Figure 12*. Pure ENR 50 is a very good electrical insulator, with a conductivity of about 3.8×10^{-16}S.cm^{-1}. The PAni.DBSA used here had an electrical conductivity of 1.2S.cm^{-1}, comparable with values found from literature for amorphous, un-aligned PAni.DBSA[26,37].

The electrical conductivity of all the blends increased with the proportion of PAni.DBSA, as observed in several studies of PAni.DBSA blends[18,20,23,25–26,29]. The blends reached an electrical conductivity in the order of 10^{-3}S.cm^{-1} with about 40 wt% of PAni.DBSA loading. The conductivity percolation threshold for all ENR-PAni.DBSA blends was estimated by fitting the data from *Figure 12* to a percolation model as defined by *Equation 4*[25,43].

$$\sigma_f = c(f - f_p)^t \qquad \ldots 4$$

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

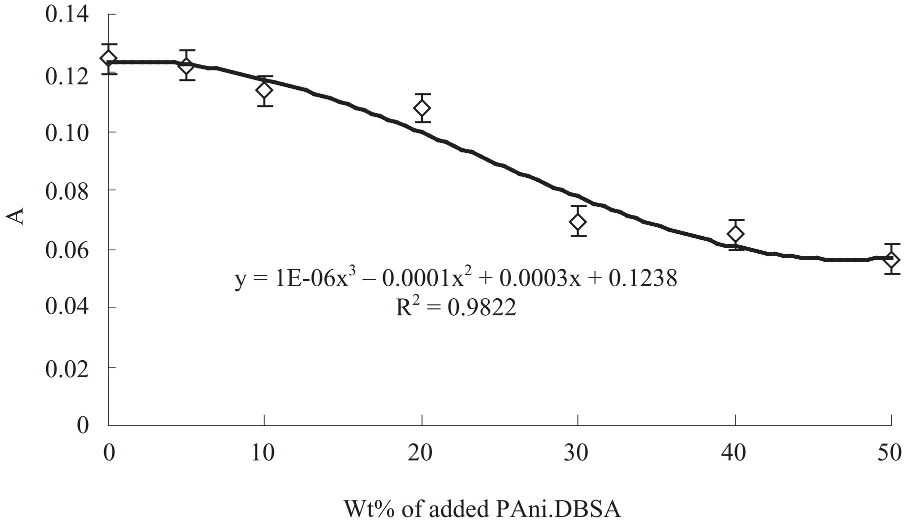


Figure 7. Chart of FT-IR peak absorbance, A (uncertainty, ± 0.005) at 2859 cm^{-1} versus the wt% of PAni.DBSA in the ENR-PAni.DBSA blends.

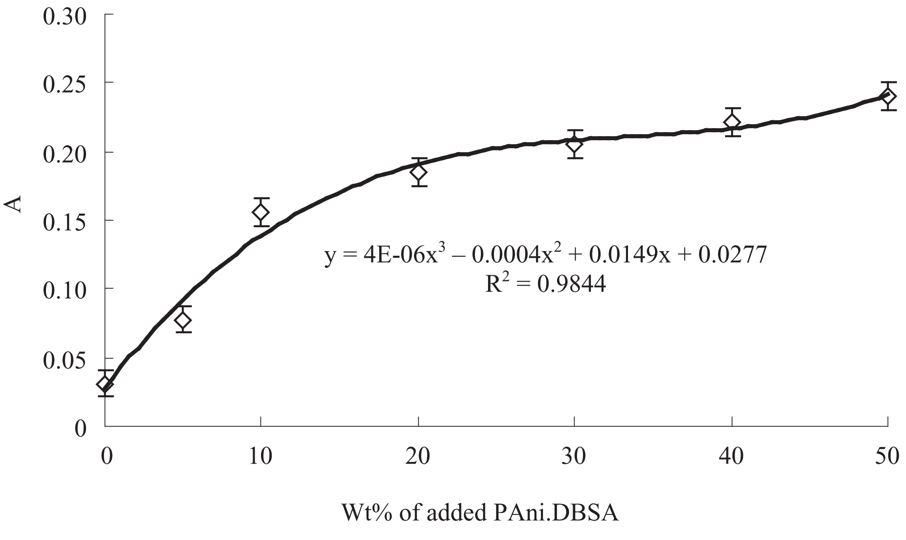


Figure 8. Chart of FT-IR peak absorbances, A (uncertainty, ± 0.01) at 3390 cm^{-1} versus the wt% of PAni.DBSA in the ENR-PAni.DBSA blends.

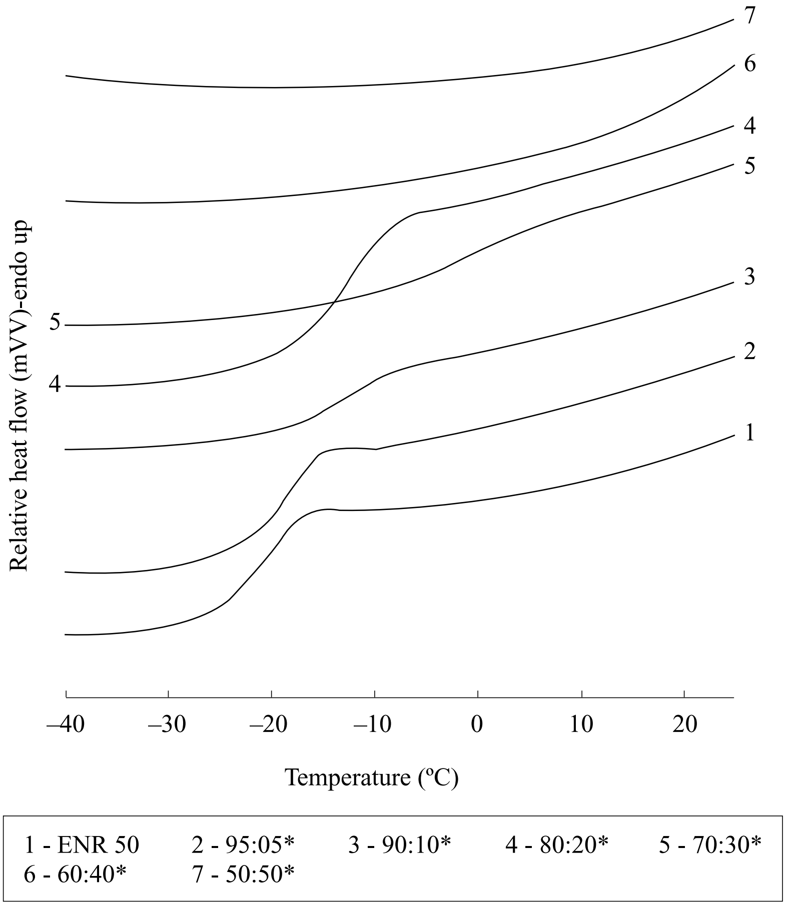


Figure 9. Sub-ambient temperature DSC thermograms for pure ENR 50 and its blends (wt% ENR:wt% PAni.DBSA) with 10 to 50 wt% of PAni.DBSA.

Line 1-ENR 50, Line 2-Blend (95 wt% ENR:5 wt% PAni.DBSA),
Line 3-Blend (90 wt% ENR:10 wt% PAni.DBSA), Line 4- Blend (80 wt% ENR:20 wt% PAni.DBSA),
Line 5- Blend (70 wt% ENR:30 wt% PAni.DBSA), Line 6- Blend (60 wt% ENR:40 wt% PAni.DBSA),
Line 7- Blend (50 wt% ENR:50 wt% PAni.DBSA).

fractions for this analysis. The values of t and correlation coefficient (R) for each case were estimated by fitting the data to a plot of log electrical conductivity (σ) versus log ($f - f_p$).

The estimated first electrical conductivity percolation threshold for the ENR 50-PAni. DBSA blends is 2.9 wt% (or 2.5 volume %) of PAni.DBSA (with t = 4.9 and R = 0.98). A second stage of percolation threshold with about 5 wt% (or 4.4 volume %) of added PAni. DBSA (with t = 5.4 and R = 0.99) was also observed. It corresponded to the separated phases of both polymers, *i.e.* the dark-

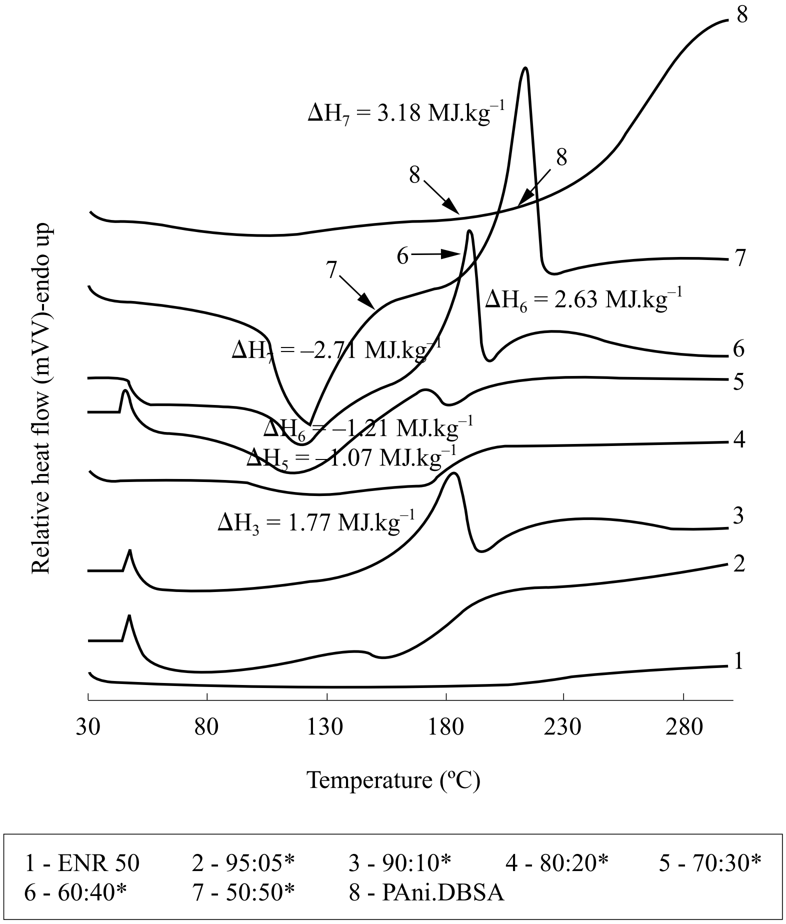


Figure 10. Above-ambient temperature DSC thermograms for PAni.DBSA, pure ENR 50 and its blends (wt% ENR:wt% PAni.DBSA) with 10 to 50 wt% of PAni.DBSA.

Line 1-ENR 50, Line 2-Blend (95 wt% ENR:5 wt% PAni.DBSA), Line 3-Blend (90 wt% ENR:10 wt% PAni.DBSA), Line 4- Blend (80 wt% ENR:20 wt% PAni.DBSA), Line 5- Blend (70 wt% ENR:30 wt% PAni.DBSA), Line 6- Blend (60 wt% ENR:40 wt% PAni.DBSA), Line 7- Blend (50 wt% ENR:50 wt% PAni.DBSA), Line 8-PAni.DBSA.

coloured regions in the optical and electron micrographs.

A very low threshold value was seen here, for which the conductivity is likely to be contributed by those regions with well dispersed conducting polymer (the pale-green regions of the optical and electron micrographs). The values of *t* for a classical double-percolation model as described in the literature[43] are in the range between 2 and 4. Here, *t* is estimated with a value greater than

TABLE 2. THE MEAN GLASS TRANSITION TEMPERATURE (Tg) VALUES FOR PURE ENR 50 AND ENR-PAni.DBSA BLENDS

Pure material/Blend (wt% ENR : wt% PAni.DBSA)	Glass transition temperature, ºC
Pure ENR 50	–26.6
Blends	
95:05	–24.5
90:10	–20.9
80:20	–19.1
70:30	–15.4
60:40	6.0
50:50	6.7

TABLE 3. THE MEAN ONSET TEMPERATURES OF THE EXOTHERM AND ENDOTHERM BEFORE THE MAJOR EXOTHERM IN THE ABOVE-AMBIENT TEMPERATURE DSC THERMOGRAMS OF PANI.DBSA, PURE ENR 50 AND ENR-PAni.DBSA BLENDS

Pure material/Blend (wt% ENR : wt% PAni.DBSA)	Onset temperature, ºC	
	Endotherm	Exotherm
Pure ENR 50	–	206.0
Blends		
95:05	–	162.5
90:10	–	137.0
80:20	94.0	173.0
70:30	92.0	124.0
60:40	106.0	173.0
50:50	104.0	197.0
PAni.DBSA	36.0	234.0

4 and it is likely to be attributed by some on-going chemical reactions of the blended ENR 50 and PAni.DBSA, *e.g.* formation of furan and 'diol' group.

CONCLUSION

The ENR 50-PAni.DBSA blends prepared in this work had good electrical conductivities, comparable with those of the nitrile rubber-based ones[26] due to appreciable miscibility between the two polymers (as shown by the proportion of pale-coloured regions in both optical and electron micrographs). Significant ring-opening of the ENR occurred (as detected by NMR and FT-IR spectroscopy) for blends with a high loading of PAni.DBSA (*i.e.* 30 wt% or above) and this was attributed to the sensitivity of the epoxide group of the rubber to acidic conditions. A progressive rise in the Tg values and increasing of the endothermic events with the proportion of PAni.DBSA as recorded by low and high temperature DSC thermograms respectively, are also proposed to be the results of ring-opening.

Two stages of electrical percolation threshold were observed for the ENR 50-PAni.DBSA blends, *i.e.* the first one (2.9 wt%/2.5 volume

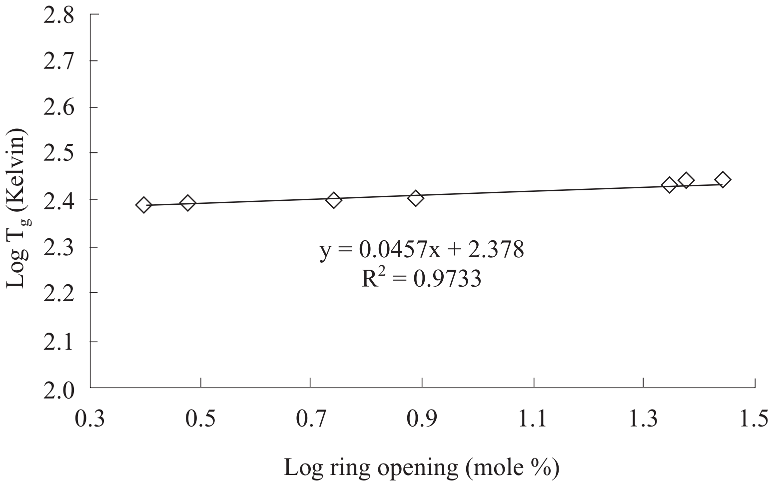


Figure 11. Chart of log glass transition temperature, Tg (Kelvin) versus log ring opening (Mole%) of ENR-PAni.DBSA Blends.

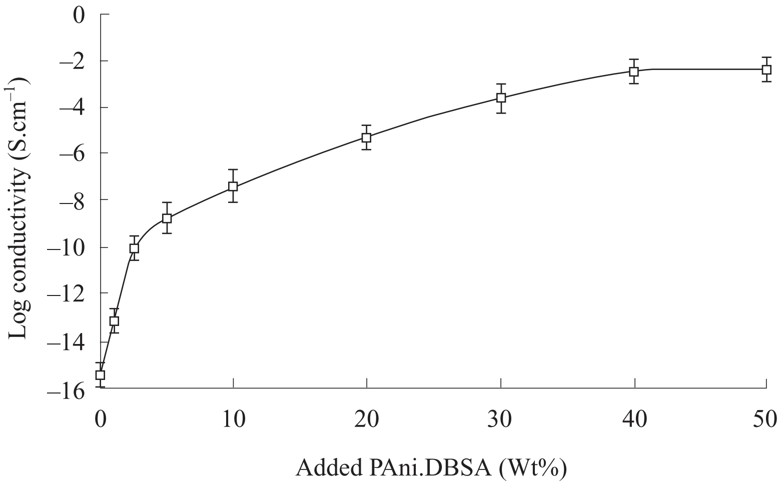


Figure 12. Electrical conductivities for the ENR 50-PAni.DBSA blends as a function of PAni.DBSA Content (wt%).

% of PAni.DBSA) which corresponded to the well-blended regions (pale green in optical micrographs) and the second one (5 wt%/4.4 volume % of PAni.DBSA) which corresponded to the phase separated regions (dark-coloured in optical micrographs). It has been shown here that the ring opening does not seriously affect the electrical properties of the ENR 50-PAni.DBSA blends. However, it is well known that the ring opening of ENR will decrease its elastomeric properties and can ultimately lead to formation of a hard thermoplastic material, called furanised natural rubber[34]. Hence, the tolerable loading of PAni.DBSA is likely to be no more than 30 wt% in practice (based on the mole % of total ring opening).

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