Characterization of polyurethane and polyaniline blends for thermo-mechanical and electro-mechanical properties

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2016

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This research thesis is submitted to the Department of Polymer and Process Engineering, University of Engineering and Technology Lahore, Pakistan for the Partial Fulfillment of the requirements of Master’s degree in Polymer & Process Engineering.

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In the name of Allah

The Most

Gracious, the Most

Merciful

“O Allah, give me greater knowledge”.

(Taha-114)

Abstract

In this study electrical conductivity of organic polymers is enhance by addition of intrinsically conducting polymers (ICPs). ICPs are also organic polymers having both optical and electrical properties. Polyaniline is one of the most commonly used ICP due to its ease of processability, good thermal stability and low cost. The major problem and limitation in processing is the intractability of ICPs. There mechanical properties can be improved by using them in blends with elastomers. The blends of polyaniline and thermoplastic polyurethane with different ratios of Pani are investigated for thermo-mechanical and electro-mechanical properties.

First of all the blends are prepared by in situ polymerization method. Different ratios of Aniline.DBSA /TPU (20/80, 30/70, 40/60 and 50/50 wt %) are prepared. Once the sheets casted and dried, these are examined for various properties including **a)** spectroscopic analysis by using Fourier transforms infrared spectroscopy **b)** thermal properties by using thermo gravimetric analysis **c)** thermo mechanical properties by using dynamic mechanical thermal analyzer and electromechanical properties by using potentiostate.

By increasing the amount of aniline.DBSA wt%, the conductivity of the blends increased but on the other hand their mechanical properties are decreased by increasing aniline.DBSA upto certain limit.

This thesis is dedicated to

My parents and siblings

for their love and support during the time I spent away from home for my studies

&

My teachers

for their guidance and time which they spent on me for my studies

Acknowledgements

I would like to thanks my supervisor Dr. Muhammad Shafiq Irfan for giving me the opportunity to work on this project. His deep sense of knowledge, guidance, thoughtfulness and dedication to his work always inspired me to great extent. I am also hugely indebted to Engr. Dr. Shafiq Irfan's immense support during the write-up of my thesis.

I would also like to thanks Engr. Dr. Asif Ali Qaiser, Engr. Dr. Atif Javaid, Engr. Dr. Farhan Saeed, Engr Sajid Naseem and Engr. Nida Qamar for providing the moral support during my work.

I would like to thanks the laboratory staff of Department of Polymer and Process Engineering. I also wish to extend my thanks to the Department of Polymer and Process Engineering, University of Engineering and Technology Lahore for the funding and support.

I am grateful to my friends with whom I spent some great time during my stay in the UET Lahore.

Finally, I am indebted to my parents and siblings for their support and unconditional love. I can never re-pay their dedication and the sacrifices they have made for me.

Engr. Iqra Abdul Rashid

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Chapter 1

Introduction

1.1 Intrinsically conducting polymers (ICPs)

The polymers which can conduct electricity by virtue of their chemical structure are known as intrinsically conducting polymers (ICPs). In 1957 the first intrinsically conducting polymer was synthesized by doping polyacetylene which exhibit metal like properties(Svirskis et al. 2010). From last few decades a lot of work has been done on the synthesis and development of ICP's because of their advantageous properties like optical, electrical, flexibility, light weight, and ease of processing. Due to these properties they have been used in a wide variety of applications. They exhibit both electrical and optical properties; and have good environmental stability(Barra et al. 2008). Some prominent examples of ICPs are Polyanilie (Pani), Polythiophene (PTh) and Polypyrrole (PPy) as shown in figure 1.

Polyaniline is the most widely used ICP due to its low cost and ease of process ability(Bhadra et al. 2009)(Gospodinova & Terlemezyan 1998)(Bhadra et al. 2007). Polyaniline was first synthesized in 1960 from the polymerization of aniline in acid. After the complete characterization of polyaniline in 80's its excellent conductive and other properties were recognized(Bhadra et al. 2009).

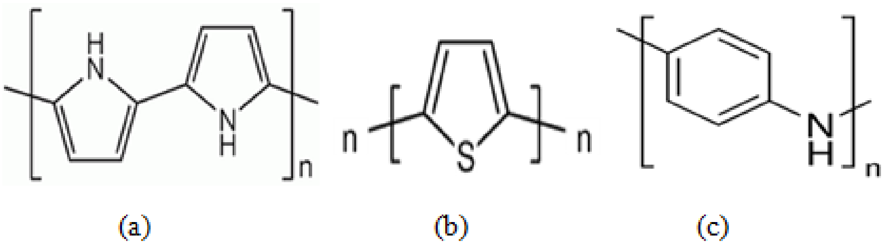

Figure 1 Structure of ICPs (a) Polyaniline (b) Polythiophene and (c) Polypyrrole

ICPs were synthesized by the oxidative polymerization of monomers usually through chemical oxidant or electrochemically to achieve the desired electromechanical and morphological properties by optimizing the polymerization process. In oxidation process a hole produced in ICP shows positive charge which was balanced by anionic doping (Svirskis et al. 2010). These were also called advanced functional polymers. These ICP's replaced the traditional intrinsically conducting polymers like metals and carbon black. They exhibit both electrical, optical properties and have good environmental stability(Barra et al. 2008).

Intrinsically conducting polymers were used for various applications like antistatic coatings, light emitting diodes, batteries, electrolytic capacitors, in sensor applications, and as corrosion inhibitors due to its ease of processing and were light in weight. In the field of biomedical ICPs were used for controlled drug delivery system(Holze& Wu 2014)(Holze 2011)(Guimarães et al. 2012)(Campos et al. 2010).

1.2 Polyaniline (Pani)

Among all the ICPs like polyaniline, polypyrrole, polythiophene and their derivatives, polyaniline was most widely used conducting polymer due to its ease of processability, high thermal and chemical stability, low cost and compatibility with other polymers(Han et al. 2002). It has good electrical and mechanical properties at ambient conditions and compatibility with common solvents(Hopkins et al. 2008). Electrical properties of polyaniline were controlled by a mechanism called protonation or doping(Luo et al. 2007). Pani has three different oxidation states leucco emeraldine, emeraldine and pernigraniline(Elkais et al. 2011).

Pernigraniline and emeraldine exist in base and salt forms due to protonation and deprotonation which depends upon the PH as shown in figure 2. Emeraldine base has blue color while emeraldine salt has green color, and they have excellent conductivity for various applications. Pernigraniline base shows purple color and pernigraniline salt has blue or black color.

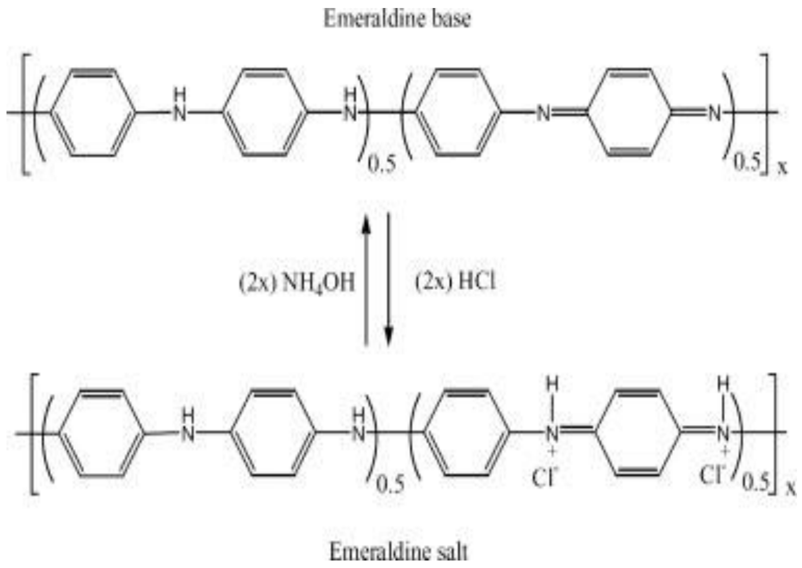

Figure 2 Polyaniline protonation and deprotonation (Pretula et al)

The properties of polyaniline was enhanced by polymerization with different acids like phosphoric acid, sulfuric acid, sulfonic acid and phosphonic acids(Tahir et al. 2005). Different methods were used for the synthesis of polyaniline like chemical polymerization, electrochemical polymerization and enzymatic polymerization. All these methods are used with the passage of time and depend on the applications.

The disadvantage of chemical oxidation reaction was conducted in severe conditions like acidic media and excess quantity of ammonium persulfate. But the yield of Pani in chemical oxidation reaction was high and about 90% of Pani has been obtained. Another method used for the synthesis of polyaniline was enzymatic polymerization because it was carried out in less severe conditions in comparison with chemical polymerization method. Pani was also synthesized by electrochemical oxidative polymerization method. This method showed higher solubility, low conductivity, lower crystallinity and larger particle size than chemical polymerization method(Universit et al. 2006).

1.3 Blends of polyaniline and elastomers

The poor mechanical properties and processability of polyaniline limits its use in different commercial applications for that reason it was blended with different polymers(Lakshmi et al. 2009). Polyaniline has solubility issues with the polymers and its blends undergone phase separation which caused lower conductivity and decreased the mechanical properties. To overcome these problems, Pani was blended with different block copolymers or protonic acids with long alkyl chains including dodecyl benzene sulfonic acid (DBSA) and hydrochloric acid (HCl). These were soluble in dimethyl formamide, toluene and xylene solvents (Wang et al. 2003)(Pan et al. 2005).

There were various methods used for the polymerization and preparation of these polymer and ICPs blends. These were either chemical or electrochemical synthesis method depends on our requirements. Chemical synthesis can be classified into solution blending, dispersion and emulsion polymerization, melt processing and chemical in-situ polymerization(Njuguna& Pielichowski 2004).

Blends of Pani with a number of polymers have been reported in the literature for various applications(Rodrigues & Akcelrud 2003). An interesting category in the polymer-Pani blends is the elastomer-Pani blends where the elastomers act as the host matrix and Pani is added to it as the conducting reinforcing filler. There were two types of elastomers thermosetting and thermoplastic elastomers. Thermoset elastomers were cured or vulcanized for cross linking between the chains of polymers. These were introduced commercially in 1960(Anon n.d.). They have the properties of vulcanized rubber. But the major difference in thermoplastic and thermosetting elastomers, one is re-useable and other is non re-useable material respectively.

Thermoplastic elastomers were used in a wide range of applications like footwear, automobile parts, sensors etc. but the drawback was their poor resistance to heat and chemicals. We have different types of elastomers like natural rubber (NR)(Jonas et al. 2014), Ethylene propylene diene monomer (EPDM), Polyurethane (PU)(Li et al. 2013) and Styrene butadiene rubber (SBR) etc.

1.4 Thermoplastic Polyurethane (TPU)

Thermoplastic polyurethane (TPU) is one of the widely used engineering thermoplastic due to its elastic properties and it was developed in 1937(Anon n.d.). It was categorized in two groups based on soft segments containing polyether (Tetra hydrofuran ethers) and polyester (derived from adipic acid esters) reinforced with hard domain consists of aromatic diisocyanate through condensation expended with short chain diol. TPU has high elasticity, abrasion resistance, oil resistance, low temperature performance and high shear strength(Boubakri et al. 2010). It was used in electronic devices, protectors for laptop keyboard, sheets, medical devices, and in sport goods applications(Anon n.d.).

1.5 Purpose of the study

The purpose of this research was to investigate the thermo-mechanical and electro-mechanical properties of Pani/TPU blends. The blends were prepared by in-situ polymerization of Pani in the TPU/DMF solution. It was shown that the proposed blends can be used in strain sensing application.

Chapter 2

Literature Review

2.1 Stretchable electronics

In present world, the electronic devices are intelligent, advance and portable. Stretchable electronics have both conducting and flexible properties which made them most widely used materials for breath detection, pulse movement, human motion and in other fields as shown in figure 3(Li et al. 2013). Conductivity, flexibility and sensitivity are three main parameters on which stretchable electronics works. For making different types of stretchable electric materials, fibers, Graphene, and different elastomers like natural rubber, polyurethane, ethylene propylene etc were used with conducting materials. Polyanilne was preferred ICP because of ease in processing with elastomers and environmental stability(Li et al. n.d.).

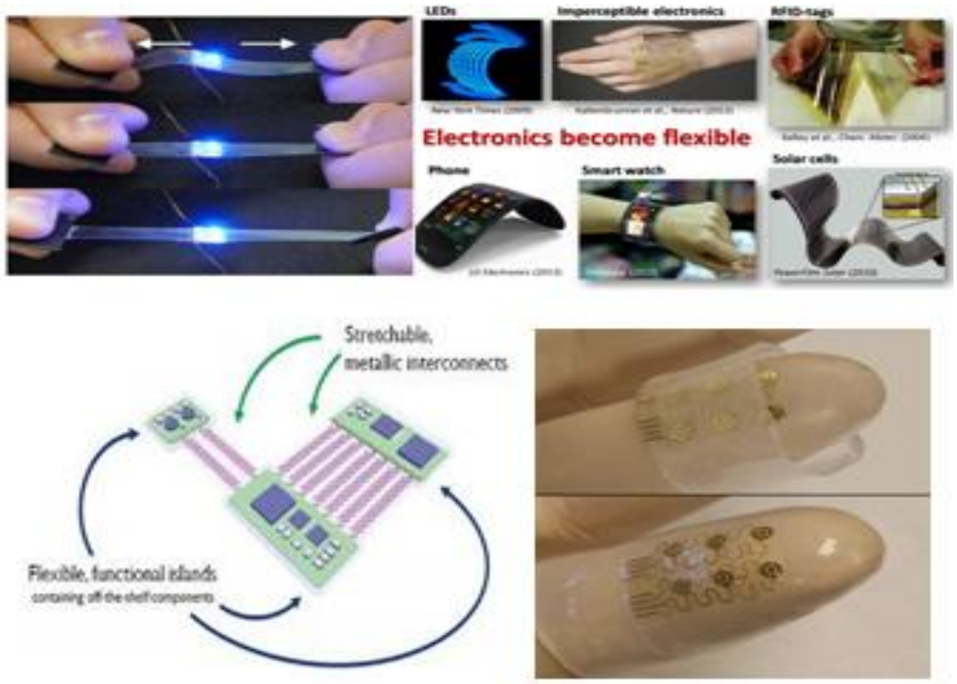

Figure 3 Applications of strain sensor (Kim & Kim 2011)(Li et al. 2013)

In these materials, elastomeric base provided the mechanical strength, stretching and flexibility while the conducting filler provided the path to the electric current. As the local clustering of the filler changed with the strain the amount of current passing through the sample varied that correlate to the amount of strain.

Eliana L. Tassiet al prepared elastomeric electroactive material of nitrile rubber with aniline through electrochemical graft copolymerization(Tassi 1992). They have reported polyaniline and nitrilic rubber graft copolymer and studied their electro chromic, electromechanical properties through frequency response and cyclic voltametry. Mechanical properties were studied through stress strain measurements. R. Vallim et al prepared polyaniline and nitrilic rubber blends through mechanical mixing by using roll mill and then vulcanized in compression molding machine. These blends were brittle and harder than crude rubber. It was shown that in elastomers, polyaniline increased the reinforcing effect and degree of cross linking was decreased(Vallim et al. 1999).

Bluma G. Soares et al prepared polyaniline and nitrile rubber based electrically conductive blends doped with dodecyl benzene sulfonic acid through in-situ polymerization method. The conductivity values deceased after vulcanization of the blends. The conductivity values of the in-situ polymerized blends were better rather than the blends prepared through mechanical mixing(Dbsa et al. 2006).K. C. Yong prepared NBR and Pani blend doped with dodecyl benzene sulfonic acid and vulcanized with dicumyl peroxide (DCP). Blends were prepared using thermo mechanical mixing. These blends showed good electrical conductivities and mechanical properties (tear strength and tensile strength). Due to these excellent properties these blends were used as flexible stain sensors(Yong 2011). R.A. Zoppi et al prepared polypyrrole/EPDM based conductive elastomeric blends through chemical oxidation of monomer with $FeCl_{3.}$ These blends were characterized through electrochemical impedance spectroscopy and cyclic voltametry(Zoppi 1997). Roselena Faez et al prepared polyaniline based elastomeric conductors through mechanical mixing and their thermal, electrical, morphological and mechanical characteristics were studied. By increasing the polyaniline concentration in the blends their modulus increases which showed a good reinforcement effect(Faez et al. 1999). They also prepared polyaniline and EPDM based conductive blend and DBSA was used as dopant. Grinding in a mortar, solution and reactive processing methods were used for doping. EPDM was partially soluble which showed partial interaction in the components. The blends were prepared without crosslinking agent through reactive processing(Faez& Paoli 2001). They prepared polyaniline and EPDM based conductive blend by using crosslinking methods. The first one was electron beam irradiation and secondly through phenolic resin SP-1045. The first method produced highly conductive blends(Faez et al. 2002) .

S. C. Domenech et al prepared functionalized EPDM and polyaniline base conductive blends through casting. Maleic anhydride was used for the functionalization of EPDM. Oscillating disk rheometer was used for optimization of vulcanization conditions. The blends were analyzed by wide-angle X-ray scattering, thermogravimetric analysis, atomic force microscopy and transmission electron microscopy(Domenech et al. 2004). V. Schmidt et al prepared polyaniline and EPDM blends by casting from organic solvents. For the crosslinked blends the activation energy was higher than those of non-crosslinked blends and pure components(Xie et al. 2004). Daniela A. Alvares et al prepared Pani and EPDM blends by mechanical process. These blends showed good conductivity and were used for devices like pressure, weight measure and touch pads(Moreira et al. 2006). Bjorn Sonerud et al prepared polyaniline, EPDM and carbon black filler based blends. The mechanical properties were unaffected by variation in filler content(Sonerud et al. 2013).

2.2 Blends of Polyaniline and Thermoplastic polyurethane

A summary of the previous work performed in the field of TPU/Pani and PU/Pani blends is provided in Table 1. T. Jeevananda et al worked on Pani filled PU/PMMA IPNs and studied the effect of amount of Pani on the properties like dissipation factor, dielectric constant, percentage elongation at break and tensile strength. The results showed that CSA doped pani incorporated with PU/PMMA interpenetrating polymer networks(IPNs) has improved tensile strength from 1.16 to 1.38 MPa. Pani acted both as a conducting and reinforcing filler in PU/PMMA matrix. Due to the individual component network the surface morphology showed two distinct phases. Upon the addition of CSA doped pani above 5% in PU/PMMA network crystal growth was observed (Jeevananda 2008). Paula C. Rodrigues et al prepared polyaniline and polyurethane blends and networks and also studied there dynamic mechanical, thermal and electrical properties. The interaction between the Pani and PU chains was studied by new decomposition temperature in TGA, shifts of –NH- and carbonyl absorption peaks in infrared spectra as compared to pure components and good mechanical properties showed in DMA analysis(Rodrigues & Akcelrud 2003).They prepared Pani/PU networks for spectroscopic study. Morphological study showed that through interphase Pani was embedded in polyurethane that was responsible for connectivity. In doped or non-doped phase the crosslinking of pani with polyurethane has no effect on the electronic transition showed in UV-Vis spectra. While the blends shifted 21nm compared to pani which showed that due to the covalent linkages with polyurethane pani chains were more extended in networks than in blends(Rodrigues et al. 2005).

Table 1 Literature survey of blends prepared through PU, TPU and aniline

Author	**Year**	**Rubber**	**Conducting polymer**	**Method**	**Conductivity**	**Characterization**
Y. Zwang	2002	PU	Pani	Solution mixing	6.17×10^{-5}S/cm	FTIR, 4 Probe
T. Jeevananda	2002	PU/PMMA	Pani	Solution mixing	3.78×10^{-2} S/cm	SEM, TGA
Ching-PiouChwang	2003	PU	Pani	Solution mixing / in-situ polymerization	10^{-4} S/cm	TGA, SEM, conductivity test
Paula C. Rodrigues	2003	PU	Pani	Mechanical mixing	10^{-4} S/cm	FTIR, TGA, 4 Probe
Paula C. Rodrigues	2005	PU	Pani	Mechanical mixing	10^{-4} S/cm	FTIR, conductivity test

Hitoshi Yoshikawa	2006	PU	Pani	Co-dissolution	10^{-5} S/cm	OPM, TEM
Erika Hrehorova	2007	PU	Pani	Solution mixing	10^{-5} S/cm	Optical microscope,
Denice S.Vicentini	2007	TPU	Pani	Solution mixing / in-situ polymerization	1.7×10^{-5}/6.9×10^{-5}S/cm	4 Probe, Keithley electrometer 614, TGA, FTIR
Jing Luo	2007	PU	Pani	Mechanical mixing	10^{-4} S/cm	FTIR, conductivity test, SEM
T. Gurunathan	2012	PU	Pani	In-situ polymerization	1.5×10^{-2} S/cm	DMA, Conductivity test

Denice S. Vicentini et al studied the electrical and thermal properties of Polyanilne and thermoplastic polyurethane based blends. They used tetrahydrofuran as a common solvent for both polyaniline (Pani) and thermoplastic polyurethane (TPU). Dodecyl benzene sulfonic acid was used as a doping agent. Solution casting and in-situ polymerization techniques were used. They measured electrical conductivity by using four- probe method and thermal characterization was performed by using thermo gravimetric analyzer. Low conductivity values were observed due to the immiscibility of TPU with Pani.DBSA and gross phase separation occurs in the solution casting blends. In-situ polymerized blends showed enhanced compatibility of the blends, higher conductivity values and fine dispersion(Vicentini et al. 2007). Erika Hrehorova et al studied the polyurethane elastomer and polyaniline composite fractal behavior and electrical properties under mechanical deformation. Pani was doped with HCl and PU/Pani-HCl film composites were prepared. They used chemical polymerization and solution mixing techniques. Chemical polymerization technique showed nonlinear electrical behavior with surface modified composites. Solution mixing showed volume modified composites with linear current voltage characteristics. Mechanical stress showed change in conductivity and electrical behavior. Conducting paths were fractured by increasing mechanical stress (elongation) due to the increase in distance between the conductive chains. Increase in electrical conductivity was depend on the interaction between the component of the composite(Hrehorova et al. 2007).

Jose Humberto Santos et al studied thermoplastic polyurethane and castor oil based membranes which were modified with polyaniline which was doped with p-toluene sulphonic acid. These membranes were characterized by Fourier transform infrared spectroscopy, electrical conductivity, thermogravimetric analysis and dynamic mechanical analysis. These membranes have good thermal stability up to 220^{0}C and good mechanical properties. These were used in separation techniques(Almeida Júnior et al. 2013).

F.D.R. Amado worked on polyaniline/polyurethane membranes for the recovery of zinc through electro dialysis. Pani doped with camphor sulfonic acid (CSA) and p-toluene sulfonic acid (pTSA). These membranes showed better results than Nafion 450 commercial membrane and show thermal stability upto 200^0C. Degradation of membranes started above this temperature. FTIR results showed the polyaniline blend in polyurethane matrix, the peak at 1034 cm^{-1} showed the S=0 group(Amado et al. 2005). Mufang Li et al studied Polypyrrole (PPy)/Polyurethane (PU) strain sensors. They used scanning electron microscope (SEM) for morphological study. The electrical conductivity was measured using four point probe resistivity meter and LCR meter. FTIR and SEM results showed that Py was diffused completely into the porous structure of PU due to the in-situ polymerization technique(Li et al. 2013).

Chapter 3

Experimentation

3.1 Materials

Thermoplastic polyurethane (Hardness Shore A 85, density 1.02 g/dm^3) was locally purchased from Tariq plastics Lahore. Aniline was purchased from Merk Schuchardt, Germany. Dodecyl benzene sulphonic acid (DBSA) was purchased from Aldrich chemistry. Ammonium per sulphate (APS) and Dimethyl formamide (DMF) were purchased from Dae Jung Kosdaq.

3.2 Synthesis of Ani.DBSA/TPU blends

Ani.DBSA/TPU blends were prepared using in situ polymerization method. TPU was dissolved in dimethyl formamide (DMF). DBSA and aniline were dispersed in 50 ml of DMF and this solution was added into dissolved TPU. APS solution was added drop wise to the previously prepared solution. The whole mixture was stirred for at least 6 hours in an ice bath at 5°C so that the polymerization reaction was completed. Then green solution was casted with the help of an applicator on a glass plate and left to dry for 24 hours. These films were washed with hot distilled water for the removal of all the solvent, impurities and unreacted monomers. The sheets were dried in a vacuum oven for 12 hours. The films were prepared varying the ratio of aniline as shown in table 2. The whole procedure is shown in schematic figure 4 and the prepared sheet is shown in figure 5.

The sheets were then characterized by using Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), dynamic mechanical thermal analyzer (DMTA) and potentiostate.

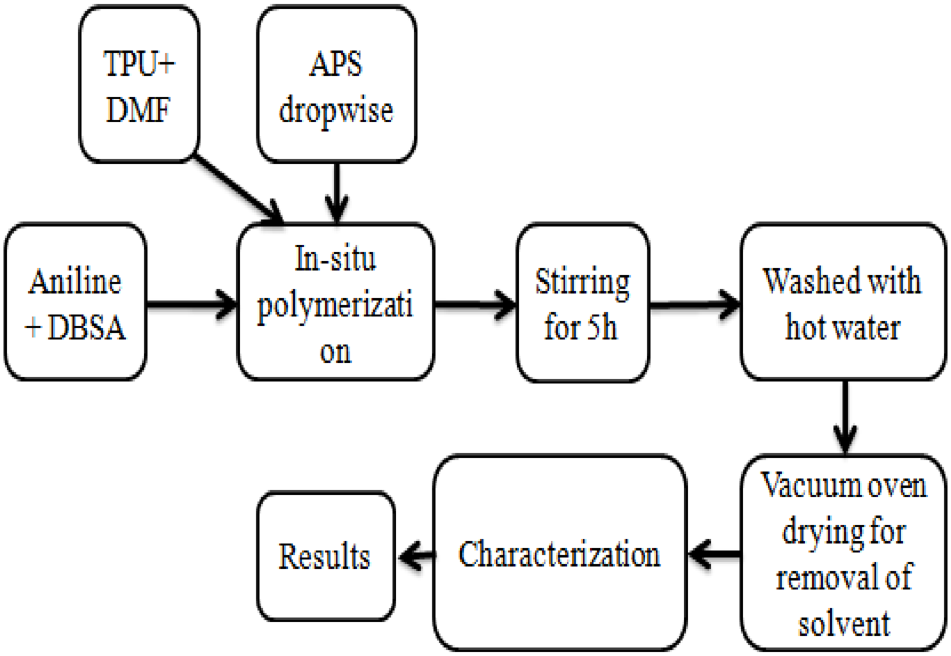

Figure 4 Step-wise emulsion polymerization process

Table 2 Different weight ratios of Ani.DBSA/TPU

Sr. no	**Ani.DBSA/TPU**
1	0/100
2	20/80
3	30/70
4	40/60
5	50/50

Figure 5 Aniline.DBSA/TPU prepared sheet

3.3 Characterization of Ani.DBSA/TPU films

3.3.1 Conductivity measurement

Electrical conductivity of the films was measured using potentiostate. The value of voltage and current were obtained and then resistance was calculated by using the following formula:

$$R = V/I \tag{1}$$

By using the calculated mean resistance values electrical conductivity was calculated by using the formula:

$$\sigma = [1/R][L/A] \tag{2}$$

σ = Electrical conductivity

R = Mean resistance of the film sample

L = Electrode spacing distance

A = Cross sectional area of the film sample

Samples were prepared in rectangular shape and dimension was 6×5×0.5mm. Then these samples were clamped on manual rig which measured the change in strain values. The rig was attached with the potentiostate for electrical resistance measurements.

Through potentiostate we can also find the electrical conductivities of different blends of rubbers with polyaniline, electrolytes and different types of composites. It gives us the value of voltage and current and then we can calculate the value of resistance by using the formula

$$V = IR$$

3.3.2 Attenuated total reflectance (ATR)

ATR spectra of different blends were recorded using JASCO FT/IR-4100 infrared spectrometer as shown in figure 6 for peak analysis. This showed either the required functional groups were present or absent. Obtained ATR spectra were compared with standard peaks of polyurethane and polyaniline. The spectra of the blends were obtained in the wave number range of 400-4000 cm^{-1}. Samples were cut from the prepared sheet and direct place into ATR for analysis.

Figure 6 Fourier transform infrared spectroscopy

3.3.3 Thermo gravimetric analysis (TGA)

Thermo gravimetric analysis of pure TPU film, Ani.DBSA and different blends of aniline.DBSA/TPU was performed using Shimandzu Thermo gravimetric Analyzer TGA-50 as shown in figure 7. Experiments were performed under inert atmosphere and at 25 - 600°C at the heating rate of 20°C min^{-1} and rate of flow 100 ml/min. Samples were completely dried in a vacuum chamber before analysis. For TGA testing nitrogen was preferred rather than air atmosphere. Sample of 10 mg were prepared in an aluminum pan and an empty pan was used for reference. These both pans were placed in TGA chamber with heating rate of 20ºC/min till the temperature reached up to 600ºC.

Figure 7 Thermogravimetric analysis

3.3.4 Dynamic mechanical thermal analyzer (DMTA)

Dynamic thermo-mechanical behavior of Aniline.DBSA/TPU blends were characterized by using DMA (Q-800, TA Instruments USA) as shown in figure 8. The experiment was performed using rectangular samples in tension mode to calculate tensile strength, elongation at break and modulus. The dimensions of the samples used in DMTA analysis was 5.00×7.00×0.5 mm.

Figure 8 Dynamic mechanical thermal analyzer

Chapter 4

Result and discussion

4.1 Attenuated total reflection (ATR)

Attenuated total reflection provides absorption spectra. It tells us at each wavelength how a sample absorbs light. ATR is used to analyze the different functional groups in the blends of polyaniline and TPU. The ATR spectra of Ani.DBSA, pure TPU and blends of Ani.DBSA/TPU are shown in Figure 9.

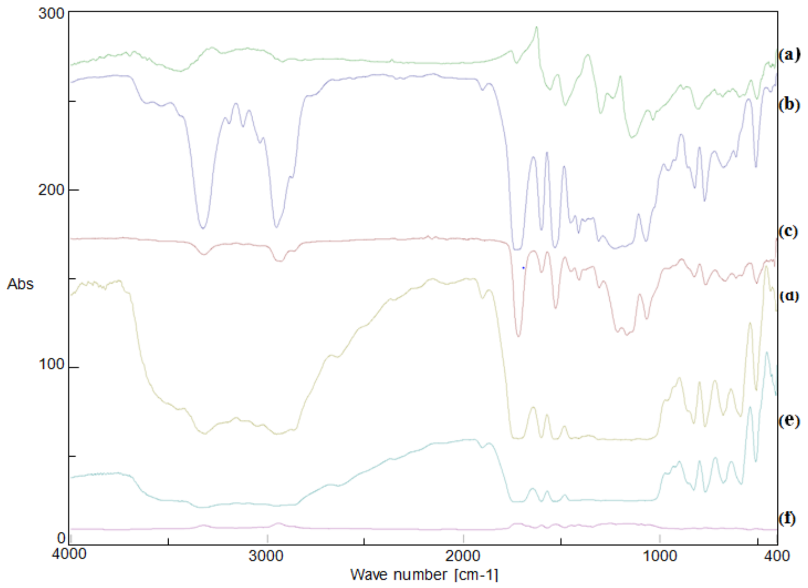

Figure 9 ATR spectra of (a) Ani.DBSA (b) Pure TPU (c), (d), (e) and (f) are Ani.DBSA /TPU blends 50/50, 40/60, 30/70 and 20/80 ratios prepared through in-situ polymerization

ATR spectra of pure Ani.DBSA shows absorption peaks in the region of 1481cm^{-1} due to C=N stretching and another peak shows in the region 1141 cm^{-1} due to C-H in plane bending. A peak in the region of 804 cm^{-1} due to C-H out of plane bending observes which shows the sulfonic group stretching vibrations. A pure TPU and Ani.DBSA/TPU blend shows absorption peaks in the region 3325-3240 cm^{-1} is due to N-H strong stretching. The peaks in the region 2950 cm $^{-1}$ shows

CH_2 medium anti-symmetric stretching. The C=O strong stretching shows a peak in the region 1740-1720 cm^{-1} due to parent molecules hydrogen bonding.

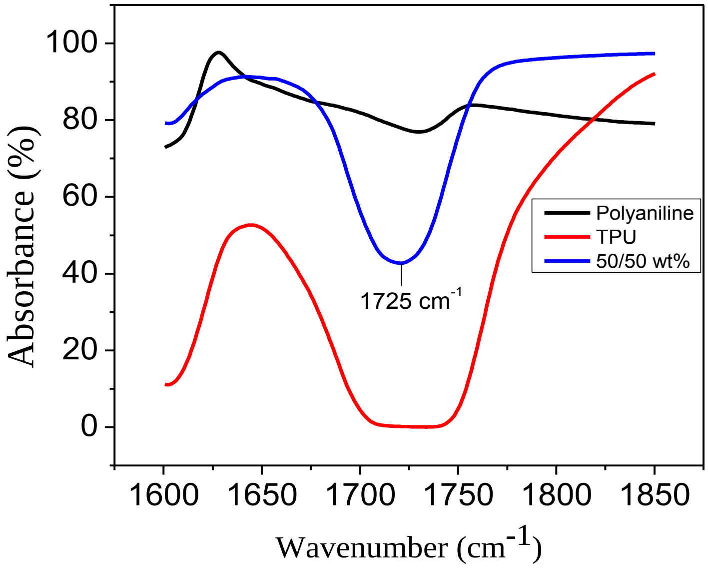

Figure 10 ATR finger prints shows overlay of polyaniline, pure TPU and 50/50 wt% of Ani.DBSA/TPU blends shows peak at 1725 cm-1

Figure 10 in range 1850–1600 cm^{-1} show the ATR spectra of polyaniline, pure TPU and 50/50 wt% blend of Ani.DBSA/TPU prepared by in situ polymerization method shows amine and carbonyl groups interactions at around 1725 cm^{-1}. These blends and pure TPU shows amine and carbonyl group interactions at around 1725 cm^{-1}(Vicentini et al. 2007). The graph clearly shows that pure pani has weak intensity, pure TPU has medium intensity of peak and the blend of aniline.DBSA/TPU has sharp peak which shows the completion of chemical reaction.

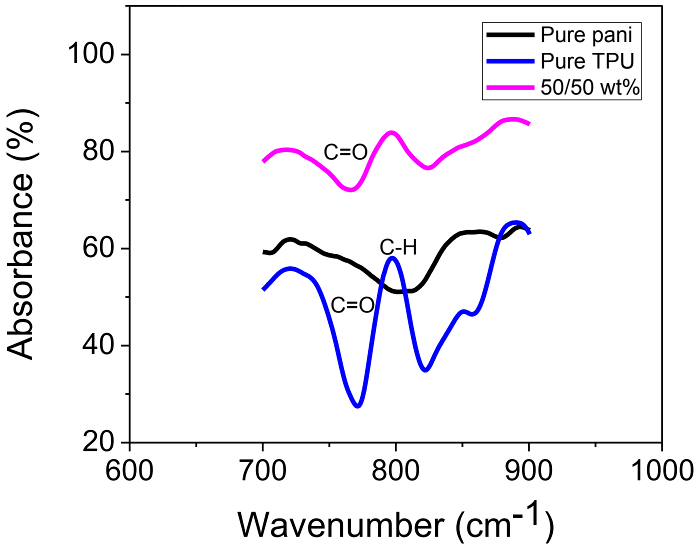

Figure 11 ATR fingerprint representing peak shift at 767cm-1

Figure 11 shows the shift of peaks in the blend of TPU and aniline.DBSA. From the graph it is clear that Pure TPU has C=O functional group at around 771 cm^{-1} while the blend has this functional group at 767 cm^{-1} shows the peak shift. Pure pani in this region has no such peak. At 806 cm^{-1} pure pani has C-H stretching while the blend has peak shift at around 825 cm^{-1}. It is concluded that aniline.DBSA/TPU blends contain both the functional groups of aniline.DBSA and pure TPU but with variation in peak intensities which confirms the chemical reaction occurs in the blends.

4.2 Thermo gravimetric analysis (TGA)

Ani.DBSA/TPU films ratios 20/80, 30/70, 40/60 and 50/50 wt% shows three main regions of mass loss. The first degradation region is due to the evaporation of water molecules. The second region degradation is due to the solvent and water molecules removal. The third region shows the combustion of the materials. If we dry the films completely in the vacuum oven and then characterize them the mass loss is reduced.

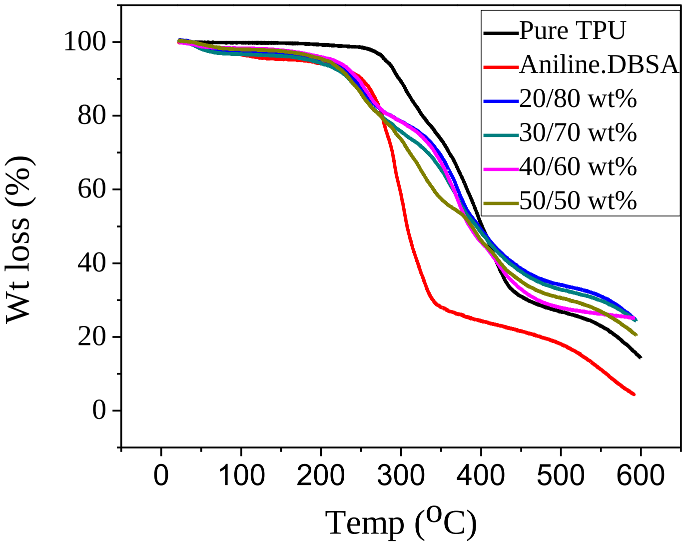

Figure 12Thermo gravimetric curves for pure TPU, Pure Pani, and Ani.DBSA/TPU blends in ratios20/80, 30/70, 40/60 and 50/50

Ani.DBSA/TPU blends are chemically bounded and mass loss is decreased because they are thermally stable.

Figure 12 shows that the pure TPU is stable upto 266.1°C. A little drop in weight is due to evaporation of moisture and volatile components. Onset occurs at 266.1ºC and a decrease in mass is observed. Offset occurs at 432.24ºC. Total mass loss of pure TPU is 85.22% and residual about 14.78%.

The presence of different components in aniline.DBSA the region before 261ºC is stable due to the long chain acidic medium of doping agent (DBSA). Small decrease in mass occurs due to the unreacted components methanol and other impurities. Onset occurs at 262ºC and offset at 334ºC, mass loss is 95.6% and residual about 4.35%.

Blends of aniline.DBSA and TPU prepared through in-situ polymerization shows different values of mass loss. The blend with 20/80 wt% shows onset at 247.4ºC before onset point a weight loss upto 5.06% occurs due to the thermally unstable components like impurities and moisture present in the blend. Between onset

247.4ºC and endset 423.77ºC region a decrease in mass is due to the thermal degradation of the blend. At higher temperature the blend is stable and mass loss of 75% occurs.

Increase aniline concentration shows increase in mass loss and less residual remain. 30/70 wt% blend shows onset at 221.7ºC and offset occurs at 385.12ºC. The mass los is 76%. Figure 12 show that the onset temperature of all the blends with different ratios of aniline.DBSA is almost same which shows the thermal stability of the blends.

The optimum blend is 30/70 wt% which shows 76% mass loss. Overlay of all the blends, pure TPU and aniline.DBSA shows that pure TPU and blends are thermally more stable than pure aniline.DBSA and blends show less mass loss than pure TPU and pure aniline.DBSA.

4.3 Dynamic Mechanical Thermal Analyzer (DMTA)

The thermo mechanical properties like tensile strength, modulus and elongation at break of conductive blends of polyaniline and TPU were measured using dynamic thermal analyzer at temperature 30°C using tension mode. All the specimens have length, width and thickness of 5, 7 and 0.7 mm respectively. Three samples of aniline.DBSA, pure TPU and each ratio 20/80, 30/70, 40/60, 50/50 wt% of aniline.DBSA/TPU was tested and then average value was calculated.

The tensile strength of the films decreases with the increase in aniline ratio in the blends because of the weak hydrogen bonding between urethane blocks and aniline oligomers. Young’s modulus decreases and then increase with the increase in aniline content in the blends. Elongation at break values decreases with the increase in Ani.DBSA concentration because there is weak interaction between TPU and Ani.DBSA blends and there is weak hydrogen bonding between them. As shown in table 3 and figure 13.

Table 3Thermo mechanical properties of Ani.DBSA/TPU different wt% at 30^{0}C.

Aniline/TPU	**Tensile strength MPa**	**Elongation at break %**	**Young's modulus MPa**	**Surface Hardness (shore A)**
0/100	12.5±0.35	738±29	4.8±0.20	85±1
20/80	1.13± 0.31	597±12.74	0.87±0.23	84±1
30/70	1.08± 0.03	421±39.9	0.64±0.21	83±1
40/60	0.91±0.08	189±29.6	0.90±0.08	82±1
50/50	0.2±0.02	132 ±5.0	0.29±0.28	80±1

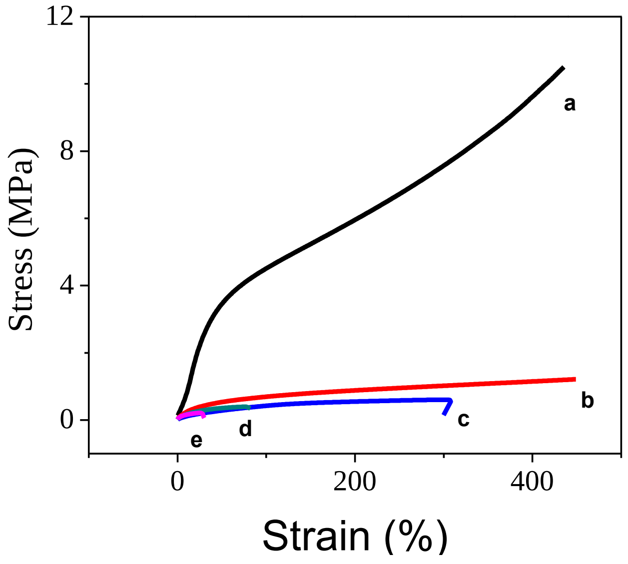

Figure 13 Stress strain curves of (a) Pure TPU (b), (c), (d) and (e) blends of Ani.DBSA/TPU 20/80, 30/70, 40/60 and 50/50 wt% respectively

4.4 Conductivity measurement

4.4.1 Volumetric and surface conductivity

The Ani.DBSA/TPU blends in the ratio 20/80, 30/70, 40/60 and 50/50 wt% prepared through in-situ polymerization shows electrical conductivities in the range 7.0 ×10^{-6}, 2.24 × 10^{-5}, 8.46 × 10^{-6} and 9.5 × 10^{-6} S/cm respectively. In Fig 14 the behavior shows that the volumetric conductivity value increases by increasing the amount of Ani.DBSA in the blends but decreases at higher values of Ani.DBSA e.g. at 40 and 50 wt%.. This decline behavior in conductivity was due to the fracture in connecting paths and weak interactions between the chains(Anon n.d.).This means maximum conductivity achieved at 30 wt% of polyaniline.

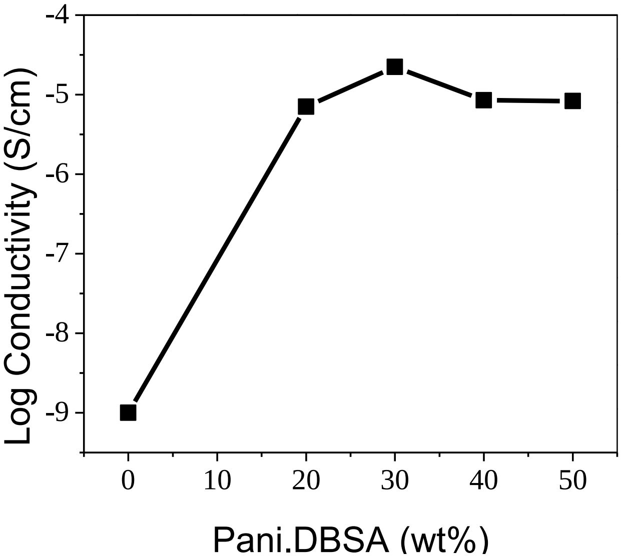

Figure 14 Electrical conductivities of Ani.DBSA/TPU blends

Surface conductivity

Figure 15 and figure 16 shows the electromechanical properties of the blends prepared through in-situ polymerization. Surface conductivity is measured as a function of stretching and compressing cycles of specimen Ani.DBSA 30 and 40 wt% ratios respectively. The graph shows clearly that at strain upto 10% the electrical conductivity has direct relationship with strain which shows good repeatability when the test was performed for 10 consecutive cycles.

A small deflection in conductivity values is due to the manual adjustment of strain rate. The change in conductivity value appears at 10% elongation is due to the breakage in electronic flow path. Conductivity values changes after compressing and stretching due to the change in chain alignments. By stretching the conductivity value decreases because of the cracks produced between Ani.DBSA and TPU blended samples(Soares et al. 2006). Upon compressing conductivity again increases. In figure 14 and figure 15 "C" corresponds to compressing and "S" corresponds to stretching.

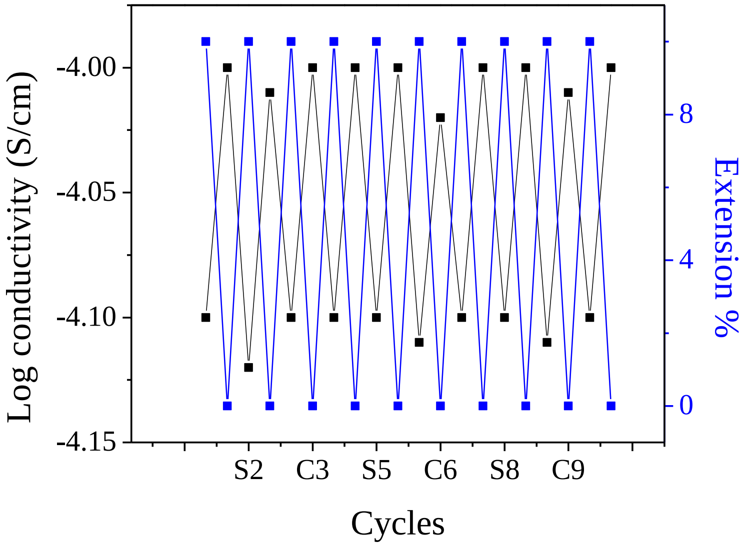

Figure 15Conductivity as a function of stretching and compressing cycles of Ani.DBSA/TPU 30/70 wt% blend

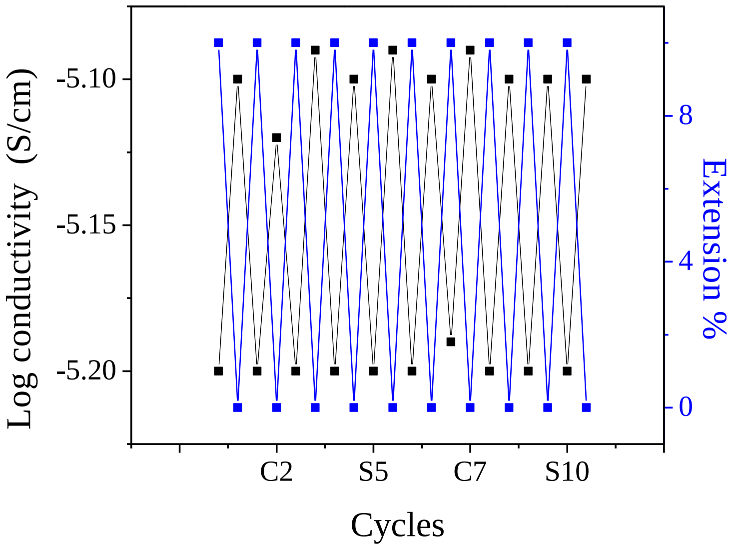

Figure 16 Conductivity as a function of stretching and compressing cycles of Ani.DBSA/TPU 40/60 wt% blend

Chapter 5

Conclusions and future work

The conducting polymer blends of Ani.DBSA/TPU were prepared via in-situ polymerization process which shows better dispersion, compatibility, elasticity and conducting paths. These blends were used for different applications for example in flexible strain sensors. These blends were thermally stable upto 230°C. The electrical conductivity values increased with the increase in Ani.DBSA wt% at a certain limit in the blends. Maximum conductivity showed at 30 wt% of Ani.DBSA. The electromechanical properties of the blends were good and the pattern of the electrical conductivity with the mechanical properties was uniform. By compressing the conducting films the electrical conductivity increased because of the better interaction in Ani.DBSA and TPU blends. But by stretching the conductivity values decreased because less interaction between Ani.DBSA and TPU blends due to the fracture in conductive paths. These blends were also used in application for flexible strain sensors because of their good electrical conductivity, repeatability and thermal stability.

Future work recommendations

Different doping agents like Sulfonic acids, Phosphonic acids, and Phosphoric acid diesters may be used with aniline

Polypyrrole and polythiophene (ICPs) may be used with other elastomers (NBR, NR, and EPDM)

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