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Water based process for polyaniline composites

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Water Based Process for Polyaniline Composites

A Thesis
Presented to
The Faculty of the Department of Chemical and Materials Engineering
San Jose State University

In Partial Fulfillment
Of the Requirement for the Degree
Master of Science

by
Ming-Hung Shih
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ABSTRACT

WATER BASED PROCESS FOR POLYANILINE COMPOSITES

By Ming-Hung Shih

Water based formulations for polyaniline (PANI-DBSA) composites were developed and the conductivity-composition (*f*) profiles were determined. The polymers employed were polyvinyl acetate (PVA), polyacrylic acid (PAA) and polyvinyl pyrrolidinone (PVP). The critical volume fractions (*fc*) for conductivity percolation threshold were determined using the scaling law of percolation theory. The *fc* values were 0.113, 0.220 and 0.288, respectively. These values were higher than the literature values for similar materials. PANI-DBSA/PVP was also processed in N-methyl pyrrolidinone (NMP) and it had a lower *fc* value, 0.185. The addition of NaOH to the PAA/water formulation reduced the conductivity of PANI-DBSA/PAA composites. The particle distribution in the composites was inspected using a scanning-electron microscope. The PANI-DBSA particles were mostly spherical and distributed uniformly in the polymers and there was no evidence of special ordering. With the PANI-DBSA/PVP composites, the *fc* could be detected visually by the luster of the films.

Acknowledgement

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Also, I would like to thank Mr. Wayne W. Lee, a materials engineering student, who helped me conduct the SEM analysis. As to my parents, Mr. Tsai-Chien Shih and Mrs. Chih-Hui Tsai Shih, I would like to show my deep appreciation for their financial supports and concern for all the years of my education.

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Chapter I

Introduction

1. Polymer composites

A polymer composite consists of two or more components, a selected filler and a polymer binder, and is designed to have certain characteristics and properties. The filler acts as a reinforcing agent while the binder holds the filler together and protects it from adverse environmental effects. These two components do not dissolve in each other but act in concert [1]. The filler materials can be fibers, particles, or whiskers.

The simplest technique to fabricate a modern composite is called lay-up, lay-up molding or contact laminating. This application involves laying the dry reinforcement, which is the chosen filler, into the mold and then applying the polymer matrix. The wet composite is rolled to distribute the polymer matrix uniformly and to remove air pockets. Another layer of reinforcement is then laid on top, after which more polymer matrix is sprayed over the reinforcement [2]. In other words, the filler is saturated with the liquid binder and the lay-up is made by building layer upon layer to obtain the desired final thickness.

The polymer binder can also be fused, mixed with the filler, and then applied to a mold. Alternatively, the polymer binder can be dissolved in a solvent while the filler remains insoluble, but well distributed in the polymer solution. The composite is then formed by extrusion or by applying the mixture to a mold.

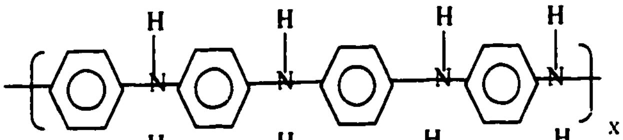
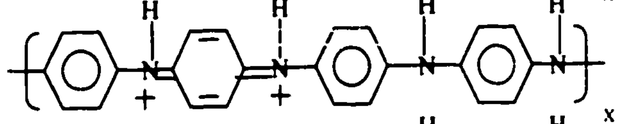
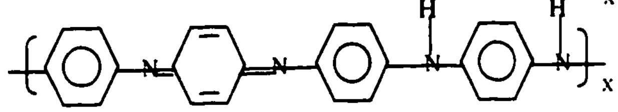
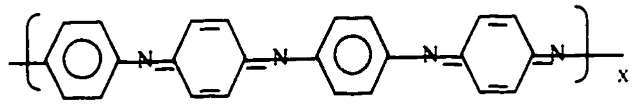
2. Conductive composites

The term " conductive composite" has two quite different definitions. The first and most commonly known are the polymers filled with conductive materials such as carbon black, carbon fibers, metal flakes and so on. The major function of the polymer matrix is to act as a "glue" to hold the conductive elements together in a solid state. The advantages of such materials are low cost, light weight, mechanical durability, and easy processing. For convenience, these composites are classified as category I conductive composites in this thesis. Metal particles, such as Ni, Cu, Ag, Al and Fe, have been used in the form of metal flakes and offer a value of conductivity up to 10^3 S/cm, which is much higher than that of the carbon black filler [3]. However, the volume fraction of conducting particles in the composite should not exceed 0.25, in order to maintain reliable material properties [4].

Another type of conductive composite is the combination of conjugated polymers with common thermoplastics, in which the backbone of the conjugated polymers are responsible for the generation and propagation of charge carriers. These are classified as category II conductive composites. For example, the conductive polyaniline (PANI) can be processed with a polymer binder to produce a category II composite. A potential advantage of such materials is the adjustable conductivity which can be controlled by the extent of oxidation or reduction of the conjugated polymers. Other advantages are the ability to dictate the nature of the majority carriers, and facile cycling between conductive and insulating states [5].

Among all conductive materials, high molecular weight polyaniline has been recognized as one of the most promising conductive polymers. It is represented by the following general formula:$—[(B—NH—B—NH)_y(B—N{=}Q{=}N)_{1-y}]_n$, where B denotes a benzenoid reduced unit and Q, a quinoid unit [6]. PANI exists in four different forms, each of which has different color as shown in Table 1.

Table 1. The Forms of Polyaniline

Name	Structure
a) Leucoemeraldine	
b) Emeraldine Salt	
c) Emeraldine Base	
d) Pernigraniline	

The emeraldine base form (type "c" in Table 1) of polyaniline is half-oxidized and is insulating, but its iminic nitrogen can be protonated (oxidized) by a strong acid to form an acid-base complex, the emeraldine salt form (type “b”), which is conductive. The fully protonated conductive complex is formed when 0.5 mole of protonic acid is consumed by each mole of a phenyl-N repeating unit of polyaniline.

The electrical properties of polyaniline attract the most interest. It has high levels of electrical conductivity (can be as high as 200S/cm) and the characteristics of variable conductivity by controlling the extent of oxidation or reduction. For example, the conductivity of the polyaniline composites can range from 10^{-9} ~200 S/cm. Polyaniline is readily available. The monomer (aniline) is relatively inexpensive, the polymerization of the monomer to polyaniline is straightforward and the reaction proceeds in high yield [8]. However, due to its semi-rigid nature, electrically conductive polyaniline is an intractable material with intrinsic poor processibility, and has poor mechanical properties. This limits its use in commercial applications. This intractability is caused by its highly aromatic nature, the interchain hydrogen bonding, and the charge delocalization effects [9]. Melt processing of polyaniline is not possible, since the polymer decomposes at temperatures below its softening and melting temperature. Polyaniline lacks thermal stability since the deprotonation of the polymer chain gradually starts around 100°C, resulting in loss of conductivity. Complete deprotonation and degradation of PANI is observed at temperatures above 200°C [10]. At this temperature, PANI loses its conductivity completely. PANI has limited solubility in common organic solvents. It has been generally accepted that it is impossible to dissolve doped (oxidized) high molecular weight polyaniline (conducting form) in common non-polar or even weakly polar organic solvents [11]. Despite these drawbacks, polyaniline is one of the first conductive polymers to be commercialized and it is now used in coatings, light-emitting diodes (LED) and the electrodes in rechargeable batteries.

Two methods have been reported where PANI was dissolved and processed without changing the molecular structure of the polymer. One is the solution method, where polyaniline is dissolved in N-methylpyrrolidinone (NMP), in selected amines, in concentrated sulfuric acid or other strong acids. The other uses a functionalized protonic acid to dope polyaniline and to make it soluble in common organic solvents [8]. The latter method has been widely used in processing polyaniline composites and it generally produces materials with a percolation threshold at extremely low volume fractions.

3. Conductivity percolation threshold, *fc*

The addition of a conductive filler to a polymer can produce a composite material with a reasonably good bulk conductivity (σ) and material properties. The conductivity of the composites is usually not a linear function of the conductive filler content, but instead shows the behavior of the type, which is shown schematically in Figure 1.

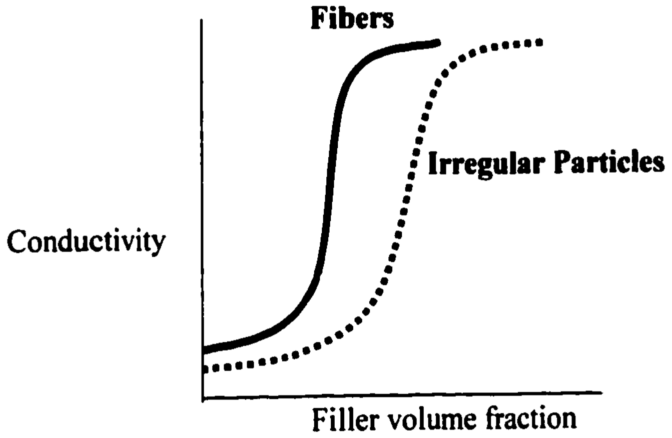


Figure 1. Conductivity-composition plot showing the influence of filler geometry on conductivity

At the low filler content range, the conductivity is insensitive to the composition until the so-called percolation threshold is reached. The volume faction of the conducting filler at the percolation threshold is called critical volume fraction, which is denoted as *fc*. In the low content region, the small filler particles (aggregates or agglomerates) are distributed in the insulating matrix, but still too far apart to form a continuous, conductive network. With increasing filler content, the distance between the particles decreases and at a certain critical filler content, the particles come in contact with each other and form one, two, or more three-dimensional conductivity networks within the insulating matrix. This filler content is called the percolation threshold. The formation of this network results in a dramatic increase in conductivity. The conductivity increases as additional filler is added because the number of connective paths increases.

The shape of the filler influences the conductive behavior of the composite. Fibrous fillers produce a percolation threshold at a lower filler content than spherically shaped particles like carbon black, because the former produces much more interparticle contact [5].

The procedure employed to prepare the composite can have a big effect on the conductivity profile of the polyaniline composites. If the process produces extended polyaniline chains, the resulting conductivity profile of the composites will resemble the case with fiber fillers as shown in Figure 1. The extended polyaniline chains produce more interparticle contact, and the conductivity percolation threshold will appear at a lower polyaniline content. If the process produces polyaniline particles, the resulting conductivity profile of the composites will resemble the case with irregular particle fillers, since there will be fewer interparticle contacts. Therefore, the conductivity percolation threshold will appear at a higher polyaniline content.

4. Motivation

Conductive polymers with intermediate and variable conductivities are suitable for many technical applications like light-emitting diodes (LED), electrochromic display devices and rechargeable batteries. Category II conductive composites, which are the composites of the conjugated polymers with common thermoplastics, have variable conductivity which can be controlled by changing the oxidation levels of the polymers. Accompanying the switching reaction between the insulating and conductive states is a corresponding change in the electrical, optical, physical and chemical properties of the polymer.

The objective of this thesis is to prepare polyaniline composites with different host polymers and to determine the conductivity-polyaniline content relationships. The percolation thresholds will also be determined for each of the composites. The conductivity-composition relationships can then be used to design materials with a prescribed conductivity.

Chapter II

Literature Review

1. PANI/PPTA processed in sulphuric acid

Andreatta et al. [11] described the preparation of polyaniline (PANI)/poly(p-phenylene terephthalamide) (PPTA) composites in a concentrated sulphuric acid solvent. Composites with various PANI-sulfate/ PPTA ratios were spun from the polymer blend solutions and used to determine the conductivity-composition profile. The PANI concentration ranges from very dilute to more than 20 wt %. In concentrated acids such as H_2SO_4, CH_3SO_3H and CF_3SO_3H, both the PANI emeraldine base and salt forms are completely soluble at room temperature. It is well known that PPTA is processed in concentrated H_2SO_4 to yield one of the strongest and stiffest fibers that are commercially available. The solubility of both PANI and PPTA in H_2SO_4 presents a unique opportunity for co-dissolving and blending polyaniline and PPTA, while still possessing the excellent mechanical properties of PPTA and the electrical conductivity of PANI.

Table 2 lists the mechanical properties and conductivities of the PANI-sulfate/PPTA composites. The conductivity ranges from 5.3 S/cm for PANI-sulfate to approximately 10^{-12} S/cm for PPTA. The mechanical properties (modulus, tensile, etc.) increase with the PPTA content. The dependence of conductivity (σ) on the volume fraction (f) of conducting PANI in the composites is determined by the number of connected pathways for carrying direct current across the specimen.

Search: CD-ROM Access Network and On-Line Catalog at the SJSU library.
Keywords: Conducting polymers, polyaniline composites, polyaniline copolymers, percolation threshold, water soluble, solubility, dodecylbenzenesulfonic acid (DBSA). 60 articles were found; 16 articles were closely related to the subject.

Table 2. Mechanical properties and conductivity of PANI/PPTA composites [Ref. 11]

Wt % PANI	Diameter (μm)	Tenacity (GPa)	Modulus (GPa)	Conductivity (S/cm)	Strain at break
100	30	0.05	1.9	5.3	0.040
70	55	0.09	4.6	9.5	0.020
65	50	0.12	5.0	8.6	0.023
60	44	0.12	6.3	9.9	0.031
55	45	0.15	6.3	3.72	0.056
50	43	0.19	7.6	1.0	0.064
40	34	0.18	8.0	0.40	0.095
35	35	0.15	7.9	0.1	0.072
25	34	0.25	10.6	0.01	0.086
20	25	0.29	13.1	0.001	0.093
10	27	0.35	15.7	10^{-6}	0.075
0	35	0.30	12.8	$\sim 10^{-12}$	0.137

The data in Table 2 are plotted on a semi-log plot in Figure 2. The densities used to convert between wt % and vol % are ρ PANI = ρ PPTA = 1.4 g/ml. The plot in the insert indicates that the conductivity follows the simple power law shown in Equation (1) for f values between 10–60 vol %.

$$\sigma = \sigma_0 f^{\alpha} \qquad (1)$$

In this equation, f is the volume fraction of PANI in the composites. The solid curve in Figure 2 shows that the experimental data can be fit to equation (1) using $\alpha = 8.15$ and $\sigma_0 = 1.9 * 10^{-14}$. The conductivity varies with f (from 10–60 vol %) and follows equation (1) over a range spanning nearly seven orders of magnitude.

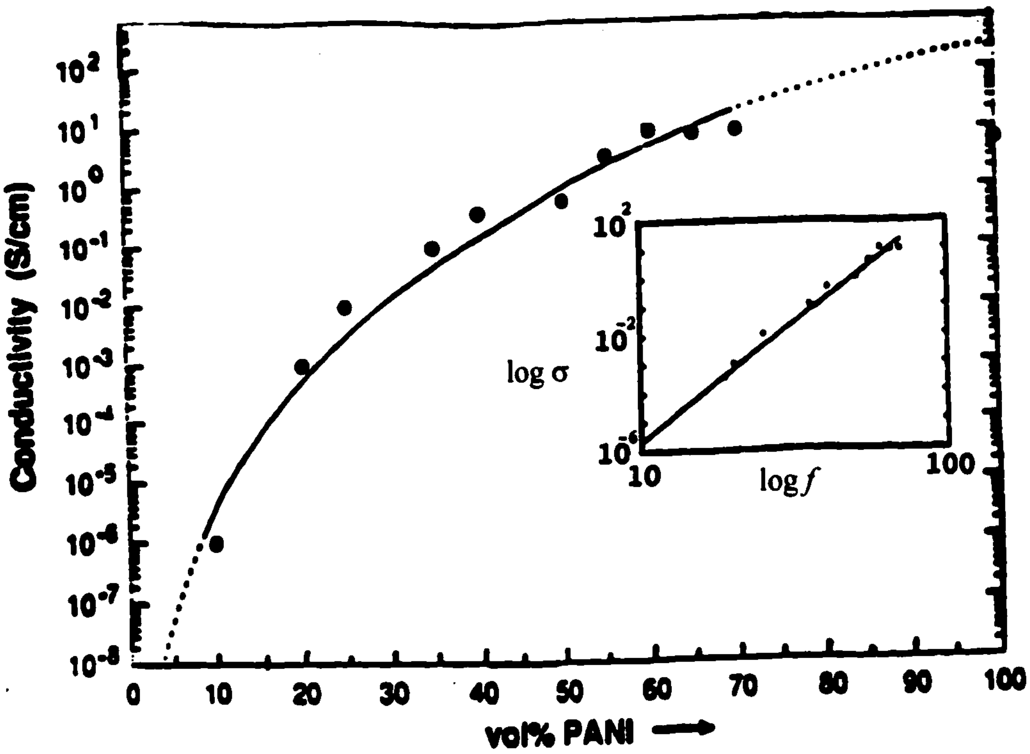


Figure 2. Conductivity vs. volume fraction of PANI in PANI/PPTA fibers [From Reference 11]

In the context of percolation theory, at sufficiently dilute filler concentrations such that there are no connected paths, the conductivity would be infinitesimal. As the concentration of the conducting polymer is increased above the percolation threshold, the conductivity would become finite and increase as the connectivity (i.e., the number of connecting paths) increases. In contrast, the data presented in Figure 2 did not show the percolation threshold explicitly. Andreatta and co-workers successfully produced the polyaniline-PPTA composite in concentrated sulphuric acid solvent. However, because of the high corrosivity of H_2SO_4, the process is not practical for industrial use.

2. PANI protonated with functionalized protonic acids

Heeger et al. [8] proposed the use of functionalized protonic acid to dope polyaniline and render it soluble in common organic solvents. A ‘functionalized protonic acid’ is denoted as $H^{+}(M^{-}\text{–}R)$, in which the R functional group in the counter-ion anionic species is chosen to be compatible with nonpolar or weakly polar solvents. The long chains of the R functional group also makes the PANI compatible with bulk polymers which have similar structures. The functionalized protonic acids act as surfactants that assist the intimate mixing of PANI in a variety of bulk polymers. They have discovered that by the judicious choice of the functionalized protonic acid, PANI can be made soluble in a variety of common organic solvents, as summarized in Table 3.

Table 3. Solubility and conductivity of protonated emeraldine salt with (SO_3^{-}–R) counter ion [Ref. 8]

R	σ (S/cm)		Solubility[b]				
	Pellet	Film[a]	Xylene	CH_3Cl	m-cresol	Formic Acid	DMSO
C_6H_{13}	10		O	O			
C_8H_{17}	19		O	O			
$C_8H_{17}COOH$	2.7						
C_8F_{17}	3.7						
(L,D) camphor	1.8	100–400		⊕	⊕	⊕	O
4-dodecylbenzene(DBSA)	26.4	100–250	⊕	⊕	⊕	O	
o-anisidine-5-	$7.7*10^{-3}$				O	O	O
p-Chlorobenzene	7.3				O	O	O
4-Nitrotoluene-2-	$5.7*10^{-2}$			O	O	O	
Dinonylnaphthalene	$1.8*10^{-5}$		O	⊕	⊕		
Cresol red	$2.2*10^{-4}$[c]			O			
Pyrrogallol red	$1.2*10^{-1}$[c]			O			
Pyrrocatechol violet	$1.9*10^{-1}$[c]			O			

[a] Films are cast from concentrated solution.

[b] O= soluble at room temperature; ⊕ = very soluble at room temperature.

[c] Pressed at 165°C

Table 3 also lists the electrical conductivities obtained (in pellets and in films cast from solution) for the emeraldine salt protonated with several functionalized counter ions. For example, with dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA) dopants, electrical conductivities in excess of 100 S/cm are achieved. An example is shown in Figure 3, where electrical conductivity (σ) of the films cast from the composites is plotted (open circle) versus weight fraction (*f*) of the PANI-DBSA system blended with polyethylene (PE).

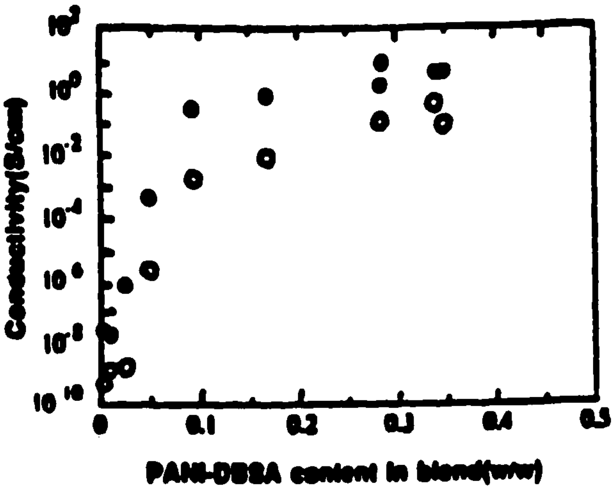


Figure 3. Electrical conductivity (σ) for the PANI-DBSA system blended with polyethylene (O) [From Reference 8]

Similar results were obtained for PANI blended with nylons, polycarbonate, polystyrene, polysultone, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer (ABS), etc. They found that in all the polyblend systems which utilize the counter ion-induced processibility of PANI, the critical volume fraction (f_c) for the conductivity percolation threshold is at least one order of magnitude below 0.16, which is the value found for globular objects or globular aggregates of the conducting polymers dispersed in an insulating matrix in three dimensions.

The Heeger and co-workers' report is of great significance since it provides a method to process the intractable polyaniline by protonating the polyaniline with appropriate functionalized protonic acid and thus render the resulting polyaniline soluble in common organic solvents. The most significant discovery is that *fc* can be reached at such a low value. This approach has been used in many subsequent studies.

3. PANI-CSA/PMMA processed in m-cresol

Reghu et al. [12] produced polyaniline composites by blending PANI-CSA in insulating polymethylmethacrylate (PMMA), in which m-cresol was used as the solvent. It was proposed that the formation of a self-assembled network of the PANI-CSA in the PANI-CSA/PMMA composites produced extremely low *fc* value of 0.003 (0.3 %). The composites exhibited a continuous increase of conductivity with filler content, while retaining the mechanical properties of the PMMA.

Polyaniline-camphor sulfonic acid solutions were prepared by dissolving the PANI emeraldine base and CSA in m-cresol. This solution was then mixed in the appropriate ratio with a solution of PMMA in m-cresol. Film thickness of 20–60 μm were obtained by casting the blend solutions onto a glass plate. After drying at 50°C in air for 24 hours, the films were then peeled off the glass substrate to provide a freestanding film for use in the transport measurements. The molecular weight of PMMA used was kept low to permit a greater mobility of the macromolecules during the process of liquid-liquid phase separation. This enhances the diffusion of PANI-CSA in PMMA and facilitates the self-assembled network of PANI-CSA in PMMA.

Figure 4(a) and 4(b) shows the transmission-electron microscopy micrographs of the PANI-CSA/PMMA composites with 0.005 and 0.0025 volume fractions, respectively. The details of the PANI-CSA network can be seen clearly. These figures show the scenario imagined for a percolating medium with " links" (PANI-CSA fibers), " nodes" (crossing points of the links), and "blobs" (dense, multiply connected regions). The specimen containing 0.005 PANI-CSA has numerous links, with diameters of about 100-500 Å, which are clearly visible; while the 0.0025 specimen has few links between the nodes and blobs. Thus, the formation of conducting networks depends on the PANI-CSA content.

The relationship between conductivity and volume fraction of PANI-CSA is shown in Table 4 and Figure 5(a). This relationship is critically dependent on the distribution of the links, nodes, and blobs. The distribution is influenced by the molecular weight of PANI and PMMA, and the process parameters such as the viscosity of the polyblend concentration, the solvent, the drying temperature, preparation conditions, etc [12].

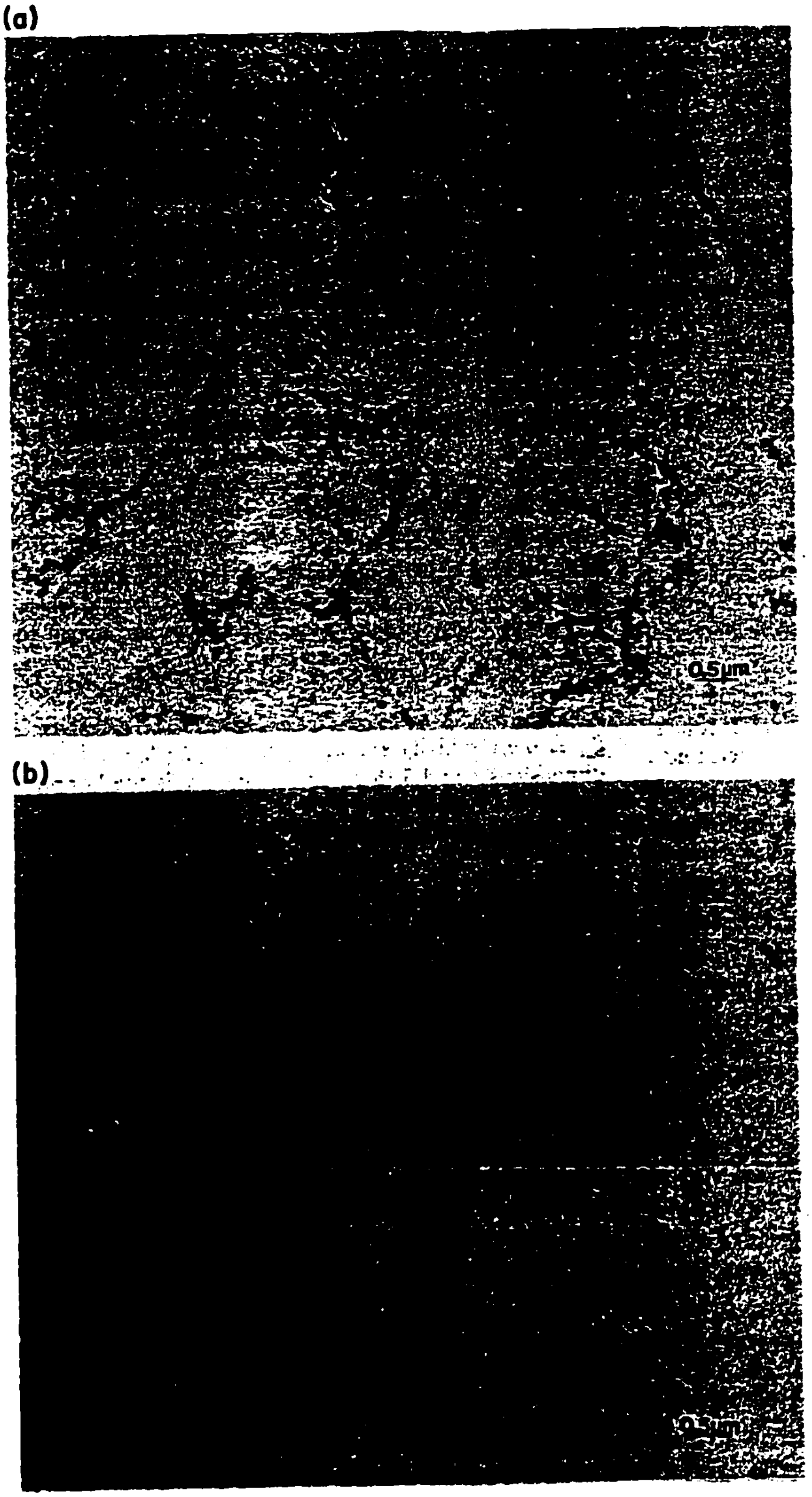


Figure 4. Transmission-electron micrographs of cast PANI-CSA/PMMA composite film containing (a) $f = 0.005$ and (b) $f = 0.0025$ PANI-CSA [From Reference 12].

To determine the percolation threshold more precisely, the data was treated using Equation (2) which is derived from the *scaling law of percolation theory* [13].

$$\sigma(f) \approx \sigma_T \times (f - f_c)^t \qquad (2)$$

In this Equation, σ_T is interpreted as the conductance for each basis unit and " t" is the critical exponent, which is the dimensionality of the transport mechanism (t equals 1 for two dimensions and t equals 2 for three dimensions).

Table 4. Room temperature conductivity (σ) and resistivity (ρ) ratio of PANI-CSA/PMMA composites at various volume fractions (f) of PANI-CSA [Ref. 12]

f	σ(300 K) S/cm	ρ(4.2 K)/ρ(300 K)
1	200–400	1.3–10
0.8	140	11
0.67	110	13
0.5	66	18
0.33	21	19
0.12	9	30
0.08	4	60
0.04	1.8	210
0.02	0.7	710
0.015	0.4	1830
0.012	0.22	2200
0.010	0.17	2600
0.008	0.12	
0.006	0.074	3780
0.004	0.014	5250
0.003	0.003	
0.002	0.0012	
0.001	10^{-4}	
0.0005	10^{-5}	

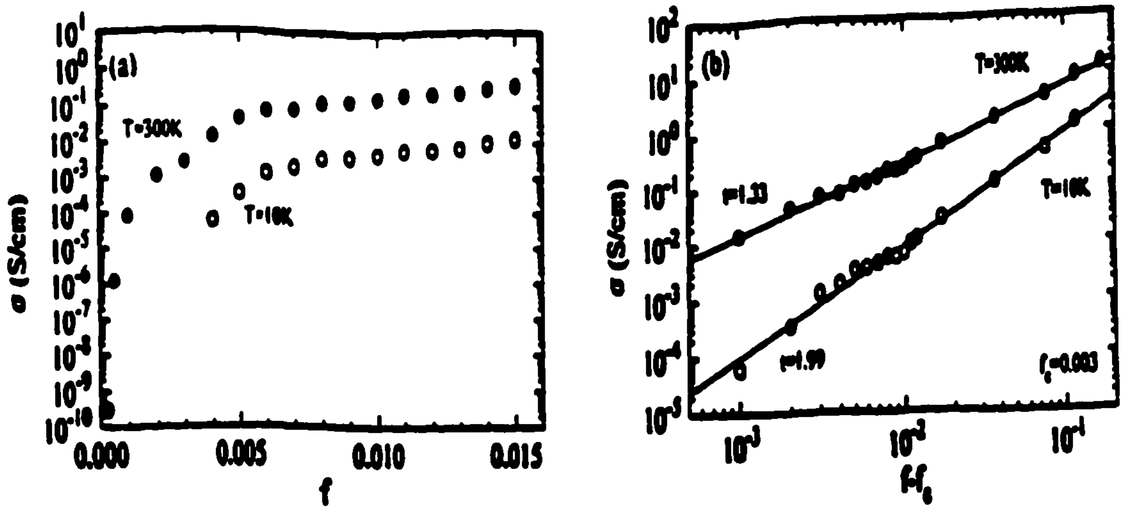


Figure 5. (a) Conductivity vs. volume fraction (*f*) of PANI-CSA at 300K and 10K; (b) log-log plot of conductivity vs. (f-f_c) at 300 K (•) and 10 K (O), where f_c = 0.003 [From Reference 12].

The fit to equation (2) is shown in Figure 5(b). At 10 K, *fc* equals 0.3± 0.05 % and t equals 1.99± 0.04, which agrees with the predicted universal t value of 2 for percolation in three dimensions. The authors fabricated the PANI-CSA/PMMA composites with an extraordinary low filler content and precisely determined *fc* values using TEM micrographs.

4. Nanoparticles of PANI-HCl by sonication

Banerjee and Mandal [14] fabricated the nanoparticles of PANI-HCl blended with poly(vinyl chloride)(PVC), polystyrene (PS), poly(methyl methacrylate)(PMMA), and poly(vinyl alcohol)(PVA). The composites were prepared by suspending preformed submicronic PANI-HCl particles in the solutions of matrix polymers and exposed to ultrasonics for 1.5 hours. The PANI-HCl colloid particles with surface-absorbed poly(vinyl methyl ether) (PVME) were prepared by oxidative dispersion polymerization of aniline in acidic (1.25 M HCl) water, where PVME was the steric stabilizer. The PANI-HCl particles containing 4.4 wt % PVME had a conductivity of 4.96 S/cm. Sonication reduced the particle sizes to less than 20 nm and thus provided many more interparticle contacts between the PANI-HCl particles. The films of this composite exhibit an extremely low fc value. The conductivity-composition profile for the films of the PANI-HCl/PVA composites is shown in Figure 6. The results for the specimens with very low fc values (smaller than 0.3 wt %) are plotted in the insert plot. As can be seen in Figure 6, there is no percolation threshold. However, in the same method taken by Heeger et al., the data used in Figure 6 were fitted to Equation (3) derived from the *scaling law of percolation theory*. The plot is shown in Figure 7.

$$\sigma(f) = C\times(f-fc)^{t} \tag{3}$$

This equation is a variation of equation 2 and the parameters are the same as those in Equation 2. The method yields a value of $3.6* 10^{-4}$ for fc and 1.96 for t.

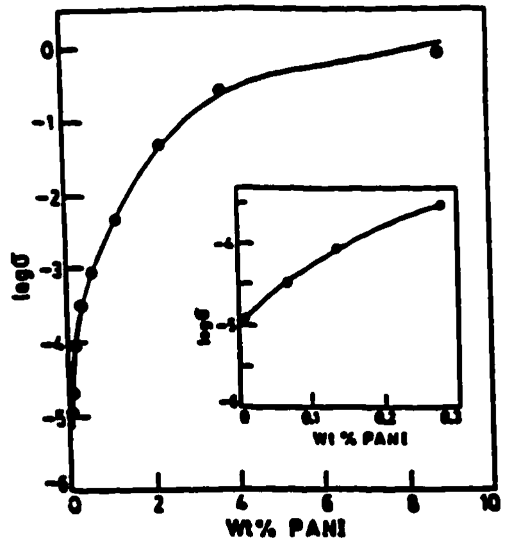


Figure 6. Plot of log conductivity vs. weight fraction of PANI-HCl in PANI-HCl/PVA [from reference 14].

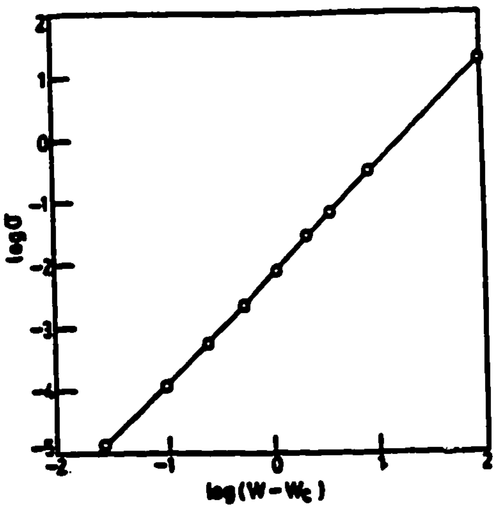


Figure 7. Plot of log (conductivity) vs. log (W-Wc), where W and Wc are the weight fraction and critical weight fraction of PANI-HCl, respectively [from reference 14].

A summary of the *fc* and t values for the various composites is listed in Table 5. In each case an extremely low percolation threshold (*fc*) value was obtained.

Table 5. *fc* and t for various blends of PANI-HCl with conventional polymers [Ref. 14]

Polymer Matrix	10^4*fc*	t
Poly(vinyl chloride) (PVC)	4.02	1.87
Polystyrene (PS)	4.19	1.91
Poly(vinyl acetate) (PVA)	3.18	1.94
Poly(methyl methacrylate) (PMMA)	2.14	1.89
Poly(vinyl alcohol) (PVA)	3.60	1.96

The information from the other literature reports with relevance to PANI processing is as follows. Conn et al. [15] prepared PANI-CSA/PVC composites by coating unplasticized PVC particles with PANI-CSA in m-cresol. The resulting particles were hot-pressed at 150°C and 28MPa to form a connective network of PANI-CSA in PVC. The percolation threshold was below 1 wt % of PANI-CSA. Yang et al. [16] prepared PANI/polypropylene composites by oxidative polymerization of aniline in biaxially stretched polypropylene microporous films with ammonium persulfate as the oxidant. The composite films are flexible, have tensile strength of 60–100 MPa and conductivities as high as 5-6 S/cm. Vikki et al. [9] reported an exceptionally high solubility of PANI-DBSA and PANI-CSA in a crystalline compound, 1,3-dihydroxylbenzene (i.e. resorcinol). Up to 20-30 wt % of PANI-DBSA and PANI-CSA can be dissolved in resorcinol at 200-220°C to form particle-free films as observed by optical microscopy. The conductivity of these polyaniline salts was not measured. Ruckenstein and Sun [17] reported two inverted emulsion pathways to prepare PANI/styrene-butadiene-styrene (SBS) composites. In method 1, the polymerization was proceeded by introducing an organic solution of aniline into an inverted emulsion containing the host polymer (SBS), an oxidant and a dopant. In method 2, the polymerization was proceeded by introducing an aqueous solution of an oxidant and a dopant into an inverted emulsion containing aniline and SBS host polymer. The PANI/SBS composites prepared by method 1 and 2 had conductivity as high as 0.35-0.48 S/cm and 2.9-2.8 S/cm, respectively. The *fc* values were reported to be between 9.63 and 13.1 wt % for the composites from method 1, and between 6.9 and 20.5 wt % for those from method 2. Method 2 was more successful, since the PANI-SBS composites prepared by this method had higher conductivity and better mechanical properties.

Laska et al. [18] prepared the thermally processable conducting polyaniline by protonation of the emeraldine base with diphenyl phosphate (DPHP). The PANI-DPHP is conductive and thermally stable at processing temperature up to 200°C. The composites of PANI-DPHP and plasticized PVC (PVC: tricrezyl phosphate = 100:40) were prepared by hot pressing. The materials had a low percolation threshold (6 wt % PANI-DPHP). In stead of producing polyaniline composites, Nguyen et al. [19] reported the synthesis and properties of water-soluble conducting polyaniline copolymers. The poly(aniline-*co*-N-(4-sulfophenyl)-aniline)(PAPSA) copolymers were synthesized by chemical polymerization. The copolymers were soluble in aqueous NH_4OH and had conductivities which varied with the molar fraction of the monomers. The fc values were not indicated in this article. The data from the article were treated using equation 3 and the fc value was 0.48. Nguyen and Diaz [20] prepared the poly(aniline-*co*-*o*-anthranilic acid) (PAA) copolymers which are soluble in aqueous alkaline solutions and in some organic solvents. The electrical conductivity of PAA copolymers decreases from the polyaniline value of 5.2 S/cm to the poly(*o*-anthranilic acid) value of 10^{-8} S/cm, depending on the monomer ratio. The fc value was not indicated in the article. The data from this article were treated using equation 3 and an fc value of 0.723 was obtained.

5. Conclusion

This literature survey reveals several reports in processing the polyaniline composites. However, the processing procedures were not described in detail in most articles. This is unfortunate because the processing conditions have a strong effect on morphology of interconnected networks near the conductivity percolation threshold and the overall conductivity-composition response. Thus, a large number of processing parameters can be varied to affect the resulting polyaniline composites, such as the choice of solvent, process temperature, the molecular weight of polyaniline and the polymer matrix, the viscosity of the polyblend solution, etc. More research on the processing of polyaniline composites is needed to obtain materials with desired properties in a reproducible manner.

Chapter III

Proposal

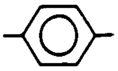
1. Hypothesis

The focus of this research is to verify the hypothesis that composites of the commercially available polyaniline, protonated by dodecylbenzenesulfonic acid (DBSA) which are processed in N-methyl pyrrolidinone (NMP) have a lower f_c than those processed in water. Secondly, composites which are processed in aqueous solutions instead of organic solvents have a distribution of particles which has a f_c value in the range of those of globular conducting particles dispersed in a non-conducting polymer matrix.

2. Approach

The relationship between conductivity (σ) and the volume fraction (f) of polyaniline in composites will be determined. The optimization of the process is not the main focus of this research. The effect of acidity on the conductivity of the resulting composites will also be explored.

2. 1 Process for polyaniline composites

Polyaniline available from Allied-Signal Inc. will be used to prepare the composites. This material consists of polyaniline polymer protonated by dodecylbenzenesulfonic acid (DBSA), which is one of the protonic acids proposed by Heeger [8], with $M^- = SO_3^-$ and R =  $C_{12}H_{25}$. PANI-DBSA is reported to be soluble in organic solvents like m-cresol and chloroform [8]. These two solvents have been widely used in processing PANI composites. N-methyl pyrrolidinone (NMP) has been reported to dissolve polyaniline and emeraldine base form [21], and hence we plan to use NMP to dissolve PANI-DBSA. Table 6 shows the volume fractions (f) of PANI-DBSA in the composites to be formulated, and blended with polyacrylic acid (PAA), polyvinyl acetate (PVA) in water, and with polyvinyl pyrrolidinone (PVP) in NMP and water individually.

The composites will be processed at room temperature. In the aqueous process, PAA and PVP are expected to be soluble, while PVA and PANI-DBSA are expected to be insoluble and suspended. The composites from this process are expected to have conductivity profiles which resemble those for the irregular particle fillers, since the polyaniline molecules will be "balled up" and there will be less interparticle contact. In NMP, both PANI-DBSA and PVP are expected to be soluble in NMP and the composites from this process are expected to have conductivity profiles which resemble those for the fiber fillers, because the polyaniline chains are swollen and more extended, thus producing much more interparticle contact, and a lower fc.

Table 6. List of polymers, solvents, and volume fractions (f) of PANI-DBSA in the composites to be prepared

Polymer Matrix	Process Conditions and Solvents	f of PANI-DBSA in Composites							
PVA	Dry Blend	0.10	0.14	0.15	0.20	0.25	0.30	0.35	0.40
PVP	Water	0.12	0.17	0.19	0.22	0.24	0.26	0.28	0.31
PAA	Water	0.10	0.18	0.20	0.22	0.25	0.28	0.30	0.34
PVP	NMP	0.10	0.14	0.16	0.19	0.21	0.24	0.26	0.29
PAA	Aqueous NaOH	0.30	0.34						

2.2 The effect of acidity on conductivity

One PANI-DBSA/PAA specimen will be processed in aqueous NaOH solution to determine the effect of acidity on the conductivity (the aqueous PAA solution has a pH of 2.5~3.0). If the conductivity is lowered, one or two more specimens will be processed. These composites are expected to have a lower conductivity since PANI-DBSA will be deprotonated to form the emeraldine base, which is insulating. This experiment will also demonstrate that the conductivity of the PANI-DBSA composites can be controlled by adjusting the pH of the formulation.

2.3 Measurements

2.3.1 Conductivity

The conductivity of each specimen in Table 6 will be measured to determine the relationships between conductivity and composition for each composite system. The critical volume fraction (fc) will be determined by applying the *scaling law of percolation theory* [13], which is Equation (3), where C is a constant and t is the critical exponent ($t \approx 1$ in two dimensions and $t \approx 2$ in three dimensions). The fc values of the PANI-DBSA/PVP composites processed in NMP and in water will be compared. The fc value of the former is expected to be smaller.

$$\sigma(f) = C\,(f - fc)^{t} \tag{3}$$

2.3.2 Distribution of Polyaniline

The distribution of PANI-DBSA in the composites will be inspected using a scanning electron microscope (SEM). The specimens will be cooled in liquid nitrogen and be manually fractured. The fractured specimens will then be coated with a layer of gold and used in SEM analysis. When NMP is used for processing, PANI-DBSA dissolves and forms "free" moving chains. During the drying step, when the solvent content is low, the PANI-DBSA chains become incompatible with the host polymer and this may result in some phase separation. The PANI-DBSA separates to produce a string-like network with long-range connectivity. This provides conductive paths for the composites and the formation of conducting networks at low *fc* values. When the process is carried out in water, the PANI-DBSA remains insoluble and retains its particle shape. In this case, higher *fc* values may be needed to produce a connective path for conductivity. The connectivity relies on the relative distances between PANI molecules, as in the case of globular fillers in the host polymers.

Chapter III

Experimental Procedures

1. Processing for PANI-DBSA composites

1.1 PANI-DBSA/PVA formulation

Commercial Elmer's glue (EG) which contains polyvinyl acetate (PVA), and PANI-DBSA from Allied Signal Inc. were used as received. Elmer's glue contains 44 % solids which are mostly PVA, while the rest is water plus additives. The PANI-DBSA powder was added to the glue and stirred gently to prevent the formation of bubbles. The mixture was then sonicated for 10 minutes. Sonication was adopted instead of mechanical mixing because the latter produces bubbles. Sonication also prevents the blend from sticking to the walls of the beaker and facilitates mixing by disintegrating the PANI-DBSA aggregates. A black, fudge-like mixture was formed. The blend was then cast onto a glass substrate and allowed to dry at room temperature for 24 hrs. Thickness of the films did not reduce significantly during drying. The formulations with higher PANI-DBSA content dried faster. For example, less than 2 hrs were needed to dry a specimen with 40 vol % PANI-DBSA (specimen 71). Some of the formulations had bubbles and the bubbles were removed by tapping. The bubbles rose to the surface of the films and escaped spontaneously with tapping. The amounts used in each preparation are listed in Table 7. The values of f were calculated using the weights of PANI-DBSA and PVA only. The specific gravities used for the calculation of f values are 1.07 g/cm^3 for PVA and 1.36 g/cm^3 for PANI-DBSA.

Formulations with $f \geq 0.25$ were too viscous to process (specimen 49), unless a small amount of water was added (specimen 67). These formulations could not be left standing in ambient for more than 60 minutes since they would lose water and become too dry to be cast. The films from the formulations with $f \geq 0.346$ cracked during drying in ambient. These films were covered with a funnel to reduce the evaporation rate of the water. The top end of the funnel was covered with Parafilm with a 1.5mm hole. The drying time with the funnel cover was about 24 hrs and the cracks were absent in the film from the formulation with $f=0.346$ (specimen 66a). For the films from the formulations with $f=0.4$, the cracks were not removed with a funnel cover.

Table 7. Compositions of the PANI-DBSA/PVA formulations

No.	f	PANI-DBSA, g	PVA Glue, g	PVA, g	H_2O, ml	Solvent/Solids Ratio
82	0.082	0.06	1.23	0.541	0	0
46	0.10	0.10	1.61	0.708	0	0
74	0.10	0.10	1.61	0.708	0	0
75	0.11	0.11	1.59	0.700	0	0
76	0.12	0.12	1.57	0.691	0	0
77	0.13	0.13	1.56	0.686	0	0
78	0.14	0.14	1.54	0.678	0	0
47	0.15	0.15	1.52	0.669	0	0
48	0.20	0.20	1.43	0.629	0	0
49	0.25	0.25	1.34	0.590	0	0
67	0.25	0.25	1.34	0.590	0.5	0.595
68	0.30	0.30	1.25	0.550	0.5	0.588
68a	0.30	0.30	1.25	0.550	0.5	0.588
66	0.346	0.35	1.18	0.519	1.0	1.151
66a	0.346	0.35	1.18	0.519	1.0	1.151
71	0.40	0.40	1.07	0.472	1.0	1.147
71a	0.40	0.40	1.07	0.472	1.0	1.147

Notes: 1. Specimens with remarked "a" were dried under a funnel.

1.2 PANI-DBSA/PVP formulation in water

Polyvinyl pyrrolidinone (PVP) from Scientific Polymer Product Co. was used as received. PVP was first dissolved in a designated amount of water. The resulting solution had a pH of 4.5~5.0. The amount of water used was equal to 1.0~1.5×(the total weight in grams of PANI-DBSA and PVP). Thus, the solvent/solids ratios are 1.0 to 1.5. The amounts used in each of the preparations are listed in Table 8. The values of *f* were calculated using the weights of PANI-DBSA and PVP only. The specific gravities used for the calculation of *f* values are 1.25 g/cm^3 for PVP and 1.36 g/cm^3 for PANI-DBSA. When the PVP/water mixture was stirred intensely, a lot of bubbles were produced. However, these bubbles would vanish quickly. The solution was then left standing in ambient for 5 minutes to allow the trapped bubbles to escape. PANI-DBSA powder was then added to the aqueous PVP solution and the blend was sonicated for 15 minutes to disperse PANI-DBSA particles. The PANI-DBSA powder disintegrated quickly in the aqueous PVP solution. The blend was then stirred gently and periodically during sonication to prevent bubble formation. Bubbles were always formed on the walls of the beaker during sonication. It was hard to determine if the PANI-DBSA particles had been dissolved, since no PANI-DBSA particles were observed in the PANI-DBSA/PVP solution. A homogeneous, black PANI-DBSA/PVP blend was formed after sonicating for 15 minutes. The blend was then cast on the glass substrates. Tapping the glass substrates helped remove the few bubbles remaining in the films. The specimens were dried at room temperature for 24 hrs. The thickness of the films was not reduced significantly during drying. Formulations with higher PANI-DBSA content dried faster.

The films from the formulations with $f \geq 0.351$ cracked during drying in ambient. These films were covered with a funnel to reduce the evaporation rate of the water. The top end of the funnel was covered with Parafilm with a 1.5mm hole. The drying time with the funnel cover was about 48 hrs and the cracks were absent in the films from the formulations with $f \leq 0.365$ (specimens 117, 69).

Table 8. Compositions of the PANI-DBSA/PVP formulations

Specimen No.	f	PANI-DBSA, g	PVP, g	H2O, ml	Solvent/Solids Ratio
53	0.063	0.02	0.280	0.4	1.333
55	0.116	0.04	0.280	0.4	1.250
56	0.145	0.05	0.271	0.4	1.246
57	0.170	0.059	0.264	0.4	1.238
58	0.194	0.10	0.383	0.7	1.449
79	0.217	0.11	0.365	0.7	1.474
59	0.243	0.125	0.359	0.6	1.240
59a	0.243	0.125	0.359	0.6	1.240
72	0.262	0.135	0.350	0.6	1.237
73	0.277	0.285	0.684	1.0	1.032
60.1	0.292	0.15	0.335	0.5	1.031
116	0.310	0.20	0.410	0.7	1.148
61.1	0.332	0.20	0.370	0.6	1.053
61.1a	0.332	0.20	0.370	0.6	1.053
117	0.351	0.20	0.340	0.8	1.481
69	0.365	0.20	0.320	0.8	1.538
62	0.392	0.4	0.57	1.5	1.55

Note: 1. 59a and 61.1a were cast after 20 min of intense mechanical mixing.

1.3 PANI-DBSA/PAA formulation in water

Polyacrylic acid (PAA) purchased from BFGoodrich Specialty Chemicals Co. was used as received. PAA is soluble in water, but is not as easily dissolved as PVP. The amounts used in each formulation are listed in Table 9. The values of f were calculated using the weights of PANI-DBSA and PAA only. The specific gravities used for the calculation of f values are 1.40 g/cm^3 for PAA and 1.36 g/cm^3 for PANI-DBSA. While several different processes were tried, only the following process produced the most homogeneous distribution of PANI-DBSA and eliminated the formulation of bubbles in the blend solution. The other processes will be discussed in Appendix B. PANI-DBSA and PAA powder were dry mixed manually and the dry blend was sonicated for10 minutes. Sonication keeps the powder from clinging to the beaker and better pre-mixing can be achieved. The designated amount of water was then added to the dry blend. Some PANI-DBSA/PAA aggregates started sticking to the beaker wall. They were scrapped off and the mixture was sonicated for additional 30 minutes. It was found that using glass beakers during sonication was more effective than using plastic beakers in disintegrating the PANI-DBSA/PAA aggregates.

A small amount of acetone was added during the intense mechanical mixing to minimize bubble formation and the beakers were covered. This reduces the surface tension of the solution. Mechanical mixing with a magnetic stirrer was introduced gently in the beginning to prevent bubble formation. Some bubbles appeared, but vanished gradually. After about 15 minutes, mechanical mixing could be intensified without producing bubbles. The mixing time increased from 45 minutes for the formulations with

f=0.419, to 2 hrs for those with f=0.05. This is a result of the increase in viscosity of the formulation. The solution appeared uniformly dark green and opaque. It did not have large suspended green PANI-DBSA particles, as was observed with the other procedures in Appendix B. The homogeneity of the final blend solution was judged by the size of PANI-DBSA particles, which were almost the same size as the original PANI-DBSA powder, 3~100 μm. The solution was cast on the glass substrates. The thickness of the films was between 750 and 1200 μm (wet) and 15~65 μm after drying at room temperature for 12 hrs. This was close to the range of film thickness in the literature presented by Heeger et al. [Ref 12].

Table 9. Compositions of the PANI-DBSA/PAA formulations

No.	f	PANI-DBSA, g	PAA, g	H_2O, ml	Acetone, ml	Solvents/Solids Ratio
81a	0.05	0.03	0.57	18	6.5	40.833
106	0.075	0.03	0.38	12	3.0	36.585
41	0.103	0.04	0.36	10	4.0	35.000
120	0.154	0.06	0.34	11.5	3.0	36.250
121	0.178	0.04	0.19	6.5	2.0	36.957
105.2	0.205	0.05	0.20	7.0	2.5	38.000
104.3	0.222	0.05	0.18	6.5	1.0	32.609
103.2	0.255	0.05	0.15	5.0	1.0	30.000
100	0.279	0.06	0.16	6.6	1.0	34.545
102.2	0.306	0.06	0.14	5.0	1.0	30.000
101.3	0.34	0.06	0.12	4.5	1.0	30.556
42	0.36	0.06	0.11	5.0	1.0	35.294

1.4 PANI-DBSA/PVP formulation in NMP

N-methyl pyrrolidinone (NMP) from Aldrich Chemical Co. was used as received. Both PANI-DBSA and PVP could be dissolved in NMP. Selection of the amount of NMP to be used became a crucial problem in processing. PANI-DBSA was first dissolved in NMP. PVP was added to the solution with gentle stirring. The solution was sonicated for 20 minutes and then cast on the glass substrates. The films were dried at room temperature for one to three weeks, depending on both the solvent/solute ratios and *f*. In general, the drying time increased as the solvent/solute ratio or PANI-DBSA content decreased. The amounts used in each preparation are listed in Table 10. The *f* values were calculated using the weights of PANI-DBSA and PVP only. The specific gravities used for the calculation of the *f* values are 1.40 g/cm^3 for PVP and 1.36 g/cm^3 for PANI-DBSA.

Since PANI-DBSA was soluble in NMP, the amount of NMP used was expected to have substantial effects on conductivity and processibility. Specimens with the same *f* and different solvent/solids ratios were prepared. As shown in Table10, specimens labeled with an asterisk, "*", that had smaller solvent/solids ratios took about 20 days to dry, while the specimens with the same *f* value but a larger solvent/solids ratio dried in about 10 days. Specimen 88.1 was too viscous to process, and more NMP was added to process adequately (specimen 88). The determination of the amount of NMP needed to produce the best film conductivity will be discussed in the next chapter.

Table 10. Compositions of the PANI-DBSA/PVP formulations in NMP

Specimen No.	*f*	PANI-DBSA, g	PVP, g	NMP, ml	Solvent/Solids Ratio
84	0.048	0.03	0.546	0.7	1.22
113.2	0.061	0.04	0.57	0.8	1.31
113.1	0.061	0.04	0.57	1.1	1.80
112	0.097	0.05	0.43	0.8	1.67
111	0.121	0.06	0.40	0.8	1.74
110	0.144	0.075	0.41	0.8	1.65
*** 94**	**0.145**	**0.15**	**0.813**	**1.0**	**1.04**
109	0.163	0.085	0.40	0.8	1.65
*** 93**	**0.165**	**0.17**	**0.79**	**1.0**	**1.04**
108.1	0.195	0.10	0.38	1.4	2.92
*** 92**	**0.195**	**0.20**	**0.76**	**1.0**	**1.04**
107.1	0.217	0.22	0.73	3.0	3.16
*** 91**	**0.217**	**0.22**	**0.73**	**1.0**	**1.05**
90	0.242	0.125	0.36	1.1	2.27
89	0.262	0.135	0.35	1.1	2.27
88.1	**0.274**	**0.14**	**0.34**	**0.82**	**1.71**
88	0.274	0.14	0.34	1.2	2.50
87	0.292	0.15	0.35	1.2	2.40
85	0.332	0.20	0.37	1.7	2.98

Note: Specimens labeled with asterisks, "*", have smaller NMP/PANI-DBSA ratios than the corresponding specimens with the same *f*.

1.5 PANI-DBSA/PAA composites formulation in aqueous NaOH solution

The purpose of this processing was to determine the effect of acidity on the conductivity of the resulting PANI-DBSA composites. Aqueous PAA solution has a pH of 2.5~3.0, which is good for conducting PANI-DBSA salts, since the conductivity of PANI-DBSA decreases with alkalinity. Aqueous 5 wt % NaOH solution was prepared by dissolving 1 g NaOH in 19 g water. PANI-DBSA and PAA powder were mixed as described previously (p. 31). Water and aqueous NaOH solution were added to the dry blends and the mixture was sonicated for 30 minutes. Table 11 lists the quantities used in the formulations. The amount of NaOH (aq) used was half the equivalence of PAA. Acetone was added to the mixture with the beaker covered and then mechanical mixing was applied. The solution was then cast on glass substrates and allowed to dry at room temperature for 24 hrs.

Table 11. Compositions of the PANI-DBSA/PAA formulations in NaOH (aq)

Specimen No.	114.2	115
f	0.306	0.36
PANI-DBSA, g	0.06	0.06
PAA, g	0.14	0.11
H2O, ml	14.25	11.4
Acetone, ml	2.0	0.5
5 wt % NaOH, ml	0.79	0.61
Solvent/Solids ratio	62.63	59.75
Mixing Time, hr	1.5	0.75

2. Film thickness and conductivity measurement

The thicknesses of PANI-DBSA/PVA and PANI-DBSA/PVP films were measured using calipers. The measurement was made at four different locations and the minimum and maximum values were recorded. The PANI-DBSA/PAA films were thinner and their thicknesses were measured using a TENCOR, Alpha-Step 200. An Alpha-Step printout indicating the thickness of the PANI-DBSA/PAA film with f=0.205 (specimen 105.2) is shown in Appendix A. The resistivities were measured using a four-probe MAGNE-TRON (Model M-700) instrument. The instrument can measure resistivities up to 10^7 Ω*cm. The initial readings of resistivity showed a large variation, which then settled to a minimum value after 1~2 minutes. These readings were recorded.

The resistivity readings were made at four or five different locations for each specimen. Arithmetic average of the resistivities was taken as the average resistivity for each specimen.

3. Scanning electron microscope (SEM) analysis

A HITACHI model S-520 scanning electron microscope was used to inspect the distribution of PANI-DBSA in the composites. Specimens with dimensions of one square inch were fractured after cooling in liquid nitrogen. The fractured specimens were mounted and sputtered with a very thin film of gold in vacuum before each SEM analysis.

Chapter IV

Results and Discussion

1. Conductivity and *fc* of PANI-DBSA composite films

1.1 PANI-DBSA/PVA formulation

The films were black, opaque and had a rough surface. The adhesion of the films to the slides was strong. The films were difficult to scrape off. The films with $f \geq 0.4$ cracked during the drying step, whether they were dried in the ambient or covered with a funnel. The PANI-DBSA/PVA films had good material properties. They were stronger and tougher than the PANI-DBSA/PAA films, and less brittle than the PANI-DBSA/PVP films. The resistivities of the PANI-DBSA/PVA composites are listed in Table 12, where f is the volume fraction of PANI in the composites. The variation in the resistivity values had percentage errors between 5 %– 20 % for all the measurement. Comparing specimens 67 and 49 in Table 12 revealed that the addition of water to facilitate the processing (specimen 67) did not affect the resistivity. Comparing specimens 68 and 68a revealed that reducing the water evaporation rate during the drying step resulted in a small increase in resistivity. Reducing the evaporation rate of water does not significantly affect the resistivities of the film when f is less than 0.34. Good PANI-DBSA/PVA films resulted when the PANI-DBSA content was less than 40 vol %. It is reported that with metal particles, f should not exceed 25 vol % to maintain reliable material properties [4]. Film 71a cracked during the drying step. This indicated that reducing the evaporation rate of solvent did not prevent the films with $f \geq 0.4$ from cracking. The resistivities of these films were not measured.

Table 12. The resistivities (ρ) of the PANI-DBSA/PVA composite films

No.	f	Thickness, μm	Resistivity, Ω*cm	Average ρ, Ω*cm	Average σ, S/cm
82	0.082	228~280	2.15, 2.71, 3.05 (E+6)	2.6± 0.32 (E+6)	3.79E-7
46	0.10	457~482	0.52, 0.61, 0.74 (E+6)	6.2± 0.78 (E+5)	1.61E-6
74	0.10	482~520	0.45, 0.6, 0.54, 0.8 (E+6)	5.9± 1.0 (E+5)	1.67E-6
75	0.11	600~660	0.03, 0.06, 0.07, 0.08 (E+6)	6.0± 1.5 (E+4)	1.67E-5
76	0.12	430~520	4.5, 5.2, 3.1, 5.0 (E+3)	4.5± 0.68 (E+3)	2.24E-4
77	0.13	560~635	374, 377, 473, 465	422± 46.8	2.37E-3
78	0.14	610~635	236, 237, 282, 286, 322	273± 28.9	3.67E-3
47	0.15	457~508	74.2, 78.3, 67.7, 68.5	72± 4.1	1.39E-2
48	0.20	381~508	21.8, 21.5, 22.1, 22.7	22± 0.38	4.54E-2
49	0.25	457~470	8.3, 7.6, 7.4, 9.2, 8.1, 7.9	8.1± 0.45	1.24E-1
67	0.25	431~482	6.5, 6.7, 7.4, 7.3, 8.3, 9.2	7.6± 0.79	1.32E-1
68	0.30	228~305	2.6, 2.9, 3.4, 3.6	3.1± 0.38	3.20E-1
68a	0.30	254~280	4.6, 5.3, 6.1, 4.3	5.1± 0.63	1.97E-1
66	0.346	152~203	N/A	N/A	N/A
66a	0.346	152~228	1.2, 1.3, 1.5, 1.8, 2.0, 2.3	1.7± 0.35	5.94E-1
71	0.40	130~150	N/A	N/A	N/A
71a	0.40	127~140	N/A	N/A	N/A

Note: 1. Specimens with remarked "a" were dried in a funnel.
2. "N/A" means no measurement was taken as a result of cracks of the films.

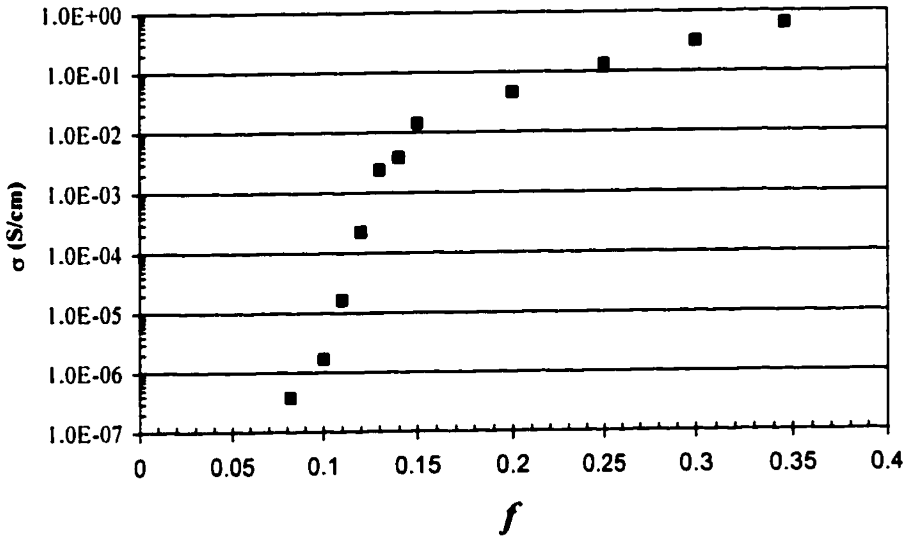


Figure 8. Plot of conductivity vs. f for the PANI-DBSA/PVA composite films

The average conductivity values (σ) for each PANI-DBSA/PVA composite were plotted against f in Figure 8. The plot shows that the films had a rather high residual conductivity at low f values, possibly due to the presence of ionic additives or a high moisture retention in the films. A value of 0.1 for fc was estimated using the beginning of the rise in the curve. On the other hand, a value of 0.11 was estimated using the center of the rise in the curve. This second method attempted to correct for the residual conductivity. The data were treated using the scaling law of percolation theory ($\sigma = C\times(f\text{-}f_c)^t$) [13]. There was a good agreement between the data and the line with R^2=0.98. As can be seen in Figure 9, fc and t were found to be 0.113 and 2.00, respectively. The value of experimental critical exponent is very close to the theoretical t value of 2 for a three-dimension transport mechanism [13]. The value of fc equal to 0.113 agrees with the value from Figure 8 when estimated using the center of the rise in the curve. Thus, the letter method will be used in the subsequent treatments to estimate fc from the σ versus f plots. The fc value for 0.113 is smaller than the value of 0.16 reported in the literature for globular conducting fillers in bulk polymer matrix [22]. It is, however, much larger than the value 0.0003 reported for the PANI-CSA/PMMA composites [12]. This is not surprising since there are several differences between the composites. The conducting polymer used in reference 12 was PANI-CSA. This study used PANI-DBSA. PANI-CSA was used as a liquid which dissolved and then formed a string-like, phase separated conducting network during the drying step. In this study, the PANI-DBSA is dispersed and not dissolved. Thus the PANI-DBSA polymer chains remained localized in particles. The PANI-DBSA particle kept the globular shape throughout processing.

Thus, the higher value *fc* for the PANI-DBSA composite is not unreasonable. Secondly, unlike the literature reported, there was no evidence of additional phase separation, aggregation or string formation during the drying step. In stead, the distribution remained uniform in the PVA. This resulted in higher *fc*.

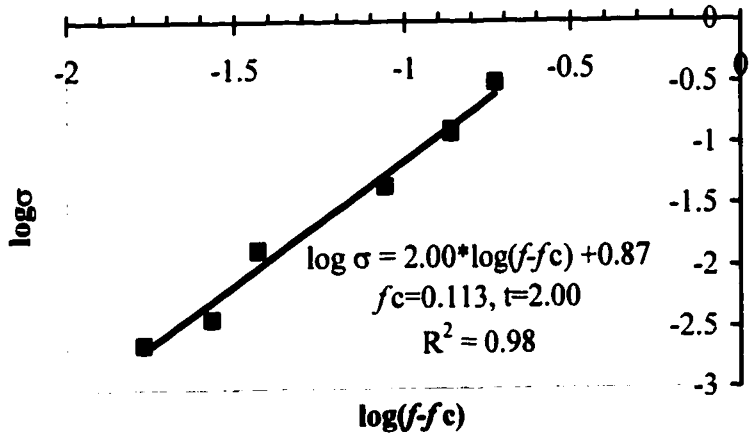


Figure 9. Plot of logσ vs. log (*f*-*fc*) for the PANI-DBSA/PVA composite films

1.2 PANI-DBSA/PVP formulation in water

The films were black and had a smooth surface. The adhesion of the films to the slides was strong. The films were hard to scrape off. The appearance of the PANI-DBSA/PVP films, whether formulated in NMP or in water, was interesting. The higher the PVP content, the brighter, and shiner the appearance of the film. There was a dramatic change of the appearance of the film at *fc*, which helped locate *fc* by visual inspection. The films with *f*>*fc* appeared dull and opaque. The films with *f*<*fc* appeared shiny and glossy. The same was observed with the PANI-DBSA/PVP films formulated in NMP.

The resistivities of the PANI-DBSA/PVP composites formulated in water are listed in Table 13. The effectiveness of the mixing was assessed by comparing the resistivities of films 59a and 61.1a, which had additional mechanical stirring for 20 minutes, with films 59 and 61.1, respectively. The resistivities were in close agreement, indicating that the processing produced a homogeneous blend, even without the mechanical stirring.

Table 13. The resistivities (ρ) of the PANI-DBSA/PVP composite film formulated in water

No.	*f*	Thickness, μm	Resistivity, Ω*cm	Average ρ, Ω*cm	Average σ, S/cm
53	0.063	101~127	>1.0E+7	>1.0E+7	<1.0E-7
55	0.116	330~342	>1.0E+7	>1.0E+7	<1.0E-7
56	0.145	260	7.2, 5.89, 4.47 (E+6)	5.8± 0.92 (E+6)	1.71E-7
57	0.170	300	3.56, 3.5, 4.8 (E+6)	3.9± 0.56 (E+6)	2.53E-7
58	0.194	210	2.31, 1.96, 2.05 (E+6)	2.1± 0.14 (E+6)	4.75E-7
79	0.217	155	1.34, 1.19, 1.07 (E+6)	1.20± 0.09 (E+6)	8.33E-7
59	0.243	203~279	0.61, 0.63, 0.73 (E+6)	6.6± 0.49 (E+5)	1.52E-6
59a	0.243	229~254	0.57, 0.64, 0.71 (E+6)	6.4± 0.47 (E+5)	1.56E-6
72	0.262	310	0.16, 0.17, 0.21, 0.24 (E+6)	1.9± 0.30 (E+5)	5.13E-6
73	0.277	280	2.1, 2.4, 2.7, 1.9 (E+4)	2.3± 0.28 (E+4)	4.40E-5
60.1	0.292	290~350	3.45, 4.61, 3.86, 4.12 (E+3)	4.0± 0.36 (E+3)	2.49E-4
116	0.310	150~200	290, 340, 450, 410	372± 57.5	2.69E-3
61.1	0.332	230~300	41, 42, 33, 40, 44	40± 2.8	2.50E-2
61.1a	0.332	140~178	31, 45, 37, 39, 41	38± 3.7	2.59E-2
117	0.351	200~240	11,13,15,12,14	13± 1.2	7.69E-2
69	0.365	160~180	9.4, 8.9, 10.2, 11.0	9.9± 0.73	1.01E-1

Note: Specimens 59a and 61.1a were cast after introducing 20min intense mechanical stirring.

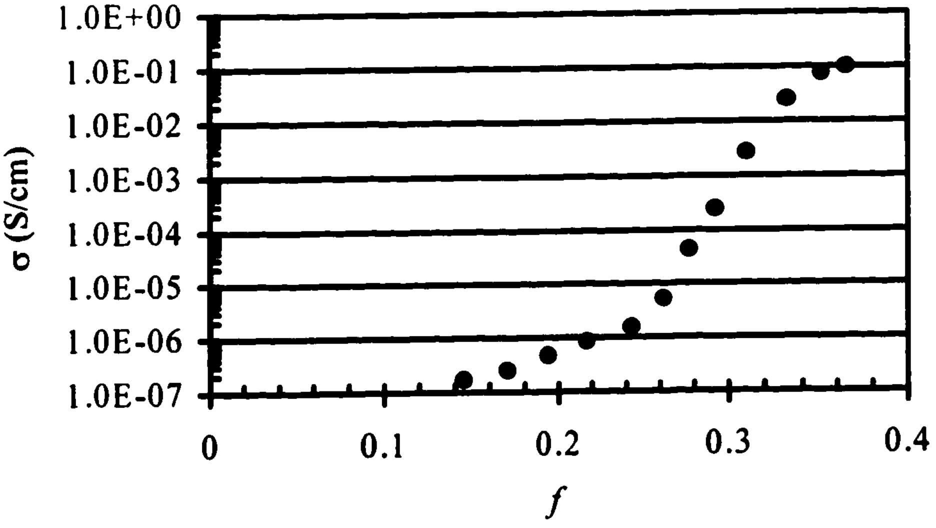


Figure 10. Plot of conductivity vs. *f* for the PANI-DBSA/PVP composite films formulated in water

The average conductivity value for each PANI-DBSA/PVP composite is plotted against *f* in Figure 10. From this plot, *f*c was estimated equal to 0.29 from the center of the rise in the curve.

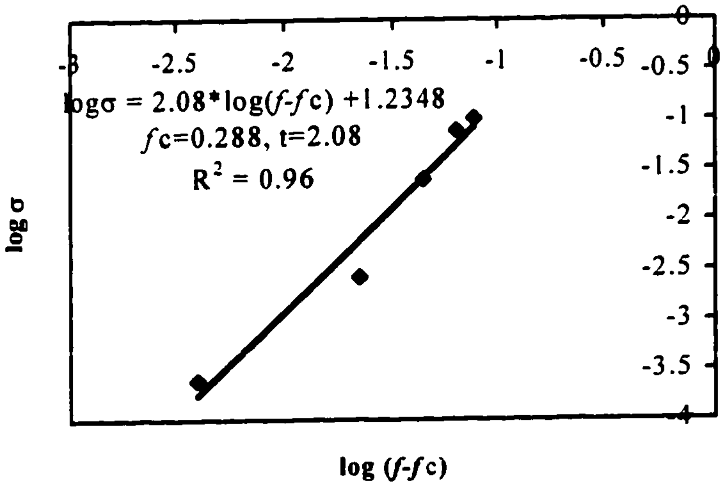


Figure 11. Plot of logσ vs. log (*f*-*f*c) for PANI-DBSA/PVP composite films formulated in water

The data was also treated using the scaling law of percolation theory ($\sigma = C\times(f-f_c)^t$) [13]. There was a good agreement between the data and the line with $R^2=0.96$. As can be seen in Figure 11, the fc and t were found to be 0.288 and 2.08, respectively.

The solvent/solids ratio is very important and affects both the processibility and performance of the films.

Table 14 shows two formulations with inappropriate solvent/solids ratios. When the ratio is less than 0.67, the formulation is too viscous to process (specimen10); and when it is greater than 2.46, the formulation is too dilute to be cast as a film (specimen 44).

Table 14. PANI-DBSA/PVP composite films with inappropriate solvent/solids ratios

No.	f	PANI-DBSA, g	PVP, g	H2O, ml	Solvent/Solids Ratio	Effects
10	0.093	0.372	3.35	2.5	0.672	Too viscous to process
44	0.061	0.04	0.57	1.5	2.459	Too dilute to cast

Good PANI-DBSA/PVP films resulted when the PANI-DBSA content was less than 39 vol %. It is reported that with metal particles, f should not exceed 25 vol % to maintain reliable material properties [4]. Six formulations with f equal to 0.39 were prepared using different processing conditions. These films cracked during drying and had poor mechanical properties. The films could not be improved by introducing intense mechanical stirring for 20 minutes (specimen 62.1), by slowing the drying process using a funnel to cover the specimens (specimen 69a, 70a), or by reducing the amount of water used (specimen 70, 70a).

Table 15. PANI-DBSA/PVP composites formulation in water with *f* equal to 0.39

No.	*f*	PANI-DBSA, g	PVP, g	H2O, ml	Solvent/Solids	Result
62	0.39	0.4	0.57	1.5	1.55	Cracking
62.1	0.39	0.4	0.57	1.5	1.55	Cracking
69	0.39	0.4	0.57	1.5	1.55	Cracking
69a	0.39	0.4	0.57	1.5	1.55	Cracking
70	0.39	0.4	0.57	1.0	1.03	Cracking
70a	0.39	0.4	0.57	1.0	1.03	Cracking

Note: Specimens 69a and 70a were dried in a funnel.

1.3 PANI-DBSA/PAA formulation in water

The films were green, dull and had a rough surface due to the presence of the PANI-DBSA particles. The films with lower PANI-DBSA content (f<0.205) were translucent and light green, while those with higher PANI-DBSA content were opaque and dark green. The thicknesses of the dry films in the molds were appropriately less than those of the formulations due to the large solvent/solids ratios in the specimen formulations. These films were relatively thinner than the other composites and contained a lot of visible PANI-DBSA particles. The adhesion of the films to the glass substrates was weakest among all composite films and they were a little brittle. The resistivities of the PANI-DBSA/PAA composites are listed in Table 16. The average conductivity value for each PANI-DBSA/PAA composite is plotted against f in Figure 12. From this plot, f_c was estimated equal to 0.225.

Table 16. The resistivities (ρ) of the PANI-DBSA/PAA composite films

No.	*f*	Thickness, μm	Resistivity, Ω*cm	Average ρ, Ω*cm	Average σ, S/cm
81a	0.05	50	>1.0E+7	>1.0E+7	<1.0E-7
106	0.075	56	>1.0E+7	>1.0E+7	<1.0E-7
41	0.103	40	8.12, 9.12, 8.94, 9.51 (E+6)	8.9± 0.40 (E+6)	1.12E-7
120	0.154	43	1.65, 2.07, 1.83, 2.33 (E+6)	1.9± 0.23 (E+6)	5.08E-7
121	0.178	39	0.79, 0.93, 1.03, 0.86 (E+6)	9.0± 0.78 (E+5)	1.11E-6
105.2	0.205	34	78, 90, 83, 86 (E+3)	8.4± 0.38 (E+4)	1.19E-5
104.3	0.222	33	21.5, 30.2, 31.4, 16.8 (E+3)	2.5± 0.58 (E+4)	4.06E-5
103.2	0.255	46	145, 156, 161, 148, 110	144± 13.6	6.94E-3
100	0.279	39	72, 92, 85, 75, 78	80± 6.5	1.24E-2
102.2	0.306	50	9.0, 7.3, 10.2, 8.7, 9.1	8.6± 0.69	1.16E-1
101.3	0.34	49	5.6, 5.1, 4.9, 4.6	5.0± 0.30	1.98E-1
42	0.36	43	2.5, 3.2, 3.3, 2.7, 3.7, 2.6	3.1± 0.40	3.21E-1

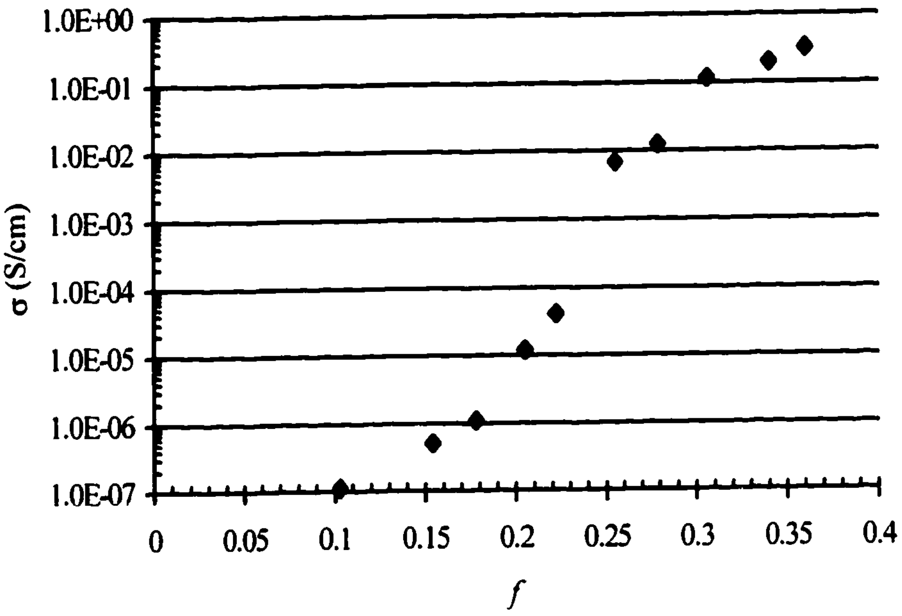


Figure 12. Plot of conductivity vs. *f* for the PANI-DBSA/PAA composite films formulated in water

The data was treated using the scaling law of percolation theory [13]. There was a good agreement between the data and the line with $R^2=0.98$. And as can be seen in Figure 13, the *fc* and t were found to be 0.220 and 2.10, respectively.

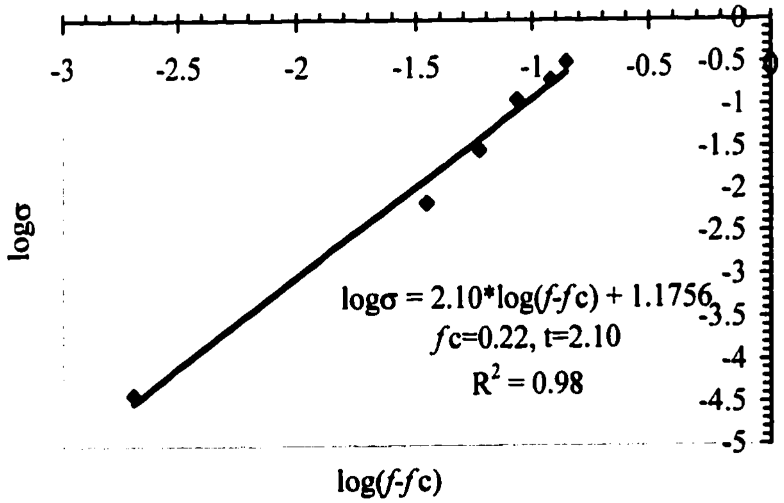


Figure 13. Plot of logσ vs. log (*f*-*fc*) for the PANI-DBSA/PAA composite films formulated in water

Several variations on the formulation procedure were conducted. These are labeled I~IV and are listed in Appendix B. Only process I produced a homogeneous distribution of PANI-DBSA with high conductivity and the absence of bubbles in the formulation. Whether acetone was blended with water prior to mixing with the dry blends, or after made no difference to the final solution. Acetone must be added during the mechanically mixing to make up for its evaporation. However, the amounts of water and acetone used, critically affected the processibility and the drying step. When the solvent was low, the final formulation was not homogeneous and had bubbles and agglomerates. When it was excessive, a liquid-liquid (water and acetone) phase separated at the edges of the films during the drying step, which resulted in poor appearance of the final films. It was difficult to determine the correct amount of each co-solvent needed for the formulation. Table 17 shows the effects of water/solids and acetone/solids ratios on the appearance of the films. It was found that more acetone was needed as f decreased. The water/solids ratio was between 22–30 for all formulations, while acetone/solids ratio was between 4.5–7 for $f > 0.205$ and between 7–10 for $f \leq 0.205$. However, when one of these ratios was high, the other one had to be low to prevent a dilution at the edges of the films (specimens103, 102). Table 18 shows that dilution of the formulation reduces the conductivity of the film.

Table 17. The effect of the solvent/solids ratio on the appearance for the PANI-DBSA/PAA composite films formulated in water

No.	f	PANI-DBSA, g	PAA, g	Water/Solids Ratio	Acetone/Solids Ratio	Film Appearances
80	0.05	0.03	0.57	24.2	7.5	Good
3	0.05	0.03	0.57	66.7	N/A	Can not be cast
81a	0.05	0.03	0.57	30.0	10.8	Edge dilution
41	0.103	0.04	0.36	25.0	10.0	Good
105.2	0.205	0.05	0.2	28.0	10.0	Good
39a	0.152	0.06	0.34	28.8	7.5	Good
39a	0.152	0.06	0.34	30.0	10.0	Edge dilution
104.3	0.222	0.05	0.18	28.3	4.3	Good
104.1	0.222	0.05	0.18	30.4	10.0	Edge dilution
103.2	0.255	0.05	0.15	25.0	5.0	Good
103	0.255	0.05	0.15	30.0	7.5	Edge dilution

Table 18. The effect of dilution on the resistivities (ρ) for PANI-DBSA/PAA composite films formulated in water

No.	*f*	Resistivity, Ω*cm	Average ρ, Ω* cm
103.2	0.255	145, 156, 161, 148, 110	144± 13.6
*103	0.255	1450, 1436, 1440, 1348, 1604	1455± 59.4
102.2	0.306	9.0, 7.0, 10.0, 8.0, 9.0	8.6± 0.88
*102	0.306	580, 740, 740, 640, 720	684± 59.2

Note: Specimens labeled with asterisks, "*", represented the dilute solution.

There was a question about the effect of acetone on conductivity. Table 19 lists some specimens which were processed without acetone. All the resistivities were much higher than those processed with acetone. Thus acetone improved the processibility and the conductivity of the resulting film.

Table 19. Resistivities (ρ) of the PANI-DBSA/PAA composite films processed without acetone

No.	*f*	Resistivity, Ω*cm	Average ρ, Ω*cm
104.3	0.222	21.5, 30.2, 31.4, 16.8 (E+3)	25± 5.83 (E+3)
*31	0.222	2.31, 1.87 (E+6)	2.1± 0.22 (E+6)
103.2	0.255	145, 156, 161, 148, 110	144± 114
*28	0.255	1830, 1840, 1070, 760, 470, 3000	1495± 728
102.2	0.306	9.0, 7.3, 10.2, 8.7, 9.1	8.9± 0.69
*25	0.306	348, 560, 655, 470	508± 99

Note: Specimens labeled with asterisks, "*", indicated formulations without acetone.

1.4 PANI-DBSA/PVP formulation in NMP

The films were black and thinner than those of PANI-DBSA/PVP formulations in water and had a smooth surface. The higher the PVP content, the brighter, more shiner the appearance of the film. There was a dramatic change of the appearance of the film at fc. The films with $f>fc$ appeared dull and opaque. The films with $f<fc$ appeared shiny and glossy. The process was conducted by first dissolving PANI-DBSA in NMP to insure that PANI-DBSA particles are fully dissolved. It was found that PVP dissolved in the PANI-DBSA/NMP solution, when sufficient NMP was used to dissolve PANI-DBSA.

Table 20 lists both the NMP/solids ratio and NMP/PANI-DBSA ratio. The amount of NMP needed to fully dissolve PANI-DBSA was determined by the latter ratio due to following observation. Comparing specimens 88.1 with 110 (or 109), the NMP/solids ratios were very close, but the NMP/PANI-DBSA ratio for the former was much smaller than for the latter. However, specimen 88.1 was too viscous to process, while specimens 109 and 110 were processible and the films had good conductivity. Thus, the NMP/solids ratio did not provide a good method for estimating the amount of NMP needed to fully dissolve PANI-DBSA. This was the reason why the NMP/PANI-DBSA ratio was used to determine the amount of NMP needed. When this ratio was less than 7, the PANI-DBSA particles did not totally dissolved, and the result was a lower σ value. This places the solubility of PANI-DBSA in NMP at around 14 %. The difference in the σ's was much as 1000 times as can be seen, by comparing specimens 107.1 and 91. As the ratio increased, the resistivity of the film decreased and was closer to the resistivity for fully dissolved PANI-DBSA, even though the PANI-DBSA particles were not fully dissolved. This was the case even when NMP appeared to partially dissolve PANI-DBSA. When NMP/PANI-DBSA ratio was larger than 27, the formulation was too dilute to be cast (specimen 131.1). The NMP/PANI-DBSA ratio affected the σs of the composites, as well as the required drying time. Specimens with a NMP/PANI-DBSA ratio> 7 had a drying time of approximately10 days, while those with a ratio< 7 had a drying time of approximately 3 weeks. The longer drying time may have result from trapped NMP due to the incomplete dissolution of PANI-DBSA.

Table 20. The effect of the NMP/PANI-DBSA and NMP/Solids ratios on the resistivity (ρ) of PANI-DBSA/PVP composite films formulated in NMP

No.	f	NMP/Solids Ratio	NMP/PANI-DBSA Ratio	Resistivity, Ω*cm	Average ρ, Ω*cm
88.1	0.274	1.70	**5.83**	N/A	N/A
* 91	0.217	1.05	**4.55**	760, 890, 910 (E+3)	853± 62 (E+3)
107.1	0.217	3.16	13.64	570, 520, 530, 498, 554	534± 22
* 92	0.195	1.04	**5.00**	850, 912, 1100 (E+3)	954± 97
108.1	0.195	2.92	14.00	1.1, 2.3, 2.1, 2.6, 2.7 (E+3)	2.1± 0.45 (E+3)
* 93	0.163	1.04	**5.88**	440, 381, 560 (E+3)	460±66 (E+3)
109	0.163	1.65	9.41	182, 143, 170, 133 (E+3)	157± 19
* 94	0.144	1.04	**6.67**	1.12, 1.34, 1.28, 1.01 (E+6)	1.2± 0.12 (E+6)
110	0.144	1.65	10.67	0.59, 0.60, 0.81, 0.77 (E+6)	6.9± 0.98 (E+5)
113.1	0.061	1.80	**27.5**	N/A	N/A
113.2	0.061	1.31	20.00	4.7, 4.2, 3.86, 3.79 (E+6)	4.1± 0.31 (E+6)

Note: 1. Specimens labeled with asterisks, "*", have smaller NMP/PANI-DBSA ratios than the corresponding specimens with the same f.

2. "N/A" represents no measurement was taken because of a highly viscous solution (specimen 81.1) or dilute formulation (specimen 113.1).

The resistivities of the PANI-DBSA/PVP composites formulated in NMP are listed in Table 21. The maximum PANI-DBSA content for producing good films was below 33.2 vol %. The average conductivity values for the PANI-DBSA/PVP composite formulated in NMP were plotted against f in Figure 14. From this plot, the f_c was estimated equal to 0.18.

Table 21. The resistivities (ρ) of the PANI-DBSA/PVP composite films formulated in NMP

No.	f	Thickness, μm	Resistivity, Ω*cm	Average ρ, Ω*cm	Average σ, S/cm
84	0.048	170	8.26, 9.14, 7.82, 8.84 (E+6)	8.5± 0.48 (E+6)	1.17E-7
113.2	0.061	190	4.7, 4.2, 3.86, 3.79 (E+6)	4.1± 0.31(E+6)	2.42E-7
112	0.097	135~150	2.12, 1.77, 1.83, 2.0 (E+6)	1.9± 0.13 (E+6)	5.18E-7
111	0.121	130	1.10, 0.98, 1.13, 0.95 (E+6)	1.04± 0.08 (E+6)	9.62E-7
110	0.144	130	0.59, 0.6, 0.81, 0.77 (E+6)	6.9± 0.98 (E+5)	1.44E-6
109	0.163	110~140	0.18, 0.14, 0.17, 0.13 (E+6)	1.5± 0.20 (E+5)	6.37E-6
108.1	0.195	85	1.1, 2.3, 2.1, 2.6, 2.7 (E+3)	2.1± 0.45 (E+3)	4.63E-4
107.1	0.217	70~80	570, 520, 530, 498, 554	534± 22.1	1.87E-3
90	0.242	140~150	124, 151, 101, 98, 146	124± 19.6	8.06E-3
89	0.262	120~130	44, 47, 38, 42, 40	42± 2.6	2.37E-2
88	0.274	170~200	33, 34, 24, 28, 30	29± 3.0	3.36E-2
87	0.292	150~170	23, 22, 20, 19, 21	21± 1.2	4.76E-2
85	0.332	100	N/A	N/A	N/A

Note: "N/A" represents no measurement was taken due to cracks in the films.

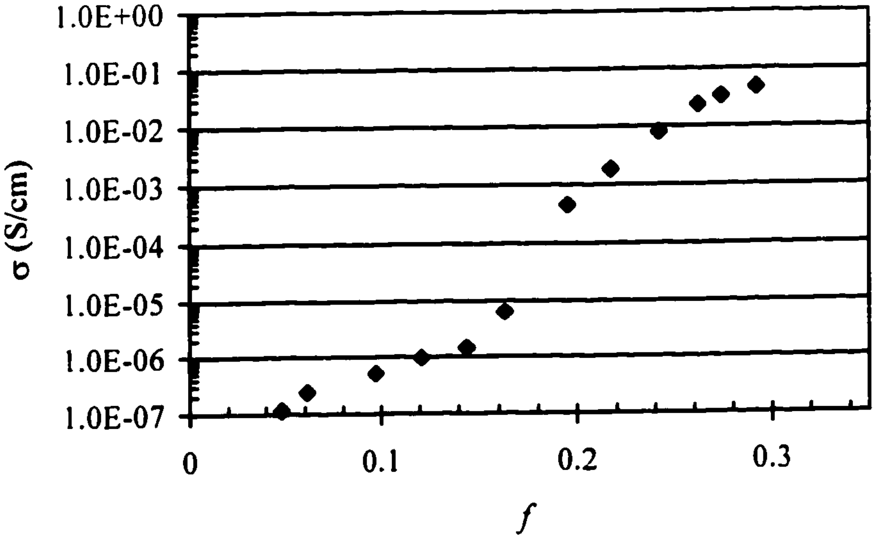


Figure 14. Plot of conductivity vs. *f* for the PANI-DBSA/PVP composite films formulated in NMP

The data was treated using the scaling law of percolation theory [13]. There was a good agreement between the data and the line with R^2=0.96. As seen in Figure 15, the *f*c and t were found to be 0.185 and 2.03, respectively.

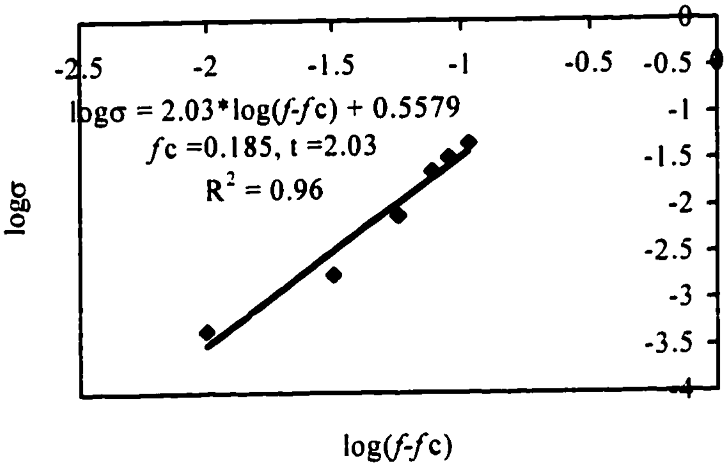


Figure 15. Plot of logσ vs. log (*f*-*f*c) for the PANI-DBSA/PVP composite films formulated in NMP

The *fc* value of the PANI-DBSA/PVP film formulated in NMP is smaller than in water. This may be because the dissolution of PANI-DBSA in NMP extends and separates the PANI-DBSA chains. One cluster of chains may contact another cluster. The chains become entangle with each other. The dissolution of PANI-DBSA in NMP also produced small, well-distributed PANI-DBSA particles in solution, which increased the chance of PANI-DBSA particles contacting each other. During the drying step, the PANI-DBSA polymer tended to go back to its originally globular shape, and the entangled clusters may retain their physical shape through drying step. All of this resulted in more contact between PANI-DBSA particles, and produced a lower *fc* value.

1.5 PANI-DBSA/PAA formulation in aqueous NaOH solution

The films were shallow black and dull, with a rough surface. The adhesion of the films to the slides was weaker than that for the other composites. The films were easily removed from the glass substrates. The thicknesses of the wet films still decreased dramatically during the drying step, as did the PANI-DBSA/PAA formulated in water, which is the result of the large solvent/solids ratios in specimen preparation. The addition of NaOH (half equivalence based on PAA content) partially neutralized PAA and was expected to enhance the mechanical properties of the films, and partially neutralized the PANI-DBSA emeraldine salt, transforming it to the PANI-DBSA emeraldine base form which is non-conducting. Indeed it was found that there was an increase in the resistivities, as seen in Table 22.

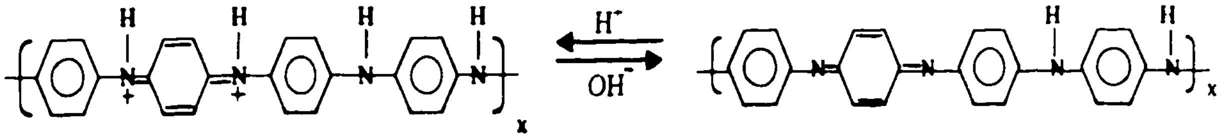
All particles aggregated after adding the aqueous NaOH solution. The solution was then very viscous and intractable. The amount of water used had to be increased by about a factor of three to make the solution processible. Table 22 lists the amount of water used to process the specimens with or without neutralization. The resistivities of the neutralized specimens were 3 orders of magnitude higher. There was no visible change in the mechanical properties of the resulting films. They were still easy to break, like those from the PANI-DBSA/PAA formulations in water, and the adhesion of the films to the slides was not changed.

Table 22. The effect of NaOH on the film resistivity (ρ)

No.	f	Water/Solids Ratio	Thickness, μm	Resistivity, Ω*cm	Average ρ, Ω*cm
102.2	0.306	22.5	50	9.0, 7.0, 10.0, 8.0, 9.0	8.6± 0.88 (E+6)
* 114.2	0.306	75.0	40	11.1, 12.3, 12.6 (E+3)	12.0± 0.6 (E+3)
42	0.36	29.41	43	2.5, 3.3, 2.7, 3.7, 2.6	2.9± 0.43
* 105	0.36	75.0	21~23	3.8, 4.3, 3.1, 2.5 (E+3)	3.4± 0.63 (E+3)

Note: Specimens labeled with asterisks, "*", were neutralized with 0.5 equivalent NaOH/1 equivalent PAA.

The increase in resistivity and the change in color, from green to black, plus the lack of change in the mechanical properties suggests that NaOH neutralizes mainly the PANI-DBSA, not the PAA. The chemical equation for neutralizing of PANI-DBSA is shown schematically below. The PANI emeraldine salt is deprotonated to emeraldine base in the basic environment.



Emeraldine Salt
"Conducting"

Emeraldine Base
"Insulating"

2. Scanning electron microscope (SEM) analysis

A scanning electron microscope was used to determine the particle size and distribution. The specimens used in the SEM analysis had f values near top of the rises in the plots of σ versus f. The size of the original P ANI-DBSA particles was between 3~100 μm, while that in the composites was mostly less than 15 μm. This showed that the distribution of the PANI-DBSA particles was uniformly. Additional micrographs, which are not included in this chapter, are listed in Appendix C.

2.1 PANI-DBSA/PVA formulation

Figure 16 shows the scanning electron micrograph of the surface of the PVA composite film (f=0.15). In this figure, the PANI-DBSA particles are the black dots, and the white area is the PVA and additives. The PANI-DBSA particles were mainly spherical, 6~8 μm in diameter, and distributed randomly in the composite. No large particles, clumps or aggregates of PANI-DBSA were observed, even though the size of the original PANI-DBSA particles is 3~100μm. The conducting paths were constructed by the random contacts between PANI-DBSA particles. There were no string-like phase separations. The small white particles may be the additives in the commercial PVA formulation.

The films were still intact after immersion in liquid nitrogen for 10 seconds. The films did not crack in vacuum, and had good adhesion to the glass substrates. Also, the films did not fuse or "move" during the SEM analysis of the film cross section.

Figure 16. Scanning electron micrograph for the top surface of the PANI-DBSA/PVA film, f= 0.15

2.2 PANI-DBSA/PVP formulation in water

Figure 17 shows the scanning electron micrograph of the cross sections of the PANI-DBSA/PVP composite film (f=0.322). The upper part of the figure is magnified 1.2 K, and the lower part (the insert) is for 2.4 K. The black particles in the figure are the PANI-DBSA polymers, and the white area is the PVP polymer. The PANI-DBSA particles were mainly spherical, 5~15 μm in diameter and distributed randomly in the composites. PANI-DBSA particles were not aggregate, and their distribution was quite uniform. As the case above, the connecting paths were based on the random contacts between PANI-DBSA particles.

Figure 17. Scanning electron micrograph for the fractured edge of the PANI-DBSA/PVP film formulated in water, f=0.332

The adhesion of the PANI-DBSA/PVP films to the slides was worse than that of PANI-DBSA/PVA films. The films cracked severely after immersion in liquid nitrogen for 10 seconds. The films also cracked in vacuum, which resulted from the evaporation of the residue solvent in the films. The films were fused slightly by the irradiating beam during the SEM analysis of the cross section of them. This showed that the films were thermally less stable.

2.3 PANI-DBSA/PAA formulation in water

Figure 18 shows the scanning electron micrograph of the cross sections of the PANI-DBSA/PAA composite (f= 0.255). As shown in this figure, the PANI-DBSA particles were distributed randomly in the composites and were 5~12 μm in diameter.

Figure 18. Scanning electron micrograph for the fractured edge of the PANI-DBSA/PAA film formulated in water, f= 0.255

The PANI-DBSA particles were not aggregated to form string-like phase separated connective networks. The films were intact after cooling in liquid nitrogen, and they were not fused by the irradiating beam during the SEM analysis of the cross section of the films.

2.4 PANI-DBSA/PVP formulation in NMP

Figure 19 shows the scanning electron micrograph of the surface of the PANI-DBSA/PVP composite film (*f*=0.195). The PANI-DBSA particles are the black dots, and the white area is the PVP polymer.

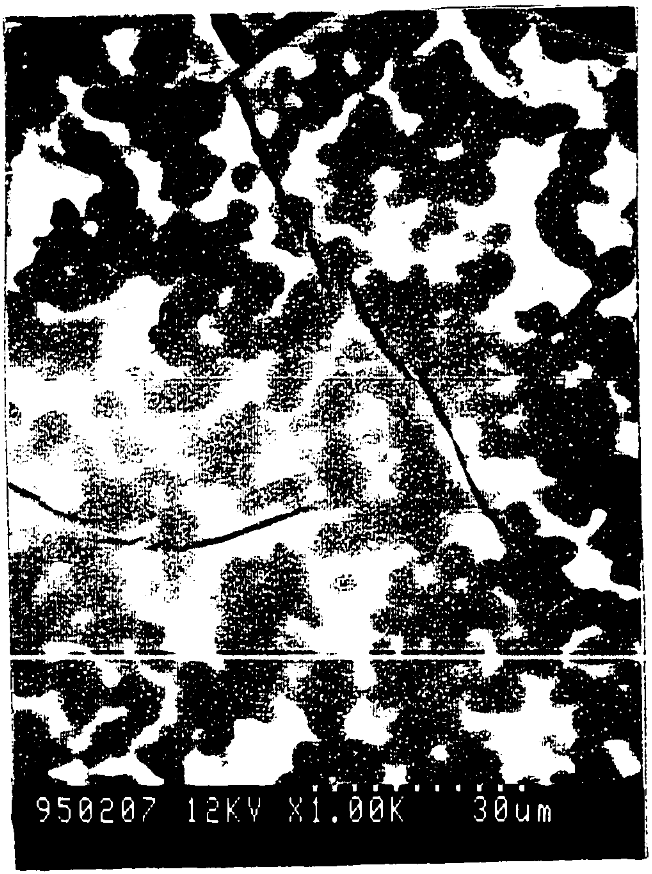


Figure 19. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in NMP, *f*=0.195

The connections between PANI-DBSA particles were more visible here than in the SEM of the other composites. The size of PANI-DBSA particles was approximate 3~8 μm. Some of the larger dark clusters in the photo are the aggregates of several small PANI-DBSA particles. These clusters may result from a little string-like phase separation. Some cracks were observed on the surface of the films, as shown in the Figure 26 and 29 in Appendix C. The films cracked and lifted off the glass substrate right after immersion in the liquid nitrogen. The films also cracked in vacuum, which should result from the evaporation of the residue solvent in the films. The films fused and lifted up from the glass slide during the SEM analysis of the cross section. Thus, the films are thermally sensitive.

3. Overall experimental results & the comparison with literature

Figure 20 summarizes the conductivity results. The conductivity-composition profiles for these composites can be generally classified into three regions- the region below *fc* with a small slope, the sharp slope region near *fc* and the region of saturated conductivities for the high PANI-DBSA contents. The residual low conductivities (~10^{-7} S/cm) of these composites may be due to moisture or ionic impurities.

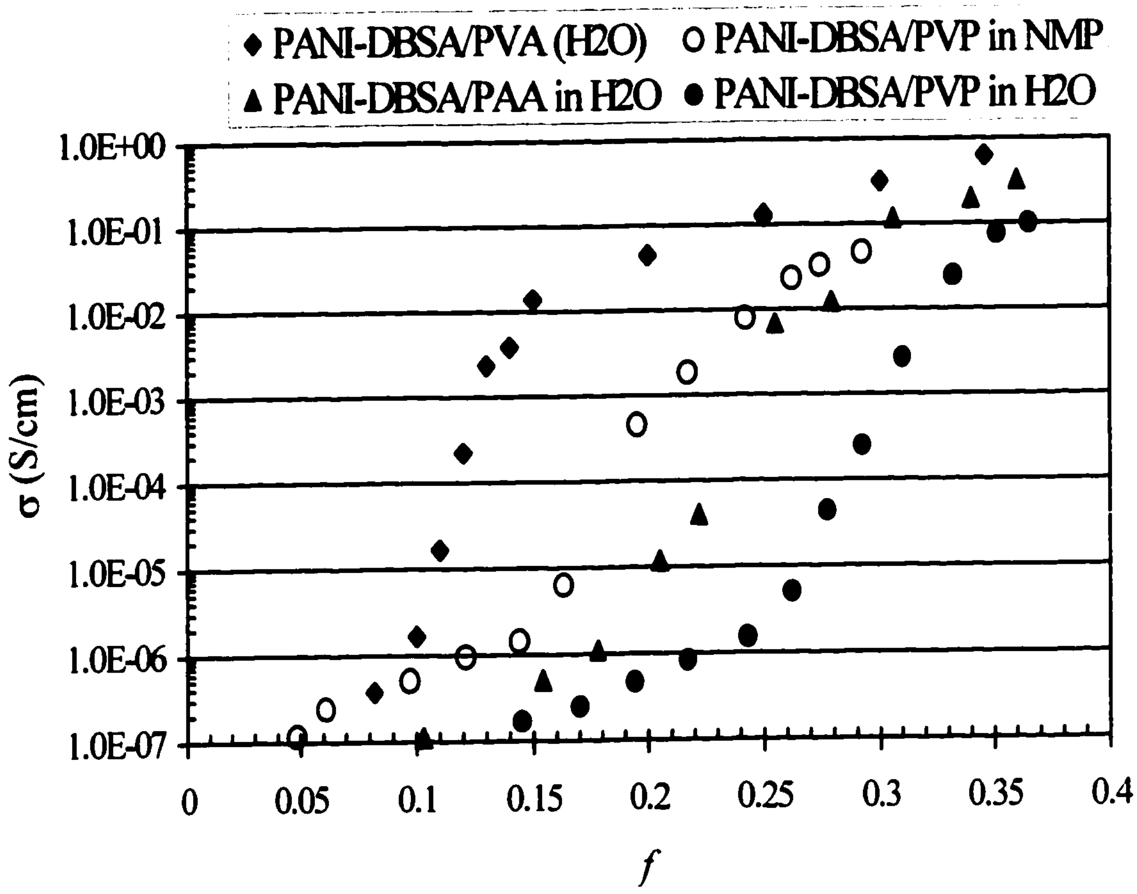


Figure 20. Plot of conductivity vs. *f* for the PANI-DBSA/PVA, PANI-DBSA/PVP and PANI-DBSA/PAA composite films formulated in water and NMP

The composites prepared in this study have *fc* values between 0.11 and 0.29. The PANI-DBSA/PVA composites have the lowest value, 0.113. The PANI-DBSA/PVP composites formulated in water have the highest value, 0.288. This may be due to the unusual binding ability of PVP, and the higher wettability of the PANI-DBSA by the PVP. Small quantities of PVP are known to stabilize suspensions, by adsorbing as a thin layer on the particles [23]. Hence, PVP surrounds the PANI-DBSA particles and reduces the interparticle contacts. In addition to this, the higher wettability of the PANI-DBSA by the bulk polymer was expected to influence the conductivity-composition profiles, since it may improve the distribution of the particles. The wettability of the PANI-DBSA by the bulk polymer has been reported to depend on the difference in surface tension (γ) between them. It has been shown with carbon black composites that the values of *fc* relate well to the surface tension of polymer [24]. When the difference in surface tension ($\Delta\gamma$) was large, the PANI-DBSA tended to aggregate and self-assembling conducting networks were formed. This resulted in a lower *fc* value. When $\Delta\gamma$ was small, the PANI-DBSA tended to distribute itself homogeneous in the bulk polymers, since the PANI-DBSA-polymer interactions were favorable. This produced a higher *fc* value because the particles were separated by the polymer coating. Unfortunately, the surface tensions of PANI-DBSA and PVP are not available. In this study, PANI-DBSA appeared to be wetted better by PVP than by PAA. The PANI-DBSA particles disintegrated quickly in the aqueous PVP solution, and a very homogeneous blend resulted. On the contrary, the PANI-DBSA aggregated in aqueous PAA solution. Accordingly, the PANI-DBSA/PVP composites had a higher *fc*.

The PANI-DBSA/PVP formulated in NMP has a lower f_c value, 0.185. This may be a consequence of the solubility of PANI-DBSA in NMP, which may swell and separate the PANI-DBSA chains and ultimately produce smaller well-distributed PANI-DBSA particles in the film. This may result in more contact between the particles and a lower f_c. The PANI-DBSA/PVA films have the strongest adhesion to the glass substrates and have good thermal stability.

Table 23 summarizes the estimated f_c values from the σ vs. f plots and the f_c and the t values from the log σ vs. log $(f\text{-}f_c)$ plots for the composites prepared in this study. These f_c values are all higher than those reported in the literature. Table 24 summarizes the f_c and t values reported in literature and includes the type of PANI, polymer matrix and solvent used in each case, for which "N/A" means the information was not provided. The f_c values from the data in reference 8 were estimated by the author to be less than 0.16. PANI copolymers are the materials in reference 19 and 20 and the values of f_c and t were calculated for this study using Equation 3.

Table 23. Summary of the estimated f_c, f_c and t for the PANI-DBSA/PVA, PANI-DBSA/PVP and PANI-DBSA/PAA composite films formulated in water

	PANI-DBSA /PVA	PANI-DBSA /PAA	PANI-DBSA /PVP	PANI-DBSA /PVP *
Estimated f_c	0.11	0.225	0.29	0.18
f_c (Equation 3)	0.113	0.220	0.288	0.185
t value (Equation 3)	2.00	2.10	2.08	2.03

Note: "*" composite was formulated in NMP.

Table 24. Summary of literature results for different PANI composites

Reference No.	Type of PANI	Polymer Matrix	Solvent	*fc*	t
8	PANI-CSA	Polymethyl Methacrylate (PMMA)	m-cresol	< 0.16	N/A
8	PANI-DBSA	Polyethylene (PE)	m-cresol	< 0.16	N/A
11	PANI (Base or Salt)	Poly (p-phenylene Terephthalamide) (PPTA)	Sulphuric Acid	N/A	N/A
12	PANI-CSA	Polymethyl Methacrylate (PMMA)	m-cresol	0.003± 0.0005	1.33 (300K) 1.99 (10K)
14	PANI-HCl	Polyvinyl Chloride (PVC)	THF	0.000402	1.87
14	PANI-HCl	Poly Styrene (PS)	THF	0.000419	1.91
14	PANI-HCl	Polyvinyl Acetate (PVAc)	THF	0.000318	1.94
14	PANI-HCl	Polymethyl Methacrylate (PMMA)	THF	0.000214	1.89
14	PANI-HCl	Polyvinyl Alcohol (PVA)	1.2 M HCl (aqueous)	0.00036	1.96
15	PANI-CSA	Polyvinyl Chloride (PVC)	m-cresol	< 1wt %	N/A
19	PANI	Poly(N-4-(sulfophenyl) aniline)	1.25 M HCl (aqueous)	0.48[a]	1.90
20	PANI	Poly(o-anthranilic acid)	1.2 M HCl (aqueous)	0.723[a]	2.06

Note: [a] calculated using Equation 3. PANI-CSA= Polyaniline-camphor sulfonic acid; PANI-DBSA= Polyaniline-dodecylbenzene sulfonic acid; THF= Tetrahydrofuran. The specimen geometry was films except fibers for reference 11, and pellets for reference 15.

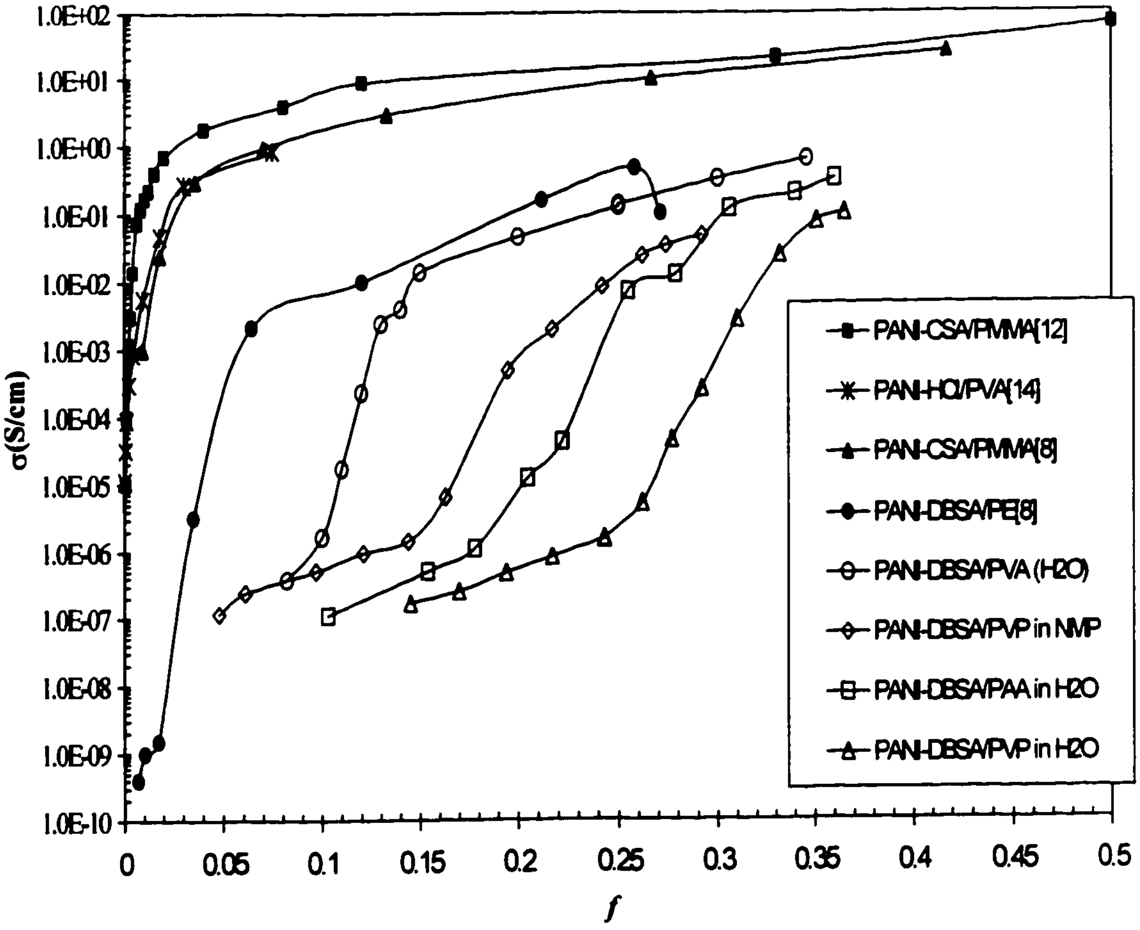


Figure 21. Plot of conductivity vs. *f* of PANI for different PANI composites

Figure 21 summarizes the results from the literature and this study. Some of the literature reported the composition in weight fraction of PANI, and these were converted to volume fraction using the densities listed in Table 25. These densities were obtained either from MSDS sheets or from calculation based on the information provided in literature [8, 14]. It can be clearly seen that the materials fall into two profile sets, depending on the PANI type. Several factors contribute to the *fc* difference between these two sets. The first set appears in the upper left corner of Figure 21, which are for the PANI-CSA and PANI-HCl composites. These reached a relatively higher conductivity and had lower *fc* values. In these cases, conducting PANI formed a self-assembling conducting network in the composites during drying. The PANI-CSA had greater intrinsic conductivity of 100–400 S/cm, while PANI-DBSA had a conductivity of 100–250 S/cm [8, 11]. PANI-CSA was used as a liquid, which dissolved and then formed a string-like, phase separated conducting network during the drying step [11]. In reference 14, a stabilizer (poly(vinyl methyl ether)(PVME)) was absorbed on PANI-HCl colloid particles. When the solvent was removed, the stabilizer phase separated since it was not miscible in the bulk polymer PVA and helped form aggregates of the nano-size PANI-HCl particles. The aggregation formed the self-assembling network of PANI-HCl, which had a percolation threshold at an extremely low PANI-HCl content.

Table 25. Density values used to convert the weight fraction to volume fraction of the PANI composites

Reference No.	Polymer Matrix	Density, g/cm^3
8	PMMA	5.0
8	PE	0.93
8	PANI-CSA	1.36
14	PVA	1.07
14	PANI-HCl	1.278

The second set is for the PANI-DBSA composites which reached a lower conductivity level and had higher *fc* values. The values of this set appear in the middle region of Figure 21. The lower conductivity reflected the lower intrinsic conductivity of

PANI-DBSA. A σ value of 100–250 S/cm (films) is reported [8], and we measured 2–4 S/cm. With PANI-DBSA composites the conductivity of increased more slowly with *f* than with the PANI-CSA composites. Both composites from reference 8 were believed to have a bi-continuous morphology, i.e., a string-like conducting network. On the other hand, the conducting PANI-DBSA in this study was distributed uniformly as particles in the bulk polymer and there was no evidence of a string-like, self-assembling conducting network. The lack of a string-like conducting network resulted in a higher *fc* value than with the PANI-DBSA and PANI-CSA composites from reference 8, and the PANI-HCl composites from reference 14. The PANI/PPTA and PANI-DPHP/PVC-TCP composites (Table 23) fall into a separate group. These materials were prepared as fibers or pellets. They have no additional phase separation, and the PANI-sulfate (σ = 5.3 S/cm) [11] and PANI-DPHP are less conducting.

Chapter VI

Conclusions

The PANI-DBSA composites in this study had σ-f profiles different from those for the other PANI materials reported in the literature. These composites had higher values of f_c and reached a lower maximum conductivity. For the region below the f_c, there was a residue conductivity which was fairly high. There was no network-like phase separation visible for the composites of PANI-DBSA with PVA, PVP or PAA whether formulated in water or NMP. The PANI-DBSA particles were distributed uniformly in all host polymers. This resulted in higher f_c than those composites with the bi-continuous morphology [11, 14].

The composites of PANI-DBSA with polyvinyl acetate (PVA)(Elmer's glue) had the lowest f_c. The PANI-DBSA/PVP composites which were processed in NMP had a lower f_c than those processed in water and the amount of NMP used strongly influenced the conductivity of the resulting composites. Because PVP dissolves easily, PANI-DBSA can be processed with the preformed polymer solutions, either water or NMP. However, with PAA which is marginally soluble and forms aggregates in water, it is recommended that PANI-DBSA and PAA powders be dry mixed prior adding the water solvent. The addition of acetone to the solution reduced the surface tension and prevented bubble formation during processing. However, the amount of acetone used should be minimal to prevent the dilution of the process solution.

The PANI-DBSA/PVA films had the best mechanical integrity of the sample studied. Good films of PANI-DBSA/PVA and PANI-DBSA/PVP composites existed when the PANI-DBSA content was below 40 vol % when formulated in water, and below 33 vol % when formulated in NMP. For the PANI-DBSA/PVP composites formulated in water or NMP, there was a dramatic change of the appearance of the film at *f*c, which helped locate *f*c by inspection. The films with *f*>*f*c appeared dull and opaque. The films with *f*<*f*c appeared shiny and glossy.

The addition of NaOH to the PANI-DBSA/PAA formulation in water resulted in a sharp increase in resistivity of the composite and a change in color, from green to black. There was no change in the mechanical aspects. This result suggests that the NaOH neutralizes mostly PANI-DBSA, and not PAA.

Proposals for Further Research

Several suggestions are listed as follows.

1. The processes carried out were in ambient and room temperature. This required the use of chemical solvent. The amount of solvent often needed to prevent bubble formation seemed to effect the mechanical integrity of the resulting films. This problem may be eliminated if the process is conducted at a higher temperature, e.g., 50°C, thus less solvent is required and bubble formation may be less.
2. The instrument used in measuring resistivity was limited to 10^7 Ω*cm, which is not useful for specimens with lower PANI-DBSA contents. It is recommended that an instrument with a wider range be used.
3. A stabilizer, like polyvinyl methyl ether (PVME), absorbs on the PANI-DBSA colloid particles [14]. With such a stabilizer, the resulting PANI-DBSA-PVME/PVP (or PAA) composites formulated in water may phase separated to form a bi-continuous morphology because the PVME is not miscible in the bulk polymers. This will produce a lower fc value. The process is a 2-step process as follows:
    a. PVME is first coated on PANI-DBSA colloid particles in tetrahydrofuran (THF).
    b. Then the coated PANI-DBSA particles are dispersed in a PVP (or PAA)/water solution.
    c. The films are cast from the solution and dried in ambient.

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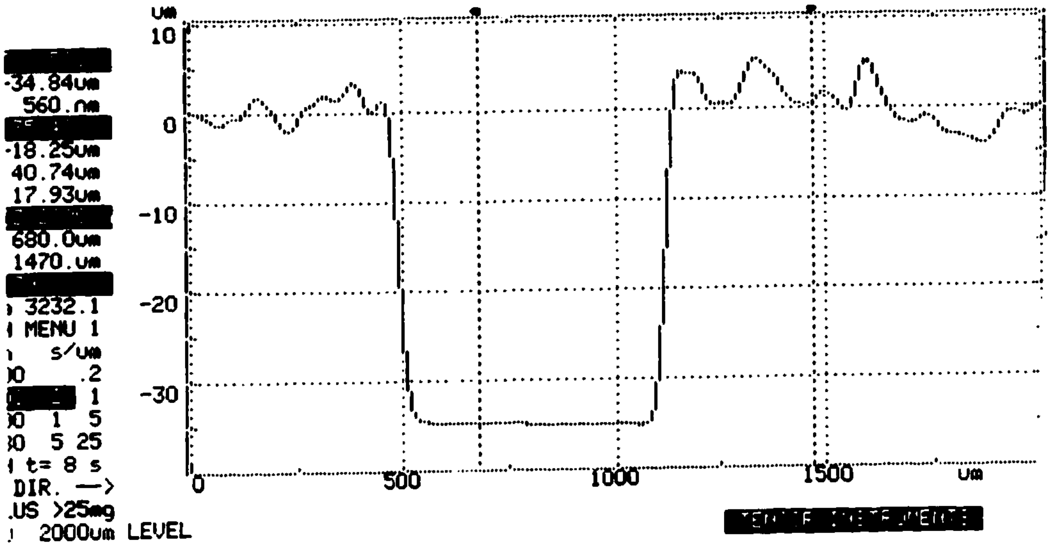
Appendix A

The instrument used in measuring film thicknesses is TENCOR instrument Alpha-Step 200. The thickness is measured by fixing the two cursors at the top of the plot and the vertical difference between these two cursors will be the thickness. The following printout is for the specimen of PANI-DBSA/PAA formulation in water with *f*=0.205. The thickness of this film is approximately 35 μm.



Appendix B

Four variations on the PANI-DBSA/PAA formulation procedure were conducted. Only the process I produced a homogeneous distribution of PANI-DBSA with high conductivity and the absence of bubbles in the formulations.

I) Addition of Water to Premixed Dry PANI-DBSA/PAA

The details of the processing were described in the page 31. Upon addition of water, PANI-DBSA/PAA aggregates formed and this reduced the viscosity of the mixture. This also reduced the trapped air (the bubbles all rose to the surface of the solution) and increased the processibility of solution significantly. Unlike all previous processes, sonication at this stage effectively disintegrated the large PANI-DBSA/PAA agglomerates to some extent and facilitated the mechanical mixing thereafter. Comparing specimens 80 and 81 revealed that the application of sonication here was essential. Without sonication there were larger aggregates, though the mechanical mixing was introduced for 4 hrs (specimen 80). The PANI-DBSA/PAA agglomerates were much easier to disintegrate than the PAA aggregates. The disintegration of PANI-DBSA/PAA agglomerates was observable and was accompanied by a slow increase in the viscosity of the solution.

To achieve improved homogeneity, intense mechanical mixing was essential and inevitable, but this produced bubbles. Unlike the PANI-DBSA/PVP and PANI-DBSA/PVA composites, the bubbles were trapped in the films or solution of PANI-DBSA/PAA composites and did not escape by tapping. The addition of more water facilitated the process by reducing viscosity and helped remove the air bubbles. The bubbles escaped spontaneously. Further intense mixing did not produce more bubbles with the presence of the appropriate amount of acetone.

II) Addition of PANI Powder to Aqueous PAA Solution

According to reference 14, the PANI-HCl particles are dispersed in the polymer solution and sonicated. The authors state that a higher viscosity of the polymer solution facilitates the disintegration of PANI-HCl particles and produces nanos size particles with a low f_c, 0.0005[14]. However, it was found that this approach was not good for processing PANI-DBSA/PAA in water. PAA dissolves slowly in water and intense mechanical mixing was needed to disintegrate the PAA aggregates. This mixing produced a lot of air bubbles which were difficult to eliminate. The PAA aggregates are transparent, and it was hard to tell when they had dissolved. Sonication for 1 hr after adding PANI-DBSA did not help disintegrate or disperse the PANI-DBSA particles in the PAA solution, or in removing or breaking the bubbles. The further intense mechanical mixing produced more bubbles but did not produce a homogeneous blend solution. The PANI-DBSA remained suspended in the solution (specimen 2). The final solution was mostly transparent, and had dark green lumps of PANI-DBSA. Hence, this process did not make the PANI-DBSA powder uniformly disperse in the aqueous PAA solution.

III) Addition of Aqueous PANI Solution to Aqueous PAA Solution

Separate aqueous solutions of PAA and PANI-DBSA were prepared. The PANI-DBSA particles separated quickly and becoming fine particles through sonicating. When the PANI-DBSA solution was poured in the aqueous PAA solution, the PANI-DBSA aggregated immediately. The solution was sonicated for 1 hr then mixed mechanically for 2 hrs. The resulting solution was similar to the previous one. There was an inhomogeneous distribution and large aggregates of PANI-DBSA, as well as trapped bubbles (specimens 14, 22). The final solutions were transparent, and filled with dark green lumps of PANI-DBSA. These resulted in a dramatic decrease in conductivity. Both specimens 22 and 105.2 were formulated with f=0.205, and were fabricated using process III and I, respectively. The former had a conductivity value of less than 10^{-8}, while the latter was around 10^{-4}.

IV) Addition of PAA Powder to PANI Solution

The addition of PAA to the aqueous PANI-DBSA solution produced aggregates of PAA and PANI-DBSA/PAA. The solution was sonicated for 1 hr then mixed mechanically for 2 hrs. The final blend solution was not improved (specimen 7).

Appendix C

Figure 22 through 27 show the scanning electron micrographs for the film surfaces or cross sections of the films of PANI-DBSA/PVA, PANI-DBSA/PVP and PANI-DBSA/PAA composites formulated in water or NMP. Figure 23 shows the adverse image as shown in the monitor of the SEM.

Figure 22. Scanning electron micrograph for the fractured edge of the PANI-DBSA/PVA film, f=0.15.

Figure 23. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in water, f=0.332.

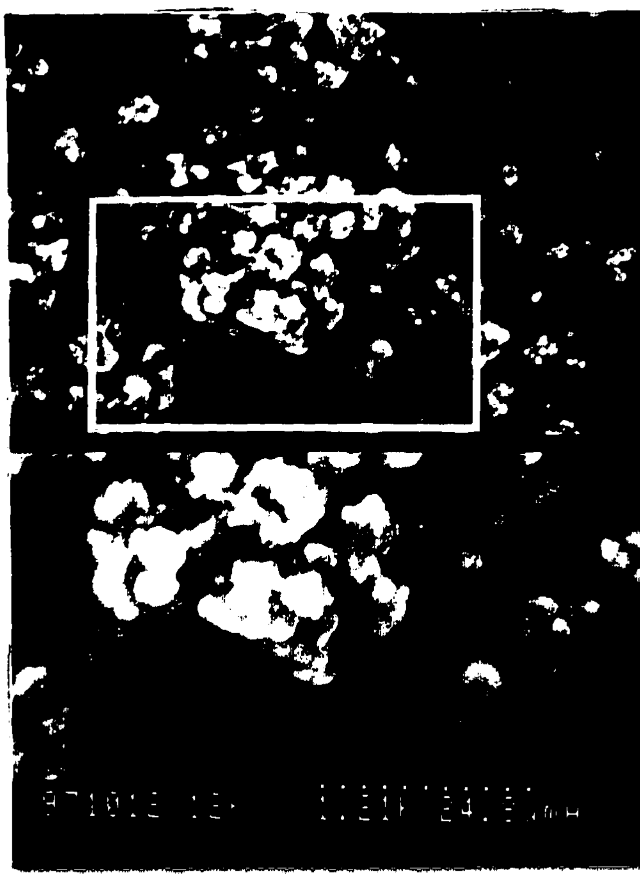


Figure 24. Scanning electron micrograph for the fractured edge of the PANI-DBSA/PAA film formulated in water, *f*=0.255.

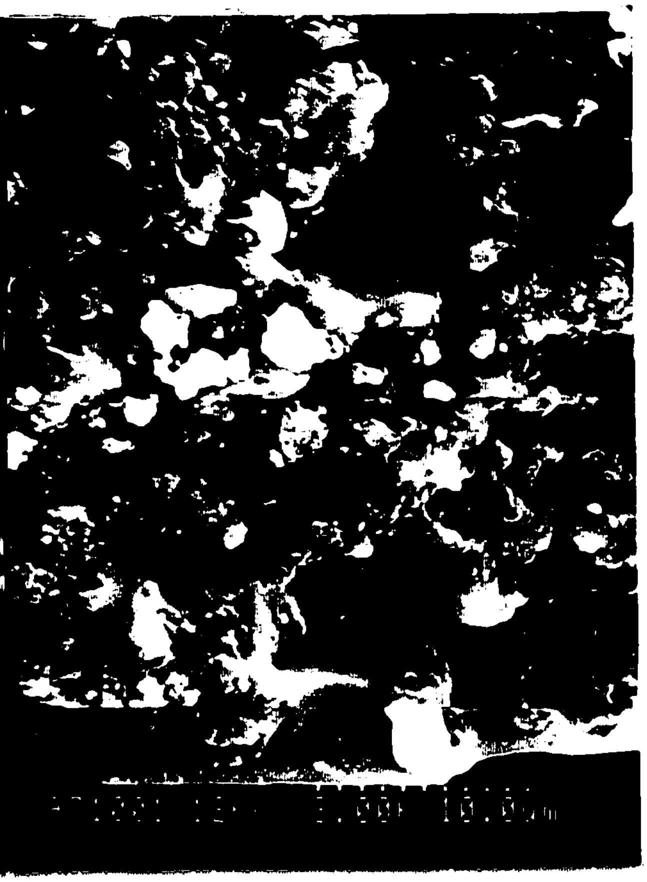


Figure 25. Scanning electron micrograph for the top surface of the PANI-DBSA/PAA film formulated in water, *f*=0.255.

Figure 26. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in NMP, f=0.097.

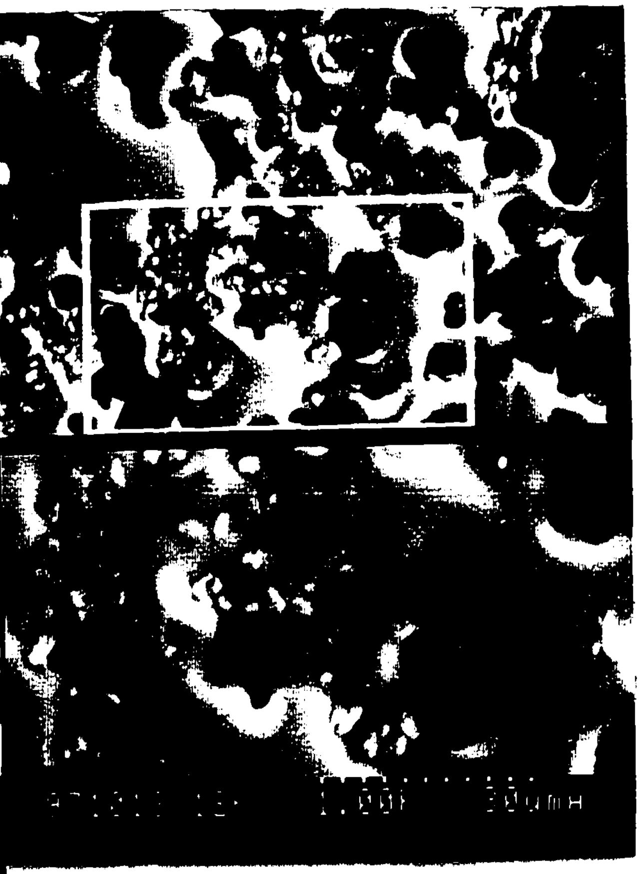


Figure 27. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in NMP, f=0.144.

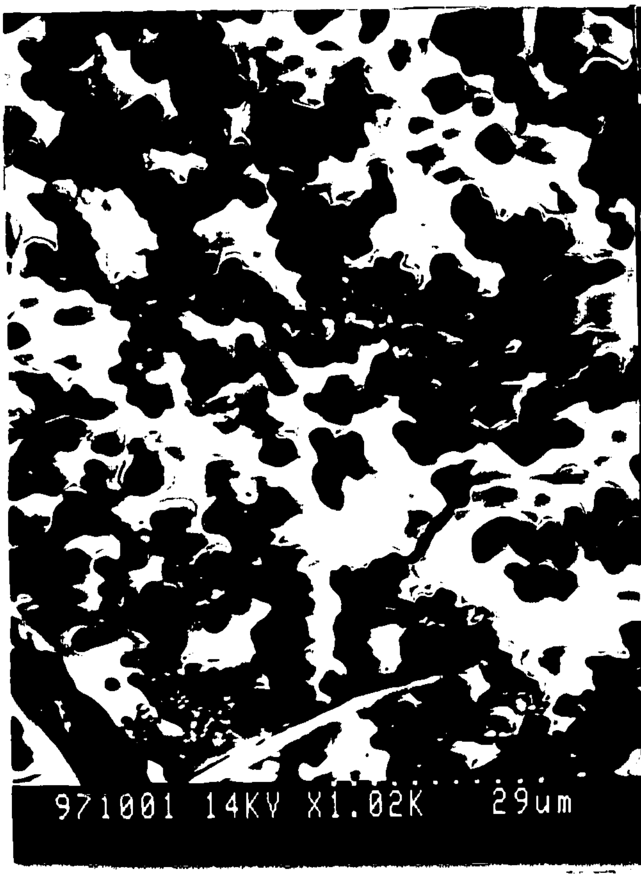


Figure 28. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in NMP, f=0.163.

Figure 29. Scanning electron micrograph for the top surface of the PANI-DBSA/PVP film formulated in NMP, f=0.195.

November 20, 1997

L. Smith
US Associate Editor, POLYMER COMMUNICATIONS part of Polymer
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Gaithersburg, MD 20899, USA

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I would appreciate permission to include Table 2. Mechanical properties and conductivity of PANI-PPTA fibres, and Figure 2. Conductivity vs. volume fraction of PANI in PANI/PPTA fibers........, which appear in " Electrically Conductive Polyblend Fibres of Polyaniline and Poly-(p-phenylene terephthalamide).", by Andreatta, Alejandro, Heeger, Alan J. and Smith, Paul, 1990, Vol. 31, July, pp. 275-278 in my master thesis with the title " Water Based Process for Polyaniline Composites" in the Department of Chemical Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records a returning envelope is provided.

Sincerely,

Shih. Ming-Hung

Ming-Hung Shih
C/O Dr. ART DIAZ
College of Engineering
Department of Chemical and Materials Engineering
San Jose State University
One Washington Square, San Jose, CA 95192-0086, USA

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University of California, Santa Barbara, CA 33106, USA

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Sincerely,

Shih, Ming-Hung

Ming-Hung Shih
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San Jose State University
One Washington Square. San Jose, CA 95192-0086

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Dear Sir:

I would appreciate permission to include Figure 1. Transmission-electron micrographs of cast PANI-PMMA composite film……, and Figure 2. (a) Conductivity ($\log_{10}$ scale) vs. volume fraction (f) of PANI-CSA at 300 K and at 10 K; (b) $\log_{10}$-$\log_{10}$ plot of conductivity…….., and Table I. Room temperature conductivity (σ) and resistivity (ρ) ratio of PANI-CSA/PMMA composites at various volume fractions (f) of PANI-CSA, which appear in" Transport in Polyaniline Networks Near the Percolation Threshold.", by Reghu, M. Yoon, C.O., Yang, C. Y., Moses, D., Smith, Paul and Heeger, A.J., 1994, Vol. 50, n. 19, Nov. 15, pp. 13931-13941 in my master thesis with the title " Water Based Process for Polyaniline Composites" in the Department of Chemical Engineering at San Jose State University.

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Shih, Ming-Hung

Ming-Hung Shih
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Dear Sir:

I would appreciate permission to include Table 1. *fc* and t for various blends of PANI-HCl with conventional polymers, Figure 1. log (electrical conductivity) vs. PANI-HCl concentration in PANI-PVA, and Figure 2. log (conductivity) vs. log(W-Wc), which appear in " Conducting Polyaniline Nanoparticle Blends with Extremely Low Percolation Thresholds." , by Banerjee, Pallab and Mandal, Broja M., Macromolecules 1995, Vol. 28, pp. 3940-3943 in my master thesis with the title " Water Based Process for Polyaniline Composites" in the Department of Chemical Engineering at San Jose State University.

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Sincerely,

Shih, Ming-Hung

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