CONDUCTIVE POLYMER - ELASTOMER BLENDS

PETER FOOT

KINGSTON UNIVERSITY LONDON

IOM3 RIEG MEETING

11TH DECEMBER 2009

Overview

- Introduction
  - Conducting polymers
  - Polyaniline (PAni)
  - Limitations
  - Aim of study
  - Elastomers
- Methodology - Discussion
  - Synthesis of polyaniline
  - Preparation and properties of blends – 1 : EO-EPI Elastomer
  - Preparation and properties of blends – 2 : NBR Elastomer

Conclusions

Conducting Polymers

- Conjugated organic macromolecules
- Conduct electricity in the "**DOPED**" state (i.e. when charged)

POTENTIAL APPLICATIONS

- Electrochromic and electro-luminescent devices
- Anti-corrosion paints & coatings
- Radar absorbing materials
- Printed circuits
- Antistatics

Polyaniline

Why Polyaniline ?

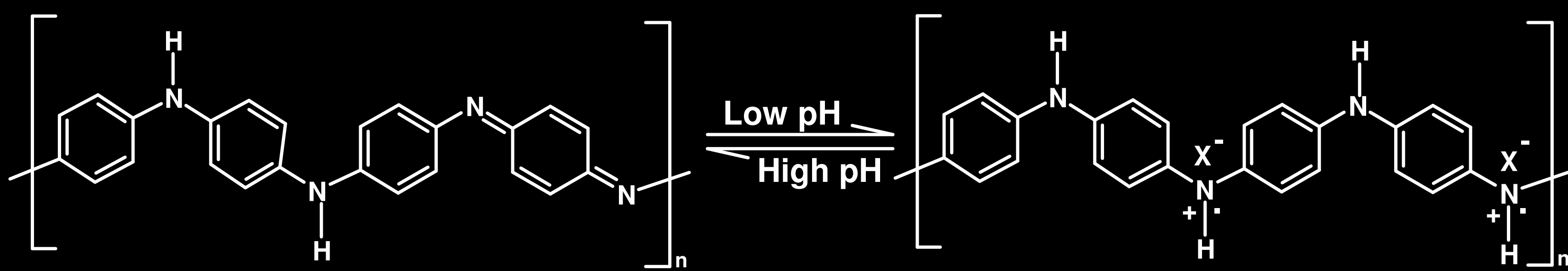
- Monomer inexpensive (aniline)
- High yield polymerisation & low-toxicity polymer
- High thermal and environmental stability
- Good electrical and optical properties

Drawbacks of PAni for industrial applications ?

- Low processability
- Poor mechanical properties

Polyaniline

- Electrical properties reversibly controlled via protonation



Conductivity=2.6x10^{-8} S/cm

Conductivity=9.8S/cm

Aim of study

- Synthesis, optimisation and analysis of conducting PAni
- Blending solubilised PAni with elastomers

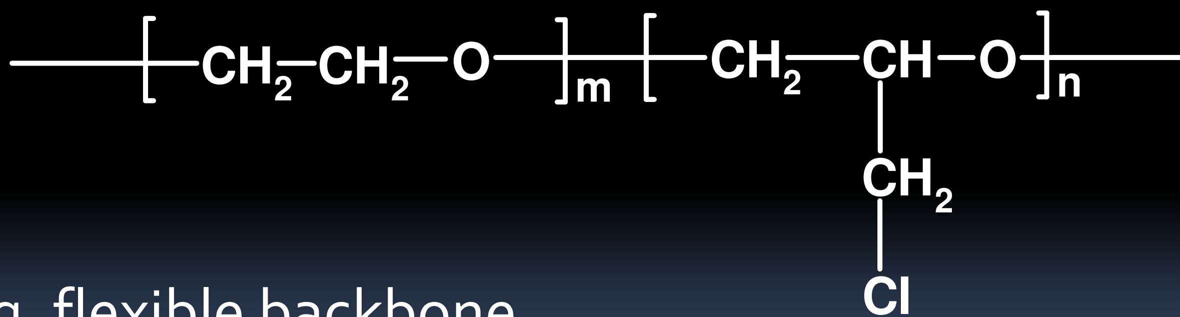
↓

Conducting rubbers with good electrical & mechanical props.

Elastomer 1

Epichlorohydrin-ethylene oxide

- Similar solubility parameter and H-bonding potential to polyanilines



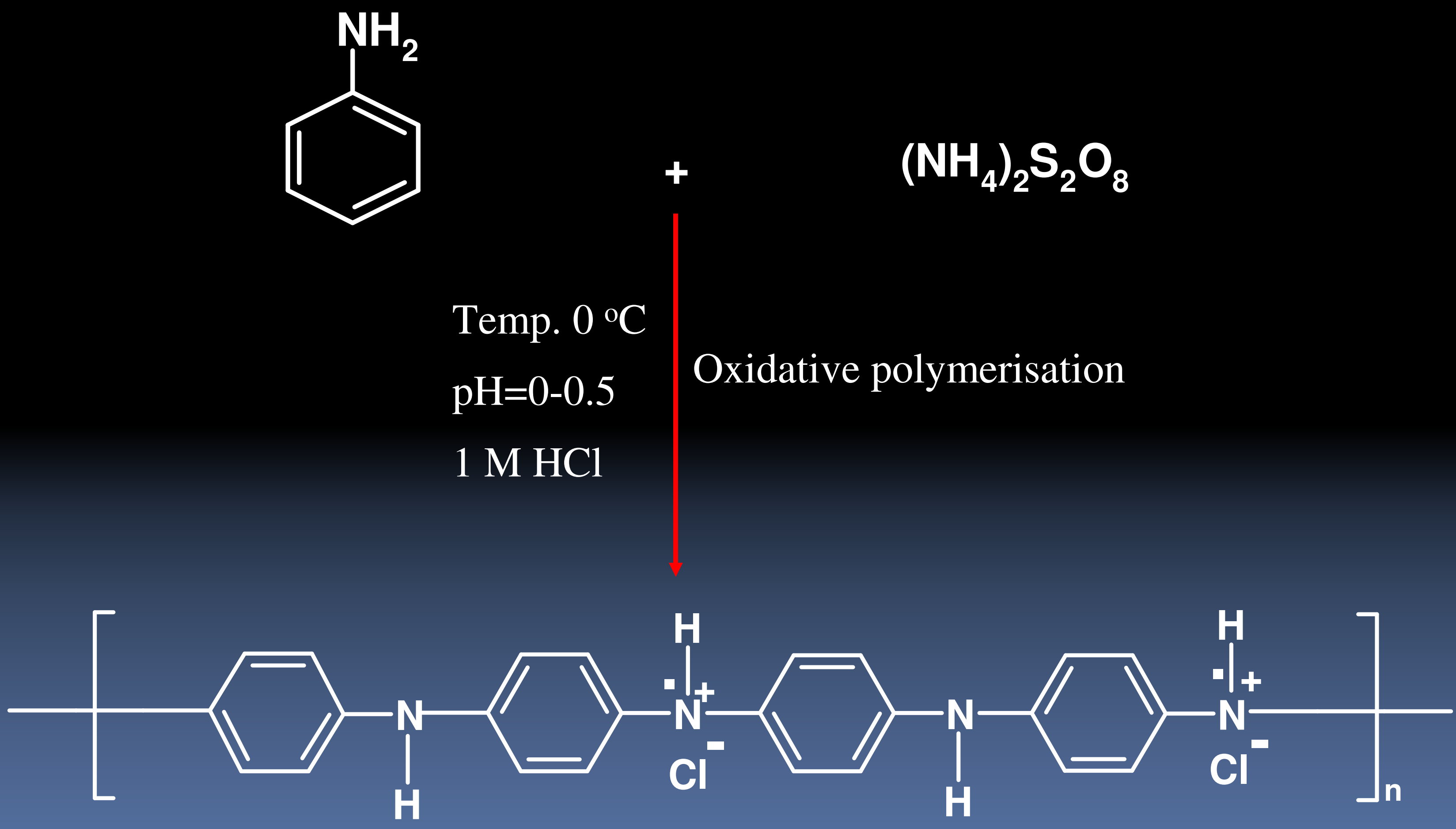
- Strong, flexible backbone
- Good oil, fuel and solvent resistance.
- Good heat resistance.

Synthesis of Polyaniline

Chemical polymerisation -- two-step route chosen:

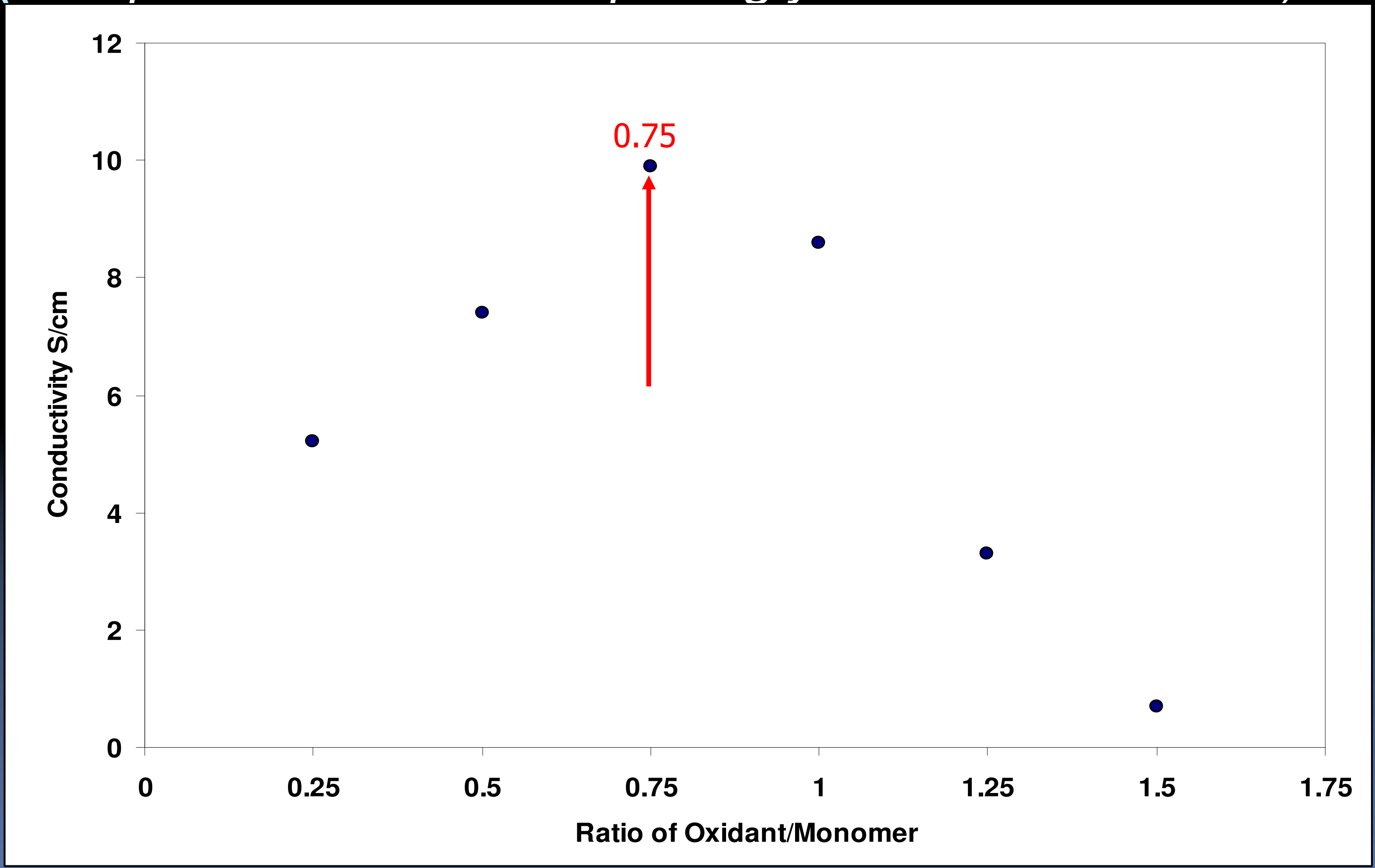
- Synthesis of PAni Hydrochloride salt
- Deprotonation to prepare PAni base
- Reprotonation (doping) of base with solubilising agent, e.g. ionic surfactant or other sulfonic acid

Polyaniline - HCl

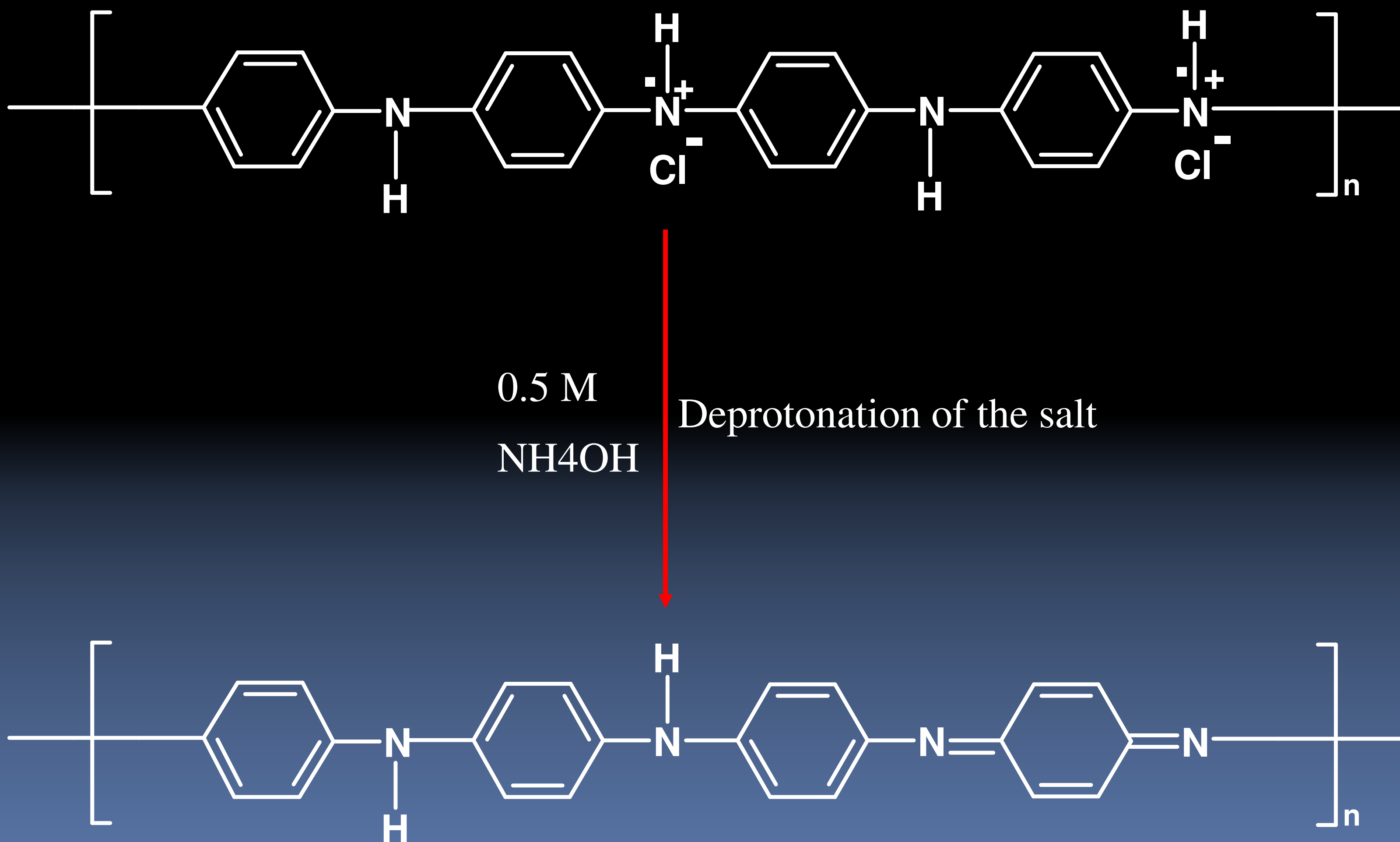


Effect of oxidant/monomer ratio on conductivity of Polyaniline.HCl

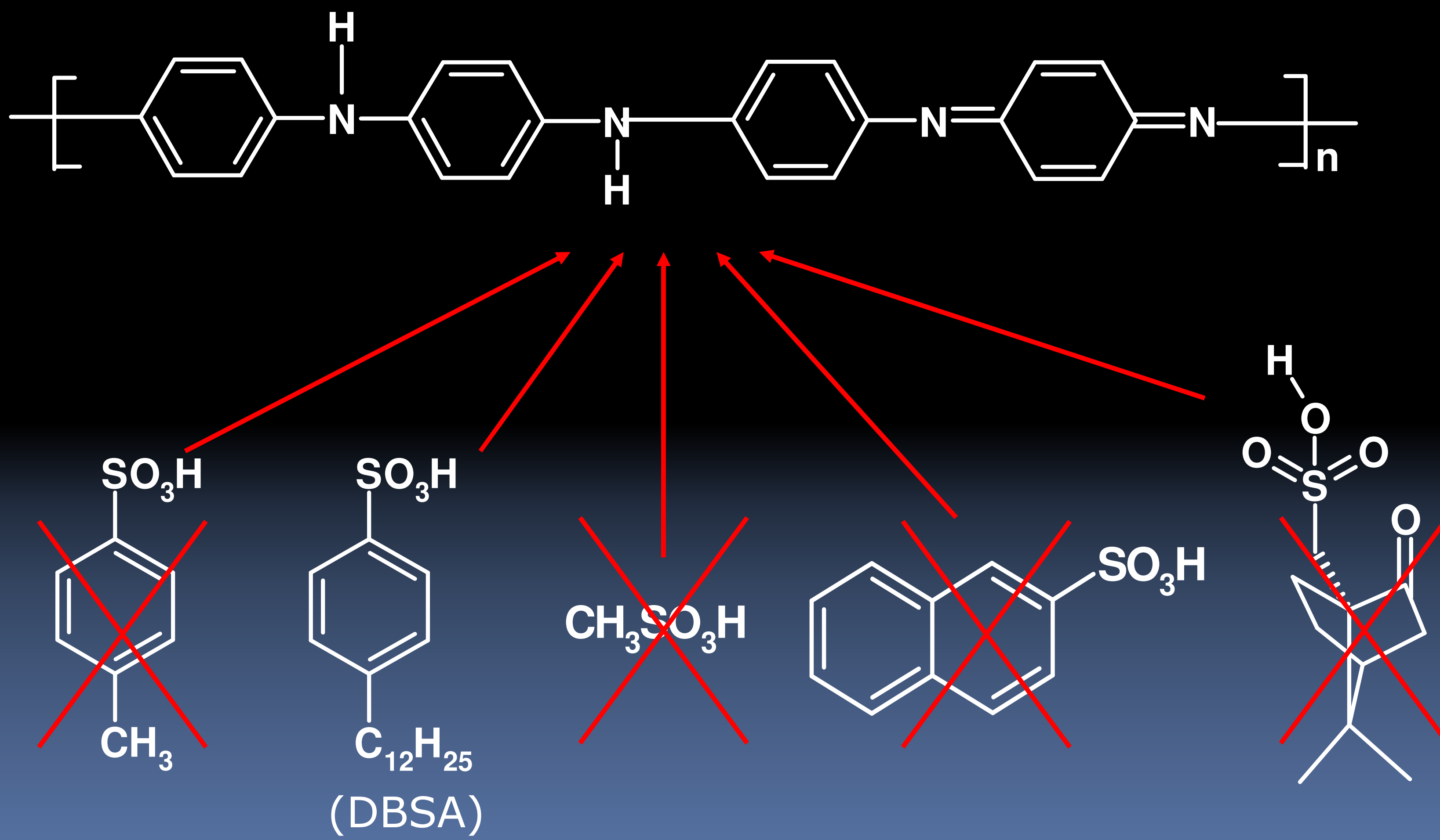
(→ Optimum value is surprisingly sub-stoichiometric)



Polyaniline Base



Doping (Re-protonating) PAni Base



Conductivity and Solubility Parameters

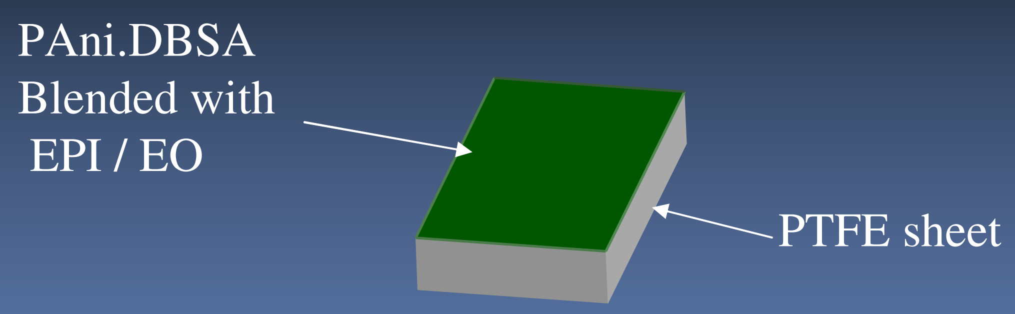
→ *Only PAni.DBSA gave a reasonable match…*

Polymer	Conductivity ($S.cm^{-1}$)	Solubility parameters $(J.cm^{-3})^{1/2}$
Epi-EO	$2x10^{-10}$	19.9
PAni-DBSA	0.6	20.8
PAni-CSA	0.9	22.9
PAni-MeSA	2.7	23.9
PAni-TSA	1.6	24
PAni-NSA	1.5	25

Preparation of Blends

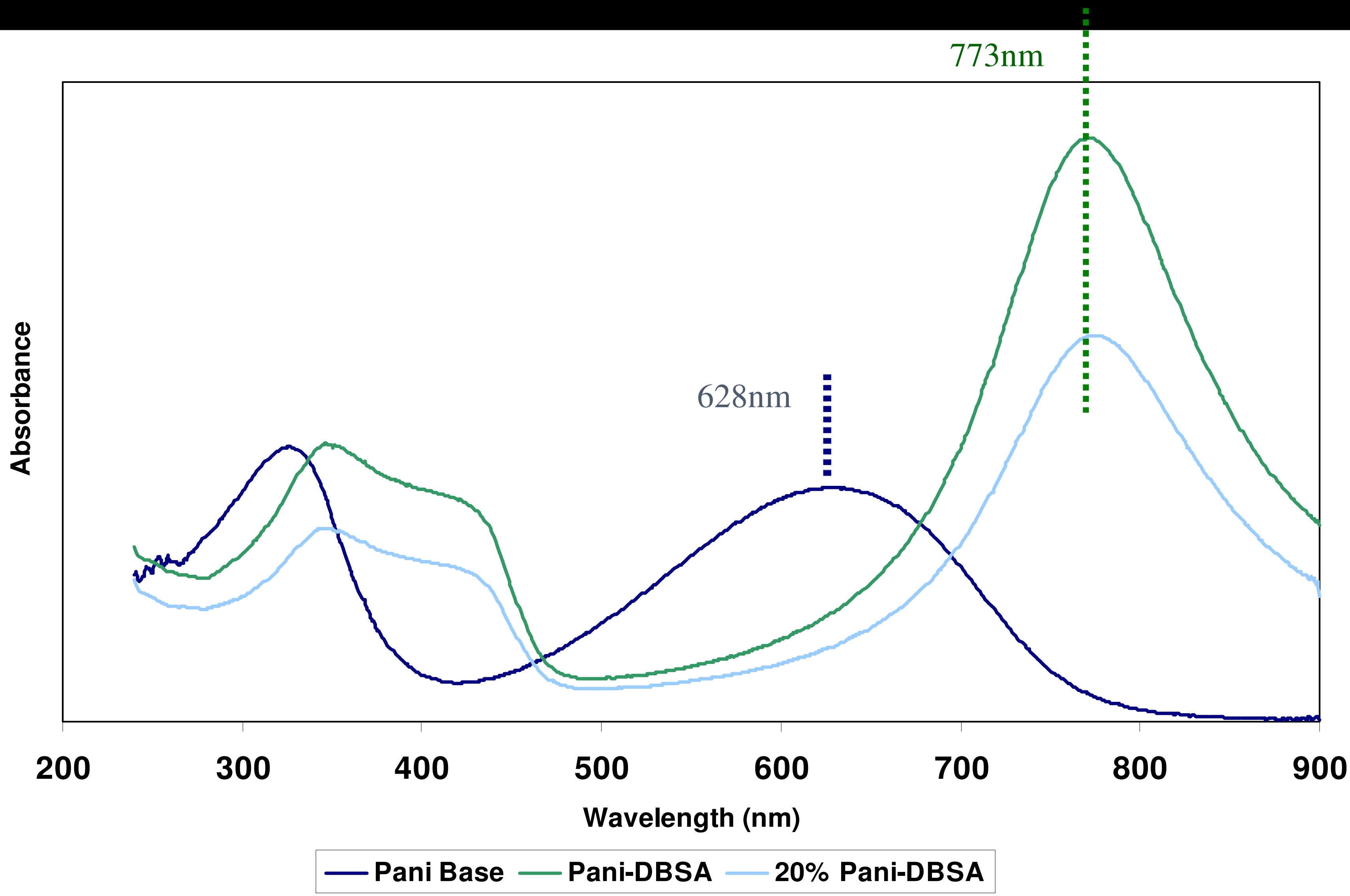
Blends prepared by co-dissolution method

- Polymers (PAni.DBSA & EPI.EO) dissolved in THF
- Solvent evaporated on PTFE sheets to obtain conducting blend films



UV-Vis Analysis of PANI.DBSA BLENDS

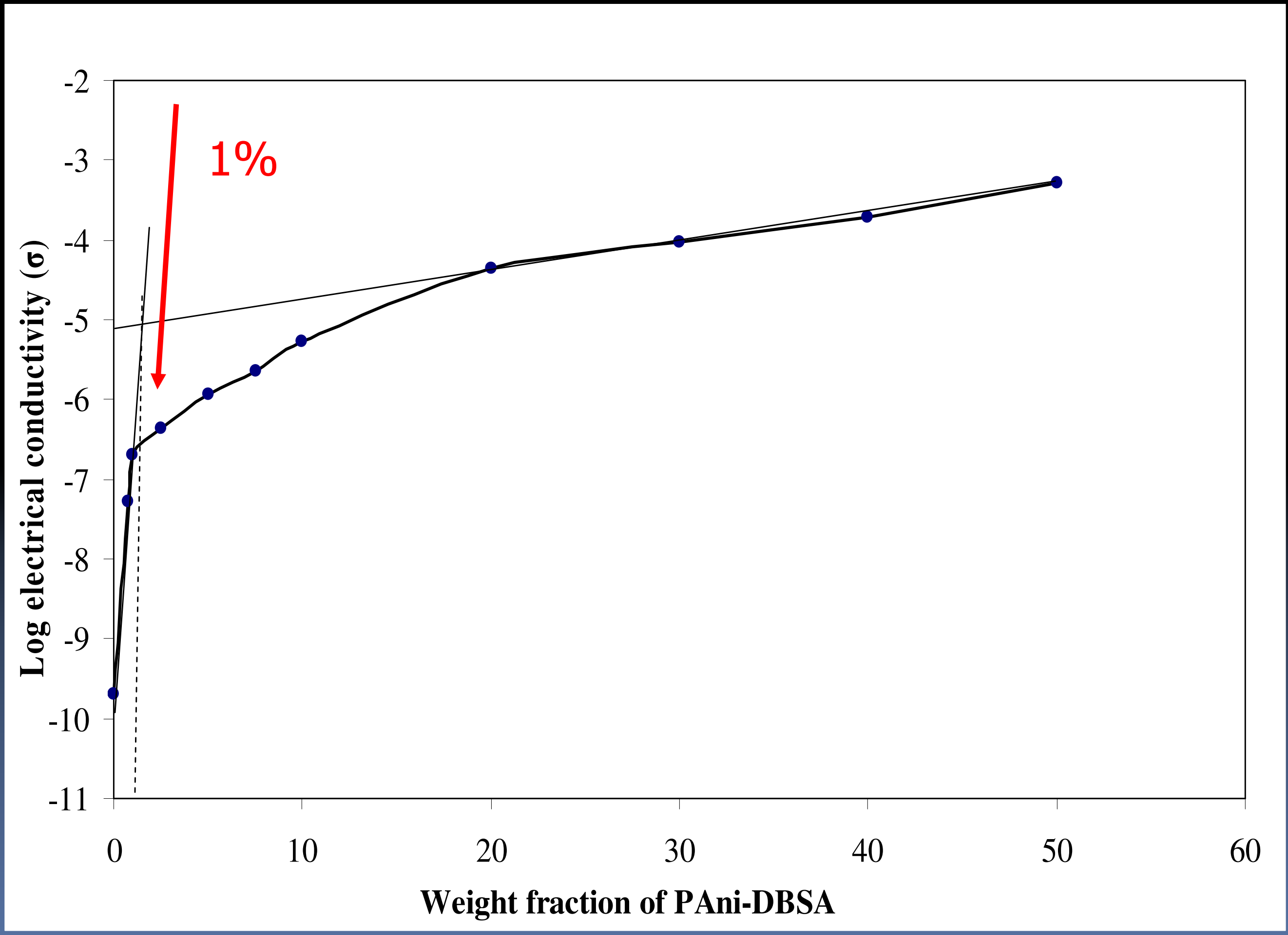
→ *Shows the dispersed polyaniline remains in conductive state*

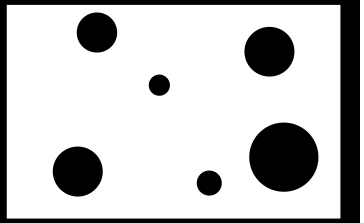


Conductivity of Pani.DBSA Blends

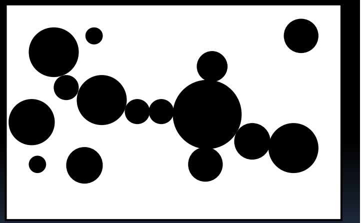
→ *Percolation threshold apparently <1vol.%*

(Some elongated particles present, as well as larger "globules")

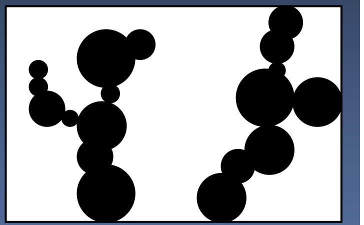




(a) Before percolation



(b) After percolation



(c) Totally connected

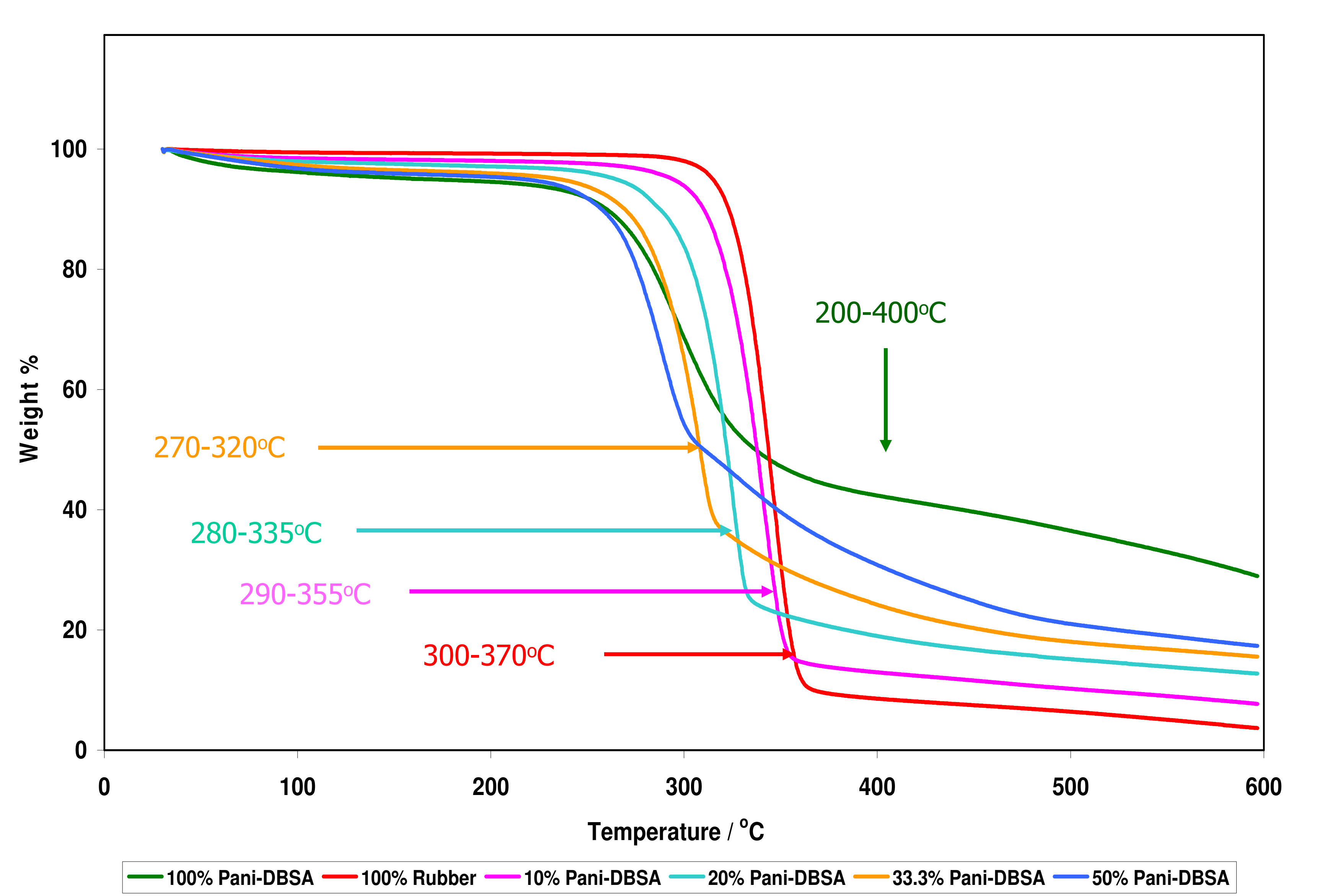
GLASS TRANSITION OF PANI-DBSA BLENDS

→ *also indicate that the PAni.DBSA dissolves in the elastomer*

Blends	PANI-DBSA Content (wt%)	Tg °C
Epi-EO	0	-40
PAni-DBSA/Epi-EO	10	-37
PAni-DBSA/Epi-EO	20	-36
PAni-DBSA/Epi-EO	25	-35
PAni-DBSA/Epi-EO	33.3	-33
PAni-DBSA/Epi-EO	50	-23

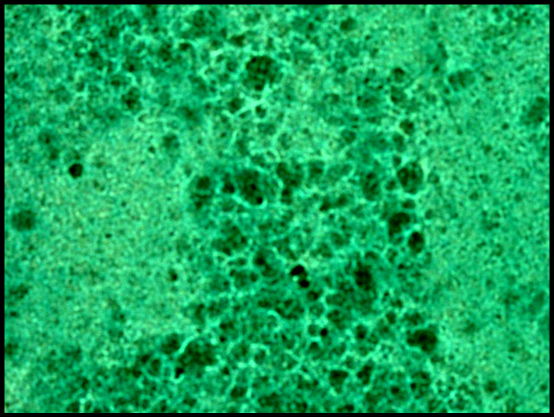
TGA analysis of PANI-DBSA BLENDS

… reveals a compositional trend in the high-T degradation event

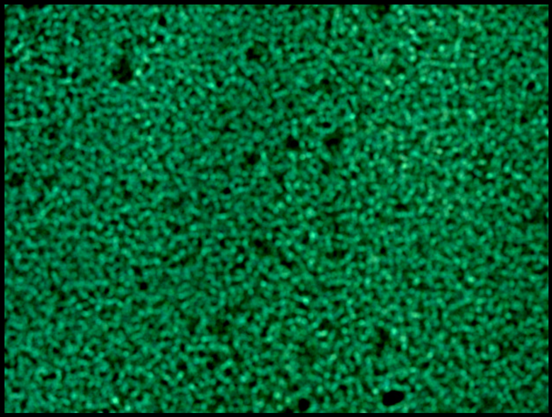


Blend Morphology : Optical Microscopy (200x)

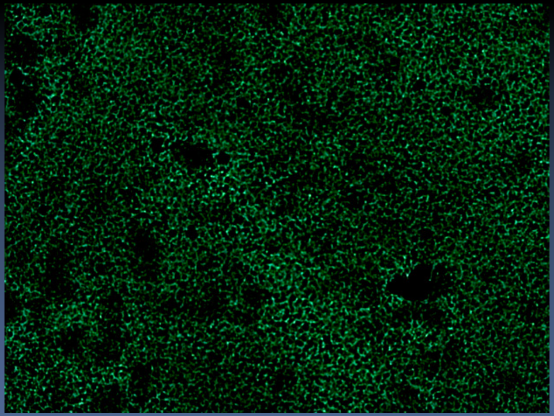
→*Reveals PAni-rich and PAni-poor regions on the μm scale (both contribute to bulk conductivity)*



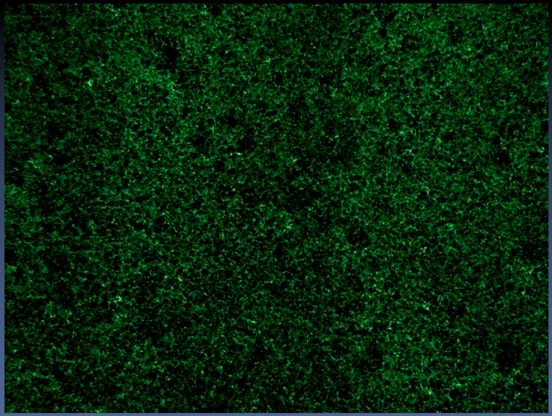
10% Pani-DBSA



20.0% Pani-DBSA



33.3% Pani-DBSA



50.0% Pani-DBSA

Summary

- Increasing oxidant ratio → higher concentration radical cations shorter polymer chain → lower conductivity
- Increased pH → decrease level of protonation → lower conductivity

- PAni-DBSA has good compatibility with Epi-EO elastomer
- Level of conductivity of the blends can be modified according to desired application
- Percolation threshold of blends ~1% w/w
- UV-visible spectrometry shows PAni-DBSA remains in the doped form upon blending with Epi-EO copolymer.

ELASTOMER 2: STUDY OF NITRILE RUBBER (NBR)-PANI.DBSA BLENDS

INTRODUCTION

- Elastomer-intrinsically conducting polymer blends were prepared by:

- Solution mixing, i.e. by using a shared solvent
- Mechanical mixing, using an internal mixer

- Criteria for selection of main components:

- High chemical attack resistance (elastomer).
- Good solubility and miscibility with selected partner-polymer (for elastomer and conductive polymer).
- Good thermal stability (both polymers).
- Good electrical conductivity (conductive polymer).
- Both polymers were blended by using solution mixing, with chloroform as the shared solvent
- NBR (with 48 wt% acrylonitrile content) and PAni.DBSA were chosen as the elastomer and conducting polymer respectively

Solubility Parameter Values

- Calculated by using *Equation 1* and molar attraction constant s calculated by Hoy.

  Equation 1 : $\delta_p = (\rho \times \Sigma F_i) / M_o$

  where δ_p = solubility parameter for polymer , ρ = density of polymer , Σf_i = sum of group molar attraction constants of polymer repeat unit & M_o = formula weight of the polymer repeat unit

Polymer	*Solubility Parameter Value* $(J.cm^{-3})^{1/2}$
NBR (48 wt% ACN content)	20.8
PAni.DBSA	20.8

FT-IR Spectroscopy

- *Spectra of blend films resemble a superposition of spectra for NBR and PAni.DBSA but a few notable peak shifts provide evidence of molecular-scale interaction between the two polymers*

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	-CΞN stretching
PAni.DBSA	3447W	1030M	-
NBR	-	-	2237M
Blends			
90:10	3411W	1081W	2237W
50:50	3437W	1029W	2236W

DSC Analysis

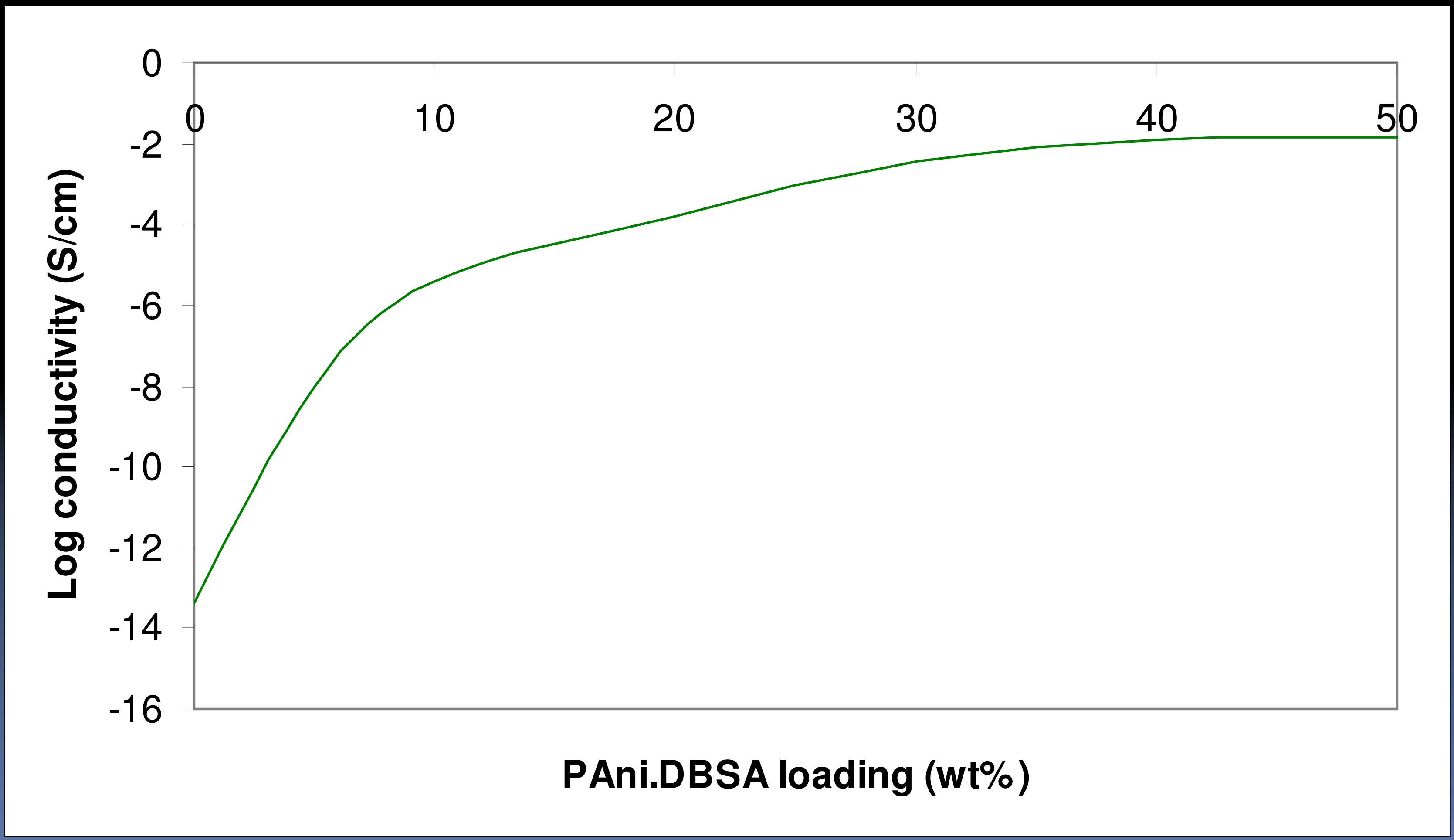
- Samples of pure NBR, pure PAni.DBSA and their blends (with 10, 20, 30, 40 and 50 wt% of added PAni.DBSA) analyzed by DSC (-30°C to 400°C, heating rate 20°C/min).
- DSC thermograms of all blends show some degree of temperature shifting for their thermal processes (based on the onset value of endotherm or exotherm)
- Blends with 10 to 30% PAni.DBSA showed largest shifts. Other evidence showed good miscibility for these blends

DC Electrical Conductivity

- 100 µm films of pure NBR, pure PAni.DBSA and their blends were cast onto glass slides for this purpose
- Electrical conductivity measured by van der Pauw 4-probe technique, except for films with low conductivity ($<10^{-7}$ S/cm) which were measured by using a 2-probe technique
- Apparently two stages of conductivity percolation, with thresholds < 1 vol.% and ~16 vol.% of PAni.DBSA

Electrical Conductivity of NBR-PAni.DBSA Blends as a Function of PAni.DBSA Content

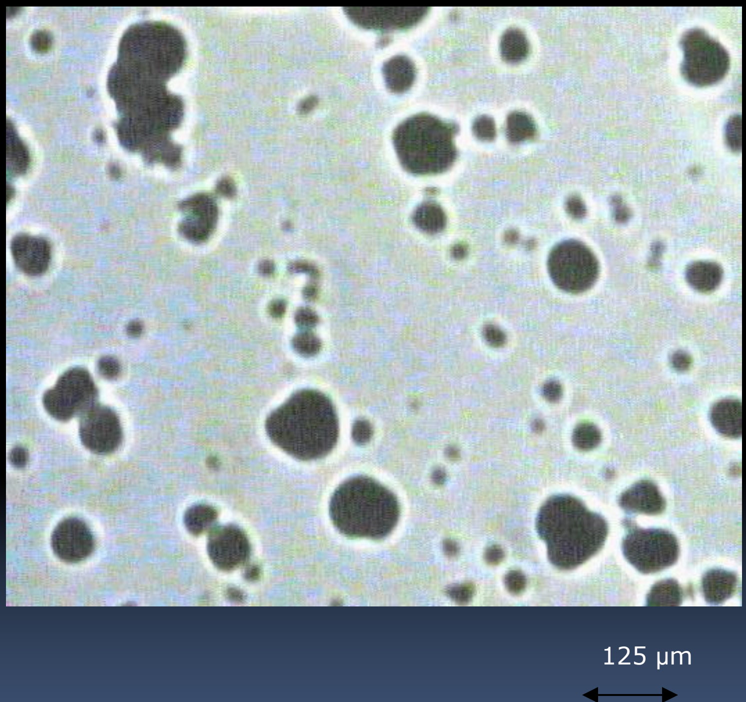
(→ 2 stages of percolation apparent)



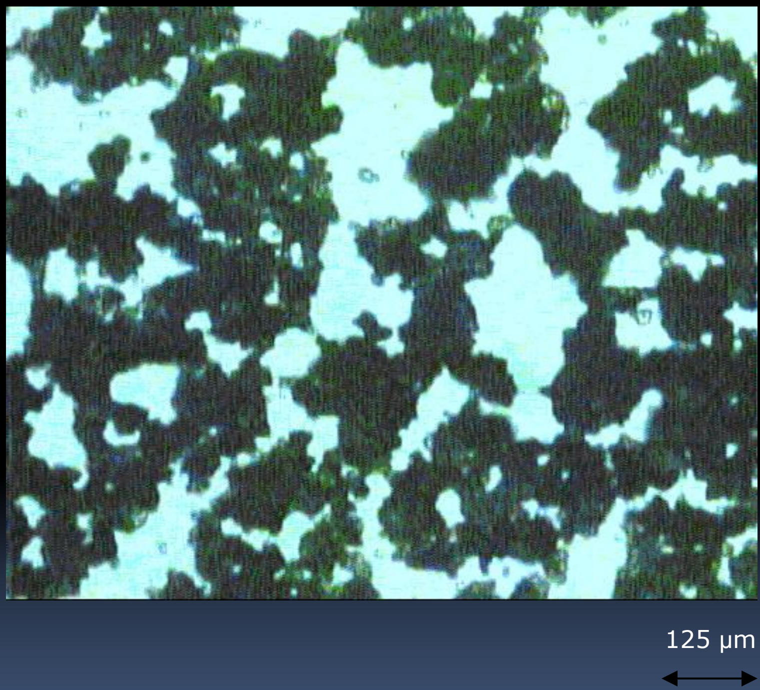
Optical Microscopy

- All blends studied by optical microscopy (200 x magnification) and images captured digitally
- As before, the observed bright green regions are well-blended regions of both components (rich in NBR). TEM reveals nano-sized particles & in these regions.
- The dark green regions (rich in PAni.DBSA) are large particles or agglomerates of PAni. DBSA

Optical Micrographs for Blends: (a) with 5 wt% of Added PAni.DBSA and (b) with 40 wt% of Added PAni.DBSA



(a)



(b)

Thermal Mixing/Cross-Linking of NBR Blends

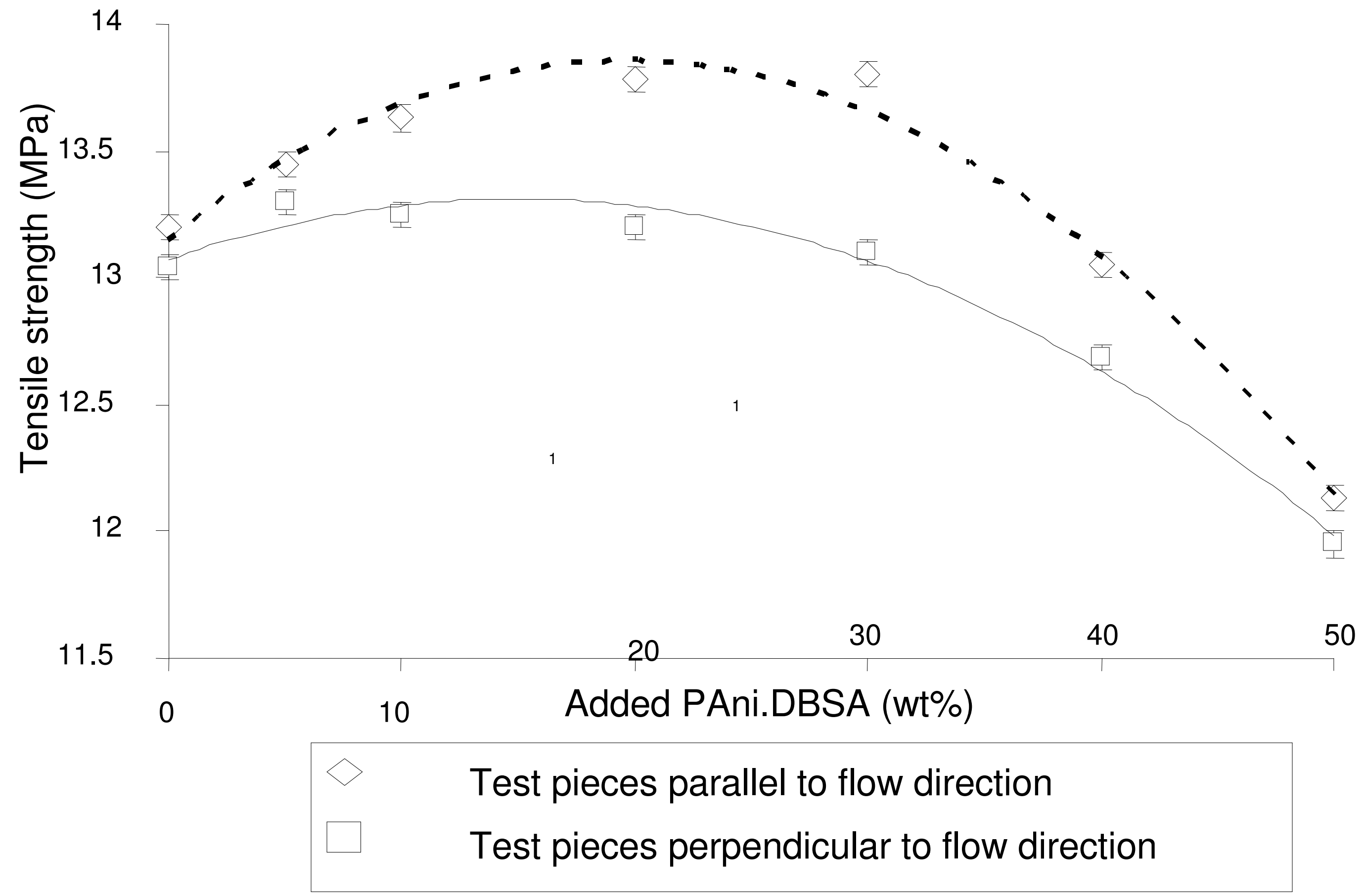
- Polymers blended in an internal mixer (Brabender)
- Cross-linked by dicumyl peroxide
- Vulcanisation studied by MDR
- Samples characterised as for solvent-cast blends
- Anisotropic mechanical & electrical properties (i.e. parallel & perpendicular to flow) also measured

Mean Glass Transition Temperatures (Tg) for Peroxide-Vulcanised NBR and NBR-PAni.DBSA Blends

Composition (wt% NBR : wt% PAni.DBSA*)	Glass transition temperature (Tg), ^{o}C
Vulcanised NBR (48.2 wt% ACN)	-10
Vulcanised blends	
90:10	-7
80:20	-7
70:30	-5
60:40	-8
50:50	-8

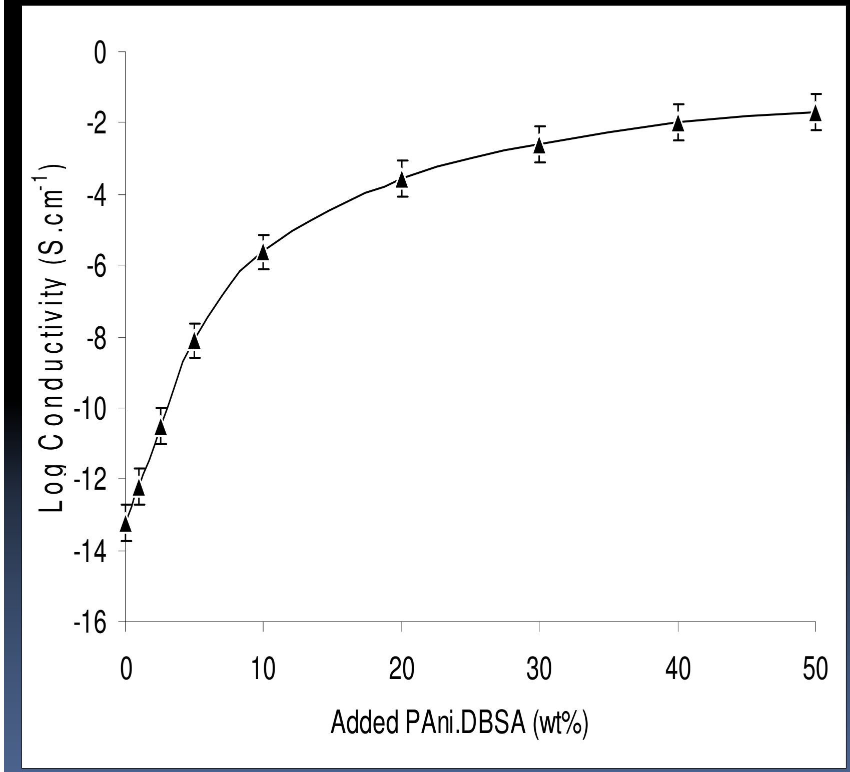
Tensile Strength of Blends vs. Composition

→ *PAni gives some initial reinforcement, then weakens the rubber*

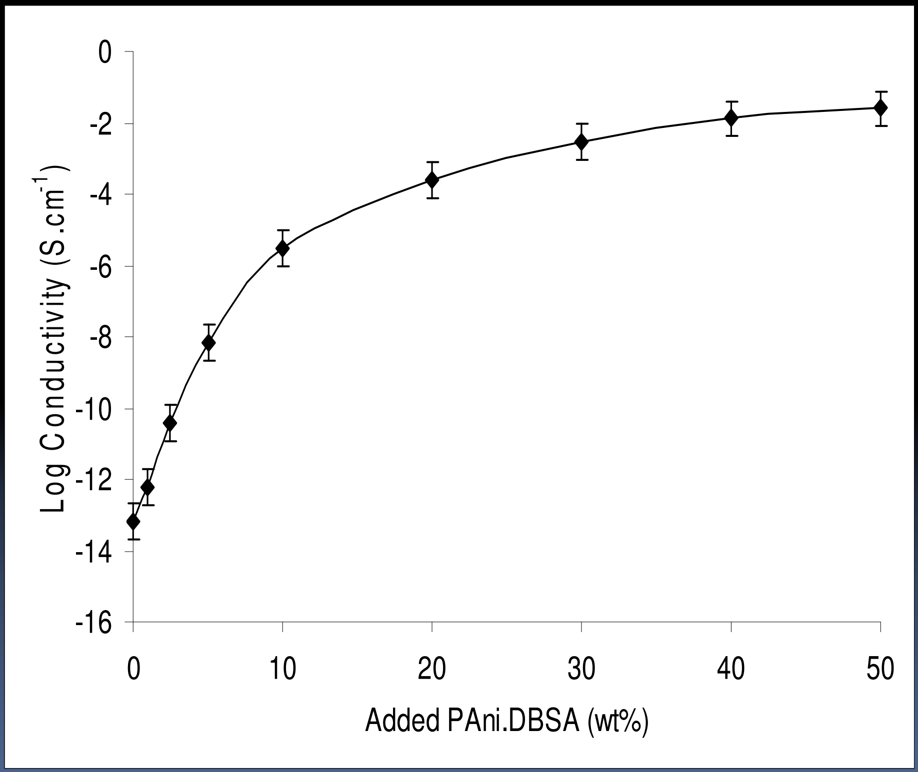


Electrical Conductivity

- *Un-strained samples: surprisingly little effect of thermal treatment or cross-linking*



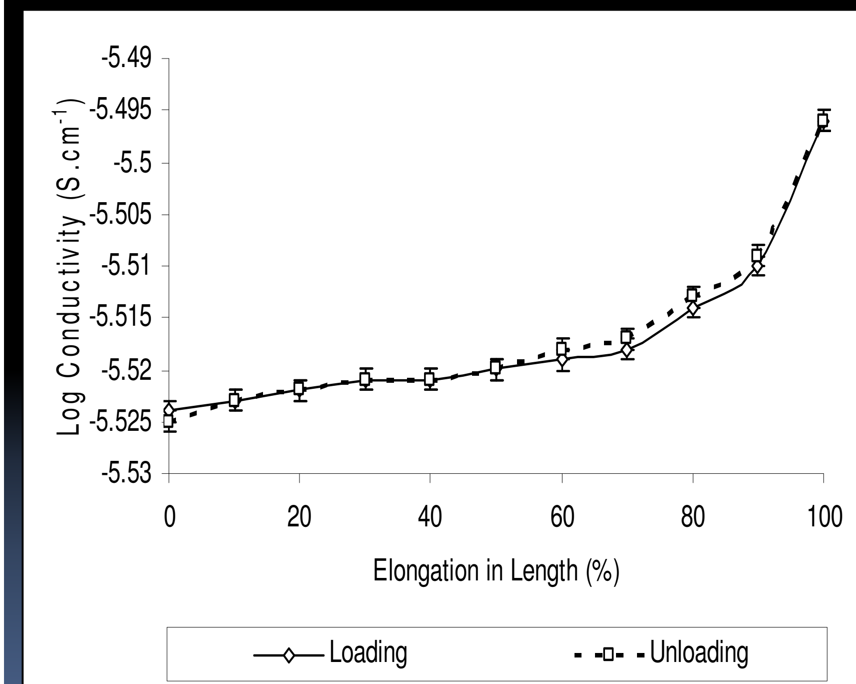
Non-vulcanised



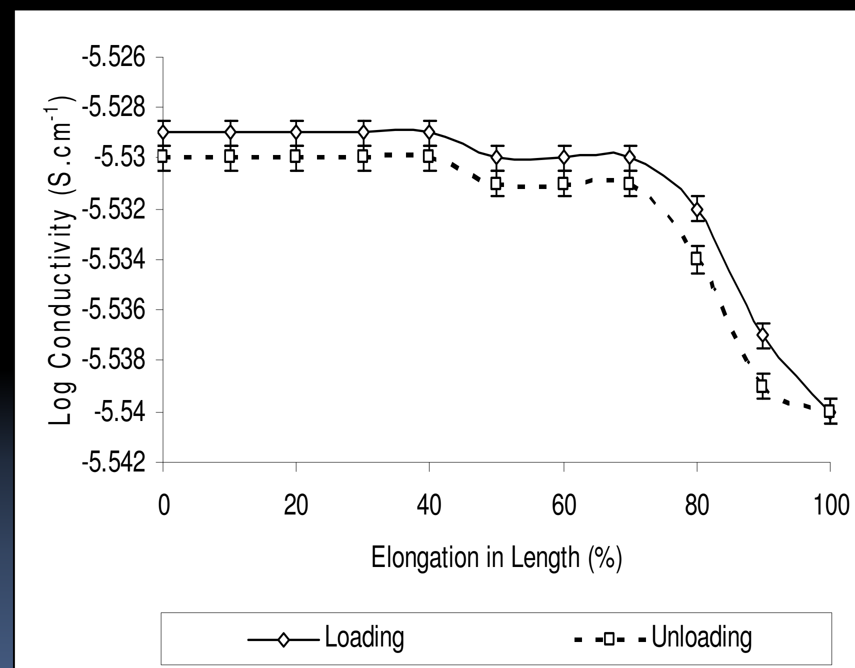
Peroxide-Vulcanised

Electrical Conductivity: Effect of Strain - 1

- *10% Pani.DBSA Blend - 3rd cycle (shows little fatigue)*



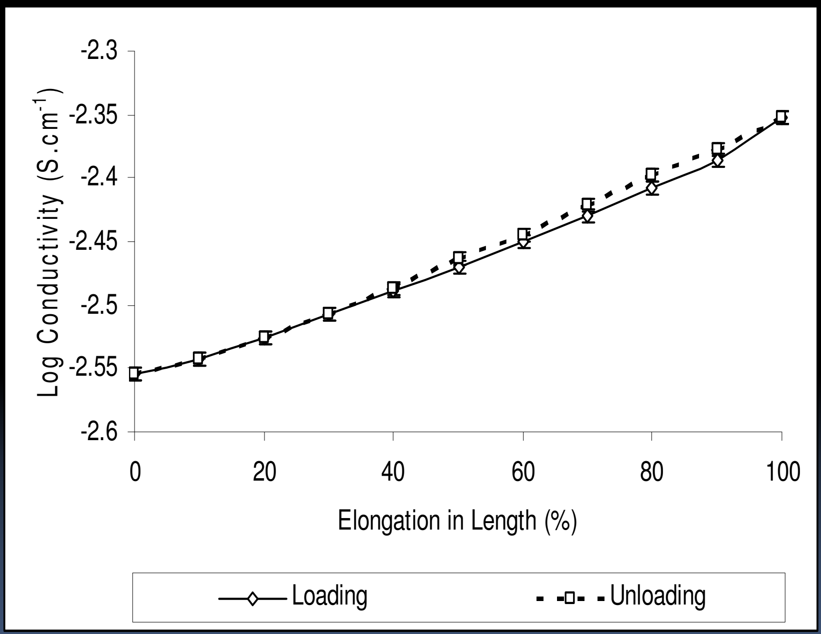
Strain parallel to flow (milling) direction

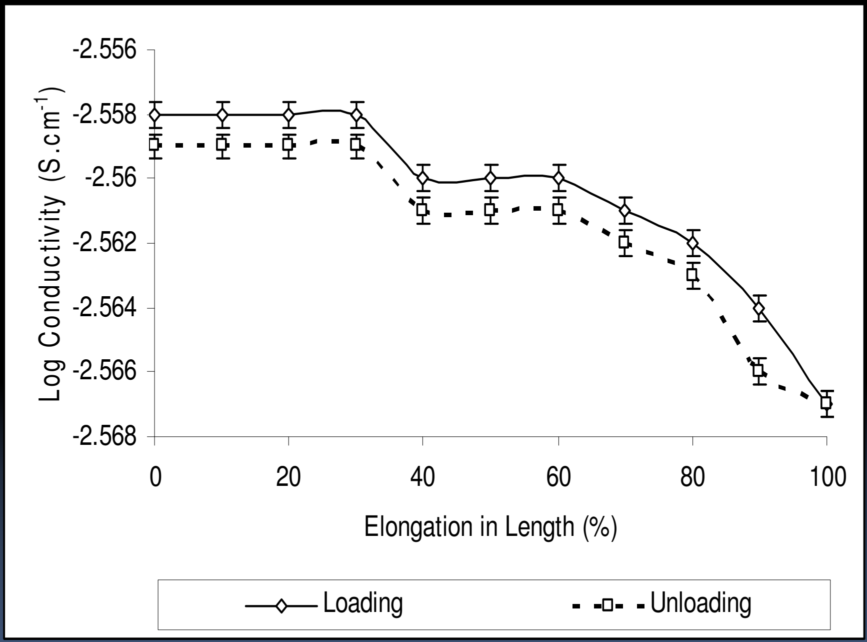


Strain perpendicular to flow

Electrical Conductivity: Effect of Strain - 2

- *30% Pani.DBSA-NBR Blend (3rd cycle again)*





Strain parallel to flow direction

Strain perpendicular to flow

CONCLUSION

- Polyaniline-nitrile rubber blends with reasonable miscibility and useful electrical properties have been prepared. (Miscibility between both polymers could be further improved by using a coupling agent.)
- Intermolecular interactions revealed by IR peaks and DSC transition temperatures shifts
- Two stages of conductivity percolation threshold observed. The earlier one corresponds to the well-blended phase and the later one to the separated phase.

- Thermal blends: conducting polymer appears to have both reinforcing or plasticising effects on NBR
- Conductivity of strained samples is anisotropic; samples strained in the flow direction show a repeatable <u>increase</u> in conductivity under tension.
- Mechanism still under analysis .

Acknowledgements

PEO-ECH Blends:

- **Dr Zaid Abbas**
- Dr. S. Barton
- Dr Ahmed Farid (London Metropolitan University)

NBR and ENR Blends:

- **Malaysian Rubber Board**
- **Dr. Stuart Cook (TARRC, Hertford)**
- **Dr. Huda Morgan**
- **Dr. Andrew Tinker (Director of R&D, TARRC)**
- **Dr K-C Yong (on study leave from MRB)**

Some Relevant Publications

1. **The Effects of Composition and Processing Variables on the Properties of Thermoplastic Polyaniline Blends and Composites. H Morgan, PJS Foot and NW Brooks, J Mater. Sci. 36, 5369-77 (2001).**
2. **The Electronic Properties of Metal-Complexed Poly(3-Alkylthiophene) Films. PJS Foot, M Miah, V Montgomery and I Youngs, Mater. Res. Bull. 37, 2055-66 (2002).**
3. **Thermal Doping of Polyaniline by Sulfonic Acids. D Poussin, H Morgan and PJS Foot, Polymer International 52, 433-38 (2003).**
4. Synthesis and properties of a novel thiophene conducting copolymer with mesogenic groups attached parallel to the polymer backbone. J W Brown, G J Lambe, P J S Foot and J A Clipson. Macromol. Rapid Commun. **25,** 1000 (2004).
5. **Synthesis of Liquid Crystalline Conducting Polymers for Laser Alignment.** J W Brown, P J S Foot, L Gabaston, P Ibison and A Prevost. Macromolecular Chemistry & Physics **205**, 1823 (2004).
6. **Conductive Poly(Butadiene-*co*-Acrylonitrile)-Polyaniline Dodecylbenzenesulfonate [NBR-PAniDBSA] Blends prepared in Solution. K C Yong, P J S Foot, S J Cook and A J Tinker, European Polymer J. 42, 1716-27 (2006)**
7. **Conductive Polyaniline/Poly (Epichlorohydrin-*co*-Ethylene Oxide) Blends Prepared in Solution. Z K Abbas, S J Barton, P J S Foot and H Morgan. Polymers and Polymer Composites 15, 1-8 (2007).**
8. **Electrically-Conductive Epoxidised Natural Rubber-Polyaniline DBSA Blends. KC Yong, PJS Foot, H Morgan, S Cook, A Tinker, M Ahmad, J Rubb. Res. 11, 59-77 (2008).**
9. **Synthesis and Characterisation of Polyaniline/Montmorillonite Nanocomposites. A Shakoor, T Z Rizvi and P J S Foot, Polym. Polym. Comp. 17 (6), 347-52 (2009).**
10. **Properties of Thermally-Mixed Poly(Butadiene-*co*-Acrylonitrile)-Polyaniline Dodecylbenzenesulfonate Blends. *Submitted to J. Appl. Polym. Sci.***