

STRUCTURE AND PROPERTIES OF PROCESSIBLE CONDUCTIVE POLYANILINE BLENDS

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List of Patents:

1. “A process for the preparation of polymer films having high solvatochromic effect”, S. Radhakrishnan, **V. Sreejith**, Indian Patent Applied, 937 / DEL / 2002, dated 16.09.2002.
2. “A process for the preparation of conducting polymer films with high optical transparency”, S. Radhakrishnan, **V. Sreejith**, Indian Patent Applied, NF – 356 / 2003, dated 19.08.2003.
3. “A process for the preparation of conducting polymer moulding compound with improved processability”, S. Radhakrishnan, **V. Sreejith**, Indian, European and United States Patents Applied, NF-420 / 2003, dated 01.10.2003

CHAPTER - I
INTRODUCTION

1.1 INTRODUCTION:

The twentieth century witnessed a tremendous change in the human life style due to the revolutionary discoveries and developments in the field of polymer science and engineering. There is a long history of successful development, which came from the enormous contributions of numerous people¹. The development of conducting polymers become one of the most promising field since the discovery of intrinsically conducting polymers by Alan J. Heeger, Hideki Shirakawa and Alan G. MacDiarmid ² in 1977, for which they were awarded the Nobel Prize in Chemistry, 2000. These polymers are assumed to have tremendous applications in different fields, especially in the electronic industry. But the major concern in this area is the processibility of these polymers as most of them are not stable at processing conditions. Hence, the main objective of the present work is the attainment of processibility in these conducting polymers and their blends.

1.1.1 CONDUCTING POLYMERS:

Conducting polymers can be classified mainly into three types:

- a) Intrinsically / inherently conducting polymers (ICPs),
- b) Conducting polymer composites, and
- c) Ionically conducting polymers.

Our field of interest is mainly concentrated on Intrinsically conducting polymers and improvement of its processability.

INTRINSICALLY CONDUCTING POLYMERS (ICPs):

An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical

properties, processibility etc. commonly associated with a conventional polymer, is termed an “intrinsically conducting polymer” (ICP) more commonly known as “synthetic metal”³. In 1975, the first papers on the novel metallic polymer, poly (sulfur-nitride), (SN)_x appeared in the literature. It was in 1976 that A.G.MacDiarmid, H.Shirakawa, A.J.Heeger and coworkers discovered organic conducting polymers and their ability to dope these polymers over the full range from insulator to metal^{2,4}. They had carried out doping experiments on polyacetylene with bromine at the University of Pennsylvania on Tuesday, the 23rd of November 1976 and subsequently with iodine^{2,4,5}. That event heralded the dawn of a new era of conducting polymers.

The most common examples of intrinsically / inherently conducting polymers are Polyacetylene, Polyaniline, Polypyrrole, Polythiophene, Poly(p-phenylene), Poly(phenylene vinylene) etc. The Figure 1.1 shows some of the conjugated polymers, which have been studied as intrinsically conducting polymers.

The unique electronic properties of the conjugated polymers are derived from the presence of Π - electrons, the wave functions of which are delocalized over a long portion of the polymer chain when the molecular structure of the backbone is planar. It is therefore necessary that there are no large torsion angles at the bonds, which would decrease the delocalization of the Π - electrons system⁶.

The essential properties of the delocalized Π - electrons system, which differentiate a typical conjugated polymer from a conventional polymer with σ - bonds are as follows: (a) the electronic (Π) band gap (E_g) is relatively small (~ 1 to 3.5 eV), with corresponding low excitation and semi-conducting behaviour; (b) the polymer molecules can be easily oxidized or reduced, usually through charge transfer with atomic or molecular dopant species, to produce conducting polymers; (c) net charge mobilities in the conducting state are large enough so

that high electrical conductivities are realized, and (d) quasi – particles, which, under certain conditions, may move relatively freely though the material ^{7,8}.

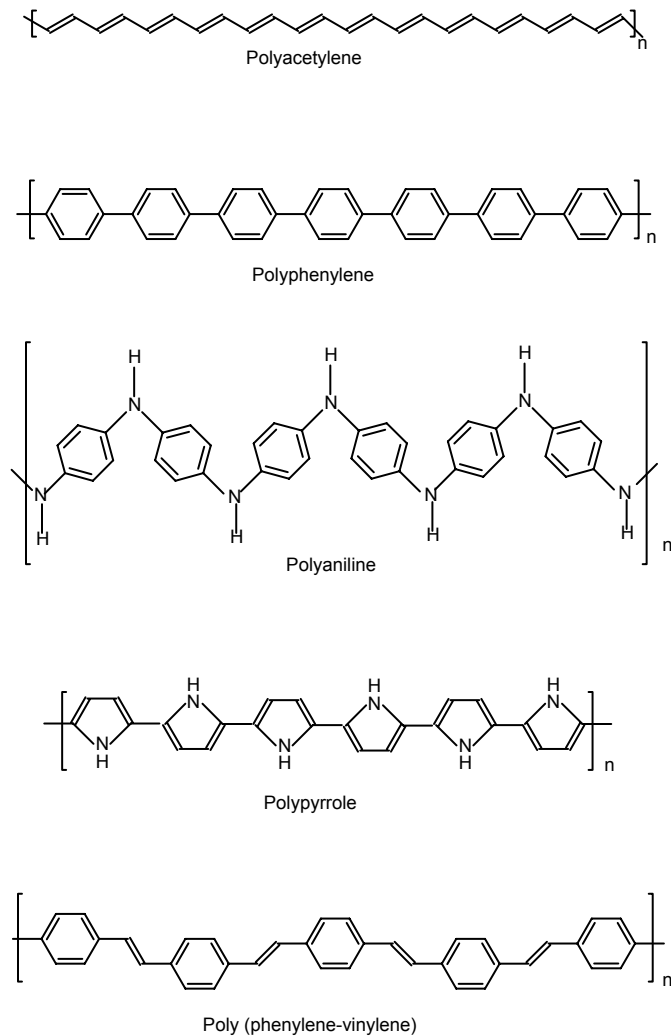


Figure 1.1: Examples of ICPs

The electrical and optical properties of these materials depend on the electronic structure and basically on the chemical nature of the repeating unit. The general requirement of the electronic structure in these polymers were recognized and described many years ago. The electronic conductivity is

proportional to both the density and drift mobility of the carriers. The carrier drift mobility is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated.

CONDUCTING POLYMER COMPOSITES:

These are usually prepared by the addition of conducting fillers in the insulating polymer matrix. The conductive filler commonly used are metal flakes, graphite, conductive carbon black, etc. These filler are loaded in the common insulating polymers like PP, PVC, LDPE, etc, to get conducting polymer composites or master batches. These are the materials exclusively used as the commercial conducting polymers. These are used as semiconducting layers in high voltage applications, EMI shielding materials, etc.

The major problem in this area is the processing problems created due to the filler loading. To get sufficient conductivity for these applications, filler loading of more than 20% is required. This higher addition of these rigid fillers will cause a drastic increment of melt viscosity, which causes serious processing problems. Moreover, these fillers also affect the properties of finished products like aesthetics, brittleness, poor finish, etc. Hence, there is need to develop process where an alternative material or blend can be prepared preferably from conducting polymers.

1.2. POLYANILINE

Due to its ease of synthesis and processing, environmental stability, relatively high conductivity and cost economics, polyaniline is probably the most industrially important conducting polymer today ⁹⁻¹¹. Polyaniline is a typical phenylene based polymer having a chemically flexible -NH- group in the polymer chain flanked by phenyl ring on either side. Polyaniline represents a class of

macromolecules whose electrical conductivity can be varied from an insulator to a conductor by the redox process. This polymer can achieve its highly conductive state either through the protonation of the imine nitrogens or through the oxidation of amine nitrogens. For example the conducting state of PANI can be obtained in its 50% oxidized emeraldine state in aqueous acids like HCl and the resulting material is a p-type semiconductor¹²⁻¹⁴. With the extent of doping polyaniline can have four different oxidation states¹⁵⁻¹⁶ like Leucomeraldine base (LEB), Emeraldine (EB), Emeraldine salt (ES) and Pernigraniline (PNB) shown schematically in the Figure 1.2.

Oxidative doping of the leucomeraldine base or protonic acid doping of the emeraldine base material produces the conducting emeraldine salt whose conductivity varies between 0.5 S/cm and 400 S/cm depending on the means of preparation. Extensive studies of the emeraldine salt (ES) material have shown that the metallic state is governed by inhomogeneous disorder. That is, in the conducting state, there are regions that are three-dimensionally ordered in which the conducting electrons are three-dimensionally delocalized and regions where the polymer is strongly disordered, in which conduction electrons diffuse through one-dimensional polymer chains that are nearly electrochemically isolated. One-dimensional localization in these nearly isolated chains lead to decrease in conductivity with decrease in temperature.

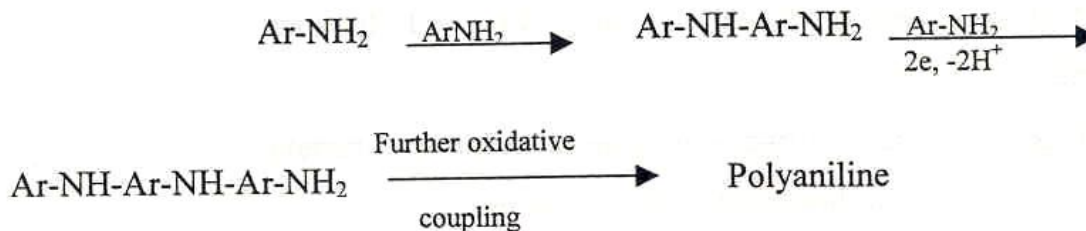
Polyaniline can be synthesized mainly by chemical or electrochemical oxidation of aniline under acidic conditions. The method of synthesis depends on the intended application of the polymer. For bulk production chemical method, where as for thin films and better patterns electrochemical method is preferred.

a) Chemical Synthesis:

The conventional method of synthesis of emeraldine salt is the emulsion polymerization of aniline monomer in aqueous media in presence of a mineral

acid like HCl^{11, 17-20}. An oxidant like ammonium per sulphate or potassium dichromate can be used to initiate the reaction^{21- 23}. The ideal molar ratio of monomer to acid to oxidizing agent is proved to be 1: 1: 1^{24, 25}. The aniline salt of protonic acid in the protonic acid medium is mixed with aqueous solution of ammonium per sulphate with a continuous stirring for 4 hrs. The precipitate obtained is then filtered and washed with distilled water so as to obtain emeraldine salt.

The principle function of the oxidant is to withdraw a proton from the aniline monomer. The polymerization reaction is summarized as follows:



The factors affecting the polymerization process are the pH of the solution, type of the acids used, its concentration, effective size, solvation and electronegativity of the conjugate base associated with a given acid.

b) Electrochemical synthesis:

Electrochemical polymerization is a radical combination reaction and is diffusion controlled. The anodic oxidative polymerization is the preferable method to obtain a clean and better-ordered polymer as a thin film. Electrochemical synthesis is achieved by:

1. Galvanostatic method

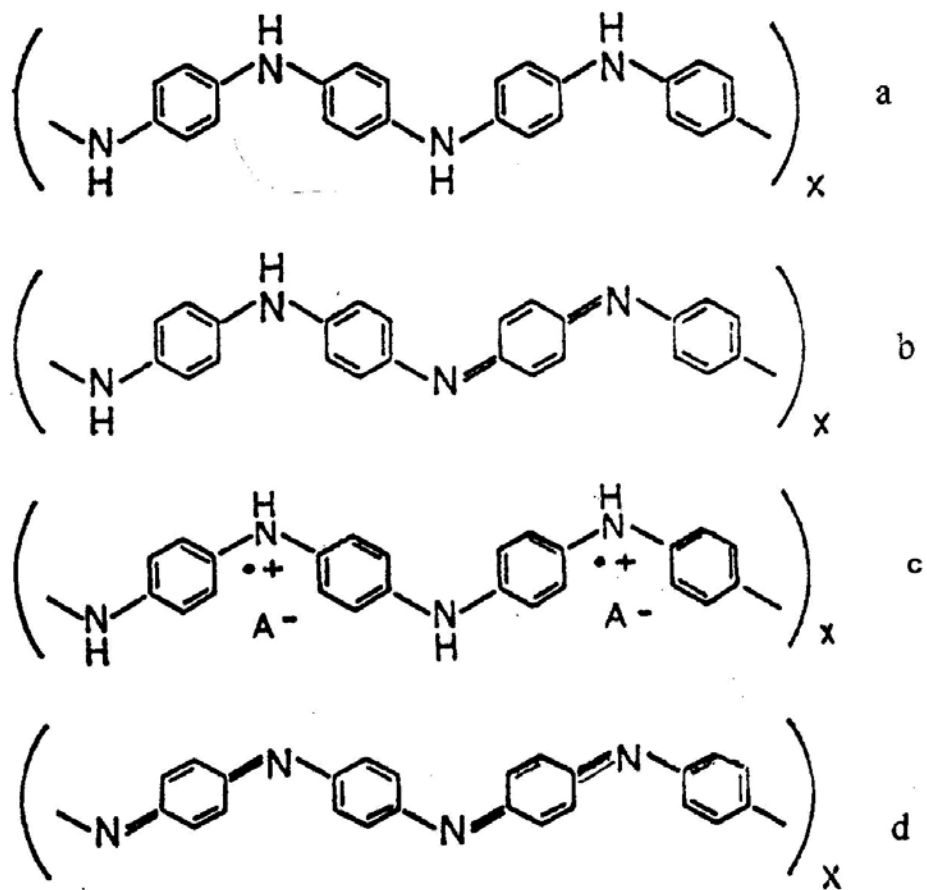
2. Potentiostatic method - keeping potential constant 0.7 – 1.1 V versus SCE
3. Potential sweep method – between two potential limits –0.2 to + 1.0 V versus SCE.

Electrochemical reaction is carried out by dissolving 0.1 mole of protonic acid in distilled water at platinum electrode. The first step in the oxidation of aniline is the formation of a radical cation, which is independent of pH. Mohilner et.al²⁶ classified the oxidation of aniline as an ECE reaction (a succession of rapid electrochemical – chemical – electrochemical reactions). The radical coupling is predominantly through a 1, 4 coupling of monomer units. The colour changes observed with polyaniline are yellow (–0.2 V), blue (0.0 V) and green (0.65 V), which are associated with different oxidation states (doping levels).

1.3. DOPANTS FOR POLYANILINE:

Polyaniline can be easily doped by non-redox doping method. Polyaniline holds a special position amongst conducting polymers in that its highly conductive doped form is accessible by two completely different processes – protonic acid doping (non-redox) and oxidative doping. Protonic acid doping of emeraldine base units results in the complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine salt.

Doped polyaniline can be obtained by chemical oxidation (p-doping) of leucomeraldine base. This actually involves the oxidation of the σ/π -system rather than just the π -system of the polymer, as is usually the case of p- doping.



(a) Leucoemeraldine base (LEB), (b) emeraldine base (EB), (c) emeraldine salt (ES), (d) pernigraniline base (PNB).

Figure 1.2: Various oxidation states of polyaniline.

There are plenty of reports available on different acid as well as ester dopants used for polyaniline. They include common mineral acids, high molecular weight long-chain organic sulfonic acids, phosphoric acids and their esters, etc. The standard route of synthesis of doped polyaniline is the one with Hydrochloric acid (HCl) as dopant ions as reported by many authors²⁷⁻³⁰. The other mineral acids commonly used include Sulfuric acid (H₂SO₄)³¹⁻³³, Hydrofluoric acid (HF)^{34,35}, Perchloric acid (HClO₄)^{36,37} etc. The low molecular weight organic acids include Formic acid, Acetic acid, Acrylic acid, etc³⁸⁻⁴⁰. High molecular weight long-chain organic sulfonic acids include Camphor sulfonic acid (CSA)⁴¹⁻⁴⁷, Methane sulfonic acid (MeSA)⁴⁸⁻⁵⁰, p-Toluene sulfonic acid (PTSA),⁵¹⁻⁵³, Dodecylbenzenesulfonic acid (DBSA)⁵⁴⁻⁶³, Polystyrenesulfonic acid (PSSA)⁶⁴⁻⁶⁶, etc. Other than the above-mentioned acid dopants, esters of phosphoric acid [67-69] as well as phthalic acid⁷⁰ were also used as effective non-redox dopant ions. Some examples of the organic sulfonic acid dopants used in the present work are shown in the Figure 1.3.

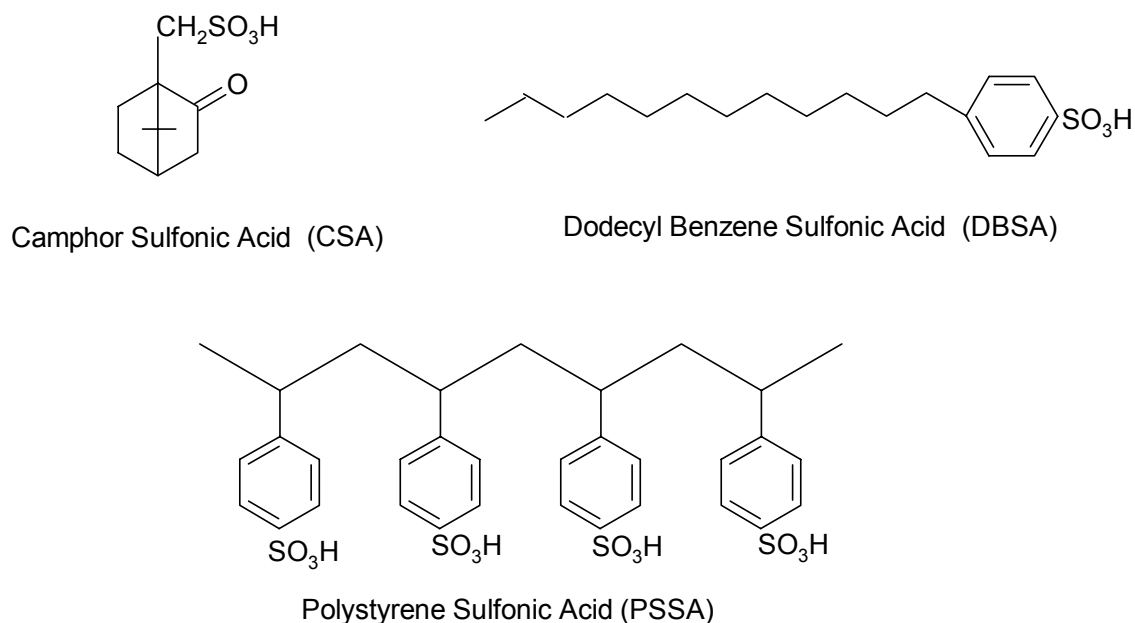


Figure 1.3: Represents the structures of the sulfonic acid used in the present work as dopant ions for polyaniline.

It was seen that the dopant ion could alter the properties of the conducting polyaniline formed. It can affect properties like conductivity, crystallinity, solubility and, hence, processibility. Amongst these, the organic sulfonic acids have been found to impart many interesting properties like high solubility and thermal stability to polyaniline. The sulfonic acids like DBSA, PSSA, etc., which have long-chain alkyl groups can plasticize the polyaniline formed by increasing the interchain separation, thereby facilitating the solvent molecules penetrating into the polyaniline lattice. Also, the alkyl chain can act as an effective solvent compatible group to improve the solubility of the polymer. These groups can also acts as compatibilizers as well as plasticizers when blended with other polymers. In the present work these sulfonic acids were selected as dopant ions for polyaniline. The efficiency of these dopants to provide better properties and processibility to polyaniline were examined and one among these was selected for the present work to examine the improvement of processibility by various techniques in detail.

1.4. PROCESSIBILITY IN CONDUCTING POLYMERS:

The attainment of processibility is the hottest issue today in the field of intrinsically conducting polymers. Intrinsically conducting polymers have assumed tremendous importance due to the large number of applications in electronics. However, the main limitations in this field are the lack of processibility and long-term stability of these electroactive polymers. It is mainly due to the lack of thermal stability of conductivity. Amongst the different conducting polymers, polyaniline has drawn considerable attention due to its relatively better stability and ease of synthesis. However, in its doped state as synthesized, polyaniline is insoluble in most solvents and does not show thermal stability above 160° C. There were already some attempts to study the processibility of polyaniline and the improvement in processibility in the past ^{71, 72}. As a consequence, its

conducting composites are very close to applications on a large scale for industrial applications⁷³⁻⁷⁶.

The processing method adopted to make polymer blends or composites is a sensitive issue, as it significantly determines the properties of the manufactured composite material. Known methods to produce polyaniline containing composites⁷⁷ may be essentially narrowed down to two types; (1) Synthetic method based on aniline polymerization in the presence of or inside a matrix polymer, and (2) Blending method to mix a previously prepared polyaniline with a matrix polymer⁷⁸. Roughly, these include:

(1) Synthetic methods:

- Dispersion polymerization of aniline in the presence of a matrix polymer in a disperse or continuous phase;
- Chemical insitu polymerization of aniline in a matrix or in a solution with a matrix polymer;
- Electrochemical polymerization of aniline in a matrix covering an anode;
- Polymer grafting to a polyaniline surface;
- Copolymerization of aniline with other monomers resulting in the formation of soluble aniline copolymers, which can be considered as composite polymers.

(2) Blending methods:

- Solution blending of soluble matrix polymers and substituted polyanilines;
- Solution blending of soluble matrix polymers and polyaniline doped by functionalized protonic acids (counter ion induced processibility);
- Solution blending of undoped polyaniline with soluble amide or acidic solvents;
- Dry blending followed by melt processing.

The synthetic methods involve the insitu dispersion of polyaniline particles inside other polymer matrices by synthesizing polyaniline in presence of dispersion or a solution of the second polymer matrix. There are different ways of producing polyaniline composites by synthetic route. One method is the polymerization of aniline at lower temperatures using an appropriate oxidant in presence of water soluble polymers or tailor-made reactive copolymers like poly (2-vinylpyridine-co-p-aminostyrene) ⁷⁹, PVA ^{80, 81}, poly (N-vinylpyrrolidone) ^{82, 83}, PEO ⁸⁴, cellulose derivatives ^{85, 86}, poly (methylvinylether) ⁸⁷, etc. This technique results in sterically stabilized colloidal dispersions of PANI particles of different size and morphology. These colloids can be further mixed with film-forming latex particles or with stable matrix polymer dispersions to produce conducting composites ^{81, 83, 88}.

Ruckenstein et al. ^{89 - 91} have developed emulsion pathways for the preparation of conducting PANI composites using the stabilization of an emulsion by a surfactant. In particular, they have reported a method to produce PANI / PMMA and PANI / PS composites via oxidative aniline polymerization carried out by adding an aqueous solution of ammonium per sulfate and HCl dopant to a concentrated emulsion containing an aqueous solution of the ionic surfactant (sodium dodecylsulfate) as the continuous phase and an organic (benzene) solution of the host polymer and aniline as the dispersed phase. The corresponding composites were obtained by co-precipitation of the host polymer and PANI, with a percolation threshold of ~ 2 – 10 vol.% PANI.

Another method of preparing PANI composites in synthetic route is by emulsion polymerization of aniline or pyrrole in functionalised polymer latex. Yassar et al. ⁹² reported the emulsion polymerization of pyrrole in sulfonated and carbonated PS latex samples, in which PS particles were over coated by polypyrrole. These composites have core-shell morphology with PS forming the

core and polypyrrole forming the shell. Armes et al.⁹³ examined the feasibility of the method with polyaniline. Non-uniform PANI coatings were obtained for the polymerization of aniline in presence of HCl in latex medium at ambient temperatures (25°C), but more homogeneous PANI coatings were obtained at 0°C. The maximum PANI coverage was found to be around 57 – 59%, which is much lower than the surface composition 94 – 100% for polypyrrole deposited onto a similar micro-sized PS latex⁹⁴.

The strong effect of interactions of PANI with its host polymer was shown by Jeon et al.⁹⁵. They investigated the effects on PANI-DBSA / PC composites prepared by an inverted emulsion polymerization method developed in accord with Ruckenstein et al.^{89 – 91} pathways, in which the role of surfactant and dopant was played by DBSA⁹⁵. These composites showed an increase in tensile modulus with PANI loading. The determination of percolation threshold, conductivity and SEM studies together with mechanical behaviour suggests that the structure of the PANI /PC composite is changed at high content of PANI due to a physical-chemical interaction of the components. Jeevanada et al.⁹⁶ used sodium laurylsulfate (SLS) and TSA, which acts as a surfactant as well as a protonating agent, to prepare these blends. The better interactions of blend components are displayed by improved thermal stability of PANI / PC blends.

Unlike the dispersion systems described above, there are other methods of chemical polymerization of aniline in the presence of a polymer matrix, which do not demand the presence of surfactants in the reaction mixture. These are done in many ways: in a solution of aniline and a matrix polymer^{97, 98}; at the surface of a polymer substrate dipped in aniline and oxidant solution⁹⁹; directly in a polymeric matrix, swelled in aniline and in contact with a oxidant solution^{100, 101}; or in a polymeric matrix containing an oxidant and in contact with a solution or vapors of a monomer¹⁰².

Another way of preparation of PANI composites is the electrochemical polymerization of aniline on a matrix. Although electrochemical polymerization in large-scale technologies is not practical, it can be useful for small geometry systems (sensors, microelectronics and optical devices, batteries, etc.) due to advantages such as precise control of PANI properties produce at an electrode surface, the possibility to avoid by-products of the process, etc.^{103, 104}. Polymerization at an electrode (anode) surface coated by a non-conductive polymer film at the aniline oxidation potential results in the formation of a PANI / polymer composite⁷⁷. Electrochemical polymerization technique is already being used to produce polyaniline composites with polymers like PU, PMMA, PC, poly-p-phenylene terephthalamide / diphenylether, etc.

A typical synthetic method to obtain PANI composites is probably the grafting of some polymers to a PANI surface. Thus, Chen et al.¹⁰⁵ demonstrated chemical modification of EB via its UV-induced surface graft polymerization with methoxy – poly (ethylene glycol) monomethacrylate macromonomer in aqueous media. These modified PANI films doped with HClO₄ were effective in reducing protein adsorption and platelet adhesion, and were claimed to have potential application as biomaterials and blood compatible materials. Thermally initiated graft copolymerization was used in the case of EB and acrylic acid¹⁰⁶. This grafting method can be used effectively where the adhesion properties are important.

In the industrial viewpoint, blending method is important in large-scale production than the synthetic route discussed above. There were many attempts to blend polyaniline with other polymer matrices. Many blending techniques like solution blending, melt blending etc. were explored. Among these most of the researchers used solution pathway, as conductivity of PANI is not stable at higher processing temperatures. The present work also deals with the blending techniques. Here also both techniques of solution as well as melt blending were used. This work presents a major leap in the achievement of highly processible polyaniline blends. The characteristics of blending techniques, the polyaniline

blending techniques already used by others, and the route towards the achievement of real processibility in polyaniline are discussed below.

1.5. POLYMER BLENDS:

Polymer blends can be simply defined as the mixture of two or more polymers or copolymers. Blends of two polymers are usually prepared to achieve desired properties, which cannot be given by the individual polymers. To attain processibility in polyaniline, it can be blended with other highly processible thermoplastics or elastomers. There are many techniques which can be adopted for blending of two polymers like melt blending, powder blending, solution blending, reactive blending, etc. Among these, melt blending is the most feasible and industrially viable processes. The blend of two polymers can be of different kind depending on the compatibility of these polymers. Depending on this, there can be different classifications like miscible blends, immiscible blends, compatible blends and polymer alloys. The main factors affecting the miscibility of the blend components are polarity of the components, specific group attraction, molecular weight, ratio of the components taken and crystallinity¹⁰⁷.

The properties and performance of the blends are highly dependent on the morphology. Morphology of any blend is mainly decided by the miscibility of the components. Depending on this polymer blends can be classified as miscible and immiscible blends. A truly compatible blend can be defined as the mixture of the two polymers with “miscibility in molecular scale”. This has the merit of clarity, but has the disadvantage of confirming the definition of compatibility to encompass only those blends showing true thermodynamic miscibility, thereby excluding a very large number of blends. Another way of defining compatibility is “polymer blends which do not exhibit gross symptoms of phase separation”. This widens the scope considerably, but still excludes some blends, which have been modified to facilitate the generation of preferred, but not necessarily fine,

morphology and, hence, preferred physical properties. A third definition is simply “to consider blends as compatible when they possess a (commercially) desirable set of properties”¹⁰⁸. Some properties of truly compatible blend can be (a) miscibility in molecular scale, (b) no phase separation, (c) single T_g and other physical properties, (d) synergic effect of physical properties, etc. The mechanical properties of a blend or alloy will be determined not only by the properties of the components, but also by the phase morphology and interphase adhesion.

Compatibilization of an immiscible blend is necessary to achieve stable and reproducible dispersion, which would lead to desired morphology and properties. The ways of compatibilization can be broadly classified into two types: as addition of a third component (compatibilizer) and by inducing ‘insitu’ chemical reaction between blend components (reactive blending). According to L.A. Utracki, compatibilization can be achieved by addition of linear or star-shaped block copolymers, addition of graft or random copolymer, co-reaction within the blend to generate either insitu either copolymers or interacting polymers, using IPN technology, cross-linking the blend ingredients, modification of homopolymers, addition of co-solvents, high stress shearing, etc.¹⁰⁹.

Existence of a single T_g is an indirect way of confirming the compatibility of the blend. Glass transition is the generalized Ehrenfest type second order transition existing glass and a liquid super cooled below its melting point. The generalization involves specifying definite values of the structure parameter, which in turn has a kinetic character. The glass transition is not a pure thermodynamic phenomenon. The change in the extensive thermodynamic functions during classification of liquid depends not only on the initial and final set of temperature and pressures, but also on the way the change has been accomplished. The transition is associated with an increase of the density fluctuations, resulting in a discontinuous jump of the first derivatives dF/dT and dF/dP , where T and P are temperature and pressure and F stands for any

thermodynamic quantity, e.g. G, S, H or V. The temperature at which the transition occurs is the glass transition temperature (T_g), which depends on the sample preparation, rate of scanning, pressure, frequency, additives (plasticizers and fillers), molecular parameters (molecular weight and its distribution, branching, tacticity, etc.), crystallinity, etc. "In polymers, glass transition is related to co-operative segmental motion", Boyer (1966) suggested that T_g involves 50 – 100 backbone chain carbon atoms, i.e. a domain with diameter $d_d = 2 - 3$ nm. In agreement with this Warfield and Hartman (1980) calculated that in the glass transition of amorphous thermoplastics there are 15 to 30 statistical segments involved. Much larger values $d_d = 15$ and from 10 to less than 5 nm were assigned respectively by Kaplan (1976) and by Blair and Warren (1981). The use of T_g in the determination of polymer / polymer miscibility is based on the premise that a single T_g indicates that the domain size is below d_d , where $2 \leq d_d \leq 15$ nm. This is confirmed by several studies of T_g of multiphase systems. It is found that there are two T_g values in an IPN system of domain size 10 to 50 nm large. It is important to note that single T_g is not a measure of thermodynamic miscibility, but only of the state of dispersion.

In order to improve processibility, intrinsically conducting polymer can be blended with other polymers as discussed earlier. Blending can be carried out by different techniques, among which solution blending and powder blending were used in research purposes in the case of conducting polymers. Powder blending was done mostly to mix two polymers, which are not processible by other useful techniques, and these blends were mostly prepared for academic interests. Solution blending is a better technique to blend the polymers, which are completely or partially soluble in a common solvent. This technique also finds some application in coatings. But the melt blending technique is the most useful one as far as industrial processing and applications are concerned. To attain thermal processibility, the thermal stability and miscibility in molten state of both polymers are the important factors to be considered. To obtain better processibility and end properties for the blend, some additives in low phr level

can be added while blending. These additives are usually referred to as processing aids¹¹⁰. Processing aids are more compatible with the major matrices of the blend and are included to ensure a more uniform flow and act as lubricant to the melt to increase the rate of flow. It provides better mixing; increased flow rate and imparts superior surface finish to the product. The detailed discussion about the blends of polyaniline is given below.

1.6. BLENDS OF POLYANILINE:

1.6.1. SOLUTION BLENDING.

The development of solution methods to process polyaniline is based on the understanding of the fact that difficulties in its processibility are related to its aromatic structure, interchain hydrogen bonding and effective charge delocalization in its structure¹¹¹. Different approaches have been adopted which can be classified as follows:

- a) The synthesis of substituted polyanilines, which are soluble in organic solvents, realized through the introduction of alkyl^{112, 113}, alkoxy¹¹⁴ and other substituents on the monomer aromatic ring.
- b) The introduction of sulfonic groups on PANI benzene rings, to form water-soluble sulfonated self-acid-doped PANI^{115, 116}. Another kind of sulfonated PANI can be produced through substitution of hydrogen in imine sites of PANI, e.g. by propanesulfonic acid¹¹⁷.
- c) Copolymerization of aniline with other monomers to form soluble aniline copolymers¹¹⁸.
- d) Doping of undoped PANI by functionalized protonic acids (CSA, DBSA, phosphoric acid diesters, etc.) and an R- functional group (alkyl substituted aromatics, long alkyl chains, etc.), imparting dopant compatibility with non-polar or weakly polar organic solvents^{67, 71, 119, 120}; Cao et al.⁷¹ called this method to dissolve PANI 'counter-ion induced processibility'.

- e) The use of amide solvents such as NMP, in which PANI base is soluble ¹²¹.
- f) The use of an acid – base interaction of the PANI base with concentrated acids ¹²² or solvents having strong acidic functions ¹²³.

Synthesis of substitute PANI to make it more soluble will cause the adverse effect of decrease in conductivity, due to disturbance of the electronic delocalization in the polymer chains ^{124, 125}. Nevertheless, the conductivity of PANI with some non-bulky substituents is high enough for some purposes. Some polyaniline derivatives like poly (o-toludine), poly (m-toludine) and poly (o-methoxyaniline) exhibit higher conductivities in the order of 0.01 – 3 S/cm ^{51, 126}. Moreover, Raghunathan et al. ¹²⁷ found that an electron localization length was much larger in poly (o-alkoxyaniline) compared with corresponding poly (o-alkylaniline) and, hence, encourage the investigators to use alkoxy substituents for solution blending. Thus there are number of investigation done on poly (o-methoxyaniline) [POMA], with different dopant ions like HCl, TSA, etc. POMA blends with PVDF, PU, Hydrin-C[®], etc. as well as poly (alkylaniline) blends with PVC, ABS, etc. were investigated in detail ^{128 – 130}.

Another method to produce soluble polyaniline is by synthesizing block or graft polymer of PANI with blocks of more conventional dielectric polymers. This method is based on the ability of aniline or imine units of EB or LEB to interact with the reactive end group of dielectric polymers. Li et al. ¹³¹ synthesized A-B-A block polymer with PANI as segment A and segment B a PEG with a – C₆H₄-NH₂ end group. This was the extension of their earlier work to produce PANI graft copolymers ¹³². There are many more reports on block and graft polymers of polyaniline ^{133 – 135}.

Solution blends can be prepared due to ‘counter-ion’ induced solubility of PANI. These polyaniline were mostly prepared by doping PANI with organic sulfonic acids like CSA, DBSA, etc. This discovery of a processing route for the conductive form of the PANI – emeraldine salt of functionalized sulfonic acids by

Cao et al.⁷¹ marked a significant advance. The film cast of PANI-CSA from m-cresol solution had a conductivity of ~ 400 S/cm. These secondary doping phenomena were attributed to an expanded coil-like conformation, which was proven by viscosity studies^{136, 137}. Ikkala et al.¹³⁸ believe that this conformation resulted in supermolecular structures due to the combination of three specific simultaneous interactions; first the sulfonic acid is bonded to PANI through proton transfer; second, the hydroxyl group of m-cresol forms a hydrogen bond with the carbonyl group of CSA; and third, the phenyl group of m-cresol and PANI stack, yielding enhanced mutual dispersion forces. These provide the requirement for what was called 'molecular recognition'. Such interactions promote a more extended conformation of PANI chains, which leads to the improvement in solubility and conductivity.

Considerable interest has been focused on this processing route, including the possibility of stretch aligning of the PANI doped fibers and films, resulting in an increased conductivity in the stretch direction^{139, 140}. It was demonstrated that PANI with functionalized sulfonic acids could be processed in blend with common insulating polymers, such as PMMA, PC, nylon 4,6 and nylon 12, PVAc, PVB, ABS, etc by mixing the two solutions, followed by film casting^{71, 120} to obtain blend materials with interesting characteristics. In particular, PANI-CSA / PMMA displayed probably the most unique conductivity, transparency and other properties.

It is known that PANI doped with a binary mixture of sulfonic acids possesses peculiar thermal stability, conductivity and other characteristic features as compared to the polymer doped separately by sulfonic acids. Koul et al.¹⁴¹ have shown enhanced electrical and optical properties along with higher solubility in all common organic solvents, for PANI doped with a mixture of DBSA / PTSA (1:1). Using this double-doped PANI, they prepared composite films with ABS by casting from the chloroform solution. The surface resistance of these

composites changed from 300 M Ω /cm² to 1.302 K Ω /cm², dependent on the PANI doped content and the method of mixing the system components.

The ability of polyaniline to form hydrogen bonds can affect the final properties of the composite prepared. Naturally, this is more intrinsic to polymers with polar groups in their main or side chains. This dependence provides a means to affect to some extent of miscibility, mechanical, thermal and an electrical property of the conducting blends through a change of the functional compositions of the matrix polymer. Various methods to enhance the properties of immiscible blends include the use of precursors, compatibilizers such as block copolymers or ionic polymeric groups. The last was used by Ho et al.¹⁴² when making a rubber like conducting polymer blend of thermoplastic PU with PANI-DBSA by mixing in chloroform. The sulfonic chain extender (2,5-diaminobenzene sulfonic acid) of PU allowed additional hydrogen bonding with PANI-DBSA. As a consequence, the blend composition led to variation of glass transition points, different degrees of miscibility and a tensile strength of the modified PU blends that increased with the incorporation of PANI-DBSA. A similar approach of introducing ionic groups, such as sulfonic moiety, to the insulating polymer PC to enhance its coulombic interaction with PANI phase in the composite was used by Lee et al.¹⁴³. They reported the preparation of conductive flexible composites of PANI and sulfonated PC, with improved compatibility.

Other than organic sulfonic acids, phosphoric acid esters as well as phthalic acid esters were also used as dopant ions by Pron et al⁶⁷⁻⁷⁰ to enhance the solution processibility. These were used to prepare conducting solution blends of PANI with polymers like PS, ABS, PMMA, etc., with a very low percolation threshold. These aliphatic diesters protonated EB under mechanical mixing that resulted in the heavily plasticized mixture which could be hot-pressed into conducting, freestanding films. However, at higher temperatures above 140°C, partial degradation of PANI-phosphoric acid diester complex occurs, leading to a decreased conductivity.

1.6.2. THERMALLY PROCESSIBLE POLYANILINE BLENDS.

Thermally processible conducting polymer blends and composites are more important and practical in the industrial scale than solution processed system. Three main approaches exist to produce such materials. The first is realized through the mechanical dispersing of infusible conducting polymers in melt thermoplastic matrices to achieve conventionally mouldable or extrudable conductive composites. The second is the development of melt-processible electrically conductive polymers. The third combines the preparation of a mixture of PANI in a dispersion with a thermoplastic polymer solution or dispersion, followed by the separation of the mixture and its melt treatment.

a) Composites with infusible PANI.

The principle requirements for the use of PANI as an infusible component in a composite are easy dispersion in thermoplastic matrix polymers and sufficient thermal stability in processing and operation conditions. Standard polyaniline doped with mineral acids have a high surface tension, resulting in their tendency to agglomerate, and a lowered specific surface area, which creates serious problems while dispersing in other matrices. Use of functionalized protonic acid as dopant can improve the situation.

The commercial form of PANI doped with TSA -Versicon™ was dispersed in thermoplastic PVC, PETG and nylon 12 using conventional compounding in a Brabender mixer ¹⁴⁴. The good performance of these polyaniline blends was derived from its thermal stability and its dispersibility as fine sub-micron particles. Percolation curves followed a standard function form, but the fit parameters and maximum achievable conductivity are a strong function of processing history and of choice of matrix polymers. The significance of the dispersion of PANI phase

for conductivity properties of its blends and their dependence on a matrix polymer was demonstrated by Zilberman et al.^{145,146}. They investigated Versicon™ melt-mixed blends with thermoplastic polymers such as PS, PS plasticized with DOP, PCL, LLDPE and LDPE. The blending temperature was chosen depending on the matrix polymer. The results showed that the blend morphology and the level of interaction between components of the blends strongly affected the electrical conductivity of the blend. PANI-TSA blends with elastomer like EPDM was also studied in detail¹⁴⁷. Here PANI-TSA was also found to contributing to an increase in the rubber cross-linking density.

b) Polymer blends and composites with fusible PANI.

The discovery of counter-ion induced solubility⁷¹ appeared to be the base of resolution of the problem of imparting the melt processible capability to PANI through the use of some functionalized sulfonic acids, e.g. DBSA or alkyl or aryl diesters of phosphoric acid as doping agents. Ikkala et al.¹⁴⁸ developed conducting polymer blends by conventional melt mixing of thermoplastic bulk polymer with PANI-DBSA. The percolation threshold for conductivity was observed at a low weight fraction of PANI-DBSA, differing with the matrix. These composites were proposed for applications such as electrostatic dissipation (ESD), static discharge and EMI shielding; which require conductivities of approximately $10^{-5} - 10^{-9}$ S/cm for ESD and > 1 S/cm for EMI.

In PANI-DBSA blends, an extra amount of DBSA yielded a plasticized melt processible complex^{149, 150}. Use of an excess amount of DBSA led to a decrease of Tg and a plasticizing effect, resulting in easier melt processing. Thus, Tg was $\sim 135^{\circ}\text{C}$ for a molar ratio of 1: 0.7, compared with the much higher Tg ($\sim 230^{\circ}\text{C}$) observed for molar ratio of 1: 0.5.

Zilberman et al.^{145, 151} also investigated a conductive PANI-DBSA complex prepared by a thermal doping process in Brabender plastograph at

140°C for 5 min. It was used melt mixing with thermoplastic polymers like PS, LLDPE, CoPA (Copolyamide), etc. at suitable temperature varied with matrix polymer. Naturally, the electrical conductivity of the blends depended markedly on the matrix polymer and on the compatibility of the components. This resulted in a low percolation threshold with PS blends than others. Perhaps, since their components exhibited similar solubility and solubility parameters, the PANI-DBSA / PS blends appeared the most suitable system among those considered to obtain an electrical conductivity high enough for use, while the PANI-DBSA / CoPA blends were the least suitable ones. The DOP plasticizer increased the solubility parameter of the PS towards that of PANI-DBSA, resulting in enhanced dissolution of PANI-DBSA in the PS matrix during melt processing, and in a slightly higher conductivity.

Koul et al.¹⁵² reported blends of conventional thermoplastic ABS copolymer and PANI doped with a specific ratio of mixed dopants, consisting of DBSA and PTSA at dopant ratios ranging from 1: 1 to 9: 1. It was found that the lowest loading of PANI doped with hybrid dopants in the moulded conducting composites might be effectively used for the dissipation of electrostatic charge. With higher loading a shielding effectiveness of 60 dB at 101 GHz was achieved, which suggested the potential of these conducting composites being used as EMI shielding materials.

Alkyl and aryl phosphoric acid diesters also constitute an excellent group of PANI dopants, which not only render this polymer conductive and solution processible, but also plasticize it to be melt-processible^{67 - 70}. Thus rheological parameters are characteristic of a Bingham liquid, with the viscosity decreasing with an increase of the diester content. Protonation of EB with dioctyl hydrogen phosphate resulted in a heavily plasticized mixture that could be thermally processed to give freestanding films, with better conductivity. It was shown that blends with excellent mechanical properties could be prepared by hot pressing (160 °C) PANI-DiOHP / PVC plasticized by DOP or PANI-DPHP / PVC

plasticized by tricresylphosphate (TCP). These conductive blends also demonstrated a low percolation threshold less than 10%. Many other authors like Ikkala et al.¹⁵³ and Yang et al.¹⁵⁴ also showed that the effect of compatibilizers and plasticizers like different esters favored the formation of a continuous PANI network in thermally processed blends.

Thermal effects and aging of polyaniline in their blends and composites have been the major concern when talking about the processibility of these materials. The conductivity of these blends should be stable at its processing conditions as well as the operating conditions. It was found that polyaniline loses conductivity at much lower temperatures, due to the loss of dopant ions. The processibility and the properties of these blends also depend highly on the compatibility and dispersibility of polyaniline in the matrix polymer. The addition of polyaniline also dramatically changes the melt viscosity, which can also lead to the severe processing difficulties. So there is need for designing a polyaniline blend system, which can overcome these problems and very well go for different industrial applications.

1.7. RHEOLOGY AND PROCESSIBILITY:

Rheology is the science that deals with the way materials deform when forces are applied to them. This term is most commonly applied to the study of liquids and liquid like materials such as paint, oil well drilling mud, blood, polymer solutions and molten plastics, i.e. material that flow, although rheology also includes the study of the deformation of solids such as occurs in metal deforming and the stretching of rubber.

The visco-elastic properties of molten polymers are of importance to plastic engineers, because it is these properties that govern flow behaviour whenever plastics are processed in the molten state. For example, in order to optimize the design of extruders, the viscosity must be known as the function of

temperature and shear rate. In injection moulding, the same information is necessary in order to design the mould in such a way that the melt will completely fill it in every shot. In blow moulding, the process of parison formation and swell are governed entirely by the rheological properties of the melt.

1.7.1. MELT VISCOSITY.

As discussed earlier, viscosity of the molten polymer or polymer composite at the processing stage determines the processing parameters to be employed. Determination of Melt Flow Index (MFI) is a means of studying the melt viscosity of the polymer melt at a particular temperature with a constant low shear. MFI is usually expressed as the weight of the polymer melt extruded through a standard die in 10 minutes at constant temperature and with a constant weight on the piston. This method is illustrated in the international standards ASTM D1238 and BS 2782. It is a useful test to check batch-to-batch constancy or effect of processing by taking measurements at intervals. Manufacturers produce different MFI polymers and copolymers to match different processing requirements. These measurements have disadvantage of sources of errors such as end effects and slip at the barrel wall when using for fundamental rheological studies. But these measurements can be used for the viscosity studies at lower shear rates.

1.7.2. MATHEMATICAL MODELS FOR VISCOSITY OF FILLED POLYMERS.

The logical starting point for a discussion on the effect of rigid fillers is Einstein's equation for viscosity of a very dilute suspension of rigid spheres in a Newtonian fluid. Einstein showed that the presence of a sphere perturbs the flow field of the surrounding fluid in such a way that more energy is dissipated¹⁵⁵. The

effect is to increase the viscosity by an amount proportional to the volume fraction of filler particles regardless of their size.

$$\eta = \eta_f (1 + 2.5\phi) \quad \text{-----} \quad (1.1)$$

Here, η is the viscosity of suspension, η_f that of the suspending fluid, and ϕ the volume fraction of filler. The relative viscosity can be written as:

$$\eta_r = 1 + 2.5\phi \quad \text{-----} \quad (1.2)$$

Difficulties arise as soon as any Einstein's assumptions no longer apply. If the suspension is not very dilute, the flow field and the particles interact with each other to further increase the viscosity. If the particles are not spherical, the suspension is no longer Newtonian and cannot be characterized by a single viscosity. If the filler is not rigid, it is deformed by flow, and the suspension becomes non-Newtonian and viscoelastic. And above all if the fluid medium is already a visco-elastic material, such as molten polymer, additional complications are encountered. Other complexities can occur due to the density difference, particle size, tendency of the fillers to agglomerate, etc.

The probability of continuous network being formed by filler particle in a matrix is related to the statistical average number of contacts each particle makes with neighboring particles and the maximum number of contacts per particles that are sterically possible ¹⁵⁶. The packing of any particulate filler can take any possible close packing arrangement and accordingly it acquires a definite number of contacts with the neighboring filler particles. So one particle posses a definite value of Z, which is the maximum number of possible contacts,

or co-ordination number. Values of Z and maximum packing fraction, ϕ_m are given in the Table 1.1.

Table 1.1: Values of Z and maximum packing fraction, ϕ_m for cylindrical filler and different mode of packing of spherical fillers.

Shape of filler	Type of lattice	Z	ϕ_m
Spherical	Face-centered cubic	12	0.74
	Body-centered cubic	8	0.68
	Simple Cubic	6	0.52
	Diamond	4	0.34
	Random	6	0.637
Cylindrical	Random	--	0.45

Many equations were derived for more concentrated suspensions¹⁵⁷. One of them is the Mooney equation, which takes into account particle shape C and morphology of the saturated suspension. This parameter is K. The equation is:

$$\eta = \eta_s^{C\theta / (1-K\theta)} \quad \text{-----} \quad (1.3)$$

For polydispersed particles the packing density is another variable that affects the viscosity of the suspension. Random close-packed spheres will have a maximum packing fraction of 0.637, 0.68 for sphere with b.c.c packing, and 0.74 for spheres with f.c.c packing. This equation can also be shown as:

$$\eta_r = e^{KE\phi / (1-\phi/\phi_m)} \quad \text{-----} \quad (1.4)$$

Where ϕ is the volume fraction and ϕ_m is the maximum packing fraction.

There are many other mathematical models¹⁵⁸ for the discussion of viscosity and phase behaviour in filled polymers and the present work considered some of them as given in the Table 1.2.

Table 1.2: The comparison of different models for viscosity of polymer dispersed system.

<u>Author</u>	<u>Equation</u>
Einstein (1911)	$\eta_r = (1 + 2.5\phi)$
Eilers (1941) ¹⁵⁹	$\eta_r = [1 + 1.25 \phi(1 - \phi/\phi_m)]^2$
Mooney (1951) ¹⁶⁰	$\eta_r = e^{K_E \phi / (1 - \phi/\phi_m)}$
Krieger and Dougherty (1959) ¹⁶¹	$\eta_r = (1 - \phi/\phi_m)^{-[K_E] \phi^m}$
Quemada (1977) ¹⁶²	$\eta_r = (1 - \phi/\phi_m)^{-2}$

Where, $\eta_r = \eta / \eta_0$ (relative viscosity)

$K_E = 2.5$ (Einstein's constant)

$\phi =$ Volume fraction of PANI particles

$\phi_m =$ maximum packing fraction.

1.8. CHARGE TRANSPORT IN CONDUCTING BLENDS AND COMPOSITES:

The charge transport behaviour in blends and composites is dominated by the morphology that consists of an insulating matrix and conductive filler. The composite changes from an insulator to a conductor over a very narrow range of filler concentration. A typical curve of resistivity vs. filler concentration is shown in the Figure 1.4. At lower concentrations, the composite remains an insulator. At a critical volume fraction, the resistivity of the composite falls sharply to a level at which the composite can readily conduct electricity. This is due to the formation of a fine conducting network formation at that critical concentration of conducting material. The conversion of a blend / composite from an insulator to conducting is known as percolation phenomenon. The critical fraction of the filler to form a fine network, above which the composite will become conducting, is known as percolation threshold.

The addition of a conductor to an insulator affects the electrical properties according to the degree of filling and proximity of the conducting particles. Three situations are possible: (1) No contact between the conductive particles, (2) Close to proximity, and (3) Physical contact. When the particles are isolated, the conductivity of the blend / composite is only slightly changed. The blend / composite may remain an insulator although its dielectric properties may change significantly.

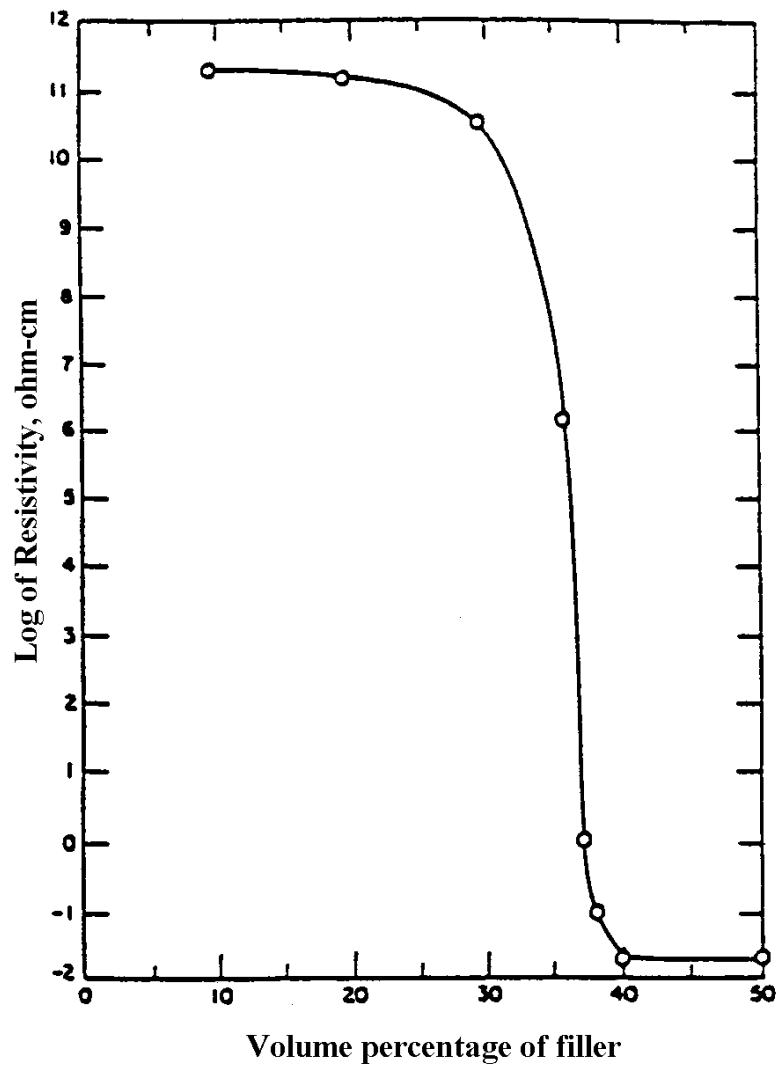


Figure 1.4: Typical curve of resistivity vs. filler concentration.

When the conductive particles are in close proximity, the electron can jump the gap between the particles, creating current flow. The ability of the electron to jump a gap under a given voltage field, increases exponentially with the decreasing gap size. The gaps as large as 10 nm can be jumped. The process of electron transfer across an insulator gap is referred to as 'hopping or tunneling'. Tunneling consists of jumping or tunneling of electrons from the valance band of ions or molecules on one side of the gap to conduction band at

other side without energy exchange. The equation for the probability that an electron will tunnel from one energy state to another through the insulator is then form,

$$P = a e^{-\tau \Delta E / kT} + e^{\Delta E_p / kT} \quad \text{-----} \quad (1.5)$$

Where 'a' is a constant, E is the activation energy to travel the energy gap, T is the sample temperature, Ep is the local polarization across the barrier, and τ is the tunneling factor. The tunneling factor can be expressed as:

$$\tau = e^{-\alpha r} \quad \text{-----} \quad (1.6)$$

Where α is a constant, r is the special distance through which the electron must tunnel. The exponential form of the tunneling factor shows the importance of maintaining close proximity between the adjacent conductive particles.

The third condition, which is possible when conductive filler is introduced in to an insulating matrix, is that the conductive particle will physically contact each other to form a continuous network throughout the blend / composite. Under this condition the composites conduct through the particle network by conduction mechanism of the particles. In highly loaded composites actual touching does occur and such composites have shown a linear current-voltage characteristics, but in some cases a non-ohmic behaviour was also observed.

Gurland¹⁶³ has also shown that the sharp transition from insulator to conductor is due to the formation of a network among the conductive fillers. As mentioned earlier, this does not imply a physical contact.

The network formation has been most frequently treated as a percolation process. The percolation model simply refers to a means of continuous network

formation through a lattice, taking into account relative concentration of the concentration of the two materials comprising network.

Quantum mechanical tunneling has been also used to explain the conduction through the insulating materials. According to this theory, two conductors whose separation is large ($> 100 \text{ \AA}$) compared to atomic dimensions see each other through a resistance controlled by the bulk resistivity of polymer itself. However, when this distance is small ($< 100 \text{ \AA}$) electrons may tunnel quantum mechanically between the conductive elements, leading to a lower resistance than would be expected from the insulator alone. Thermal expansion of the polymers has been used to explain the importance of critical volume fraction in such materials. Due to the difference in thermal expansion coefficient of polymers and fillers, with increase in temperature the distance between the adjacent filler particles increases. If the initial volume fraction is just greater than the critical volume fraction (and therefore resistance is low), then the increase in temperature will cause the filler particle to move apart. Due to this the distance between the filler particles may increase beyond the critical value, thus causing a large increase in the resistance value.

Jean-Pierre Reboul¹⁶⁴, in a review, has discussed the conduction in carbon black filler polymers and also effect of electrode material on the conduction process. In such systems non-linear current-voltage characteristics have been observed and different conduction have been proposed. According to Reboul the resistance of such material is influenced by many parameters such as length, orientation, voltage, temperature etc. Therefore, no significant value for the conductivity of the material can be deduced from a single measurement of current and voltage. It is therefore necessary to distinguish between properties of the medium and properties of a particular sample with given shape, length, and electrode material.

Jachym¹⁶⁵ mentioned that the polymeric conducting powder at very high concentration, the mechanism of conduction is characteristics of the doping agent alone. At concentration close to critical value, there is a large change in resistance with change in temperature, resulting from the different linear expansion coefficients of the polymer and the filling material. Frequently, the tunneling effect takes place, which induce corresponding temperature dependencies. At low concentrations, the temperature dependence of conductivity, σ , on temperature takes the form:

$$\sigma = \sigma_0 \exp \{- (W / k_B T)\} \quad \text{-----} \quad (1.7)$$

Where σ_0 is a constant and W is the activation energy.

The activation energy can be defined by the equation

$$W = -k_B \frac{\partial (\ln \sigma)}{\partial (1/T)} \quad \text{-----} \quad (1.8)$$

Various values of activation energy are observed for different cross-linking agents and for their variable concentrations. It is also observed that above the glass transition temperature of the resin, the activation energy decreases with temperature.

For increase in carbon black content, above some critical value, this is an abrupt increase in the conductivity of the composite. In this highly conducting region, the conductivity varies according to the following relation:

$$\sigma = \sigma_0 (1/T)^n \quad \text{-----} \quad (1.9)$$

Where n depends on the particular resin system.

1.9. FREQUENCY DEPENDENT CONDUCTIVITY:

Conduction in localized sites of a conductive blend / composites has to be considered in this treatment. Carriers in localized sites can move into adjacent empty states by thermally assisted tunneling called hopping. The hopping probability depends on the mutual overlap of the wave functions, determined by the ratio of the intersite distance to the localization length r_0 .

There is a derived equation for the conductivity considering the hopping mechanism by the carriers in localized sites. The relation obtain can be expressed as¹⁶⁶:

$$\sigma(\omega) = (\pi / 96) e^2 kT [N(E_F)]^2 r_0^5 \omega [\ln(1 / (\omega\tau_0))]^4 \text{ -----(1.10)}$$

Frequency-dependent conductivity shows the characteristic features represented by above extended pair-approximation. A frequency dependent conductivity at low frequencies, equal to the dc value, is followed by monotonous increase with a frequency exponent $n < 1$ at higher frequencies. The low frequency branch varies with temperature in the same way that dc conductivity does, whereas the high frequency branch varies in general considerably less.

Thus, for the charge transport among disordered induced localized sites, $\sigma(\omega)$ should vary approximately as a function of a simple power law dispersion ω^n with $n < 1$ ¹⁶⁷, which can be described by the well-known relation¹⁶⁸:

$$\sigma(\omega) = \sigma_{dc} + A\omega^n \text{ -----(1.11)}$$

Where σ_{dc} is the DC conductivity, 'A' a temperature dependent parameter, ω is the frequency and n is the fractional exponents.

The dielectric property measurements of the conducting polymers with sweep in frequency can give the frequency depended conductivity. It can be measured from the imaginary part of the relative permittivity (ϵ'') of the material. It can be expressed as:

$$\epsilon'' \cdot \omega = 1.8 \cdot 10^{12} \cdot \sigma \quad \text{-----} \quad (1.12)$$

Where ϵ'' is the imaginary part of the relative permittivity, ω is the frequency and σ is the conductivity. From the above equation (1.12), the frequency dependent conductivity at each applied frequency can be calculated.

It can also be seen that this exponent also depends on the experimental temperature and can be expressed as:

$$n = (T_{ch} - T) / (T_{ch} + T) \quad \text{-----} \quad (1.13)$$

Where, T is the experiment temperature in Kelvin scale and T_{ch} is a characteristic temperature specific to the material depending on the nature and mobility of charge carriers. From the above equation the characteristic temperature for each compositions of blends can be calculated.

1.10. APPLICATIONS OF PROCESSIBLE CONDUCTING POLYMERS:

Conducting polymers are assumed to have tremendous applications in various fields especially in electronic appliances. They have importance in large number of application like LED display, conductive surfaces, solid phase

sensors, optical storage lithographs, transducers, EMI/ESD shielding, plastic batteries, membrane for gas separation, magnetic recording, etc. But as discussed the problem hindering these wonderful applications is the poor processibility in these polymers. Improvement of the processibility will enable scientists and technologists to explore this to create a new looking world of conducting polymers. Some of the possible applications of processible conducting polymers are discussed below.

By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the buildup of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry. In the computer industry the sudden discharge of static electricity can damage microcircuits. This has become particularly acute in recent years with the development of modern integrated circuits. To increase speed and reduce power consumption, junctions and connecting lines are finer and closer together. The resulting integrated circuits are more sensitive and can be easily damaged by static discharge at a very low voltage. By modifying the thermoplastic used by adding a conducting plastic into the resin results in a plastic that can be used for the protection against electrostatic discharge.¹⁶⁹ The solution processible polyaniline blends can contribute to this application.

Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. This can cause malfunctions in nearby electrical devices. The plastic casing used in many of these devices are transparent to such radiation. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed. This can best be achieved by using conducting plastics. This is cheap, easy to apply and can be used with a wide range of resins. The final finish generally has good adhesion, gives a good coverage, thermally expands approximately the same as the polymer it is coating, needs just one step and gives a good thickness. Processible conductive

polyaniline and blends either solution processible or, more promisingly the melt processible blends can provide wonderful material for EMI shielding.

Corrosion is a part of our everyday life. When metal donates some of its electrons to oxygen it causes the formation of impurities that weaken the structure, which is known as corrosion. Painting a metal with zinc or covering the metal with plates of zinc can delay corrosion. Zinc, being more reactive and a good electron donor reacts with oxygen more readily and the metal underneath is not affected. Unfortunately, coatings and plates of zinc cannot last long. All of the problems caused by corrosion can be reduced considerably by a wonderful “plastic coating that virtually eliminates rust and corrosion-which could help cars, bridges, pipelines and other metal structures last up to 10 times longer” This coating can be prepared by using polyaniline. Coatings like zinc paint create a physical barrier, but polyaniline works completely different. Polyaniline is a “catalyst that mediates the reaction that leads to rust”. Polyaniline halts corrosion by “accepting electrons from the metal and in turn, donates them to oxygen” creating a two-step reaction that “forms a layer of pure iron oxide”. In the laboratory, under controlled conditions “polyaniline prevented rust 10,000 times more effectively than zinc” and in the field polyaniline “proved three to 10 times more effective” reported Bernard Wessling president and managing partner of Ormecon Chemie GmdH & Co in Ammersbek, Germany. The polymer coating polyaniline is not a heavy metal and does not propose a threat to human health and “it is also cheaper than zinc”, Wessling described it as an “organic metal” that could last forever. Processible polyaniline or blends can provide a promising material in this respect.

In high voltage cables, there is a high probability of occurrence of spark due to the accumulation of heavy static charges on the insulating material used as sheathing for the cable. It can lead to hazardous fire and cause damages for cable system and neighboring materials. To avoid this, there used to be a semiconducting inner layer for the sheathing in contact with the actual conductor.

This gives a gradual reduction of conductivity from the conductor to the outer insulating sheath, thereby, facilitating the discharge of the static charge accumulation and protects from any sparking problems. This semiconducting layer is usually made by conducting carbon black composites in polymers like LDPE and PVC. It needs 15 - 20% of carbon black loading to obtain useful conductivity, which leads to considerable processibility problems due to the dramatic increase in melt viscosity while extrusion. If carbon black could be replaced by conducting polymers like polyaniline, it can reduce the above-discussed processing problem. For this, the conducting polymer has to be thermally stable (retaining of conductivity) at processing temperatures and, hence, melt processible. So the melt processible conducting polymer or its blends offer great potential in high voltage cables applications.

1.11. CRITERIA FOR PROCESSIBILITY:

The main criteria to attain processibility in any polymer blend are the thermal stability of all the materials in the blend, lower melt viscosity even at higher useful loading of the fillers or the minor matrix, miscibility between the blend components, compatibility and the mouldability. The major criteria of the present work have been designed on the basis of the information already discussed. Even though there are many attempts of preparation of polyaniline blends and composites, the attainment of real processibility in terms of industrial processes were still not satisfactorily achieved. The main concern over the processibility of these polymeric conducting blends is the thermal stability. This specifically means the thermal stability of conductivity at processing conditions. So it has to be thoroughly investigated. It was assumed that the incorporation of different dopant ions could alter this thermal stability of polyaniline, as the conductivity loss was identified as due to the loss of dopant ions at higher temperatures^{170 - 173}. Hence, there is a need of investigating the thermal stability

and the degradation kinetics of the polyaniline with different dopant ions. Then checking of real processibility is the most important in process development. For this, the investigation of melts viscosity and solution viscosity, and this behaviour at different polyaniline has to be investigated. The increase in melt viscosity with the conductive material loading can cause serious processing difficulties. This problems remains the major concern over the already commercially used conductive composites were carbon black or graphite are the conductive filler. Also these composites become more brittle at higher filler loading. These problems can be resolved by using more flexible polymeric material as conducting part. If one could prepare the processible polyaniline blend by any of the known techniques like melt processing or solution processing (preferable melt processible as it is most important in industrial view point); next step is the investigating its utility in different applications. The applications like anti-static layers and coatings, EMI shielding are the most important for these conductive blends. Moreover, its applicability in display systems, circuit printing, corrosion resistance, etc, also has to be investigated. Measurements of frequency dependent conductivity of these blends can give an idea about the charge transfer through hopping mechanism, and hence, it gives an idea of its applicability as EMI shielding material in different frequency ranges.

1.12. OBJECTIVES AND SCOPE OF THE WORK:

Attainment of real processibility for inherently conducting polymers was the main aim of the present work. Although there were some investigations in the past, there was hardly any success in this regard. Till now, the melt processing of these polymers or their blends has not found real success mainly due to the loss of conductivity of these polymers at the processing temperatures. The present studies are directed towards improving the processibility and stability of the conducting polyaniline by suitable modifications such as blending and using dopants that act as compatibilizers or plasticizers. Such modifications can lead to changes in crystalline structure, morphology, electrical properties and optical properties. Hence detailed studies are needed in these aspects as well.

In order to improve the processibility and thermal stability of conducting polyaniline, three different methods were adopted for modifying the polymer: (a) Doping the polymer with molecules having electron acceptors and long alkyl chains, (b) Solution blending of modified polyaniline with thermoplastics having good solubility and processibility in common organic solvents such as PVC, PMMA, PC etc. and, (c) Melt blending of polyaniline with polymers with low processing temperature such as LDPE.

The thermal stability, solubility, compatibility as well as conductivity and, hence the processibility of polyaniline could be improved tremendously by incorporation of a long-chain organic acid as the dopant ion. It was also expected that the single step, direct doping procedure could be used for synthesizing these polyanilines with different long-chain dopant ions instead of the standard route of synthesizing, to avoid tedious steps involved like de-doping, re-doping etc. The conductivity as well as the solubility of polyaniline can also be improved by using these long chain acid dopants. So PANI doped with one of this long chain acid dopant was selected as the ideal candidate for further studies on processibility.

This thermally stable polyaniline was melt-blended with polymers like LDPE and its real processibility was checked in terms of ease of processing and thermal stability of conductivity. The effect of polymeric dispersing agents like PEO and PEG that are ionically conductive in nature were explored as processing aids, with an expected improvement of processibility along with electrical properties of these blends. This blends were identified various applications such as a semiconducting layer in high voltage cables and various ESD / EMI shielding applications.

Solubility of the polyaniline can also be improved by the use of long chain acid dopants. This polyaniline with improved solubility in common organic solvents can be solution blended with soluble polymers like PMMA, PVC, PC, etc. These blends could also provide processible conducting material with better optical properties. These blends could also be used for anti-static coatings, corrosion protective coatings, coating for EMI shielding, etc.

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CHAPTER 2
EXPERIMENTAL METHODS

2.1. INTRODUCTION:

Synthesis and doping of polyaniline (PANI) can be done by many methods as discussed in the earlier chapter. This work deals with chemical synthesis of polyaniline followed by doping with different dopants using two methods; (a) Direct doping (in-situ doping), where the PANI was synthesized in presence of respective acids (DBSA, CSA, PSSA etc.), and (b) Indirect doping method, where the PANI is prepared by standard route using a mineral acid, then dedoped with an alkali and redoped with respective acids. Among various blending methods possible, this work mainly made use of two methods; solution casting method using a common solvent to PANI and the blending polymer matrix and melt – blending method, which have utmost importance in processing and application viewpoint. These blends were prepared mostly in the form of films, sheets or strips and checked the processibility and properties with various means.

2.2. MATERIALS USED:

The various polymeric materials and chemicals used are given in the Table 2.1.

Table 2.1: Specifications of polymeric material and chemicals used and their sources:

Material	Acronym	Source
Ammonium persulfate, A.R	APS	S D Fine chemicals, India.
Aniline, A.R	ANI	S D Fine chemicals, India
Camphorsulfonic acid.	CSA	Merk Ltd., Germany.
Chloroform, G.R.	CHCl ₃	E -Merk Ltd., India.
Dodecylbenzenesulfonic acid	DBSA	Fluka Chemi, Switzerland.
Hydrochloric acid (35%), G.R.	HCl	E-Merk Ltd., India.

Low Density Polyethylene (Lotrene CD – 0230)	LDPE	Qatar Petrochemicals, Qatar.
Polycarbonate (Laxan)	PC	G.E. Plastics.
Poly (ethylene glycol)	PEG	Merk Ltd., Germany.
Poly (ethylene oxide)	PEO	BDH Chemicals Ltd., England.
Poly (methyl methacrylate) [GSFC injection moulding grade]	PMMA	Gujpol, India
Poly (Styrene Sulfonic acid) 30% aq. solution	PSSA	Polysciences, USA.
Poly (Vinyl Chloride)	PVC	Finolex, India.
Tetrahydrofuran, G.R.	THF	Merk Ltd., India.

2.3. SYNTHESIS OF POLYANILINE:

Polyaniline can be synthesized by chemical and electrochemical routes. This work deals only with chemical route of synthesis with the use of different dopant ions. The total synthesis of polyaniline with different dopant ions was done in two different ways.

2.3.1. POLYANILINE SYNTHESIS WITH INDIRECT WAY OF DOPING:

Polyaniline was synthesized in conventional route in aqueous medium using mineral acid such as HCl as dopant ion and oxidizing agent ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as initiator. Aniline monomer, acid dopant and oxidizing agent were taken in the molecular ratio of 1:1:1.1. Hydrochloric acid was taken in distilled water into which aniline monomer was added and stirred to get aniline-acid complex and kept in the freezing mixture to attain the

reaction temperature of 0 - 5 °C. In another beaker $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was dissolved in distilled water and kept in the freezing mixture. After both of these solutions attained the reaction temperature, they were mixed together and stirred well, and kept for six hours for the completion of reaction. Polyaniline powder formed was filtered, washed thoroughly with water to remove excess salts and dried under the vacuum (10^{-3} torr) for 24 hrs to make it moisture free.

Polyaniline (PANI) so obtained was first neutralized with ammonia solution (2M), filtered, washed thoroughly (till pH was 7), dried and then crushed to fine powder. This powder was mixed with dodecyl benzene sulfonic acid (DBSA) externally (1:2 mole / monomer) and then dropped in chloroform and stirred for 24 hrs to obtain PANI-DBSA (Redoped). The same procedure was also applied to get redoped polyaniline with dopant acid ions as camphor sulfonic acid (CSA), polystyrene sulfonic acid (PSSA) etc.

2.3.2. POLYANILINE SYNTHESIZED WITH DIRECT DOPING (IN-SITU DOPING METHOD):

In-situ doping method can be made use in synthesizing polyaniline with different dopants. Instead of going through the conventional mineral acid route, the final dopant acid was taken directly in the aqueous reaction medium. The required aniline monomer and organic acid were taken in aqueous medium in 1:1 molar ratio; into which solution of oxidizing agent (initiator) was added at the reaction temperature and kept for 6 hours with stirring to complete the reaction as mentioned above to get the polyaniline with desired dopant ions in single step.

Polyaniline doped with dodecyl benzene sulfonic acid (PANI-DBSA) was synthesized by one-step micellar chemical oxidative polymerization of aniline in the presence of dodecylbenzenesulfonic acid (DBSA) using ammonium

persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as oxidizing agent. The dark green polyaniline powder doped with DBSA obtained was washed thoroughly with distilled water, filtered and dried. This PANI-DBSA was dried under vacuum (10^{-3} torr) for 24 hrs to make it moisture free.

Similarly, one-step chemical oxidative polymerization was also used to synthesize polyaniline doped with polystyrene sulfonic acid (PSSA), camphor sulfonic acid (CSA), etc., as dopants to get PANI-PSSA, PANI-CSA, etc.

2.4. PREPARATION OF LDPE POWDER:

LDPE granules obtained were converted into powder for getting efficient mixing with polyaniline powder. LDPE granules were dissolved in xylene at a temperature above 80°C . The clear solution obtained was cooled to room temperature, stirred well to break the agglomerates and LDPE was precipitated by adding it drop wise to excess of methanol with constant stirring. The fine powder of LDPE obtained was washed well with methanol and then with acetone. This was dried well under vacuum to remove the solvent traces.

2.5. PREPARATION OF SOLUTIONS OF THERMOPLASTICS IN DIFFERENT COMMON ORGANIC SOLVENTS:

For the purpose of solution blending of polyaniline with thermoplastics, the stock solutions of each thermoplastic in suitable solvents were prepared. Solvents used in this work were chloroform for PMMA, tetrahydrofuran for PVC and dichloromethane for PC. All these stock solutions were made with the concentration of 1g / 30 ml.

2.6. MECHANICAL MIXING OF LDPE AND POLYANILINE POWDERS:

Dodecylbenzenesulphonic acid doped polyaniline (PANI-DBSA) and LDPE powders were taken separately and accurately weighed for making different compositions of PANI-DBSA / LDPE with PANI-DBSA content ranging from 5% to 50%. These powders were mixed well using a mortar and a pestle. The details of amounts of different powders taken for different compositions are given in the chapter 3. Similar way the powder compositions containing LDPE and PANI-HCl as well as LDPE and carbon black (acetylene black) also were prepared.

2.7. LOW SHEAR MELT BLENDING AND DETERMINATION OF MELT-FLOW INDICES OF PANI / LDPE BLENDS:

All blend mixtures prepared as mentioned above were melt-blended by passing through the barrel of MFI tester, so as to get low shear rate melt-blended material. All the compositions were processed at 125°C and the melt-blended material was collected as strip form.

Simultaneously, MFI values of these blends were also determined as per the standard ASTM D1238. MFI is good measure of melt processibility of the material. These values were also used to study the effect of various fillers and other additives on the melt viscosity behavior of each kind. As the LDPE grade used was low MFI extrusion grade, all the MFI measurements were done at 125°C, using 5kg load on the piston. From the MFI values relative viscosity of each composition was calculated as discussed in the Chapter 3, and compared with the existing mathematical models discussed in the Chapter 1.

2.8. PREPARATION OF LDPE / CARBON BLACK COMPOSITES AND DETERMINATION OF ITS MELT-FLOW INDEX VALUES:

LDPE and conductive Carbon Black (Acetylene Black) were mixed – same as PANI / LDPE as mentioned – in different compositions to get different composite mixtures of 2%, 5%, 7%, 10%, 15% and 20% carbon black content.

Melt-Flow Index (MFI) values of all these composites were also determined at 125°C with a load of 5kg on the piston.

2.9. PREPARATION OF PANI / LDPE BLEND FILMS BY COMPRESSION MOULDING TECHNIQUE:

All the melt-blended compositions mentioned earlier were taken in the required quantity and the films of different thickness were moulded using a polymer film making compression moulding equipment. Thicknesses of these films were adjusted with the help of spacers.

2.10. HIGH SHEAR MELT COMPOUNDING OF PANI / LDPE BLENDS:

High shear rate melt compounding of PANI / LDPE blends were carried out in a twin-screw micro-compounder (DSM MICRO-5) with a set temperature of 130°C and the rpm of the co-rotating screws were kept at 100. A batch weight of 4g was taken for compounding. Different blend compositions ranging from 10% to 40% of PANI-DBSA were prepared. Similarly, PANI-DBSA / LDPE blends with 5phr PEO as processing aid were also compounded. The machine specification of this micro-compounder is given in the Table 2.2.

Table 2.2: Specifications of Micro-Compounder

Sr. No	Specifications	Micro-Compounder	Unit
1	Total Capacity	+/- 6	cm ³
2	Net Capacity	5	cm ³
3	Screw Speed	5 – 400	rpm
4	Screw Length	107.5	mm
5	Controlled Heating Zones	4	No.
6	Maximum Operating temperature	350	°C
7	Heating Time (from 20 to 240°C)	< 15	mins.
8	Cooling Time (from 240 to 80°C)	14	mins.
9	Cooling Time Using Extra Cooling Element (Water)	8	mins.
10	Cooling Water Flow	3	min ⁻¹
11	Weight	95	kg
12	Dimension	W70 D40 H80	cm
13	Main Voltage	208 / 240	Volt
14	Power	1.75	K Watt
15	Drive Motor(DC)	0.35	K Watt

The above melt compounded blend materials were fed into the cylinder of a micro injection-moulding machine (DSM), which was maintained at a temperature of 140°C. These melts were injected in the mould at room temperature to get the standard test specimen for tensile and impact / flexural tests. The moulds given with this injection-moulding unit were used to mould rectangular (for flexural) and dumbbell (for tensile test) shaped test specimens. The machine specifications of the micro injection-moulding unit are given in the Table 2.3.

Table 2.3: Specifications of Micro Injection Moulding Machine:

Sr. No	Specifications	Micro Injection Moulding Machine	Unit
1	Dimension	650 x 300 x 250	mm
2	Barrel Capacity	+ / - 3.5	cm ³
3	Duration of the injection cycle	5	mins.
4	Heating Zone	2	No.
5	Max. Service Temperature	350	°C
6	Heating Time (from 20 to 240°C)	2	mins.
7	Compressed-air pressure	3 – 16	Bar
8	Compresses-air consumption for 0.5s stroke	9.5	sec ⁻¹
9	Total Heating Power	0.7	KW
10	Weight	20	Kg
11	Main Voltage	208 – 240	Volt

2.11. SOLUTION CASTING OF POLYANILINE BLENDS WITH THERMOPLASTICS:

Polyaniline blends with different thermoplastics were carried out by solution casting technique. Solubility of PANI-DBSA in different common organic solvents was determined by adding 10 gm of each polyaniline in 100 ml of different solvents and stirred for 24 hrs. The solutions obtained were filtered and the total solid content in 1 ml was determined from the weight obtained after complete evaporation of the solvent. The solubility of PANI-DBSA in different solvents like CHCl₃, THF, NMP and DCM were determined.

Stoke solutions of PMMA in CHCl₃, PVC in THF and PC in DCM were prepared with the definite concentrations of 1g / 30ml, 1g / 20ml, etc. The PANI solution and the thermoplastic solutions to prepare the blends were taken in accurate quantities to make different weight fractions of polymer in the

required blends. These solutions in a common solvent were taken and mixed by stirring continuously for 6hrs and then sonicated for half an hour to get homogeneous blend solution. These blend solutions were casted in different petri dishes to get the blend films of different thickness. These castings were carried out at ambient conditions with controlled rate of evaporation. These petri dishes were kept undisturbed till complete evaporation of the solvent and then the films of PANI-DBSA blends with thermoplastics were peeled off and dried thoroughly under vacuum for complete removal of solvent.

2.12. UV-VISIBLE SPECTROSCOPY:

The creation of mid-gap state in the conducting polymers due to charge transfer complex formation due to doping can be studied by UV – Visible spectroscopy. It can also be used to detect the homogeneity of the polyaniline blend. The homogeneous blends will show the increasing intensity for the characteristic absorption bands for polyaniline with the increase in PANI content, which will obey the well-known Beer – Lamberts law:

$$O D = C . \alpha . d$$

Where OD is the optical density, C is the concentration, α the molar extinction coefficient, and, d the thickness of the sample (i.e. the path length).

UV – Visible spectroscopy also provides a measure of solubility of polyaniline with different dopant ions in a solvent. The intensity, or even the existence of bands of characteristic polyaniline while the solutions are subjected for the scan directly gives the measure of solubility.

UV-Visible spectroscopy was done using the “Shimadzu UV-240 spectrometer” sweeping the incident wavelengths from 900nm to 300nm. The

transmittance and reflectance of the solution casted blends films was measured using spectrophotometer model “HR 2000 CG-UV-NIR High Resolution Spectrometer, Ocean Optics Inc.” with the light source from “Mikropack DH 2000”. Transmittance of these blends was recorded with respect to air.

2.13. INFRA-RED SPECTROSCOPY:

Infrared spectroscopic studies were carried out for material characterization of polyaniline samples with different dopant ions as well as blend compositions.

The fine powdered PANI samples with different dopant ions were analyzed by using “Shimadzu FTIR 8201” by diffusion reflectance scanning disc technique.

2.14. VISCOSITY MEASUREMENT:

The measurement of solution viscosity is an important tool to understand the molecular characteristics of the polymer dissolved or dispersed in a solvent medium. The studies on dilute solutions are always of theoretical interest to understand the molecular parameters like molecular weight and molecular interactions, while that of concentrated solutions and polymer dispersions are of practical importance. Many industrial problems associated with adhesives, coatings, cast films and spun fibres cannot be fully appreciated without a proper knowledge of properties of concentrated polymer solutions. At higher concentration of above 5% by weight, polymer molecules do not exist in isolated chain coils, but are interpenetrating and entangled with each other. Therefore at high concentrations the polymer solutions will behave differently and the separate study of concentrated solutions is of high importance.

Viscosity of the dilute polymer solutions was determined using Ostwald viscometer. The schematic diagram of the apparatus is shown in the Figure 2.1. The suitable concentration range for this measurement is 0.1 to 1.0 wt.%, which usually gives a linear relationship of the viscosity with the concentration of the solution. From this the parameters like relative viscosity, specific viscosity, etc. of the polymer / solvent system can be determined. The molecular weight of any polymer can be determined using the popular equation:

$$\eta_{sp} = k \cdot (M_n)^\alpha$$

Where, η_{sp} is the specific viscosity, M_n is the number average viscosity of the dissolved polymer, and 'k' and α are the constants depending on the polymer / solvent / temperature system. Hence, the above equation can be used to determine the number average molecular weight of the polymer.

In the blends of more than one polymer, the interaction between the polymers and the polymer solvent interaction of each polymer can affect the overall viscosity of the solution. If the blend is miscible in molecular level and these interactions are equivalent, the resultant viscosity will be an additive function of individual combination. Any deviation from homogeneity like agglomeration of one component, partial insolubility, etc. will cause the deviation of properties from the expected one. Analysis of these deviations of the blend solution can be used for the prediction of molecular miscibility and homogeneity of resultant blends.

For industrial applications like paints and coatings, the study of the properties of concentrated solutions and dispersions are of high importance. For the viscosity measurements of these highly concentrated solution and dispersions, there are many viscosity cups available like Ford-Cup viscometer and Zahn flow-cup viscometers. In the present work, an arrangement that is

similar to the Ford-Cup was used as shown in the Figure 2.2. The upper cup was made of steel with maximum capacity of 3ml and the bottom orifice on 1mm. There is a glass measuring cylinder kept at the bottom to collect the solution, which comes from the steel cylinder. The time of flow for a definite quantity of solution were measured, from which the relative viscosity was calculated.

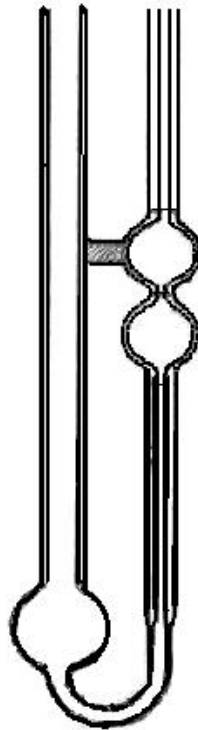


Figure 2.1: Schematic diagram of the Ostwald Viscometer used for the viscosity measurement of the dilute polymer solutions.

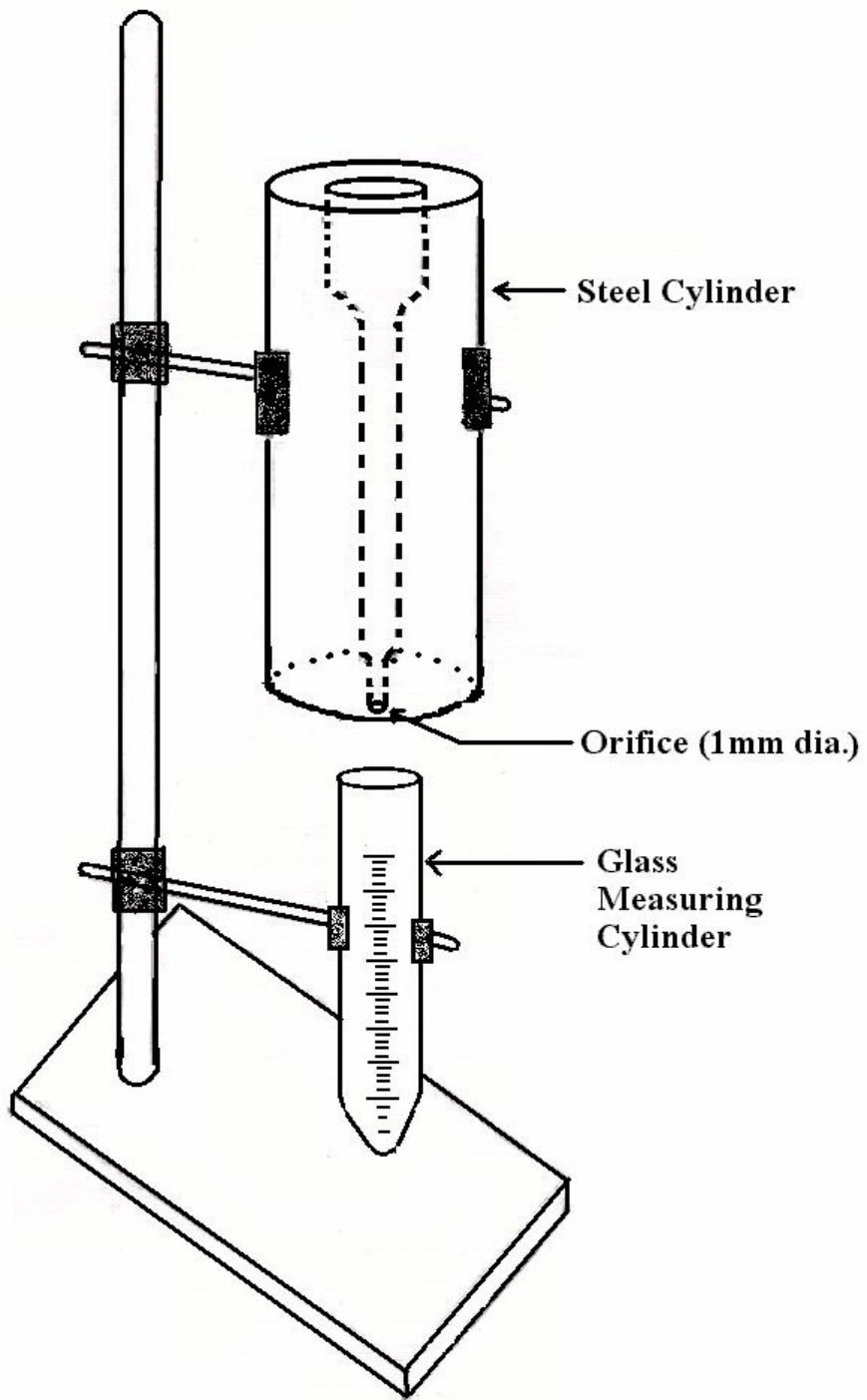


Figure 2.2: Schematic diagram of the Ford-Cup Viscometer type arrangement used for the viscosity measurement of the concentrated polymer solutions and dispersions.

2.15. SPIN COATING:

Spin coating of these solution blends were carried out using a spin coater having a spinning chuck with variable rpm. The different substrates used were steel; glass as well as ABS. Efficiency of spin coating was checked with various viscosities of the corresponding blend solutions.

2.16. X-RAY DIFFRACTION ANALYSIS:

Wide-angle X-Ray Diffraction (WAXD) studies were done in order to analyze the structures of polyaniline synthesized with different dopants as well as the blends prepared by both solution and melt blending techniques. The crystalline structures of various polymeric compositions were investigated by WAXD, using a powder X-Ray diffractometer (Phillips PW 1830 model) with $\text{CuK}\alpha$ source and βNi filter. All the scans were recorded in the 2θ regions of 5 - 45° at a scan rate of 4° per minute. From the 2θ values for reflections; 'd' values were calculated using well-known Brag equation:

$$2 \cdot d \cdot \sin\theta = n \cdot \lambda$$

The conducting polymers synthesized by the chemical route generally offer a semi-crystalline structure. The crystallinity of the polyaniline with different dopants as well as the blends prepared can be estimated by calculating the area under the crystalline and amorphous region of the each peak.

For the amorphous polymeric materials the average inter chain distance (R) can be estimated from the position of the broad peak seen in the above-mentioned figure by using the relation:

$$R = \{(5/8)\lambda / \sin\theta\}.$$

Where, R is the average interchain separation, λ is the wavelength of the X-ray used and θ is the diffraction angle.

The WAXD analysis also can be used for the estimation of the crystallinity Index (C_i) values from simple rule of mixture, which holds true for non-interactive phase segregated systems:

$$C_i = \Phi_A / (\Phi_A + \Phi_C) \dots\dots\dots (3.6)$$

Where, Φ_A = Area under the amorphous region,
 And Φ_C = Area under crystalline region.

2.17. DIFFERENTIAL SCANNING CALORIMETRY:

Differential Scanning Calorimetric studies on PANI-DBSA / LDPE melt blends were carried out using a METTLER thermal analyzer. DSC gives an idea about the primary and secondary transition with change in temperature. It gives the exothermic and endothermic changes occurring over a particular temperature range. DSC was recorded from 50°C to 200°C for LDPE, PANI-DBSA as well as all the compositions of PANI-DBSA / LDPE blends. The heating rate was kept constant at 10°C per minute. DSC was recorded for both heating and cooling cycles. Endothermic changes like melting were recorded during heating cycle, and exothermic changes like crystallization were recorded during cooling. The melting point (T_m) as well as temperature of crystallization (T_c) and corresponding endothermic (ΔH_m) and exothermic (ΔH_c) changes in heat capacity was recorded.

2.18. THERMOGRAVIMETRIC ANALYSIS (TGA / DTG):

TGA of PANI-DBSA / LDPE blends were recorded over a temperature range of 26°C to 600°C in nitrogen atmosphere using a METTLER thermal analyzer, to analyze the degradation pattern of these blends. Simultaneously, Differential Thermogram (DTG) data was also recorded. The different stages of degradation of polyaniline with different dopant ions as well as the effect of blending on the thermal stability of conducting polyaniline can be studied by noting the on set temperatures of each degradation steps, the percentage of degradation at a particular temperature, etc. From the thermogravimetric data, the degradation pattern and kinetics of thermal degradation were studied in detail. A thorough investigation of the effect of blending on the stability of polyaniline was also carried out.

2.19. OPTICAL MICROSCOPY:

In order to study the morphology of the blends, an optical polarizing microscope (Leitz LaborLux 12 pol, Germany) coupled to an image analyzer system (VIDPRO 32, Leading Edge, Australia) was used in the present work. Figure 2.3 shows essential parts of the optical polarizing microscope. The microscope contains essentially a light source (Tungsten Lamp 25W), a condenser, a polarizer, a sample stage with controlled heating arrangement, objective assembly, an analyzer and eyepiece / microphotography arrangement. In another arrangement, image analyzer was connected in place of microphotography. The image analysis system contains a video camera connected to a computer via a software which provide image grabbing, image storage and analysis facilities.

Optical microscopy was used in order to understand the morphology of the LDPE / PEO blends after melt processing. The strands of extruded blends were collected, and the fine sections were cut in both vertical and horizontal directions. Both longitudinal and cross sections were stained with a dye (methylene blue) and images were recorded.

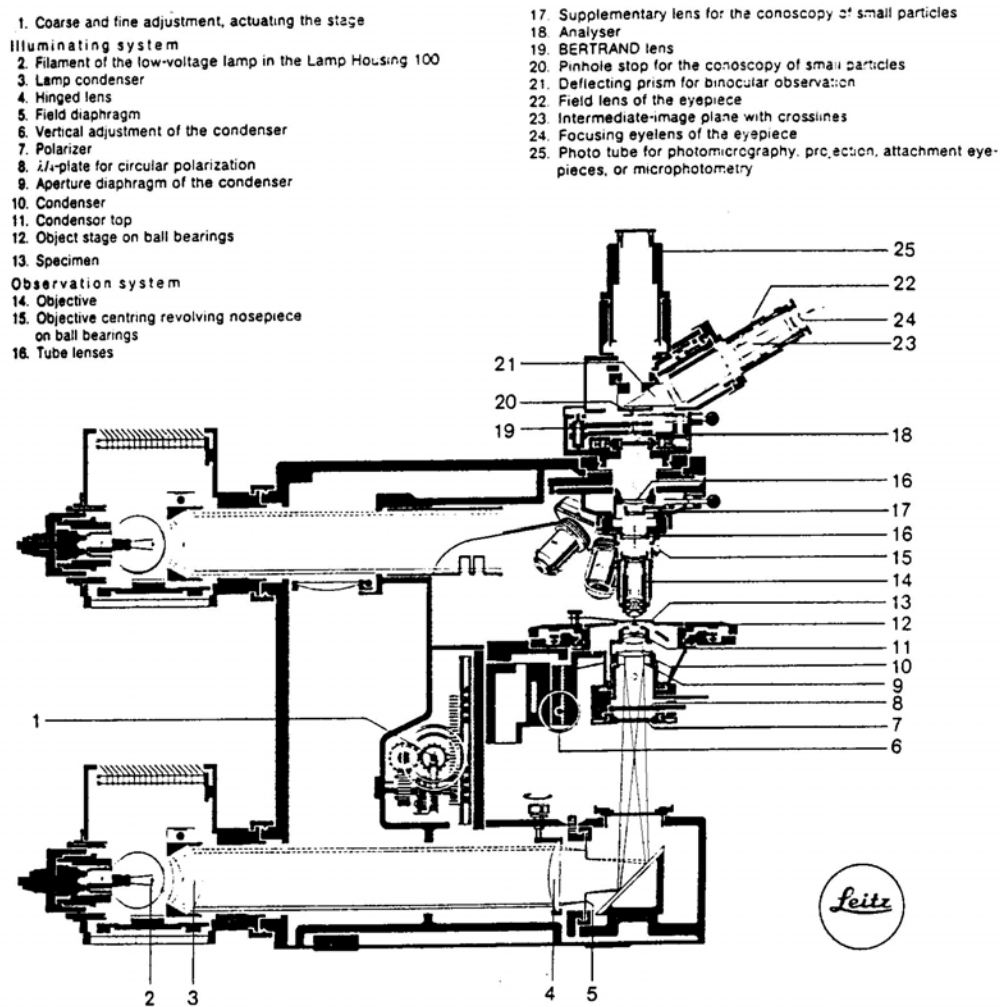


Figure 2.3: Represents the essential parts of optical polarizing microscope.

2.20. CONDUCTIVITY MEASUREMENTS:

The conductivity measurements were carried out by a two-probe technique recorded by a Kiethley electrometer model - 614. Conductivity measurements were done for the films of different blends and pellets of polyaniline with different dopant ions. The specific resistivity was calculated as:

$$\rho = (R * A) / t$$

Where, ρ is the resistivity, R is the resistance measured, A is the area of the electrode used and t is the thickness of the sample. And,

$$\sigma = 1 / \rho$$

Where, σ is the conductivity of the material.

Conductivity of these polyaniline blends with change in temperature also was studied. The integrated electrodes were placed in the sample holders as shown in the Figure 2.3. The apparatus consisted of a sample holder that was enclosed in an electromagnetic shielded cell, which in turn was mounted inside a glass jacket, which could be sealed and connected to a rotary pump. A small heater was mounted close to the film or pellet and using a suitable control device controlled the rise in temperature to 4°C / min. The temperature was varied from room temperature to 100°C, while in the some cases it was varied from -15°C to 100°C using liquid nitrogen.

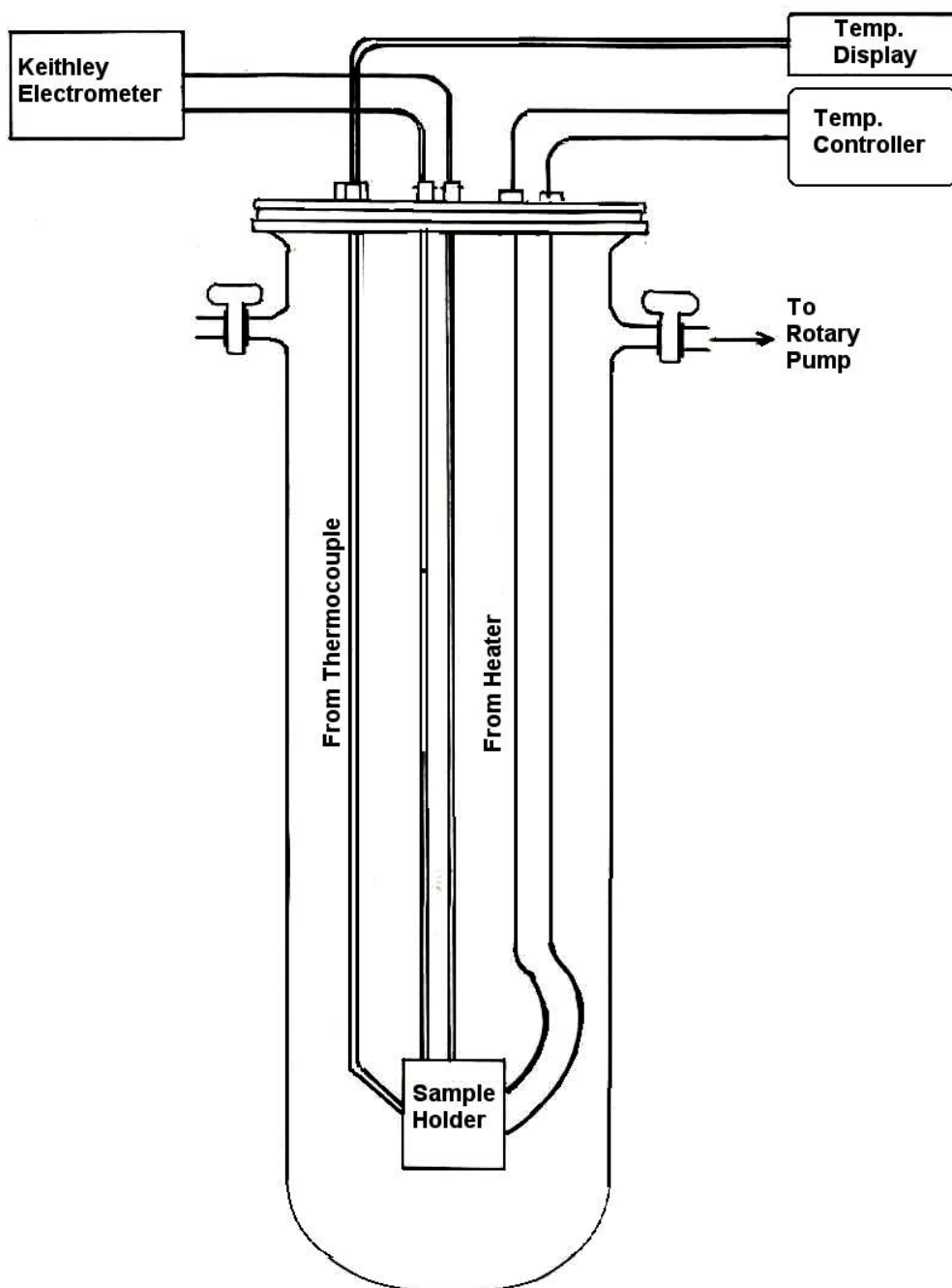


Figure 2.4. Apparatus used for studying the temperature dependence conductivity of conducting polymers and their blends.

2.21. DIELECTRIC MEASUREMENTS:

Dielectric properties of the polymers can give information about the dielectric relaxations occur in the polymeric lattice due to molecular rearrangements. These relaxation studies can be carried out in two ways – with respect to the frequency and with temperature fixing the other constant. These relaxations can be made use to study especially the secondary molecular reorientation like one which occurs during glass transition. So the change in T_g with additives can be understood from the dielectric relaxation curves. The effect of DBSA as a plasticizer on thermoplastics like PMMA and PVC was determined by measuring the dielectric properties of PMMA and PVC films with different DBSA content in it. These measurements were carried out by measuring the resistance and capacitance values at different temperatures using “Aplab 4910 LCR-Q meter. The film samples were loaded in the cell with controlled temperature programming that can sweep the temperature with the rate of 4 degrees per minute.

2.22. Electrical Impedance Measurements:

Electrical impedance of the conducting polymer blends and composites can give the behaviour of these materials in the alternating field at different frequency. These measurements were carried using the ‘Solatron SI 1255 HF Frequency Response Analyzer’ connected with a ‘Solatron 1296 dielectric Interface’. Here Relative permittivity values of these PANI / LDPE blends were recorded, from which conductivity of these materials with frequency can be calculated. This can be used as an important tool to understand the hopping mechanism of these blends with respect to polyaniline loading.

2.23. EMI SHEILDING MEASUREMENTS:

Samples of PANI-DBSA / LDPE blend and those with PEO were moulded to get the sheets of 5 cm diameter and 1mm thickness for EMI shielding measurements. The EMI shielding measurement set up is given in the Figure 2.4. Here, the signal generator generates the signal and transmitted to the loop antenna placed in a metal box. Samples were placed on the sample holder, which was placed in between the loop antenna and a HP RF probe.

All the signals, which were generated by the loop antenna connected to APLAB Frequency Generator (Model: 2219-U) will pass through the sample if it has no shielding effectiveness (SE). These transmitted signals were detected by the EMI near field probe (HP 11941A) and then amplified using a wide band preamplifier (HP 11909A). The amplified signals were then fed to a Hewlett Packard Spectrum analyzer (Model E 4411B). The spectrum analyzer gives the spectral distribution curve (SDC) depending upon the signals transmitted or shielded. The unshielded condition was considered as reference. The comparison of the curves obtained for various samples with this reference was used analyzed to get the shielding effectiveness of the samples.

EMI SHEILDING MEASUREMENT SET UP

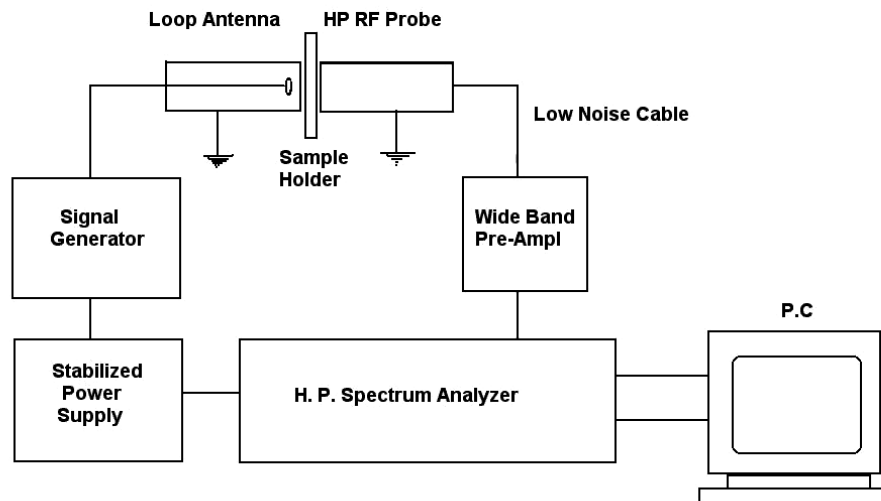


Figure 2.4: EMI shielding measurement set up

CHAPTER – 3
MELT COMPOUNDING AND PROCESSING OF
POLYANILINE / LDPE BLENDS

3.1 INTRODUCTION:

Processibility of a polymer depends on so many factors like thermal stability, viscosity at processing conditions, crystallization behaviour and molecular alignments, molecular structure and its miscibility with other polymer matrices, interaction with other additives etc. In the field of conducting polymers, the true processibility remains the “Achilles heel” even today. Methods of synthesis and the types of dopant ions used are the main driving forces, which decide the processibility and conductivity of intrinsically conducting polymers like polyaniline. Selection of dopant acids can alter the stability of polyaniline; especially conductivity, its molecular structure, molecular interactions and the interactions with other polymers etc.

This work has been structured in such a way that the material selection was done in the earlier stage of the work, according to stability of the polyaniline obtained, and, hence, thermal stability was studied for polyaniline containing various dopant ions introduced during synthesis. From the results ‘Polyaniline doped with dodecylbenzenesulphonic acid’ (PANI-DBSA) was chosen as the major conducting polymer component in all the blends. Selection procedure for this has been described in detail in this chapter. This chapter mainly deals with the melt blending of polyaniline (PANI) with low-density polyethylene (LDPE) having a low melting point of 108°C. The processing characterization, physical characterization and testing were done along with other structural studies. Some other polymers like polyethylene oxide (PEO) and polyethylene glycol (PEG), which have very low melting temperatures and low melt viscosities were used as processing aids in separate sets of blends. These blends showed better processibility and end properties. These blends can fetch numerous applications like semi-conducting layer in cables, anti-static elements in other electronic appliances etc.

3.2. EXPERIMENTAL:

3.2.1. SYNTHESIS OF POLYANILINE WITH DIFFERENT DOPANTS:

Polyaniline was synthesized by two different routes as described in the earlier experimental part (chapter 2). The route used in this work was the direct synthesis path, which gives the in-situ doping of the desired dopant ion in a single step compared to the multi-step conventional way of doping. Different dopants like Hydrochloric acid (HCl), Camphorsulphonic acid (CSA), Polystyrenesulphonic acid (PSSA) and Dodecylbenzenesulphonic acid (DBSA) were used as different acid dopants for the synthesis of polyaniline.

a) Polyaniline Doped with HCl:

Polyaniline doped with hydrochloric acid was synthesized through conventional route, where emulsion polymerization was done in presence of HCl and using ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as oxidizing agent ^{1, 2}. 2ml of aniline monomer (0.02M) and 2.1ml of 35% HCl solution (0.02M) were taken in aqueous medium at the reaction temperature of 0 - 5°C and an aqueous solution of 5.3g ammonium persulphate (0.02M) was added to it and kept for 4hrs to complete the reaction. The polyaniline formed was washed and thoroughly dried.

b) Polyaniline Doped with Camphorsulphonic acid (CSA):

Polyaniline doped with Camphorsulphonic acid (CSA) was also synthesized through direct in-situ doping route, where single-step emulsion polymerization was done in presence of CSA and using ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as oxidizing agent. 2ml of aniline monomer (0.02M) and 5.108g of CSA (0.02M) were taken in aqueous medium at the reaction temperature of 0 - 5°C and an aqueous solution of 5.3g ammonium persulphate (0.02M) was added to it and kept for 4hrs to complete the reaction. The polyaniline (PANI-CSA) formed was washed and thoroughly dried.

c) Polyaniline Doped with Polystyrenesulphonic acid (PSSA):

Similarly, polyaniline doped with polystyrenesulfonic acid (PSSA) was also synthesized in single-step polymerization method. Here, the amount of PSSA taken was 12.2ml of 30% aqueous solution of PSSA (0.02M).

d) Polyaniline Doped with Dodecylbenzenesulphonic acid (DBSA):

Polyaniline doped with Dodecylbenzenesulphonic acid (DBSA) was also synthesized through direct in-situ doping route, where single-step emulsion polymerization was done in presence of DBSA and using ammonium persulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, as oxidizing agent. 2ml of aniline monomer (0.02M) and 7.1ml DBSA (0.02M) were taken in aqueous medium at the reaction temperature of 0 - 5°C and an aqueous solution of 5.3g ammonium persulphate (0.02M) was added to it and kept for 4hrs to complete the reaction. It was found that in this case, the polyaniline formed did not settle immediately and hence 10g KCl was added to the suspension to facilitate quicker precipitation. The dark green polyaniline powder (PANI-DBSA) formed was washed and thoroughly dried.

3.2.2. THERMOGRAVIMETRIC ANALYSIS OF POLYANILINE WITH DIFFERENT DOPANTS:

Thermal stability of polyaniline synthesized with different dopants as above was studied by thermogravimetric analysis (TGA). TGA was done from room temperature to 600°C in nitrogen atmosphere. The dopant degradation and main chain degradation of each polyaniline was determined and kinetics of degradation was also studied thoroughly. Differential Thermogravimetry (DTG) was taken simultaneously and analyzed carefully to get stability parameters of each polyaniline.

3.2.3. PREPARATION OF LDPE POWDER.

Low-density polyethylene (Lotrene CD-0230' grade, mp = 108°C) granules were dissolved in xylene by heating it to above 80°C. The clear solution obtained was cooled to room temperature, stirred well to break the agglomerates and LDPE was precipitated by adding it drop wise to excess of methanol with constant stirring. The fine powder of LDPE obtained was washed well with methanol and then with acetone. This was dried well under vacuum to remove the solvent traces.

3.2.4. MECHANICAL MIXING OF LDPE AND POLYANILINE POWDERS:

Dodecylbenzenesulphonic acid doped polyaniline (PANI-DBSA) and LDPE powders were taken separately and accurately weighed for making different compositions of PANI-DBSA / LDPE with PANI-DBSA content ranging from 5% to 50%. These powders were mixed well using a mortar and a pestle. The amounts of different powders taken to make 1g of the mixtures of different compositions are given in Table 3.1.

In the same way PANI-PSSA / LDPE blend mixture is also made containing 40% of PANI-PSSA. 0.4g of PANI-PSSA and 0.6gm of LDPE powder was taken to make a 1g mixture.

The conventional hydrochloric acid doped polyaniline (PANI-HCl) also taken and mixed with LDPE powder in the same way as mentioned above to get a range of compositions from 10% to 40%. The compositions were exactly the same as in the case of PANI-DBSA / LDPE as mentioned in the table.

Table 3.1: The amount of PANI-DBSA and LDPE powders taken to make 1gm of various compositions (wt.%) of PANI-DBSA / LDPE blend mixture:

PANI-DBSA Content (Weight %)	Amount of PANI-DBSA (g)	Amount of LDPE (g)
5%	0.05	0.95
10%	0.10	0.90
20%	0.20	0.80
30%	0.30	0.70
40%	0.40	0.60
50%	0.50	0.50

Another set of blend mixtures of PANI-DBSA / LDPE were prepared from a range of 5% to 50% PANI-DBSA content, which contains different amounts of PEO (MW = 300,000) (in phr level) as processing aids. Different sets of blend mixtures were prepared with 3phr, 5phr as well as 7phr of PEO contents. The details of the contents taken are given in Table 3.2.

Similarly, 5phr PEG (MW = 35,000) was also used as processing aid in another set of PANI-DBSA / LDPE blends

Table 3.2: The amounts of LDPE, PANI-DBSA and PEO taken in different blend mixtures of LDPE / PANI-DBSA with varying amount of PEO as processing aid [Total quantity = 1g]:

Basic Composition (% PANI-DBSA Content)	Amount of PANI-DBSA (g)	Amount of LDPE (g)	Amount of PEO		
			For 3phr	For 5phr	For 7phr
0%	0.00	1.00	0.03	0.05	0.07
5%	0.05	0.95	0.03	0.05	0.07
10%	0.10	0.90	0.03	0.05	0.07
20%	0.20	0.80	0.03	0.05	0.07
30%	0.30	0.70	0.03	0.05	0.07
40%	0.40	0.60	0.03	0.05	0.07
50%	0.50	0.50	0.03	0.05	0.07

3.2.5. MELT BLENDING AND DETERMINATION OF MELT-FLOW INDICES OF PANI / LDPE BLENDS:

All blend mixtures prepared as mentioned earlier were melt-blended by passing through the barrel of MFI tester, so as to get low shear rate melt-blended material. All the compositions were processed at 125°C and collected the melt-blended material was collected as strip form.

Simultaneously, during the melt-blending process MFI values of these blends were also determined as per the standard ASTM D1238. As the LDPE grade used was low MFI extrusion grade, all the MFI measurements were done at 125°C, using 5kg load on the piston.

3.2.6. PREPARATION OF LDPE / CARBON BLACK COMPOSITES AND DETERMINATION OF ITS MELT-FLOW INDEX VALUES:

LDPE and conductive Carbon Black (Acetylene Black) were mixed – same as PANI / LDPE as mentioned – in different proportions to get different composite mixtures of 2%, 5%, 7%, 10%, 15% and 20% carbon black content.

Melt-Flow Index (MFI) values of all these composites were also determined at 125°C with a load of 5kg on the piston.

3.2.7. PREPARATION OF PANI / LDPE BLEND FILMS BY COMPRESSION MOULDING TECHNIQUE:

All the melt-blended compositions mentioned earlier were taken in the required quantity and moulded the films of different thickness were moulded using a polymer film making compression moulding equipment at 120°C with

residence time of 12 min. Thicknesses of these films were adjusted with the help of spacers and these ranged from 200 μm to 240 μm .

3.2.8. HIGH SHEAR MELT COMPOUNDING OF PANI / LDPE BLENDS:

High shear rate melt compounding of PANI / LDPE blends were carried out in a twin-screw micro-compounder (DSM MICRO-5) with a set temperature of 130°C and screw rpm of 100. A shot-weight of 4g was taken each time for compounding. Different blend compositions ranging from 10% to 40% of PANI-DBSA were prepared. Similarly, PANI-DBSA / LDPE blends with 5phr PEO as processing aid were also compounded.

The above melt compounded blend materials were fed into the cylinder of a micro injection-moulding machine (DSM), which was maintained at a temperature of 140°C. These melts were injected in the mould at room temperature to get the standard test specimen for tensile and impact / flexural tests.

3.2.9. STRUCTURE AND PROPERTY STUDIES OF PANI / LDPE BLENDS:

a) XRD Studies for Structural Investigations:

X-Ray diffraction analysis was carried out for all the blends prepared to study the structural behaviors. WAXD was also done for the blend of PANI / PEO films with different compositions of 1:2, 1:1, 2:1, 3:1, 4:1 and 6:1 respectively to analyze the effect of PEO on PANI orientation. The crystallization indices and crystallinity changes were calculated and studied in detail. XRD patterns were analyzed carefully to investigate the phase morphology of these blends.

b) Thermogravimetric Analysis (TGA):

TGA of PANI-DBSA / LDPE blends were recorded over the temperature of 26°C to 600°C in nitrogen atmosphere using a METTLER thermal analyzer, to analyze the degradation pattern of these blends. Simultaneously, Differential Thermogram (DTG) data was also recorded. From these, the degradation pattern and kinetics of thermal degradation were studied in detail. A thorough investigation of the effect of blending on the stability of polyaniline was also carried out.

c) Differential Scanning Calorimetric Analysis:

Differential Scanning Calorimetric (DSC) analysis was carried out, using METTLER DSC machine, for different PANI / LDPE blends. It was recorded from room temperature to 200°C to analyze the primary and secondary molecular changes.

d) Optical Microscopy:

Optical microscopy was used in order to understand the morphology of the LDPE / PEO blends after melt processing. The details of the Optical Polarizing microscopy used are discussed in the Chapter 2. The strands of extruded blends were collected, and the fine sections were cut in both vertical and horizontal directions. Both longitudinal and cross sections were stained overnight with a dye (methylene blue) and images were recorded in normal mode.

3.3. RESULTS AND DISCUSSIONS:

The processibility of a polymer or a blend of two polymers depends mainly on the stability of each component at the processing conditions. Conducting polymers such as polyaniline face severe problems of losing its conductivity when heated above 150°C^{3,4}. However, it has been mentioned by some authors that PANI has better stability with certain dopants. Hence, the synthesis of polyaniline with different dopant ions and investigating its thermal stability was undertaken in order to select the best option for melt-blending process and fixing the temperature of blending process. The effect of blending and doping on the melt processing behavior of polyaniline was investigated so as to optimize the composition. In this portion of the work, low melting grade of low-density polyethylene was chosen to blend polyaniline since it offers lower processing temperatures as well as it is the most extensively used polymer for formulating masterbatches.

3.3.1. SYNTHESIS AND SELECTION OF POLYANILINE WITH MORE STABLE DOPANT IONS:

Polyaniline can be synthesized easily with acid dopants^{5,6}. The standard way of synthesizing is the oxidative emulsion polymerization of aniline in an acid medium so as to get the insitu acid doped polyaniline. It has been reported that polyaniline can also be doped with organic acids like different sulfonic acids such as CSA, PSSA, DBSA, PTSA, MeSA, etc.⁷⁻¹². These polyanilines can be prepared in two ways. (i) The PANI-HCl synthesized using HCl is first neutralized with ammonia solution (2M), filtered, washed thoroughly till pH is 7, dried and crushed to fine powder. This powder is then mixed with sulfonic acid by which PANI is doped externally (1:2 mole / monomer) which is then dropped in a solvent and stirred for 24 hrs to obtain PANI doped with a new organic dopant ion. (ii) The second route is the one-step emulsion polymerization of aniline in presence of the sulfonic acid. The general way of synthesizing has been found to

be the first route where a number of tedious steps like neutralizing, washing and re-doping is involved. In this work, the second route was selected as it offers one-step synthesis giving the product in the final form of doped polyaniline, which is attractive for industrial large-scale production. More over, there are no tedious steps like neutralization with ammonia, washing of emeraldine base and again doping it with another acid.

In all these reactions yield the final product of doped polyaniline in the form of dark green powder. The agglomeration of the powder as well as the intensity of the green colour varies with the dopant ion used. These agglomerations can be easily broken to get the fine powder by mechanical grinding. On the other hand, in the case of DBSA doped polyaniline the final product was found very soft and sticky powder with intense green colour. The drying process also was found to take longer time in DBSA doped case. The yield of the polyaniline formed was determined in each case and is given in the Table 3.3. The pure form of all these PANIs showed very good conductivity of the order of 10^{-2} - 10^{-1} S/cm. Among these, the one, which was doped with DBSA, gave the highest conductivity. These values are given in Table 3.4.

Table 3.3. Yield of polyaniline formed with different dopant ions synthesized by direct doping method.

Dopant acid used	Yield (%)
HCl	77.2
CSA	86.7
PSSA	52.9
DBSA	88.0

Table 3.4. Conductivities of polyaniline doped with different acids synthesized by direct doping method:

Dopant acid used	Conductivity (S/cm)
HCl	$1.015 * 10^{-2}$
CSA	$3.561 * 10^{-2}$
PSSA	$2.101 * 10^{-2}$
DBSA	$4.767 * 10^{-1}$

The most important property associated with the processibility of these conducting polymers is the thermal stability of their conductivity. Thermal stability of emeraldine base as well as standard HCl doped polyaniline has already been studied and reported elsewhere^{3, 13-16}. This stability was studied in the present case for all samples by thermo gravimetric analysis (TGA), after drying thoroughly under vacuum at 45°C for three days to remove entire moisture. Thermograms of these four polyanilines are shown in Figure 3.2. Two-stage degradation of polyanilines is obtained, the first step being the degradation due to the escape of dopant ions from the polyaniline and the latter being the main chain scission. The temperature point at which the dopant ion starts to escape from the polyaniline matrix can be determined from the onset temperature of the first degradation in each case. These values are given in Table 3.5. It shows the lowest onset temperature of dopant ion degradation for PANI-HCl and highest for PANI-DBSA. The order of increasing onset temperature for dopant ion degradation was found to be in the order of PANI-HCl < PANI-CSA < PANI-PSSA < PANI-DBSA.

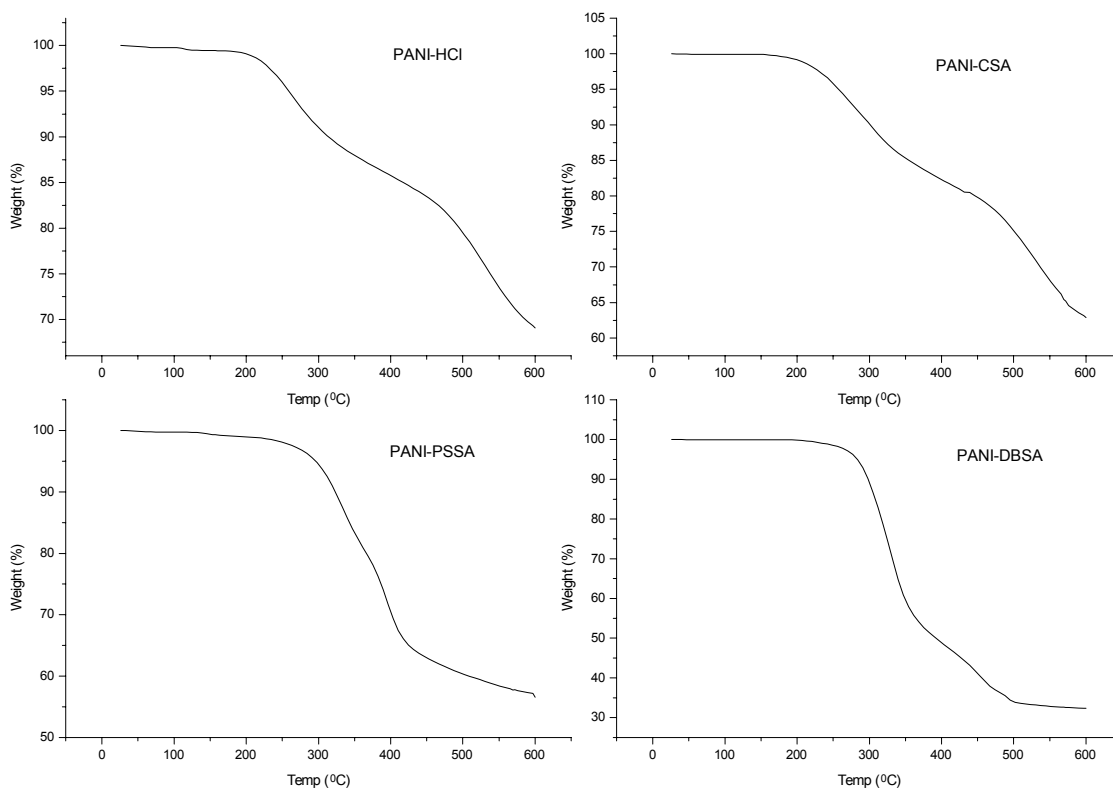


Figure 3.1: Thermograms of polyanilines doped with HCl, CSA, PSSA and DBSA.

Table 3.5: Onset temperatures of first stage of degradation of different polyanilines obtained from TGA (corresponding to loss of dopant ions):

Polyaniline Type	Onset temperature of first degradation (T_{onset}) (°C)
PANI-HCl	210
PANI-CSA	219
PANI-PSSA	284
PANI-DBSA	285

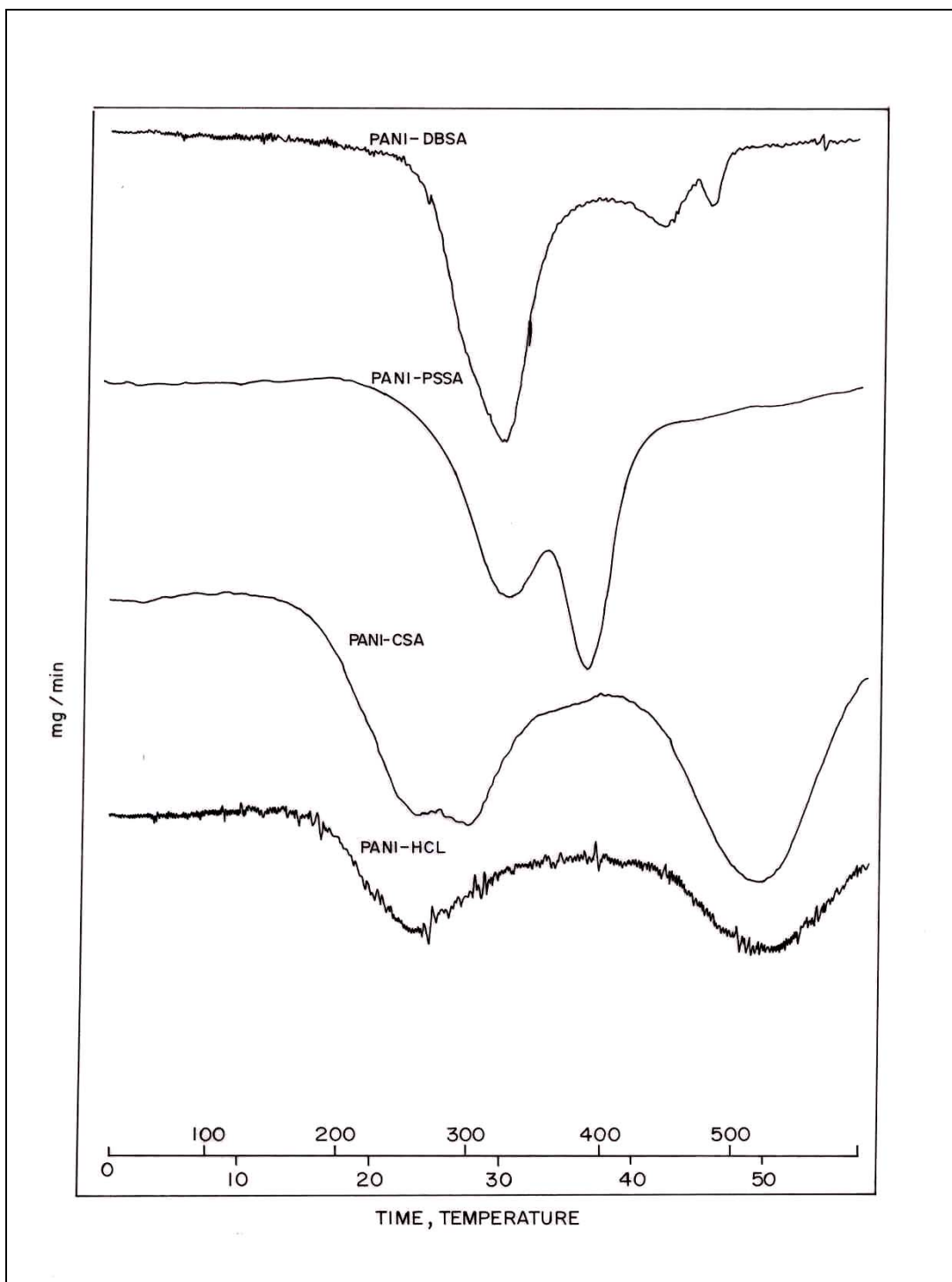


Figure 3.2: Differential Thermograms (DTA) of polyanilines doped with HCl, CSA, PSSA and DBSA.

The differential thermogram (DTG) also can be analyzed for the accurate determination of T_{onset} as well as T_{max} of each degradation step involved. T_{onset} is the point at which intense change to any dip starts and T_{max} is the lowest point of each dip of these derivative curves. These values give a clear idea of the temperature region, to be considered for the study of kinetic parameters like activation energy and order of reaction. DTG curves for all polyanilines with different dopant ions are shown in Figure 3.2. All these curves show the existence of two stages of polyaniline degradation. Separate minima show the separate degradation steps. It may be noted that the position and the nature of the first peak depends very much on the dopant present while the second step changes little. In all cases, the first step can be assigned to the dopant and the second to the main chain degradation. In the case of CSA it can be seen that there is an existence of double degradation of dopant ion itself indicating by the two components in the first peak. It causes the rapid degradation of CSA above 220°C. These DTG shows the highest T_{max} for the first degradation step for DBSA doped polyaniline.

The second stage of the degradation shown in the thermograms is the main chain degradation of polyaniline. It is already reported that degradation of conducting polyaniline is found to have two major stages. First one is associated with the degradation or evolution of the dopant ions from the polymer and the second stage is the actual thermal degradation of the main polymer chain^{3, 5}. Since the first stage of degradation is dopant ion dependent, it can vary with the dopant ion used. This work elucidates the supremacy of DBSA over the other common sulfonic acids and mineral acid dopants in bringing about thermal stability as desired for melt process. Detailed study of degradation temperatures and the kinetics of degradation with each dopant ion were studied in detail.

The degradation kinetics can be examined by using existing kinetic equations. The derivation of equation by combining Arrhenius equation with the general kinetic expressions (Petrović and Zavargo, 1986; Nishizaki and Yoshida,

1980) takes into consideration that experiments are carried out either isothermally or at a constant rate of heating¹⁷. The equation is as follows:

$$(\frac{d\alpha}{dT}) = (A/\beta) (1-\alpha)^n \cdot e^{-E_a/RT} \quad \text{----- (3.1)}$$

Where, α is the degree of conversion, β is the heating rate, n is the order of the reaction, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature in Kelvin scale and $d\alpha/dT$ is the rate conversion / degradation with temperature. For a process with constant rate of heating, $(d\alpha/dT) \cdot \beta$ gives the rate of conversion / degradation with respect to time, $(d\alpha/dt)$. So the above equation can be re-written as:

$$(\frac{d\alpha}{dt}) = A \cdot (1-\alpha)^n \cdot e^{-E_a/RT} \quad \text{----- (3.2)}$$

Taking natural logarithm for the above equation,

$$\ln (d\alpha/dt) = \ln A + n \ln (1-\alpha) - E_a / RT \quad \text{----- (3.3)}$$

This equation now assumes the form of an equation of a straight line. Plotting $\ln(d\alpha/dt)$ against $(1/T)$ gives a straight line with a slope of $(- E_a / R)$, from which the activation energy (E_a) can be calculated.

The heating rate was kept constant at 10°C per minute for all thermogravimetric analysis of polyanilines with different dopant ions. Different points at tiny intervals of half a minute were taken and the rate of degradation of each point was determined. Such points in between the T_{onset} and T_{max} of each case, which are, also more near to the T_{onset} were taken into consideration for the detailed kinetic studies to determine the activation energy as well as order of degradation in each case. Figure 3.3 shows the points taken with a constant temperature interval for PANI-DBSA.

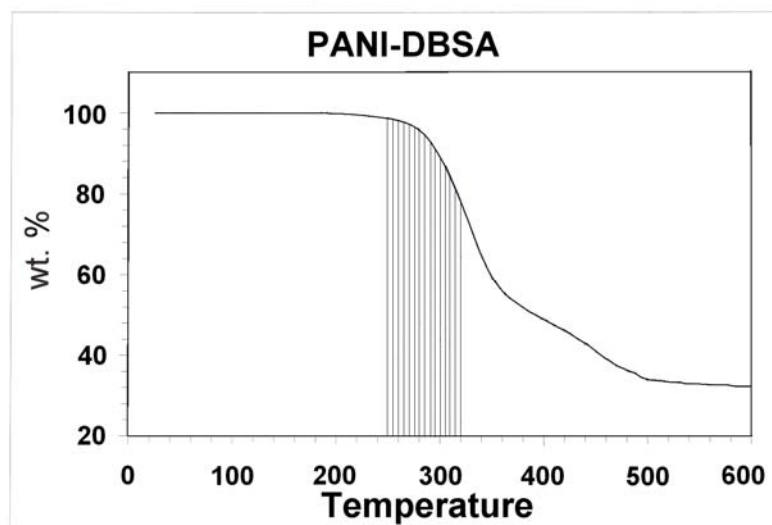


Figure 3.3: The points taken from TG with a constant temperature interval for PANI-DBSA.

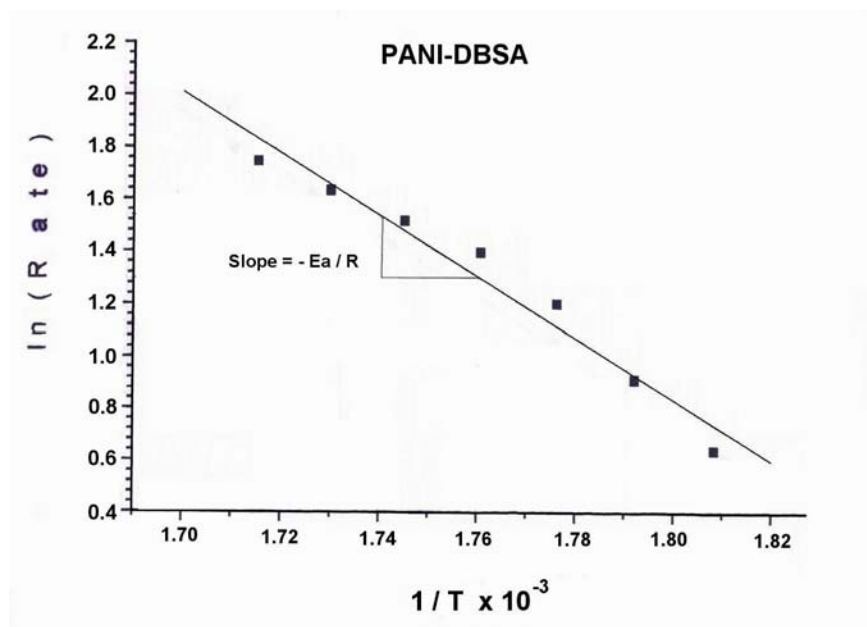


Figure 3.4: Plot of $\ln(dw/dt)$ against $1/T$ for PANI-DBSA

The values of $\ln(d\alpha/dt)$ were plotted against $(1/T)$ for all the four cases considering the point in between T_{onset} and T_{max} as discussed above. This plot for PANI-DBSA is given in Figure 3.4. From the slope obtained in each case, the activation energy of degradation was calculated. These values are given in the Table 3.6.

The activation energy indicates the energy required for the reaction to be feasible. Here, lesser activation energy indicates the higher rate of degradation. PANI-HCl gave the lowest E_a of 8.9 kcal/mol indicating its fast degradation of dopant ions. E_a of PANI-DBSA was found to be the highest at 23.1 kcal/mol. E_a was found to increase in the order PANI-HCl < PANI-CSA < PANI-PSSA < PANI-DBSA. It indicates the highest stability of PANI-DBSA among all the cases considered in terms of the rate of degradation also.

Table 3.6: Activation energy calculated from the plot of $\ln(d\alpha/dt)$ against $(1/T)$ for the thermal degradation of dopant ions from polyanilines with different dopant ions.

Polyaniline	Slope obtained (- E_a/R)	Activation energy, E_a (kcal / mol)
PANI-HCl	-4250	8.98
PANI-CSA	-5362	10.65
PANI-PSSA	-9500	18.88
PANI-DBSA	-11670	23.19

As expected, the Cl^- ion in PANI-HCl showed the least thermal stability. As it is the smallest dopant anion considered, it can escape faster than other large chain anions. There are already some reports on the degradation of the dopant ions occurring in the first step of the thermal degradation of polyaniline and its derivatives^{15, 18}. It was reported with the help of TG/Mass analysis that the fragment dissociating in the first step is that of dopant ions¹⁸. The CSA dopant showed lesser stability compared to other sulfonic acids like PSSA and DBSA. This can be due to the fact that CSA is a highly crystalline material, which is reported to dissociate itself in two stages, resulting in rapid degradation above 220°C. The other two polyanilines, that is, PANI-PSSA as well as PANI-DBSA showed better stability. This is due to the polymeric backbone of PSSA and a very long alkyl group in DBSA. These can interact with the polyaniline main chain much better as they have an inter-penetrating nature or have better compatibility with the long alkyl chain portions. Also, due to the higher molecular weight of these anions, their mobility inside another polymeric system with the raise in temperature will be less as compared to smaller anions. So it won't escape from the polyaniline easily with the rise in temperature. From these results, PANI-DBSA was selected as the most suitable material for blending.

3.3.2. MELT – BLENDING OF POLYANILINE WITH LDPE:

As discussed in the earlier chapter, blending is a useful technique to achieve processibility in conducting polymers. Amongst all the blending techniques, melt blending is the most feasible and important technique from the industrial point of view. Considering the lower thermal stability of conductivity of polyanilines, the second polymer matrix with which it has to be blended should be as low melting as possible and thermally very stable. More over, it should be compatible with polyaniline so as to get a better dispersion of polyaniline in that matrix. In the present work use of low melting LDPE grade whose melting point is 111.8°C, as confirmed by DSC, was made for main matrix so that it can be

processed at a temperature below 120°C, which assures stability of the polyaniline during melt processing.

Although some authors have already reported the melt compounding of HCl doped polyaniline¹⁹⁻²⁴ and other inherently conducting polymers, they were not very successful in terms of real processibility that could contribute to fabricating final products for electronic and electrical applications. These composites reported were seem to have inferior dispersion and can lose conductivity at the processing temperature. Carbon black composites are the commonly used for all practical applications where semiconducting layer or parts are needed²⁵⁻³⁰. In carbon black composites, higher loading is always needed even for attaining reasonable conductivity, which leads to increase in melt viscosity and resulting in cumbersome processing. Hence, the main criteria for checking the processibility of these ICP blends is the achievement of low melt viscosity at the processing temperature, as well as the attainment of required conductivity with low percentage of loading.

To study the melt viscosity of the blends, melt-flow index (MFI) values were recorded at its processing temperature of 125°C with 5kg load on the piston. These were noted for PANI-DBSA / LDPE blends ranging from 10% to 50% of PANI-DBSA content and are given in the Table 3.7. MFI values of the PANI-HCl / LDPE blends were also recorded and are shown in the Table 3.8. The MFI of 40% PANI-PSSA / LDPE was found to be 0.155 g/10min. at 125°C with a load of 5kg on the piston

The MFI values for PANI-DBSA blends were found to be higher in comparison with other polyanilines. Higher MFI indicates the lower melt – viscosity of PANI-DBSA blends. This clearly shows the better processibility of PANI-DBSA blends than other polyanilines. This also indicates the better compatibility of these blends than others. It can be also due to the very small particle size of the DBSA doped polyaniline. The standard polyaniline, that is

PANI-HCl, acts as a less interactive filler in the LDPE matrix, thereby, resulting in increased melt viscosity with increased loading, as in the case of carbon black fillers. These MFI values are compared with the values of LDPE / Carbon Black composites of 2% - 20% of carbon black (Acetylene Black) content at the same conditions used to measure PANI blends and are given in Table 3.9.

Table 3.7: MFI values of PANI-DBSA / LDPE blends at 125°C with a load of 5kg on the piston:

Basic Composition of the blend (% PANI-DBSA Content)	MFI (g / 10min.)
0% (Pure LDPE)	0.865
10%	0.635
20%	0.485
30%	0.380
40%	0.290
50%	0.230

Table 3.8: MFI values of PANI-HCl / LDPE blends at 125°C with a load of 5kg on the piston:

Basic Composition of the blend (% PANI-HCl Content)	MFI (g / 10min.)
10%	0.450
20%	0.200
30%	0.050
40%	0.010

It is found that the MFI of these blend are too low as there is no flow at 20% loading, indicating the very high melt viscosities of these composites, which can cause severe processing difficulties. It is clear that the melt viscosity is predominantly low for PANI blends than Carbon Black composites showing its potential application as processible blends. This in turn shows that the PANI-DBSA is a better choice for melt blending as compared to the other materials considered. The comparison of change in MFI values of the PANI-DBSA / LDPE as well as PANI-HCl / LDPE with PANI-DBSA loading is illustrated in the Figure3.5.

Table 3.9: MFI values of LDPE /Carbon Black composites at 125°C with a load of 5kg on the piston:

Basic Composition of composites (% Carbon Black Content)	MFI (g / 10min.)
2%	0.5150
5%	0.2980
7%	0.2400
10%	0.1075
15%	0.03835
20%	0.0 (No Flow)

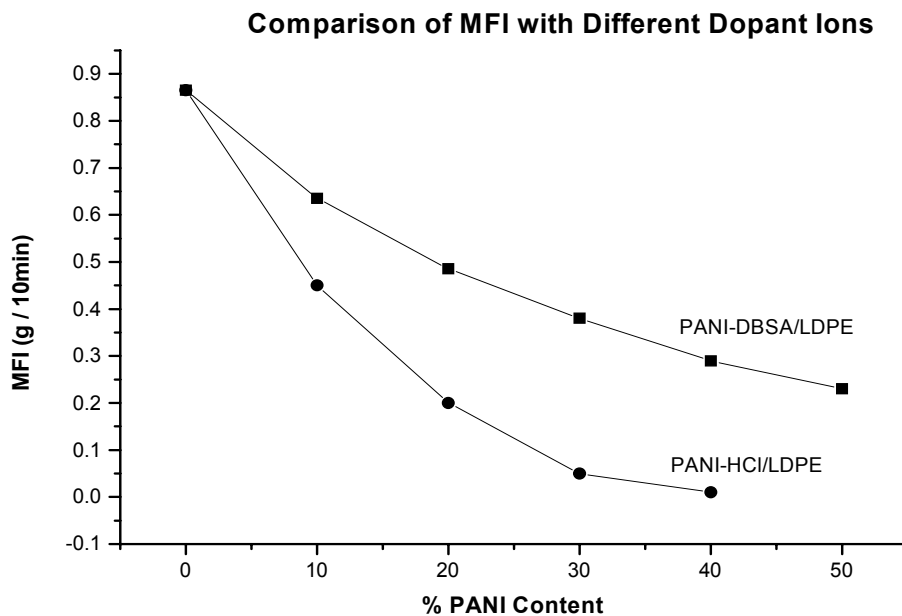


Figure 3.5: Comparison of MFI values of the PANI / LDPE blend with different dopant ions against percentage polyaniline content

Finally, these values can be compared to that of carbon black composites to get a better idea of the superior processibility of PANI / LDPE blends, which is illustrated in figure 3.6.

The granules of these blends obtained can be processed easily by any of the known technique. These blend films were found to mould well with uniform nature of blending.

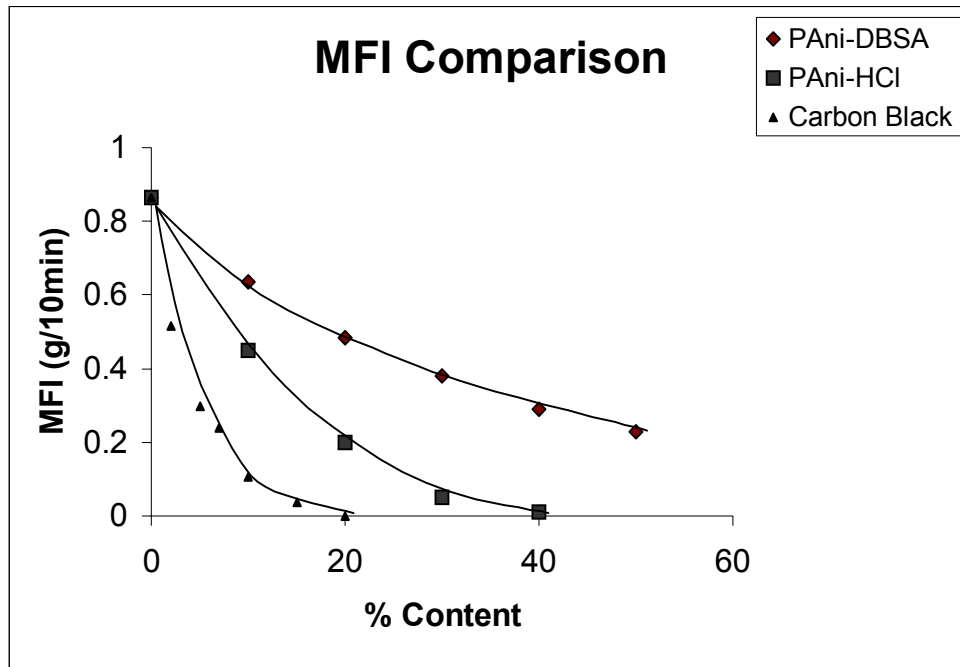


Figure 3.6: Comparison of MFI values of LDPE / Carbon Black composite with that of LDPE / PANI Blends.

The same blends were also made at higher shear rate using micro – compounder (DSM MICRO – 5) as discussed in experimental chapter. Batch weight of each blend mixture for a single compounding was fixed at 4gms. From these compounded material tensile specimen as well as impact testing specimens were made using micro -injection moulding machine. Compounding was done at 130°C at a fixed screw rpm of 100 and the injection moulding was carried out at 140°C (barrel temperature), keeping mould temperature at 25°C.

Apart from processibility of the blends, MFI values also give the relative melt viscosity of each blend with composition, which in turn gives the better indication about its processibility. These values can be examined thoroughly to study the melt flow behavior, to get an idea of the particle size of the dispersed phase, shape, domain size, phase morphology and its flow pattern. It was done by calculating the relative melt viscosity values of each blend composition with

respect to the flow of pure LDPE keeping the temperature and load on the piston constant for all compositions. These relative viscosity values were plotted against composition of conducting polymer and compared with five of the already accepted mathematical models.

The melt viscosity of a polymer melt is inversely proportional to the melt-flow index ³¹ at the same conditions. Then the Melt Viscosity,

$$\eta \propto (1/\text{MFI}) \quad \text{----(3.4)}$$

Hence, the relative melt viscosity of the blend can be calculated directly from MFI values from the following expression:

$$\begin{aligned} \eta_r &= \eta_{\text{blend}} / \eta_0 \\ &= (\text{MFI})_0 / (\text{MFI})_{\text{blend}}, \end{aligned} \quad \text{----(3.5)}$$

Where η_0 and $(\text{MFI})_0$ are the viscosity and melt-flow index of the pure LDPE without any filler or additive and η_{blend} , and $(\text{MFI})_{\text{blend}}$ are those of blends respectively.

The relative melt viscosity of various blends of PANI-DBSA / LDPE blends with respect to that of pure LDPE are given in table 3.10. The values of PANI-HCl / LDPE are given in Table 3.11. LDPE / carbon black composite behavior was also studied so as to compare the values with conventional conducting particles filled polymer system, which is extensively used in the industry. The relative melt viscosity values of LDPE / Carbon Black composites are given in Table 3.12.

In order to understand the melt processibility in these various blends, theoretical models have been developed which have been described in Chapter 1 of this thesis. The models are named by their authors, viz. Einstein, Eilers, Mooney, Krieger and Dougherty and Quemada. It is known that the particle size,

shape, their dispersion and concentration in the melt / solution control the viscosity. Hence, the values for these compositions were estimated from the respective equations taking into account the cylindrical and spherical shape of the dispersed system.

Table 3.10: Relative melt viscosity of PANI-DBSA / LDPE blends with respect to the pure LDPE calculated from the MFI values determined at 125°C with a load of 5kg on the piston:

MFI of pure LDPE, $(MFI)_0 = 0.865$ g/10min.

Blend Composition (% PANI-DBSA)	$(MFI)_{blend}$ (g/10min)	Relative viscosity, $\eta_r = \eta_{blend} / \eta_0$ $= (MFI)_0 / (MFI)_{blend}$
10%	0.635	1.3622
20%	0.485	1.7835
30%	0.380	2.2763
40%	0.290	2.9828
50%	0.230	3.7609

Table 3.11: Relative melt viscosity of PANI-HCl / LDPE blends with respect to the pure LDPE calculated from the MFI values determined at 125°C with a load of 5kg on the piston:

MFI of pure LDPE, $(MFI)_0 = 0.865$ g/10min.

Blend Composition (% PANI-HCl)	$(MFI)_{blend}$ (g/10min)	Relative viscosity, $\eta_r = \eta_{blend} / \eta_0$ $= (MFI)_0 / (MFI)_{blend}$
10%	0.450	1.9222
20%	0.200	4.3250
30%	0.050	17.30
40%	0.010	86.50

Table 3.12: Relative melt viscosity of LDPE / Carbon Black composites with respect to the pure LDPE calculated from the MFI values determined at 125°C with a load of 5kg on the piston:

MFI of pure LDPE, $(MFI)_0 = 0.865$ g/10min.

Composition (% Carbon Black)	$(MFI)_{blend}$ (g/10min)	Relative viscosity, $\eta_r = \eta_{blend} / \eta_0$ $= (MFI)_0 / (MFI)_{blend}$
2%	0.5150	1.6796
5%	0.2980	2.9027
7%	0.2400	3.6042
10%	0.1075	8.0465
15%	0.03835	22.5554

Volume Fraction (ϕ) of PANI-DBSA, PANI-HCl as well as Carbon Black content in each blend was calculated considering the density of each component. PANI-DBSA as well as PANI-HCl shown to have the powder density of 0.59 g/ml, Carbon Black has 0.1515 g/ml where as LDPE has a density of 0.92 g/ml. Accordingly, volume fraction of all these contents in the respective blends were calculated using the conversion formula:

$$\text{Volume} = \text{Mass} / \text{Density}.$$

And,
$$\text{Volume Fraction } (\phi_1) = V_1 / (V_1 + V_2)$$

Corresponding theoretical values of relative viscosity for each volume fractions were calculated for each models discussed in Chapter 1.

The behavior of LDPE / Carbon black composites was first analyzed, as since the commercial conducting polymers are carbon black filled composites. It shows the trend fitting to Mooney model, as reported elsewhere³². This behavior itself shows the sharp increment with the melt viscosity with filler loading, causing severe problems while compounding and moulding of components. Figure 3.7 clearly illustrates this behavior. PANI-HCl / LDPE blends was seen to fit the trends given by Krieger and Dougherty model. It was also seen that the curve is more fitting to that of $\Phi_m = 0.45$, which corresponds to the cylindrical shape of fillers. It is shown in the figure 3.8. It may be due to the existence of oblong morphology for polyaniline as reported elsewhere³³. This fitting to the Krieger and Dougherty model suggests that these blends have uniform dispersion of polyaniline particles in LDPE, which follows the trends as expected for particulate filled polymer with little or no additional interaction between two phases.

Interestingly, DBSA doped polyaniline showed lesser increase in relative viscosity with polyaniline loading. It showed a large deviation from Krieger and Dougherty model, especially in higher loading levels above the volume fraction of 0.3. The curve lies even below the curve corresponds to $\Phi_m = 0.74$, which was

calculated for the particulate spherical filler with f.c.c mode of packing. These are illustrated in the Figure 3.9(a) and 3.9(b). In fact, the curve is almost close to the predicted one from Einstein's equation. These observations suggest the existence of highly interactive phase morphology and very uniform dispersion. This can arise from the fact that DBSA present in the polyaniline phase acts like a compatibilizer as well a plasticizer for LDPE matrix. The plasticizing effect provided by DBSA on LDPE can be seen by the MFI values of LDPE with different DBSA contents given in the Table 3.13. Typically, a part of DBSA dopant (maximum 5%) can diffuse in to LDPE and interact with the same and lowering the viscosity or increasing the MFI. This confirms the role of DBSA in the formation of highly uniform dispersion of PANI in the LDPE matrix.

Table 3.13: MFI values of LDPE with different DBSA contents (Temp = 125°C, Load = 5kg)

DBSA Content (%)	MFI (g/10min)
0 % (pure LDPE)	0.865
1%	0.955
2 %	1.022
3 %	1.256
4 %	1.626
5%	1.782

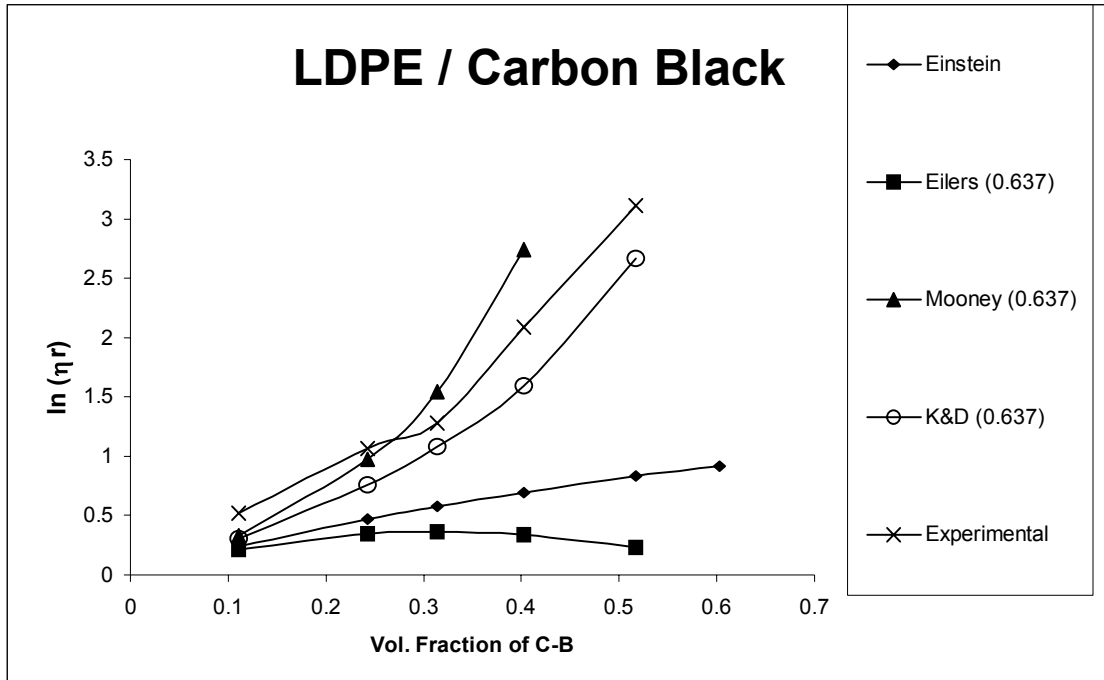


Figure 3.7: Comparisons of theoretical models with LDPE / Carbon Black Composites.

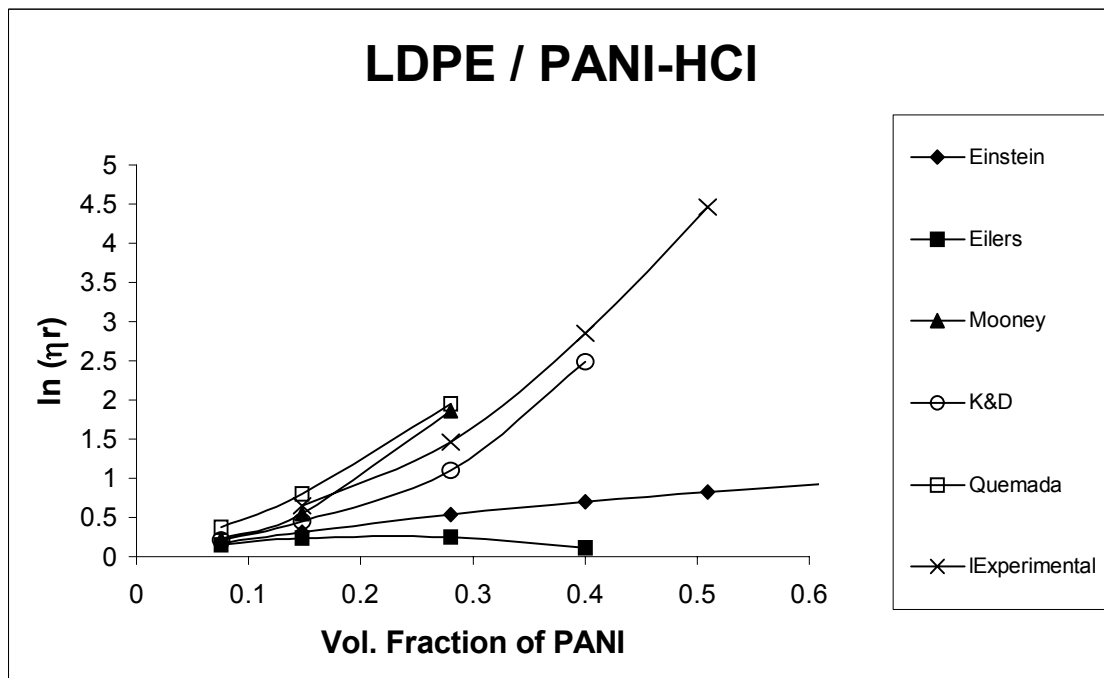


Figure 3.8(a): Comparisons of theoretical models for cylindrical shaped dispersed medium with $\phi_m=0.45$ with PANI-HCl / LDPE blends

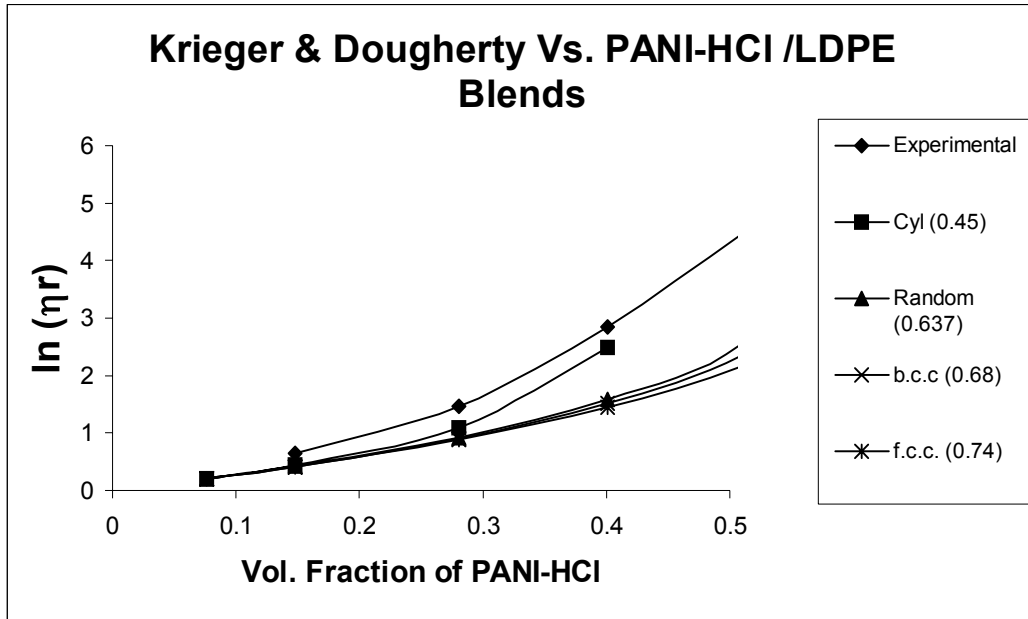


Figure 3.8 (b): Comparisons of Krieger and Dougherty model with PANI-HCl / LDPE blends.

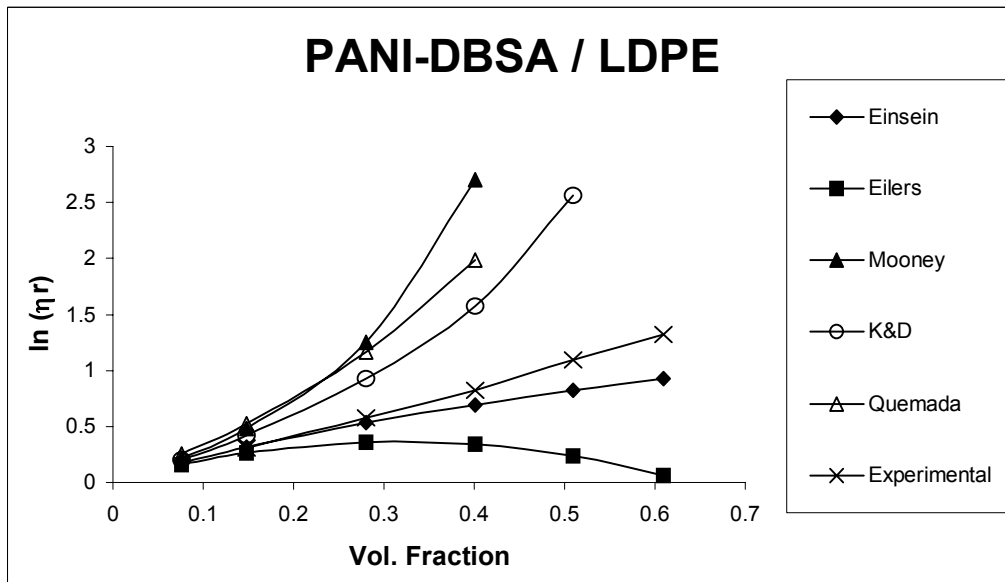


Figure 3.9: Comparisons of theoretical models for random arranged dispersed medium with $\phi_m=0.637$ with PANI-DBSA / LDPE blends. It shows the fitting with Einstein Model.

3.3.2.a. PANI-DBSA/ LDPE MELT-BLENDS WITH PEO AS PROCESSING AID:

Low melting polymers like PEO (MW 300,000) can be used as processing aids as discussed earlier. PEO is already known for its lubricating effect in other polymer melt systems as reported by many authors elsewhere^{34, 35}. PEO is also known to be used in ionically conducting gels and as polymer electrolyte^{36 - 39}. In this work it has been considered as a dispersing agent and, hence, can act as a good processing aid for PANI-DBSA / LDPE blends with enhanced conductivity too.

Selection of processing aids among these low melting polymers were done mainly considering the Melt Flow Index values of blends with 5phr of these polymers in the blends; which directly indicates the processibility in each case. These values very well show the better processibility for the PANI-DBSA / LDPE blends with PEO as processing aid. These values are given in Table 3.14 and the improvement in the processibility is demonstrated in the Figure 3.10. It is more pronounced and well supported with conductivity measurements, which shows reasonably large improvement of conductivity with PEO than with PEG and the blends without any of these processing aids. Conductivity and other properties of these blends are discussed in detail in Chapter 5. Moreover, the ease of uniform mixing in the blend mixture was found better in the case of PEO. From these results, PEO was chosen as more efficient processing aid for the PANI-DBSA / LDPE blends and, hence, the further studies were restricted to PEO as the processing aid.

Table 3.14: Comparison of MFI values of PANI-DBSA / LDPE blends with different polymers like PEO and PEG as processing aids:

(Temp = 125°C, Load = 5kg)

Basic Blend Composition (% PANI-DBSA)	MFI (g / 10 min)		
	Without Processing Aids	5 phr PEG	5 phr PEO
0%	0.865	1.378	1.385
10%	0.635	1.250	1.235
20%	0.485	1.075	1.060
30%	0.380	0.935	0.965
40%	0.290	0.480	0.865
50%	0.230	0.380	0.590

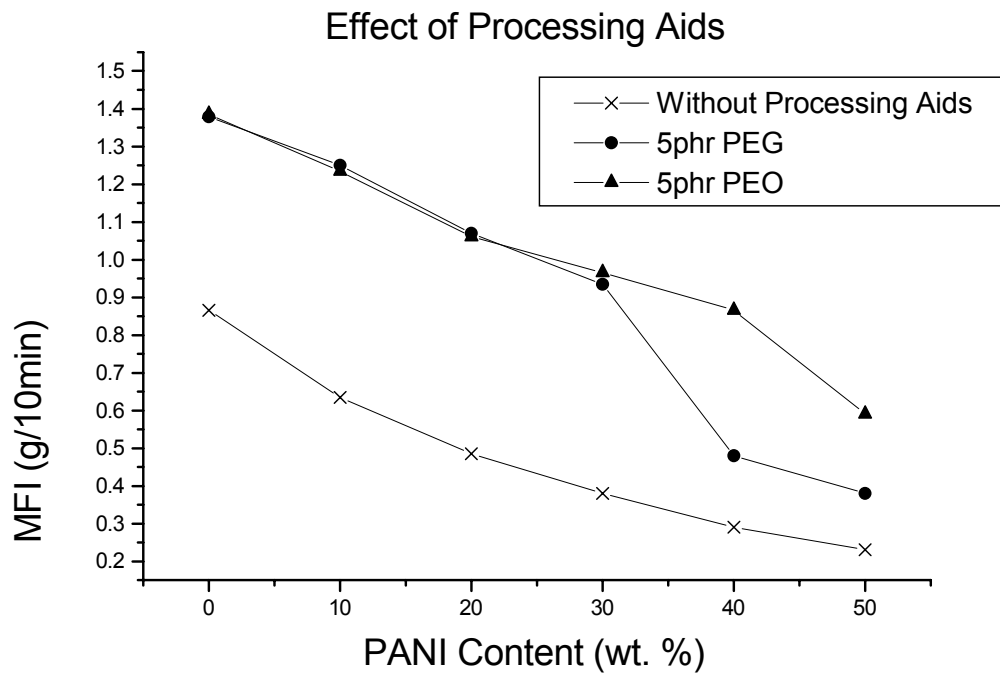


Figure 3.10: Comparison of MFI values of the PANI-DBSA / LDPE blends with different processing aids.

As in the case of pure blends, MFI of the blends with different amounts of PEO in different phr levels were also determined to compare its melt viscosity with polyaniline loading and, hence, to examine their processibility. MFI of different PANI-DBSA / LDPE blends with different PEO contents of 0phr, 3phr, 5phr and 7phr are compared in the Table 3.15. It clearly shows the increase in MFI of respective blends with the increase in PEO loading, which is more clearly explained in the Figures 3.11 and 3.12.

Table 3.15: Comparison of MFI values of PANI-DBSA / LDPE blends with different contents of PEO as processing aid: (Temp = 125°C, Load = 5kg)

Basic Composition of the Blend (% PANI)	MFI (g / 10 min)			
	Amount of PEO (as processing aid) in the blend.			
	0 phr PEO	3 phr PEO	5 phr PEO	7 phr PEO
0%	0.865	1.230	1.385	1.450
10%	0.635	1.065	1.235	1.367
20%	0.485	0.780	1.060	1.180
30%	0.380	0.725	0.965	1.020
40%	0.290	0.535	0.865	0.866
50%	0.230	0.245	0.590	0.5913

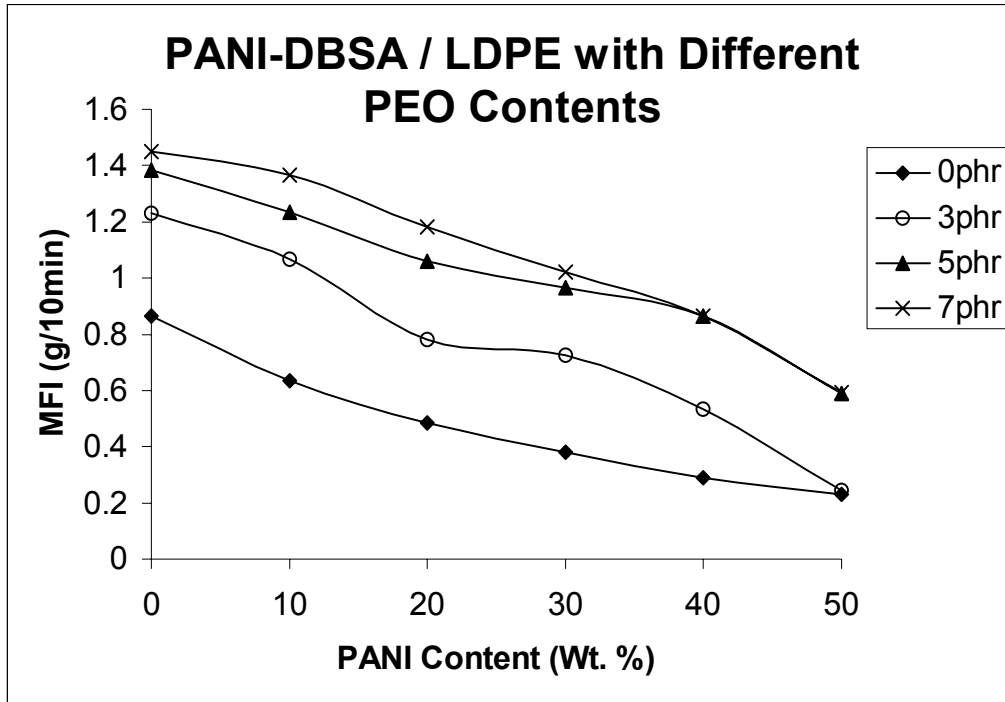


Figure 3.11: Plot of MFI Vs. Polyaniline content of blends with different phr content of 0, 3, 5 and 7phr PEO as processing aid.

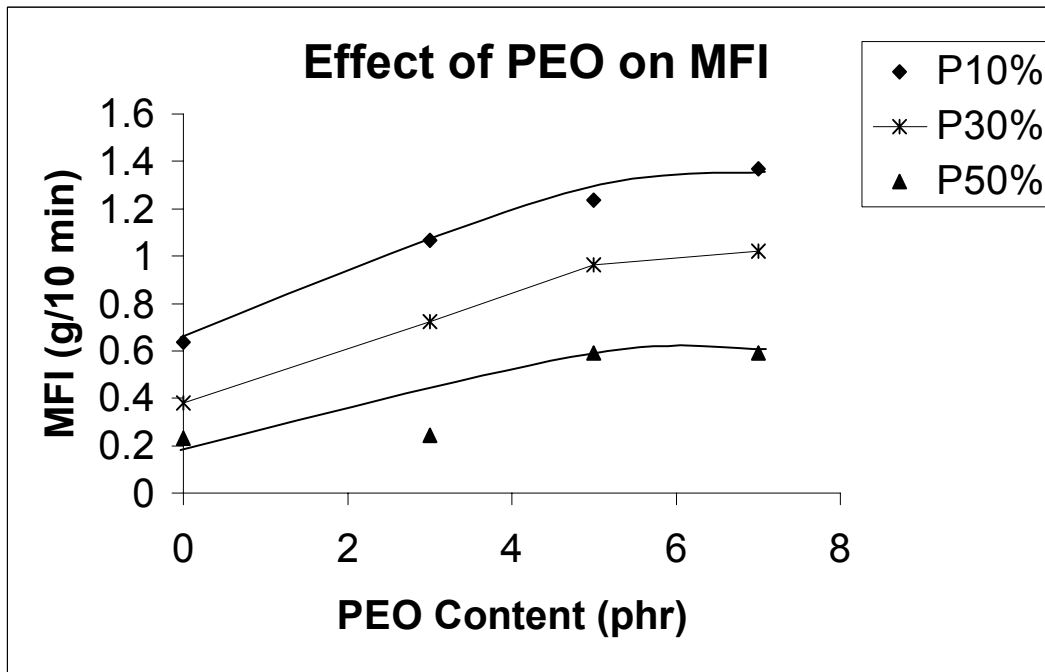


Figure 3.12: MFI Vs. PEO content in phr level of different PANI-DBSA / LDPE blends with different polyaniline loading.

These trends in melt-viscosity show that there is a considerable improvement in the processibility of these blends when PEO is added as a processing aid. In the coming chapter, it shall be seen that the conductivity of these blends also show considerable increase in the presence of PEO. The above table and figures illustrates the trend in improvement of processibility of these blends with the increase in PEO content. Both the plots show that there is a slight improvement with 3phr PEO, then a considerably large improvement in 5phr case and then only a slight improvement only from 5phr to 7phr. So PEO at 5phr was optimized as processing aid, as there is some kind of saturating effect observed after that. It can be due to the existence of skin-core morphology, where PEO forms the skin layer. PEO is having a very low melting point of 70°C. So it melts very fast and acts like a lubricant between particles. On higher loading, the PEO flows more towards the outer part of the melt extrudate and forms an effective skin layer, which give higher flow to the melt. The phenomena of lowering of MFI of PANI-DBSA / LDPE blends with PEO suggests the existence of “Skin-Core” morphology of these blends. So further studies on structure and properties were restricted to the comparisons of those of blends without processing aids and the blends with 5phr PEO as processing aid.

The above blends with 5phr PEO as processing aid were moulded to get films, which were used, for further studies. These mouldings were done by compression moulding. Spacers were used while moulding to adjust the thickness of the film as required. About 0.2 mm thick films were made for all these blends at a temperature of 115°C with an applied pressure of 3 tons. Films were found well moulded with uniform nature of blending.

The above blends were also made at higher shear rate using micro – compounder as discussed in the experimental part. Batch weight of each blend mixture for a single compounding was fixed at 4gms. From these compounded material, tensile specimens as well as impact testing specimens were made using micro -injection moulding machine. Compounding were done at 135°C at a

fixed screw rpm of 100 and the injection mouldings were done at 145°C (barrel temperature), keeping mould at the room temperature.

As discussed in the case of pure blends, MFI values also gives the relative viscosity of each blend with composition, which in turn gives a better indication of its processibility. These values can be examined to study the flow behavior and get an idea about the phase morphology and its flow pattern. It was done by calculating the relative viscosity values of each blend composition with respect to the flow of pure LDPE with 5phr PEO keeping the temperature and load on the piston constant for all compositions. These relative viscosity values were plotted against composition of conducting polymer as well as its volume fraction and compared with five of the already accepted mathematical models as discussed earlier. Relative melt viscosity (η_r) calculations and the respective standard values for each mathematical models were calculated same as for the pure blend cases discussed earlier. The relative melt viscosity of various blends of PANI-DBSA / LDPE + 5phr PEO blends with respect to that of pure LDPE + 5phr PEO are given in Table 3.16. These were also compared with different models for filled polymers like Einstein, Eilers, Mooney, Krieger and Dougherty and Quemada as discussed earlier.

Similarly, the relative melt viscosity of various blends of PANI-DBSA / LDPE + 3phr PEO blends with respect to that of pure LDPE + 3phr PEO are given in Table 3.24. Similarly, the relative melt viscosity of various blends of PANI-DBSA / LDPE + 3phr PEO blends with respect to that of pure LDPE + 3phr PEO are given in Table 3.17.

Table 3.16: Relative melt viscosity of PANI-DBSA / LDPE blends with 5phr PEO as processing aid with respect to the LDPE + 5phr PEO calculated from the MFI values determined at 125°C with a load of 5kg on the piston:

MFI of LDPE + 5phr PEO, $(MFI)_0 = 1.385$ g/10min.

Blend Composition (% PANI-DBSA)	$(MFI)_{blend}$ (g/10min)	Relative viscosity, $\eta_r = \eta_{blend} / \eta_0$ $= (MFI)_0 / (MFI)_{blend}$
5%	1.280	1.0820
10%	1.235	1.1214
20%	1.060	1.3066
30%	0.965	1.4352
40%	0.865	1.6012
50%	0.590	2.3475

Table 3.17: Relative melt viscosity of PANI-DBSA / LDPE blends with 3phr PEO as processing aid with respect to the LDPE + 3phr PEO calculated from the MFI values determined at 125°C with a load of 5kg on the piston:

MFI of LDPE + 3phr PEO, $(MFI)_0 = 1.230$ g/10min.

Blend Composition (% PANI-DBSA)	$(MFI)_{blend}$ (g/10min)	Relative viscosity, $\eta_r = \eta_{blend} / \eta_0$ $= (MFI)_0 / (MFI)_{blend}$
10%	1.065	1.1549
20%	0.780	1.5769
30%	0.725	1.6965
40%	0.535	2.2991
50%	0.245	5.0204

LDPE / PANI-DBSA blends with PEO as processing aid show very high MFI. Also the changes in melt viscosity with polyaniline loading being lower with PEO loading indicates the effective lubrication provided by PEO, which is meant for any processing aid ⁴⁰. The result of comparison of these mathematical models was consistent with the phase morphology of these blends. Due to very low melt viscosity, the relative viscosity is also very low compared to those without processing aids. It can be seen from here that it is further deviating from the Einstein model and more fitting to Eilers model. Since the PEO is expected to form cylindrical morphology, it also effects the orientation of PANI along with it. Hence, the treatment here was done considering the cylindrical morphology of the filler. These are explained in the Figures 3.13 and 3.14. It suggests the existence of skin-core phase morphology, where PEO form the skin of melt extrudate and thus giving high lubricating effect to provide high MFI and, hence, better processibility.

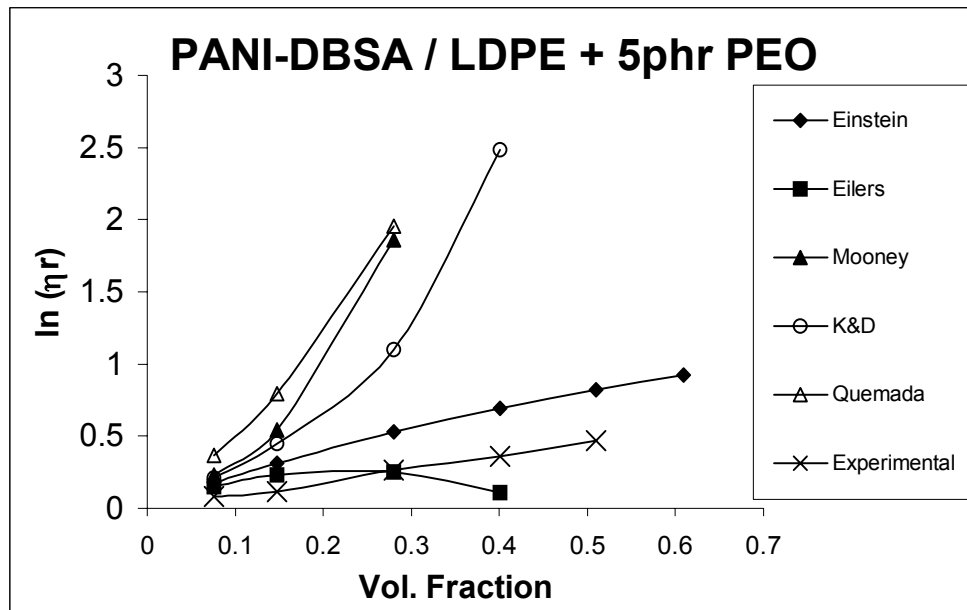


Figure 3.13: Comparisons of relative viscosity predicted by different theoretical models with that given by PANI-DBSA / LDPE blends with 5phr PEO.

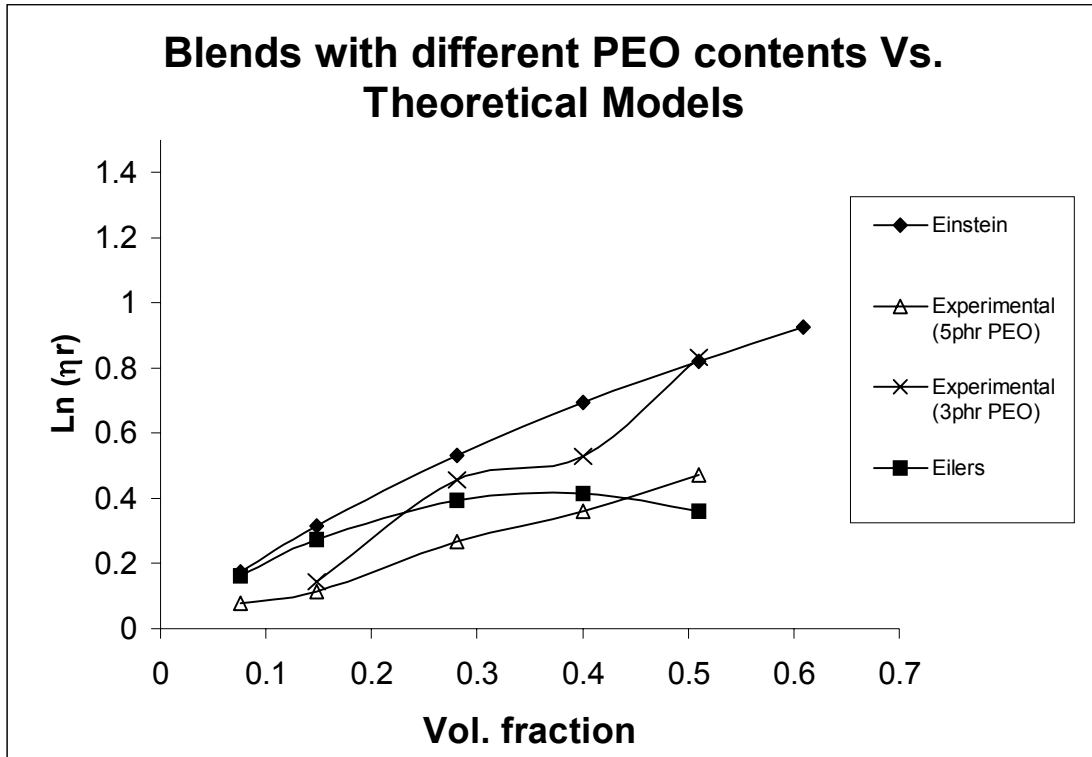


Figure 3.14: Comparisons of Einstein and Eilers models with PANI-DBSA / LDPE blends with different PEO contents.

3.3.3 STRUCTURE DEVELOPMENT IN PANI / LDPE BLENDS:

These melt processed PANI / LDPE blends were thoroughly characterized for structure, morphology, thermal stability, etc by various techniques like X-Ray Diffraction (XRD), Differential Scanning Calorimetric (DSC), Optical Microscopy, Thermogravimetric Analysis (TGA), etc.

X-Ray Diffraction Analysis:

In order to confirm the effect of blending of PANI-DBSA with LDPE on the supermolecular structure, the samples were examined by x-ray diffraction. Figures 3.15 shows the wide angle XRD for the individual components and Figure 3.16 shows wide angle XRD for these blends having percentage PANI content ranging from 10% to 50%.

The XRD for the individual components in the blends was also recorded to estimate the crystallinity values. These are given in the Table 3.25. Since PANI-DBSA has much lower crystallinity than LDPE, the XRD scans are dominated mainly by the LDPE component. It can be noted from the Figure 3.16 that although the two major reflections of LDPE are seen in all cases, the intensities of these peaks varies with composition. This suggests changes in the overall crystallinity due to blending. In order to determine the extent of these changes, the crystallinity Index (C_i) values were estimated from simple rule of mixture, which holds true for non-interactive phase segregated systems ⁴¹:

$$C_i = \Phi_A / (\Phi_A + \Phi_C) \dots\dots\dots (3.6)$$

Where, Φ_A = Area under the amorphous region,

And Φ_C = Area under crystalline region.

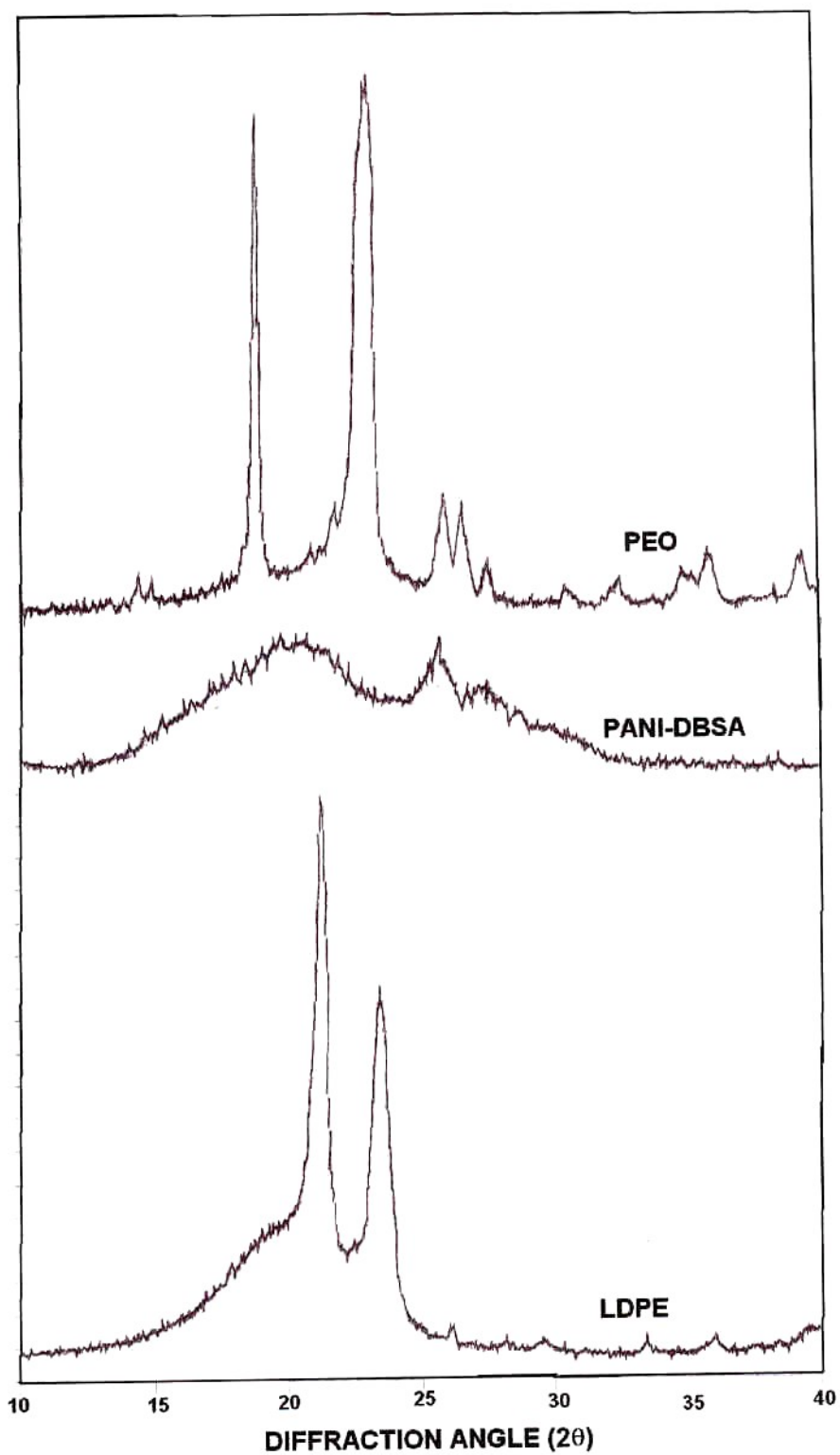


Figure 3.15: XRD of Pure LDPE, PANI and PEO

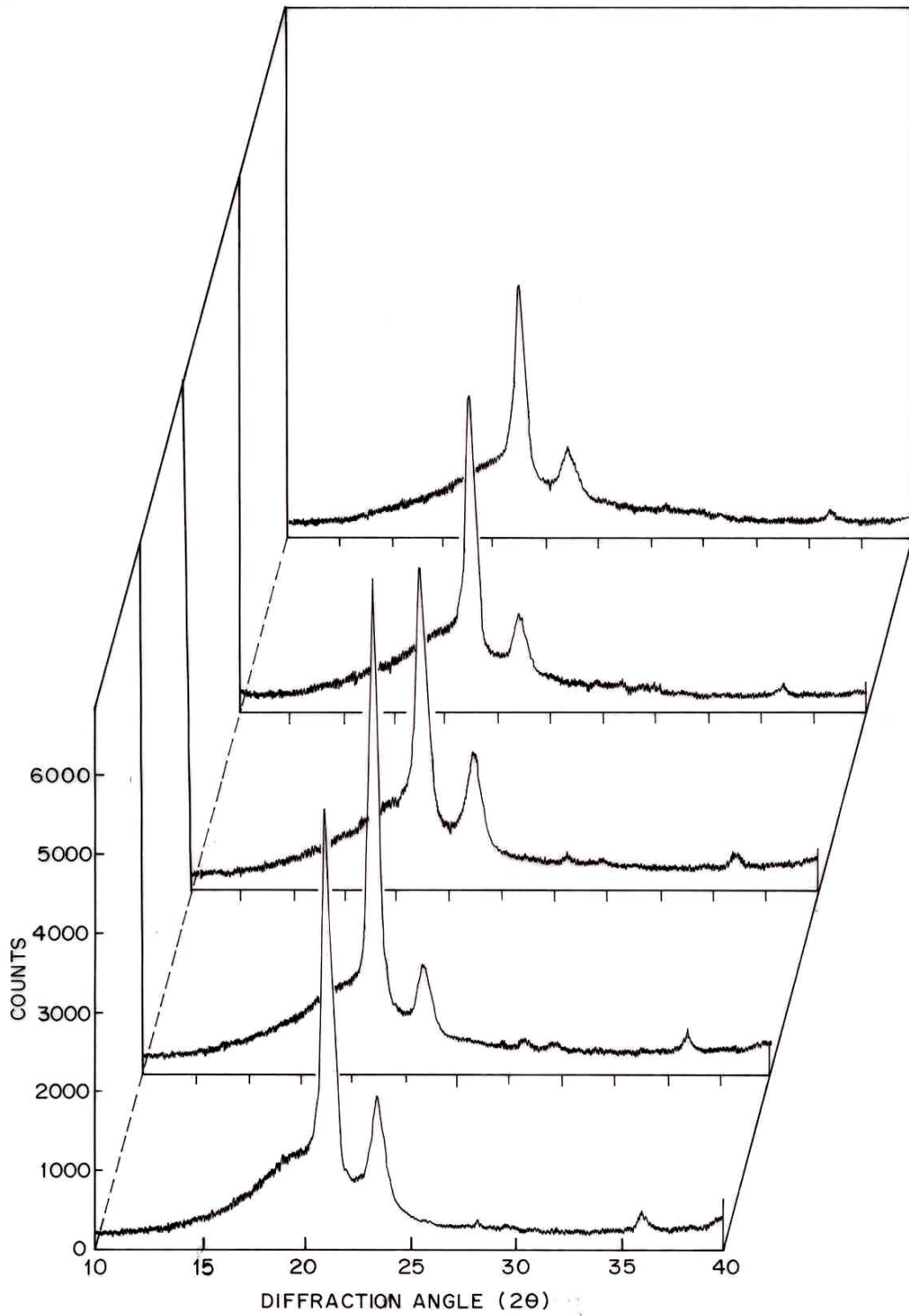


Figure 3.16 : XRD of different composition of PANI-DBSA / LDPE blends with PANI contents of 5%, 10%, 20%, 30%, 40% and 50%.

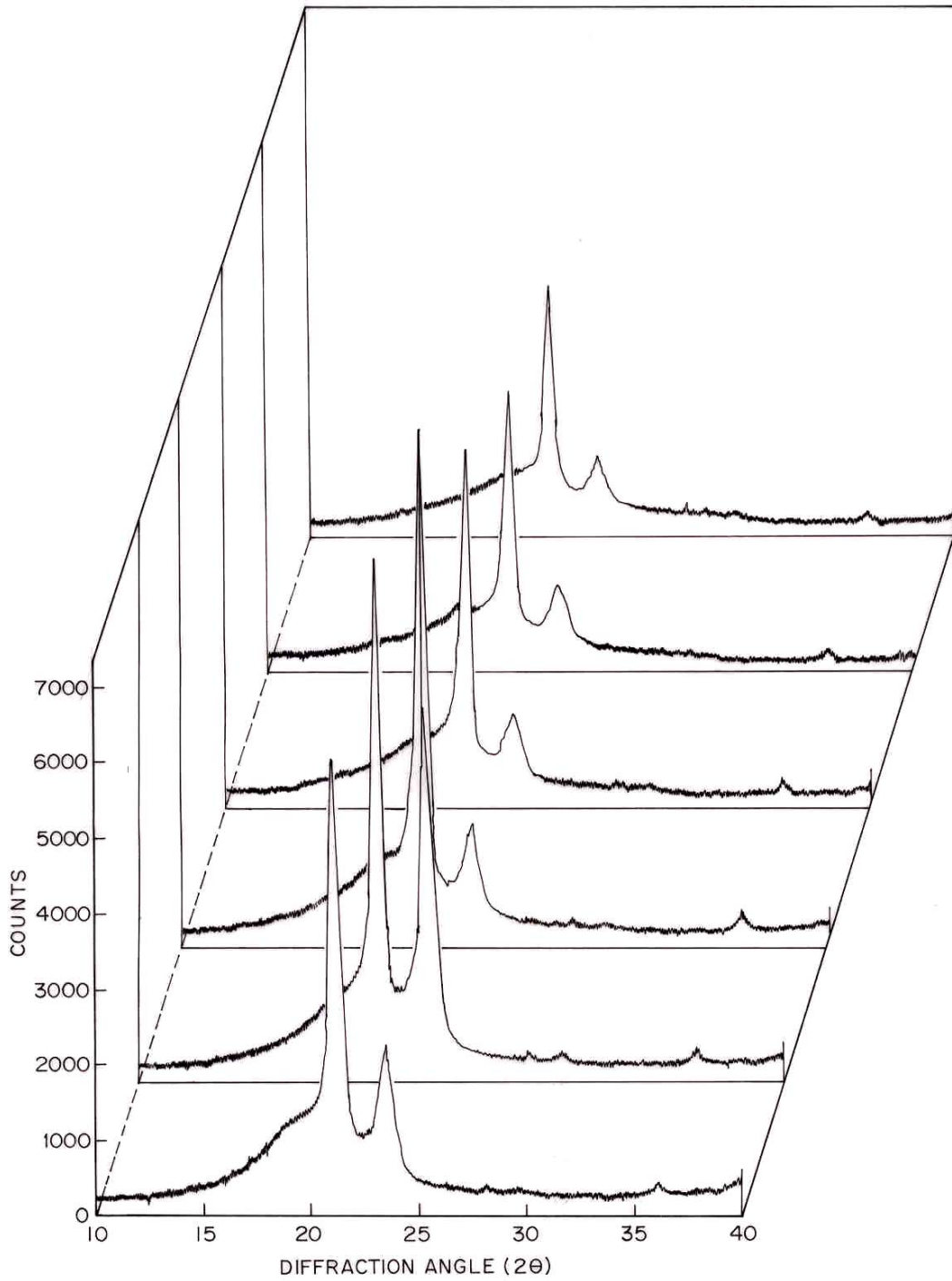


Figure 3.17: XRD of different composition of PANI-DBSA / LDPE blends with 5phr PEO as processing aid having PANI contents of 5%, 10%, 20%, 30%, 40% and 50%.

Table 3.18: Crystallinity Index values of pure components used in the various compositions of PANI-DBSA / LDPE blends:

Material	Crystallinity Index (C_i)
LDPE (Lotrene CD-023)	0.44
PANI-DBSA	0.26
PEO	0.71

C_i values of all PANI-DBSA / LDPE blends prepared were calculated from the respective XRD patterns as mentioned in earlier cases and denoted as C_i(Observed). Also the expected values of each blends were calculated from those of pure materials and denoted as C_i(Expected), which was calculated as:

$$C_i(\text{Expected}) = C_i(\text{PANI-DBSA}) * x + C_i(\text{LDPE}) * (1-x) \text{ -----(3.8)}$$

Where, 'x' is the weight fraction of PANI-DBSA in the blend.

C_i(Observed) as well as calculated values of C_i(Expected) for PANI-DBSA / LDPE blends are given in table 3.19 and the comparison of these values are illustrated in the figure 3.18.

Table 3.19: Crystallinity Index values [$C_i(\text{Observed})$] for PANI-DBSA / LDPE blends and $C_i(\text{Expected})$ of the respective blends calculated from the values of pure components.

Composition of blends (% PANI-DBSA)	C_i (Observed)	C_i (Expected)
10%	0.40	0.43
20%	0.39	0.41
30%	0.38	0.39
40%	0.33	0.37
50%	0.28	0.35

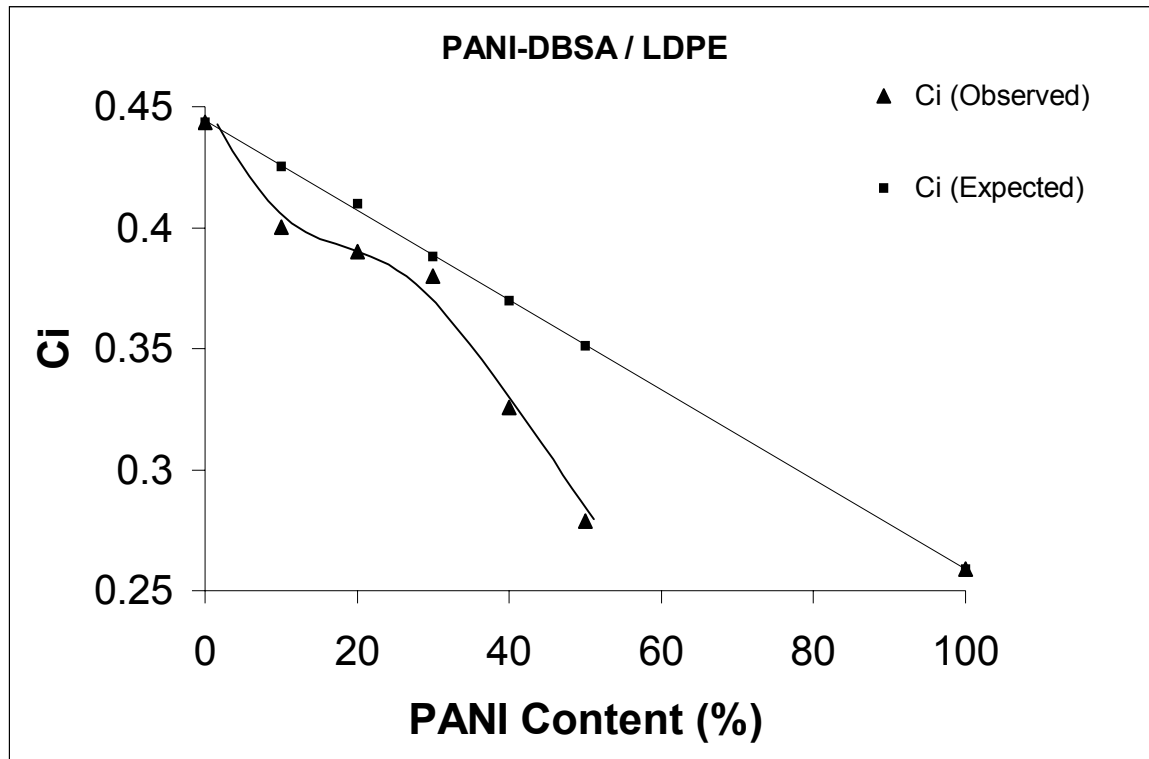


Figure 3.18: Comparison of C_i (Observed) and C_i (Expected) of PANI-DBSA / LDPE blends calculated from XRD analysis.

It shows that the actual crystallinity values of these blends are considerably lower than the values calculate from the crystallinity indices of pure LDPE and PANI-DBSA. It indicates the interactive phase morphology of these blends. It can be seen from the earlier reports that there is an existence of two major crystalline peaks for LDPE as seen in the Figure 3.15. The peaks are corresponds to (1,1,0) as well as (2,0,0) planes of orthorhombic structure of LDPE. The first peak corresponds to (1,1,0) plane, which is the plane parallel to c-axis, and the (2,0,0) plane is the one parallel to b and c axes and perpendicular to a-axis. Considering these crystallographic data already reported it could be seen that there is considerable lowering of the ordered structure along both the planes of LDPE. It indicates the interaction of DBSA doped polyaniline with LDPE matrix.

Similarly, values of $C_i(\text{Observed})$ as well as $C_i(\text{Expected})$ were calculated for PANI-DBSA / LDPE blends with 5phr PEO as processing aid. The values of $C_i(\text{Expected})$ were calculated from C_i values of pure PANI-DBSA and that of LDPE + 5phr PEO sample. C_i value for LDPE + 5phr PEO was 0.4871. These values of $C_i(\text{Observed})$ as well as $C_i(\text{Expected})$ are given in Table 3.20 and the comparison of these values are illustrated in the Figure 3.19.

Table 3.20: Crystallinity Index values [$C_i(\text{Observed})$] for PANI-DBSA / LDPE blends with 5phr PEO as processing aid and $C_i(\text{Expected})$ of the respective blends calculated from the values of LDPE + 5phr PEO and pure PANI-DBSA.

Composition of blends (% PANI-DBSA) + 5phr PEO	$C_i(\text{Observed})$	$C_i(\text{Expected})$
5%	0.44	0.48
10%	0.47	0.46
20%	0.42	0.44
30%	0.38	0.42
40%	0.35	0.40
50%	0.31	0.37

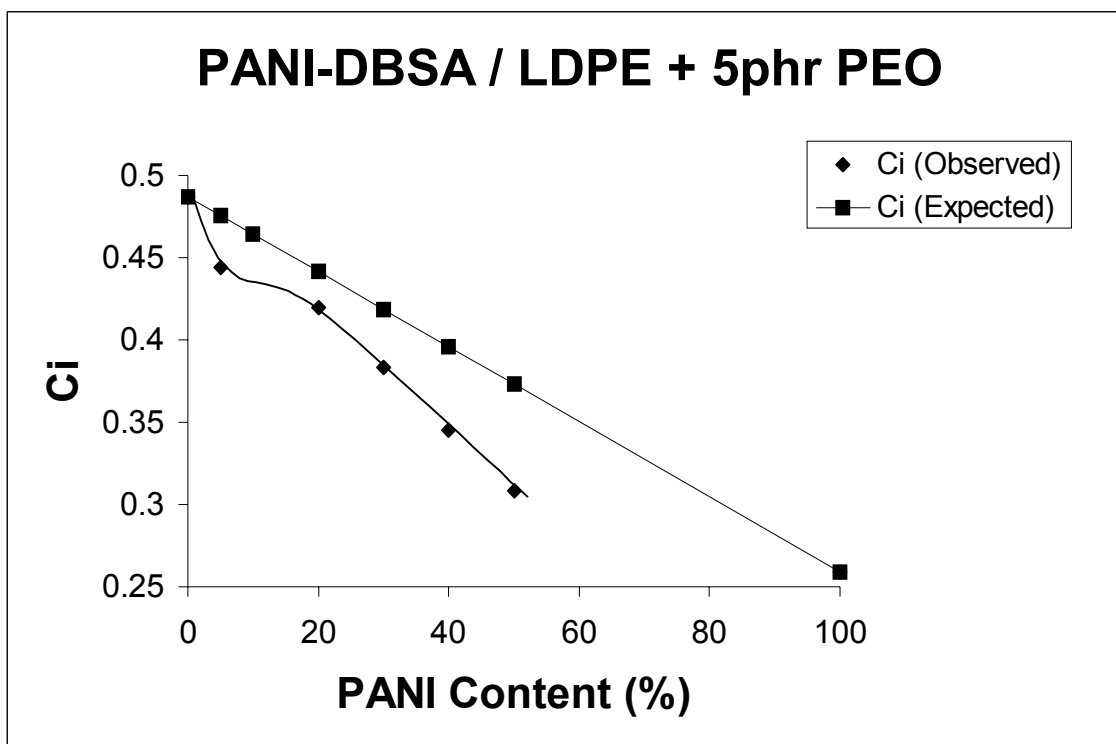


Figure 3.19: Comparison of C_i (Observed) and C_i (Expected) for PANI-DBSA /LDPE blends obtained by XRD analysis.

C_i values of PANI-DBSA / LDPE blends without any processing aid were compared with that of blends with 5phr PEO as processing aid. They are given in the Table 3.21. It follows that the crystallinity is increased in the presence of PEO in all cases. The PEO chains present in the melt seem to orient the LDPE chains along the 2,0,0 plane, which can be explained considering the crystallographic parameters ('a', 'b', 'c' parameters) of these polymers ⁴². The 'a', 'b', 'c' parameters are 2.55 Å, 5.0 Å and 4.7 Å for polyethylene and 8.0 Å, 13.4 Å and 19.2 Å for poly (ethylene oxide) respectively. Considering the orientation in (2,0,0) plane, which is parallel to the b and c axes and perpendicular to the a-axis; it can be seen that the c parameter (19.2 Å) of PEO is equivalent to hold 7 – 8 unit lengths of polyethylene along the a-axis (2.55 Å), inducing high degree of orientation along the plane causing the increment of crystallinity.

Table 3.21: Comparison of Crystallinity Index values [C_i] for PANI-DBSA / LDPE blends without any processing aids (0phr PEO) and that of the respective blends with 5phr PEO as processing aid.

Composition of blends (% PANI-DBSA)	Crystallinity Index (C_i)	
	Amount of PEO in the blend	
	0 phr	5phr
0%	0.44	0.49
10%	0.39	0.47
20%	0.41	0.42
30%	0.38	0.38
40%	0.33	0.35
50%	0.28	0.31

Optical Microscopy:

In order to understand the morphology developed during melt processing, optical microscopy was used for observing the LDPE / PEO blends sectioned after melt extrusion. The strands of extruded blends were collected, and the fine sections were cut in both vertical and horizontal directions. Both longitudinal and cross sections were stained with a dye (methylene blue) and images were recorded. Since PEO absorbs the dye preferentially, the domains become more visible with enhanced contrast. Figure 3.20 (a) shows the Longitudinal section of the blend and that of Figure 3.20 (b) is the cross sectional view of the extruded strand of these blends. Both these images confirm the fibrous morphology of PEO inside the LDPE matrix with the orientation along the flow direction of the melt. This type of morphology has profound effect on the electrical and mechanical properties of these blends moulded in final shape. These aspects are discussed in later chapters of this thesis.

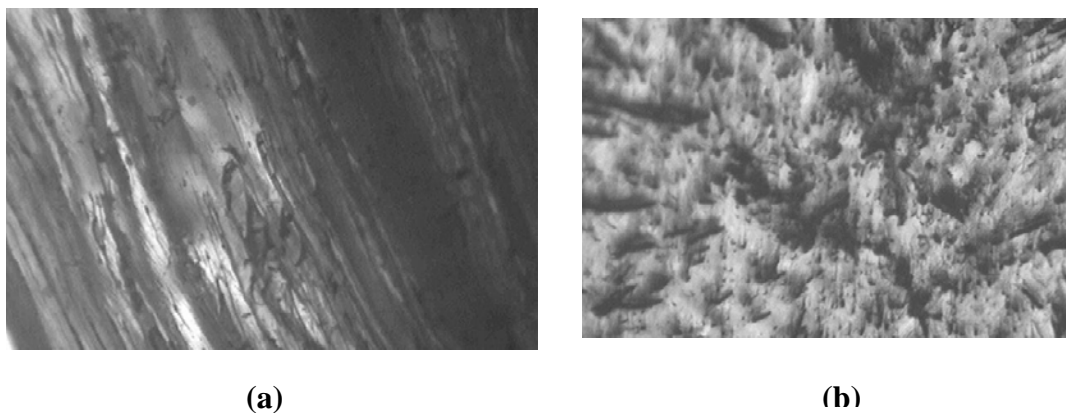


Figure 3.20: Optical microscopic images of PANI / PEO Blends. (a) Longitudinal and (b) Cross-sectional.

Differential Scanning Calorimetry (DSC):

DSC gives an idea about the primary and secondary transition with change in temperature. It gives the exothermic and endothermic changes occurring over a particular temperature range. In a blend, it can yield more information about miscibility, fractional crystallization, etc. DSC was recorded from 50°C to 200°C for LDPE, PANI-DBSA as well as all the compositions of PANI-DBSA / LDPE blends. The heating rate was kept constant at 10°C per minute. DSC was recorded for both heating and cooling cycles. Endothermic changes like melting were recorded during heating cycle, and exothermic changes like crystallization were recorded during cooling. In this temperature region, there were no secondary transitions like T_g for any of the above cases considered.

In the case of pure PANI-DBSA there were no transitions seen in this temperature region. As expected there was a melting point (T_m) as well as temperature of crystallization (T_c) for pure LDPE at 111.8°C and 94.5°C respectively. The corresponding endothermic (ΔH_m) and exothermic (ΔH_c) changes in heat capacity are also recorded as 39.5 j/g and -35.7 j/g respectively. The corresponding T_m and T_c were found to be near to the above-mentioned values without much difference for different PANI-DBSA / LDPE blends. So, it is assumed that these changes are due to the LDPE content in each blend and its crystallization behaviour. It may be noted that PANI has much higher melting point (expected to be > 220°C) and hence will not show transition in the temperature range studied. Hence, the heat capacity changes (ΔH_m and ΔH_c) are also expected proportional to LDPE content in each of these blends. These values were determined by DSC in each case and compared with the expected values calculated from concentration of LDPE in the blend, and, which are shown in Tables 3.22 and 3.23. It also confirms the existence of interactive phase morphology in these blends. This observation can be more clearly explained by

the Figures 3.21 and 3.22. These values indicate the reduction in heat of crystallization than expected in each case and, hence, indicate the reduction in crystallinity.

Table 3.22: Heat capacity change at melting [ΔH_m (Observed)] for PANI-DBSA / LDPE blends and ΔH_m (Expected) of the respective blends calculated from the value of pure LDPE and its ratio in the blend.

Composition of blends (% PANI-DBSA)	ΔH_m (Observed) (j/g)	ΔH_m (Expected) (j/g)
Pure LDPE	39.5	39.5
10%	30.3	35.55
20%	24.4	31.6
30%	22.4	27.65
40%	18.4	23.7
50%	14.7	19.75

Table 3.23: Heat capacity change at crystallization [ΔH_c (Observed)] for PANI-DBSA / LDPE blends and ΔH_c (Expected) of the respective blends calculated from the value of pure LDPE and its ratio in the blend.

Composition of blends (% PANI-DBSA)	ΔH_c (Observed) (-j/g)	ΔH_c (Expected) (-j/g)
Pure LDPE	35.7	35.7
10%	24.4	32.13
20%	16.4	28.56
30%	16.6	24.99
40%	8.47	21.42
50%	10.1	17.85

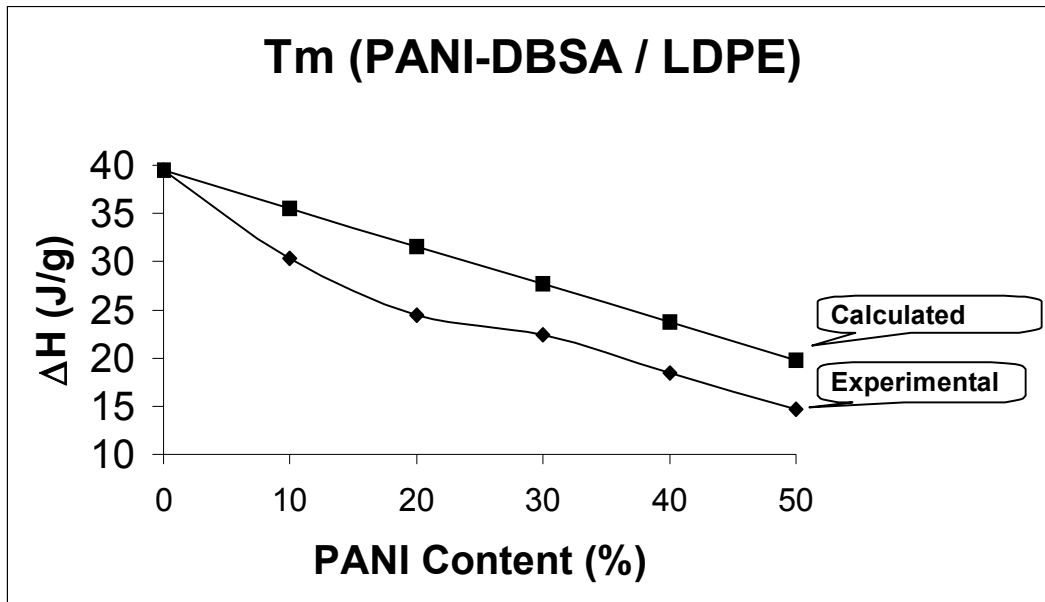


Figure 3.21: Comparison of ΔH_m (Experimental) and ΔH_m (Calculated) of PANI-DBSA / LDPE blends obtained from DSC.

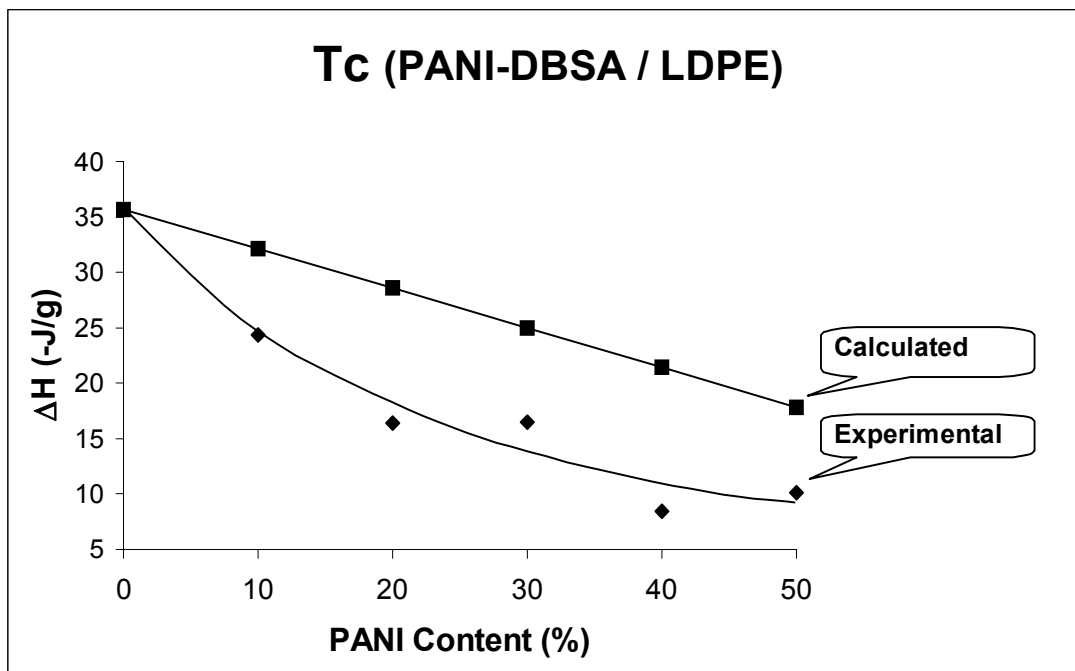


Figure 3.22: Comparison of ΔH_c (Experimental) and ΔH_c (Calculated) of PANI-DBSA / LDPE blends obtained from DSC.

In the same way DSC of the PANI-DBSA / LDPE blends with 5phr PEO was also done and the comparison of all the values as mentioned above were carried out. As expected there was a melting point (T_m) as well as temperature of crystallization (T_c) for pure LDPE with 5phr PEO at 111.1°C and 92.7°C respectively similar to the case of pure blends as discussed above. The corresponding endothermic (ΔH_m) and exothermic (ΔH_c) changes in heat capacity are also recorded as 41.6 j/g and -44.3 j/g respectively, which are higher than that for LDPE itself. It is interesting to note that the PEO melts at 77°C and as such would not contribute to the ΔH_m or ΔH_c values for transitions >92°C. the PEO in the molten state thus appears to promote crystallization of LDPE. This can be due to lubricating properties of PEO^{34, 35} giving better alignment prior to crystal formation. The corresponding T_m and T_c were found to be near to the above-mentioned values without much difference for different PANI-DBSA / LDPE with 5phr PEO blends. So, these changes can be attributed to the LDPE content in each blend. Hence, the changes in ΔH_m and ΔH_c are also expected in the same manner with LDPE content in each of these blends. These values were determined by DSC in each case and compared with the expected values calculated from the pure LDPE + 5phr PEO values and its ratio in the blend. These observed and expected values of ΔH_m and ΔH_c are given in Tables 3.24 and 3.25. It also confirms the existence of interactive phase morphology in these blends. These observations are more clearly explained by the Figures 3.23 and 3.24. These values indicate the reduction in heat of crystallization than expected in each case and, hence, suggest the reduction in crystallinity. The crystallinity is more than expected value at lower percentage as the orientation effect of PEO on LDPE is more pronounced than that of the plasticization effect of DBSA and the fibrous morphology of the PEO, which can also affect the orientation of PANI along with it. It can be seen that the ΔH_m and ΔH_c values of all the blends of PANI-DBSA / LDPE with 5phr PEO are more than that of the blends without PEO content, indicating the induced orientation of LDPE in the presence of PEO and, hence, higher crystallinity. The comparison of ΔH_c of

PANI-DBSA / LDPE blend with 0phr as well as 5phr PEO contents are illustrated in the Table 3.26.

Table 3.24: Heat capacity changes at melting [ΔH_m (Observed)] for PANI-DBSA / LDPE blends with 5phr PEO and ΔH_m (Expected) of the respective blends calculated from the value of pure LDPE and its ratio in the blend.

Composition of blends (% PANI-DBSA)	ΔH_m (Observed) (j/g)	ΔH_m (Expected) (j/g)
0%	41.3	41.3
5%	24.3	39.24
10%	34.6	37.17
20%	30.7	33.04
30%	22.9	28.91
40%	19.4	24.78
50%	16.5	20.65

Table 3.25: Heat capacity changes at crystallization [ΔH_c (Observed)] for PANI-DBSA / LDPE blends with 5phr PEO and ΔH_c (Expected) of the respective blends calculated from the value of pure LDPE with 5phr PEO and its ratio in the blend.

Composition of blends (% PANI-DBSA)	ΔH_c (Observed) (-j/g)	ΔH_c (Expected) (-j/g)
0%	44.3	44.3
10%	42.2	39.87
20%	35.1	35.44
30%	28.1	31.01
40%	26.6	26.58
50%	19.9	22.15

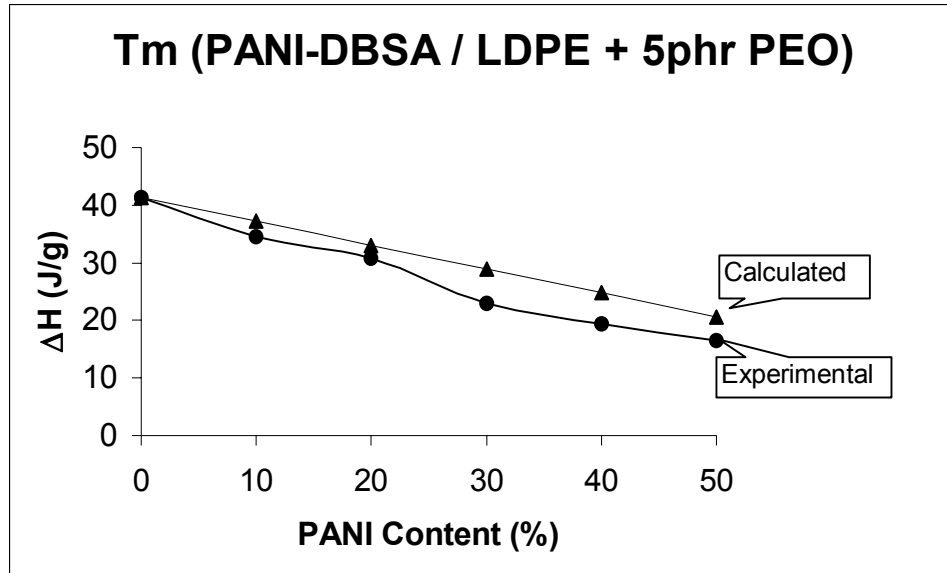


Figure 3.23: Comparison of ΔH_m (Experimental) and ΔH_m (Calculated) of PANI-DBSA / LDPE blends with 5phr PEO obtained from DSC.

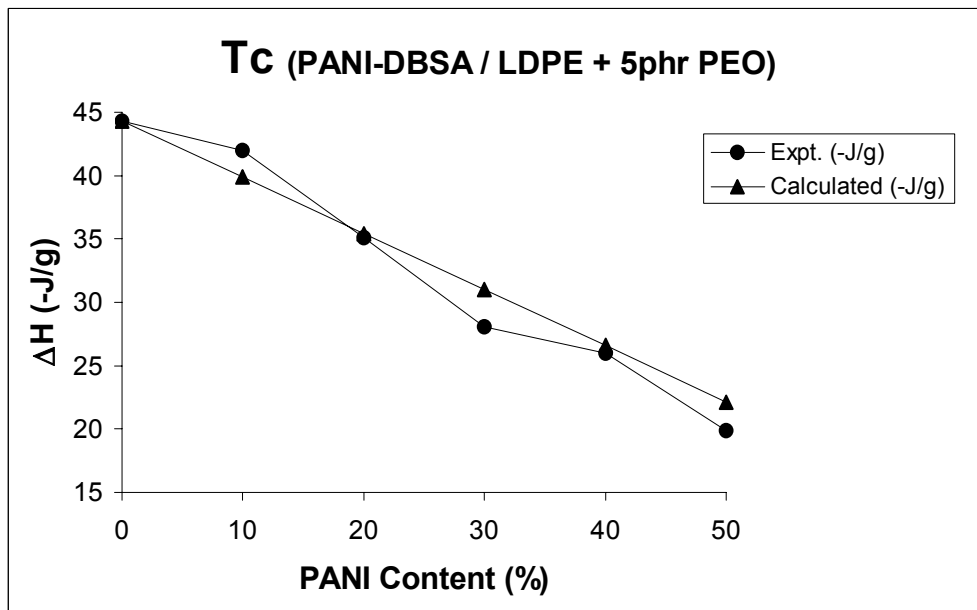


Figure 3.24: Comparison of ΔH_c (Experimental) and ΔH_c (Calculated) of PANI-DBSA / LDPE blends with 5phr PEO obtained from DSC.

Table 3.26: The comparison of ΔH_c of PANI-DBSA / LDPE blend with 0phr as well as 5phr PEO contents:

Composition of blends (% PANI-DBSA)	ΔH_c (-j/g)	
	0phr PEO	5phr PEO
Pure LDPE	35.7	44.3
10%	24.4	42.2
20%	16.4	35.1
30%	21.1	28.1
40%	8.47	26.6
50%	10.1	19.9

Thermogravimetric analysis (TGA):

Thermogravimetric analysis of these PANI-DBSA / LDPE blends was also carried out as mentioned in the experimental part. TGA of pure LDPE was also carried out to analyze the relative degradation that occurs in the blends. Blends with PANI-DBSA content of 10%, 20%, 30%, 40% and 50% were taken for this analysis. It was found that the relative degradation of dopant ions is lower in the blends, especially when LDPE content is more in the blend. It indicates that the presence of sufficient LDPE matrix around each PANI-DBSA molecule traps the dopant ion well within itself thereby protecting the dopant from the thermal degradation or release from polymer. This phenomenon is well explained in the Figure 3.25.

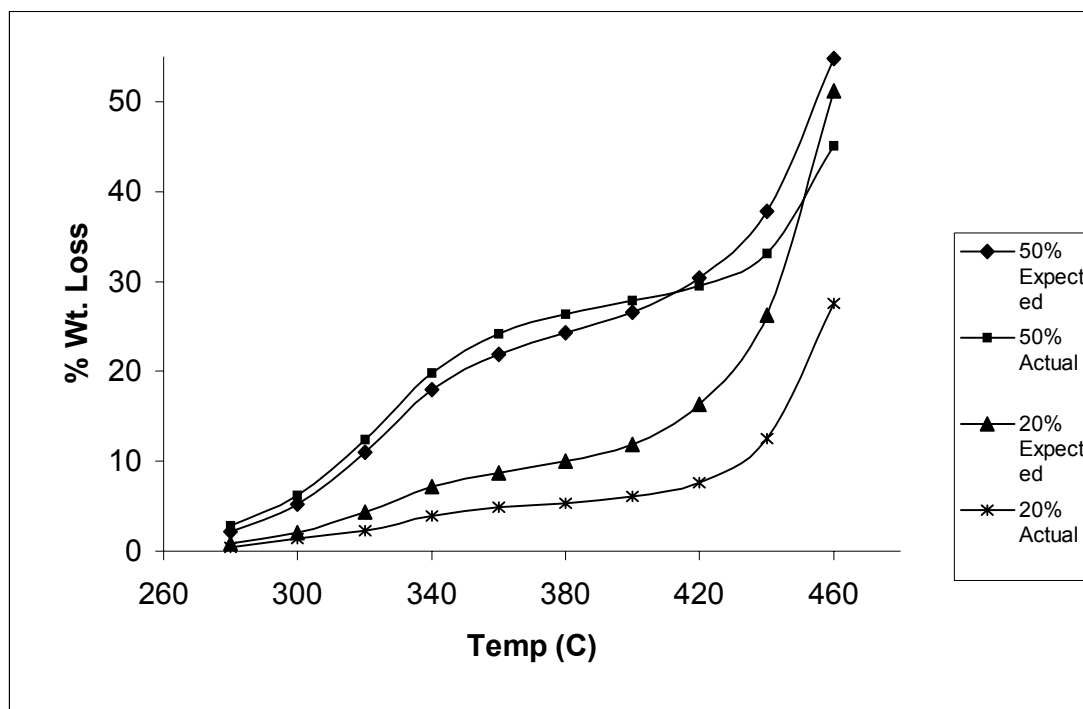


Figure 3.25: Comparison of expected and actual degradation of dopant ion from PANI-DBSA / LDPE blend with 20% as well as 50% polyaniline content.

The effect of blending on the thermal stability of doped PANI is clearly evident. It is seen that this effect is almost negligible in the case of 50% PANI blend but very much prominent in the case of 20% PANI blend. In the former case there is insufficient amount of LDPE matrix to encapsulate the entire PANI-DBSA molecule, thus allowing the exposure of unprotected polyaniline molecules within the bulk as well as on the surface, resulting in a similar degradation pattern as that of original polyaniline. However, in the case of 20% blend, sufficient LDPE matrix is present which protects the dopant ion from thermal degradation.

3.4. CONCLUSIONS:

This chapter has described the mode of selection of the polyaniline with suitable dopant ion, which could give better thermal stability as well as solubility and, hence the processibility. This chapter also described the detailed procedure and results obtained for melt processing and blending of polyaniline with LDPE.

Polyaniline was incorporated with different dopants in single step by directly synthesizing polyanilines in presence of these dopant ions instead of the conventional route of synthesizing, where a number of tedious steps are involved like initial synthesis followed by de-doping and re-doping. Amongst the different dopant studied like HCl, CSA, PSSA and DBSA, it was found that the thermal stability improved tremendously when the polyaniline was directly doped with DBSA. Also, the conductivity as well as solubility was found to maximum for the polyaniline doped with DBSA. Hence, PANI-DBSA was selected as the ideal candidate for further studies on processibility and blending.

It was shown that the melt processing of polyaniline doped with DBSA can be easily carried by blending it with low melting polymers like LDPE. The melt processibility of these blends was monitored by MFI measurements, which indicates the superior processibility of PANI-DBSA / LDPE blends over PANI-HCl / LDPE blends and LDPE / Carbon Black composites. The changes in melt viscosity due to addition of conducting component to a major polymer matrix were investigated in detail and compared with different theoretical models suggested. These studies clearly brought out the differences in the melt flow behaviour in the case of PANI-DBSA in comparison with filler containing conducting polymers. Conductivity studies also confirms the supremacy of PANI-DBSA / LDPE blends over other systems discussed above. XRD studies indicate the interactive phase morphology of these blends. Crystallinity of these blends monitored through XRD and DSC analysis was found to decrease than expected indicating the existence of interactive phase morphology. Detailed melt viscosity

studies monitored through MFI determination and comparisons of these values with the existing mathematical models are consistent with the phase morphology of these blends.

It can also be concluded that large improvements in processibility could be achieved by the addition of processing aids such as PEO and PEG. The PEO was found to be more effective on the basis of ease of incorporation, enhancement of conductivity as well as improvement of processibility. XRD studies also reveal molecular interactions between the phases in presence of PEO giving higher crystallinity due to induced orientation of LDPE. Interesting observations have been made regarding the oriented fibrous morphological features getting developed during melt processing of these blends in presence of PEO.

In short, it can be seen that these blends of PANI-DBSA with low melting polymers like LDPE can provide a better alternative for carbon black composites, which gives serious processing problems due to high melt-viscosity and need of high filler loading. These blends demonstrate the stability of conductivity at the processing temperature along with high processibility. Additions of dispersing agents such as PEO as processing aid ensure even better processibility with enhanced flow. The feasibility of preparing excellent melt processible inherently conducting polymer has been clearly brought out in this chapter. The products such as films, sheets, injection moulded test pieces have been made from these conducting polymer blends. These have been studied for their mechanical and electrical properties, which are described in the later chapters of this thesis.

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CHAPTER - 4
SOLUTION BLENDING OF POLYANILINE
WITH THERMOPLASTICS

4.1 INTRODUCTION:

Amongst different techniques available for the polymer processing, the most successful technique till now in the field of conducting polymers is the solution casting technique. Even though it is not a very useful way of processing in the industrial viewpoint, it can prove to be useful in certain applications like conductive coatings, anti-static paints, corrosion protection layers etc. The processability in this mode is also dependent on many parameters such as stability towards exposure to air / chemicals, thermal stability, solubility in common solvents etc. Blending with other processible polymers provide a better way to improve processability of these inherently conducting polymers. From the point of view of long-term stability, conducting polymers have been blended with other commodity polymers such as polyvinyl chloride (PVC), polycarbonate (PC), polystyrene (PS) etc.¹⁻⁴. However, the main aim of the earlier efforts was only to obtain sufficient conductivity at low PANI concentrations and the details regarding the compatibility, processability or other properties of the blends have not been investigated before. The essential requirements in the solution blending are the solubility of both polymers in a common solvent, miscibility and compatibility of the ICP with the other polymer matrix, film forming properties and more importantly the electrical properties and performance of the end products.

First and foremost, the solubility of PANI needs to be improved and hence detailed studies were undertaken to investigate the effect of dopant ion on the solubility of PANI. Then there is the blending of selected polyaniline with other common insulating processible polymers like poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC), polycarbonate (PC) etc. Miscibility and compatibility of polyaniline with these polymers, processability of these blends by solution casting technique, the molecular and structural developments and orientations were undertaken which are discussed in detail in this chapter.

4.2. EXPERIMENTAL:

4.2.1. SYNTHESIS OF POLYANILINE WITH APPROPRIATE DOPANT IONS

Polyaniline with different dopant ions were synthesized by two routes as discussed in earlier chapter; by the direct route of doping (insitu doping method) and also by the conventional way of synthesizing where polyaniline is first prepared with HCl, de-dope by neutralizing and re-dope with suitable sulfonic acid dopant. Details of these routes of synthesis were given in the chapter 3. The preferred route is one with direct doping method where less number of steps are involved. Different dopants like hydrochloric acid (HCl), Camphorsulphonic acid (CSA), polystyrenesulphonic acid (PSSA) and dodecylbenzenesulphonic acid (DBSA) were used for the synthesis of polyaniline.

In order to attain good processability in solution casted blends, the major driving factor is always the solubility of the each component in a common solvent. The solubility of polyaniline, containing each dopant ion considered, was examined by determining the weight of polyaniline dissolved in 100ml of different common organic solvent after 24 hours of stirring at ambient conditions. The solubility was also examined by UV-spectroscopy. It was done by putting 1gm of each polyaniline in 10ml of different solvents like chloroform and tetrahydrofuran, stirring it for one day. The resultant solution was filtered and taken the UV-Visible absorption spectra of each case. The more concentrated solutions were diluted for accurate measurements. UV-Visible spectroscopy was done using the "Shimadzu UV-240 spectrometer" sweeping the incident wavelengths from 900nm to 300nm.

To determine the molecular weight of the obtained soluble DBSA doped polyaniline viscosity measurement was carried out using Ostwald viscometer.

PANI-DBSA solutions were made in chloroform with varying weight percentage from 0.5 to 3.0 %.

4.2.2. BLENDING OF POLYANILINE WITH PMMA.

Poly (methyl methacrylate) is a well-known optically transparent engineering plastic. PMMA is known for its good solubility in many of the organic solvents. Chloroform is a good solvent known for it. Since the PANI-DBSA synthesized as mentioned above is found highly soluble in chloroform, it can be made use for the solution blending of PANI-DBSA with PMMA.

Atactic PMMA was used in this work. PMMA stock solution was prepared by dissolving 5gms of PMMA in 150 ml of chloroform, so as to get the PMMA concentration of 1gm per 30ml. The solubility of polyaniline doped with dodecylbenzenesulfonic acid (PANI-DBSA) was found to improve with additional doping (extra-doping) with DBSA. The solubility of PANI-DBSA (extra-doped) was found to be 6.7g per 100 ml of chloroform. To make different compositions of PANI-DBSA / PMMA blends; calculated quantity of solutions of PMMA and polyaniline were mixed as given in the table 4.1.

Required quantity of both solutions were taken as mentioned in the table and mixed well. The resultant solutions were stirred on magnetic stirrer continuously for 6hrs and then sonicated for half an hour to get homogeneous blend solution. These blends solutions were casted in petri dish to get the blend films of different thickness. The thickness was adjusted by using petri dishes of different diameters. The thicknesses of the films obtained were around 60 microns as well as 130 microns. These castings were carried out at ambient conditions with controlled rate of evaporation. These petri dishes were kept undisturbed till complete evaporation of the solvent was over and then the films

of PANI-DBSA / PMMA blends were peeled off and dried thoroughly under vacuum for complete removal of solvent.

Table 4.1: Amount of different components in the different PANI-DBSA / PMMA blend as well as the quantity of each solutions taken to make the total 1g of each blend.

Composition of the blend (% PANI-DBSA)	Amount of PMMA (g)	Amount of PANI-DBSA (g)	Quantity of PMMA solution taken (ml)	Quantity of PANI-DBSA solution taken (ml)
2%	0.98	0.02	29.4	0.30
5%	0.95	0.05	28.5	0.75
10%	0.90	0.10	27.0	1.50
15%	0.85	0.15	25.5	2.24
20%	0.80	0.20	24.0	3.00
30%	0.70	0.30	21.0	4.50

4.2.3. BLENDING OF POLYANILINE WITH PVC.

Poly (vinyl chloride) also can be blended with polyaniline doped with DBSA by solution blending technique. Solvent used here was tetrahydrofuran, in which extra-doped PANI-DBSA can be dissolved. The stock solution of PVC was prepared with the concentration of 1g / 30ml. 3% solution of polyaniline were prepared. To make different compositions of PANI-DBSA / PVC blends calculated quantity of solutions of PVC and polyaniline were mixed as given in the table 4.2.

Table 4.2: Amount of different components in the different PANI-DBSA / PVC blend as well as the quantity of each solutions taken to make the total 1g of each blend.

Composition of the blend (% PANI-DBSA)	Amount of PVC (g)	Amount of PANI-DBSA (g)	Quantity of PVC solution taken (ml)	Quantity of PANI-DBSA solution taken (ml)
2%	0.98	0.02	29.4	0.67
5%	0.95	0.05	28.5	1.67
10%	0.90	0.10	27.0	3.33
15%	0.85	0.15	25.5	5.0
20%	0.80	0.20	24.0	6.67
30%	0.70	0.30	21.0	10.0

The desired quantity of both solutions were taken as mentioned in the table and mixed well. The resultant solutions were stirred on magnetic stirrer continuously for 6hrs and then sonicated for half an hour to get homogeneous blend solution. These blends solutions were casted in petri dish to get the blend films of different thickness. The thickness was adjusted by using petri dishes of different diameters. The thickness values of the films obtained were around $100 \pm 5 \mu\text{m}$ as well as about $200 \pm 5 \mu\text{m}$. Theses film castings were carried out at 40°C with controlled rate of evaporation. The petri dishes were kept undisturbed till complete evaporation of the solvent was over and then the films of PANI-DBSA / PVC blends were peeled off and dried thoroughly under vacuum for complete removal of solvent.

4.2.4. BLENDING OF POLYANILINE WITH POLYCARBOBATE.

PANI-DBSA / PC blends were prepared using dichloromethane (DCM) as the common solvent for blending. The stock solution of PC was prepared with the concentration of 1g / 30ml. The solubility of PANI-DBSA (extra-doped) was found to be 3.53g per 100 ml of chloroform.

In order to make different compositions of PANI-DBSA / PC blends, calculated quantity of solutions of PMMA and polyaniline were mixed as given in the table 4.3 and cast in to form of films under controlled conditions as described above for other cases.

Table 4.3: Amount of different components in the different PANI-DBSA / PC blend as well as the quantity of each solutions taken to make the total 1g of each blend.

Composition of the blend (% PANI-DBSA)	Amount of PC (g)	Amount of PANI-DBSA (g)	Quantity of PC solution taken (ml)	Quantity of PANI-DBSA solution taken (ml)
2%	0.98	0.02	29.4	0.57
5%	0.95	0.05	28.5	1.42
10%	0.90	0.10	27.0	2.83

4.2.5. Viscosity measurements

Viscosity of the blend solutions was measured using ‘Ostwald Viscometer’. Readings were noted for different solutions of PMMA concentrations in chloroform as well as PANI-DBSA concentrations in chloroform. Viscosities of blends were noted with increasing in polyaniline loading in the solution of constant concentration of the major matrix. Behavior of these blend solutions can be compared with the expected values obtained from the individual polymer solutions and can be compared to get the homogeneity of these solutions as well as the inter phase interactions of the blend components.

Viscosity of concentrated solutions is important from viewpoint of thick paint like coatings application. This measurement was carried out for the PANI-DBSA / PMMA blends and PANI-HCl / PMMA blend solutions using a Ford-Cup like arrangement, where the cylindrical stainless steel viscometer carries an orifice of 1mm diameter (see chapter II of this thesis). In all measurements 10%

solution of PMMA was taken and polyaniline powders were added to it to make different blend / dispersion compositions. These were stirred for 10 hrs on a magnetic stirrer and then sonicated for 1hr before passing through the viscometer. The time taken for 1ml of each blend solution to come out through the orifice was determined and relative viscosity in each case with respect to zero polyaniline loading was calculated.

4.2.6. Spin coating of PANI solutions

Spin coating of these blends solutions were carried out using a spin coater having a spinning chuck with variable rpm. The different substrates used were steel, glass as well as moulded ABS sheets. Efficiency of spin coating was checked with various viscosities of the corresponding blend solutions.

4.2.7 Structure and morphology

a) XRD Studies for Structural Investigations:

Wide angle X-ray diffraction (WAXD) analysis was carried out for all the samples of polyaniline doped with different dopants as well as the blends prepared to study the structural behaviors. These patterns were analyzed to get the effect of dopant acid used on the crystallinity of polyaniline formed. XRD patterns were analyzed carefully to investigate the phase morphology of these blends. Inter-chain separation of the major matrices was calculated from the $(2\theta)_{\max}$ of the amorphous diffraction.

b) FT-IR spectroscopic analysis:

Polyaniline samples with different dopant ions were characterized with FTIR spectroscopy. This was carried out using “Shimadzu FTIR 8201” by diffusion reflectance scanning disc technique. PMMA, PANI-DBSA and their different blends were characterized with FT-IR spectroscopic technique. Samples were prepared as the solutions in chloroform. These solutions were dropped between two NaCl windows and recorded the IR absorption with the background scan of chloroform alone.

c) UV – Visible spectroscopy:

UV visible spectroscopy was carried out extensively for different purposes. These analyses were carried out using “Shimadzu UV 240” spectrometer. The blends of polyaniline with different thermoplastics were characterized for uniformity of dispersion or the molecular miscibility other than the characterization of polyaniline for this polyaniline. The solutions of respective blends as well as the casted films were separately analyzed. Homogeneity of these blends can be analyzed by the agreement of intensities of characteristic absorption of polyaniline with polyaniline loading with the Beer Lamberts law.

d) Differential Scanning Calorimetric Analysis:

Thermal analyses of the blends were carried out to understand the primary and secondary phase changes with temperature. Differential Scanning Calorimetric (DSC) analysis were carried out, using PERKIN ELMER DSC machine, for different PANI-DBSA / PMMA blends, as well as the PMMA with different DBSA content to examine effect of dopant ion on the T_g of the PMMA

and the blends. It was recorded from 50°C to 250°C to analyze the primary and secondary molecular changes.

e) Dielectric Measurements:

Dielectric properties of the polymers can give the in formations about the dielectric relaxations occur in the polymeric lattice due to molecular rearrangements. These relaxation studies can be carried out in two ways – with respect to he frequency and with temperature fixing the other constant. These relaxations can be made use to study especially the secondary molecular reorientation like one which occurs during glass transition. So the change in Tg with additives can be understand from the dielectric relaxation curves. The effect of DBSA as a plasticizer on thermoplastics like PMMA and PVC were determined by measuring the dielectric properties of PMMA and PVC films with different DBSA content in it. Theses studies were out by measuring the a.c. resistance and capacitance values at different temperatures using “Aplab 4910 LCR-Q meter. The film samples were loaded in the cell with controlled temperature programming that can sweep the temperature with the rate of 4 degrees per minute.

4.3. RESULTS AND DISCUSSIONS:

Solution blending technique also can be successfully applied for the blending of polyaniline with other polymers to improve processibility. Here, the attainment of processibility mainly depends on the solubility of the concerned polymers in a common solvent. Sufficient solubility of polyaniline is the most important factor governing the processibility in this contest. As discussed in the earlier chapter, polyaniline can be doped with different long chain organic acids to improve its solubility and compatibility. The soluble polyaniline thus formed can be solution blended with polymers like poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC), polycarbonate (PC), etc. PMMA and PC are known for their optical properties. So the blends of polyaniline with these polymers can fetch importance in optical applications like transparent conductive coatings for anti-static properties even on the printed surfaces. Whereas, PVC blends with polyaniline can be used for various ant-static layers and coatings as well as the corrosion protection coatings.

4.3.1 SOLUBILITY OF POLYANILINE IN ORGANIC SOLVENTS

Solubility of polyaniline doped with different dopant ions was determined in different common organic solvents like CHCl_3 , THF, NMP and DCM. It is important to attain a reasonable solubility for the polyaniline in any of the common organic solvents, which are less toxic, to consider it feasible for solution blending with other soluble polymers. There have been some reports on the solubility of polyaniline in different aqueous and non-aqueous media ⁵⁻⁸. However, those investigations were on the derivatives of polyaniline, which resulted in the tremendous decrease of conductivity. Here the PANI with different dopant ions were examined. It was found that only PANI-DBSA gives considerable solubility in these solvents. Other polyanilines like PANI-HCl, PANI-

PSSA and PANI-CSA were completely insoluble or have very little solubility to detect by solid content measurements. It was also found that the solubility of the PANI-DBSA improves when extra dopant 0.5 molar DBSA is added. It was found that the solubility of PANI-DBSA in chloroform improved from 2.5 g / 100 ml to 6.7 g / 100ml when doped additionally with DBSA. In order to characterize the solubility of each type of polyaniline in chloroform as well as tetrahydrofuran 1g of these polyanilines were added to 10 ml of both solvents, stirred for 24 hrs, filtered and their UV-Visible spectra recorded from 200nm to 900nm. It was found that both solution of PANI-DBSA showed very high absorbance, which in fact increased beyond the detectable range of the instrument due to its high solubility. Hence, these solutions were diluted 20 times in chloroform and 10 times in THF to give the optical density less than 2.0 in these cases. The UV-Visible spectrum of these solutions in chloroform is given in Figure 4.1, and that of in THF were given in Figure 4.2. It is seen from these spectra that not only the PANI-DBSA shows tremendous absorbance in the original polymer region (280 to 400 nm) but also in the dopant induced bipolaronic transition region (850 nm). This indicates that the doped state of PANI - DBSA remains intact even after dissolution in organic solvents without any leaching out of the dopant. It may be pointed here that some authors have reported the solubility of PANI in its undoped state in NMP. On the other hand, in the present case it is the doped polymer which is soluble. Also, the figure clearly indicates that the highest solubility of PANI-DBSA amongst the polyaniline samples containing different dopant ions. The order of solubility can be as PANI-DBSA > PANI-PSSA > PANI-CSA > PANI-HCl in both the solvents studied.

The solubility of DBSA doped polyaniline obtained by one-step synthesis was also determined from the solid contents in the solution. Solubility in different common organic solvents was determined by adding 10 gm of each polyaniline in 100 ml of different solvents and stirred for 24 hrs. The solutions obtained were filtered and the solid content in 1 ml was determined by determining the weight

after complete evaporation of the solvent. The solubility of PANI-DBSA in different solvents like CHCl_3 , THF, NMP and DCM were given in the Table 4.4

Table 4.4: The solubility of PANI-DBSA in different solvents determined by the total solid content in 1ml of each solution.

Solvent	Solubility of PANI-DBSA (g / 100 ml)
CHCl_3	6.73
THF	4.15
DCM	3.53
NMP	2.12

In order to determine the effect of dopant ion on crystallinity, X-Ray Diffraction (WAXD) studies were carried out on each polyaniline with different dopant ions. The XRD patterns of these polyaniline are shown in the Figure 4.3. The crystallinity of the resultant polyaniline was calculated by the method discussed in the Chapter 3. The C_i values calculated are given in Table 4.5. It can be noted that the CSA doped polyaniline showed maximum crystallinity among the cases studied of 0.37 and the DBSA doped polyaniline showed the least of 0.26. It shows the effect of long-chain present in DBSA as well as polymeric structure of PSSA in interacting through the polyaniline lattice and disturbing the crystalline order. It also confirms the possibility of the easy

penetration of solvent molecules through PANI-DBSA than that of any other polyaniline considered.

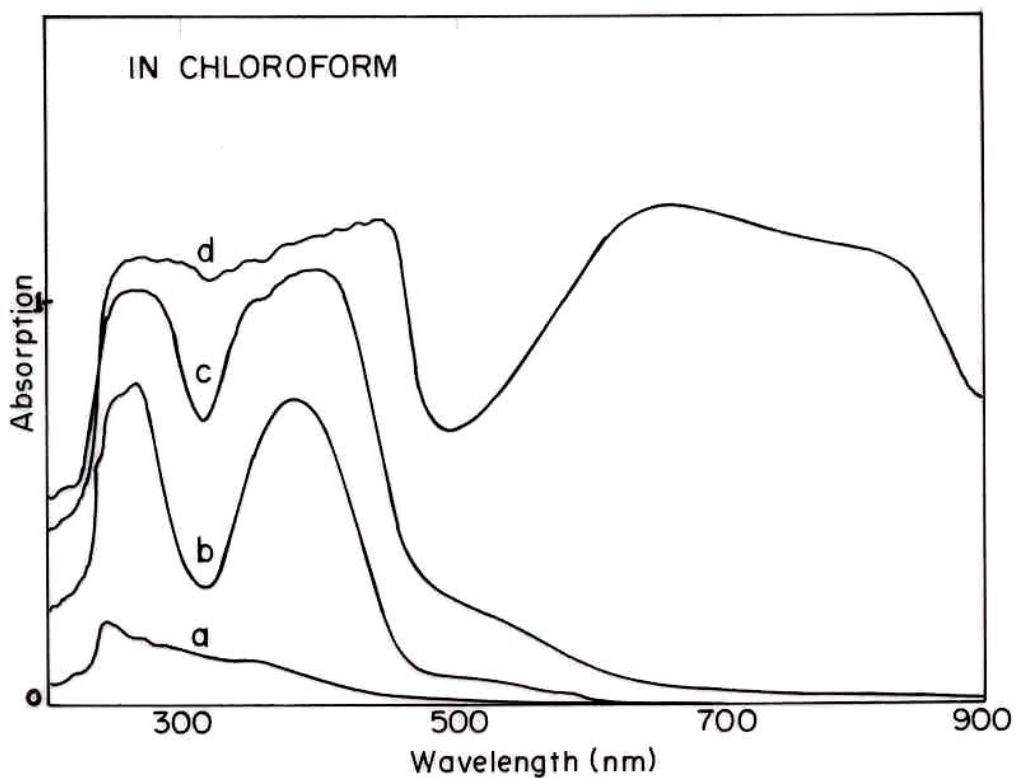


Figure 4.1: UV-Visible Spectra of solutions of polyaniline doped with different dopants in chloroform; (a) PANI-HCl, (b) PANI-CSA, (c) PANI-PSSA and (d) PANI-DBSA (20 times diluted).

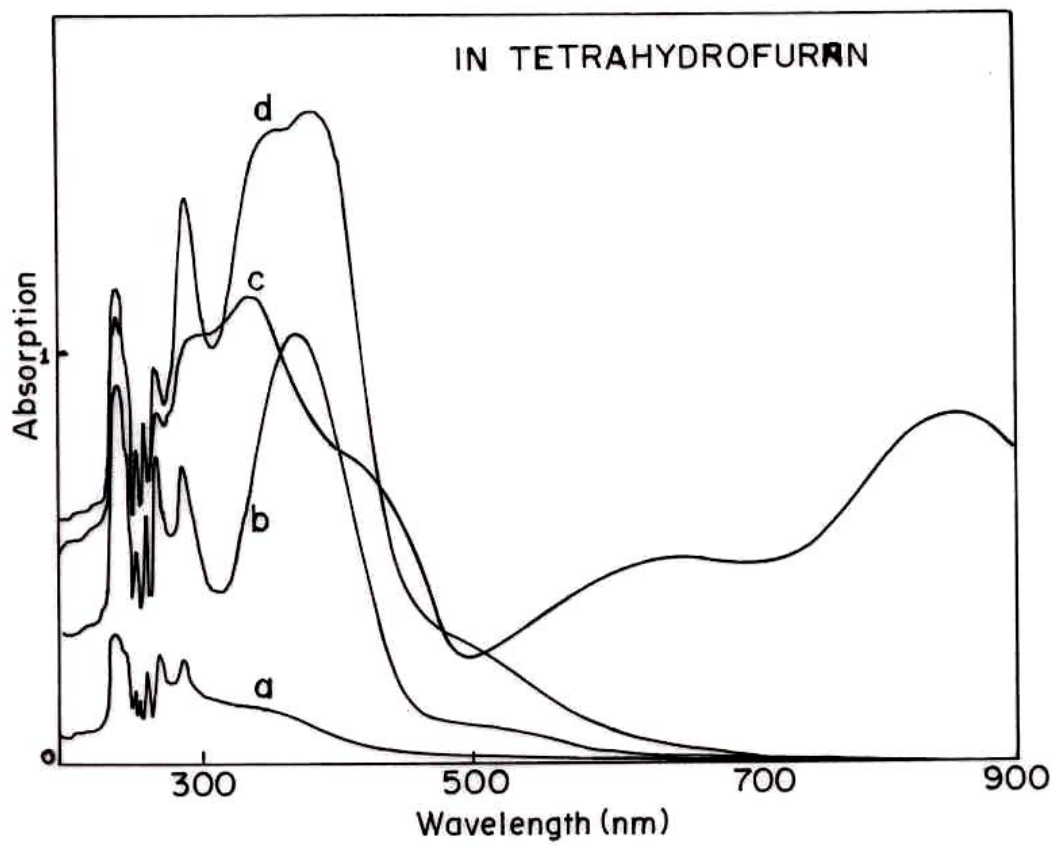


Figure 4.2: UV-Visible Spectra of solutions of polyaniline doped with different dopants in THF; (a) PANI-HCl, (b) PANI-CSA, (c) PANI-PSSA and (d) PANI-DBSA (10 times diluted).

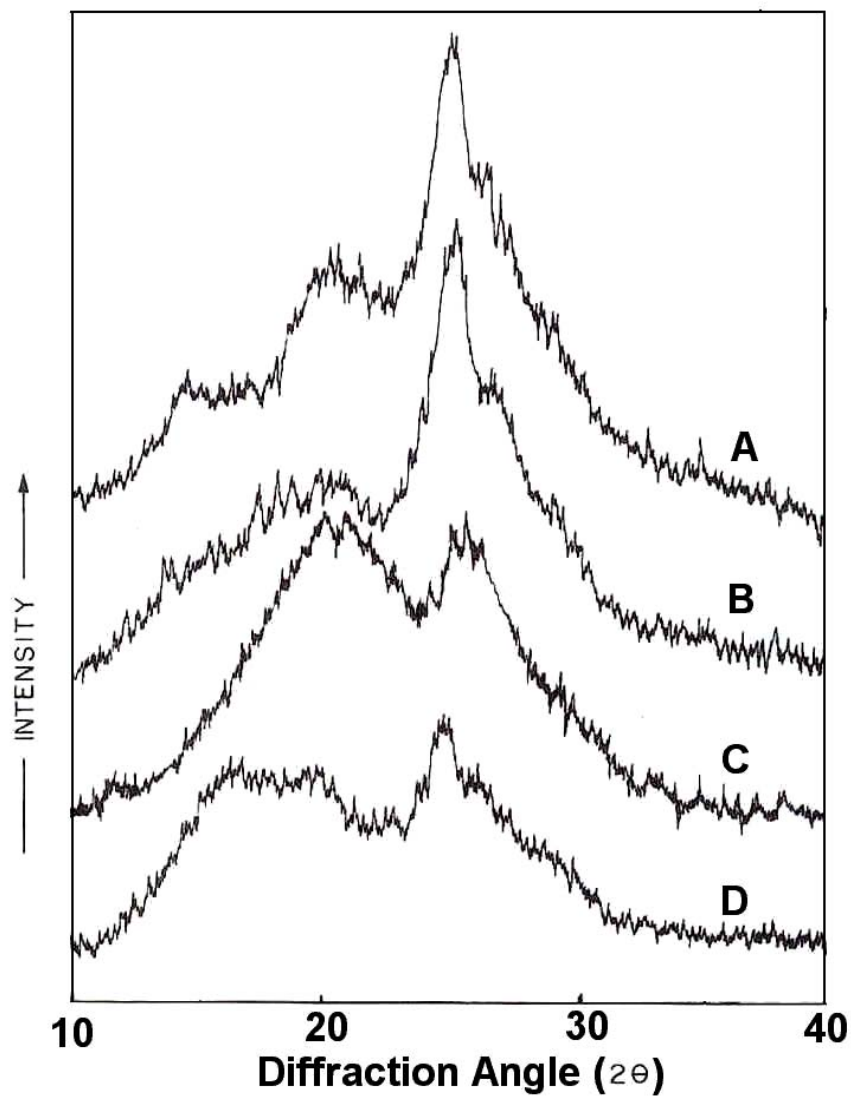


Figure 4.3: X-ray diffraction scans for PANI with different dopant ions. (A) PANI-HCl, (B) PANI-CSA, (C) PANI-DBSA, and (D) PANI-PSSA.

Table 4.5: The crystallinity index (Ci) values of polyanilines with different dopant ions determined from WAXD.

Polyaniline Sample	Crystallinity Index (Ci)
PANI-HCl	0.36
PANI-CSA	0.37
PANI-PSSA	0.28
PANI-DBSA	0.26

4.3.2 POLYANILINE / PMMA BLENDS:

As explained in the experimental part, PANI / PMMA blend films were cast using chloroform as solvent, with controlled rate of evaporation in order to avoid phase separation during the solvent evaporation when polymer concentration increased beyond the cloud point. The PANI / PMMA blend films from PANI-DBSA were very uniform, homogenous and flexible at all compositions whereas those from PANI-HCl were grainy, rough and brittle even at low concentrations of PANI. This may arise from the higher compatibility / miscibility of PANI-DBSA with PMMA solution than that of PANI doped with HCl. It may be mentioned here that the blend solutions in the case of PANI-DBSA were transparent green with no cloudiness whereas in the case of HCl doped PANI suspension of particles was noted at all concentrations.

4.3.3. POLYANILINE / PVC BLENDS:

PANI / PVC blend films were cast using tetrahydrofuran as solvent, under controlled rate of evaporation while casting to avoid phase separation during the solvent evaporation when polymer concentration increased beyond the cloud point. The concern over this cloud point is more serious in the case of PVC as reported in the past,⁹ it caused severe problems giving rise to white patches and hence, the castings temperature of 40°C was maintained. Here also homogeneity was observed in the cases of blends with PANI-DBSA and those with PANI-HCl were found to be grainy and brittle. This suggests the role of DBSA as compatibilizer giving good miscibility of the two components. It was also noted that the flexibility of the blend was improving with polyaniline loading indicating the plasticizing effect of DBSA.

4.3.4. POLYANILINE / POLYCARBONATE BLENDS:

As explained in the experimental part, PANI / PC blend films were cast using dichloromethane as solvent, with controlled rate of evaporation. As discussed in above cases, here also the PANI / PC blend films from PANI-DBSA were very uniform, homogenous and flexible at all compositions whereas those from PANI-HCl were grainy, rough and brittle even at low concentrations of PANI. This also shows the higher compatibility / miscibility of PANI-DBSA with PC solution than that of PANI doped with HCl. It may be also be mentioned here that the blend solutions in the case of PANI- DBSA were transparent green, as in earlier cases, with no cloudiness whereas in the case of HCl doped PANI, suspension of particles was noted at all concentrations.

4.3.5. Viscosity measurements

The viscosity of a dilute polymer solution depends on several factors, mainly, the nature of the polymer and that of the solvent, their concentrations, the polymer molecular weight, the temperature and shear rate. At the molecular level, the viscosity of a polymer solution is a direct measure of hydrodynamic volume of the polymer molecules. For the blend of two polymers the solution viscosity depends on the interaction of each polymer with the common solvent as well as the inter-polymer interactions. These measurements were carried out in two ways. One for dilute solution of blends and the second set was for concentrated solutions where Ford-Cup viscometer type arrangement was used.

The measurements for diluted solutions were carried out in Ostwald viscometer. The solutions of PMMA and PANI-DBSA in chloroform were mixed together to get the blend composition of different polyaniline content from 5, 10, 20, 30, 40 and 50%. Total concentration of these solutions was fixed as 0.5%. The time of flow for 10 ml of these solutions were measured. The viscosity measurements of the solutions of PMMA and PANI-DBSA in chloroforms also carried out separately. From this measurement the trend of time of flow of these pure components were platted against concentration. This is shown in the Figure 4.4.

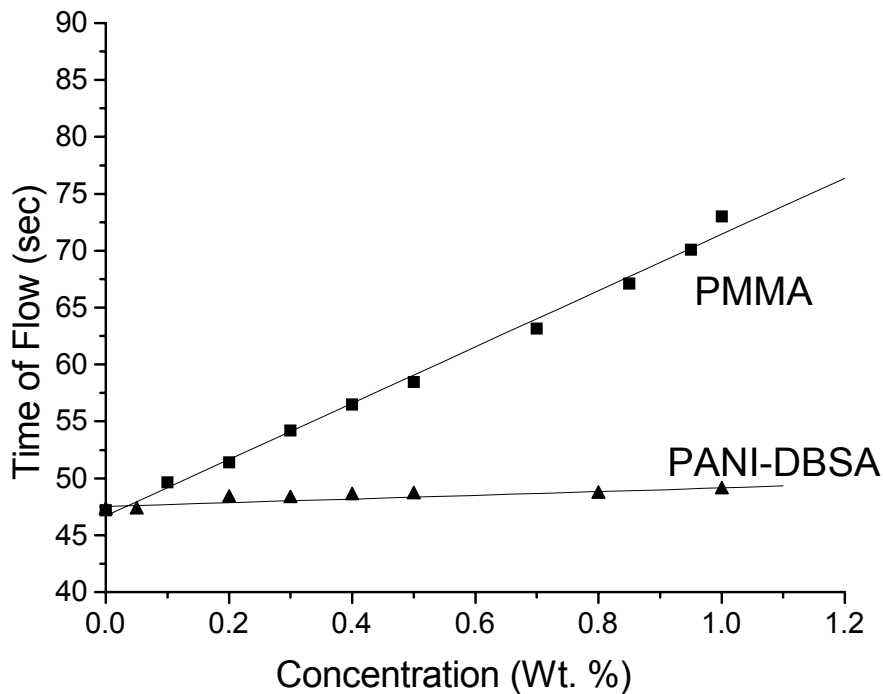


Figure 4.4: The time of flow for PMMA and PANI-DBSA solutions in chloroform.

From the above curve the effect of each component on the viscosity of chloroform solution can be obtained. The next step was the measurement of flow time for the same volume of blend solution. The blend solution of 0.5% total polymer concentration was used with varying the blend composition from 5 to 50% of PANI-DBSA. From the blend composition and time of flow obtained for individual polymers at that concentrations the expected time of flow and hence the relative viscosity of those solutions with respect to the pure solvent were calculated. The time of flow obtained were used to calculate the actual value of relative viscosity of the blend and compared with that of expected value calculated from individual polymer viscosity values. These are given in the Figure 4.4

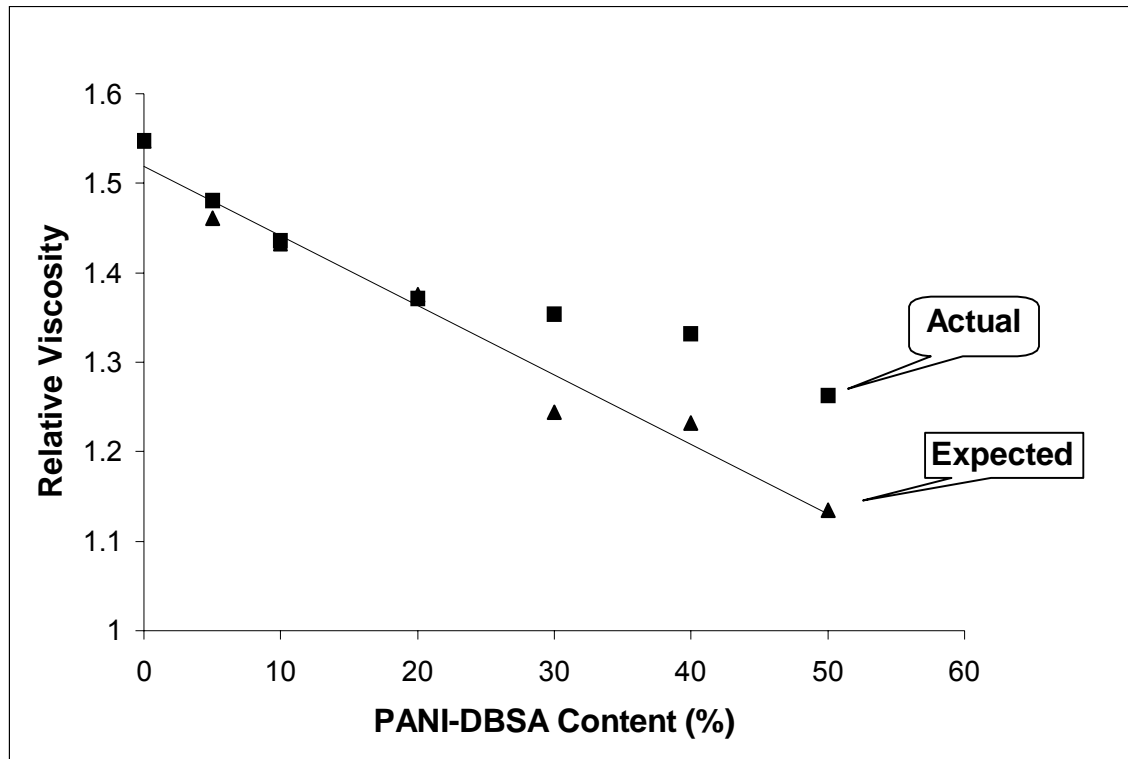


Figure 4.5: Comparison of expected and actual values obtained for the 0.5% solution of PANI-DBSA / PMMA blend solutions.

It can be seen from the above plot that the blends were showing the exact behavior as calculated till the 20% loading of polyaniline. It shows the homogeneous nature of the solution where the relative viscosity is mere addition of individual component. It indicates the uniform mixing of the components with each other and good interaction with the solvent molecules. Hence, the simple rule of mixture is followed in this regime. However, above 20% there is the agglomeration of the polyaniline particles and thus the mixture is phase separated in which the polyaniline is in dispersed state rather than dissolved state. The insoluble fraction of polyaniline particles then act as particulate fillers and thus there is an increase in relative viscosity as observed for the dispersions, which is different from homogeneous solutions.

While the study of the viscosity behavior of dilute polymer solution is of significant theoretical importance; that of the flow behavior of a concentrated

polymer solution is of practical importance for coatings ¹⁰. Many industrial problems associated with adhesives, coatings, cast films and spun fibres cannot be fully appreciated without a proper knowledge of properties of concentrated polymer solutions / dispersions. At higher concentration of above 5% by weight, polymer molecules do not exist in isolated chain coils, but are interpenetrating and entangled with each other. Therefore at high concentrations the polymer solutions will behave differently and the separate study of concentrated solutions is of high importance.

For concentrated solutions and dispersions, the flow behaviour can be studied by using Ford-Cup type viscometer arrangement as described in the ASTM D1200. Here 10% solution of PMMA in chloroform was used as the reference solution and the polyaniline powders were added to this solution to make different blend concentrations. The time of flow for 1ml solution was measured and the relative viscosity of different blend solutions were calculated with respect to the pure PMMA solution. The relative viscosity with polyaniline loading were calculated in the case of PANI-DBSA / PMMA blends and that of PANI-HCl / PMMA blends. The relative viscosity increase with polyaniline loading in each case is given in the Figure 4.6.

It can be seen that the increase in relative viscosity is more rapid in the case of PANI-HCl than that of PANI-DBSA. It can be due to the fact that the HCl doped polyaniline is insoluble in chloroform and is acting like non-interactive particulate filler. But in the case of DBSA doped polyaniline there is solubility in chloroform and better miscibility with PMMA and, hence, the relative viscosity is low. After 20% loading there is sharp increase and it was found to be difficult to get the flow of 1ml at 40% polyaniline loading. It is because more of physical blocking due to fast film formation at the tip and formation of high agglomerates, rather than high viscosity. It shows confirms the interactive nature of the PANI-DBSA / PMMA blends.

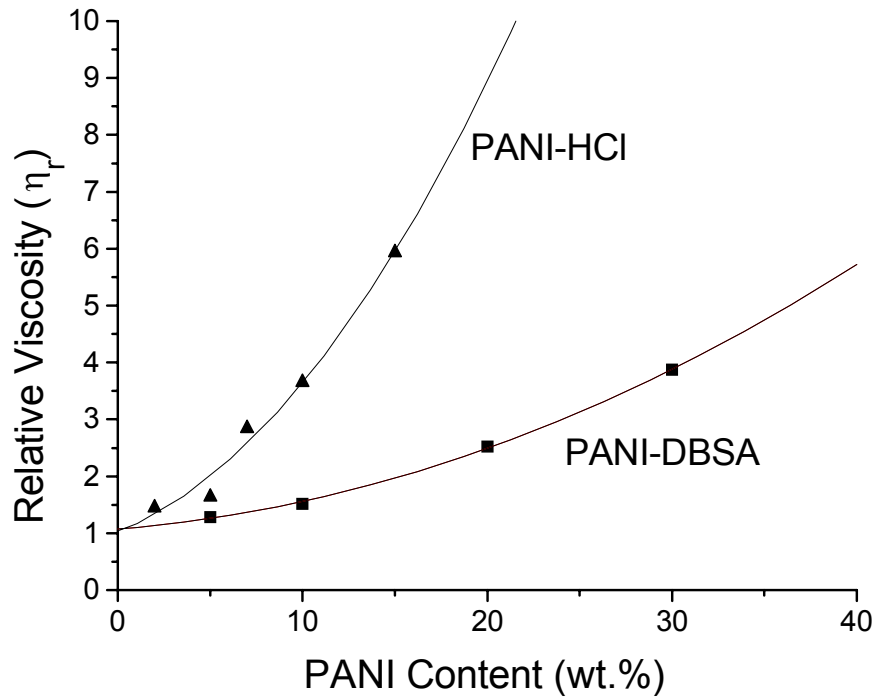


Figure 4.6: The change in relative viscosity for PANI-DBSA / PMMA and PANI-HCl / PMMA solution blends in chloroform with polyaniline loading.

As discussed in the Chapter 3, here also the change in relative viscosity with filler loading can be compared with existing mathematical models for the behavior of polymer melt / solution with particulate fillers ¹¹. The details regarding these mathematical models are already discussed in Chapter 1. The models considered were Einstein, Eilers, Mooney, Krieger and Dougherty and Quemada. It was considered that the polyaniline is having oblong morphology as discussed in earlier Chapter. The relative viscosity of these blends was plotted against the volume fraction of polyaniline in each composition to compare the behavior with these models. And the maximum packing fraction was considered as that of cylindrical shaped particles.

The comparison of the behavior of relative viscosity of PANI-HCl / PMMA blends with different mathematical models were shown in the Figure 4.7. It can be seen that the behavior of the PANI-HCl / PMMA blends were more fitting to that of Mooney model where the exponential rise in relative viscosity is observed, indicating that the HCl doped polyaniline act like non-interactive filler dispersed in PMMA solution.

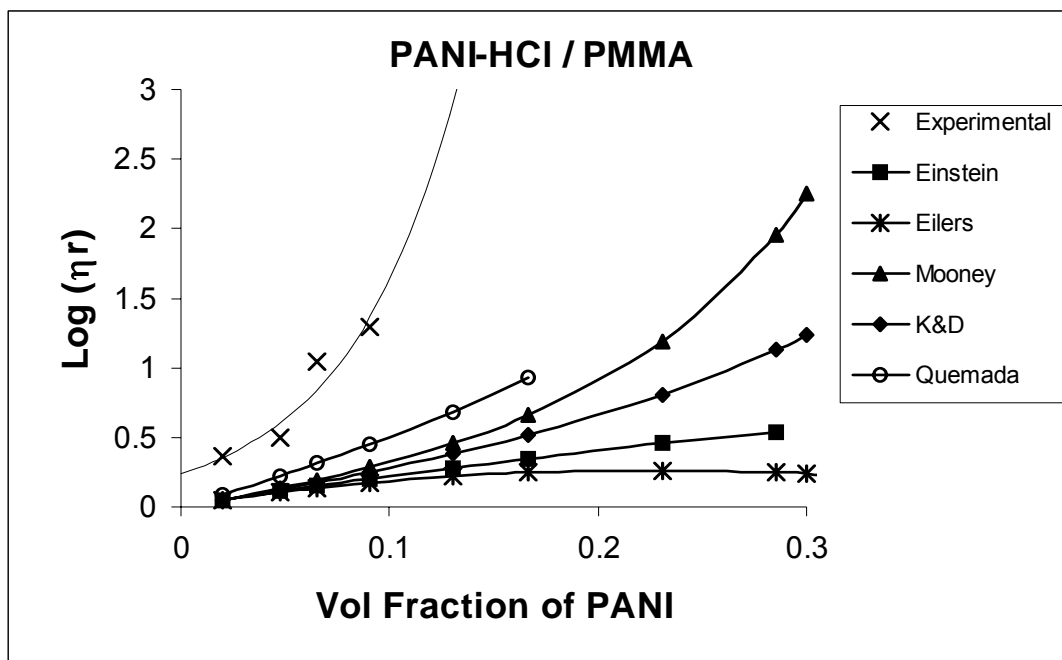


Figure 4.7: The comparison of relative viscosity of PANI-HCl / PMMA blend solutions with different mathematical models.

The behavior of solution viscosity of PANI-DBSA / PMMA blends with PANI-DBSA loading were also compared with different models as shown in the Figure 4.8. It comes more fitting to the Quemada model rather than Mooney model as it is not showing any exponential increase and almost following the same path of theoretically calculated values of Quemada model. It indicates that there is better interaction of blend components in this case. It also shows the miscible nature of these blends, which is absent in the case of HCl doped polyaniline.

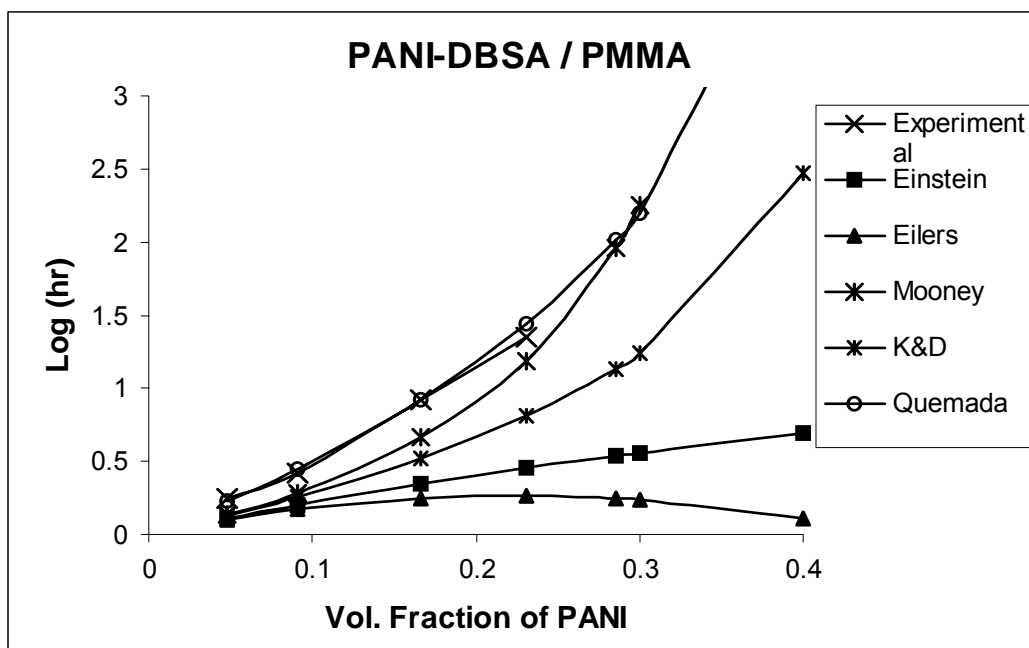


Figure 4.8: The comparison of relative viscosity of PANI-HCl / PMMA blend solutions with different mathematical models.

4.3.5. Spin Coatability

These solution blends were spin coated on different substrates like steel and ABS. As expected, as the viscosity increases the coatability also improved. The rotation of the chuck was adjusted as low as possible in the initial stage and gradually increased to get the solvent evaporated fully. Chloroform solutions of these blends showed easy coating properties over THF and DCM blend solution due to slower evaporation rate. These coated substrates can be used as the material for ESD / EMI shielding measurements.

4.3.7. CHARACTERIZATION AND STRUCTURAL EVALUATION:

a) UV – Visible Spectroscopy:

The UV-Visible spectroscopy can be used to characterize the doped state of the conducting polymers. It can also be made used to determine the homogeneity of the optically transparent blends. The UV – Visible absorption spectra for these PANI-DBSA / PMMA blends are shown in Figure 4.9. Curves A to E correspond to increasing concentration of PANI-DBSA in PMMA blend from 2% to 20%. It is evident that the intensity of the broad absorption band at 850 nm corresponding to doped PANI bipolaronic state increases with increase of PANI content in the blend. The exact dependence of the absorption intensity with the concentration is shown in Figure 4.10. It is interesting to note that this plot is linear upto PANI concentration of 15% above, which there is deviation, observed in the graph. According to Beer Lambert's law for optical absorption (optical density OD) for homogeneous solutions the following relation is expected: ¹²

$$O D = C . \alpha . d \quad (4.1)$$

Where C is the concentration, α the molar extinction coefficient and d the thickness of the sample. Thus, it appears that the Beer Lambert's law is followed in the present case of DBSA-PANI blends with PMMA at least up to the concentration of 15% of PANI. The above equation (4.1) is commonly used for homogenous solutions which contain solutes having absorption in the visible / UV region and when there are no particulate suspensions. The excellent agreement between the experimentally observed data in the present case with the above equation (4.1) suggests that there is good homogeneity of the blends and that the component polymers mix well with each other. The deviation from the linear

graph at high concentrations of PANI above 15% can be due to phase segregation of the additional PANI. Thus it appears that the upper limit for the formation of homogeneous DBSA-PANI / PMMA blend is 15% of PANI. It may be noted that the HCl-PANI gave particulate dispersions at all compositions in PMMA and the OD was very high even at 10 % due to large background scattering of the UV-Visible beam with very little changes with wavelength, i.e. no distinct spectra, noted from the sample.

Figure 4.9. Optical absorption spectra of PANI-DBSA blends with PMMA. Curves correspond to increasing PANI concentration in the blend from 2%, 5%, 10%, 15% and 20%.

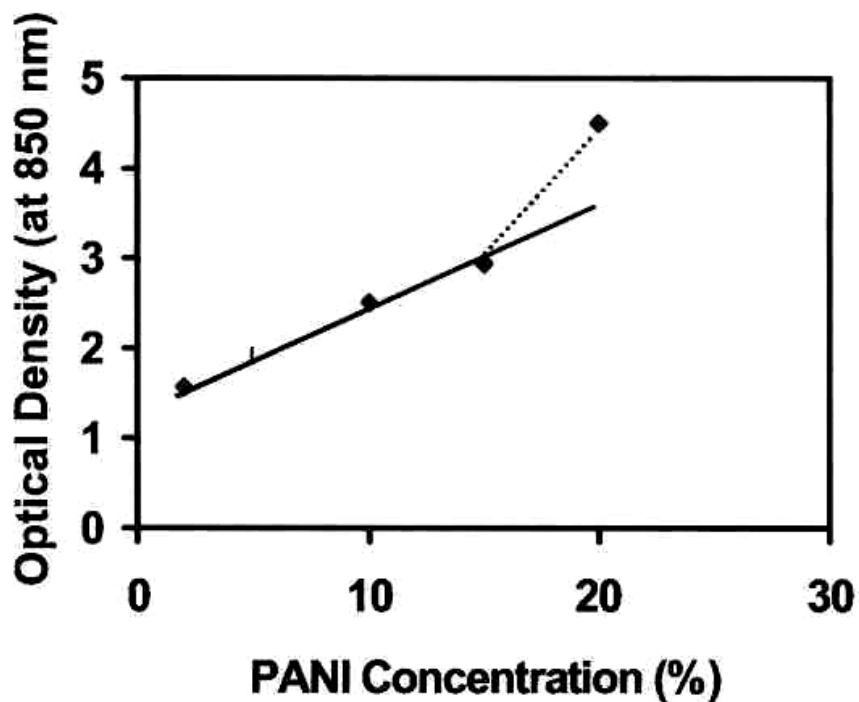


Figure 4.10: Optical absorbance (Optical Density) at 850 nm for DBSA-PANI blends with PMMA with concentration of PANI showing Beer Lambert's Law.

The UV-Visible absorption spectra for PANI-DBSA / PVC blends are shown in Figure 4.11. Curves A to E correspond to increasing concentration of PANI-DBSA in PVC blend from 2% to 20%. It is evident that the intensity of the broad absorption band at 850 nm corresponding to doped PANI bipolaronic state increases with increase of PANI content in the blend. The exact dependence of the absorption intensity with the concentration is shown in Figure 4.12.

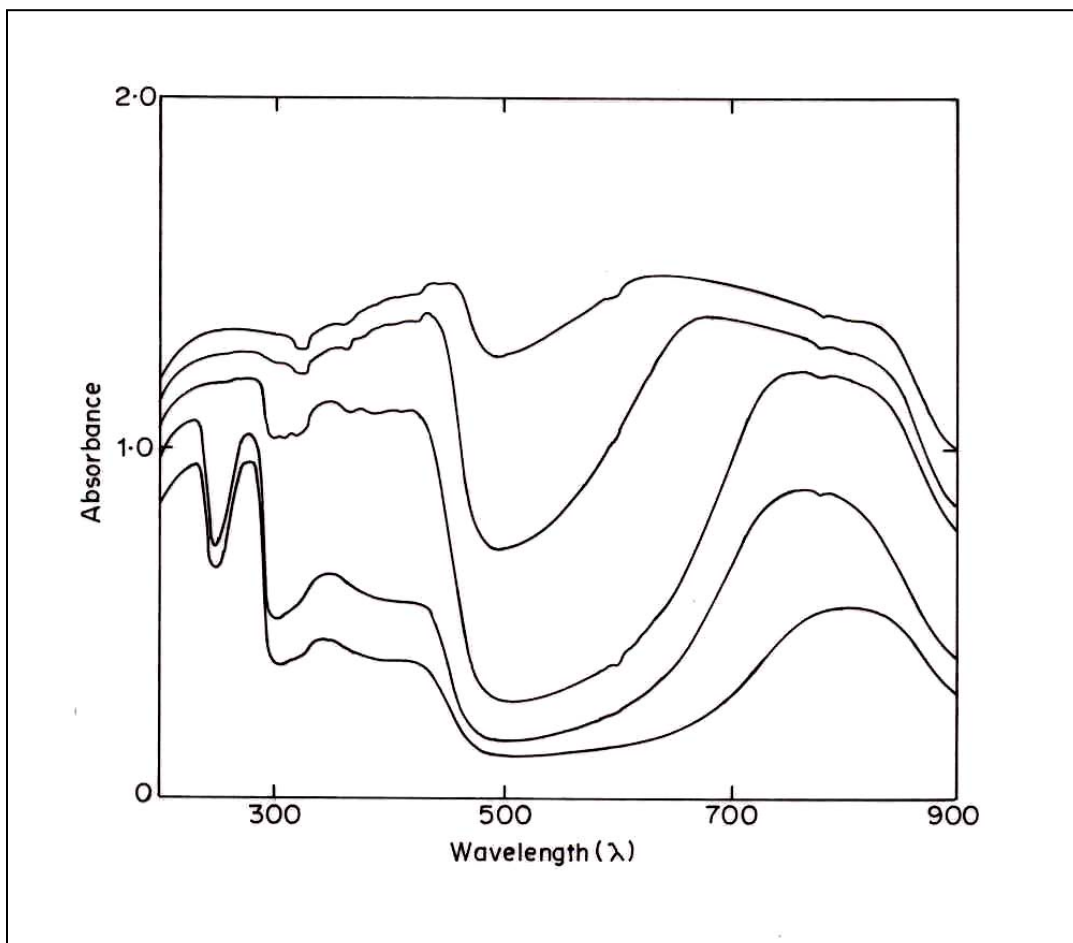


Figure 4.11: Optical absorption spectrum of PANI-DBSA blends with PVC. Curves A to E correspond to increasing PANI concentration in the blend.

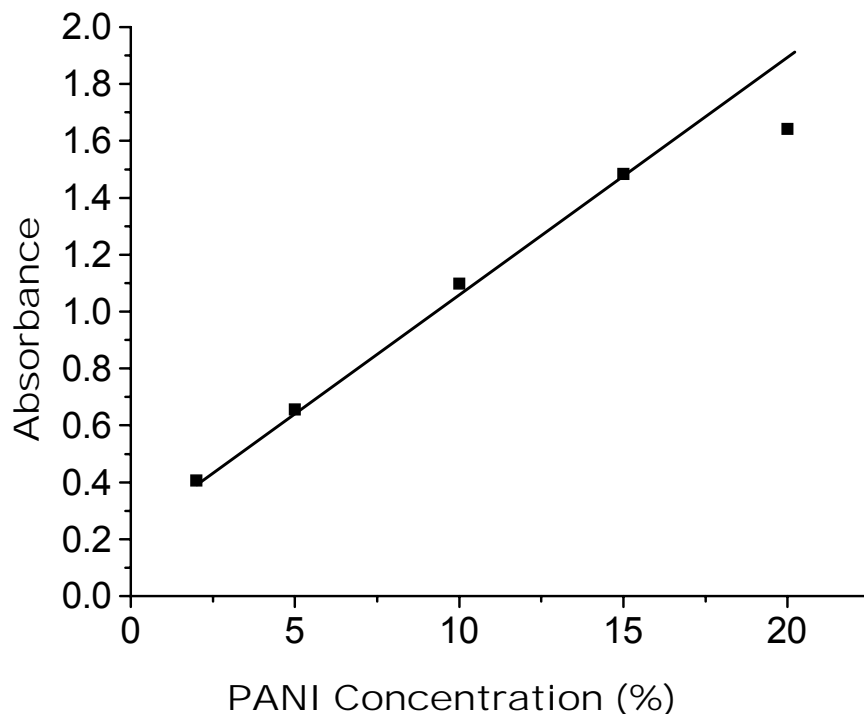


Figure 4.12: Optical absorbance (Optical Density) at 850 nm for DBSA-PANI blends with PVC with concentration of PANI showing Beer Lambert's Law.

It is interesting to note that here also the plot is linear upto PANI concentration of 15% above, from which there is deviation, observed in the graph. It appears that the Beer Lambert's law is followed in the present case of DBSA-PANI blends with PVC at least up to the concentration of 15% of PANI. The excellent agreement between the experimentally observed data in the present case with the above equation (4.1) suggests that there is good homogeneity of the blends and that the component polymers mix well with each other. The deviation from the linear graph at high concentrations of PANI above 15% can be due to phase segregation of the additional PANI. Thus it appears that the upper limit for the formation of homogeneous PANI-DBSA / PVC blend is 15% of PANI. It may be noted that the PANI-HCl gave particulate dispersions at all compositions in PVC and the OD was very high even at 10 % due to large

background scattering of the UV-Visible beam with very little changes with wavelength, i.e. no distinct spectra, noted from the sample.

The UV-Visible absorption spectra for PANI-DBSA / PC blends are shown in Figure 4.13. Curves correspond to increasing concentration of PANI-DBSA in PVC blend from 2% 5% and 10%. It is evident that the intensity of the broad absorption band corresponding to doped PANI bipolaronic state increases with increase of PANI content in the blend. The exact dependence of the absorption intensity with the concentration is shown in Figure 4.14.

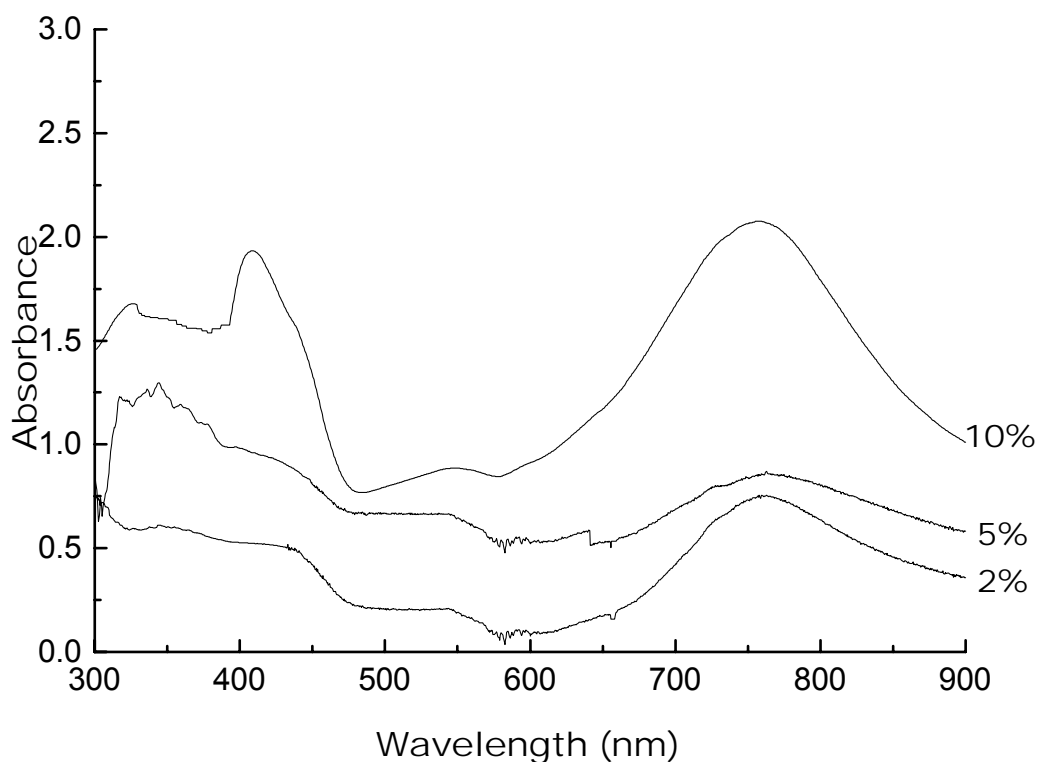


Figure 4.13: Optical absorption spectrum of PANI-DBSA blends with PC. Curves A to C correspond to increasing PANI concentration in the blend.

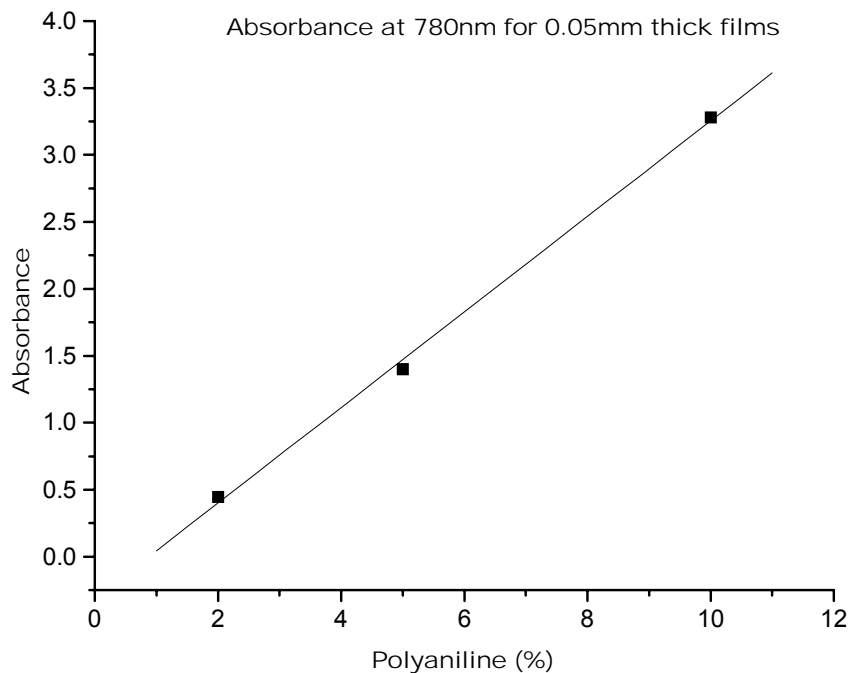


Figure 4.14: Optical absorbance (Optical Density) at 780 nm for DBSA-PANI blends with PC with concentration of PANI showing Beer Lambert's Law.

It is interesting to note that in this case also the plot is linear with PANI concentration. It appears that the Beer Lambert's law is followed in the present case of DBSA-PANI blends with PC also as in earlier cases. The excellent agreement between the experimentally observed data in the present case with the above equation (4.1) suggests that there is good homogeneity of the blends and that the component polymers mix well with each other.

b) Infra-Red Spectroscopy:

Infrared spectroscopy was used to characterize the polyaniline powders with different acids as dopants. The IR spectrum obtained is given in the Figure4.15. Infrared spectrum of these polyaniline powders was recorded from

400 cm^{-1} to 2000 cm^{-1} to analyze mainly the fingerprint region. The peaks at 1015 and 1045 cm^{-1} appearing only in the case of PSSA and DBSA doped PANI correspond to the aromatic rings present in the dopant acids. On the other hand the sharp peak around 540 cm^{-1} belonging to halogens appears for HCl doped PANI. Other peaks are common for all the cases suggesting that the quinoid to benzenoid ratio remains more or less same.

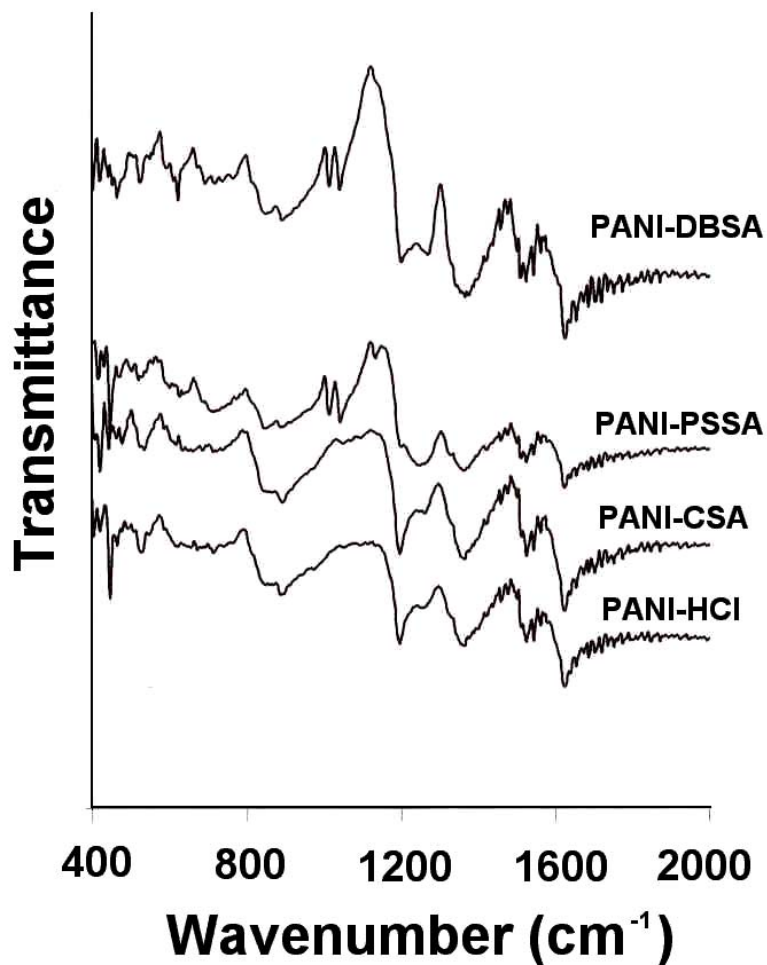


Figure 4.15: IR spectrum of polyaniline doped with different dopant ions

c) X-Ray Diffraction Analysis:

In order to confirm the formation of homogeneous blends, the samples were examined by x-ray diffraction (WAXD). XRD pattern of PANI-HCl as well as PANI-DBSA were given in Figure 4.16. PANI is known to be semi-crystalline as it exhibits sharp XRD peaks in the diffraction angle (2θ) region of 15 to 35 degrees¹³.

However, for PANI-DBSA blends with PMMA, the XRD scans contained mainly broad amorphous halos as indicated in the Figure 4.17. Curves A to D of this figure correspond to increasing concentration of PANI (5%, 10%, 15% and 20%). This clearly suggests that there are practically no discrete PANI domains / ordered crystallites present in these blends thus indicating thorough mixing of the component polymers in molecular level. The position of the broad amorphous band depends on the PANI concentration in the blend and these results are discussed below.

These various results obtained by different techniques suggest that there is good mixing / compatibility between DBSA-doped PANI and PMMA while very little miscibility is present for HCl-doped PANI and other polymer matrix. Thus, it appears that the dopant DBSA plays an important role in bringing about the miscibility of the two components. It is quite likely that the sulfonic acid group of DBSA while being close to PANI, the rest is miscible with the PMMA, which can lead to its action of compatibilizer. Some evidence for the penetration of these molecules in host matrix is seen from the XRD results. The average inter-chain distance can be estimated from the position of the broad peak seen in the above-mentioned figure by using the relation ¹⁴;

$$R = \{(5/8)\lambda / \sin\theta\}. \quad \dots\dots\dots (4.2)$$

Where, R is the average interchain separation, λ is the wavelength of the X-ray used and θ is the diffraction angle.

These values for different concentrations of PANI are shown in Table 4.6. It shows the increase in interchain distance with addition of PANI-DBSA. The calculated interchain distance is 6.88 \AA for pure PMMA, which increases with the addition of PANI-DBSA to reach the value of 7.68 \AA for 20% loading. The increase of the inter-chain distance is clearly associated with the penetration of the externally added molecules within the PMMA chains. It may be mentioned here that DBSA also acts as a plasticizer for PANI.

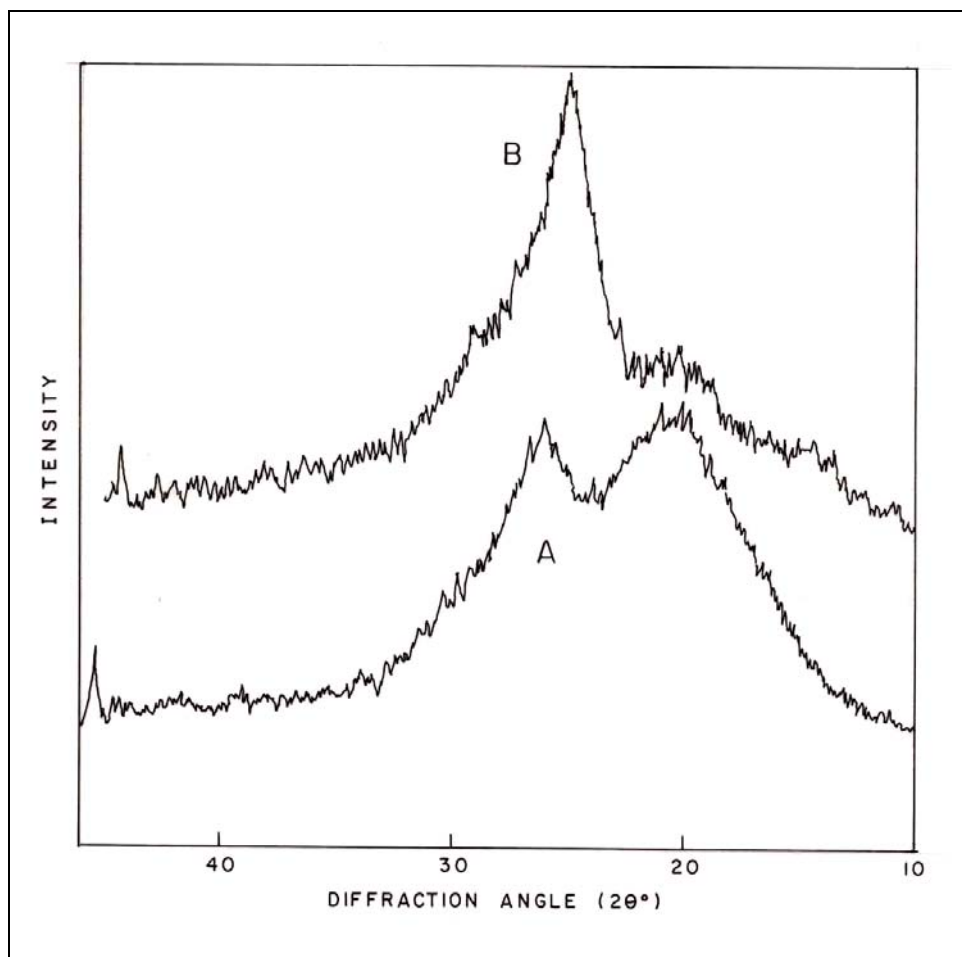


Figure 4.16: X-ray diffraction scans for PANI. (A)DBSA doped PANI and (B) HCl doped PANI.

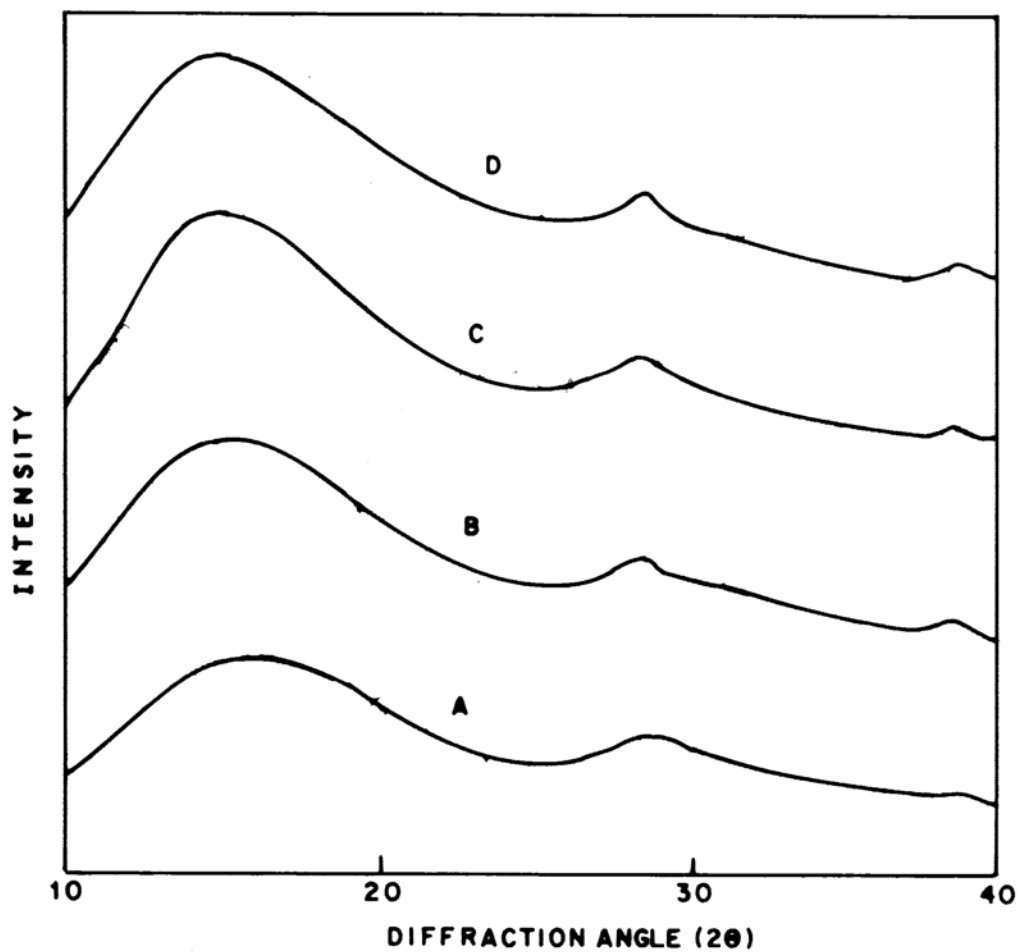


Figure 4.17: XRD scans for PANI-DBSA blends with PMMA having different concentrations of PANI-DBSA ; curves A to D correspond to PANI-DBSA concentration of 5,10,15 and 20% respectively

Table 4.6: Interchain separation in PMMA blend with different percentage of PANI-DBSA (directly doped):

Percentage Of PANI/DBSA	2θ For the first peak in the amorphous region	θ	λ [Å ⁰]	Inter-chain Separation, $R = (5/8)(\lambda/\sin\theta)$ [Å ⁰]
0 (PMMA)	16.2	8.1	1.54	6.831
5	15.6	7.80	1.54	7.093
10	15.3	7.65	1.54	7.231
15	14.9	7.45	1.54	7.421
20	14.4	7.2	1.54	7.682

Similarly X-Ray Diffraction (WAXD) were carried out for PANI-DBSA / PC blends also to confirm their homogeneity. As in the case of PANI-DBSA / PMMA blend, these blends of DBSA-PANI with PC also contained mainly broad amorphous halos in the XRD scans as indicated in the Figure 4.18. Curves A to D of this figure correspond to increasing concentration of PANI (0%, 2%, 5% and 10%). This clearly suggests that there are practically no discrete PANI domains / ordered crystallites present in these blends thus indicating thorough mixing of the component polymers in molecular level. The position of the broad amorphous band depends on the PANI concentration in the blend and these results are discussed below.

These various results obtained by different techniques suggest that there is good mixing / compatibility between DBSA-doped PANI polycarbonate also. Thus, it appears that the dopant DBSA plays an important role in bringing about the miscibility of the two components. It is quite likely that the sulfonic acid group of DBSA while being close to PANI, the rest is miscible with the PC, which can lead to its action of compatibilizer. Some evidence for the penetration of these molecules in host matrix is seen from the XRD results. The average inter-chain distance can be estimated from the position of the broad peak seen in the above-mentioned figure by using the relation (4.2).

These values for different concentrations of PANI are shown in Table 4.7. It shows the increase in interchain distance with addition of PANI-DBSA. The calculated interchain distance is 6.55 Å for pure PMMA, which increases with the addition of PANI-DBSA to reach the value of 7.13 Å for 10% loading. The increase of the inter-chain distance is clearly associated with the penetration of the externally added molecules within the PC chains.

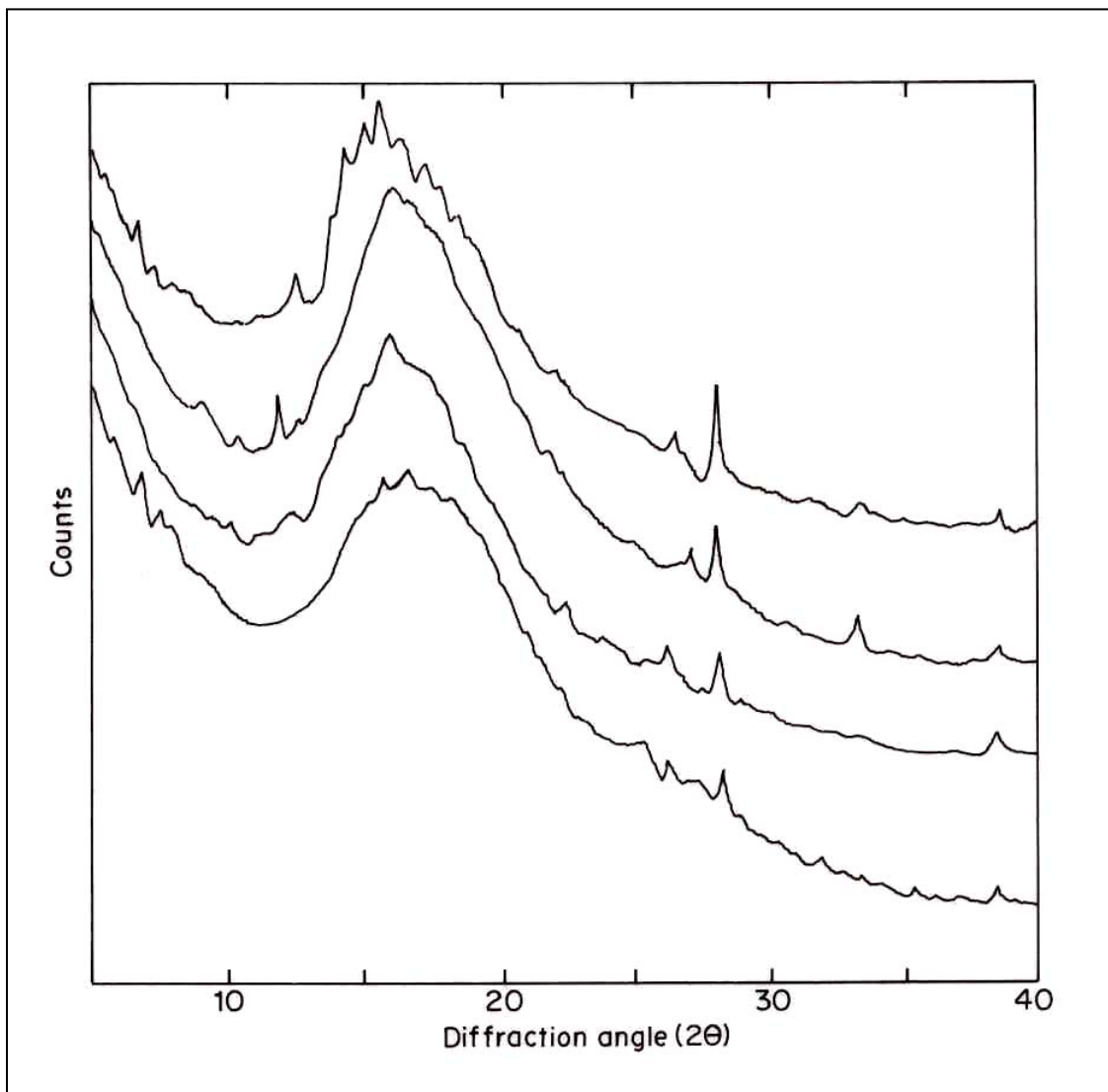


Figure 4.18: XRD scans for PANI-DBSA blends with PC having different Concentrations of PANI-DBSA; curves A to D correspond to PANI-DBSA concentration of 0, 2, 5 and 10% respectively.

Table 4.7: Interchain separation in PC blend with different percentage of PANI-DBSA (directly doped):

Percentage Of PANI/DBSA	2θ For the first peak in the amorphous region	θ	λ [Å ⁰]	Inter-chain Separation, $R = (5/8)(\lambda/\sin\theta)$ [Å ⁰]
0 (PC)	16.9	8.45	1.54	6.550
2	16.4	8.2	1.54	6.748
5	16.0	8.0	1.54	6.916
10	15.5	7.75	1.54	7.138

d) Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) can be used to understand the primary and secondary phase changes with temperature. In polymers the molecular orientation changes can be determined by DSC. These can be melting, crystallization, glass transition, etc. The homogeneity of a polymer blend can be characterized by the existence of single T_g , as it is a phenomenon where cooperative molecular motions are involved. The detailed discussion on this is already given in the Chapter 1.

The glass transition temperatures of PMMA with different DBSA contents were measured by DSC by sweeping the temperature range from 50°C to 250°C. Since the PMMA used is atactic one it won't give any melting point and also the shifts correspond to other changes like T_g will be very primitive. So the DSC curves were analyzed carefully to get the T_g of these PMMA samples. The T_g values obtained were given in the Table 4.8.

Table 4.8: The T_g values of PMMA / DBSA, with different DBSA contents.

DBSA Content (%)	T_g (°C) (DSC)
0	115.6
1	114.1
2	108.0
5	104.8

It is evident from these results that the DBSA can act like a plasticizer in PMMA matrix. So it can be understood from this that the DBSA present in the polyaniline can interact with PMMA when blended with it. This DBSA can thus act like a compatibilizer as well as plasticizer to the PMMA matrix. It justifies the observed flexibility of the PANI-DBSA / PMMA blends formed. This flexibility improvement with increased PANI-DBSA content also can be understood as the plasticizing effect of DBSA.

e) Dielectric Measurements:

This is the measurement that can be very well carried out in the insulating polymers, which have high electric resistance, low permittivity (dielectric constant), small dielectric loss, and resistance to high voltages. The dielectric constant (ϵ') is the ratio of the capacity of an electric capacitor filled with the substance to that of the same capacitor in vacuum, at a definite external field frequency. Dielectric loss is the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric.

A molecule possesses a constant dipole moment if the centers of gravity of its positive and negative charges are displaced relatively to each other. In an electric field the dipole molecules orient themselves predominantly in the direction of the field and the total electric moment of all the dipoles differs from zero, resulting in what is known as an orientation moment. The time needed for orientation depends on temperature, which determines the intensity of molecular moment. With increasing temperature the mobility of the molecule increases, and therefore orientation of the polar molecules in the direction of external electric field is faster. In a temperature frequency range there is a phase shift between the voltage applied at any given instant and the orientation moment, or more precisely the electric displacement vector, as the result of which the moment lags

somewhat behind the applied voltage. This phase shift is a result of dissipation of part of the energy as heat. It is customary to characterize phase shift by the angle δ . Since the energy dissipated per unit volume of dielectric as heat (dielectric loss) is proportional to the field frequency and to $\tan\delta$, the angle δ is usually called the loss angle. Besides $\tan\delta$, dielectric loss is characterized by the loss factor $\varepsilon'' = \varepsilon' \tan\delta$, where ε' is the permittivity of the material.

A characteristic feature of polymers is independent movement of chain sections consisting of a large number of monomer units. Besides this there may be smaller and more mobile kinetic units such as side chains or polar substituents. The relaxation time of the orientation moments of such groups is smaller than the relaxation time of main chain segment, and for this reason they can retain mobility at lower temperatures, where the segments of the main chain are practically immobile. Mainly two types of dielectric loss have been established for all polymers. The first type of dielectric loss, called dipole-segmental, is associated with orientation rotation of the polar units of the macromolecule under conditions where segmental moment is possible. The second type, called dipole-group, is due to orientation of the polar groups themselves. Losses of this kind may also occur below and above the T_g of the polymer.

The addition of plasticizers lowers all these dielectric characteristics. As a result of decrease in viscosity of the polymer when a plasticizer is added to it, its relaxation time decrease and, hence, the maximum of its dielectric loss angle shifts towards lower temperatures¹⁶. The absolute value of loss angle and permittivity depend on the polarity of the plasticizer.

Since the maximum of loss angle $\tan \delta_{MAX}$ occurs at glass transition temperature (T_g) of the polymer, its shift is equivalent to a depression in the T_g . Hence, the plasticizer efficiency can be assessed by the shift of $\tan \delta_{MAX}$: the

lower the temperature corresponding to $\tan \delta_{MAX}$, the more the efficient the plasticizer.

In PANI-DBSA blends with all the above-mentioned thermoplastics, were observed the increasing flexibility with increased PANI-DBSA content. It can be understood that there is a decrease in T_g of the blend formed. It can be due to the fact that the DBSA in polyaniline is also acting as plasticizer for the second polymer matrix blended with it. This is already given by the DSC analysis. It can be confirmed by dielectric measurements of polymers films of PMMA, PVC, etc., with different DBSA content.

Different PMMA films were casted with DBSA content varies from 1% to 10% to study the dielectric properties to analyze plasticizing effect. The dielectric relaxation in PMMA containing DBSA is given in the Figure 4.19. Both ϵ' and ϵ'' measured at 100 Hz are plotted against temperature to get the maximum relaxation corresponding to the T_g of the PMMA. The exact value of the T_g of PMMA with different DBSA content is given in the Table 4,9.

These studies carried out separately on dielectric properties on PMMA containing different amount of DBSA revealed shifts in the primary relaxation peak (α relaxation of PMMA) towards lower temperature, which is expected for any plasticizer in a polymer¹⁵. It may be mentioned here that the T_g values obtained here are different from those in DSC since the measurement conditions here are in high frequency mode. Nonetheless, there is shift towards lower temperature in presence of DBSA. This suggests that there is good miscibility of the DBSA with PMMA, and it acts as a plasticizer in the PMMA matrix. Thus the dopant ion in this case acts a compatibilizer for PANI – PMMA blends through mutual interaction and miscibility with individual components.

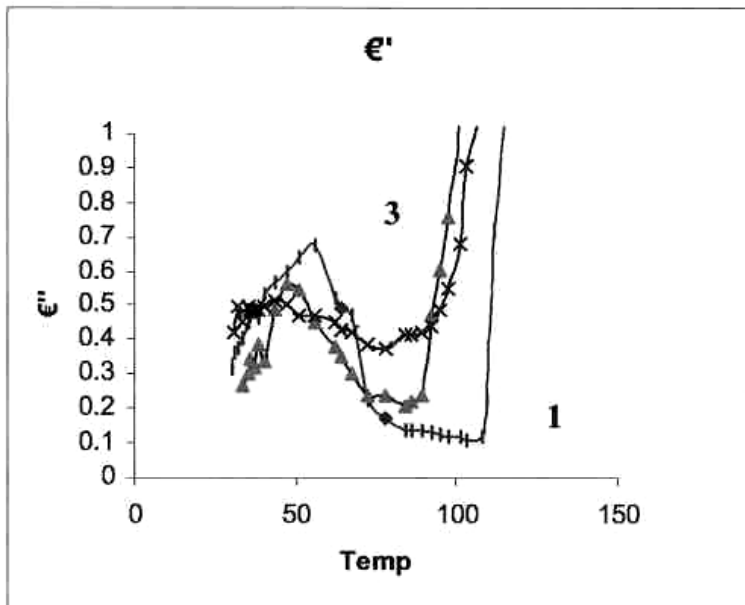
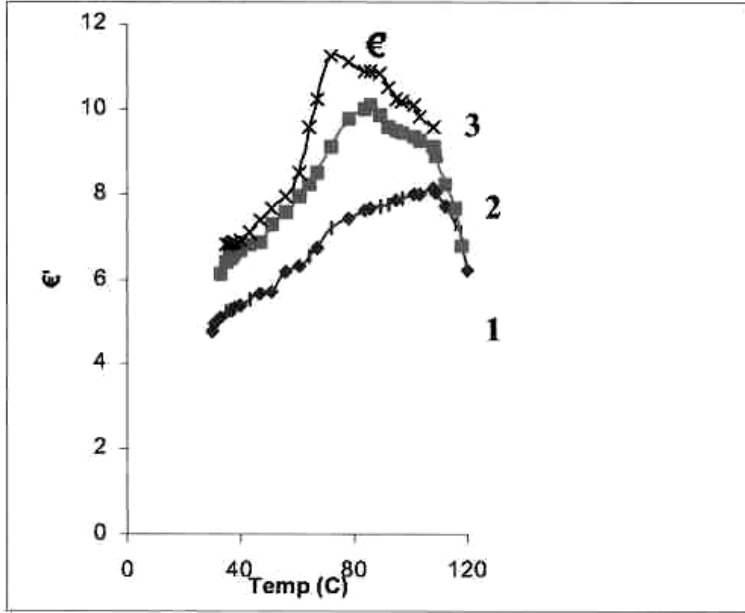


Figure 4.19: Dielectric relaxation in PMMA containing DBSA showing shift in T_g. Curves marked I, II and III correspond to DBSA concentration of 0, 2 and 5 % respectively.

Table 4.9: Effect of DBSA on T_g of PMMA determined from dielectric measurements.

Percentage of DBSA in PMMA matrix	T _g determined from dielectric transitions (K)
0	379
1	359
2	352
5	348

Similarly, the effect of DBSA in the PVC matrix also can be well studied by dielectric measurements. The dielectric relaxation in PMMA containing DBSA is given in the Figure 4.20. The ϵ' measured at 100 Hz are plotted against temperature to get the maximum relaxation corresponding to the T_g of the PMMA. The exact value of the T_g of PMMA with different DBSA content is given in the Table 4.10. These studies carried out separately on dielectric properties on PVC containing different amount of DBSA revealed shifts in the primary

relaxation peak (α relaxation of PVC) towards lower temperature, which is expected for any plasticizer in a polymer. This suggests that there is good miscibility of the DBSA with PVC, and act as a plasticizer in the PVC matrix. Thus the dopant ion in this case acts a compatibilizer for PANI-DBSA / PVC blends through mutual interaction and miscibility with individual components

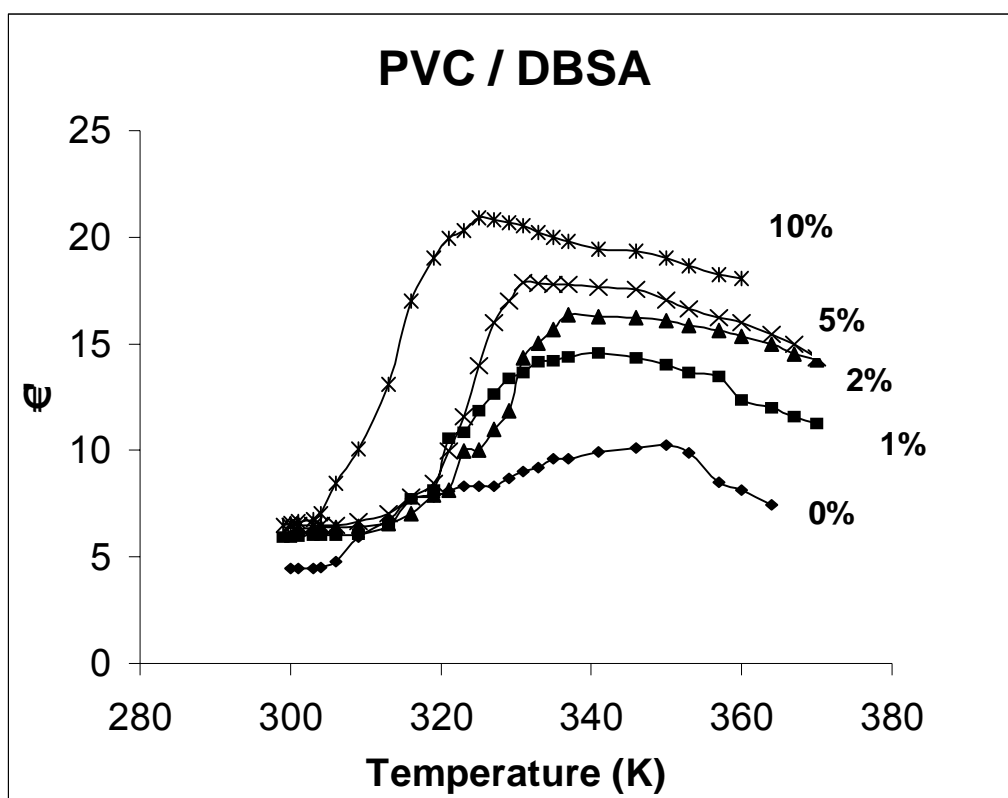


Figure 4.20: Dielectric relaxation in PVC containing DBSA showing shift in T_g. Curves marked I, II III and IV correspond to DBSA concentration of 0, 2, 5 and 10% respectively.

Table 4.10: Tg of PVC matrix with different DBSA content calculated from Dielectric loss measurement.

Percentage content of DBSA (%)	Tg calculated from Dielectric loss measurement (K)
0	350
1	341
2	337
5	331
10	325

4.4. CONCLUSIONS:

The solution processability of polyaniline has been studied by investigating its solubility in different solvents after incorporation of certain dopants, monitoring the viscosity, film formation and homogeneity of the blends. It has been observed that the solubility can be improved by the use of long chain organic acid (DBSA) as the dopant. Amongst the different doping agents studied, DBSA doped polyaniline showed very high solubility in common organic solvents like chloroform, tetrahydrofuran, dichloromethane, etc. The solubility followed the trend as PANI-DBSA > PANI-PSSA > PANI-CSA > PANI-HCl. This enables the easy processability of the PANI-DBSA in solution casting technique. To improve processability, the polyaniline can be blended with thermoplastics, which are also soluble in these solvents mentioned above. Hence, PANI-DBSA was easily blended with polymers like PMMA, PVC and PC by solution processing and casting technique using solvents like chloroform, THF and DCM respectively.

Processability of these blends was studied in terms of increase in viscosity of the blend solutions with polyaniline loading. It reveals the better processability and coatability for blends of PANI-DBSA than those with PANI-HCl or conventionally used carbon black composites. It was found that the behavior of these blends was fitting to the Mooney model and that of Quemada models when PANI-HCl and PANI-DBSA were used as conducting part respectively. It indicates the existence of better interactive phase morphology in the PANI-DBSA / PMMA blends.

The films of these blends thus formed showed a very good optical transparency, miscibility and flexibility. This flexibility was attributed to the

lowering of Tg of the blend. It was found that there is existence of single Tg for these blends indicating the higher molecular miscibility of these thermoplastics with DBSA doped polyaniline. This miscibility was seen till 15% of the polyaniline content in these blends. The homogeneous nature of these blends were characterized by the UV-Visible spectroscopy these the increase in intensity of the absorbed light by these blend films with polyaniline loadings were in accordance with the Beer – Lambert's law.

The plasticizing effects of the DBSA in PMMA and PVC matrices were characterized by the dielectric measurements where the peak corresponding to the relaxation at the glass transition was found to shift to the lower temperatures with the addition of DBSA. This effect was seen both in the PMMA and PVC matrices. XRD studies also reveal the plasticizing of DBSA in these matrices. It was seen here that the inter-chain separation of these thermoplastics were increased with polyaniline loading indicating the penetrating capacity of DBSA molecules into these polymer matrices. It can be understood here that the DBSA added as dopant in polyaniline gives additional functions of compatibilizer and plasticizer in these blends.

These polyaniline blends can be used for different applications such as antistatic coatings and the coatings for corrosion resistance. These blends also form films of excellent optical properties and, hence, can be made used in the optical applications such as conductive coatings on printed surfaces and display units. The electrical, optical and other properties of these films and coatings made from the above blends are described in Chapter 5 of this thesis.

4.5. REFERENCES:

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CHAPTER – 5

**PROPERTIES AND APPLICATIONS
OF MELT / SOLUTION PROCESSED BLENDS OF
DBSA DOPED POLYANILINE**

5.1. INTRODUCTION:

Amongst the large number of applications reported in literature for inherently conducting polymers, those which require melt and solution processability are antistatic coatings, transparent conducting coatings, EMI/RF shielding, ESD protection and electronic packaging. As mentioned in the earlier part of this thesis, the processability of polyaniline can be achieved by appropriate dopant incorporation, blending with low melting polymer and addition of processing aid such as PEO and PEG.

This chapter deals with the properties of the end products made from these blends and the possible applications of the blends of polyaniline prepared via melt blending as well as solution blending techniques. Hence, this chapter is further divided into two sections: (i) properties and applications of PANI-DBSA melt processed blends, and (ii) properties and applications of PANI-DBSA solution blends.

SECTION – 1:

5.2 PROPERTIES AND APPLICATIONS OF PANI MELT PROCESSED BLENDS.

This section deals with the properties and the possible applications of PANI-DBSA melt processed blends, which are prepared as discussed in chapter 3. Melt processing is the one, which can offer easy and direct implementation in many applications in industrial viewpoint. It is already proved in earlier chapters that the melt processability of the polyaniline can be improved by using long chain organic acids as dopants. It offers improved thermal stability of dopant ions as

well as improved melt processibility when blended with other polymers like polyethylene. In order to examine its real applicability in specific fields, the measurements of various properties of these blends are essential. The properties measured for these PANI / LDPE melt processed blends are conductivity at room temperature, conductivity variations with temperature, frequency dependent conductivity, EMI shielding measurements, mechanical properties, etc.

5.2.1. EXPERIMENTAL:

a) Conductivity Measurements:

Conductivity of the films or sheets of the blends were measured using KEITHELY electrometer. The details of the instrumental parts and the method were delineated in the experimental chapter (Chapter 2). Conductivities of all the PANI / LDPE blends were determined by measuring the resistance of about 0.2mm thick films of these blends. The thicknesses of these films were measured using a screw-gauge. Two probe resistance measurements were carried out by loading these films between the two electrodes of the cell. Resistance readings were noted from which the conductivity were calculated for each case. The cell has the provision for heating so as to sweep the temperature in a required range at a constant rate of heating. Conductivities of pure PANI / LDPE blends as well as these blends with processing aids were determined. Room temperature conductivities as well as the conductivity values at a range of temperatures from room temperature to 85°C were determined.

b) Electrical Impedance Properties:

Electrical properties under a.c. electrical fields for the conducting polymer blends and composites can give the response of these materials in the different

frequency ranges which is important for their applications in EMI shielding. These measurements were carried using the 'Solatron SI 1255 HF Frequency Response Analyzer' connected with a 'Solatron 1296 dielectric Interface'. Here Relative permittivity values of these PANI / LDPE blends with respect to frequency were recorded, from which conductivity of these materials with frequency can be calculated.

c) EMI Shielding Measurements:

Samples of PANI-DBSA / LDPE blend and those with PEO were moulded to get the sheets of 5 cm diameter and 1mm thickness for EMI shielding measurements. Here, the signal generator used was 'APLAB Frequency Generator Model: 2219-U and these signals were transmitted to the loop antenna placed in a metal box. Samples were placed on the sample holder, which was placed in between the loop antenna and a HP RF probe. These transmitted signals were then amplified using a wide band preamplifier. The amplified signals were then fed to a 'Hewlett Packard spectrum analyzer'. The spectrum analyzer gives the spectral distribution curve (SDC) depending upon the signals transmitted or shielded. The unshielded condition can be considered as reference. Then compared this with the curves obtained for various samples. These differences were analyzed to get the shielding effectiveness of the samples.

d) Mechanical Properties:

Mechanical Properties of these blends were carried out using an INSTRON Universal Testing Machine. These physical testing of PANI / LDPE blends were carried out with injection moulded test samples. The tensile tests

were done with dumbbell shaped samples and the flexural testing was done with rectangular shaped ones. The detailed measurements of these samples were given in the experimental chapter.

Tensile tests were done according to the standard ASTM D 638; keeping the grip distance of 55mm, gauge length 35mm and crosshead speed 50 mm/min.

. Flexural tests also were carried out as per the standard ASTM D 790 using the injection moulded rectangular samples having about 3mm thickness and 12mm width.

These testing were carried out for PANI-DBSA / LDPE blends both with and without processing aids. The results were compared with that observer for LDPE / carbon black composites and discussed in detail.

5.2.2. RESULTS AND DISCUSSION:

a) Conductivity Measurements:

The room temperature conductivities of these blends were determined and compared. The resistance of each blend films across its thickness was measured using electrometer. Knowing the exact thickness, the resistivity and, thus conductivity of these blends can be calculated. Since the path length of the current flow across the electrode through the medium is the thickness of the film and the area of cross section of the conducting medium is the area of electrodes, the conductivity can be calculated from the fundamental equation:

$$\rho = (R * A) / t \quad \text{-----} (5.1)$$

Where, ρ is the resistivity, R is the resistance measured, A is the area of the electrode used and t is the thickness of the sample. And,

$$\sigma = 1 / \rho \quad \text{-----}(5.2)$$

Where, σ is the conductivity of the material.

Typically, conductivity (σ) of the blend, which contains one conducting, as well as on insulating matrix is given by ¹

$$\sigma = A (\phi - \phi_c)^m \quad \text{-----}(5.3)$$

Where A is a constant, ϕ the concentration of PANI, ϕ_c the percolation threshold and m is the critical exponent. It should be noted that the above equation

assumes that the conducting phase is different and distinctly separate than the insulating matrix.

The conductivity stability with temperature is the major concern in the field of intrinsically conducting polymers. Hence, the effect of dopant ion on the thermal stability of polyaniline also has to be investigated to justify the selection of appropriate dopant ion. Pellets of each polyaniline samples with different dopant acids were heat treated at different temperatures for 20 minutes and the conductivities of each pellet after reaching back to room temperature were measured using electrometer. These values are given in the Table 5.1. The conductivity degradation of each polyaniline sample is illustrated in the Figure 5.1.

Table 5.1: The conductivity values of the various Polyaniline samples with different dopant ions after heat treatment at different temperatures.

Treatment Temp. (°C)	PANI-HCl	PANI-CSA	PANI-PSSA	PANI-DBSA
26	1.015×10^{-2}	3.561×10^{-3}	2.101×10^{-3}	2.46×10^{-1}
80	1.068×10^{-2}	4.413×10^{-3}	1.847×10^{-3}	1.23×10^{-1}
120	2.537×10^{-3}	4.143×10^{-4}	1.974×10^{-3}	4.1×10^{-2}
200	1.317×10^{-5}	6.722×10^{-6}	1.091×10^{-4}	6.15×10^{-3}
240	5.457×10^{-8}	2.519×10^{-8}	5.011×10^{-6}	3.905×10^{-4}
300	2.03×10^{-10}	2.08×10^{-10}	4.946×10^{-9}	1.75714×10^{-6}

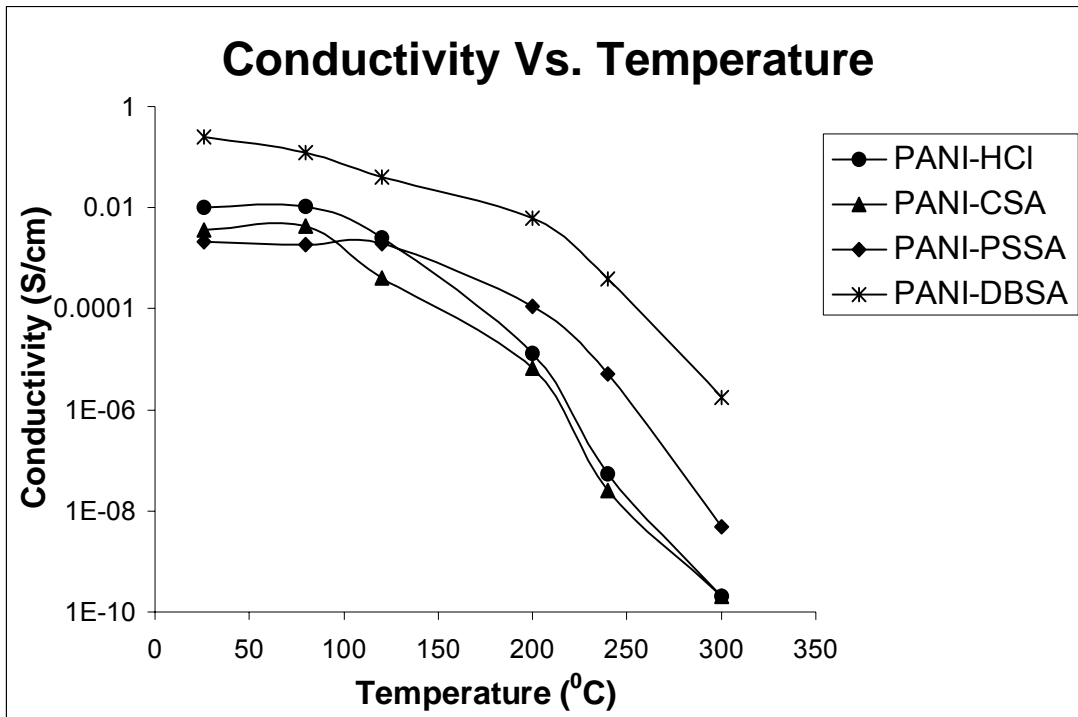


Figure 5.1: Comparison of variation in conductivity of Polyaniline with different dopant ions after heat treatment.

It has to be noted that the measurement shown above were isothermal process where the sample were kept at a definite temperature for 20 minutes and measured the conductivity after cooling to room temperature. Hence, it cannot be same as TGA where heat treatment is dynamic one with constant rate of heating. This measurement gives the idea of effect of different processing temperature where the samples will have some residence time at isothermal condition. Hence, it gives the idea about the properties of finished product after processing. It can be seen form the above figure that the thermal stability of conductivity in polyaniline is heavily dependent on the nature of acid dopant. It can be noted that the conductivity loss on HCl doped polyaniline starts even after 120°C where as the most stable DBSA doped PANI is showing the retention of useful conductivity even after the heat treatment at 240°C. This shows the feasibility of DBSA doped polyaniline to go through the processing temperatures during melt processing.

In the present investigation, the conductivities of PANI / LDPE blends were measured at the room temperature and plotted against the increasing polyaniline content. The room temperature conductivities of the PANI-DBSA / LDPE blends as well as those with different processing aids like PEG and PEO at 5phr levels are given in the Table 5.2 and the comparison is well illustrated in Figure 5.2.

Table 5.2: The conductivity values of the various PANI-DBSA / LDPE blends with different processing aids content in 5phr level.

Basic Composition of the Blend (% PANI)	Conductivity (S /cm)		
	Without Processing Aid	With 5phr PEG	With 5phr PEO
10%	1.71×10^{-15}	2.255×10^{-10}	2.20×10^{-7}
20%	1.17×10^{-5}	1.183×10^{-5}	6.77×10^{-5}
30%	2.08×10^{-5}	2.472×10^{-5}	8.33×10^{-5}
40%	5.13×10^{-5}	6.176×10^{-5}	1.10×10^{-4}
50%	8.70×10^{-5}	1.00×10^{-4}	1.16×10^{-4}

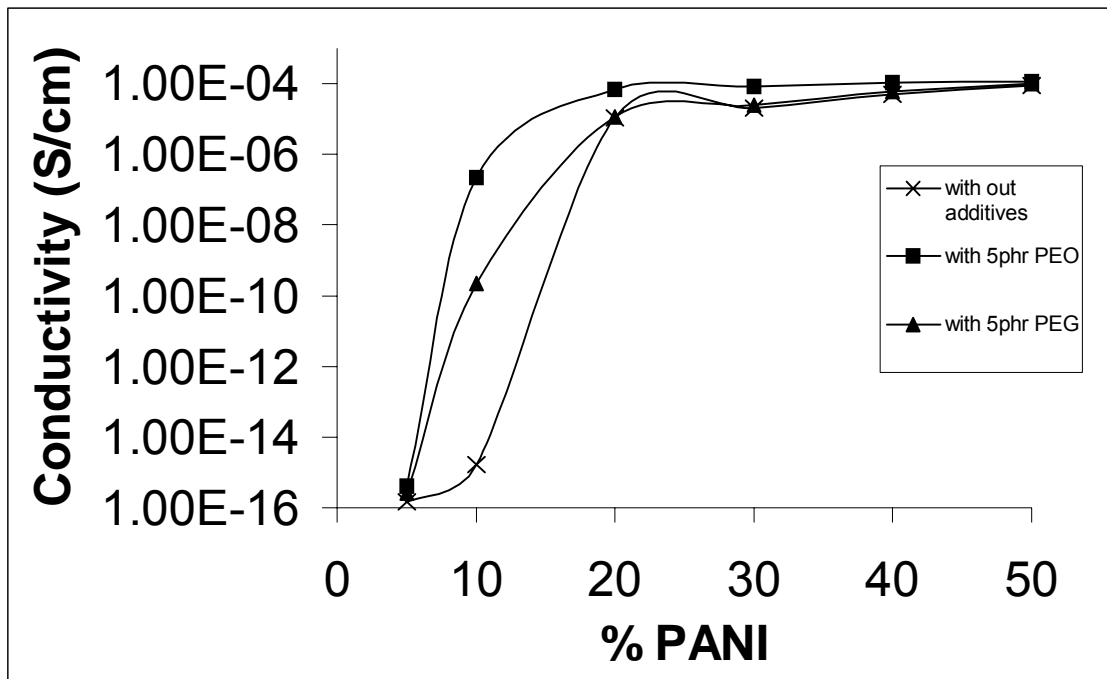


Figure 5.2: Comparison of variation in conductivity of PANI-DBSA / LDPE blends with different processing aids at 5phr level. (a) Without processing aids, (b) with 5phr PEO and (c) with 5phr PEG.

The above figure indicates the enhancement of conductivity of PANI-DBSA / LDPE blends with the addition of processing aids. It was also found that this enhancement in conductivity is more pronounced in presence of PEO. It can also be seen that the percolation threshold also shifts towards the lower loading level with the addition of processing aids. It can be due to the fact that the ionic additives like PEO and PEG that can bridge in between the conductive network of polyaniline to help to achieve the formation of effective network even in level loading level.

As the addition of PEO is giving pronounced conductivity improvement, the effect of amount of PEO on the conductivity also were studied. The

conductivity values of PANI-DBSA / LDPE blends with different amount of PEO as processing aid were determined and are given in the Table 5.3. The comparison of these values is illustrated in the Figure 5.3.

Table 5.3: The conductivity values of the various PANI-DBSA / LDPE blends with different levels of PEO content.

Basic Composition of the Blend (% PANI)	Conductivity (S /cm)		
	0phr PEO	With 3phr PEO	With 5phr PEO
5%	1.49×10^{-16}	1.50×10^{-16}	4.08×10^{-16}
10%	1.71×10^{-15}	2.50×10^{-11}	2.20×10^{-7}
20%	1.17×10^{-5}	1.10×10^{-6}	6.77×10^{-5}
30%	2.08×10^{-5}	9.80×10^{-6}	8.33×10^{-5}
40%	5.13×10^{-5}	5.53×10^{-5}	1.10×10^{-4}
50%	8.70×10^{-5}	1.11×10^{-4}	1.16×10^{-4}

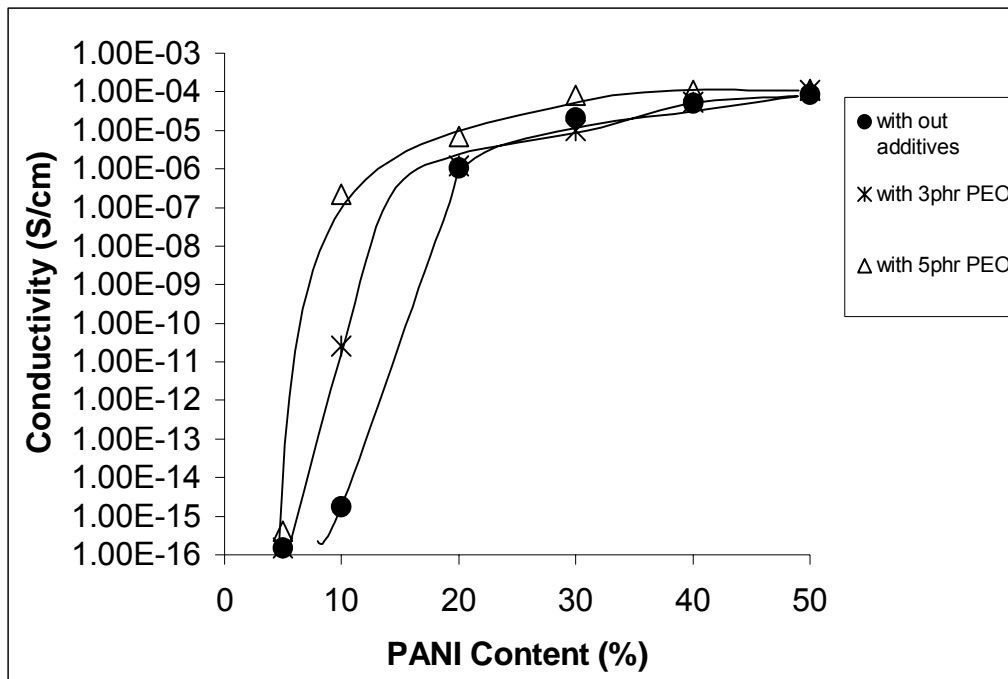


Figure 5.3: Comparison of variation in conductivity of PANI-DBSA / LDPE blends with different phr level of PEO contents. (a) Without PEO, (b) with 3phr PEO and (c) with 5phr PEO.

It can be seen from the above figure that the percolation threshold is shifting towards the lower polyaniline loading with the increase in PEO content. For the pure blend it was seen to be near to the 10%, which is shifting to around 5% in the case of blend with 5phr PEO. PEO is known to use as ionically conducting polymer electrolyte, which can have sufficient ionic mobility to conduct electricity²⁻⁵. Percolation threshold in a conducting blend or composite with a non-conducting medium can be considered as the minimum amount of conducting material required to form a three dimensional fine network so as to conduct easily. Hence, across this threshold there will be a sudden increase in the conductivity of the material, which shows a saturation effect after that, as shown in the above figure. In the case of blend with PEO as processing aid,

ionically conducting nature of the PEO can act as an efficient conductive bridge in between the immaturely formed polyaniline network even below the actual percolation threshold and bring it to the state of above percolation threshold. The efficiency of this ionic bridging increases with the amount of PEO added and, thereby, shifting the percolation threshold more and more towards the lower polyaniline loading level with the increase in the PEO level.

The conductivity of these blends with the change in temperature also was studied by measuring the resistance value as above with sweeping the temperature from room temperature to 85°C. The conductivity curve verses temperature for different blend composition is given in Figure 5.4.

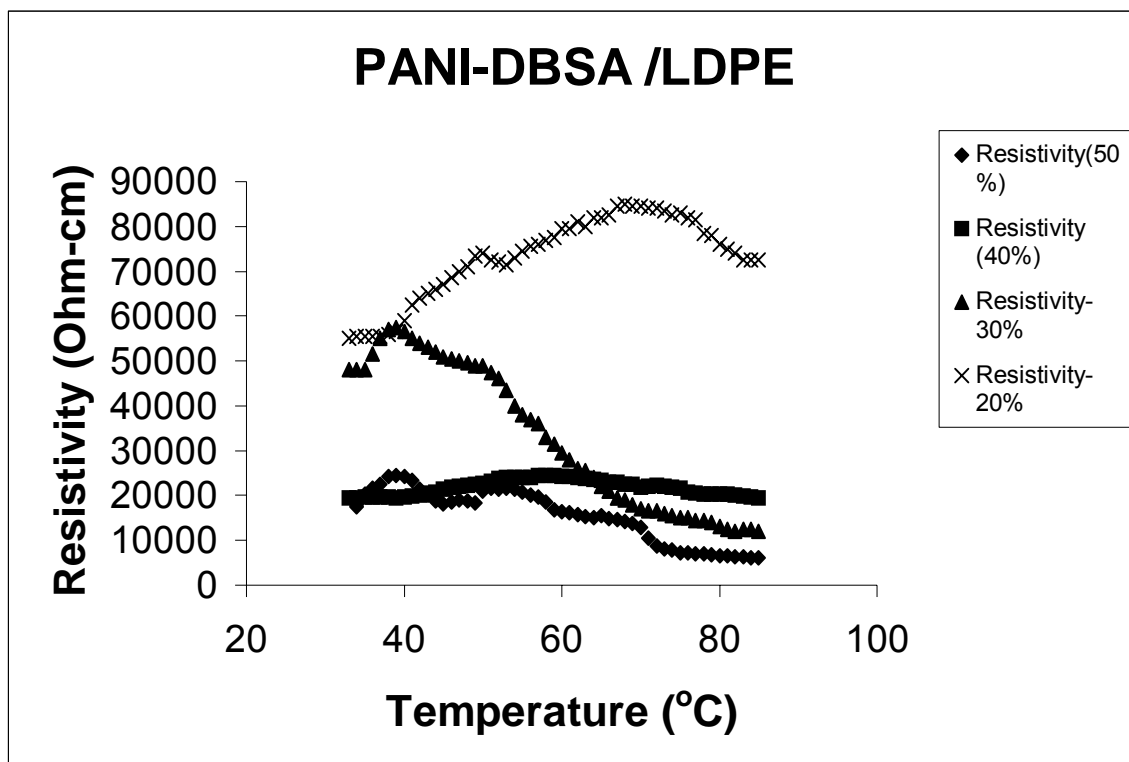


Figure 5.4: Conductivity of PANI-DBSA / LDPE measured in the temperature range of room temperature (28°C) to 85°C. The curves shown from top to bottom is 20%, 30%, 40% and 50% of PANI-DBSA loading respectively.

The above figure shows that there are no primary or secondary phase changes in this temperature range for these blends. For higher polyaniline loading, the conductivity is almost constant with temperature with very small activation energy. However, at lower polyaniline loading, it can be seen that there is large change in resistivity with temperature. In fact, at 20 and 30 % loading in these melt processed blends, the resistivity increases first and then decreases with increase of temperature. This can arise due to the predominant expansion of the major LDPE matrix, which causes the disturbance in the polyaniline domains, inter-domain distance and break of some contacts in the network. However, since this is reversible process, there was no permanent change or dopant degradation observed after thermal cycling in these experiments.

b) Electrical Impedance Properties:

The dielectric property measurement can be used as a tool to understand the charge transport mechanism in the conducting polymers and their blends. The measurements of dielectric properties with sweeping the frequency from 1 Hz to 10 MHz. Conductivity of a material depends on the temperature and the frequency. The details of the charge transfer in conducting polymer and their composites like tunneling and hopping mechanisms are discussed in the introduction Chapter 1. The frequency depended conductivity can be expressed as ⁶:

$$\sigma(\omega) = (\pi / 96) e^2 kT [N(E_F)]^2 r_0^5 \omega [\ln(1 / (\omega\tau_0))]^4 \text{ ----- (5.4)}$$

Here, the transport is assumed to take place by carriers with energy close to Fermi energy. Here r_0 is the localization radius of localized charge carrier.

The dielectric property measurements of the conducting polymers with sweep in frequency can give the frequency depended conductivity. It can be

measured from the imaginary part of the relative permittivity (ϵ'') of the material. It can be expressed as:

$$\epsilon'' \cdot \omega = 1.8 \cdot 10^{12} \cdot \sigma \quad \text{-----} \quad (5.5)$$

Where ϵ'' is the imaginary part of the relative permittivity, ω is the frequency and σ is the conductivity. From the above equation (5.5), the frequency dependent conductivity at each applied frequency can be calculated.

It can be seen that the conductivity change with the frequency is also dependent on a characteristic frequency exponent, n , given as:

$$\sigma(\omega) = \sigma_0 \omega^n \quad \text{-----} \quad (5.6)$$

Here, σ_0 is the frequency independent conductivity. Therefore, it can be expressed as:

$$\log(\sigma) = n \log(\omega) \quad \text{-----} \quad (5.7)$$

The above equation (5.7) is in the form of a straight line. Hence, $\log(\sigma)$ can be plotted against $\log(\omega)$, which will give a straight line with slope 'n'.

For metallic behaviour, the value of n will be zero and the unity value indicates the one dimensional charge transfer. The values of n less than one indicated the three-dimensional charge transfer through hopping, which will be complex phenomena.

It can also be seen that this exponent is also depend on the experimental temperature and can be expressed as:

$$n = (T_{ch} - T) / (T_{ch} + T) \text{ ----- (5.8)}$$

Where, T is the experiment temperature in Kelvin scale and T_{ch} is a characteristic temperature specific to the material depending on the nature and mobility of charge carriers. From the above equation the characteristic temperature for each compositions of blends can be calculated.

In present work, the melt processed blends of PANI / LDPE were analyzed for the frequency dependent conductivity behaviour. Various PANI-DBSA / LDPE blends of different polyaniline loadings were analyzed using the films of each blend. The conductivity values at each frequency readings were calculated using the equation 5.5 and log (σ) values were plotted against log (ω). The plots for PANI-DBSA / LDPE blends were shown in the Figure 5.5.

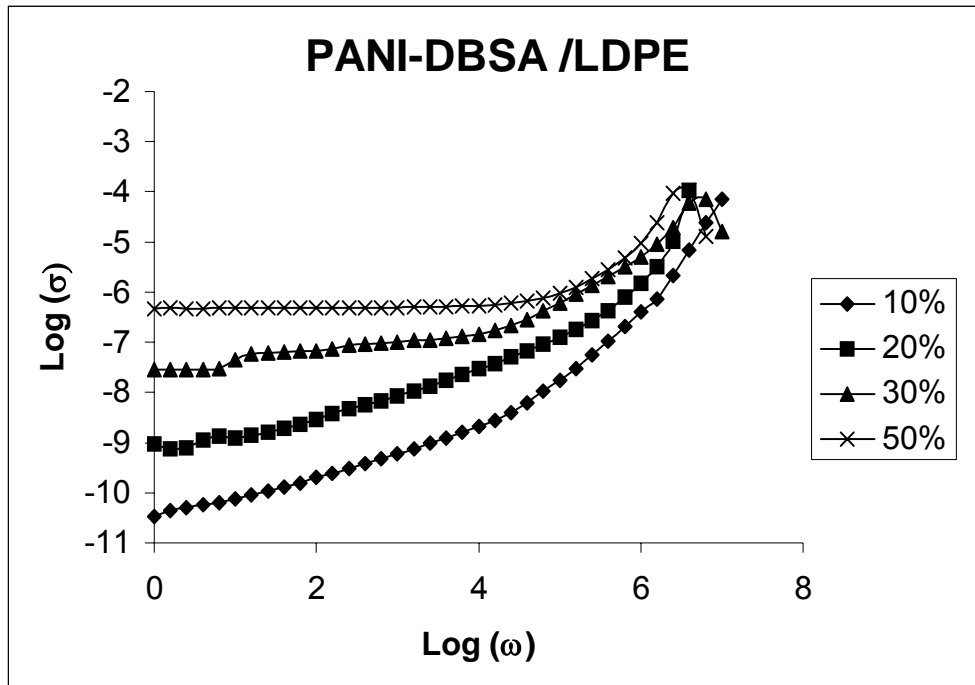


Figure 5.5: log (σ) Vs. log (ω) plots for PANI-DBSA / LDPE blends

Here the slope of each curve was calculated in the lower frequency region (i.e.; from 1 Hz to 1MHz). The slope gives the values of corresponding exponent, 'n'. From this the characteristic temperature (Tch) of each blends were calculated using the equation 5.8. The values of 'n' and 'Tch' for each blend are given in the Table 5.3.

Table 5.3: The values of 'n' and 'Tch' for PANI-DBSA / LDPE blends.

Blend Composition (% PANI-DBSA)	n	Tch (K)
10	0.597	1189.5
20	0.455	801.3
30	0.313	573.4
50	0.109	373.5

It can be noticed here that the conductivity increased with polyaniline loading, but the exponential factor, n, is getting decreased with the polyaniline loading. This is because of the fact that, at higher loading the network formation of the conducting sites are more efficient in conduction by hopping even at low frequency, and, hence the exponent factor becoming lower and lower with loading. Hence, the corresponding values of Tch also are seen to decrease for 1189K for 10% to 373K for 50% of polyaniline loading. It may be mentioned here that the characteristics temperature is inversely related to the localization distance, i.e., lower the Tch value more is the delocalization of charge carrier. Thus, at higher PANI concentrations the charge carriers can move longer distances easily. It will be interesting to note that the conductivity of all compositions is merging at very high frequency level. It is because of the fact that the composite matrix acts as efficient combinations of parallel capacitors and resistances and release assist to get high charge mobility even at low polyaniline loading. It shows the efficiency of low polyaniline concentrated blends to act as a

good EMI shielding material at very high frequencies. However, the blends with higher polyaniline loading are very efficient in all ranges of frequency, even at very low frequency.

These values were also compared with that containing HCl doped polyaniline and that of PSSA doped polyaniline. As observed in dc conductivity the PANI-DBSA doped polyaniline gave better conductivity than others. The conductivity values for the 40% blends of each case were compared and are shown in the Figure 5.6.

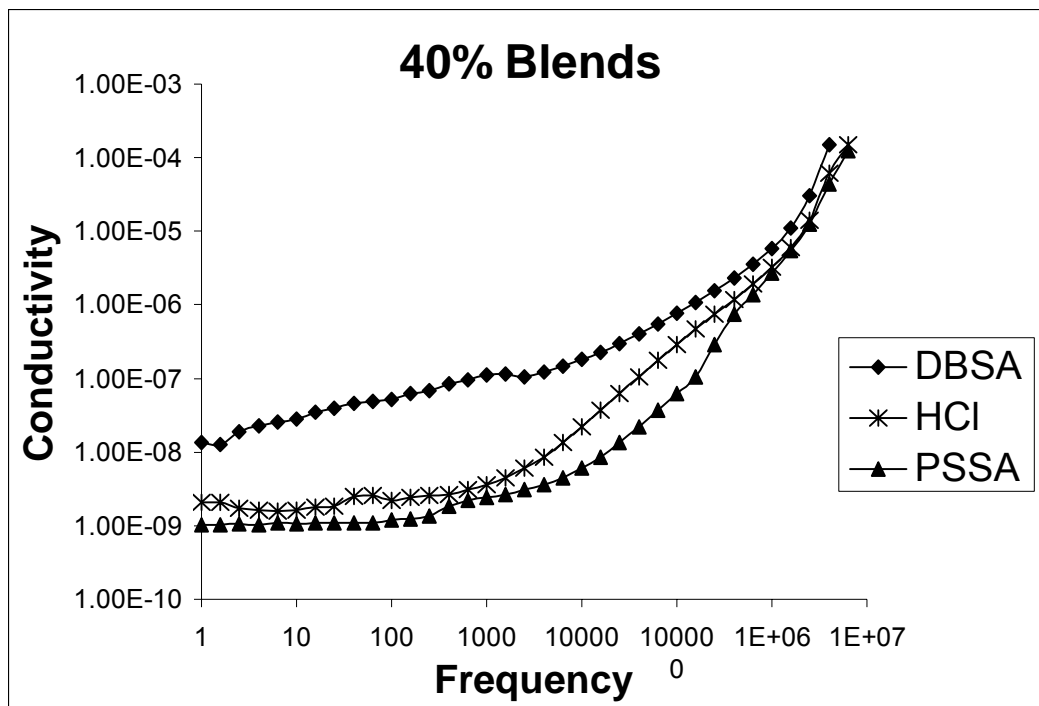


Figure 5.6: Comparison of frequency dependent conductivity values for the 40% PANI /LDPE blends with different dopant ions.

As in the case of PANI-DBSA blends, different loading level for PANI-HCl / PANI blends also were analyzed. The Figure 5.7 shows the frequency dependent conductivity of these blends with different polyaniline loading level. Here also it

can be seen that the exponent factor is slightly decreasing with polyaniline loading as in earlier case. The values of 'n' and 'Tch' are given in the Table 5.4. Also the conductivity values are merging together at very high frequency level. As explained in earlier case it is also due to the efficient parallel combination of capacitor and resistance arrangement at very high frequencies and gives better conductivity at higher frequency even at lower polyaniline loading.

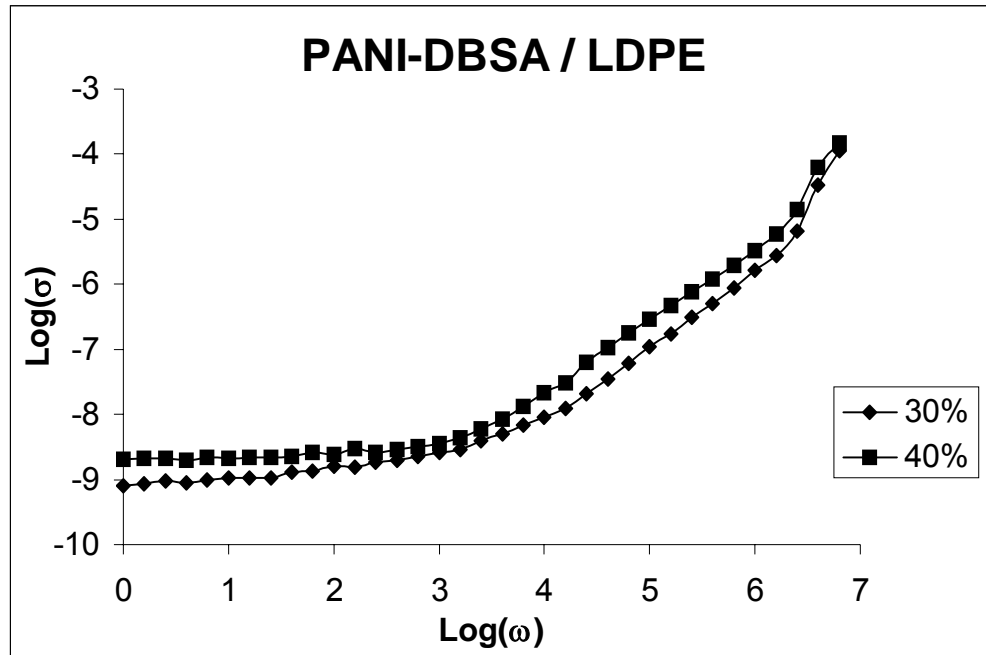


Figure 5.7: log (σ) Vs. log (ω) plots for PANI-HCl / LDPE blends

Table 5.4: The values of 'n' and 'Tch' for PANI-HCl / LDPE blends.

Blend Composition (% PANI-HCl)	n	Tch (K)
30	0.265	516.3
40	0.256	506.7

The frequency dependent conductivity of PANI-DBSA / LDPE blends with 5phr PEO also was measured and compared. These blends are more conducting than those without PEO. The pots of $\log(\sigma)$ vs. $\log(\omega)$ are shown in the Figure 5.8, from which the exponent factor, n , was calculated. The values of 'n' and 'Tch' are given in the Table 5.5.

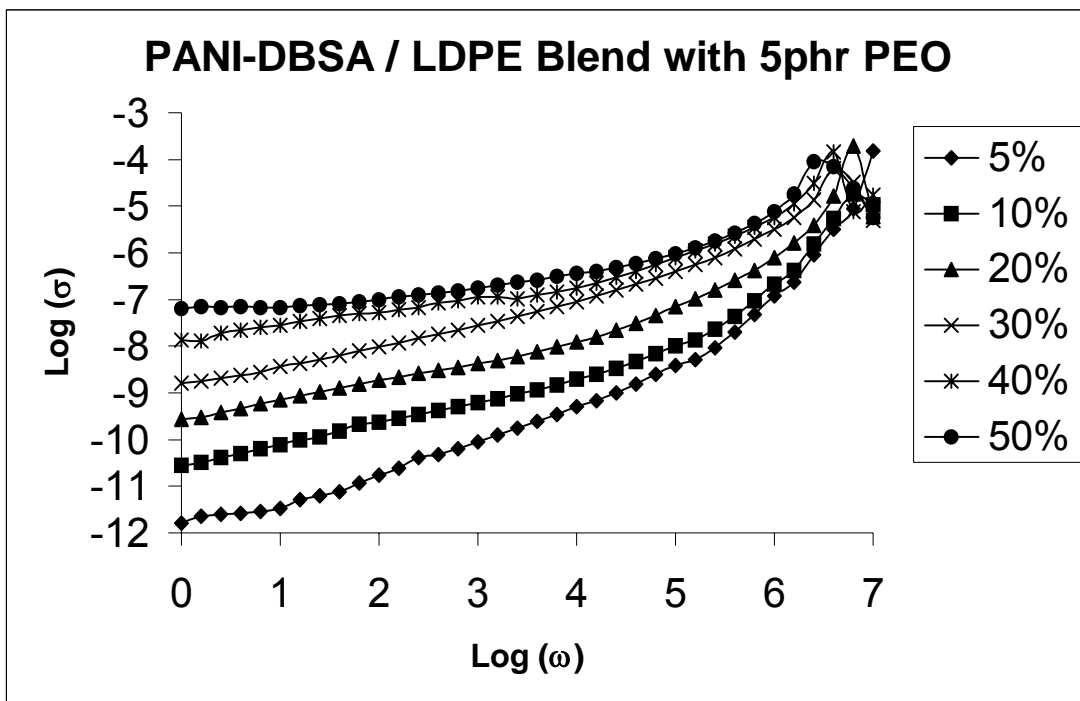


Figure 5.8: $\log(\sigma)$ Vs. $\log(\omega)$ plots for PANI-DBSA / LDPE blends

Table 5.5: The values of 'n' for PANI-DBSA / LDPE blends with 5phr PEO.

Blend Composition (% PANI-DBSA)	n	Tch (K)
5	0.697	1682.0
10	0.539	1003.8
20	0.514	936.0
30	0.498	844.7
40	0.383	671.9
50	0.267	518.6

Here also, the exponential factor, n , is getting decreased with the polyaniline loading. As explained earlier, this is because of the fact that, at higher loading the network formation of the conducting sites are more efficient in conduction by hopping mechanism even at low frequency, and, hence the exponent factor becoming lower and lower with loading. Hence, corresponding value of Tch is decreasing with polyaniline loading. It will be interesting to note that here also the conductivity of all compositions is merging at very high frequency level. It is because of the fact that the composite matrix acts as efficient combinations of parallel capacitors and resistances and release assist to get high charge mobility even at low polyaniline loading. It shows the efficiency of low polyaniline concentrated blends to act as a good EMI shielding material at very high frequencies. However, the blends with higher polyaniline loading are very efficient in all ranges of frequency, even at very low frequency.

c) EMI Shielding Measurements:

Electromagnetic interference is the unwanted electrical and magnetic energy that causes disturbances in the receiving device. Such interferences have been considered as a form of pollution, which we can't see, touch, hear, smell or taste. This interference, which comes from one electronic unit, can effect severely the functioning of the other devices. For practical purposes, the majority of EMI problems are limited to a part of spectrum known as radio frequency band, which covers the radio and audio frequencies ⁷. Hence, the processible conducting polymers play an important role in the construction of EMI shielding layers and coatings of electronic device housings.

Various melt-processed blends of PANI with LDPE can be used as the EMI shielding components. The shielding effectiveness (SE) of these blends were investigated between 1MHz to 50 MHz using HP frequency analyzer as discussed in the experimental part. The reference level was taken as -40 dB. The Figure 5.9 shows the reference level, which was recorded with out any shielding. The various EMI shielding effectiveness of the PANI-DBSA / LDPE blends are given in the Table 5.6. The corresponding output signal are shown in the Figure 5.10

Table 5.6: EMI shielding effectiveness (SE) of various PANI-DBSA / LDPE blends:

Blend Composition (% PANI-DBSA)	Shielding Effectiveness (SE) dB
10	14
20	20
30	22
40	28
50	30

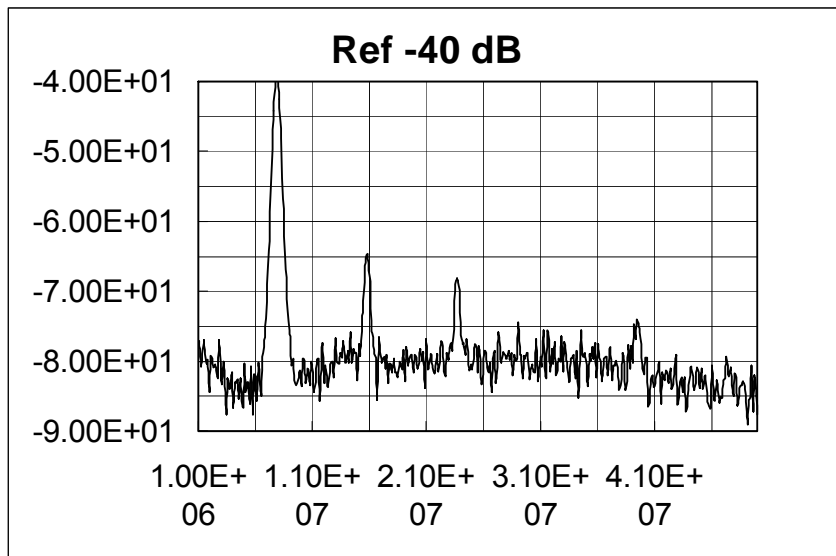


Figure 5.9: Reference scan with out shielding material.

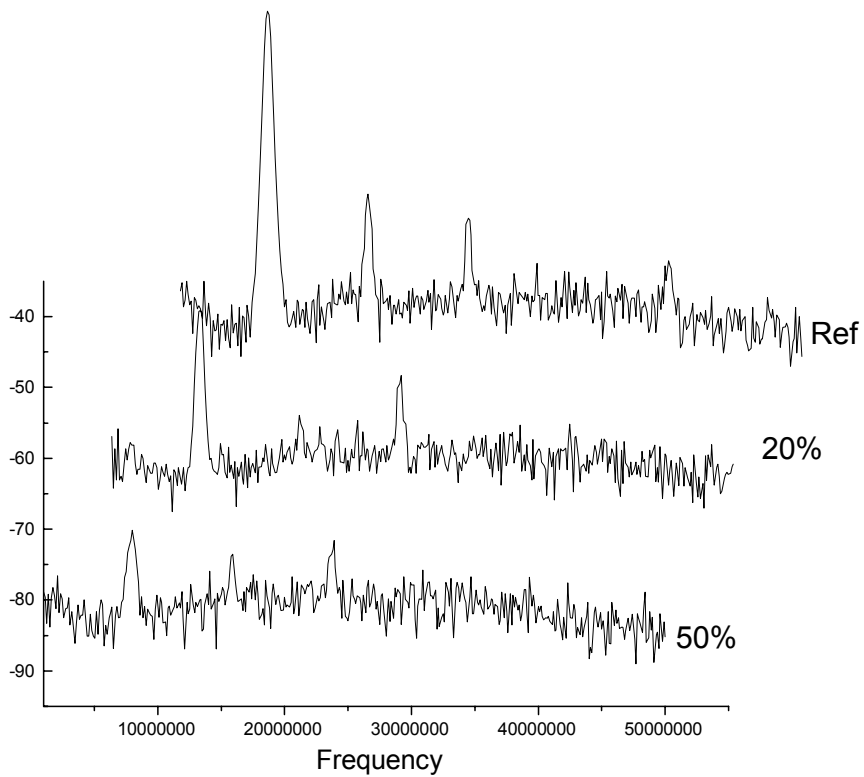


Figure 5.10: Out put signal given after sheets of different PANI-DBSA / LDPE blend used as shielding materials. This represents the out put signal with out

shielding (reference), with 10% PANI-DBSA/ LDPE and that of 50% PANI-DBSA / LDPE.

The above result shows that the PANI-DBSA / LDPE blend can be used as an EMI shielding material. The 50% blend shows the SE of 30 dB.

The PANI-DBSA / LDPE blend with 5phr PEO were also analyzed for their shielding effectiveness (SE). The various EMI shielding effectiveness of these blends are given in the Table 5.7. The corresponding output signals are shown in the Figure 5.11.

Table 5.7: EMI shielding effectiveness (SE) of various PANI-DBSA / LDPE blends with 5phr PEO:

Blend Composition (% PANI-DBSA)	Shielding Effectiveness (SE) dB
10	19
20	22
30	25
40	30
50	40

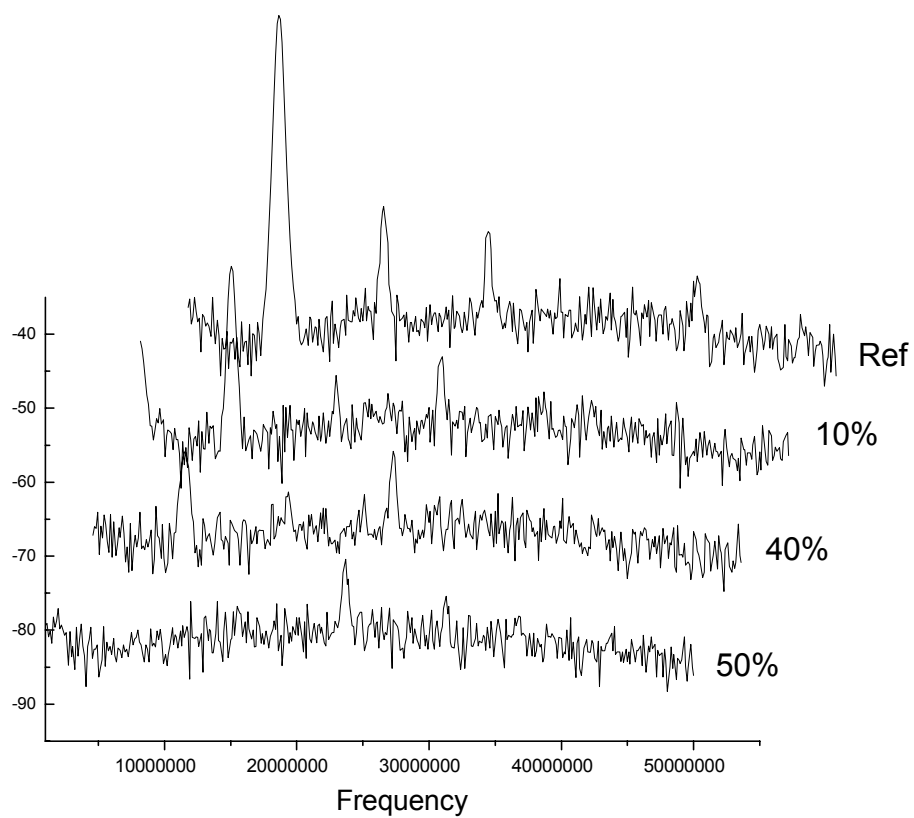


Figure 5.11: Out put signal given after sheets of different PANI-DBSA / LDPE blend with 5phr PEO, used as shielding materials. This represents the out put signal with out shielding (reference), with 10%, 40% and that of 50% PANI-DBSA / LDPE.

It can be noticed from above table that the blend with PEO are more efficient in shielding than that of without any additives. It shows better SE at all blend compositions. It gives a very useful shielding efficiency of 40 dB at 50% of polyaniline loading.

It is important to investigate the importance of DBSA doped PANI over that of conventional HCl doped one. The SE of PANI-HCl / LDPE were also measured at the same frequency level. These values are given in the Table 5.8. The comparison of the SE of these blends of PANI-HCl with that containing PANI-DBSA are shown in Figure 5.12.

Table 5.8: EMI shielding effectiveness (SE) of various PANI-HCl / LDPE blends:

Blend Composition (% PANI-HCl)	Shielding Effectiveness (SE) dB
30	19
40	22
50	25

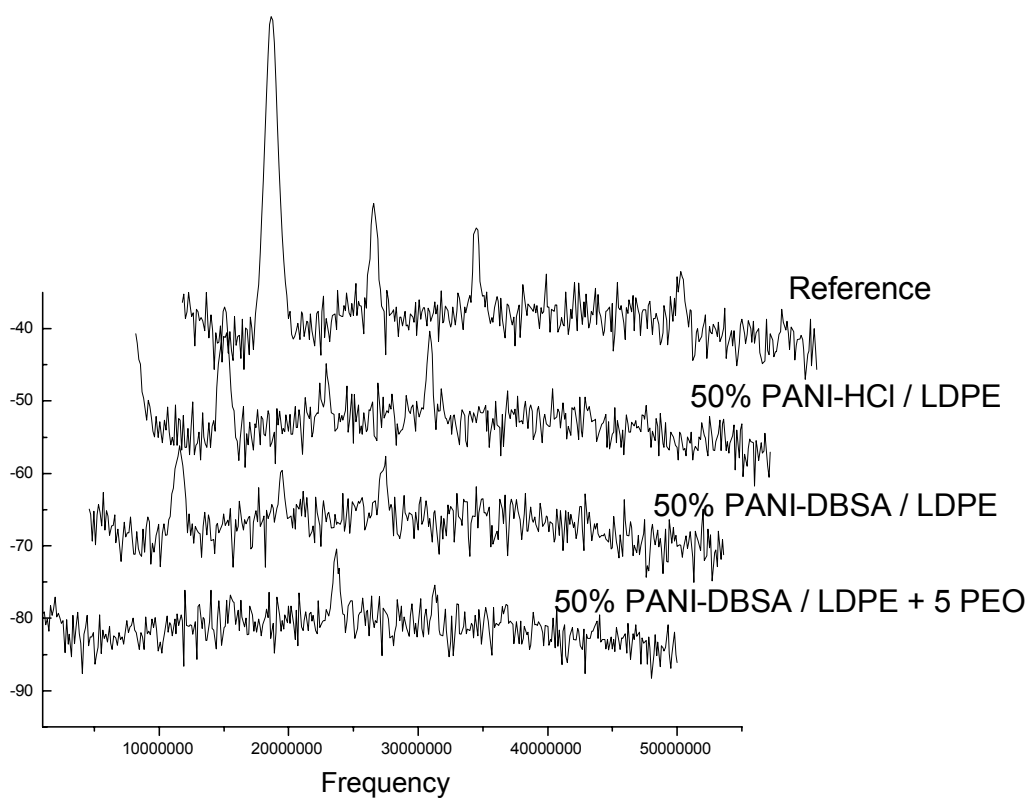


Figure 5.12: Comparison of shielding effectiveness of various 50% PANI / LDPE blends with different dopant ions and additives.

It is now clear from the above result that the blends with DBSA doped polyaniline are more efficient in EMI shielding over HCl doped polyaniline. It is also interesting to note that this efficiency is further improved by the addition of PEO as processing aid.

d) Mechanical Properties:

Mechanical properties of the polymer blends play an important role in their application in different products. The properties like flexibility, elongation, flexural modulus, tensile strength and tensile modulus are the most important physical properties to be known before assigning the applicability of these blends. Measurements of these properties of the PANI-DBSA / LDPE melt compounded blends as well as those with 5phr PEO were measured using an INSTRON Universal Testing Machine. The samples used were the dumbbell shaped as well as rectangular injection moulded samples for tensile test and flexural test respectively, as mentioned in the Chapter II of this thesis.

The tensile test of the LDPE as well as PANI-DBSA / LDPE blends with increasing polyaniline contents from 10% to 40% were done according to ASTM D – 638, keeping the grip distance of 55mm, gauge length 35mm and crosshead speed 50 mm/min. Different properties given by the tensile tests for PANI-DBSA / LDPE blends are given in the Table 5.9. Figure 13 (a to e) represents the stress – strain behaviour obtained for various blend compositions during tensile test.

Table 5.9: Physical properties of PANI-DBSA / LDPE blends given by tensile test:

Composition of Blend (% PANI-DBSA)	Tensile Modulus (MPa)	Stress at max load (MPa)	Strain at max load (%)	Stress at auto break (MPa)	Strain at auto break (%)	Toughness (MPa)
0	180.0	12.04	73.31	12.02	71.65	5.561
10	208.6	9.95	30.57	9.32	29.41	1.881
20	225.7	10.11	18.89	10.09	18.67	1.124
30	281.0	9.52	13.10	9.45	12.65	0.679
40	325.1	12.29	12.54	12.26	12.29	0.825

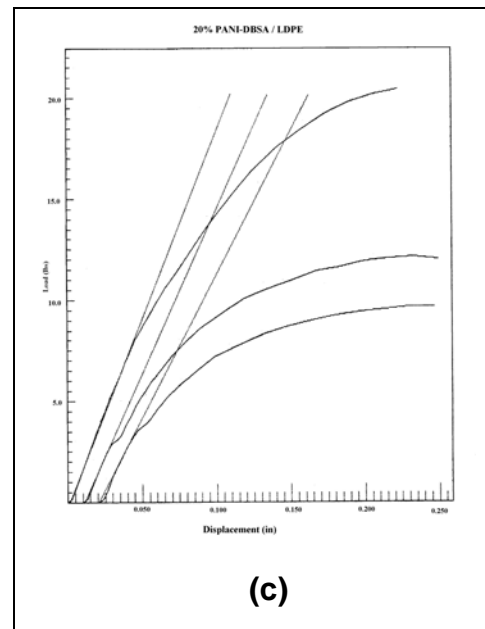
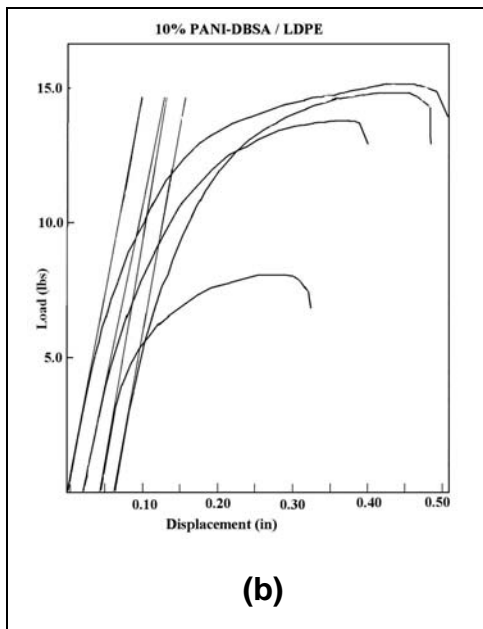
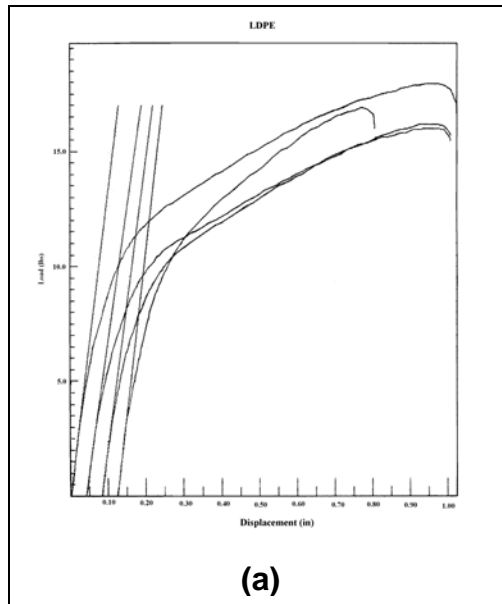


Figure 5.13: Stress – Strain curves obtained in the tensile test for PANI-DBSA / LDPE blends, (a) LDPE, (b) 10% PANI-DBSA / LDPE, and (c) 20% PANI-DBSA / LDPE

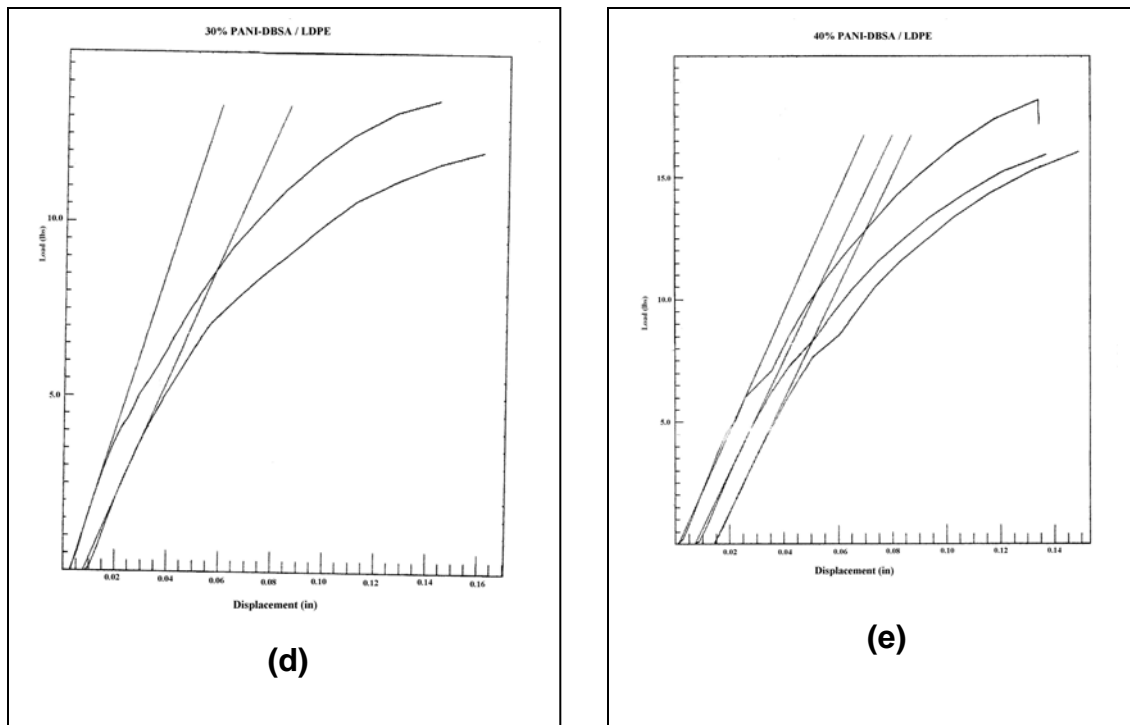


Figure 5.13: Stress – Strain curves obtained in the tensile test for PANI-DBSA / LDPE blends, (d) 30% PANI-DBSA / LDPE, and (e) 40% PANI-DBSA / LDPE

Above-mentioned table explains the changes in mechanical properties of LDPE with the PANI-DBSA loading. It can be noticed that the elongation at break remains at 12.3% even at the 40% loading. It can be seen that this reduces from 72% for pure LDPE, 29.4% for 10% loading, 18.7% for 20% loading, 12.7% for 30% loading and reaches to 12.3% for 40% loading. It indicates the retaining of the sufficient flexibility and elongation of the melt compound even at higher loading.

Another important mechanical property to be considered for any polymeric material or their blend is the tensile modulus (Young's modulus). It can be

noticed for the above table that tensile modulus is increasing with polyaniline loading. It is shown in the Figure 5.14. It can be due to the fact the PANI-DBSA is acting as highly interactive filler in the LDPE matrix as discussed in Chapter 3. It can also be attributed to the higher rigidity of polyaniline than LDPE matrix. The pure PANI has modulus of 2000 MPa as reported elsewhere ⁸. LDPE used here has tensile modulus of 180.4 MPa. From these values, one can estimate the tensile modulus of LDPE / PANI blends of different compositions using the simple rule of mixtures as given by Thakayanagi ⁹. Given two materials of elastic moduli E_1 and E_2 , which may be arranged in parallel, or in series combinations separately, the modulus of the blend can be given as:

$$E_c = \varphi_1 E_1 + \varphi_2 E_2 \quad \text{----for series} \quad \text{----- (5.9)}$$

$$1 / E_c = \varphi_1 / E_1 + \varphi_2 / E_2 \quad \text{----for series} \quad \text{----- (5.10)}$$

Where φ_1 and φ_2 are the volume fraction of the two materials.

The relation given by Davies ¹⁰ assuming the blend is macroscopically homogeneous and isotropic is given by:

$$E^{1/5} = E_1^{1/5} \varphi_1 + E_2^{1/5} \varphi_2 \quad \text{-----}(5.11)$$

The tensile modulus calculated from equations 5.9, 5.10 and 5.11 and those actually observed are given in the Figures 5.15 for varying polyaniline loading in LDPE matrix. It can be seen from these figures that the increase in modulus with polyaniline loading is more fitting to the parallel model. The comparison of the values with parallel model is separately shown in the Figure 5.16. It can be seen that the modulus obtained is slightly higher than the

expected value especially at higher loading levels. It means that the polyaniline is getting oriented in the direction parallel to the test samples, which is the melt flow direction during the injection moulding process.

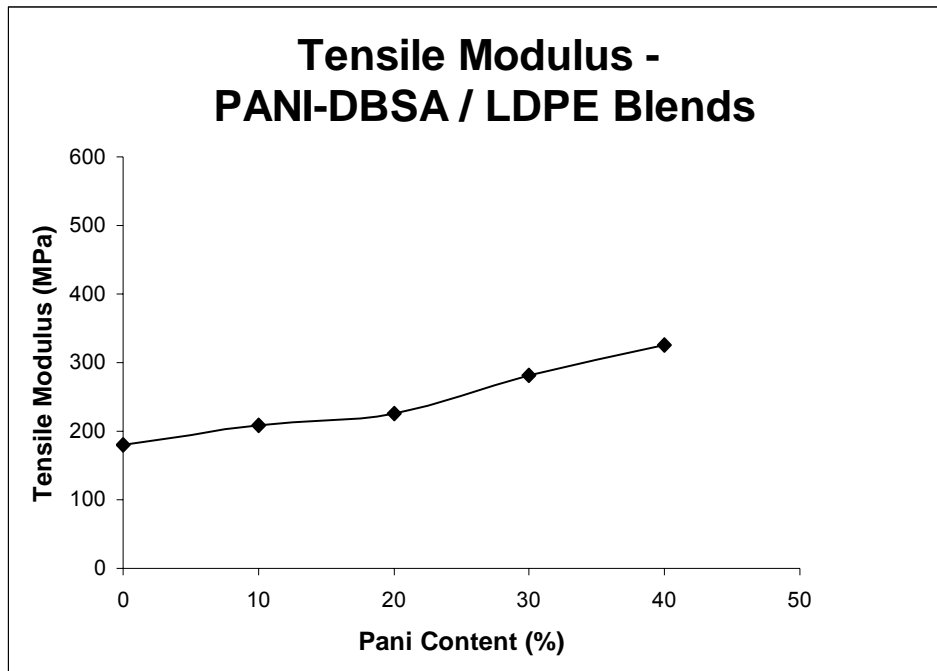


Figure 5.14: Represents increase in tensile modulus with polyaniline loading.

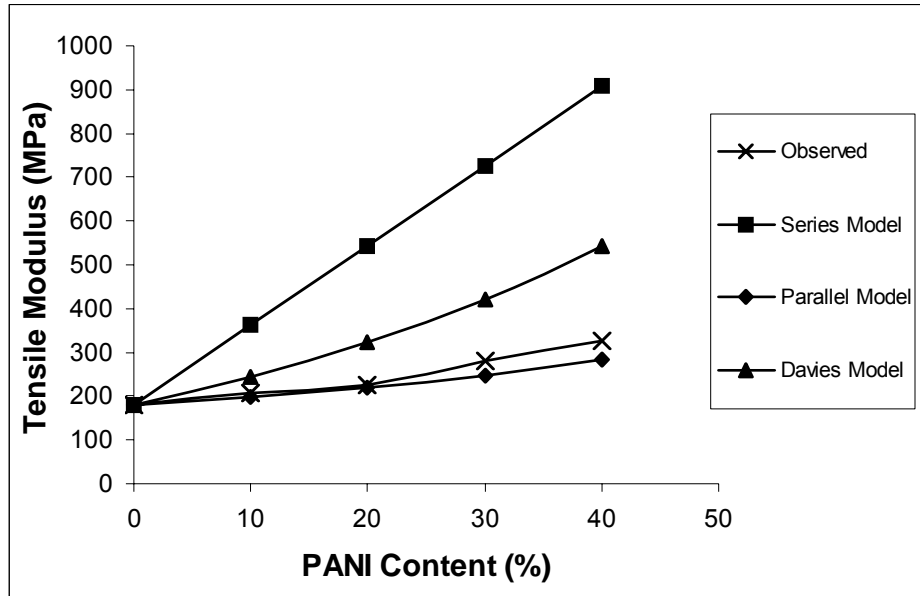


Figure 5.15: Comparison of different models for tensile modulus with the experimental data for PANI-DBSA / LDPE blends.

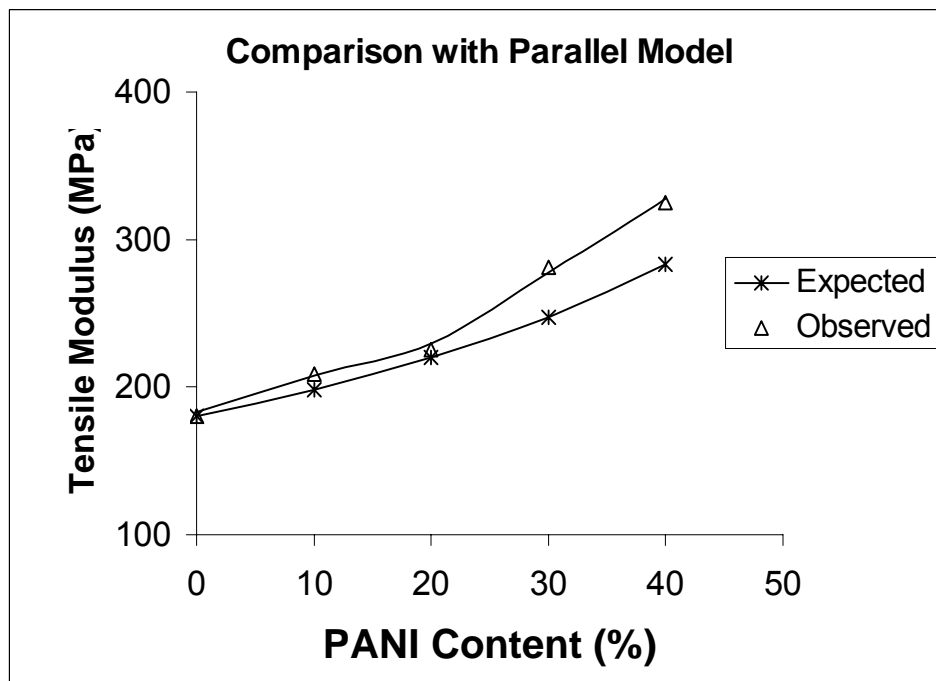


Figure 5.16: Comparison of parallel model for tensile modulus with the experimental data.

Another property to be considered is the toughness of the blend with polyaniline loading. Toughness is the energy absorbed by the material during deformation before failure ¹¹. It can be seen that for the above table that the toughness decreases with the polyaniline loading. It decreases from 5.5 M.Pa for LDPE to 0.82 M.Pa for 40% PANI-DBSA blend.

Table 5.10: Physical properties of PANI-DBSA / LDPE blends with 5phr PEO given by tensile test:

Composition of Blend (% PANI-DBSA)	Tensile Modulus (MPa)	Stress at max load (MPa)	Strain at max load (%)	Stress at auto break (MPa)	Strain at auto break (%)	Toughness (MPa)
0	186.0	14.14	47.30	13.69	50.36	3.791
10	217.6	12.97	25.05	12.41	26.48	1.611
20	226.7	10.22	17.88	10.27	18.32	0.940
30	234.0	8.61	14.10	8.62	14.19	0.679
40	245.1	7.31	10.36	7.39	10.40	0.3710

Similarly, the mechanical properties of the PANI-DBSA / LDPE blends with 5phr PEO as additive also were determined. The tensile test was carried out exactly as explained in the earlier case. The values obtained are given in the Table 5.10. Here also the tensile modulus in getting increased with the polyaniline loading, but this increase is less than that of the blends with out PEO. It can be seen here that the addition of PEO was affecting the mechanical

properties. Addition of PEO reduces the elongation of LDPE from 72% to 50%. This effect can be due to the fact that the presence of PEO effects the molecular orientations of LDPE as seen in the Chapter 3. Table 5.11 gives the comparison of tensile modulus and elongation of various blends with and without PEO addition. The comparison of the tensile modulus with that of calculated from different models are given in the Figure 5.17. Here the 0% taken was the LDPE with 5phr PEO. Due to the fibrous morphology of the PEO strands inside the LDPE matrix, the tensile modulus is higher than that of the blend without PEO. The induced orientation of the PANI-DBSA during moulding causes the hike in modulus at higher loading from that expected from the theoretical models.

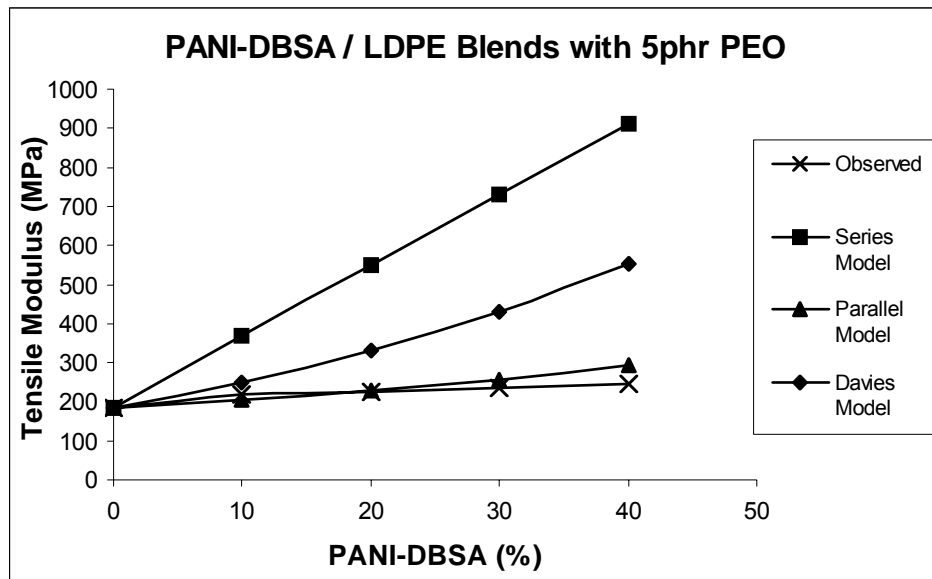


Figure 5.17: The comparison of tensile modulus of PANI-DBSA / LDPE with 5phr PEO with different theoretical models.

It can also be observed that, other than the increment in the modulus, the addition of PEO is also affecting the properties like elongation and toughness. The elongation of LDPE with PEO is inferior to the pure LDPE, but the drop with polyaniline addition is also low when PEO is added to it. Hence, at higher loading the value is almost same with that without PEO. The toughness is also lower than that of the blend without PEO.

Table 5.11: Comparison of physical properties of PANI-DBSA / LDPE blends with and without PEO:

Composition of Blend (% PANI-DBSA)	Tensile Modulus (MPa)		Elongation at auto break (%)	
	Without additives	With PEO	Without additives	With PEO
0	180.0	186.0	71.65	50.36
10	208.6	217.6	29.41	26.48
20	225.7	226.7	18.67	18.32
30	281.0	234.0	12.65	14.49
40	325.1	245.2	12.29	10.40

The flexural test was carried out by using rectangular injection moulded samples, where three-point bend test was employed. Flexural tests were carried out as per the standard ASTM D 790 using the injection moulded rectangular samples having about 3mm thickness and 12mm width. The samples found highly resistant to cracking or any kind of break. Hence, the important properties obtained here were the flexural modulus and the toughness. It is important to note that these measurements are the properties along the direction right angle to the melt flow where that obtained along the flow direction in the tensile test. It will be interesting to note that the flexural modulus is increasing with polyaniline loading as illustrated in the Figure 5. 18. The flexural tests for the PANI-DBSA / LDPE blends with 5phr PEO also were carried out and compared that of the blend without PEO. The comparison of these result obtained for PANI-DBSA / LDPE blends with and without PEO are given in the Table 5.12.

The change in flexural modulus also was compared with the different models as discussed in the case of tensile modulus. This is shown in the Figure 5.19. It is interesting to note that this behaviour is more fitting to the Davies model instead of the parallel model observed for tensile modulus. It has to be noted here that this modulus is entirely different in the fact that the force applied is perpendicular direction to the orientation of the filler. (Tensile test was along the orientation direction). This anisotropy in the mechanical properties also gives a proper evidence for the morphology of these blends, where the fillers are oriented in the direction of the melt flow.

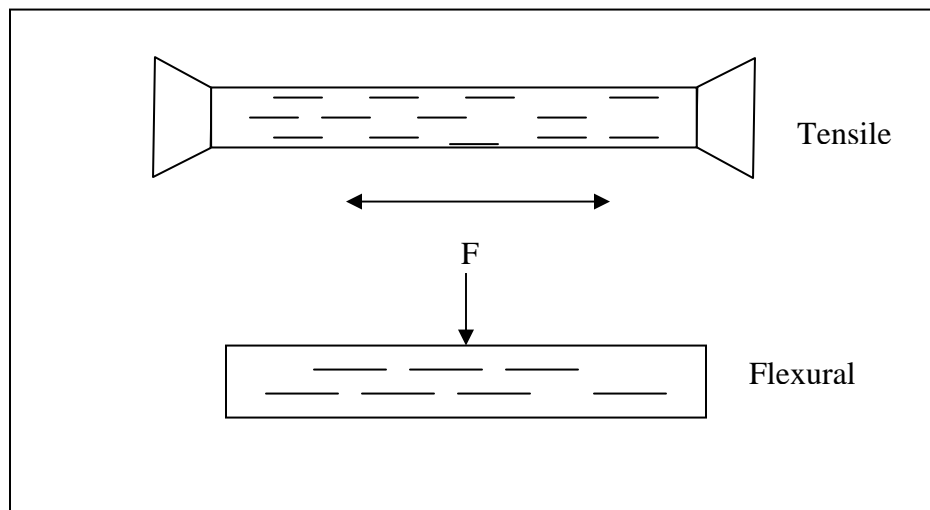


Table 5.12: The important physical properties obtained from flexural test of PANI-DBSA / LDPE blends.

Composition of the blend (% PANI-DBSA)	Flexural Modulus (MPa)		Toughness (MPa)	
	Without additives	With 5phr PEO	Without additives	With 5phr PEO
0	231.2	259.7	0.417	0.045
10	272.3	271.6	0.0538	0.043
20	392.6	312.1	0.0547	0.046
30	488.0	323.7	0.0689	0.043
40	548.8	328.1	0.0697	0.046

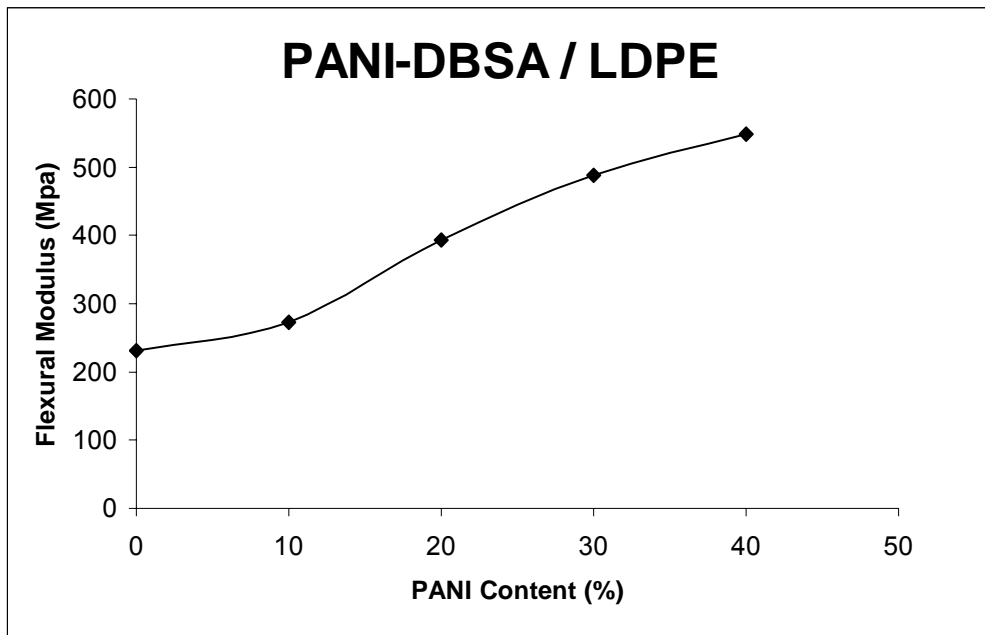


Figure 5. 18: Effect of polyaniline loading in PANI-DBSA / LDPE blends on flexural modulus

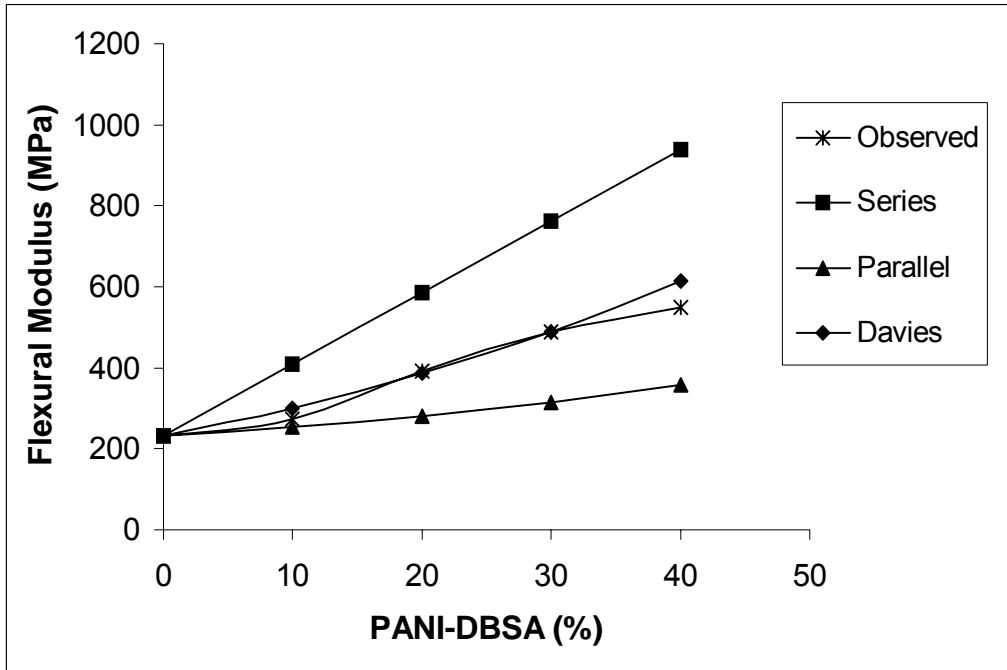


Figure 5.19: Comparison of different models for Flexural modulus with the experimental data for PANI-DBSA / LDPE blends.

SECTION – 2:

5.3. PROPERTIES AND APPLICATIONS OF PANI SOLUTION PROCESSED BLENDS WITH THERMOPLASTICS.

This section deals with the properties and the possible applications of PANI-DBSA solution blends, which are prepared as discussed in chapter 4. These solution processible blends can offer easy and direct implementation in coating applications. It is already proved in earlier chapters that the processibility of the polyaniline can be improved by using long chain organic acids as dopants. It offers improved thermal stability of dopant ions as well as solubility in common solvents and, hence, improved processibility when blended with other polymers like PMMA, PVC and PC. In order to examine its real applicability in specific fields, the measurements of various properties of these blends are essential. The properties measured for these solution blends are conductivity at room temperature, conductivity variations with temperature, EMI shielding measurements, Mandrel bend test for flexibility and crack resistance, etc.

5.3.1. EXPERIMENTAL:

a) Conductivity Measurements:

Conductivity of the films of the blends of PANI-DBSA / PMMA, PANI-DBSA / PVC as well as PANI-DBSA / PC were measured using KEITHELY electrometer. The details of the instrumental parts and the method were delineated in the experimental chapter (Chapter 2). Conductivities of all these

blends were determined by measuring the resistance of about 0.2mm thick films of these blends. The thicknesses of these films were measured using a screw-gauge. Two probe resistance measurements were carried out by loading these films between the two electrodes of the cell. Resistance readings were noted from which the conductivity were calculated for each case. The cell has the provision for heating so as to sweep the temperature in a required range at a constant rate of heating. Room temperature conductivities as well as the conductivity values at a range of temperatures from room temperature to 100°C as well as from -15°C to 100°C were also determined.

b) EMI Shielding Measurements:

As discussed in melt blend section EMI shielding is an important property also for the conductive coatings in application viewpoint. The solution prepared for various PANI-DBSA / PVC blends in THF were coated on 1mm thick moulded ABS sheets by spin coating technique. SE of these sheets was determined as discussed in earlier section using 'Hewlett Packard spectrum analyzer'.

c) Optical Properties:

Optical properties of the polymer or its blends or composites decides its application capacity in different fields like display systems, transparent coatings, anti-static coatings with optical clarity, etc. These can be decided by measuring different optical properties like transmittance and reflectance of the polymer or its blends. These properties should be measured in the visible range. These

properties of the solution casted blends films were measured using spectrophotometer model “HR 2000 CG-UV-NIR High Resolution Spectrometer, Ocean Optics Inc.” with the light source from “Mikropack DH 2000”. Transmittance of these blends with respect to air was recorded.

d) Mandrel Bend Test:

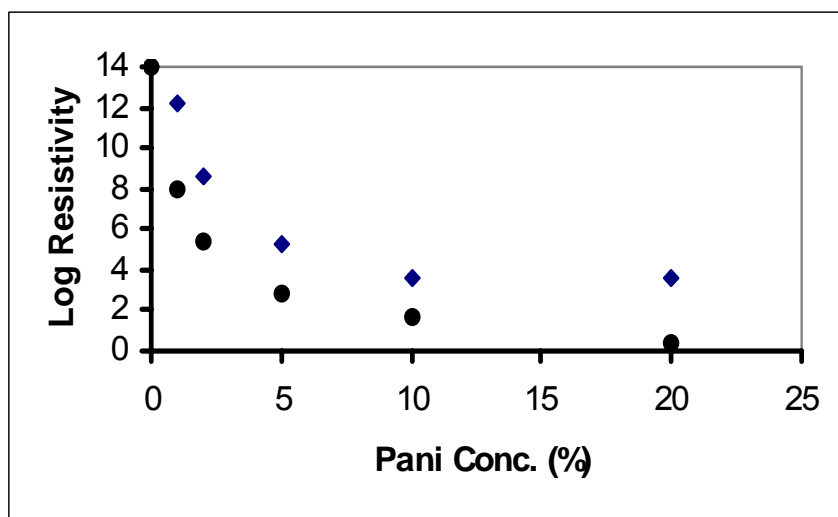
This test is for checking the flexibility (resistance to cracking) of the polymer films and coatings. It was carried out according to the ASTM D522-93a (2001). Here the films of all the polyaniline blends with different thermoplastics as well as the conductive carbon black composites were bend to 180° on a ¼” mandrel and then examined for the cracks formed. If there is no crack formed, the sample was declared passed and the formation of the cracks was regarded as the failure of the sample. This test was carried out on all the blend films of PANI-DBSA / PMMA, PANI-HCl / PMMA, PANI-DBSA / PVC, PANI-DBSA / PC, and PVC / carbon black composites.

5.3.2. RESULTS AND DISCUSSION:

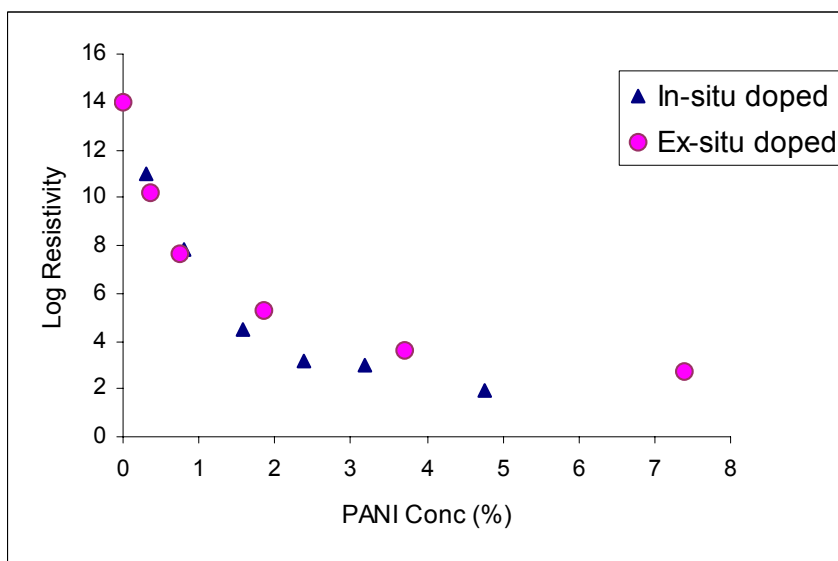
a) Conductivity Measurements:

The room temperature conductivities of these solution casted blends were determined and compared. The resistance of each blend films across its thickness was measured using electrometer. Knowing the exact thickness the resistivity and, thus conductivity of these blends can be calculated. Since the path length of the current flow across the electrode through the medium is the thickness of the film and the area of cross section of the conducting medium is the area of electrodes, the conductivity can be calculated from the fundamental relations (5.1) and (5.2) as discussed in earlier section. Conductivities of each polyaniline samples with different dopant ions are discussed in Chapter 3.

Blends of PANI-DBSA with PMMA were analyzed for its room temperature conductivities. The blends with polyaniline doped with HCl and DBSA were compared. These values of two different kind of blends containing polyaniline doped with DBSA in direct way and in re-doping pathway were also compared and plotted against the effective polyaniline content as shown in the Figure 5.17 It depicts the conductivity for the blends made from the two grades of PANI-DBSA with PMMA. It is evident that the PANI-DBSA gives sharp decrease in resistivity at much lower concentration of the conducting polymer in the blend than those containing PANI-HCl component. Further, PANI-DBSA (direct synthesized) yields more conducting blends than PANI-DBSA (ex-situ doping) for the same compositions. Such compositional dependence of conductivity has been typically observed in the past for phase segregated conducting composites and understood in terms of percolation threshold at which the inter-particulate contacts are formed.^{12, 13}



A



B

Figure 5.17: Conductivity of PANI-PMMA blends with respect to composition having different dopants. (A) Comparison of HCl doped PANI and DBSA doped PANI and (B) comparison at low concentrations for PANI-DBSA (ex-situ) with PANI-DBSA (insitu) grades.

It should be noted that the above equation (5.3) assumes that the conducting phase is different and distinctly separate than the insulating matrix. Hence, it was felt that in the present case of PANI-DBSA, the blends contain more uniform network formation and even compatibility of the components because these were very clear and transparent both in solution as well as solid film phases.

The temperature dependence of electrical conductivity for these blends was measured from -15°C to 100°C . It exhibited most interesting results. It is given in the Figure 5.18 (a) and (b). It depicts the variation of electrical resistivity with temperature for PANI-DBSA / PMMA blends. These graphs are slightly different in appearance from the usual $\log \sigma$ vs. $1/T$ plots reported for many conducting polymers in literature. This was intentionally carried out in order to bring out the transitions / relaxation processes taking place in the blends.

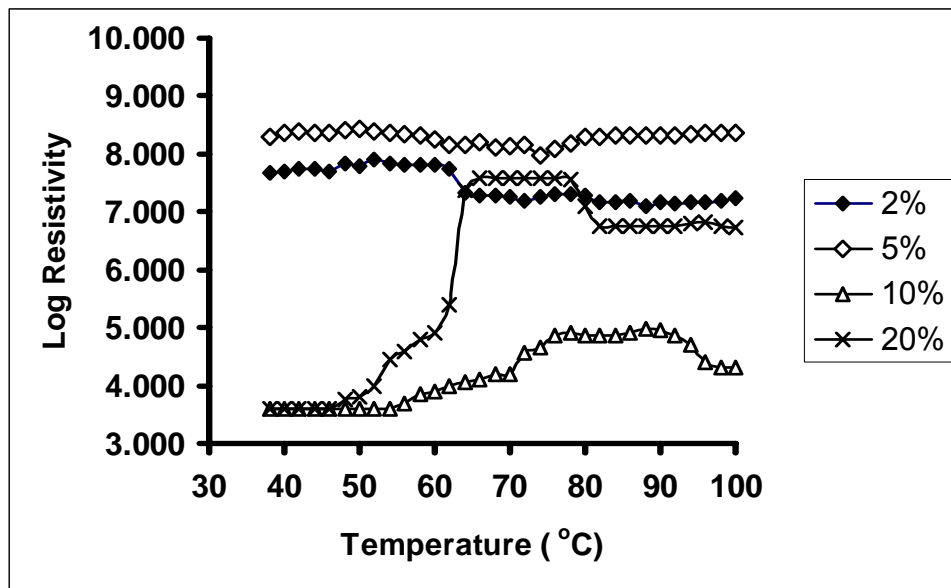


Figure 5.18 (a): Temperature dependence of electrical resistivity for DBSA-PANI blends with PMMA; scanned from room temperature to 100°C .

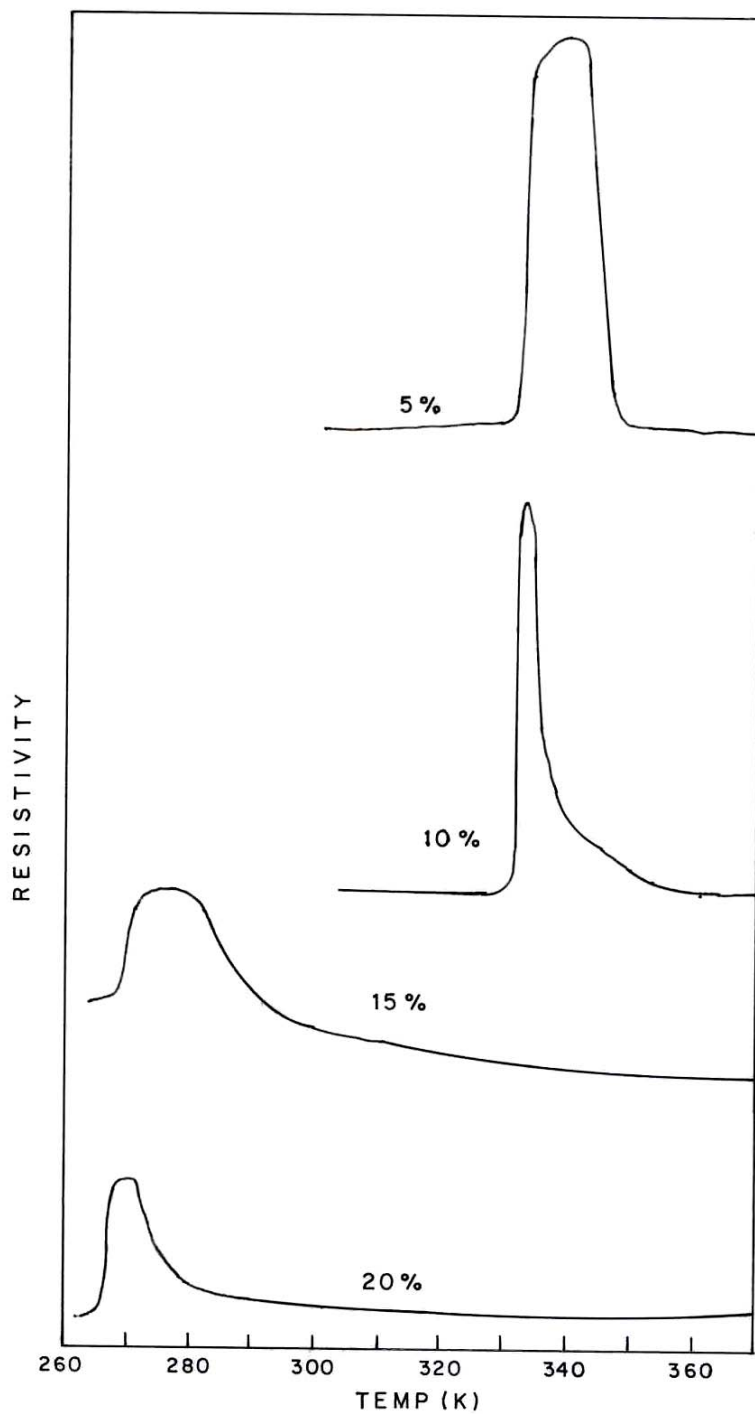


Figure 5.18 (b): Temperature dependence of electrical resistivity for DBSA-PANI blends with PMMA; scanned from -15°C to 100°C .

The data was recorded continuously at a heating rate of 10 °C / min. It is seen that there is very little change in the curves for 2 and 5% of PANI but a sharp increase of resistivity is observed for blends containing 20% PANI. Usually, the conductivity of conducting polymers is known to change in either Arrhenius manner with activation energy or following the variable range hopping (VRH) process.^{14, 15} However, in conducting polymer composites (containing phase segregation), the positive temperature co-efficient of resistance (PTC effect) has been reported by a number of authors.^{16 - 19} The PTC phenomenon is associated with discrete domains, contact formation and inter-domain distance. Hence, the observation of PTC effect is clearly suggestive of presence of discrete conducting domains in the material, which in the present case is only above 20% of PANI. Thus, it is clear that the blends having low concentration of PANI are much more homogeneous than those containing 20% PANI and there is phase segregation only when PANI concentration is above 15%.

The resistivity shoot up at certain regions depending on the polyaniline content was observed. This can be identified as the relaxation process associated with the glass transition temperature (T_g) of the blend. These values of each blend can be determined from the maximum of these resistivity peaks. These values are given in the Table 5.13. This can be noticed that there is only one relaxation observed for every blend corresponding to the existence of the single T_g indicating the homogeneous nature of these blends. Moreover, there is a reduction in T_g values with the polyaniline loading. It can be correlated with the efficiency of DBSA to interact with the PMMA matrix also. This interaction is assumed to be predominant in the fact that, the excess or the free DBSA molecules can penetrate through the PMMA matrix and act like a good plasticizer, reducing the T_g of the resulting blend. It shows that the DBSA molecule is acting like a compatibilizer that provides better inter-phase interaction, and act as plasticizer to reduce the T_g of these blends, in addition to its doping function. This can also be noticed that the T_g values are going even below the room temperature in the case where the polyaniline content is more than 20%.

Table 5.13: Tg calculation from the resistance transitions.

Percentage of PANI/DBSA in PMMA matrix	Tg determined from resistance transitions (K)
5	342
10	331
15	279
20	272

b) EMI Shielding Measurements:

The shielding effectiveness (SE) of various PANI-DBSA / PVC coated ABS sheets were investigated between 1MHz to 50 MHz using HP frequency analyzer as discussed in the experimental part. The reference level was taken as -40 dB. The various EMI shielding effectiveness of the PANI-DBSA / PVC coated ABS sheets are given in the Table 5.14. The corresponding output signals are shown in the Figure 5.19.

Table 5.14: EMI shielding effectiveness (SE) of various PANI-DBSA / PVC coated ABS sheets:

Blend Composition of the coating on ABS (% PANI-DBSA)	Shielding Effectiveness (SE) dB for 150 microns
10	10
15	12
20	14
30	15

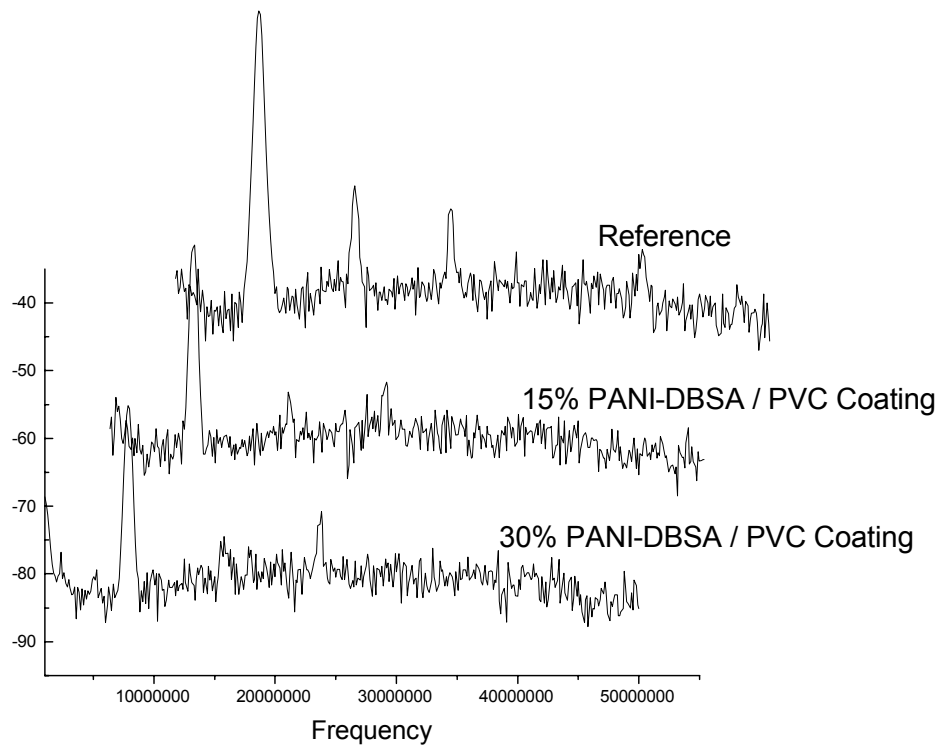


Figure 5.19: Out put signal given when different PANI-DBSA / PVC solution blend coated ABS sheets, used as shielding materials. This represents the out put signal with out shielding (reference), with 10%, 40% and that of 50% PANI-DBSA / LDPE.

Here the coatings were very thin on the ABS sheets. It is interesting to note that this coating provides the SE of 15 DB in the case of 30% PANI-DBSA / PVC blend was used. Hence, it can be interpreted that these coatings can be made use as low EMI shielding layer.

c) Optical Properties:

The optical properties of the polymer or its blends or composites decides its application capacity in different fields like display systems, transparent coatings, anti-static coatings with optical clarity, etc. Conducting polymers are assumed tremendous application in these areas. These can be decided by measuring different optical properties like transmittance of the polymer or its blends. All the above solution blends of polyaniline have high potential for these applications. Due to the presence of polyaniline these blends showed maximum transparency at the region of 580 nm. Hence, the transmittance of these blends at this region was compared as the measure of transparency.

The transmittance of the PANI-DBSA / PMMA blend with 130 micron thickness were analyzed to get the idea about its optical clarity. The UV-Visible spectra in transmittance mode were recorded from 300nm to 900nm. The transmittance at the wavelength of 580 nm was recorded to compare the transparency given by the blend film. The transmittance spectra obtained in the PANI-DBSA / PMMA blend is shown in Figure 5.20 and the transmittance value at 580nm is given in the Table 5.15. Same optical measurements were carried out for PANI-DBSA / PVC blend as well as PANI-DBSA / PC blend films. The corresponding spectra for these blends are given in the Figure 5.21 and Figure 5.22 respectively. The transmittance values of these blends are given in the Table 5.16 and 5.17 respectively. These results show that these blends can be used as transparent conductive coatings.

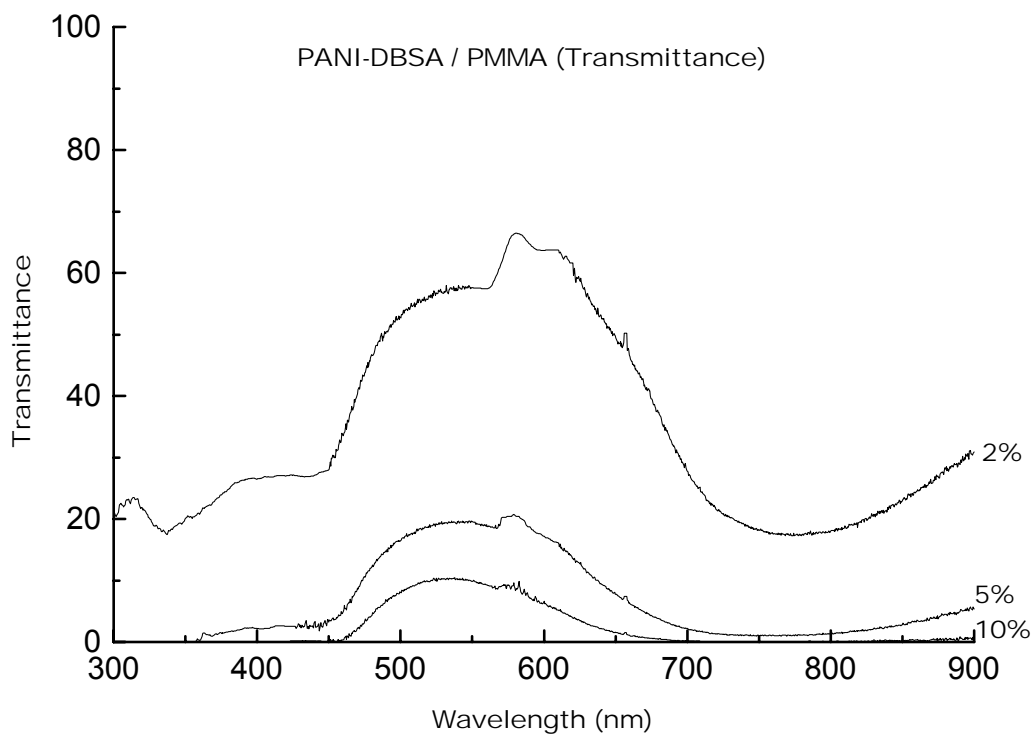


Figure 5.20: Transmittance spectra of PANI-DBSA / PMMA blend films.

Table 5.15: Transmittance of PANI-DBSA / PMMA blend films at 582 nm.

Polyaniline Content in PANI / PMMA Blends (%)	Transmittance at 582nm (%)
2%	77.3
5%	23.6
10%	9.8

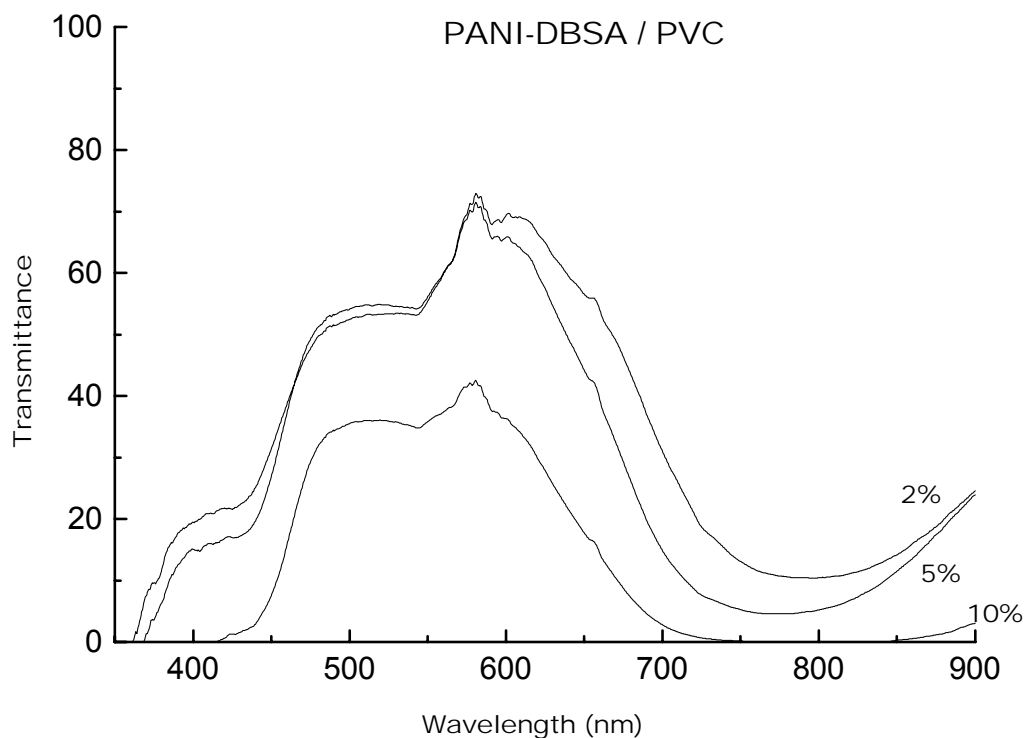


Figure 5.21: Transmittance spectra of PANI-DBSA / PVC blend films.

Table 5.16: Transmittance of PANI-DBSA / PVC blend films at 585 nm.

Polyaniline Content in PANI / PVC Blends (%)	Transmittance at 585nm (%)
2%	72.0
5%	70.4
10%	41.2

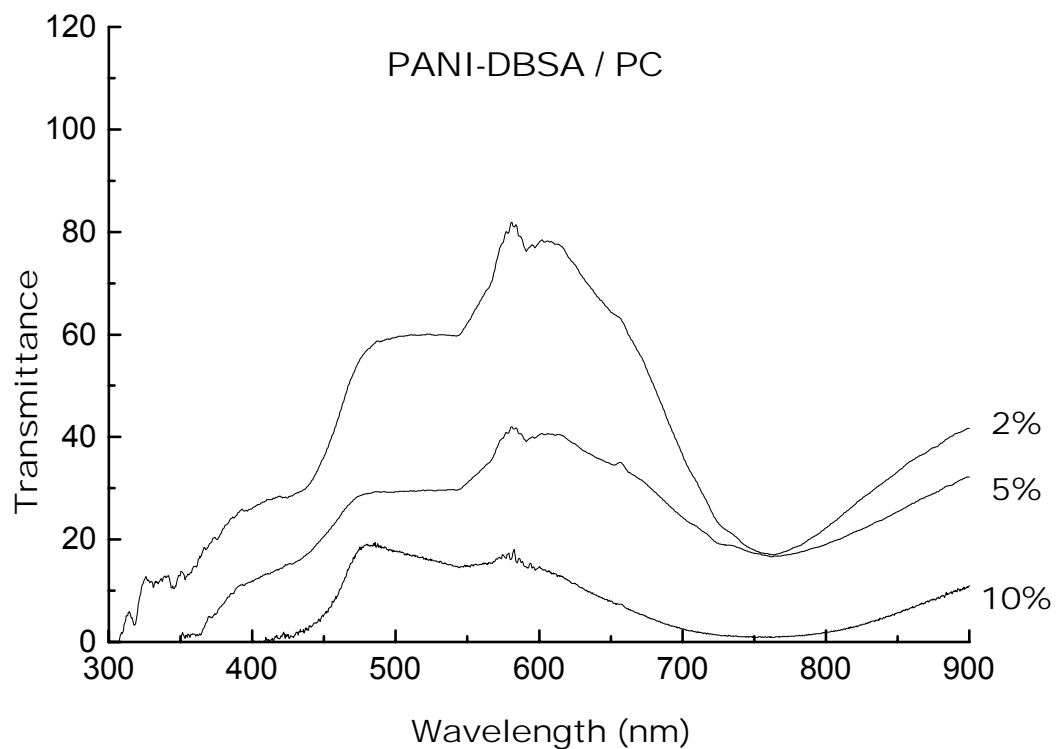


Figure 5.22: Transmittance spectra of PANI-DBSA / PC blend films.

Table 5.17: Transmittance of PANI-DBSA / PC blend films at 582 nm.

Polyaniline Content in PANI / PC Blends (%)	Transmittance at 582nm (%)
2%	87.5
5%	45.2
10%	18.1

d) Mandrel Bend Test:

As mentioned in the experimental part the Mandrel Bend test was carried out according to the ASTM D522-93a (2001). It gives the crack resistance property of these blend films. This gives the measure of flexibility of these blend films, which can give the measure of applicability of these blends as flexible coatings. These polyaniline blend films and films of carbon black composites were bend 180° over a ¼” mandrel and then examined for the cracks formed. If there is no crack formed, the sample was declared passed and the formation of the cracks was regarded as the failure of the sample. The test results for PANI-DBSA / PMMA, PANI-DBSA / PVC, PANI-DBSA / PC, PANI-HCl / PMMA, PANI-HCl / PVC and PVC / carbon black composites were given in the Tables 5.18, 5.19, 5.20, 5.21, 5.22 and 5.23 respectively.

Table 5.18: The results of Mandrel Bend Test for PANI-DBSA / PMMA Blends.

Composition of PANI-DBSA / PMMA Blend (PANI-DBSA content) (%)	Mandrel Bend Test Result.
0% (PMMA)	Failed.
1%	Passed.
2%	Passed.
5%	Passed.
10%	Passed.
15%	Passed.
20%	Failed
30%	Failed

Table 5. 19: The results of Mandrel Bend Test for PANI-DBSA / PVC Blends.

Composition of PANI-DBSA / PVC Blend (PANI-DBSA content) (%)	Mandrel Bend Test Result.
0% (PVC)	Passed.
1%	Passed.
2%	Passed.
5%	Passed.
10%	Passed.
15%	Passed.
20%	Passed.

Table 5. 20: The results of Mandrel Bend Test for PANI-DBSA / PC Blends.

Composition of PANI-DBSA / PC Blend (PANI-DBSA content) (%)	Mandrel Bend Test Result.
0% (PVC)	Passed.
2%	Passed.
5%	Passed.
10%	Passed.

Table 5 21: The results of Mandrel Bend Test for PANI-HCl / PMMA Blends.

Composition of PANI-HCl / PMMA Blend (PANI-HCl content) (%)	Mandrel Bend Test Result.
1%	Failed.
2%	Failed.
5%	Failed.
10%	Failed.

Table 5. 22: The results of Mandrel Bend Test for PANI-HCl / PVC Blends.

Composition of PANI-HCl / PVC Blend (PANI-HCl content) (%)	Mandrel Bend Test Result.
1%	Passed.
2%	Passed.
5%	Failed.
10%	Failed.

Table 5.23: The results of Mandrel Bend Test for PVC / carbon black composites.

Composition of PVC/ carbon black Blend (carbon black content) (%)	Mandrel Bend Test Result.
2%	Failed.
5%	Failed.
10%	Failed.
20%	Failed.

In PANI-DBSA / PMMA blend films the test indicate that the addition of DBSA doped polyaniline gives extra flexibility to the material. This effect also indicates the plasticizing effect of DBSA present in PANI. It again fails the test at the polyaniline loading of 20% and above. It can be due to the fact that the homogeneity of these blends looses at the higher polyaniline loading and PANI particles tend to agglomerate as seen in the Chapter 4.

The PVC films were found to pass this test, and with DBSA doped polyaniline loading it retain this flexibility or even improve this upto 20% loading. Polycarbonate blends also gave the same as PVC blends result on bend test.

It is interesting to compare this results with that of blends of HCl doped PANI and carbon black composites. PANI-HCl is the standard for of conducting polyaniline prepared in laboratories, where as carbon black is used extensively as the conductive filler for industrial applications. It can be seen in these above results that addition of HCl-doped PANI makes it more brittle indicating the formation of non-homogenous blend where PANI-HCl is acting as rigid filler. The carbon black composites were found to be worse affected and become very brittle and fail the test in all compositions.

It is evident from this test that the blends of PANI-DBSA with thermoplastics like PMMA, PVC and PC were flexible and superior to the blends with PANI-HCl and commercially used carbon black composites. Hence, these blends can be used as the flexible conductive coatings.

5.4. CONCLUSIONS:

The properties and the probable applications of melt as well as solution processed blends of polyaniline, especially doped with DBSA, have been discussed in the present chapter. The electrical conductivity of these blends was found to increase with the addition of PANI-DBSA and it attained the upper limiting value even at 15% of the conducting phase in the blend. PEO, which has been shown to be good processing aid, gave synergistic results as regards the electrical conductivity. A small addition of PEO (5 to 7 phr) lowered the percolation threshold, which arises from the formation of fibrous network structure incorporating conducting PANI. Thus, one can obtain high conductivity as well as melt processability in these blends. The important property studied here was the frequency dependence of conductivity of these blends. This also shows the higher conductivity for PANI-DBSA blends over PANI-HCl and PANI-PSSA melt processed blends with LDPE. The detailed studies of this frequency dependent conductivity revealed the complex nature of charge transport process in these blends. The power law $\sigma = \sigma_0 \omega^n$ was followed with n changing considerably with composition. These findings suggested the charge transport was dominated by the inter-domain hopping process and the charges became increasingly delocalized with increase of PANI content. In the high frequency regime, the conductivity became high for all the cases suggesting the effectiveness of these blends for the application as EMI shielding material. The

separate EMI shielding measurements showed the actual suppression of the signals (and noise) in a wide range of frequencies upto 50 MHz. All these properties were found to either remain unchanged or in some cases increase with the presence of PEO added as a processing aid. The studies on mechanical properties of these blends indicated that there is an increment in modulus and slight decrease in elongation with the addition of PANI to LDPE. These properties were in the acceptable limits especially at low concentrations of PANI at / near percolation threshold. The improvements in the mechanical properties in combination with good electrical conductivity make these blends attractive for moulding thermoplastic products.

The properties of solution processed blends were studied with a view to their applications in conductive coatings, films etc. The conductivity values showed very low percolation values for all these blends. These measurements also showed the existence of single T_g, indicating the molecular miscibility of these blends. The most important property of these blends was the optical transparency. Conductive layers having very good transparency (70%) could be made using these solutions. The EMI shielding properties also were measured for the ABS sheets coated with different composition of PANI-DBSA / PVC blend which gave fairly good shielding efficiency. All these blends of PANI-DBSA / PMMA, PANI-DBSA / PVC, PANI-DBSA / PC, PANI-HCl / PVC and PVC / carbon black composites were subjected to bend test to check the flexibility of these films. It was found that the PANI-DBSA blends are having good flexibility and crack resistance over others.

In conclusion, these blends of PANI-DBSA are identified as very useful materials for different applications such as anti-static layers, EMI shielding material, transparent flexible conductive films and coatings, etc. These blends showed better properties over conventional HCl doped polyaniline blends and commercially used carbon black composites.

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CHAPTER – 6
SUMMARY AND CONCLUSIONS

Conducting polymers have become important materials in various fields of electronics, sensors, safety devices, biomedical applications etc. Polyaniline has already been given considerable importance among conducting polymers, because of its ease of synthesis, low cost, better environmental stability as well as other properties as discussed in the first chapter. For majority of applications, the achievement of processibility is importance from the industrial viewpoint. This work presents a promising leap towards the better applicability of inherently conducting polymers, especially in electronic industry. Attainment of high processability for polyaniline both for the melt processing as well as solution coating is the real achievement of the present work.

In order to achieve high processability for polyaniline two approaches were taken in the present research. Firstly, the thermal stability of the conducting polyaniline was improved so as to retain the conductivity after melt processing. Further, the melt flow was improved by blending specially doped polyaniline with low melting polymer and incorporating processing aids in the same. In the second approach, polyaniline was doped with specific agents so as to increase the solubility in common organic solvents. It was solution blended with commodity polymers with film forming properties. The viscosity and dispersion characteristics were improved so that such solutions could form films and coatings easily. Detailed investigations were made at every stage of these modifications and large amount of data has been collected which has given in depth understanding of various processes involved.

Implementation of direct route for synthesis of polyaniline in presence of the different dopant acids (mainly sulfonic acids) reduces the number of tedious steps involved in the conventional methods of indirect doping. Among the various polyaniline varieties prepared, the one with DBSA as the dopant ion showed better conductivity, thermal stability, solubility, etc. TGA studies reveal that the thermal stability of the conducting polyaniline is dependent mainly on the dopant

ion present and increases in the order PANI-HCl < PANI-CSA < PANI-PSSA < PANI-DBSA. This led to the choice of PANI-DBSA in preparing the melt processable conducting blends.

The melt flow characteristics of the PANI-DBSA blend with low melting polymer such as LDPE were thoroughly investigated. These results indicate the better melt processibility of PANI-DBSA / LDPE blends in addition to its stable conductivity due to the DBSA present in the blend. Comparisons of relative melt viscosity, monitored through MFI measurements, with the existing mathematical models for filled polymers like Einstein, Eilers, Mooney, Krieger and Dougherty and Quemada, is consistent with the blend morphology. The processibility obtained here was far better than corresponding carbon black composite, which is extensively used for commercial purposes. The processability improvement and interactive phase morphology of these blends are also well supported by the comparison of relative melt viscosities of these blends with existing mathematical models for filled polymers. Carbon black composites behavior is found to fit the Mooney model as reported earlier. The relative melt viscosity behavior of PANI-HCl / LDPE blends were found to match with the Krieger and Dougherty model as expected for particulate filled polymer composites with good dispersion. But a considerable deviation from Krieger and Dougherty model is observed for PANI-DBSA / LDPE blends towards the lower relative melt viscosities. The lower melt viscosity is attributed to the existence of more interactive phase morphology of these blends and the plasticizing effect of DBSA on LDPE. It suggests the highly improved melt processibility of PANI-DBSA / LDPE blends

The most out standing result of the present investigations is the improvement of melt flow by the addition of polymeric dispersing agents like PEO, PEG etc which not only improved the processability but also imparted high conductivities of the melt processed blends of polyaniline. These outperform the conventional carbon black composites in many respects. These synergistic results could be understood in terms of the fibrous morphology developed in the

blends with PEO/PEG forming the network like structure in which PANI was preferentially dispersed. Thus, high processability could be attained due to the lubricating effect while the high conductivity was retained due to the shift in percolation threshold to lower concentrations of PANI. These various hypotheses have been supported by investigations on structure and morphology of the melt processed blends. It shows the formation of skin-core morphology where PEO forms the skin and LDPE the core. WAXD studies also reveal molecular interactions between the phases in presence of PEO giving higher crystallinity due to induced orientation of LDPE. In conclusion, these studies indicate the improved processability and better end product properties of PANI-DBSA / LDPE melt-blends and a further improvement when PEO was added as the processing aid in low phr level

These blends were also studied for frequency dependent conductivities and EMI shielding properties other than dc conductivity and structure and morphological investigations. The solution blends were found to ideally suit for preparing the flexible conductive films and coatings with very high optical transparency. In short these blends of polyaniline could prove useful in various applications like anti-static layers and coatings, transparent conductive coatings, corrosion protective layers, EMI / RF shielding material, etc.

In the case of solution-processed blends of PANI, firstly the solubility was investigated by different techniques for PANI doped with different doping agents. Considerable solubility was obtained for DBSA as the dopant ion, which gave, improved solubility for polyaniline in the common organic solvents like chloroform, tetrahydrofuran, dichloromethane, etc. The solubility was found to be in the order PANI-DBSA > PANI-PSSA > PANI-CSA > PANI-HCl. The solution processed blends of PANI with thermoplastics like PMMA, PVC and PC were studied for their processability by monitoring the viscosity. It was observed when the PANI-DBSA was used as the conducting material in the blend; the blend was homogeneous with low viscosity values even at high concentrations of the

additive. On the other hand, PANI-HCl blends behaved like filled polymers. In this case also the experimental results were compared with mathematical models described earlier. It was found that the behaviour of these blends was fitting to the Mooney model and that of Quemada models when PANI-HCl and PANI-DBSA were used as conducting part respectively. It indicates the existence of better interactive phase morphology in the PANI-DBSA / PMMA blends.

The solution processed films of these PANI-DBSA blends were homogeneous in nature with high miscibility of polyaniline loading up to 15%. On the other hand the blends with PANI-HCl and carbon black composites, the films casted were found grainy and phase separated even at very low polyaniline loadings. UV-visible spectroscopy studies confirmed the homogeneity of these blends since the optical density followed the Beer-Lamberts law. The origin of such homogeneity was attributed to the DBSA present in the polyaniline which was found to act as compatibilizer for the two components. Part of this dopant was also found to plasticize the second major polymer matrix. These conclusions could be made due to strong evidence obtained from various characterization techniques. The increase in interchain separation identified by WAXD studies, the decrease in the T_g obtained by DSC as well as dielectric relaxation method and flexibility of the films with mandrel bend test all pointed to the above suggestions. Thus, the DBSA molecule was found to act as compatibilizer as well as plasticizer in these blends at the same time increasing the conductivity due to its charge transfer interaction with PANI.

The dc conductivities of the melt as well as solution blends were measured both at room temperature and at a range of temperatures. These measurements reveal that the percolation threshold of conductivity of PANI-DBSA / LDPE is decreased by the addition of PEO and PEG as processing aids. Further, this decrease also depends on the amount of PEO added. The conductivity measurements carried out for solution blends reveal the attainment of very low percolation threshold at around 2% of polyaniline addition. These

measurements show that the conductivity transitions at a certain temperature range depends on the blend composition corresponding to the T_g of these blends. This also confirms the high miscibility of these blends indicated by the existence of single glass transition.

The measurement of frequency dependent conductivity was also carried out on these blends. It also follows the trend of conductivity obtained in earlier dc measurements, where blends of DBSA doped polyaniline gave the maximum conductivity. It was also found that the frequency dependent exponent values decrease with polyaniline loading indicating the formation of a fine network at higher loading. Correspondingly the value of characteristic temperature of frequency dependent conductivity decreases with polyaniline loading. At higher loading the conductivity of the different compositions approach to each other, indicating the efficient configuration of capacitor and resistance elements resulting in higher conductivity even at lower loading. It indicates that the PANI / LDPE blends at lower loading would be efficient EMI shielding material at very high frequency more than 10 MHz. But the blends with higher polyaniline loading would be efficient EMI shielding material over the entire range of frequencies.

The measurement of EMI shielding shows the better shielding efficiency of the blends with DBSA doped polyaniline than that with HCl doped polyaniline. At higher loading the shielding efficiency increases. The shielding efficiency of these blends was found to improve with the addition of PEO. In this case, a very high shielding efficiency of 40 dB was observed at 50% of polyaniline loading. The solution blends of PANI-DBSA / PVC coating on ABS sheets were also found to be useful for EMI shielding applications. It gave a high shielding efficiency of 30 dB for the coating of 30% polyaniline blends.

Finally, it can be seen that these studies on melt and solution processed blends have opened a variety of opportunities for the applications of conducting polymers where conventional materials such as carbon black filled polymers are

being used. The serious processing problems encountered in the conventional materials can now be overcome by implementing the right choice of materials, dopants, processing aids and composition. Apart from the processability, the aesthetics – colour, smooth surface finish etc- can also be considerably improved by use of these blends. This work offers a promising leap towards the melt processability of conducting polymers, with a lot of potential in industrial use. The solution blends of polyaniline could be used in speciality coating applications where high transparency and conductivity are desired. Coatings of PANI-DBSA solution blends could also provide corrosion protective layers for different applications. As has been demonstrated in the above studies, PANI polymer blend solutions and dispersions can be used as anti-static coating for various purposes and EMI shielding coatings for electronic devices. It may be mentioned here that these studies have led to the development of new processes for which patents have been filed by our group both in India as well as other countries.