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#### CONDUCTIVE POLY(EPICHLORHYDRIN)-POLYANILINE

#### DODECYLBENZENESULFONATE

#### [PECH-PANI.DBSA] RUBBER BLENDS PREPARED IN SOLUTION

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#### ABSTRACT

Blends of poly(epichlorhydrin) elastomer [PECH] and polyaniline dodecylbenzenesulfonate [PAni.DBSA], with electrical conductivities up to  $6.4 \times 10^{-7}$  S cm<sup>-1</sup>, have been prepared by solution mixing and casting. The solubility parameters were calculated and the most suitable solvent (tetrahydrofuran) was selected for mutual solubility between PAni.DBSA and the compatible elastomer poly(epichlorhydrin) [PECH].

Fourier-transform infrared (FT-IR) spectra of PECH-PAni.DBSA blends contained features of the spectra of the pure materials, but with significant peak shifts due to changing intermolecular interactions between the polymers. Thermal decomposition steps of the conductive blends were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stabilities of the blends were dependent on the ratio of PAni.DBSA to PECH. The electrical conductivities of blends with proportions of 1 to 50 wt % PAni.DBSA were measured by 2-probe and 4-probe techniques. The electrical conductivity increased with the proportion of PAni.DBSA, showing two percolation threshold stages, which were explained by a change in the conformation of the polymeric chains leading to an increase in the conductivity. The effects of composition on the glass transition in the blends were determined using thermomechanical analysis (TMA).

Keywords: Conductive blend; polyaniline; poly(epichlorhydrin), PECH rubber

#### 1. INTRODUCTION

Intrinsically conducting polymers (ICPs) have attracted a large amount of attention because of their remarkable properties and wide application possibilities <sup>1</sup>. Polymers with intrinsic electrical conductivity have commercial applications such as rechargeable batteries <sup>2</sup>, electro-rheological (ER) materials <sup>3</sup>, sensors <sup>4</sup> and many others.

Some intrinsically conductive polymers may have poor stability <sup>5</sup> and poor mechanical properties <sup>6</sup>. A successful method to overcome these problems could be the use of blends or composite materials containing the intrinsically conductive polymers with thermoplastics or elastomers. Solution mixing <sup>7</sup>, thermo-mechanical mixing <sup>8</sup> or electrochemical methods <sup>9</sup> are techniques which can be used to introduce a conductive polymer into an insulating elastomeric matrix.

Among conducting polymers, special interest has been focused on polyaniline because of its ease of synthesis, inexpensive monomer, and better stability than other ICPs. Polyaniline (PAni) was first made by Letheby as "aniline black" <sup>10</sup> in the 1860s by oxidation of aniline under mild conditions <sup>11</sup>. The conductivity of PAni can be adjusted through the selection of a suitable dopant and level of doping and also by controlling its structure during synthesis <sup>12, 13</sup>.

The aim of the present work was to study electrically conductive blends produced by combining an elastomeric material (Hydrin H) with different amounts of PAni.DBSA. It was decided to produce blends by a solution mixing method, which required that both polymers be soluble in a common solvent.

Characterisation of the resulting PECH-PAni.DBSA blends is reported here, using Fourier-transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), determination of the electrical conductivity of pure polymers and blends and morphological study by optical and electron microscopy.

#### 2. EXPERIMENTAL

#### 2.1. Materials

Aniline monomer (Ani) (99 wt%), ammonium persulfate [APS] (98 wt%), 36.5–38 wt% HCl solution (GPR), iron (III) chloride [FeCl<sub>3</sub>] (98 wt%), 33 wt% ammonia solution (GPR) and 70 wt% DBSA solution in 2-propanol (GPR) were supplied by Sigma-Aldrich UK. Poly(epichlorhydrin) rubber (Hydrin H) was supplied by Zeon Chemicals Europe, Ltd.

## 2.2. Calculation of solubility parameter values for main materials

In order to estimate the solubility parameters ( $\sigma_P$ ) for poly(epichlorhydrin) rubber and PAni.DBSA, Eq. (1) and the values of functional group molar attraction constant  $F_i$  calculated by Hoy <sup>14</sup> were used.

$$\sigma_P = \left[\frac{\rho \times \sum F_i}{M_0}\right] \tag{1}$$

where  $\rho$  is the density of the polymer (kg m<sup>-3</sup>), M<sub>0</sub> is the formula weight of the polymer repeat unit (kg mol<sup>-1</sup>) and  $\Sigma F_i$  is the sum of all the groups' molar attraction constants in the polymer repeat unit [(J m<sup>3</sup>)<sup>0.5</sup> mol<sup>-1</sup>]. The determination was based on the smallest repeat unit of the relevant polymer.

#### 2.3. 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. 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  $1^{\circ}$ C. The aniline solution was placed in an ice bath with an overhead stirrer. After the addition of a few drops of 1 M FeCl<sub>3</sub> solution 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 between 0 and  $2^{\circ}$ C while the pH was adjusted to 0 - 0.5 by the addition of concentrated HCl. The mixture was left for 8 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 de-protonating the wet PAni.HCl in 33% aqueous ammonia solution (3000–5000 mL) with 24 h stirring. The base was then washed with 10 L of distilled water and filtered under vacuum. Drying was carried out in a vacuum oven at  $40^{\circ}$ C for 24 h. Redoping was achieved by mixing the emeraldine base with DBSA in a monomer molar ratio of 1:1.The mixture was stirred for 48 h and then filtration was done with a sintered-glass funnel of grade 3 porosity (16–40 mL). All products were washed with large quantities of distilled water until the filtrates were colourless. Final drying of the powdered filter cake was carried out in a vacuum oven at  $40^{\circ}$ C for 48 h. A sample of PAni.DBSA prepared as above was submitted for elemental analysis by Medac Ltd. The approximate empirical formula from the average experimental results was  $C_{30}H_{37.7}N_{1.95}SO_{4.6}$  and the theoretical formula of PAni-DBSA is  $C_{30}H_{39}N_2SO_3$ .The atomic ratio of S to N is about 0.48, close to the expected value of 0.5 for the conductive form of PAni-DBSA.

#### 2.4. Blend preparation

Masterbatch solutions of poly(epichlorhydrin) rubber (80 mg PECH/ mL solvent) and PAni.DBSA (0.53 mg PAni.DBSA/ mL solvent) in THF were prepared at room temperature and filtered. Polymer blends were prepared by mixing solutions containing different mass ratios of PECH and PAni.DBSA (50:50, 60:40, 70:30, 80:20, 90:10, 95:5, 97.5:2.5 and 99:1, respectively). Each of the above blend solutions was magnetically stirred for 24 h at room temperature. The mixtures were cast onto PTFE sheets and left to dry at room temperature.

#### 2.5. Morphological studies (optical microscopy)

ECH-PAni.DBSA blends were studied with a Nikon OPTIPHOT-2 optical microscope (magnification  $\times 100$ ) 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 and allowed to evaporate to form a thin (3.0 µm) transparent film.

#### 2.6. Electrical conductivity measurement

The dc electrical conductivity values for PAni.DBSA, pure PECH and PECH-PAni.DBSA blends were calculated from electrical resistance values measured by 2 or 4-probe techniques. The equipment employed was a Keithley 617 programmable electrometer and a Keithley 224 programmable current

source, both under computer control. A pressed pellet of pure PAni.DBSA (diameter 13 mm, thickness 1.5 mm; prepared in a KBr press at 10 ton 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, samples of each PECH-PAni.DBSA blend were cast from solution onto PTFE sheets (100 mm<sup>2</sup>); the solvent was allowed to evaporate for 24h and they were then stuck onto square microscope slides. 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 were performed for less conductive cast films (conductivity  $<10^{-7}$  S cm<sup>-1</sup>).

For the samples measured by the 4-probe technique <sup>7</sup>, electrical conductivities were calculated from the mean resistance values using the van der Pauw equation (Eq. (2)).

$$\sigma = \frac{2\ln 2}{(R1+R2)\pi df}$$
(2)

where  $\sigma$  is the electrical conductivity [S cm<sup>-1</sup>], R1 and R2 are the values of apparent resistance 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 Eq. (3).

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

where  $\sigma$  is the electrical conductivity, R is the mean value of apparent resistance (voltage/current ratio) for the cast blend, *L* is the measured electrode spacing distance and *A* is the cross-sectional area of the cast film between the current-carrying electrodes. High-conductivity silver paint contacts were used, to minimise the electrode resistance.

### 2.7. FT-IR spectroscopy

ATR reflectance FT-IR spectra of PAni.DBSA, pure poly(epichlorhydrin) rubber and all PECH-PAni.DBSA blends were recorded on a Perkin–Elmer FT-IR spectrometer (Paragon 100). A small amount of each sample solution was used in order to obtain a reasonably thin transparent film.

#### 2.8. Thermal analysis

Thermal stabilities of the blends and the pure components were investigated by thermogravimetric analysis (TGA) using a Mettler TG 50 thermobalance coupled with a Mettler analysis controller TC10A, from 30 to  $400^{\circ}$ C (at heating rate of  $10^{\circ}$ C.min<sup>-1</sup>), under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo 822e analyser, from 25 to  $400^{\circ}$ C ( $10^{\circ}$ C.min<sup>-1</sup>), under nitrogen.

The PAni.DBSA powder, pure PECH and all the PECH-PAni.DBSA blend cast films were characterised by differential scanning calorimetry, using a Mettler Toledo DSC822e (heating rate  $10^{0}$ C/min). Each sample was sealed in a 40 µL aluminium pan and was analysed under N<sub>2</sub> atmosphere. An empty pan was used as the reference.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Calculation of solubility parameters for materials used

The solubility parameters of polymers are affected by variation in their chemical constituents such as the distribution of chain branches or substituent groups along the polymer backbones.

The solubility parameter for THF is 19.5  $[(J \text{ cm}^{-3})^{0.5}]^{15}$ , whereas that calculated for PAni.DBSA is 20.8 <sup>16</sup> (Table 1)

The above values are comparable, so it can be expected that PAni.DBSA would be somewhat soluble in THF. For poly(epichlorohydrin) the calculated solubility parameter is 20.11 (Table 2), which is also quite comparable to that of PAni.DBSA.

# Smallest repeat unit of PAni.DBSA:



Group	Group Contribution	Number of Groups	$\sum F_i$	
	[(J.cm <sup>-3</sup> ) <sup>1/2</sup> .cm <sup>3</sup> ]/mol		[(J.cm <sup>-3</sup> ) <sup>1/2</sup> .cm <sup>3</sup> ]/mol	
For EB:				
6-membered ring	-48	4	-192	
		12	2880	
-CH=aromatic	240			
>C=aromatic	201	6	1206	
-NH-	368	2	736	
CH=olefin	249	4	996	
>C= olefin	173	2	346	
-N-	125	2	250	
		Polymer	$\sum F_{i} = 6222$	
FOR 2×DBSA:	-48	2	96	
6 mombared ring	-40	2	-90	
CH-aromatic	240	8	1920	
	240	8	804	
	201	4	5019	
-Сп <sub>2</sub> .	209	22	5918	
-Сп3	505	2	000	
-6-	428	2	0J0 1440	
-O- (epoxide)	300	4	024	
-OH-	402	2	924	
		Dopant	$\sum F_{i} = 12372$	
Details of Calculation				
Density as measured from pressed pellet of PAni.DBSA powder = $1.134 \text{ g.cm}^3$ : $M_0 = 1014 \text{ g.mol}^{-1}$ $\sigma = [1.134(6222 \pm 12372)/(1014)] = 20.8 (L \text{ cm}^{-3})^{1/2}$ or 20.8 (ML m <sup>-3</sup> ) <sup>1/2</sup>				

Smallest repeat unit of EPCH:

-O-CH<sub>2</sub>-CH(CH<sub>2</sub>Cl)-

Group	Group Contribution	Number of Groups	F <sub>i</sub> ∑F <sub>i</sub>		
	$[(J.cm^{-3})^{1/2}.cm^{3}]/mol$	l	$[(J.cm^{-3})^{1/2}.cm^{3}]/mol$		
-CH <sub>2</sub> -	269	2	538		
>CH-	176	1	176		
-0-	235.5	1	235.3		
-Cl	419	1	419		
		Rubber	$\sum \mathbf{F}_{i} = 1368$		
Details of Calculation					
Density as provided by manufacturer = $1.36 \text{ g.cm}^{-3}$ ; $M_0 = 92.5 \text{ g.mol}^{-1}$					
$\sigma_{ ho} = [(1368 \times 1.36)/92.5] = 20.11  (\text{J.cm}^{-3})^{1/2}, \text{ or } 20.11  (\text{MJ.m}^{-3})^{1/2}]$					

Table 2: Calculation of solubility parameter value from molar attraction constants for PECH

# 3.2 Morphological Structure (optical microscopy)

The morphology of PAni-DBSA/ECH blends was investigated by optical microscopy (Fig. 1). For all the micrographs, two distinct coloured regions were observed, i.e., the lighter (actually pale green) ones and the darker (actually dark green) ones. The dark region appears to be polyaniline clusters, probably high molecular weight polyaniline, whilst the lighter region is attributed to PAni-DBSA forming a colloidal dispersion within the polyepichlorohydrin.

A micrograph of a blend containing 10% of PAni-DBSA is shown in Figure 1 (b). It is possible to observe PAni-DBSA particles present in the form of small agglomerates. At this concentration it is only possible for a conducting pathway to be formed via the connection between high molecular weight polyaniline particles and dispersed oligomers in the rubber. This is in agreement with the calculated percolation threshold at 10% (w/w) of PAni-DBSA content. As the amount of the

conducting polymer in the blends was increased (Figures 1 a, b, c and d), the conducting pathways became shorter and the conductivity increased.

Figure 1: Optical micrographs (100 × magnification) for the blends of PECH and PAni.DBSA. Blends contain (a) 99: 1, (b) 90: 10, (c) 60:40 and (d) 50:50 wt% PECH:PAni.DBSA.



#### 3.3 Electrical conductivity measurement

The calculated electrical conductivity values for pure PAni.DBSA, polyepichlorhydrin and blends with polyepichlorhydrin and PAni.DBSA are shown in Figure 2. Clearly PECH is a very good electrical insulator, with conductivities in the region of  $3 \times 10^{-12}$ S cm<sup>-1</sup>.

The PAni.DBSA used in this project had a high electrical conductivity of  $1.2 \pm 0.5$  S cm<sup>-1</sup>, comparable with the literature values for pressed pellet samples <sup>17</sup>. The electrical conductivities of all the blends increased with the proportion of PAni.DBSA.

# Figure 2: Electrical conductivities of PECH-PAni.DBSA blends as a function of PAni.DBSA content (wt %)



The conductivity percolation threshold for the blends was estimated by fitting the data from Figure 2 to a simple percolation model as defined by Eq. 4.  $^{18}$ .

$$\sigma = c(f - f_P)^t \quad (4)$$

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 to volume fractions for this analysis. By fitting the data to a plot of log electrical conductivity ( $\sigma$ ) versus log(f –  $f_P$ ), it was possible to estimate the values of t (Figure 3) and the correlation coefficient (R). By fitting the experimental data to a plot of log  $\sigma$  versus log(f –  $f_P$ ), values of 1% w/w or 1.36% v/v for  $f_P$  and 2.21 for t were obtained, with a correlation coefficient (R) of 0.95.



Figure 3: Log electrical conductivity ( $\sigma$ ) versus log(f – f<sub>P</sub>)

#### **3.3. Infrared spectroscopy**

ATR spectra obtained from pure polyepichlorhydrin and pure PAni-DBSA are shown in Figures 4(a) and 4(b), respectively. The spectrum of PAni.DBSA cast film has characteristic absorptions at  $3447 \text{ cm}^{-1}$  (<u>N</u>\_H stretching),  $1559 \text{ cm}^{-1}$  (N\_quinoid\_N),  $1478 \text{ cm}^{-1}$  (N\_benzoid\_N),  $1295 \text{ cm}^{-1}$  (quinoid\_N\_benzoid),  $1240 \text{ cm}^{-1}$  (C aromatic\_N stretching) and  $1030 \text{ cm}^{-1}$  (S\_O stretching). The FT-IR spectra of PECH-PAni.DBSA blends looked like a combination of the spectra of the pure materials, but with significant peak shifts due to changing intermolecular interactions between the polymers. The presence of quinoid and benzoid vibrations indicates the emeraldine state of PAni. The band at 790 cm<sup>-1</sup> was attributed to the out of plane bending mode of C-H, and the 878 cm<sup>-1</sup> band was considered to be evidence of the formation of para-linked polyaniline. The band at 2112 cm<sup>-1</sup> may be assigned to the overtones of C-H (out of plane) bending. The peak at 2910 cm<sup>-1</sup> corresponds to aliphatic stretching, and those in the region of 3212 and 3408 cm<sup>-1</sup> are related to =N-H stretching.

The IR spectrum of pure polyepichlorhydrin in Figure 4 (a) shows a band at 750 cm<sup>-1</sup> due to C-Cl stretching. The band at 1062 cm<sup>-1</sup> was assigned to C-O-C stretching, and peaks at 1284, 1347 and

1458 cm<sup>-1</sup> correspond to aliphatic  $-CH_2$ - bending. The band at 2906, 2973 cm<sup>-1</sup> is due to aliphatic  $-CH_2$ - stretching.



Figure 4: Infrared spectra of (a) pure polyepichlorhydrin and (b) pure PAni-DBSA

Figure 5 shows the IR spectra for PAni-DBSA/polyepichlorhydrin blends. As can be seen from the spectra, the intensity of the C-Cl band decreased when the percentage of PAni-DBSA increased (744-745). The intensity of the S=O stretching bands occurring at 1010 and 1030 cm<sup>-1</sup>, which are characteristic of PAni-DBSA, obviously increased as the percentage of PAni-DBSA increased in the polymer blend. The –CH- stretching vibrations for the rubber were observed at 2900 and 2975 cm<sup>-1</sup>. It is clear from the spectra that as the PAni-DBSA content increased, the intensity of the S=O band at 1030 cm<sup>-1</sup> increased and became more distinct, while the intensity of the N-H band at 3266-3285 cm<sup>-1</sup> decreased.



Figure 5:.Infrared spectra of PAni-DBSA /polyepichlorhydrin blends of the (a) 1%, (b) 2.5%, (c) 5%, (d) 20 %, (e) 30% and (f) 40%.

#### 3.4. Thermal Analysis

#### 3.4.1 Thermogravimetric Analysis (TG)

In Figure 6, the thermogravimetric curves under a nitrogen atmosphere for pure PAni-DBSA, pure polyepichlorhydrin rubber and their blends are compared. The PAni-DBSA curve shows a large mass loss at 200-380°C, attributable mainly to dopant loss and the beginning of main chain degradation. Above these temperatures, the residual polyaniline showed a slower mass loss process assigned to main chain degradation. At 400°C, the polymer left a residue, probably corresponding to crosslinked materials. The curve for polyepichlorhydrin reveals a large mass loss at 318-380°C, corresponding to dehydrochlorination. Different weight losses were observed, depending on the composition of the blends. Comparing the TG curves of blends containing 10, 20 and 30% (w/w) of PAni-DBSA with that of pure polyepichlorhydrin, it was possible to observe a mass-loss process corresponding to the polyepichlorhydrin chain degradation at the following temperatures: 300-350°C in the blend

containing 10% (w/w) PAni-DBSA, 260-332<sup>o</sup>C and 270-340<sup>o</sup>C for the blend containing 20 and 30% (w/w) of PAni-DBSA respectively.



Figure 6: Thermogravimetric curves of (a) pure PECH, (b) PAni.DBSA, blends containing, (c) 40%,



#### 3.4.2 Differential Scanning Calorimetry (DSC)

Figure 7 represents the DSC thermograms for PAni-DBSA, pure PECH and their blends. They show a decrease in the decomposition onset temperature of PECH from  $310^{\circ}$ C to 294, 290 and  $273^{\circ}$ C respectively, for blends containing 10%, 20% and 30% (w/w) of PAni-DBSA.

All the DSC thermograms for the blends showed thermal processes that were combinations of events recorded for pure PECH and PAni.DBSA, but the events showed some degree of temperature shift relative to the corresponding processes in the pure polymer. As indicated by the data in Table 3, pure PECH is thermally stable up to about  $310^{0}$ C.

PAni.DBSA also had good thermal stability up to about 250<sup>o</sup>C. For all proportions of PAni.DBSA shifts in the onset temperature of the major exotherm with composition were observed, giving further evidence for good mixing in these blends. TGA analysis supported the DSC results.



Temperature /ºC

Figure 7: DSC thermograms for PAni.DBSA, pure PECH and their blends of different composition (wt% PECH: wt% PAni.DBSA).

Table 3: The mean onset temperatures of major exotherms for the above-ambient temperature DSC thermograms of PAni.DBSA, pure PECH and PECH-PAni.DBSA blends

Composition (wt% PECH: wt% PAni.DBSA)

Onset temperature of major exotherm  $(^{0}C)$ 

Pure ECH	310.25
99:1	318
97.5:2.5	311
90:10	294
80:20	290
70:30	273
60:40	274
50:50	275
PAni.DBSA	250

#### 3.5. Electronic (UV-Visible) spectroscopy

During the mixing of PAni-DBSA and PECH, the colours of the blends remained green, indicating that PAni-DBSA remained in its doped state. In order to prove this, UV-visible spectra of PAni-DBSA/PECH blends were obtained, and the spectra of pure PAni-EB and PAni-DBSA were obtained for comparison. For the base polymer, N-methylpyrrolidone (NMP) was used as solvent and reference, while THF was used for the doped polymer. Figure 8 shows the UV-Vis spectra of the emeraldine base and PAni-DBSA solutions. In the EB spectrum, two characteristic bands were observed: one at 326 nm due to a  $\pi$ - $\pi$ \* transition of the benzenoid ring and another at 628 nm, corresponding to an n- $\pi$ \* transition between the HOMO of the benzenoid ring and the LUMO of the quinoid ring. For the doped polymer (PAni-DBSA) the peak at 326 nm was shifted to 347 nm, and two more absorptions were observed. The absorption at 430 nm represents the protonation stage of the PAni chains. The band at 773 nm is reportedly due to the presence of polarons resulting from the doping process <sup>19</sup>. The spectra of PAni-DBSA/PECH blends demonstrated the fact that the PAni-DBSA remained in its doped state, since the characteristic peaks of the doped polymer were observed.



Figure 8: UV-Visible spectra of (a) PAni-EB, (b) PAni-DBSA/PECH (20/80), (c) PAni-DBSA

#### 3.6. Thermomechanical analysis (TMA)

Analysis by TMA below ambient temperature was performed to characterize the miscibility of PAni-DBSA blends further. The glass transition temperatures (Tg) of the pure elastomer and the blends are listed in Table 4.

It was found that there was only one Tg for each blend, and the Tg values of the various blends were shifted monotonically to higher temperatures with increasing PAni-DBSA content. The glass transition behaviour indicated good compatibility between the conductive polyaniline and the polyepichlorhydrin.

Table 4.				
Blends	PAni-DBSA Content	$Tg(^{0}C)$		
	(wt %)			
PECH	0	-22		
PAni-DBSA/PECH	1	-9.64		
	2.5	-9.28		
	5	-8.44		
	10	-7.44		
	20	-0.76		
	30	4.47		
	40	8.39		
	50	11.39		

#### 4. CONCLUSIONS

PAni-DBSA/PECH blend films were obtained by solution casting. The PAni-DBSA used to prepare the solution blends was synthesized by a three-step chemical method. The theoretically calculated solubility parameters for both the conductive polymer and the polyepichlorhydrin were comparable, leading one to anticipate at least partial miscibility. This was confirmed by studies of the structures and morphologies of the blends using ATR-IR spectroscopy and optical microscopy. The IR spectra indicated changing intermolecular interaction with concentrations, shown by a shift of the amine (PAni-DBSA) absorption peak to a higher wavenumber.

The electrical conductivities of the blends were in the semiconducting region; they increased with the proportion of PAni-DBSA, and there were found to be two percolation threshold stages at 1wt% and

10wt% of the conductive polymer. UV-visible spectroscopic analysis was used to confirm that the

PAni-DBSA remained in the doped state upon blending with polyepichlorohydrin. The concentration

of PAni-DBSA had a significant influence on the thermal stability of the blends. TMA data for the

polymer blends exhibited a single Tg, indicating homogeneous behaviour in the rubber-rich phase.

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