Synthesis and Electrorheological Characterization of Polyaniline Nanoparticles and Polyaniline/Poly(vinyl butyral) Composites

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Synthesis and Electrorheological Characterization of Polyaniline Nanoparticles and Polyaniline/Poly(vinyl butyral) Composites

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PART I.

EFFECT OF POLYMERIC STABILIZERS ON SYNTHESIS AND CHARACTERIZATION OF POLYANILINE NANOPARTICLE
ABSTRACT

Monodisperse polyaniline (PANI) nanoparticles were synthesized from an oxidative dispersion polymerization using poly (sodium 4-styrenesulfonate) (PSSS) (MW=70,000) as both a polymeric stabilizer and a doping agent due to its acidity, in which poly (vinyl alcohol) (PVA) and poly(methyl vinyl ether-alt-maleic acid) (PMVEMA) were adopted as polymeric stabilizer. PANI nanoparticles were examined by dynamic light scattering to obtain their particle size distribution and their chemical and physical characterizations were analyzed by UV-VIS and FT-IR. From the TEM measurement, the diameter of spherical shaped particles was observed to be approximately 200nm. Thermogravimetric analysis of the particles was performed to measure thermal properties. Conductivity of the particles was founded to be between $10^{-1}$ and $10^{0}$ S cm$^{-1}$ by the four probe method.

The ER fluids composed of the PANI nanoparticles and silicone oil were prepared and their rheological properties were obtained using a rotational type rheometer equipped with a high voltage generator. The yield stress increased with the electric field strength and the results were interpreted based on their dielectric spectra.
국문요약

폴리아닐린은 손쉬운 합성 과정과 좋은 열적 안정성, 그리고 용이한 전도도 조절로 인해서 가장 유용한 conducting polymer 중의 하나로 알려져 있다. 그러나 그 자체로는 불용, 불용의 가공성이 매우 취약하여 거대한 분자구조를 갖는 유기산을 dopant로 사용하여 용해성을 향상시키거나, 범용 고분자들과의 blend를 통하여 이러한 문제점을 해결하려는 노력들이 계속 되어왔다. 특히, 여러 가지 수용성 고분자를 안정적으로 사용하여 PANI 입자를 colloidal상으로 중합하고, 이를 바로 전도성 film이나 coating 물 질로 응용하고자 하는 연구들이 많이 이루어졌다. 이러한 문제점을 해결하기 위해서 단분산 폴리아닐린 입자는 폴리머 안정제와 도판트 역할을 하는 poly (sodium 4-styrenesulfonate) (PSSS) (분자량=70,000)와 폴리머 안정제인 poly(vinyl alcohol) (PVA) 와 poly(methyl vinyl ether-alt-maleic acid) (PMVEMA)를 가지고 각각 산화분산중합에 의해 중합되었다. 이러한 폴리아닐린의 나노 입자는 SEM, TEM과 DLS를 통하여 크기와 형태를 확인할 수 있었고 TGA, FT-IR, 전도도와 유변학적 방법으로 물질 특성을 분석하였다. 이러한 입자들의 전도도는 four probe 방법에 의해 10^{-1} 과 10^{0} S cm^{-1} 으로 관찰되었고 유변학적 거동은 일반 폴리아닐린의 경향과 유사하게 전기장하에서 유변유체의 급격한 점도의 증가를 관찰할 수 있었고 입자 표면의 편극화 현상으로 인한 전기장의 함수로 얻어진 항복응력을 가진 Bingham 유체의 거동을 보여주었다.
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Part I. EFFECT OF POLYMERIC STABILIZERS ON SYNTHESIS AND CHARACTERIZATION OF POLYANILINE NANOPARTICLE

1. INTRODUCTION

Electrorheological (ER) fluids are dispersions of polarizable or semiconducting particles in insulating oils, representing a unique class of electroactive intelligent materials that exhibit drastic change in rheological and electrical properties (e.g., viscosity, yield stress, and dielectric constant) under an applied electric field. This change originates from particle migration and formation of a chainlike or columnar structure oriented along the electric field direction over the gap between the electrodes [1-5] and can be finely turned by an electric field applied. This fast, strong, and reversible gelation provides a novel and efficient way to transfer energy and control motion; the gelation or fibrillation structures disappear when E is removed. This effect can be implemented in many potential applications including shock absorbers, clutches, hydraulic valves, high power vibrators, chucks, torque transducers, and dampers [1,2].

The ER materials in general include both wet-base and dry-base systems. Compared to the wet-base systems such as corn starch and mesoporous molecular sieve [6] which require active substrates, such as water surfactant [7] and glycerin [8], various dry-base anhydrous systems have been developed to overcome the shortcomings that wet-base systems posses. Examples include: zeolite [9], TiO₂ [10], chitosan [11] and acene quinone radical polymers [12], polyaniline [13], copolyaniline and
polymer/clay nanocomposites with styrene acrylonitrile copolymer [14] or polyaniline [15].

Among many semi-conducting polymers, polyaniline occupies an important position in the inherently conducting polymer (ICP) family for various electrochemical applications because of its facile synthetic process, good environmental stability, doping character low cost of raw material and high conductivity control. Nevertheless, for electrically semi-conducting polymers in general and specifically for PANI, successful application depends on our ability to overcome their difficult processability, which is due to their insolubility in common solvents.

To improve the processability of PANI, various kinds of dopants (instead of HCl) such as benzenesulfonic acid, sulfosalicylic acid, camphor sulfonic acid and dodecylbenzene sulfonic acid have been developed. The improvement of dispersion quality is an attractive approach to improving processability [16], since colloidal dispersions may be applied directly to industrial applications.

Several experimental reports have appeared in the literature of preparing the dispersion by way of oxidative dispersion polymerization of aniline using polymeric stabilizer.

In a dispersion polymerization, the PANI particles prepared the polymerization of aniline through various methods such as an emulsion [17, 18], micelle [19,20] and reverse microemulsion as a polymerization medium and steric stabilizer appeared distinctive morphologies, spheres, needles and rice grains. Usually, uniform PANI particles have been prepared with conventional water-soluble polymeric stabilizers such as poly(vinyl alcohol-co-acetate), poly (N-vinyl pyrrolidone) [21], and methyl cellulose [22], which adsorbs onto the polymer nuclei and prevents aggregation via steric stabilization. However the above stabilizers adsorb poorly in PANI particles. In order to overcome the poor physical adsorption, Armes et al.
[23-26] used tailor-made stabilizers, which are capable of being chemically grafted to PANI. Some other researchers have found by proper choice of the concentrations of the reagents dispersion polymerization of PANI using poly (vinyl alcohol)(PVA)[27], poly(vinyl methyl ether)[28-31] and poly(ethylene oxide) as stabilizer.

In this study, to enhance the dispersion stability of PANI, we used poly(methyl vinyl ether-alt-maleic acid) (PMVEMA) copolymer [32-33] with acid groups (-COOH, poly(vinyl alcohol)(PVA) with hydroxyl groups(-OH) ) as polymeric stabilizer and Poly(sodium 4-styrenesulfonate) (PSSS) [34-38] with pendant benzene sulfonate group as both polymeric stabilizer and a dopant agent due to its acidity. This experimental approach to synthesize nanoparticles stabilized with different polymeric stabilizer and quantities of dopant (HCl). The conducting form of PANI powder synthesized in aqueous HCl, referred to as PANI hydrochloride, is insoluble in common organic solvents and even in 1-methyl-2-pyrrolidone (NMP), which is the only organic solvent having been found so far that can dissolve high molecular weight PANI. Additionally, these small molecular acid dopants for PANI may evaporate at room temperature or higher, causing a depression in the conductivity of the acid-doped PANI. Moreover, the small molecular acid-doped PANI not suitable for use as cathodic material in a lithium rechargeable battery, since the movable anions of the acid dopants are capable of diffusing out to the electrolyte phase and, thus, the charge compensation for the positive electrode redox reaction will be based on the doping and undoping of anions rather than the intercalation and deintercalation of lithium cations [39-40]. These obstacles can be overcome in an appropriate way, that is, by using polymeric acid dopants.

Size effect of PANI particle was examined by SEM, TEM and DLS. The particles were characterized spectroscopically by UV-VIS, FT-IR, XPS and conductivity. For thermal stability characterization, thermogravimetric
analysis (TGA) was performed on the particles. The effect of electric field strength, particle concentration and particle size on ER properties of PANI-PSSS suspensions were examined and then its viscoelastic properties were investigated under applied elastic fields using a rotational rheometer with high voltage generator in both controlled shear rate and shear stress modes.
2. THEORETICAL BACKGROUND

2.1 Conducting polymer

2.1.1 What are conducting polymers (CPs)?

The Conducting polymers (CPs, also sometimes called Conductive Polymers or Conjugated Conductive Polymers or Organic Polymeric Conductors) are quite a different beast, in the sense that they are intrinsically conducting, and do not have any conductive fillers as such. This unique intrinsic conductivity of these organic materials, which generally are comprised simply of C, H and simple heteroatoms such as N and S, and the myriad of properties emanating from it, arise uniquely from $\pi$-conjugation. That is to say a sometimes fairly extended and delocalized conjugation originating in overlap of $\pi$-electrons. This conductivity of CPs is achieved through simple chemical or electrochemical oxidation, or in some cases reduction, by a number of simple anionic or cationic species, called “dopants”. That is to say, the polymeric backbone of these materials needs to be oxidized or reduced to introduce charge centers before conductivity is observed, and the oxidation or reduction is performed by anions or cations somewhat misnames “dopants”, a term borrowed from condensed matter physics.

2.1.2 Historical

Many CPs were well known in their nonconducting forms much before
conductivity and other features of interest were discovered. Some were also known in their conductivity forms, but not well characterized and with not much interest paid to their conductivity. For example, Poly($p$-phenylene sulfide), PPS, has been commercially produced for thermoplastics applications under the brand name Ryton by Phillips Chemical Company since the early 1970’s, and well-defined syntheses of Poly(acetylene) have been reported since the early 1970’s, and well-defined syntheses of Poly(acetylene) have been reported since 1971.

Chemical oxidative polymerization of aniline was described by Letheby in 1862, and studied in more detail by Mohilner et al. in 1962. Pyrrole was known to form a conductive “pyrrole black” via spontaneous polymerization in air on the sides of pyrrole containers, and its chemical polymerization studied in some detail in 1916. Since 1957, studies of electrochemical oxidation of aromatic monomers, now widely used as one method of synthesis of CPs, have been reported under various descriptions such as “electro-organic preparations” and “electro-oxidations”. More recently, in 1967, electrically conducting polymers form pyrrole, thiophene and furan were characterized and the electric conductivity of poly(anilines) noted. As early as 1968, dall’Ollio described electropolymerization of poly(1pyrrole). In many a sense, thus, CPs are “rediscovered” materials.

The developments of importance that focused attention on CPs as potential novel materials with highly promising conductivity and other properties however started with the serendipitous discovery in a collaborative effort between the Shirakawa and Heeger/McDiarmid groups that poly(acetylene) exposed to iodine vapors develops very high and well characterized conductivities (for an organic material). A chemical route to a new, conductive organic material was thus available. Further impetus to the field was given by the route to a new, conductive organic material was thus available. Further impetus to the field was given by the repetition and
refinement, by the Diaz group at IBM, of the electrochemical polymerization of pyrrole originally ascribed to dall’Ollio, with a much better characterized polymer produced.

Poly(acetylene) was initially the most studied CP from to both scientific and practical application points of view. However, due to its high chemical instability in air and related factors, interest in it has most recently been confined to its scientific aspects. Poly(aniline), Poly(pyrrole), and the poly(thiophenes) remain the most extensively studied CPs to date, from both scientific and practical or commercial points of view.

2.1.3 Polyaniline

Interest in polyaniline (PANI) sprung up only in the late 1980’s. The relevant structural studies were all carried out after the appearance of the Handbook of Conducting Polymer. The material which has been known as polyaniline since the middle of the previous century is very intractable, and only recently have synthetic routes been developed that lead to a more well-defined polymer, which also exhibits appreciable crystallinity. The interesting variety of electronic structures that distinguish PANI from other common conducting polymers were already known from an early study by Green and Woodhead.

2.1.3.1 Polymerization Mechanisms

PANI can be prepared by the polymerization of aniline in an oxidizing medium, and the resulting polymer is found to be in a partially oxidized state. Its molecular constitution is intermediate between that of poly(paraphenylene amine), which represents the so-called leucoemeraldine form,
and that of poly((para-phenylene imine), known as the permigraniline form in scheme 1. Since the polymer is prepared under acidic conditions (HCl), it is also partly protonated, primarily at the imine nitrogens. At lower pH, protonation of the amine nitrogens will also occur to some extent. De-protonation with base and reprotonation in acid have been found to be possible, and reversible. These processes turn out to have a tremendous influence on the electronic properties of the polymer if it has a degree of oxidation equal (or close) to 0.5; this is the so-called emeraldine form of PANI. Conductivity in the solid state rises from the approximately $10^{-10}$ S cm$^{-1}$ for the emeraldine base (unprotonated) to well over 1 S cm$^{-1}$ for the form fully protonated with respect to the imine nitrogens. This phenomenon can be understood by considering a band picture. Every nitrogen atom has a hydrogen atom bonded to it and half the number of nitrogens bear a positive charge (due to added protons). A valid resonance form of this configuration is one in which every second nitrogen bears a polaron, i.e. both a charge and a spin (radical); this form is called the polaron lattice. These polarons strongly interact and their wave functions form an energy band which is half-filled and its charge carriers are therefore mobile. A chemical viewpoint is the following. The polaron state is doubly degenerate since there expected to be delocalized along the chain, resulting in electrical conductivity.

Conductivity has also been attributed to bipolarons; a bipolaron is the doubly-charged but spinless species that arises when two polarons residing on adjacent nitrogens pair up their radicals by transforming the phenyl ring between them into a quinoid one. There are indications, however, that spinless regions in PANI correspond to disordered (amorphous) domains, which also have lower conductivity. This is connected with the inequivalence of the phenyl rings in the bipolaron form of the chain. In regions where the chains have conformational defects, bipolarons will be favoured over
polarons, which at the same time restricts the mobility of charge carriers in such domains. The motion of a bipolaron requires local changes of the chain geometry, while this is not necessary for charges moving in the polaron lattice of the emeraldine oxidation state.

**General form of polyaniline (in the base form)**

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{N} \\
\end{array} \\
\text{y} \\
\text{1-y} \\
\text{x}
\]

The fully reduced poly (paraphenyleneimine), “leucoemeraldine”, y=1

**The fully oxidized poly (paraphenyleneimine), “pernigraniline”, y=0**

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\end{array} \\
\text{x}
\]

The 50% oxidized poly(paraphenyleneimine), “emeraldine”

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\end{array} \\
\text{x}
\]

**Scheme 1. Various forms of polyaniline**

Each charged site on the PANI chain is accompanied by a counteranion of course. Therefore, in analogy with the situation for other conducting polymers, the protonation process is called doping. This is a partial analogy, however, since proton doping of emeraldine is analogy, however, since proton doping of emeraldine is not an oxidative process. Results obtained with various proton-donating acids, e.g. HCl, H$_2$SO$_4$ and HClO$_4$ appear to be similar.

Initially, structural studies have been concerned with the above-mentioned form of PANI, in particular its emeraldine oxidation state in both
undoped and proton-doped form. The possibility of preparing oriented films by solution casting and subsequent drawing has greatly facilitated the interpretation of the limited diffraction data. At the same time, drawing may lead to an enhancement of the conductivity by two orders of magnitude, along the stretching direction. Fibre spinning has also been reported. Modifications obtained by substitutions on the phenyl rings have also been investigated; these have generally been found to result in reduced conductivity. Such results have nevertheless aided in our understanding of the structure-property relations. PANIs doped with the protonic acid mentioned above still have moderate processability and mechanical properties. A significant improvement has come with the use of organic sulphonic acids. These are proton donors of amphilphilic nature (‘surfactants’) that considerably change the solution properties of the polymers as well as their solid-state behavior. The solids are again found to be partially crystalline, and the incorporation of the large counterion has significantly changed the dimensions of the unit cell. Each oxidation state can exist in the form of its base or its protonated form by treatment of the base with an acid.

2.1.3.2 Conduction in Polyaniline

Any discussion of polyaniline would be incomplete without understanding transport in conducting polyaniline and before we do so we will consider the basic aspects. Polyacetylene, which units of \((\text{CH})_x\) are linked linearly with an alternating double and single bond (therefore a repeat unit) consists of two carbons and two hydrogens. The two Kekule structure derived form this structure are equal in energy, thus the structure is doubly degenerate energetically. Of the four valence electrons per carbon, three form relatively deeply bound molecular orbitals in \((\text{CH})_x\) and the remaining
single (π-orbital) electron per carbon atom determines the location of a double bond.

Two energetically equal structures at a point where they couple give a surface effect known as a kink or a soliton. The term ‘soliton’ means ‘solitary wave’, implying a non-linear phenomenon involving non-dispersive transport of energy in a dispersive medium. This means that soliton has a movement. In a conjugated systems solitons may be neutral, positively or negatively charged according to the number of electrons in the π-orbital.

Scheme 2. Internal redox reaction leading to formation of polaron and bipolaron as a function of dopant
The motionless charged states are known to organic chemists as carbonium (+ve) and carbanion (-ve) radicals. Such a situation is also encountered in polymers which do not have two degenerate ground states. That is, their ground state is non-degenerate due to the non-availability of two energetically equal Kekule structures. Therefore there cannot be a link to connect them. The conventional distortion of the molecular lattice can create a localized electronic state, thereby lattice distortion is self-consistently stabilized. Thus the charge coupled to the surrounding (induced) lattice distortion to lower the total electronic energy is known as a polaron (i.e. an ordinary radical ion) with a unit charge and spin = 1/2. A bipolaron consists of two coupled polarons with charge = 2e and spin = 0. The energy increase due to coulombic repulsion (in the formation of a bipolaron) is more than compensated for by the energy gained when the two charges share the same lattice distortion. Quantum-chemical calculations indicate that the formation of bipolaron requires 0.4eV less energy than the formation of two polarons. However, bipolarons are not created directly but must form by the coupling of pre-existing polaron (scheme 2).

At the molecular level a polymer is an ordered sequence of monomer units. The degree of unsaturation and conjugation influences charge transport via the orbital overlap within a molecular chain. The charge transport becomes obscured by the intervention of chain folds and other structural defects. The connectivity of the transport network is also influenced by the structure of the dopant molecule. The dopant not only generates a charge carrier by reorganizing the structure-chemical modification-it also provides intermolecular links and sets up a microfield pattern affecting charge transport. Any disturbance of the periodicity of the potential along the polymer chain induces a localized energy state. Localization also arises in the neighborhood of the ionized dopant molecule due to the coulomb field.
All dopants cannot induce charge transport in polymer. It depends upon the redox energy of the host and guest molecules and electrons will transfer from a high to a low redox energy. The initial charge transfer on doping will be between dopant molecule and the proximal polymer site, but subsequently some diffusion of polymer charge away from the immediate dopant to the site can be expected and polymer pair states will be generated. In equilibrium the number of polymer pair states will equil the number of ionized dopants.

In view of this, let us see how charge transport occurs in polyaniline with a general composition, which denotes that it is not a single well-defined material but a mixture of various oxidation states in which protonation induces insulator-to-metal transition. This insulator-metal transition is a function of protonation and can be studied by various techniques.

The study of electrochemical properties of polyaniline in-situ by ESR shows an increase and then decrease of spin concentration upon oxidation and has been interpreted as Curie spins-carbonion polaron- to Pauli spins, forming a metal-like polaron band.

Litzelmann et al. have used electron energy loss spectroscopy EELS to obtain information on the nature of the insulator-metal transition as a function of protonation. Their results indicate the momentum dependence of energy loss spectrum of electrons, which does not support polyaniline as a granular metal. Similarly, the NMR and ESR study by Mizoguchi et al. indicates the absence of three-dimensional metallic islands, which again does not support polyaniline as a granular metal.

2.1.4 Applications

The study of conducting polymers has become a major part of
modern material science and in many institutes and commercial establishments involves multidisciplinary research into chemical synthesis, polymer preparation, electronics, physics and applied physics. The combination of metal-like or semiconducting conductivity and processability of classical polymers has created opportunities for scientist and technological applications. Figure shows some of the known applications of polyaniline. Several reports and review papers have indicated promising applications of polyaniline and at least a hundred companies are involved in the test production of conducting polymers. It would be of interest to mention a few of the commercialized products which use polyaniline.

2.2 Electrorheological fluids

2.2.1 Electrorheological fluids

There has been increasing interest in the development of new materials that respond in some well-defined way to electrical and optical stimuli.

Electrorheological (ER) fluids are, in general, suspensions whose rheological properties are strong functions of an electric field strength imposed upon them. The suspensions behave typically fluidlike in the absence of an electric field (although they may be pastes or gels if mixed with greater concentrations of the dispersed phase), but under the electric field, the viscosity increases significantly, and the suspensions behave solidlike. Further, all the physical and mechanical changes induced in the suspensions by the applied electric are reversed virtually the moment the field is removed.

Rheological properties of an ER fluid vary when an electric field is
imposed due to a characteristic fibrillation with the strings of particles oriented along the electric field direction. This structure of particle is claimed to be caused by the dielectric constant mismatch of the particles and the insulating oil. Because of this yield phenomenon, ER fluids are known as Bingham fluids.

The increase in apparent viscosity from particle chain interactions under shear corresponds to the yield stress defined in the Bingham plastic model. When the electric field is removed, the particles return to a random distribution and fluid flow resumes demonstrating approximately Newtonian behavior as shown in Fig. 1.

The shear stress \( \tau \) for the Bingham plastic model is shown in Equation (1).

\[
\tau = \dot{\gamma} \eta + \tau_y
\]  

(1)

where \( \dot{\gamma} \) is the shear rate, \( \eta \) is the viscosity, and \( \tau_{ER} \) is the electric field induced dynamic yield stress.

It is assumed that the ER effect is the result of interactions between the viscous forces and the polarization forces. The viscous forces, for a Newtonian fluid, should be a function of the viscosity and the shear rate. The polarization forces should be a function of the field and the permittivity mismatch of the particle and the base fluid. The simplest theoretical treatment of the ratio of the viscous forces to the polarization forces is the Mason number, Mn. Mn is a dimensionless number expressed in Equation (2) and Equation (3).

\[
Mn = \frac{\eta_c \dot{\gamma}}{2\varepsilon_0 \varepsilon_c \beta^2 E^2}
\]

(2)

where
\[ \beta = \frac{\varepsilon_p - \varepsilon_C}{\varepsilon_p + 2\varepsilon_C} \]  

(3)

where \( \eta_C \) is the viscosity of the continuous phase, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_C \) is the permittivity of the base fluid, \( E \) is the applied electric field, and \( \varepsilon_p \) is the permittivity of the solid. The Mason number is based on the ratio of the viscous forces to the polarization forces. The viscous forces of a Newtonian fluid are a function of the viscosity and the shear rate; the polarization forces are a function of the field and the permittivity mismatch of the particle and the base fluid.

In general, as the Mason number decreases, ER effect increases. At \( Mn<<1 \), the dielectric mismatch of the two phases (\( \beta \)) or the electric field (\( E \)) is high and ER stress is high, because the ER stress transfer properties are dominated by the polarization forces. However, as the shear rate or viscosity of the base fluid increases, the viscous forces increase compared with the polarization forces and ER stress becomes a smaller component of total stress. At the upper limit of \( Mn>>1 \), the dynamics are those seen in the absence of the applied field. This qualitative model predicts a number of scaling relationships (e.g., \( E^2 \) and \( \beta^2 \) dependencies) that describe the ER phenomenon. However, the Mason number is only a first approximation of ER performance and cannot be used to predict a priori ER stresses [Havelka & Pialet, 1996].

The Mason number assumes that polarization forces result entirely from the permittivity mismatch of the particle and the base fluid; it does not take into account the differences in conductivity of the two phases, which can contribute significantly to the ER stress and power draw. Furthermore, viscoelasticity is another characteristic of the ER fluids which arises from particle chain structure. To improve the primary disadvantages of wet-base ER fluids such as their limited temperature range, anhydrous
ER materials has been developed vigorously. Presumably, viscous and conductive heating of the fluid cause the eventual loss of water, which results in a decrease in the effectiveness of the fluid. Additionally, the presence of substantial amounts of water can lead to dielectric breakdown, corrosion and high power consumption. ER fluid based on the semiconducting polymers is a novel, intrinsic dry-base ER system having several advantages, such as a wide working temperature range, a reduced abrasion, and a relatively low current density. There have been several reports on the electrical and rheological properties of anhydrous ER fluids composed of inorganic and polymeric materials.

Recently an increasing number of experts have become aware of the ER phenomenon and its importance. ER fluid’s sensitivity to electric field, coupled with their fast switching capabilities, allows ER devices to be directly controlled by computers. Electrorheology can be achieved in a continuously variable, wide dynamic range that is energy efficient, fast, reliable, compact-and achievable at a reasonable cost. This method allows for an extremely simple and efficient interface between electronic controls and mechanical devices without the need for moving parts such as those in conventional systems [Havelka & Pialet, 1996]. The automotive application including clutches [Havelka & Pialet, 1996; Whittle et al., 1995; Choi et al., 1998], shock absorbers [Marksmeiserm et al., 1998], engine mounts [Williams, 1993; Jeon et al., 1998] and fuel injectors, highlighted in the accompanying illustration, could be just the start for this technology. Furthermore, new promising systems have been developed which can be incorporated in structure to improve their response when excited by earthquakes. ER damper can be a practical solution to the challenging problem of protecting flexible structures from near-source earthquakes since they can provide a controllable rigid-plastic behavior [Makris, 1997; Ribakov & Gluck, 1999].
Despite the great potential of ER technology, no larger volume commercial ER devices have reached the market place. Nonetheless, U. S. Department of Energy-funded study concluded that the failure to commercialize this promising technology indicates serious deficiencies in understanding the materials and mechanisms responsible for the ER effect [Krieger et al., 1993]

2.2.2 Mechanism of ER Effect

2.2.2.1 Electrostatic Polarization Model

The electrostatic polarization model [Gast & Zukoski, 1989] of the ER response is based on the concept that due to a mismatch between the dielectric constants of the two phases, particles polarize in an electric field and apply a force to neighboring particles. The forces with which the polarization interactions compete in determining suspension microstructure and dynamics are colloidal.

If a uniform electric field is applied, bound charges in the particle and the continuous phase respond [Zukoski, 1993]. At the interface between the two phases, a mismatch in polarizability produces a perturbation to the applied field [Chen et al., 1991]. The electric potential, \( \phi \), is given by solutions to Laplace's equation.

\[
\nabla^2 \phi = 0
\]

Subject to boundary conditions of continuity of normal components of the electrical displacement and continuity of the electrical potential,

\[
\varepsilon_p \frac{\partial \phi_p}{\partial n} = \varepsilon_c \frac{\partial \phi_c}{\partial n}
\]

and

\[
\phi_p = \phi_c
\]
respectively. Here the subscripts p and c indicate the particulate and continuous phases. Equation (2) and Equation (3) are applied at the particle interface.

Outside a single particle the potential is written where the electric field is applied along the z-axis of a spherical coordinate system centered on the particle of radius, a. The particle dipole coefficient, β, is given in Equation (3) and represents the relative ability of the particle to polarize in the presence of the electric field.

\[ \phi = -E_0 r \cos \theta \left( 1 - \beta \left( \frac{a}{r} \right)^3 \right) \] (7)

If two sphere are spaced a distance r apart with their line of centers at an angle θ from the direction of the applied electric field, each feels a force from the polarization of the other sphere. This force can be found from solutions of Equation (4) subject to Equation (5) and Equation (6) and the use of Maxwell’s stress tensor to calculate the force acting on the particle. The resulting force is written where \( F_{el} \) is the electrostatic polarization force on the particle at the origin because of the particle located at r,θ, and \( \varepsilon_0 \) is the permittivity of free space. The externally applied electric field has the form \( E = E_0 e_z \) where \( e_z \), \( e_r \), and \( e_\theta \) are unit vectors pointed in the z, r and θ directions, respectively.

\[ F_{el} = 12\pi \varepsilon_0 \varepsilon_c a^2 \beta^2 E_0^2 \left( \frac{a}{r} \right)^4 \left[ 2f_{11} \cos^2 \theta - f_{\perp} \sin^2 \theta \right] e_r + f_{11} \sin 2\theta e_\phi \] (8)

The \( f_{11} \) are dimensionless functions of \( a/r \) and \( \varepsilon_p/\varepsilon_c \) and have been calculated for a range of \( \varepsilon_p/\varepsilon_c \) [Klingenberg et al., 1991]. In the point dipole limit (i.e. when \( r/a \gg a \) or \( \varepsilon_p/\varepsilon_c \) is close to unity), the \( f_{11} \) become unity. At small separations the \( f_{11} \) increase rapidly with \( \varepsilon_p/\varepsilon_c \) such that for \( \varepsilon_p/\varepsilon_c \rightarrow \infty \), \( f_{11} \)
diverges as $r/a \rightarrow 2$.

The large field intensification between two particles in this configuration results in $f_{II}$ being attractive and singular as $r \rightarrow 2a$, and can lead to dielectric breakdown of the intervening fluid [Zukoski, 1993]. If the conducting particles touch there is a rearrangement of charge and the force is no longer singular, but can be attractive or repulsive depending on the relative size of the particles. The magnitude of the polarization force scales on $12\pi \varepsilon_0 \varepsilon_c a^2 \beta^2 E_0^2$ showing quadratic dependencies of field, particle size, and the particle's relative polarizability.

The electrostatic polarization model has seen extensive application to the study of ER fluids. Mason compare predicted and measured rates of rearrangement and trajectories of two non-Brownian conducting spheres in viscous non-conducting oil and find excellent agreement.

### 2.2.2.2 Electric Double Layers Model

Even without the electric field, the solid particles have surface charge because different polarities link ions from the surrounding fluid to themselves. The so-called electric double layer develops [Block et al., 1990], and it is especially important for a relatively weak electric field.

Klass and Martinek [1967a, 1967b] first proposed double layer polarization theory as an alternative mechanism to fibril formation, starting that aggregation rates would be slow when compared with the short response and relaxation times involved in the ER effect. This mechanism takes into account the fact that strongly polarizable particles do not always produce strong ER effects [Chen et al., 1991]. They supposed that layer, toward the electrode having a charge opposite to that of the mobile ions in the double layer.

Double layer polarization or interfacial polarization as it is sometimes
termed, produces a very high electric constant (ε) at low frequencies and arises whenever mobile charge carriers are present. The permittivity decreases with increasing frequency with the development of a loss peak centered at some critical frequency. This has led many researchers to suggest that the operative polarization mechanism in ER fluid is interfacial [Block & Kelly, 1988].

While the presence of double layer polarization in many ER systems is evident, it has not yet been shown that the resultant double layer interaction and overlapping is sufficient to cause dramatic rheological changes seen in ER fluids. Klass and Martinek first presented convincing arguments for the presence of interfacial polarization based on the measurement of a low frequency dielectric dispersion. However, they presented no direct evidence that their proposal for double layer interference was the preferred mechanism over the particle interactions involved. Owing to the strong interdependence between parameters influencing ER activity, it is very difficult to vary conditions systematically in the double layer while holding all other system and material parameter constant.

2.2.2.3 Water Bridge Model

Stangroom [1983] attributed the large increase in suspension viscosity to the formation of water bridges between particles, which must be broken in order for the suspension to flow. The electric field strength dependence was associated with the migration of ions through the particle pores. When the field is applied, ions move out of the pores, carrying water to the particle surface and thus permitting the formation of bridges between particles. When the field is removed, surface tension pulls the water back into the particle pores [Parthasarathy & Klingenberg, 1996]. See et al. [1993] and Tamura et al. [1993] slightly modified this theory. Water was assumed to
migrate to the interparticle gap in order to minimized if the water resides in the gap where the electric field strength is much larger than the nominal field strength. When the field is removed, the water retreats due to surface tension [Tamura et al., 1993] or disjoining pressure [See et al., 1993].

Though water bridges may play a role in some systems, it is unlikely that they alone produce the ER effect. As water in bulk has a large dielectric constant and can generate mobile ions, its influence on particle polarization and its ability to alter the response through the electrostatic polarization mechanism should not be ignored [Parthasarathy & Klingenberg, 1996].
3. EXPERIMENTAL

3.1 Synthesis of nanoparticles

The PANI particles were prepared by an oxidative dispersion method. PMVEMA (U.S.A. \( M_w=216,000 \) Aldrich), PVA and PSSS were slowly dissolved in deionized water respectively. Poly (sodium 4-styrene sulfonate) was used as the stabilizer, but could also be considered as a dopant due to its acidity. In this project, two different methods that incorporated different quantities of dopant (HCl) were used, since PSSS was also considered a dopant. In method PAPSSS\#1, PAPSSS\#2 in table 1, 12.3 wt\%, 2.73 wt\% of HCl was used respectively. In both methods, the same amount of PSSS stabilizer was used. Depending on the conductivities of the two different methods used, effectiveness of PSSS as a dopant can be examined. Aqueous HCl and aniline in table 1 were added to the solution and the reaction mixture was continuously stirred at 0\(^\circ\)C [28-33]. An aqueous solution containing oxidant and ammonium peroxydisulfate was added through dropping. The light yellow solution gradually darkened and acquired an emerald color over a period of 40 minutes and eventually turned into dark green — a characteristic of doped PANI. This reaction mixture was then stirred for 24h at 0\(^\circ\)C. The resulting dark green dispersions were purified three times by centrifugation at about 8000rpm for 20 min, filtered and washed in order to remove oligomer and excess monomers. ER fluids were prepared by dispersing the dried PANI particles in an appropriate conductivity range in silicone oil, and then sonicated them via an ultrasonicator.

The properties of ER fluids for each PANI were measured by a
rotational rheometer (MC120, Physica) equipped with a high DC voltage generator. The polarization processes of each ER fluid were also examined using an impedance analyzer equipped with a liquid test fixture.

3.2 Rheological Measurement of ER fluids

The ER fluids were prepared by dispersing the powdery polyaniline particles in dry silicone oil. Silicone oil was dried in a vacuum oven and stored with molecular sieve before using. Before measuring, all ER fluids were dispersed again by a mechanical stirrer.

Electrorheological properties of ER fluids using PANI nanoparticles were measured by a rotational rheometer (MC120, Physica) with a Couette-type geometry (Z3-DIN and Z4-DIN) equipped a high voltage generator (HVG 5000) and concentric cylinder type measuring unit. The gaps of Z3-DIN and Z4-DIN were 1.06 mm and 0.59 mm and their maximum stresses were 1,041 Pa and 6,501 Pa, respectively. Temperature could be controlled from -40 to 150°C. To start a run, the ER fluid was placed in the gap between the stationary outer measuring cup and rotating measuring bob, and a d.c. voltage was applied to the cup. The electric field was applied for 3 min in order to obtain equilibrium chain-like or columnar structures before applying shear. The HVG 5000 could supply DC voltage up to 5 kV/mm within ± 10 µA of electric current. In order to obtain reproducible data, the ER fluid was redispersed before each experiment, and the measurements were carried out at least two or three times. The available shear rate was varied from 0.0072 to 1000 s⁻¹. The rheological properties were obtained by two different modes, namely, CSR (controlled shear rate) and CSS (controlled shear stress) at 25 ± 0.1 °C. The static yield stress was measured by using CSS mode with electric fields. Polarization processes of
each ER fluid were also determined using an impedance analyzer (HP) equipped with a liquid test fixture.

3.3 Measurements

Centrifugation. HMR-160 IV

Thermogravimetric analysis. TGA was performed using a Polymer Laboratory, PL TGA series.

Chemical composition. The PMVEMA-PANI was characterized by Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer Spectrum 2000 Explorer FT-IR Spectrometer).

Morphology. The stabilizer/polyaniline surface is found to be very rough and there were a few aggregates of PMVEMA-PANI particles by scanning electron microscope (SEM : Hitach S-4300 (made in Japan)) and transmission electron microscope (TEM : Philips CM200, EDS DX-4 (EDAX))

Microscope. Nikon Optical Microscopy

Conductivity measurements (DC-electrical conductivity). These measurements of the DC-electrical conductivity of dry samples of PANI nanoparticle were carried out at room temperature on compressed pellets by the 2-probe method using picoammeter (Keithley 487) and the usual four-probe method (237 high voltage source measurement unit, Keithley 237)

Dynamic light scattering. Brookhaven Instrument Corporation

UV-VIS spectroscopy. UV-VIS spectra of PANI dispersion in DMF and ionized water were recorded separately using ---- , using DMF and ionized water in reference cell.
3.3.1 Measurement of UV-Vis spectrum

Spectroscopy is the measured and analysis of electromagnetic radiation absorbed, scattered or emitted by atoms, molecules, or other chemical species. The absorption and emission of electromagnetic radiation is associated with changes in energy states of the species. The UV-Vis (Ultraviolet and Visible Spectroscopy of Polymers) spectrum is from 200nm to 800nm. UV-Vis spectrophotometry uses ultraviolet and visible electromagnetic radiation to energetically promote valence electrons in a molecule to an excited energy state. The UV-Vis spectrophotometer then measures the absorption of the energy to promote the electron by the molecule at a specific wavelength or over a range of wavelengths.

The amount of electromagnetic radiation absorbed by a species in a solution depends on its concentration, the path length of the electromagnetic radiation, and the specific molar absorbivity of the species. This is defined as Beer-Lambert’s Law.

\[ A = \log_{10}(I_0 / I) = \varepsilon cl \]

(dimensionless), where \( I_0 \) is the intensity of the incident light (in quanta per second). \( I \) is the intensity of the light transmitted through the sample solution (or sample film)(in quanta per second), \( \log_{10} (I_0 / I) \) is called the ABSORBANCE (A) of the solution also called the OPTICAL DENSITY (D) or EXTINCTION(E)

\( \varepsilon \) is the molar absorptivity (also called the molecular extinction coefficient)

\[ \varepsilon = A / cl \]

( \( c \) : a function of concentration, \( l \) : cell path)

When molecules interact with radiant energy in the UV-Vis regions, the absorption of energy consists of displacing an outer electron in the molecule. The UV-Vis spectrum is a function of the whole molecule’s
structure rather than individual bonds. Information provided by a UV-Vis spectrum should be used in conjunction with other means of identifying the compound. Compounds, which have only single bonds that involve only sigma orbital electrons, exhibit spectra below the UV-Vis region and cannot be analyzing using UV-Visible spectrophotometer. Heterogroups including oxygen, nitrogen, halogens, ethers, amines, sulfides, and alkyl halides contain \( pi(\pi) \)-orbital electrons in bonding and therefore can be analyzed with UV-Vis. These groups are commonly called chromophores. All molecules with double or triple bonds can be analyzed with UV-Vis. The intensity of the absorption of energy by a molecule is proportional to the number of chromophores or double bonds it contains. UV-Vis spectra are best used in comparison with standard compilations of UV-Vis spectra to identify the basis of the chemical structure.

3.3.2 Measurement of conductivity (4-probe method)

A four-probe method and a Janis closed-cycle refrigerator system were used for measuring \( \sigma_{dc}(T) \) from 300 to 10K. Four thin gold wires (0.05mm thick and 99 pure gold) were attached in parallel on the sample surface by graphite glue (Acheson Electrodog 502) for better electrical contact.
4. RESULTS AND DISCUSSION

4.1. Characterization of semiconducting polyaniline nanoparticles

The particle formation stage is the most important and the most complex period in dispersion polymerization or emulsion polymerization. Figure 1.1 shows the proposed particle formation mechanism[41-45].

A proposed description of the polymerization of aniline using a polymer surfactant is as follows. In a dispersion polymerization, initially the system is homogeneous prior to the polymerization. By initiating polymerization, primary radicals generated by decomposition of the initiator, grow by the addition of monomer units in the continuous phase until they reach their critical chain length where they precipitate to form nuclei, either by a self or aggregative nucleation mechanism. These nuclei are not considered to be stable and aggregate with each other, they adsorb the stabilizer and finally become stable (mature) particles. As long as enough mature particle are formed to capture all of the oligo-radicals and nuclei in continuous phase, no more new particles will be formed and the particle formation stage is complete. Nuclei and mature particles coexist during the whole particle of growth stage. At the end of the polymerization, nuclei formation finishes due to the exhaustion of either the monomer or the radicals (by cooling or adding inhibitor), finally mature particles are only observed.

The use of long chain macromolecules to stabilize colloidal particles has been the subject of much study as illustrated in a number of recent reviews and monographs. The basic concept is that if one can attach polymer molecules to the surface of a particle and suspend the particle in a
good solvent for the polymer, one can prevent the particles from approaching one another and aggregating. This approach is physically similar to the way surfactant molecules suspend oil droplets in water, the polymer chains, by dangling into solution, serve to solubilize the particles rendering them more lyophilic. Indeed, in some cases short chain surfactant molecules suffice to stabilize a suspension; however, most often a polymer is required to achieve the necessary surface to surface separation. The key aspect of polymeric stabilization is that the chains must extend into the solution. One approach to the stabilization of polymeric particles is to carry out their synthesis in the presence of stabilization polymers, creating a dispersion of polymerized swollen micelles. Excluding this possibility for systems not easily synthesized in this way, one must search for a means of adding stabilizer to an existing suspension. Normal physical adsorption of polymer molecules usually results in a relatively thin layer of polymer, insufficient to provide stability. This has motivated the development of two additional methods for anchoring polymers to particles, via end-grafting and block copolymer adsorption. These techniques will be described very briefly below followed by a simple scaling analysis of the range and magnitude of the repulsive interactions that can be expected for polymeric stabilization. For further information on this subject, the reader is referred to a number of excellent reviews. The size and shape of synthesized PANI particles were determined by a balance between the adsorption rate of stabilizers and the growth rate of polymerization. A spherical shape was obtained when the adsorption rate of stabilizers exceeds the rate of polymerization. Since the polymeric stabilizer chain was adsorbed onto the semiconducting polymer particles during synthesis, their agglomeration was prevented by steric stabilization. Flocculation of the particles is prevented due to the excluded volume effect of the stabilizer adsorbed on the particle surface.

Figure 1.2 and Figure 1.3 show a schemer during synthesis processing.
Figure 1.2 (a) and (b) shows that conducting polymer particles of submicronic size are prevented from aggregation by a surface overlayer of steric stabilizer. (The dispersion medium contains oligomer, monomer and dopant) and After centrifugation, dispersion particles sediment and can be separated from the medium, respectively. Figure 1.3 shows the structural model conducting polymer colloid.

Figure 1.4 shows SEM photographs of PANI without polymeric stabilizer. The shape of the particles is very irregular and the size range of the particles is approximately 1~20 μm.

Transmission electron microscopy (TEM) of figure 1.5 ~ figure 1.7 and Dynamic light scattering (DLS)[46-48] of figure 1.8~ figure 1.10 indicates that the PANI particles with polymeric stabilizer in the dispersion have a spherical shape with a uniform size. However, the larger aggregates of the primary particles might be formed during filtration and drying process of the particles, as observed via the scanning electron microscopy (SEM). The particles broken to molecular or nano size during sonication therefore undergo aggregation when the solvent is removed [49]. The size and shape of particles such as rice grain, needle, oblong or sphere are determined by a balanced between the adsorption rate of stabilizers and the growth rate of polymerization. Figure 1.11~Figure 1.15 show SEM of PANI particles with various stabilizer in table 1.1. The PANI nanoparticles have almost a uniform size and spherical shape regardless of stabilizer weight fractions but the higher aggregates seen in the SEM might have formed during isolation and drying of the particles. Figure 1.12 show SEM photographs of PANI particles with diameters of several tens micrometers indicating some aggregation of the primary particles. In fact, redispersion of the dried particles yields dispersions of only low solid content in contrast to the dispersion of wet particles yields dispersions of solid content almost as high as that obtained during synthesis. The poor redispersibility of the dried
particles may be due to such no uniform distribution of the stabilizer taking place during drying irreversibly.

Table 1.1 shows conductivity[50-51] of the nanoparticle samples prepared from various polymeric stabilizers. The $\sigma_{dc}(RT)$ of PANI particles prepared from PMVEMA, PVA, PSSS#1, PSSS#2 and PSSS#3 is 0.23, 1.32, 0.11, 0.05 and 0.45 S/cm, respectively. Figure 16 compares temperature dependence of $\sigma_{dc}(T)$ of PANI particles with polymeric stabilizer samples.

Figure 1.16 shows the temperature dependence of $\sigma_{dc}(T)$ of PAPMVEMA, PAPSSS#1 and PAPSSS#2 samples. The three-dimensional (3D) variable range hopping (VRH) model [52-65] provides the best fit for $\sigma_{dc}(T)$ of the chemically synthesized PAPSSS in the present investigation with the following equation,

$$\sigma_{dc}(T) = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/(1+d)} \right], \quad \text{where } d=3. \quad (1)$$

Here $T_0$ can be interpreted as an effective energy separation between localized states and can be written as $T_0 = 16\alpha^3/k_B N(E_F)$, where $k_B$ is the Boltzmann constant, $N(E_F)$ is the density of states at the Fermi level, and $\alpha^{-1}$ is the localization length in the parallel (perpendicular) direction. Usually, $\sigma_{dc}(T)$ of PANI particles follows a quasi-one-dimensional (1D) variable range hopping (VRH), but the experimental result of $\sigma_{dc}(T)$ shows that our nanoparticles deviate from the 1-dimensional VRH model due to the addition of the polymeric stabilizer. Polypyrrole/clay nanocomposite was recently found to follow 3D VRH model due to its quasi network structure through the interchain links and side chains.

Figure 1.17 compares the $\sigma_{dc}(T)$ of the PAPMVEMA, PAPSSS#1 and
PAPSSS#2 studied here using the reduced activation energy defined as

\[ W(T) = \log \frac{d \ln \sigma_{de}(T)}{d \ln T} \]

From the slope of the \( W(T) \) plot, one can determine the insulating, critical, or metallic state of the materials. The slope of the PAPSSS#1 and PAPSSS#2 is negative, i.e. \( W \) increases as \( T \) decreases, which indicates that the systems are in the insulating regime. However, the slope of the \( W(T) \) plot of PAPMVEMA particle is estimated to be 0 or even positive, indicating that the systems are in the critical or the metallic regime.

The absorption spectra were recorded for the PANI-nanoparticle (PAPMVEMA, PAPVA and PAPSSS) and PANI base (usual PANI) in DMF and deionized water in figure 1.18. The dry powder of the complex can readily redissolve in water and DMF. The solution spectrum of the PANI-base taken in DMF and ionized water exhibits two bands near 320 nm and 602 nm. The absorption peaks at 320 nm is attributed to \( \pi - \pi^* \) transition of benzenoid rings and the peak at 602 nm is due to \( \pi - \pi^* \) transition of quinoid ring of the polyemeraldine chain [66].

Absorption spectra for redispersed samples of PANI nanoparticles after centrifugation [67], washing and filtering showed different features form those of the PANI salt dispersion except for PAPSSS sample[68-77]. The spectra PAPVA and PAPMVEMA samples were a little shifted to a longer wavelength with greatly diminished localized polaron band or free carrier tail instead of localized polaron band around 780nm. This could be assigned to the removal of undesired components such as excess HCl, unreacted aniline monomer and oligomer. However, about the PAPSSS (the PSSS-doped PANI), the UV-visible spectra of the PAPSSS sample was characteristic of emeraldine salt, exhibiting a strong localized polaron band at 780nm (A strong, localized high wavelength polaron band was observed in the region 750~780nm), as well as a second polaron band and a \( \pi - \pi^* \)
transition band at ca. 440 and 346 nm, respectively. The excitation absorption peak of the PANI base completely disappears in the absorption spectrum of the PSSS-doped PANI, which may indicate complete protonation of the imine N atoms. Because poly (sodium 4-styrene sulfonate) was used as the stabilizer, but could also be considered as a dopant due to its acidity. This could not perfectly remove PSSS stabilizer adsorbed onto the conducting polymer nuclei.

Thermal stability of the PANI was determined by a thermogravimetric analysis, demonstrating its two-step decomposition. It shows that a slow decrease of weight loss of samples was about 10% at 500°C and a one-step weight loss was from 500°C to 800°C. Figure 1.19 shows the results of the TGA measurement of the polyaniline nanoparticle to compare the effect of the stabilizer and dopant on the thermal property. The thermogram indicated that the weight loss around 100 °C was due to water or solvent and decomposition of the PANI particles began about 300 °C and 500 °C. The result shows that the prepared PANI particles with polymer steric stabilizer were seen as a two-step process. The first step is the loss of the dopant and the second step corresponds to the decomposition of the backbone. The first decrease of mass was mainly due to the removal of dopant molecules, polymeric stabilizer and also the poss of possible impurities such as remaining monomers. The second weight loss at high temperature corresponds to the structural decomposition of the polymer.

Chemical structure of the synthesized PANI in Figure 1.20 was identified from the Fourier Transform-Infrared spectroscopy (FT-IR) spectrum using KBr pellets in Figure 1.20. The peak of FT-IR at 825 cm⁻¹ originates from the out-of-plane H deformation of aromatic rings in the PANI unit sequences, whereas the peaks at 1,145 cm⁻¹ and 1,310 cm⁻¹ are due to aromatic amine stretching, and those at 1,490 and 1,590 cm⁻¹ are the C-C
stretching modes.

4.2. Electrorheological Characterization

The PAPSSS solution was chemically doped or undoped by oxidant, acid, reductant, or base to go through the normal sequence of color changes between transparent, green, blue and purple colors [36,38]. The solution appears to be chemically and physically stable as it is doped and undoped to various color forms (or oxidation and protonation states). This indicates that the soluble polyaniline forms. This fact suggests that the electrostatic attraction is not the only force that holds the complex together and there may be other interactions (perhaps short range forces) that also help binding the components of the complex. Since the PANI backbone is expected to have no charge in its deprotonated, blue colored insulator form, the electrostatic attraction would be absent in such state of PSSS-Pani complex.

Examples of the polyanion in the polymeric complexes are poly (styrenesulfonic acid), poly (acrylic acid), poly (methacrylic acid), poly (2-acrylamino-2-methyl-1-propnesulfonic acid) and poly (methylacrylate-co-acrylic acid).

The “double –strand” polymers were synthesized by a method that encourages the formation of molecular complexes. In the first step, the aniline monomers were absorbed onto a polyanion chain dissolved in solution. In the second step, the attached aniline monomers were oxidatively polymerized to form the polymeric complex. The adduct of polyanion : aniline may take the shape of a tight coil or extended chains. The shape of the adduct controls the morphology of the polymerized product. The anionic dopants, incorporated as part of the molecular complex, are strongly attached to the PANI chain. The solubility of conductive PANI reflects the
collective properties of two components in the molecular complex. The molecular complex of PANI with PSSS is soluble in water, methanol and DMF. The solution is colored and the dried product is conductive because of PANI.

The anionic dopant of PSSS, incorporated as part of the molecular complex, is strongly attached to the PANI chain to form a double stranded structure. The complex does not decompose or unwind in acid, base, solvent, mild oxidant/reductant, or by heat. In contrast, under the same conditions the single-strand PANI loses its dopant and becomes nonconductive. Sun et al. reported that the polyelectrolyte strongly influences the pH for deprotonation of the PANI chain. With a small anionic dopant, the single-strand PANI deprotonates at pH 4. The same transition occurs at pH 9 for the molecular complex of PANI and PSSS complex in water. The origin of this effect comes from the electrostatic field near the polyanion chain. Due to these cause, their conductivity was not controlled to a range of $10^9$ to $10^{10}$ S/cm, measuring the pH which is the favorable conductivity range for particles used in ER fluids. (Usually, For the electrorheological (ER) investigation in PANI particles, their optimal conductivity was achieved via controlling solution properties during their synthesis.)

For the electrorheological (ER) investigation, their optimal conductivity was achieved via controlling solution properties during their synthesis, in which ER fluids are dispersions of polarizable or semiconducting particles in insulating base fluids. They represent a unique class of electroactive materials that exhibit drastic changes in rheological and electrical properties under an applied electric field.

Figure 1.23 and 1.24 shows flow curves of shear stress vs. shear rate for PANI particle based ER fluid with various electric field strengths.

In the absence of an electric field, the fluid is similar to that of a typical concentrated shear–thinning suspension. The slope of 0.86 in the shear
stress - shear rate plot is less than 1 (which is the Newtonian fluid limit). Shear stresses for the ER fluid increased over the entire shear rate range with an increase of electric field strength. After the plateau region, shear stress increases with shear rate similar to Newtonian fluids, implying that the hydrodynamic force begins to dominate over the electrostatic force. The behavior which depends strongly on the electric field strength at a low shear rate is due to the deformation, reformation and destruction of chainlike or columnar structures as the shear rate increases below the critical shear rate. Meanwhile, the polarization is considered to control the ER effect. In order to study the mechanism of the electrostatic interaction and the polarization properties of our samples, we investigated the polarization properties of ER fluids dielectric spectra. From these spectra, estimated the polarization (i.e. the interfacial polarization) properties of the ER fluids. A dielectric relaxation is also observed in the spectra of the ER fluid.

The slow polarizations, the Debye polarizations by the potential barrier between two equilibrium positions where the dipole would orientate from one to the other and the interfacial polarization by the dielectric constants and conductivities of the two components, should be responsible for the ER effect would be imperative and significant either in understanding the original basis of ER effect or in developing the applicable ER fluids. We investigated the polarization properties of ER fluids, by obtaining dielectric spectra of PAPMVEMA and PAPSSS in the frequency range 20~10^6 Hz. The (a) and (b) of figure 1.21 and figure 1.22 show the permittivity (e') and loss factor (e''), respectively.

Figure 1.25 shows change of static yield stress [78-80] of PAPMVEMA measured by CSS mode at various electric field strengths. Contrary to a CSR mode in which a shear rate is applied to the ER fluid and the resulting shear stress is measured giving a dynamic yield stress, the ER fluid is stressed by an applied mechanical torque until the particle chain
structure is perfectly broken so that the shear rate occurs. As the gap between the conducting particles in the fluid decreases (e.g. increasing concentration), the electric response of the fluid becomes nonlinear through electrical breakdown or particle discharge under high electric field strengths. Based on the nonlinear conductivity model, Davis showed that over a range of unscaled \( E_0 \) greater than critical electric field \( (E_c) \), the slope of \( E_0 \) vs \( \tau_y \) (yield stress on log scale) is approaches 1.5, while the slope approaches 2 for small \( E_0 \). The critical electric field \( (E_c) \) represents the critical electric field originated from the nonlinear conductivity model, and is descriptive for crossover behavior and defines the two regimes in the \( E_0 \) vs \( \tau_y \) plot. The critical electric field \( (E_c) \) of PAPMVEMA is 2 kV/mm. Two limiting behaviors at low and high electric field strengths, respectively have following equation:

\[
\tau_y = \alpha E_0^2 \propto E_0^2 \quad E_0 \ll E_c \tag{1}
\]

\[
\tau_y = \alpha \sqrt{E_c E_0^{2/3}} \propto E_0^{2/3} \quad E_0 \gg E_c \tag{2}
\]

Equation (1) shows that \( \tau_y \) is proportional to \( E_0^2 \) for low \( E_0 \) (Regime I) as shown Figure 1.25, and \( \tau_y \) changes abruptly to \( E_0^{2/3} \) for high \( E_0 \) (Regime II) as shown Figure 1.25. Choi found that \( E_c \) is influenced by the particle conductivity an conductivity mismatch between the particle and medium liquid and is weakly dependent on the volume fraction. The polarization forces between particles increase with increasing both electric field strength and particle concentration, which in turn develops the particles chain structure, thus increasing the yield stress.
5. CONCLUSION

Semi-conducting PANI particles were synthesized from oxidative dispersion polymerization of aniline using polymeric stabilizer. ER properties of PANI particles were examined using a rotational rheometer equipped with a high voltage generator in both the steady shear and dynamic modes to study the effects of electric field strength and particle concentration on ER performance. Compared to homo polyaniline-based ER fluid, PANI-based ER fluids with diameters of several tens micrometers with some aggregation of the primary particle in the drying state is not improved significantly, by showing that the ER properties are enhanced by increasing the particle concentration and electric field strength, but also exhibit typical viscoelastic properties under an electric field due to chain formation. Future studies will be focused on PANI in the dispersion state to prevent aggregation of primary particles after drying.
6. REFERENCES


Table 1.1. Dispersion polymerization of aniline with various polymeric stabilizer

<table>
<thead>
<tr>
<th>Sample</th>
<th>aniline (wt%)</th>
<th>stabilizer (wt%)</th>
<th>HCl (wt%)</th>
<th>Temperature (°C)</th>
<th>σ (S/cm)</th>
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<tr>
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<tr>
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<td>2.56</td>
<td>25</td>
<td>0.45</td>
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Figure 1.1. The proposed particle formation mechanism
Figure 1.2. (a) Conducting polymer particles (PANI, hatched spheres) of submicronic size are prevented from aggregation by a surface overlayer of steric stabilizer. The dispersion medium contains oligomer, monomer and dopant. (b) After centrifugation, dispersion particles sediment and can be separated from the medium.

Polymeric stabilizer
Conducting polymer (PANI)

After washing, drying & filtering

Dispersion state (nanoparticles)
  pH: 0.85

Aggregation of primary particle (microparticles)
  Conductivity: 9.195 S/cm

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### Figure 1.8. DLS of PAPMVEMA dispersion

<table>
<thead>
<tr>
<th>Percent</th>
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<table>
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<th>Diameter nm</th>
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**12-2g-hema**

<table>
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**12-2g-hema**

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**12-2g-hema**

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**Notes:**
- The data represents the distribution of particle sizes measured by dynamic light scattering (DLS) for PAPMVEMA dispersion.
- The mean, standard deviation, skewness, and RMS values are provided for different particle sizes.
- The graphs show the intensity distribution across different diameter ranges.
- The dispersion is divided into three categories based on particle size: 315nm, 293nm, and 544nm.

**Legend:**
- d/nm: Diameter in nm
- G(d): Intensity gradient
- C(d): Intensity cumulative percentage
Figure 1.9. DLS of PAPVA dispersion
<table>
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<tr>
<th>Percent</th>
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![Graph 1](image1.png)

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![Graph 2](image2.png)

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![Graph 3](image3.png)

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56
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PART II.

SYNTHESIS AND ELECTRORHEOLOGICAL CHARACTERIZATION OF POLY (VINYL BUTYRAL) (PVB)-POLYANILINE (PANI) COMPOSITES USING POLY (VINYL ALCOHOL)
ABSTRACT

To improve the processability of PANI for the various electrochemical applications because of its facile synthetic process, good environmental stability, low cost of raw material and conductivity control, we used Poly(vinyl alcohol) (PVA) as polymeric stabilizer by the oxidative dispersion polymerization. However PANI-PVA can not be adopted to ER system without controlling conductivity because its conductivity is too high. Thereby, Acetalization of PANI-PVA method is adopted as a substitute for dedoping method. In this study, PANI-PVB (Poly (vinyl butyral)) particles are used to the dispersed phase in ER fluids. We observed the size effect of particles by SEM, TEM, DLS and microscopy. The particles were characterized by FT-IR, TGA and conductivity. Effect of electric field strength, particle concentration and particle size on ER properties of PANI-PVB was examined and then its viscoelastic properties were investigated under applied electric fields using a rotational rheometer.

Keywords: Electrorheological fluid, Rheology, Dispersion polymerization, stabilizer Polyaniline, Polyvinylalcohol, Polyvinylbutyral
국문요약

Polyaniline은 손쉬운 합성 과정과 좋은 열적 안정성, 그리고 용이한 전도도 조절로 인해서 가장 유용한 conducting polymer 중의 하나로 알려져 있다. 그러나 그 자체로는 가공성이 매우 취약하여 거대한 분자가 구조를 갖는 유기산을 dopant로 사용하여 용해성을 항상시키거나, 범용 고분자들과의 blend을 통하여 이러한 문제점을 해결하려는 노력을 계속 이루어왔다. 특히, 여러 가지 수용성 고분자를 안정적으로 사용하여 PANI 입자를 colloid상으로 중합하고, 이를 바로 전도성 film이나 coating물질로 용융하고자 하는 연구들이 많이 이루어졌다. 이러한 polyaniline의 submicronic particle은 polymeric steric stabilizer인 film-forming ability, toughness와 biocompatibility가 우수한 water solubility한 성질을 가진 Poly(vinylalcohol)(PVA)을 가지고 oxidative polymerization에 의해 중합되었다. 그리고 전기유연유체(ER)로서 이용 가능한 입자를 위해 alcohol과 aldehyde의 acetalization을 통해서 insoluble한 Polyvinylbutyral(PVB)와Polyaniline(PANI)을 합성하였다. PANI-PVB와 PANI-PVA composite은 SEM, TEM 그리고 DLS로 물질의 morphology와 입자 크기를 확인하였고, TGA, FT-IR, 전도도와 rheological measurement로 물질 특성을 분석하였다.
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Part II. SYNTHESIS AND ELECTRORHEOLOGICAL CHARACTERIZATION OF POLY (VINYL BUTYRAL) (PVB)-POLYANILINE (PANI) COMPOSITES USING POLY (VINYL ALCOHOL)

1. INTRODUCTION

Polyaniline (PANI) is known to be one of the most useful conducting polymers for the various electrochemical and electronic applications because of its facile synthetic process, good environmental stability, low cost of raw material and conductivity control [1]. PANI is also easy to polymerize by oxidation polymerization. To enhance the dispersion stability of polyaniline, we used poly (vinyl alcohol) (PVA) [3] with hydroxyl groups as polymer stabilizer and obtained the PANI-PVA (PAPVA) particles of a uniform nanometer size and a spherical shape prepared by the oxidative dispersion polymerization in acidic aqueous media. Note that the PVA possesses good film-forming ability, toughness and good biocompatibility. However PAPVA particles cannot be directly adapted to ER system without controlling conductivity because its conductivity is too high. Thereby, acetalization of PANI-PVA method is adopted as a substitute method for dedoping in this study.

The polymer commonly reffered to as poly (vinyl butyral) or PVB [4,5] is, in the random terpolymer poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate), shown Figure 2.1. PVB is a member of the class of poly(vinyl acetal) resins. It is derived by condensing PVA with n-butylaldehyde under acidic conditions. PVA reacts with the aldehyde, to form six-membered
rings primarily between adjacent, intermolecular hydroxyl groups, leading to the structure shown Figure 2.1. Subsequent to hydrolysis of poly (vinyl acetate) to produce PVA, the latter is reacted with. The resultant polymer contains residual vinyl acetate (VAc) groups, at approximately 1-5% (w/w), and residual vinyl alcohol (VOH) groups, ranging from 10 to 30% (w/w), with the remainder of the molecule being composed of vinyl butyral (VB). As noted, these functionalities are distributed randomly throughout the polymeric backbone. The significant use of PVB is in lamination of safety glass (automotive windshields). Others are structural adhesives, binders for rocket propellants, ceramics, in metallized brake linings, lithographic and offset printing plates; protective coatings for glass, metal, wood, and ceramics; adhesion promoter in inks etc. While 100% butyralized PVB (100% VB) can be produced, it has been found that a certain amount of vinyl alcohol is highly desirable. This is due to the fact that the VOH content is responsible for a number of important end-use properties of PVB, including controlling the adhesion to surfaces, improving the properties of thermoset resins, influencing crosslinking behavior, and affecting the miscibility and morphology of blends.

In this study, PANI-PVB (Poly (vinyl butyral)) particles are used to the dispersed phase in ER fluids. We observed the size effect of particles by scanning electron microscope analysis (SEM), transmission electron microscope (TEM), dynamic light scattering (DLS) and microscopy. The particles were chemically characterized by FT-IR. Thermogravimetric analysis (TGA) was performed on the particles to measure thermal properties. Effect of electric field strength, particle concentration and particle size on ER properties of PANI-PVB was examined and then its viscoelastic properties were investigated under applied elastic fields using a rotational rheometer with high voltage generator in both controlled shear rate and shear stress modes.
2. EXPERIMENTAL

2. 1. Dispersion polymerization using poly(vinyl alcohol)

Polyaniline dispersion with Poly (vinyl alcohol) as steric stabilizer in acidic aqueous media was carried out by using oxidative dispersion method found in earlier papers. Poly (vinyl alcohol)(molecular weight (MW) 70 000 degree of hydrolysis 97.5-99.5 mol %) was slowly dissolved in ionized water. The solution was heated up to 95°C for 1 hour, cooled down at room temperature. 35 wt% HCl and aniline were added to solution and the reaction mixture was continuously stirring at 0°C. An aqueous solution containing oxidant (ammonium peroxysulfate) was added in drops for 60-90 min at 400~500 rpm. The lightly yellow solution gradually darkened and turned emerald color over a period of 20 minutes and eventually turned dark green, which is characteristic of doped polyaniline. This reaction mixture was then stirred for 24 hours at 0°C.

2. 2. Synthesis of poly(vinyl acetal)

We used precipitation method of synthesis as described below. The acetalization [6] was carried out in reactor with PVA-PANI solution, equipped with mechanical stirrer, dropping funnel, reflux condenser and inlet for inert gas. PVA-PANI solution which was included poly(vinyl alcohol) and 35 wt% HCl as catalyst was prepared at 10°C. n-Butyraldehyde was added to the solution at 10°C for 60 min (400rpm). With progress of acetalization, the solutions became heterogeneous. This
reaction mixture was then stirred for 3 hours at temperature from 10°C to 55 °C. The resulting dark green dispersions were filtered and washed by aspirator. The separated PANI-PVB composite was then washed three times with deionized water.

PAPVB composite particles are used to the dispersed phase in ER fluids. ER fluids were then prepared by dispersing the dried PAPVB 40 and PAPVB 30 particles is silicone oil by 20vol%, 15vol% and 10 vol%.

2.3. Measurements of Characterization

Thermogravimetric analysis. TGA was performed using a Polymer Laboratory, PL TGA series.

Chemical composition. The PMVEMA-PANI was characterized by Fourier transform infrared (FT-IR) spectroscopy.

Morphology. The stabilizer/polyaniline surface is founded to be very rough and there were a few aggregates of PMVEMA-PANI particles by scanning electron microscope (SEM : Hitachi S-4300 (made in Japan)) and transmission electron microscope (TEM : Philips CM200, EDS DX-4 (EDAX))

Conductivity measurements. These measurements were carried out at room temperature on compressed pellets with silver coating by the 2-probe method using picoammeter (Keithley 487).

The conductivity of the pellets was measured by the usual four-probe method (237 high voltage source measurement unit, Keithley 237)

3. RESULTS AND DISCUSSION

3.1 Characterization of polyaniline/poly(vinyl butyral) composites

PVA, like low-molecular-weight alcohols, is highly reactive lending itself to esterification, etherification and acetalization. Of these reactions, acetalization is of great importance in industrial applications. Many studies of the acetalization of poly(vinyl alcohol)(PVA) have been made since Herrmann and Haehnel, the discoverers of PVA, first investigated it.

PANI-PVA solution prepared by the oxidative dispersion polymerization reacts with n-butyraldehyde in the presence of an acid catalyst, chiefly forming six-membered intramolecular acetal rings between the adjacent intramolecular hydroxyl groups as shown Figure 2.1 and Figure 2.2. (a). However, there is also the possibility of forming intermolecular acetal links between the hydroxyl groups causing intermolecular crosslinking, as shown Figure 2.2 (b). The formation of the five-membered ring shown in Figure 2.2 (c) is also possible. Commercial PVA contains not only the 1,3-glycol bonds, but also 1-2 percent of 1,3-glycol bonds [7]. Poly (vinyl butyral) resin, made from polyvinylalcohol and butyraldehyde, is used for laminating automobile safety glass, and as a vehicle for ‘wash-primer’ paints for marine use and other applications on metal.

PAPVB composites with PAPVA series of several aniline/(aniline+PVA) wt% contents in Table 2.1 were synthesized from an acetalization reaction of a PVA with butyraldehyde [8-13]. Codes and the relevant characterization data for samples used in this study are presented as PAPVB series. Numbers of immediately followed ‘PAPVB’ and ‘PAPVA’ denote the weight percent
of aniline/aniline+PVA content in sample.

Composite particles of samples for various weight percent of aniline to PVA have been studied.

Figure 2.3 shows SEM micrographs of the surfaces for PAPVA series. At a low concentration, aniline was polymerized into the spherical nanoparticles in the case of PAPVA20 sample. The shape of particles synthesized at the other concentrations was expected to slightly derive from the spherical shape as samples of PAPVA30, PAPVA40 and PAPVA50 in Figure 3. They were very irregular. Generally, as stabilizer concentration decreases, the shape changes from sphere to irregular shape with diameters of several tens micrometers indicating some aggregation of the primary particles. The conductivities of dried PAPVA series measured by the four-probe method was about $10^{-1}$S/cm after washing, filtering and drying of PAPVA series solution in Table 2.2.

From figure 2.4 to figure 2.12 shows SEM micrographs of the surfaces for PAPVB composite series [14-17]. The size range of the particles is approximately 1-200µm, showing that the characteristic morphology depends on the weight percent of aniline/(aniline+PVA) content. The more the PANI content of the PAPVB composites increase, the higher the electrical conductivity of room temperature is from $10^{-11}$S/cm to $10^{-2}$S/cm in Table 2.3.

Chemical structure of the synthesized PAPVB composites, PVB and PANI was identified from the Fourier transform infrared spectrum (FT-IR) spectrum using KBr pellets in Figure 2.13. The peak of FT-IR at 825cm$^{-1}$ originates from the out-of-plane H deformation of aromatic rings in the PANI unit sequences, whereas the peaks at 1,145cm$^{-1}$ and 1,310cm$^{-1}$ are due to aromatic amine stretching, and those at 1,490 and 1,590cm$^{-1}$ are the C-C stretching modes. For PVB were the appearance of four additional characteristic absorption peaks appearing at 3485cm$^{-1}$, 2900cm$^{-1}$, 1750cm$^{-1}$,
1136 cm⁻¹ and 1000 cm⁻¹ which were assigned to the characteristic vibrations of a OH-group, C-H stretching, carboxyl group and bands to cyclic acetal, respectively. The more the PANI content of the PAPVB composites increase, the more PANI characteristic absorption peaks begin to appear.

Figure 2.14 shows the results of the TGA measurement of the PAPVB composites to compare the effect of composites on the thermal property. Thermal stability of the PAPVB composites was determined by a thermogravimetric analysis, demonstrating its two-step decomposition. In TGA profile, major losses of weight were observed over two temperature periods. It shows that weight losses of the first step and second step were due to dominantly degradation of PVB and PANI, respectively. The thermogram of PANI indicated that the first decrease of mass was mainly due to the removal of dopant molecules, HCl and also the possession of possible impurities such as remaining monomers and the second weight loss at high temperature corresponds to the structural decomposition of the polymer backbone. The result shows that the prepared PANI compare to PAPVB composites have a good thermal stability.

The effect of PANI content on the electrical conductivity of room temperature about the PAPVB composites with PANI loading concentration is shown in Figure 2.15. Figure 2.15 shows the plot of log electrical conductivity vs aniline/aniline+PVA (or PVB) wt% in dried PAPVB composite particles. The composites exhibit reasonably good conductivity even at very low PANI loading.

3.2. Electrorheological Characterization

Considering that the ER effect is induced by an external electric field, we think it is the polarization that controls the ER effect. The slow polarizations, the Debye polarizations by the potential barrier between two
equilibrium positions where the dipole would orientate from one to the other and the interfacial polarization by the dielectric constants and conductivities of the two components, should be responsible for the ER effect [16-20] would be imperative and significant either in understanding the original basis of ER effect or in developing the applicable ER fluids. We investigated the polarization properties of ER fluids, by obtaining dielectric spectra of PAPVB composeites in the frequency range 20~10^6 Hz. (a) and (b) of figure 2.16 and 2.17 shows the permittivity (\(\varepsilon'\)) and loss factor (\(\varepsilon''\)) respectively.

Figure 2.18 (a) shows flow curves of shear stress vs. shear rate for PAPVB particle based ER fluid with various electric field strengths [18-20]. In the absence of an electric field, the fluid is similar to that of a typical concentrated shear-thinning suspension. The slope of 0.87 in the shear stress - shear rate plot is less than 1 (which is the Newtonian fluid limit). Shear stresses for the ER fluid increased over the entire shear rate range with an increase of electric field strength. After the plateau region, shear stress increases with shear rate similar to Newtonian fluids, implying that the hydrodynamic force begins to dominate over the electrostatic force. The behavior which depends strongly on the electric field strength at a low shear rate is due to the deformation, reformation and destruction of chainlike or columnar structures as the shear rate increases below the critical shear rate. The fibril structure becomes slightly extended and the fibrils more sharply aligned as sharing takes place. This would lead to a more uniform distribution of the particles, thereby reducing the amount of overlap of the charged dipoles, and in turn yielding stronger average dipole strength per particle.

Figure 2.18(b) shows change of static yield stress of PAPVB 40 composite measured by CSS mode at various electric field strengths and volume fraction [21]. Contrary to a CSR mode in which a shear rate is
applied to the ER fluid and the resulting shear stress is measured giving a
dynamic yield stress, the ER fluid is stressed by an applied mechanical
torque until the particle chain structure is perfectly broken so that the shear
rate occurs. The ER effect of PAPVB series is only observed at the system
of PAPVB30 and PAPVB 40. Because the insulating part with PVB of
PAPVB composites increases the distance between the polarizable particles,
it reduces the electrostatic forces between them. The occurrence of
maximum yield stress may be attributed to surface polarization, which is
determined by the electron movement within the polyaniline particles and
electron hopping between the polyaniline particles under high voltage
electric field. When the electron movement within the polyaniline particles
plays an important role in the surface polarization of PANI, the yield stress
increases. However, when the electron hopping between the polyaniline
particles determines the surface polarization of the polyaniline particles, the
yield stress decreases with the increase in the content of PVB.

As the gap between the conducting particles in the fluid decreases (e.g.
increasing concentration), the electric response of the fluid becomes
nonlinear through electrical breakdown or particle discharge under high
electric field strengths. Based on the nonlinear conductivity model, Davis
showed that over a range of unscaled $E_0$ greater than critical electric field
($E_c$), the slope of $E_0$ vs $\tau_y$ (yield stress on log scale) is approaches 1.5,
while the slope approaches 2 for small $E_0$. The critical electric field ($E_c$)
represents the critical electric field originated from the nonlinear
conductivity model, and is descriptive for crossover behavior and defines
the two regimes in the $E_0$ vs $\tau_y$ plot. The critical electric field ($E_c$) of
PAPVB 40 is 2 kV/mm. Two limiting behaviors at low and high electric
field strengths, respectively have following equation :

$$\tau_y = \alpha E_0^2 \propto E_0^2 \quad \quad \quad \quad E_0 \ll E_c$$

(1)
\[ \tau_y = \alpha \sqrt{E_c E_0^{2/3} \propto E_0^{2/3}} \quad E_0 \gg E_c \]  

Equation (1) shows that \( \tau_y \) is proportional to \( E_0^2 \) for low \( E_0 \) (Regime I as shown figure 2.19, and \( \tau_y \) changes abruptly to \( E_0^{2/3} \) for high \( E_0 \) (Regime II as shown Fig 2.19). Choi found that \( E_c \) is influenced by the particle conductivity an conductivity mismatch between the particle and medium liquid and is weakly dependent on the volume fraction. The polarization forces between particles increase with increasing both electric field strength and particle concentration in figure 2.20, which in turn develops the particles chain structure, thus increasing the yield stress.

4. CONCLUSION

Conducting polyaniline particles were synthesized from oxidative dispersion polymerization of aniline using poly (vinyl alcohol) stabilizer. However PAPVA cannot be adopted to ER system without controlling conductivity because its conductivity is too high. Thereby, Acetalization of PANI-PVA method is adopted as a substitute for dedoping method. In this study, PANI-PVB particles were synthesized and used as the dispersed phase in ER fluids. Effects of electric field strength, particle concentration and particle size on ER properties of PAPVB were also examined and then its viscoelastic properties were investigated under applied elastic fields using a rotational rheometer with high voltage generator in both controlled shear rate and shear stress modes. The result show that not only the ER properties are enhanced by increasing the particle concentration and electric field, but also exhibit typical viscoelastic properties under an electric field due to chain formation.
5. REFERENCES


Table 1. Dispersion polymerization of aniline with various PVA stabilizer weight fractions and Synthesis of poly(vinyl butyral) (PVB)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PANI/(PANI+ PVA) or PVB) [wt%]</th>
<th>HCl [wt%]</th>
<th>PVA [wt%]</th>
<th>Temperature [°C]</th>
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<tbody>
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<td>11</td>
<td>4</td>
<td>0</td>
</tr>
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<td>4</td>
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<td>2</td>
<td>4</td>
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<td>PAPVB 50</td>
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<td>4</td>
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Table 2. Conductivity for PAPVA particles after filtering & washing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [μm]</th>
<th>Resistivity [Ω]</th>
<th>Conductivity [s/cm]</th>
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<tr>
<td>PAPVA 20</td>
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<td>140</td>
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<td>307</td>
<td>228.7</td>
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<tr>
<td>PAPVA 40</td>
<td>301</td>
<td>127.2</td>
<td>0.2177</td>
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<tr>
<td>PAPVA 50</td>
<td>247</td>
<td>209.5</td>
<td>0.1675</td>
</tr>
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</table>

Table 3. Conductivity for PAPVB particles after filtering & washing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [μm]</th>
<th>Resistivity [Ω]</th>
<th>Conductivity [s/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAPVB0.1</td>
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<td>...</td>
<td>1E-11</td>
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<td>43384.257</td>
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Figure 2.1. Mechanism of Acetalization of Poly (vinyl alcohol)
Figure 2.2. Acetalization of Poly(vinyl alcohol) (PVA)

(d) Intramolecular Acetalization of 1,3-glycols in PVA

(e) Intramolecular Acetalization

(f) Intramolecular Acetalization of 1,2 glycols in PVA
(a) PAPVA 20  (b) PAPVB 30
(c) PAPVA 40  (d) PAPVA 50

**Figure 2.3.** Scanning Electron Microscope (SEM) of PAPVA series
Figure 2.4. Scanning Electron Microscope (SEM) of PVB
Figure 2.5. Scanning Electron Microscope (SEM) of PAPVB 0.1
Figure 2.6. Scanning Electron Microscope (SEM) of PAPVB 1
Figure 2.7.  Scanning Electron Microscope (SEM) of PAPVB 20
Figure 2.8. Scanning Electron Microscope (SEM) of PAPVB 30
Figure 2.9. Scanning Electron Microscope (SEM) of PAPVB 40
Figure 2.10. Scanning Electron Microscope (SEM) of PAPVB 30 (a) and PAPVB 40 (b)
Figure 2.11.  Scanning Electron Microscope (SEM) of PAPVB 50
Figure 2.12. SEM of PAPVB particles with various stabilizer weight fractions
Figure 2.13. FT-IR spectra for PAPVB series

Figure 2.14. TGA spectra for PAPVB series
Figure 2.15. Plot of log electrical conductivity vs PANI/PANI+PVB wt% in dried PAPVB composite particles
Figure 2.16. (a) Dielectric constant and (b) dielectric loss factor for PAPVB40 in 30cS silicone oil
Figure 2.17. (a) Dielectric constant and (b) dielectric loss factor for PAPVB30 and PAPVB40 in 30cS silicone oil
Figure 2.18. Shear stress vs. shear rate (a) and shear viscosity vs. shear rate (b) for PAPVB40 in 50cS silicone oil (particle concentration: 15vol%)
Figure 2.19. Static yield stress for 15 vol% of PAPVB40 in 50cS silicone oil

Figure 2.20. Static yield stress for PAPVB40 in 30cS silicone oil
감사의 글

따뜻한 봄에 잔디밭에서 함께 어울리면서 놀던 친구들과 동문 선배들, 넓은 잎이 교정을 가득 메웠던 푸른 플라타너스의 여름과 여주농촌활동에서 만난덕 토목공학과 친구들, 산악동아리 백록회 그리고 낙엽 지는 가을, 쾌쾌하기만 했던 공대 도서관과 중앙 도서관에서 시험공부를 했던 그 기억이 너무나 그리워지는 2002년 마지막 겨울입니다. 97년 화공 고분자 생물공학부에 들어와서 4년간의 추억으로 기억되어버린 학부생활을 마치고 다시 다른 추억으로 기억될 대학원 졸업을 목전에 두고, 그 동안 미쳐 알로 전하지 못했던 사랑하는 사람들에게 감사의 말을 글로 대신할까 합니다.

비록 미흡하지만 이러한 결실을 맞기까지 목욕히 뒷바라지하시면서 삶을 희생하신 사랑하는 아버지와 자식들 격동에 제대로 잘 못 이루시면서도 편안한 안식처가 되어주시는 사랑하는 어머니에게 헌연할 수 없는 깊은 감사를 드리며 앞으로 그 은혜에 보답하고자 합니다. 그리고 지금까지 옆에서 소중한 벼이면서 인생의 선배가 되어준 가장 사랑하는 성실한 언니에게도 깊은 감사를 전합니다.

학부와 2년 동안의 대학원 생활을 소중한 기억으로 채우게 해주신 한결같이 성실하신 은사 최형진 교수님께 먼저 감사 드리며, 학부생활을 열심히 지도해주시신 존경하는 정성택 교수님과 박동화 교수님, 최순자 교수님, 김인주 교수님에게도 고개 숙여 감사드립니다. 고분자 공학과의 발전을 위해서 열심히 연구하시는 윤진산 교수님, 김철희 교수님, 이광희 교수님, 권용구 교수님에게도 깊이 감사 드립니다.

때로는 힘들고 와콤고 상처 받을 때 나의 마음에 작은 행복을 느끼게 해준 소중한 사랑하는 벽들, 이제 새롭게 출발선에서 열심히 노력하는 오랜 벽인 보라와 언니 같은 미혜, 알고 영광한 짝꿍 지속이에게 정말로 감사 드립니다. 그리고 단란한 나의 벽인, 멋진 예비 의사인 동화와 행복한 결혼을 할 신부 미형에게도 진심으로 고마움을 전합니다. 대학 생활뿐 아니라 대학원생활까지 함께하면서 힘이 되어준 나의 단짝 친구들인 멋진 친구 선형이, 따뜻한 해인이, 혜영이, 경선이와 동기인 준기,
윤정이 그리고 항상 결에서 많이 챙겨준 원종이와 정한이, 나의 사랑하는 고향 친구인 영길이와 재훈이에게도 감사의 말을 전합니다. 친언니처럼 그 동안 보살피 준, 지금은 성기오빠의 먼저 아내가 된 사랑하는 은주 언니에게도 감사의 말을 전하고 싶습니다. 학부 1학년 때부터 너무나 많은 고마움과 따뜻한 정을 주신 사랑하는 동문 선배들 성민 오빠, 경부오빠, 인복오빠, 재영오빠, 석봉오빠, 수현 오빠, 혁진오빠, 진국오빠, 진석오빠, 은숙언니에게도 진심으로 감사 드리고 항상 좋은 결실 맺길 바랍니다. 사랑하는 나의 후배들, 멋진 스타더스가 된 미경이와 선화, 열심히 미래를 설계하는 태규, 태행이, 대섭이, 지혜에게도 좋은 성과 염기를 기도합니다. 그리고 대학원 생활중 안 할 없이 많은 힘이 되어준 임혜오빠, 경자 언니, 상미에게도 감사드립니다.

대학원생활동안 도움을 주신 성택오빠, 지우오빠, 민성오빠와 동기인 재훈 오빠, 동필 오빠, 결과에서 말없이 힘이 되어 준 충호 오빠에게도 감사 드리며, 힘들 때 옆에서 많은 활락소가 되어 준 희봉 오빠, 터프하지 만 잘 챙겨주는 정희 오빠, 매사에 성실한 선영이와 지영이, 그리고 새롭게 대학원에 입학하는 멋진 승준 오빠, 설명하지만 항상 웃는 해승 오빠, 미소를 짓게 하는 선순오빠, 노력하는 성실한 인범 오빠에게도 좋은 결실 맺길 기원합니다.

마지막으로 헌들거나 외로울 때 항상 결에 있었다니 고맙다고 따뜻한 말 한마디 해주지 못한 사랑하는 오빠에게도 이 작은 결실을 함께 나누고자 합니다. 대학원생활동안 기억하고 싶지 않은 부분들과 기억하고 싶은 추억들이 제가 내디딜 사회 생활에서 좋은 자양분으로 남기를 바랄니다. 그리고 인하대학교에서 그 동안 제가 키워왔던 꿈들이 새로운 결실을 맺길 바랍니다.

2002년 12월 31일
사랑하는 이들의 행복을 기원하여 서고에서

황지영