Electrorheological/Magnetorheological responses of organic/inorganic materials in a medium fluid

유-무기 재료 현탁액의 전기/자기 유변물성 연구

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2012年 2月
指導教授 崔 瑩 鎭
本論文을 工學碩士 學位論文으로 提出し

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高分子工學科

金 志 殷
Electrorheological/Magnetorheological responses of organic/inorganic materials in a medium fluid

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A TEHSIS
Submitted to the faculty of
INHA UNIVERSITY
in partial fulfillment of the requirement
for the degree of MATER

Incheon, Korea
Feb. 2012

Department of Polymer Science and Engineering
Feb. 2012
본 논문을 金志殷의 工學碩士 學位論文으로 認定함

2012年2月

주심 印

부심 印

위원 印
ABSTRACTS

Part 1
Preparation and Electrorheological Responses of Polyaniline Nanofiber and Polyaniline/Phosphate cellulose mixture

Electrorheological (ER) fluids, composed in general of electrically polarizable particles dispersed in insulating oils, exhibit fascinating field-induced rheological properties including a rapid and reversible change in their suspension structure under an applied electric field. By controlling the electric field strength to vary fibrillar structures, microstructural transition from a liquid-like to solid-like phase is obtained. All physical and mechanical property changes induced by the applied electric field are virtually instantaneous within a millisecond order and are reversible upon the removal of the field.

Typically, ER fluids are suspensions of 1-100 μm particles with the volume fractions of 0.05-0.5 in hydrophobic liquid media, such as mineral oil or silicone oil. Among these ER materials, various polymeric particles have been used as dry-base ER materials. In particular, polyaniline which is a well known conducting polymer has attracted considerable attention due to its environmental stability, simplicity, relatively high levels of electrical conductivity and low cost of synthesis.
In this study, polyaniline nanofiber was adopted into ER fluid because polyaniline nanofiber based ER fluid possesses a higher yield stress and is more stable than normal polyaniline based ER fluids. And in other to improve ER performance, indole-2-carboxylic acid which has a high polarizability was used as a dopant instead of common acids, such as hydrochloric, sulfuric, or nitric acid, during process of synthesis. Enhanced ER performance was observed from the indole-2-carboxylic acid doped PANI particle system in overall shear rate ranges, in which it demonstrates that the polarizability is an important consideration in the ER behavior.

The mixtures of phosphate cellulose and conducting polyaniline were also studied for solid-phase of ER fluid. ER performance of the mixture was compared with the each material. Through mixing two materials, synergistic effects were observed showing positive changes in rheological properties and dielectric constant. Although the dielectric constant of the mixture based ER fluid was lower than that of the polyaniline based ER fluid, the molecular polarization of the mixture makes its yield stress and response time higher and shorter than that of individual.

**Keywords:** Electrorheological fluid, Conducting Polymer, Polyaniline, Phosphate cellulose, Polarization, Dielectric property.
Part 2
Preparation and Magnetorheological Responses of Magnetic Carbonyl Iron Dispersed in Various medium

Similar to electrorheological (ER) fluids, magnetorheological (MR) fluids, comprising of soft magnetic particles suspended in a nonmagnetic continuous medium such as hydrocarbon, silicone oil, or ionic liquid, is regarded as a promising material that has mechanical properties which can be controlled by an applying external magnetic field. Compared to the ER fluids, MR fluids have a high yield stress from 10 to 100 kPa ranges with an applied external field. However in the case of typical MR fluid, there is a drawback such as serious sedimentation problem within the equipment for its application due to the high density of magnetic materials (magnetite, maghemite, carbonyl iron etc). The sedimentation of MR fluid results from a density mismatch and the incompatibility of magnetic particles in the nonmagnetic medium. Therefore various methods to solve this problem have been reported. For improvement of sedimentation stability of MR fluid, changed MR carriers were studied. Initially, the polyisobutylene/polybutene (PIB/PB) was employed as viscoelastic medium matrix. The highly elastic polymer solution of PIB/PB has been described by a Boger fluid, in which PIB/PB solution is similar to MR elastomer matrix as high elastic liquid with a constant shear viscosity at certain shear rate range.
Another way to improve the sedimentation problem is to use mixture of grease and kerosene oil as MR medium. MR fluid of grease and kerosene mixture is considered to obtain a well-dispersed carbonyl iron with some decrease of its viscosity.

The MR performance such as yield stress, shear viscosity and storage modulus were confirmed at different magnetic field strength, and these systems show improvement in sedimentation.

**Keywords:** Magneto-rheological fluid, Carbonyl Iron, Polybutene, Polyisobutylene, Viscoelastic Fluid, Grease, Kerosene, Sedimentation, Yield stress.
국문요약

파트 1
폴리아닐린 나노파이버 및 폴리아닐린/포스패이트 셀룰로오즈 혼합체 제조 및 전기응답 특성 연구

일반적으로 분극성 입자가 절연오일에 분산되어 있는 유체를 전기유변유체라 한다. 이것은 외부에서 전기장을 가하게 되면 분극 된 입자들은 정전기적 인력에 의해 사슬을 형성하게 되고 고체와 같은 거동을 하게 된다. 이 현상은 수마이크로초내로 따르고 가역적이며 이에 따라 항복 응력, 점도 등 유변적 성질의 변화를 초래하며 유변적 특성이 크게 변화한다. 다양한 전기유변유체의 분산 물질 중, 고분자 입자가 사용되면 특히 폴리아닐린은 간단한 합성방법, 높은 안정성, 높은 전도도 및 고도의 전반적인 전도성 고분자로 가장 광범위하게 사용되고 있다.

본 연구에서는 폴리아닐린 나노파이버를 전기유변유체의 분산 물질로 선택하여 합성하였다. 폴리아닐린 나노파이버는 일반적인 폴리아닐린보다 가로/세로 비율이 더 크기 때문에 더 높은 전기유변효과를 나타내며 따라서 더 높은 항복응력을 가짐과 동시에 유체내에서 보다 안정적이다. 이와 더불어 폴리아닐린의 합성과정에서 도판트로 일반적으로 사용되는 염산, 황산, 질산 대신에 인돌 카르복시산을 사용하였다. 이와 같이 합성된 폴리아닐린은 주사전자현미경을 통해 파이버 구조를 확인할 수 있었으며, 이 폴리아닐린 나노파이버를 실리콘 오일에 분산시켜 전기유변유체를 제조하였다. 회전형 레오미터를 통해 전기장 유무에 따른 전기유변특성을 분석하였고 일반 산동보다 더 높은 분극성을 가지는 인돌 카르복시산을 사용함으로써 전기유변현상이 향상됨을 확인할 수 있었다.
전기유변특성의 중요한 변수인 계면 분극성 분석을 위해 유전상수와 유전손실을 측정하므로써 유전특성을 분석하였고 이를 통해 분극성이 전기유변현상에 있어서 중요한 한 요소란 사실을 증명하였다.

또한, 전기유변효과를 높이기 위해, 폴리아닐린과 포스페이트 셀룰로오즈를 합성하고 혼합시켜 전기유변유체 입자로 분산시켰다. 폴리아닐린/포스페이트 셀룰로오즈 혼합체를 이용한 전기유변유체는 단독 입자의 전기유변유체보다 향상된 전기유변효과를 보였다. 혼합체를 사용한 전기유변유체의 경우 단독 입자의 경우보다 유전특성이 낮지만 혼합체의 높은 표면 분극성은 전기장에서 반응시간을 빠르게 하고 입자들의 사슬 형성을 도움으로써 전기유변효과를 높였다.

핵심어 : 전기유변유체, 전기유변현상, 유변학, 전도성 고분자, 폴리아닐린, 포스페이트 셀룰로오조, 분극성, 전기특성
파트 2
다양한 매질에 분산된 카보닐 철의 자기유변유체의 제조 및 특성 분석

전기유변유체와 비슷한 원리를 가지는 유체인 자기유변유체는 외부 자기장에 따라 유변 물성의 변화를 가진다. 전기유변유체와 비교하여 자기유변유체는 1~100 kPa의 상당히 높은 항복응력을 가지기 때문에 실제 산업현장에서 응용 가능성이 매우 크다. 하지만 일반적인 자기유변유체들은 분산매와 입자의 밀도차이에 의한 침강과 재 분산의 어려움이라는 문제점이 자기유변유체의 홍업적 응용에 큰 어려움을 주고 있다. 이러한 문제점을 해결하기 위해 다양한 철의 변형입자를 개발하고 연구가 활발히 진행되고 있다. 본 연구에서는 관점을 다르게 하여 입자가 아닌 분산매의 향상을 통한 침강현상을 극복하고자 시도하였다.

본 연구에서는 먼저, 절연분산매로 일반적인 오일 대신에 고분자 용액을 사용하여 자기유변유체를 제조하였다. 고분자 용액으로는 보거유체로 유명한 풀리아이소부틸렌/풀리부텐 용액을 사용하였다. 이것은 점도가 높고 점합성을 높은 철 입자를 분산시키는 데 입자의 침강을 잡아주며 동시에 높은 자기유변효과를 보여주었다. 자기유변유체와 자기유변탄성 중합체의 중간 성질을 둘에 각각의 장점을 모두 가지로 침강문제를 해결하는 우수한 결과를 확인하였다.

두번째로, 그리스와 케로신 오일의 혼합용액을 분산매로 사용하여 자기유변유체를 제조하였다. 일반적인 그리스는 입자의 높은 분산성을 줄 수 있고 편의성 때문에 자기유변유체의 절연매로 많이 사용되고 있다. 여기에 5 wt%의 케로신을 첨가하여 줄으로써 절연매의 점도를 낮춤으로써
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핵심어: 자기유변유체, 카보닐 철, 폴리부텐, 폴리아이소부틸렌, 점탄성유체, 그리스 오일, 케로신 오일, 침강현상
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Preparation and Electrorheological Responses of Polyaniline Nanofiber and Polyaniline/Phosphate cellulose mixture
1. INTRODUCTION

As one of the most spectacular smart materials, electrorheological (ER) fluids, composed of a suspension consisting of polarizable particles in an insulating liquid media, in which the particles have a high dielectric property [1-2], have attracted in many researches because of their interestingly and accurately tunable rheological properties by an applied electric field. When an external electric field is applied, the ER suspensions form fibrillated chains along the electric field direction and the rheological properties (shear viscosity, yield stress, shear stress, etc.) of ER fluids transformed into a solid-like state. This is because the particles which are electrically polarized in electric fields interact with electrostatic force. These properties can easily be controlled by external electric field strength, and the effect is reversible, i.e. the structure of the fluid returns to its original state when an external electric field is removed [3-5]. Due to controllable characteristics and fast response time, ER fluid could be used as many potential applications in various devices such as dampers [6], clutches [7], actuator [8], microvalve [9], human muscle stimulators [10], and so on. However, the ER effect is not strong enough to apply practical ER devices. For engineering application of ER fluids, many studies have been done on developing high performance ER materials including inorganic [11-12], organic, and polymeric semi-conducting materials [13-17]. Among these,
various polymeric particles have been well-used as ER materials. Especially, the PANI is known to be one of the most famous ER materials due to its environmental stability, simplicity, low cost of synthesis and tunable conductivity with doping and dedoping process [18-20]. The PANI not only can control its conductivity and dielectric properties by adjusting the degree of protonation but also has repeated polar group (–NH2) which affect the ER behavior by playing the role of the electronic donor under the external electric field. This effect increase polarizability of PANI and then help the PANI possess good ER behaviors.

Many PANIs differing in structure or morphology, including derivatives [21], nanocomposites, core-shell particles, nanospherical or fibrous PANI [22] and etc., have been developed in ER research. Recently, Yin et al. [23] reported PANI a nanofiber based ER fluid which possessed a higher yield stress and was more stable than normal PANI based ER fluids.

In this study, PANI nanofiber was synthesized through interfacial polymerization method that develops uniform and template-free nanofibers. In this immiscible biphasic phases, the organic phase is composed of organic solvent and aniline monomer, while the aqueous phase is with oxidant, dopant and distilled water. The reaction takes place at the interface without any disturbance. As for the mechanism of forming PANI nanofibers by using this method, researchers performed plenty of investigations and gave many
hypothesizes. Hopkins et al. presumed that the polyacid dopant with a relatively lower pKa than that of the aniline monomer is a critical factor to drive interfacial polymerization occur. Besides this, they also suggested that some preferential electrostatic alignment of the aniline monomer onto the anionic polyelectrolyte dopant is optimized by the interfacial method [24]. Furthermore, Huang et al. demonstrated that the oxidative chemical polymerization process itself as well as the linear nature of PANI forms caused the formation of PANI nanofibers [25].

Along with this, in order to improve ER performance, indole-2-carboxylic acid which has a high polarizability was employed as a dopant instead of common acids, such as hydrochloric, sulfuric, or nitric acid, during process of synthesis. As another study, PANI/phosphate cellulose mixture is prepared. The practical ER application of PANI-based ER fluids is still limited owing to low yield stress. Therefore, the PANI has been hybridized with other materials to improve the ER performance [26-28]. As another interested ER material, the phosphate cellulose particles have been adopted. The phosphate cellulose particles have many advantages such as inherent flame resistance and ion exchange capability as well as high ER performance. The phosphate cellulose particles dispersed in medium oil have been reported as showing the high ER performance in dry-base systems [29-31]. So, both phosphate cellulose and PANI were prepared and two kinds of particles were mixed for solid-phase of
ER fluid in which both polyaniline (PANI) and phosphate cellulose are well known as ER materials due to their materials characteristics including the electroreponsibility. After that, we made ER fluids to observe their electrical and rheological properties under the external electric field. In order to understand the ER phenomenon of phosphate cellulose/PANI mixtures, we also analyzed dielectric properties.

2. EXPERIMENTAL

2.1 POLYANILINE (PANI) NANOFIBER

2.1.1 Synthesis of PANI nanofiber

Synthesis of indole-2-carboxylic acid doped polyaniline nanofibers and HCl doped polyaniline nanofibers.

In a typical synthesis route, PANI nanofibers were synthesized by an oxidative polymerization of aniline with ammonium persulfate (APS) in an acid aqueous solution. And to obtain the fiber shape, an interfacial polymerization method was used [32].

A synthesis process is shown as follow: In order to prepare the organic phase, aniline monomer (0.05mol) and indole-2-carboxylic acid (0.005mol) were dispersed in dichloromethane with energetic stirring. While for the liquid phase,
APS (Daejung, Korea, 98%, 0.05mol) was dissolved in Di-water with agitation until a transparent solution was observed. Then, the liquid phase was added to the organic phase along one side of the inner wall carefully and the obtained immiscible two phases system was kept in refrigeratory for 24 hrs. To make a comparison, HCl doped PANI nanofibers were also synthesized in the same way as above with same reagents, in which HCl (0.005mol) was used instead of the indole-2-carboxylic acid as dopant. After the polymerization was finished, the product was washed with di-water and methanol from reaction solution till the washing liquid was neutral to remove unreacted reagents. These solid products were dried in vacuum oven at 60°C.

**Figure 1.1** Experimental process of synthesizing PANI nanofiber via interfacial polymerization.
2.1.2 Preparation of ER fluid

For using PANI nanofibers as solid-phase of ER fluid, as-synthesized PANI nanofibers have to be dedoped by controlling the conductivity with 1M NaOH solution. We have to control the electrical conductivity of the obtained PANI particles by a dedoping process in which either 1M NaOH or 1M HCl solution (Figure 1.2) was used. The conductivity decreased from $10^{-1}$ to $10^{-11}$ S/cm. Then, ER fluids were prepared by dispersing as-prepared PANI nanofibers in silicone oil ($\rho = 0.96$ g/cm$^3$, $\eta = 50$ cS at 25 °C) under shaking and sonification, respectively. Here, two kinds of ER fluids with 10% volume fraction were prepared.

![Figure 1.2 Process of doped/dedoped polyaniline with acid or base.](image-url)
Table 1.1 Summary of PANI conductivity according to doping/dedoping.

<table>
<thead>
<tr>
<th>Case no.</th>
<th>dopant</th>
<th>Conductivity of doped PANI (s/cm)</th>
<th>Conductivity of dedoped PANI (s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Indole-2-carboxylic acid 0.81g (0.005mol)</td>
<td>$10^{-1}$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>2</td>
<td>HCl 0.1823g (0.005mol)</td>
<td>$10^{-1}$</td>
<td>$10^{-10}$</td>
</tr>
</tbody>
</table>

2.1.3 Characterization

The morphology of PANI nanofibers was investigated via field emission-scanning electron microscopy (FE-SEM, Hitachi S-4300, Japan). Fourier transform infrared spectrometer (FT-IR, Rerkin Elmer System 2000, Norwalk, CT) was employed to identify the chemical structure of the PANI nanofibers. The electrical conductivity was measured by a standard four-pin probe technique using a Resistivity Meter (Mitsubishi Loresta-GP and Hiresta-UP). The ER properties of PANI nanofibers suspension were characterized by steady shearing experiments using a rotational rheometer (MCR 300, Physica, Stuttgart, Germany) with a cup-cone system (CC17 ERD, the gap between cup and cone was 0.71 mm) and a DC high voltage generator. In the controlled shear rate (CSR) mode, the flow curves of each ER fluid were measured under shear rate of between 0.01 and 1000 1/s with and without an external electric field. In addition, we analyzed dielectric relaxation spectra of prepared ER fluids using the HP 4284A precision LCR meter with HP 16452A liquid test fixture at room temperature. The using frequency range for measurement of
dielectric permittivity and loss factor was $20 \times 10^6$ Hz.

2.2 MIXTURE OF POLYANILINE / PHOSPHATE CELLULOSE

2.2.1 Synthesis of PANI and phosphate cellulose

We synthesized two kinds of particles, which were PANI and phosphate cellulose, for making mixtures. At first, PANI particles were synthesized through an oxidation polymerization of aniline with ammonium persulfate (APS) in acid aqueous solution. The aniline monomer (40 g; 0.43 mol) was dissolved in 1M HCl (400 g), and APS (123 g; 0.537 mol) was dissolved in 1M HCl (300 g) at room temperature. This ratio of materials ($[\text{Aniline}]/[\text{APS}] = 0.8$) is ideal for synthesizing PANI. Then, APS solution was added by dropping to aniline solution to allow starting the oxidation polymerization of aniline and continuously stirred for 24 hours at 1 °C. After reaction, the stirring was stopped and synthesized PANI was dedoped to make a semiconductor by raising pH value to 9.5 with 1M NaOH. Then, dark green PANI particles were washed five times with acetone and washed with distilled water till the washing liquid was neutral to remove any unreacted aniline. That solid product was dried in oven at 60 °C for 3 days. The density of synthesized PANI particles is 1.15 g/cm$^3$, which was measured via a pycnometer.

Secondly, phosphate cellulose particles were synthesized through an
esterification of cellulose with an orthophosphoric acid-urea mixture (phosphorylation of cellulose) at room temperature, using the method reported by Arslanov et al [33]. A mixture containing 4M of urea and aqueous solution of phosphoric acid (orthophosphoric acid, 85 % assay) was stirred at room temperature for 1 hour. Raw cellulose particles (40 g) were added to the solution (400 ml) and stirred for 2 days to allow the esterfication of cellulose. After the reaction, the phosphate cellulose particles were washed five times with distilled water to remove any unreacted phosphoric acid and urea. Then, the phosphate cellulose particles were dried in a vacuum oven at 60 °C for 3 days. The density of synthesized phosphate cellulose particles is 1.35 g/cm³, which was measured via a pycnometer.

2.2.2 Preparation of ER fluid

The obtained phosphate cellulose particles were mixed adding the PANI particles (5 v/v %, 10 v/v %, respectively) for using as solid-phase of ER fluid. For examination of ER fluids properties, ER fluids were prepared by dispersing pure PANI, pure phosphate cellulose and phosphate/PANI mixture in dimethylsilicone oil (density \( \rho = 0.76 \text{ g/cm}^3 \) and viscosity \( \eta = 0.65 \text{ cS at 25 °C} \) under shaking and sonification for 30 minutes, respectively. The particle concentration was fixed 15 % volume fraction and the dimethylsilicone oil was dried and stored by molecular sieves prior to use.
2.2.3 Characterization

The morphology of synthesized particles was detected via field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300). In order to obtain the conductivity of particles, dried particles were pressed to using a pellet die. And then the pallets of PANI and phosphate cellulose were measured by a picoammeter (Keithley model487, Cleveland, OH, USA) with conductivity cell at room temperature.

The rheological properties of suspension based ER fluids were investigated via a rotational rheometer (MCR 300, Physica, Stuttgart, Germany) equipped with a high direct current voltage generator. In the steady shear experiment, the flow curves of each ER fluid were measured under shear rate of between 0.01 and 1000 1/s for various electric fields. A dielectric property of the ER fluid was carried out using a LCR meter (Agilent HP 4284A) with a liquid cell over a frequency range of 20-10^6 Hz at room temperature.

3. RESULTS AND DISCUSSION

3.1 POLYANILINE NANOFIBER

Figure 1.3 shows the SEM image of synthesized PANI nanofibers. The morphology of PANI which was synthesized through interfacial polymerization method is typically nanofiber. Figure 1.3 also proves the
morphology of PANI was not influenced by dopant during the polymerization process. Although the different dopants were employed, the both synthesized PANI particles mainly consist of uniform nanofibers with a diameter of 200-300 nm.

![Figure 1.3 SEM images of PANI nanofibers.](image)

(Case1: Indole-2-carboxylic acid doped PANI, Case2: HCl doped PANI)

The chemical structure of the PANI nanofibers was identified by FT-IR analysis. The FT-IR spectra of the PANI nanofibers are shown in Figure 1.4, in which the spectrum represent that two kinds of PANI nanofibers were synthesized like typical PANI of emeraldine base. As the analytical band, the characteristic peaks are summarized as follows: The absorption bands were observed at 820 cm\(^{-1}\) (out-of-plane C-H deformation of the aromatic ring in the PANI unit sequence), 1305 cm\(^{-1}\) (the C-N stretching of the secondary aromatic
amine), 1240 cm$^{-1}$ (the C-N$^+$ stretching), 1145 cm$^{-1}$ (the benzenoid ring $\text{NH}^+$ = quinonoid stretching), 1580 cm$^{-1}$ (the aromatic C=C stretching of the quinonoid ring) and 1500 cm$^{-1}$ (the aromatic C=C stretching of the benzenoid ring) [34]. The board band with multi peaks at 3500-2800 cm$^{-1}$ is attributed to N-H stretching vibration of the secondary amine in the PANI backbone and hydrogen-bonded N-H stretching [35].

![FT-IR spectra of the PANI nanofibers.](image)

**Figure 1.4** FT-IR spectra of the PANI nanofibers.

However, it should be noted that it is difficult to distinguish sharply between HCl doped PANI and indole-2-carboxylic acid doped PANI because the peaks of indole-2-carboxylic acid overlap with that of PANI. In sodium indole-2-
carboxylic acid peak, two strong peaks at 1565 and 1409 cm\(^{-1}\) were observed based on asymmetric \(\nu_a (\text{COO}^-)\) and symmetric \(\nu_s (\text{COO}^-)\) stretching vibrations, respectively [36]. As shown in Figure 1.4, these characteristic peaks of indole-2-carboxylic acid were overlapped by strong peaks of PANI.

The ER behaviors of PANI nanofibers based on ER fluids were compared shown in Figure 1.5, in which Figure 1.5 (a) presents the flow curve obtained from the controlled shear rate test for 10 vol% suspension of the PANI nanofibers with various electric field strengths. The ER performance was investigated via a controlled shear rate (CSR). Without applying an electric field, the PANI nanofibers based on ER fluids behave similarly to Newtonian fluid that shear stress increases proportionally to the shear rate. However when external electric field is applied, the ER fluids under an external electric field behave like Bingham fluid which possesses a yield stress \((\tau_y)\) because of fibrillar structure of particles aligned in the applied electric field. The relationship between shear stress \((\tau)\) and shear rate \((\dot{\gamma})\) for Bingham fluid is expressed as follows:

\[
\tau = \tau_y + \eta \dot{\gamma}, \tau \geq \tau_y \quad (1.1)
\]
\[
\dot{\gamma} = 0, \tau < \tau_y \quad (1.2)
\]
This is related that the electrostatic force gets gradually stronger to resist the hydrodynamic force. This can be interpreted in the term of polarizability. The dispersed particles are polarized and form chain-like structures because of the attractive forces generated between dipoles. This chain-like structure will resist the flow till the shear stress approaches a critical value which is called a yield stress.

After comparing the shear stress value, we found that the indole-2-carboxylic acid doped PANI nanofiber based on ER fluid has more ER effect than that of HCl doped PANI nanofiber. It explains that the ER effect not only depends on electric field, but also depends on the constitution of the suspended particles. In synthesis of PANI nanofibers, two different kinds of dopant were used, in which indole-2-carboxylic acid has a high polarizability. When the electric field is present, the indole-2-carboxylic acid can lend a hand to perform excellent ER effect through high polarizability. Therefore, the indole-2-carboxylic acid doped PANI nanofiber based ER fluid shows higher shear stress and enhanced ER performance, demonstrating that the polarizability is an important consideration in the ER behavior.
Figure 1.5 (a) Shear stress vs. shear rate, (b) Shear viscosity vs. shear rate for the PANI nanofiber based on ER fluid (10 vol%) under various electric field.

(Scatter: Indole-2-carboxylic acid doped PANI nanofiber,
Solid line: HCl doped PANI nanofiber)
Theses suspension behaviors of both ER fluids were also confirmed by Figure 1.5 (b), in which the shear viscosity increases with the electric field strength applied. Note that a slight shear-thinning behavior of shear viscosity was observed at a low shear rate region even at zero electric field applied due to its non-Newtonian suspension system. It was also found that ER behavior of the indole-2-carboxylic acid doped PANI nanofiber based on ER fluid was enhanced over the entire range. In other words, polarizability in the ER particles is an important factor.

**Figure 1.6** Shear stress as a function of shear rate for ER fluids (10 vol %) at an electric field strength 3.0kV/mm.
**Figure 1.6** represents that shear stress as a function of shear rate for two ER fluids at electric field strength 3.0 kV/mm. Despite the same electric field strength applied, the indole-2-carboxylic acid doped PANI nanofiber based on ER fluid has higher shear stress than that of HCl doped PANI nanofiber in the entire shear rate range. The indole-doped PANI nanofiber became hard broken and stiff enough to stand the shear.

We estimated the dynamic yield stress from a controlled shear rate measurement (CSR) by extrapolating the shear stress at a zero shear rate limit [37], and then plotted the dynamic yield stress as a function of various electric field strengths.

It is well known that in general, the correlation of the dynamic yield stress and electric field strength is presented as follows:

\[
\tau, \propto E^m
\]  

(1.3)

The dependency of the dynamic yield stress on the electric field strength is known to differ from the \(E^2\) (m=2) dependency suggested by a polarization model depending on the particle concentration [38, 39], particle shape, and applied electric field strength, while the applied electric field induces electrostatic polarized interactions among the particles and also between the particles and the electrodes. However, the polarization model does not describe the flow effect accurately; in that case, the ER response is influenced by the conductivity mismatch and the interaction between particles and medium.
Various ER fluids exhibit different exponents in Eq. (1.3). A correlation between yield stress and the electric field strength of two PANI based on ER fluids is represented in Figure 1.7. \( E_c \) originated from nonlinear conductivity effect can be obtained by crossover point of the slopes for all ranges of the electric field strengths corresponding to the polarization model (slope = 2) and conduction model (slope = 1.5), respectively [40]. The estimated \( E_c \) was founded to be 1.27 kV/mm and 2.02 kV/mm for indole-2-carboxylic acid doped PANI nanofiber and HCl doped PANI nanofiber based on ER fluids, respectively.

**Figure 1.7** Replotted yield stress vs. electric field strengths for PANI based on ER fluid (10 vol%).
Furthermore, in order to investigate the ER performance for the two ER fluids, the dielectric properties for ER fluids were examined. The frequency dependence of the dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$) which are typical results for the interfacial polarization of suspensions including ER fluids were presented in Figure 1.8. The interfacial polarization is considered as the origin of ER effect. And Lines in Figure 1.9 are fitted from the famous Cole-Cole formula (Eq. 1.4) [41] with parameters.

\[
\varepsilon' = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i \omega \lambda)^{-\alpha}} = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)(1 + A \cos \theta)}{1 + A^2 + 2A \cos \theta} + i \frac{A(\varepsilon_0 - \varepsilon_\infty) \sin \theta}{1 + A^2 + 2A \cos \theta} \tag{1.4}
\]

From the above Eq.1.4, the dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) can be related to be

\[
\varepsilon' = \frac{(\varepsilon_0 - \varepsilon_\infty)(1 + A \cos \theta)}{1 + A^2 + 2A \cos \theta} \quad \varepsilon'' = \frac{A(\varepsilon_0 - \varepsilon_\infty) \sin \theta}{1 + A^2 + 2A \cos \theta} \tag{1.5}
\]

Where the exponent (1-$\alpha$) characterizes the broadness of the relaxation time distribution, and $A = (\omega \lambda)^{-\alpha}$ and $\theta = (1-\alpha)\pi / 2$ in Eq. (1.5). When $\alpha=0$, the Cole-Cole formula (Eq. 1.4) reduces to Debye’s well-know single relaxation time model. Here, $\lambda$ is the relaxation time. In Figure 1.9, it is found that the adopting Cole-Cole plot not only fits the dielectric spectra of both ER fluids but also provides a better explanation in their polarizability [42].
Figure 1.8 Dielectric spectra of PANI nanofibers based on ER fluids. (close symbol and solid line for dielectric constant $\varepsilon'$, open symbol and dash line for dielectric loss factor $\varepsilon''$)

Figure 1.9 Cole-Cole fitting curves for PANI nanofibers based on ER fluids.
Table 1.2 Parameters in Eq. (1.4) for two kinds of PANI nanofibers based on ER fluids.

1: Indole-2-carboxylic acid doped PANI
2: HCl doped PANI
3 measured by pycnometer
4,5,6,7 values measured at 1kHz (impedance analyser: HP 4284A, Hewlette Packard)

Parameters in Eq. (1.5) for the two ER fluids are summarized in Table 1.2. Here, $\Delta \varepsilon = \varepsilon'_0 - \varepsilon''_0$ is an achievable polarizability in ER fluids. Because large polarization will lead to large ER effect, the $\Delta \varepsilon$ dependence on ER properties has positive effect on good ER performance. And $\lambda$, which is the relation time for interfacial polarization of ER fluids is related with yield stress and stress enhancement under the applied electric field. On the above Table 1.2, the $\Delta \varepsilon$ of indole-2-carboxylic acid doped PANI nanofiber is a little higher than that of the HCl doped PANI nanofiber, suggesting an enhanced ER performance. In addition, when analyzing the dielectric spectra, we can see that the relaxation times are 5.6ms and 6ms for the two ER fluids separately. In general, short relaxation time is known to be related with higher shear stress, in which we can note that indole-2-carboxylic acid doped PANI nanofiber has high interfacial
polarization. Therefore, it verifies that indole-2- carboxylic acid makes PANI suspension in medium be polarization. The above analysis on the dielectric spectra coincide with the results obtained from comparing the shear stress, certainly.

3.2 MIXTURE OF POLYANILINE / PHOSPHATE CELLULOSE

Figure 1.10 (a) and (b) show the scanning electron microscopy (SEM) image of synthesized PANI and phosphate cellulose particles, respectively. The PANI is typically granular particle with average 200 nm size and seems to be formed with spiderweb between PANI particles. The morphology of phosphate cellulose is rod-like and irregular particle shape with 30-100 μm.

Figure 1.10 SEM image of pure PANI (a) and phosphate cellulose (b).
**Figure 1.11** presents flow curves investigated from the controlled shear rate (CSR) mode using a rotational rheometer at different applied fields for 15 vol% suspension particles. When no electric field was applied, the flow curves of all suspensions act as nearly Newtonian behavior showing a linear constitutive relationship between the shear stress and shear rate. When electric field was applied, however, the ER effect occurred. The shear stress ($\tau$), which is a function of shear rate ($\dot{\gamma}$), steeply increased with increasing the electric field strength and exhibited a plateau region over the entire shear rate range, and the yield stress was appeared as a Bingham fluid. It is because suspended particles were electrically polarized under an electric field and induced electrostatic interaction force among the particles. So the interaction led to form chains along the electric field direction and this increased resistance of the fluid against the shear flow.

The suspension behaviors of four ER fluids were also checked out in **Figure 1.12**, in which it depicts the change of shear viscosities for pure PANI, pure phosphate cellulose and PANI/phosphate cellulose mixtures based on ER suspension as function of shear rate at different electric field strengths. From **Figure 1.12**, it is possible to observe a decrease of shear viscosity over entire shear rate, indicating shear thinning behavior that is a typical ER behavior. It results from the changes of internal structures under shear deformation. In
addition, it was found that the PANI/phosphate cellulose mixture based on ER fluid had higher shear viscosity.

Figure 1.11 Flow curves for (a) pure PANI, (b) pure phosphate cellulose, (c) Phosphate cellulose 95 vol% + PANI 5 vol%, (d) Phosphate cellulose 90 vol% + PANI 10 vol%) based on ER fluids at different electric field strengths.
Figure 1.12 Shear viscosity vs. shear rate for (a) pure PANI, (b) pure phosphate cellulose, (c) Phosphate cellulose 95 vol% + PANI 5 vol%, (d) Phosphate cellulose 90 vol% + PANI 10 vol%) based on ER fluids at different electric field strengths.

The dynamic yield stress on electric field strength for pure PANI, pure phosphate cellulose and phosphate cellulose/PANI mixtures based on ER fluids are shown in Figure 1.13. We notice that the yield stress of the PANI/phosphate cellulose mixture based on ER fluids was considered to be relatively
higher than that of the pure PANI and pure phosphate cellulose based on ER fluids. In other word, the PANI/phosphate cellulose mixture base on ER fluids have an enhanced ER effect. This phenomenon means to the fact that the dispersed particles of PANI/phosphate cellulose mixture formed more strongly fibrillated chains than that of pure PANI and pure phosphate cellulose.

**Figure 1.13** Yield stress vs. electric field strength for phosphate cellulose/PANI mixture based on ER fluid.

From **Figure 1.14** it is determinable that the ER performance of the PANI/phosphate cellulose mixture based on ER fluid appeared higher than for pure PANI and pure phosphate cellulose based on ER fluid. This is probably
because some PANI particles between the phosphate cellulose particles help the chain of phosphate cellulose particles to become strong and to increase resistance of fluid against the shear flow.

**Figure 1.14** Shear stress vs. shear rate for phosphate cellulose/PANI mixture based on ER fluids at electric field strength 1.5 kV/mm.

To understand this result, we measured the dielectric properties of the ER fluid by studying the dielectric spectra of the ER fluids. According to the bulk polarization mechanism in suspension, polarizability of suspension particles in the electric field is related to particle dielectric properties. It is definite that the ER performance of a material is closely related to the polarizability and
conductivity of the materials. The polarizability which is defined as a difference of dielectric constant was found to be a proper parameter to understand a better ER fluid [43-45]. As shown in Figure 1.15, we investigated the dielectric permittivity ($\varepsilon''$) and dielectric loss factor ($\varepsilon'''$) which are as a function of frequency. Figure 1.16 is cole-cole fitting curve of ER fluids. This plot was fitted by a following the cole-cole function Eq. (1.4) [46].

$$\varepsilon' = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega \lambda)^{\iota - \alpha}} = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)(1 + A \cos \theta)}{1 + A^2 + 2A \cos \theta} + i \frac{A(\varepsilon_0 - \varepsilon_\infty) \sin \theta}{1 + A^2 + 2A \cos \theta} \quad (1.4)$$

The dielectric parameters for each ER fluid were summarized in Table 1.3 $\Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty$ is an achievable polarizability in ER fluid, and relaxation time ($\lambda$) is related with interfacial polarization of ER fluids. In general, a large achievable polarization ($\Delta \varepsilon$) and short relaxation time of interfacial polarization give a good ER activity.
Figure 1.15 Dielectric spectra of phosphate cellulose/PANI mixture based ER fluids.

(a) dielectric permittivity and (b) loss factor as a function of frequency.
Figure 1.16 Cole-Cole fitting curves of phosphate cellulose/PANI mixture based ER fluids.

Table 1.3 Conductivity and dielectric properties for PANI/phosphate mixture based ER fluids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (s/cm)</th>
<th>$\varepsilon_0$</th>
<th>$\varepsilon_\infty$</th>
<th>$\Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty$</th>
<th>$\lambda$ (ms)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI 100</td>
<td>$10^{10}$ to $10^{-9}$</td>
<td>7.3</td>
<td>2.6</td>
<td>4.7</td>
<td>2.1</td>
<td>0.375</td>
</tr>
<tr>
<td>P.C 100</td>
<td>$10^{11}$</td>
<td>6.4</td>
<td>2.75</td>
<td>3.65</td>
<td>0.6</td>
<td>0.54</td>
</tr>
<tr>
<td>P.C 95 / PANI 5</td>
<td>$10^{11}$</td>
<td>6.4</td>
<td>2.6</td>
<td>3.8</td>
<td>0.7</td>
<td>0.55</td>
</tr>
<tr>
<td>P.C 90 / PANI 10</td>
<td>$10^{10}$</td>
<td>7.0</td>
<td>2.75</td>
<td>4.25</td>
<td>1.2</td>
<td>0.63</td>
</tr>
</tbody>
</table>

*a* P.C = Phosphate cellulose  
P.C # / PANI $\#$ : $\#$ = vol/vol% of phosphate cellulose in mixture  
$\$ = vol/vol% of PANI in mixture  

*b* achievable polarizability  

*c* relaxation time of interfacial polarization derived from $\varepsilon''$
As shown in Table 1.3, the $\Delta\varepsilon$ of pure PANI particles has higher value than that of other particles. It means that PANI particles itself can achieve high polarization. However, the PANI based on ER fluid didn’t appear better ER behavior than other mixture based on ER fluid because the PANI particles don’t have short relaxation time ($\lambda$). It disturbs to proper interfacial polarization response. Unlike the PANI particles, the phosphate cellulose particles have the short relaxation time ($\lambda$). The phosphate cellulose particles feature in high interfacial polarization which is related to yield stress and stress enhancement under the applied electric field. The high interfacial polarization of phosphate cellulose particles was occurred by fast charge migration on the polarizable particle surface. It made quickly chains of polarized particles to direction of the applied electric field. In addition, the phosphate cellulose particles have the large surface area which enables to be good polarization on surface. But the irregular shape of phosphate cellulose particle made the difficulty to form a chain along the direction of the electric field, even though its large surface area. In PANI/phosphate cellulose mixture, the PANI supplemented this fault of phosphate cellulose. Therefore, by mixing the particles, both phosphate cellulose and PANI can help each other make up for each other’s weaknesses while strengthening their strong properties.

Figure 1.17 is shown that the small size PANI particles were placed between the phosphate cellulose particles in mixture. Here, the PANI which have the
high orientational polarizability not only increased a packing density but also helped the phosphate cellulose particles to form a strong fibrillation structure in external electric field.

**Figure 1.17** Proposed schematization of phosphate cellulose/PANI mixture. circle: PANI, rectangle: phosphate cellulose.
4. CONCLUSIONS

4.1 POLYANILINE NANOFIBER

In summary, PANI nanofibers via interfacial polymerization process of the aniline were synthesized, and the influence of dopant in ER behaviors was investigated. The PANI nanofiber structure was confirmed by SEM images, in which we found that two different kinds of dopant did not have an influence on nanofiber morphology. We analyzed the flow response as a function of various electric fields to study the different behaviors for the two kinds of ER fluids. PANI nanofibers based on ER fluids indicated typical ER behaviors. The indole-2-carboxylic acid doped PANI nanofiber based on ER fluid showed higher shear stress than that of HCl doped PANI nanofiber which was attributed to the influence of dopant due to high polarizability of indole-2-carboxylic acid. Finally, investigated dielectric spectra well interpreted the difference in ER performances.

4.2 MIXTURE OF POLYANILINE / PHOSPHATE CELLULOSE

The PANI/phosphate cellulose mixtures were prepared and dispersed in dimethylsilicone oil for ER fluid. The PANI/phosphate cellulose mixture compared with the each neat particle (neat polyaniline and pure phosphate cellulose) based on ER fluids. Their electrorheological performance was
investigated using a rotational rheometer equipped with a high voltage generator, and the electric properties were measured through LCR meter. Enhanced ER performance was observed from the PANI/phosphate cellulose mixture particle system in overall shear rate ranges, possibly due to the PANI supporting effect among phosphate cellulose particles. This study signifies that an ER fluid consisting PANI/phosphate cellulose mixture should be better ER performance than that of the other pure particles, which will increase ER’s application potential.
5. REFERENCES


PART 2

Preparation and Magnetorheological Responses of Magnetic Carbonyl Iron Dispersed in Various medium
1. INTRODUCTION

Magnetorheological (MR) fluid, comprising of soft magnetic particles suspended in a nonmagnetic continuous medium such as hydrocarbon, silicone oil, or ionic liquid, is regarded as a promising material with its mechanical properties which can be controlled by an applying external magnetic field [1-4]. Without an external magnetic field, the MR fluid behaves like a Newtonian fluid. On the other hand, in the presence of an external magnetic field, the magnetic particles rapidly become active and form a chain-like structure aligning along the direction of the magnetic field and thus being changed from a liquid-like state to a solid-like state within milliseconds. It is due to the fact that magnetic-polarization interaction occurs between magnetic particles by an external magnetic field [5-7]. The chains of particles are very sensitive to the amount of magnetic field and reinforce MR properties such as yield stress, a shear viscosity, and a storage modulus, etc. with external magnetic field strength. Therefore, MR fluids along with their electrically analogous electrorheological fluids [8-10] are in the spotlight as a potential engineering application such as shock absorbers, active dampers, polishing devices and so on [11-15]. Compared to the electrorheological (ER) fluids, MR fluids have a high yield stress from 10 to 100kPa ranges with an applied external field [16]. The MR
fluids are different from ferromagnetic particle suspensions with particles of 10nm sizes that are suspended by Brownian Motions. So, Ferrofluids can flow even if applied to magnetic strength. There are lots of MR materials like ferromagnetic particles as maghemite and magnetite suspensions similar to carbonyl iron (CI) suspended system [17-19]. Among them, specifically soft magnetic carbonyl iron (CI) particles as MR fluids have been readily and widely chosen owing to its controllable magnetized, demagnetized properties and high magnetic saturation with variations of applied fields [20, 21]. For MR carrier, many oils through advanced studies are introduced. For example, mineral oil, silicone oil, kerosene and other organic oils are introduced as a carrier fluid.

In the case of typical MR fluid, there is a drawback such as serious sedimentation problem within the equipment for its application due to the high density of magnetic materials (magnetite, maghemite, carbonyl iron (CI) etc). The sedimentation of MR fluid results from a density mismatch and the incompatibility of magnetic particles in the nonmagnetic medium. Therefore various methods to solve this problem have been reported, including polymer coating on magnetic particles and introduction of additives such as surfactants or fillers in order to overcome the sedimentation problem [22-24]. However, in the case of polymer coating on the magnetic particles, the MR properties of coated particles tend to be lower than that of pure particles due to the weaker
saturation magnetization. So we tried to solve this problem by making a change not in MR particles but in the MR carriers.

First, polymer solution as MR medium oil was studied. In comparison with MR fluid which is well known as a magnetically responsible material, MR elastomers have also been investigated actively for their various advantages [25-28]. Unlike typical MR fluid, the MR elastomers which have viscoelastic and magnetorestrictive properties are the complete absence of sedimentation of the magnetic particles by adjusting elastic force of MR elastomer. These materials exhibit their interesting properties from the superposition of internal magnetic and elastic forces which can be tailored by the composition of the composite [29]. MR elastomers can also achieve an excellent durability because the magnetic particles are held in place by elastic matrix [30]. Therefore, an attempt to turn the medium oil of MR fluid into an elastic solution is an attractive way for absence of sedimentation as well as high MR performance. For this reason, in first study, we prepared MR viscoelastic samples consisting of micronsized soft magnetic CI particles and viscoelastic medium matrix. For viscoelastic medium, we used a mixture of high-molecular-weight polyisobutylene (PIB) and low-molecular-weight polybutene (PB). The highly elastic polymer solution of PIB/PB has been described by a Boger fluid, in which PIB/PB solution is similar to MR elastomer matrix as high elastic liquid [31, 32] with a constant shear viscosity up to certain shear
rate range. The magnetic properties and MR performance (yield stress behavior, shear viscosity) of the CI-PIB/PB based MR viscoelastic fluid were studied using both controlled shear rate and controlled shear stress methods. Finally, the dispersion stability of CI particles was also checked.

As second study, we tried to apply grease instead of commonly used oil such as silicone oil or mineral oil. To solve the sedimentation problem, grease which has high intrinsic viscosity gives us possibility for a magnetic carrier. This kinds of MR fluid, consisting grease instead of commonly used oil for a magnetic carrier, does not encounter sedimentation phenomenon, exhibiting the novel dispersed property against gravity during experiment and represent a non-Newtonian fluid showing a yield stress property with either applying field or not. Because of the special characteristics of this-like MR fluids, a representative application such as magnetorheological dampers can be used and developed in many automobile companies [33, 34]. P.J. Rankin et al. turned out that sedimentation phenomenon of the grease MR fluids did not appear with stable dispersion and unchanged its rheological properties by showing that a gravity yield value was superior to critical yield stress [35]. Zhang et al. investigated shear thickening phenomenon of soft magnetic carbonyl iron microspheres dispersed in ethylene glycol using silica nanoparticle additives with no sedimentation [36]. Therefore, the general grease with the outstanding dispersion stability was chosen because it is very
cheap and easy to obtain. And 5 wt% kerosene oil was added to reduce viscosity of the grease medium for better dispersed system. The purpose of this experiment in a mixture of grease and kerosene oil is to find out various rheological properties with the desired degree of reduction of viscosity for obtaining practical use in real industries.

2. EXPERIMENTAL

2.1 CARBONYL IRON (CI) DISPERSED IN POLYISOBUTYLENE/POLYBUTENE (PIB/PB) SOLUTION

2.1.1 Sample preparation

In this experiment, the polymer mixture was used for a magnetic carrier instead of commonly used oil. The CI \( \rho = 7.86 \text{ g/cm}^3 \), standard CM grade, BASF, Germany) with a mean particle size of 7 \( \mu \text{m} \) was used as magnetic particles, and PIB/PB solution which is a viscoelastic fluid is employed to a MR medium. To prepare viscoelastic medium, high molecular weight PIB (Vistanex, MM grade L-100, \( M_v = 9.9 \times 10^5 \text{ g/mol} \) was dissolved in low molecular weight PB (Daelim Chemicals, Korea) which is a chemically stable liquid with relatively high zero-shear-rate viscosity (104 poise at 30 °C). Even if the PIB is compatible with PB, it is difficult to dissolve PIB in PB directly. So we used a
heptane which is a good solvent for both PIB and PB as a cosolvent. First, a small amount (0.25 wt %) of PIB was dissolved in heptane with magnetic stirring in a sealed glass flask at room temperature for 2 days. This solution of PIB in heptane was mixed with PB (99.75 wt %) at room temperature for 2 days. Then, CI particles were dispersed in prepared PIB/PB solution using a low-speed mixer for mixing well without degradation of the long chain molecule (PIB), to prepare MR fluids with a particle concentration of 25 vol %. Finally, for CI-PIB/PB based MR viscoelastic fluid, the heptane was removed as completely as possible on vacuum oven at 60 °C.

In addition, in order to make compare MR characteristics of the CI-PIB/PB system to those of CI-general oil system, another MR fluid was prepared by dispersing CI particles in a mineral oil ($\rho = 0.862 \text{ g/cm}^3$, heavy, Sigma-Aldrich) at the same volume concentration (25 vol %).

2.1.2 Characterization

Rheological properties of the MR fluid were conducted using a rotational rheometer (MCR 300, Physica, Stuttgart, Germany) with a magneto-rheological device (MRD 180, Physica, Stuttgart, Germany) which generates a homogeneous magnetic field. A parallel-plate measuring system with a diameter of 20 mm was used at a gap of 1 mm and a magnetic field direction was set to be perpendicular to the shear flow direction [24]. The MR
characterizations were carried out at room temperature for all tests of a controlled shear rate sweep and shear stress sweep. Dispersion stability of the CI dispersed in PIB/PB solution was confirmed for 1 month period.

2.2 CARBONYL IRON (CI) DISPERSED IN MIXTURE OF GREASE AND KEROSENE

2.2.1 Sample preparation

Soft magnetic carbonyl iron (CI, standard CM grade, BASF, Germany) microspherical particles were used as received without further process. The density and average particle size of CI particles were about 7.86 g/cm³, and 7 μm, respectively. Commercial grease (Multiservice Grease E, Hankook Shell Oil Co., Ltd, Korea) was used as a suspending medium. Kerosene Oil (Yakuri Pure Chemicals Co., Ltd, Japan) were used to obtain a better dispersed suspension with some decrease of viscosity.

We fabricated two MR fluids with a kerosene concentration of 5 wt% and without kerosene oil in the grease medium. And, we respectively mixed above two mediums and CI particles at a ratio of 1:1 weight percent for 15 min by a mechanical stirrer at room temperature.

2.2.2 Characterization

The rheological properties of the MR fluids were measured by a rotational
rheometer (MCR 300, Physica, Germany) with the external device MR equipment (MCR 300, Physica, Stuttgart, Germany) from 0 to 342 kA/m. A parallel-palte measuring system with a diameter of 20 mm was used at a gap of 1mm and magnetic field direction was set to be perpendicular to the shear flow direction. The shear viscosity and shear stress were measured in the shear rate ranging from 0.01 to 1000 s$^{-1}$. Storage and loss modulus were measured in the angular frequency ranging from 1 to 100 rad/s at room temperature. Relaxation modulus was determined by previously known equation [37].

3. RESULTS AND DISCUSSION

3.1 CARBONYL IRON (CI) DISPERSED IN POLYISOBUTYLENE/ POLYBUTENE (PIB/PB) SOLUTION

The MR performances of both CI dispersed in PIB/PB and CI dispersed in mineral oil were conducted by using a rotational rheometer via a controlled shear rate (CSR) mode with a shear rate ranging from 0.01 to 1000 s$^{-1}$. Figure 2.1(a) and (b) present the flow characteristics of two MR fluids under various external magnetic field strengths ranging from 0 to 343 kA/m. When no external magnetic field was applied, the CI-mineral oil based MR fluid showed typical particle suspension characteristics, in which the shear stress increases with a shear rate and Newtonian viscosity characteristics characteristics at a
low shear rate and then shear thinning behavior. On the other hand, the CI-PIB/PB based MR viscoelastic fluid showed that the shear viscosity is fairly constant regardless of shear rate, resulting from Boger fluid characteristics of the PIB/PB solution with non shear-thinning and constant viscosity behaviors as a second-order fluid [32]. In addition, the CI-PIB/PB based MR fluid has higher shear stress and higher shear viscosity than the corresponding CI-mineral oil based MR fluid in the whole shear rate range. It indicates that the medium matrix of MR fluid play an important role.

Furthermore, when external magnetic fields were applied, both MR fluids exhibited Bingham fluid behavior with a yield stress, representing a wide plateau shear stress range over an entire shear rate region. It is also observed that the shear stress and shear viscosity increased with an increase of magnetic field force. Since the CI particles were magnetically polarized and resulted in induced dipole-dipole interaction force under a magnetic field, they formed the chain or cluster structure along the magnetic field direction and this increased resistance of the fluid against the shear flow [38]. When the magnetic field is being increased, shear stress becomes also higher due to the stronger interaction among magnetic particles in medium matrix. It thus requires much more shear stress to make MR viscoelastic fluid flow in the case of being applied under a stronger magnetic field.
Figure 2.1 (a) Shear stress as a function of shear rate (b) Shear viscosity as a function of shear rate for the CI-PIB/PB based MR viscoelastic fluid (points) and CI-mineral oil based MR fluid (lines) under various external magnetic field strengths.

Compared to the shear stress value with a magnetic field, the both MR fluids
exhibited similar value of yield stress and shear stress in low shear rate. However, the CI-PIB/PB based MR viscoelastic fluid showed a relatively higher shear stress than the CI-mineral oil based MR fluid in a high shear rate region. This observation is due to the elasticity of the PIB/PB solution, in which its high elasticity enhances resistance of the fluid against the shear flow. Here, the important thing is that the new system using Boger fluid instead of general oil as MR medium matrix is possible for MR fluid without worsening the MR properties.

![Graph](image)

**Figure 2.2** Shear stress curves (CSS mode) for CI-PIB/PB based MR viscoelastic fluid under various magnetic field strength.
Generally, there are two kinds of yield stresses for MR fluids that are dynamic yield stress and static yield stress. The dynamic yield stress is the extrapolated value obtained from flow curve via the CSR mod 
mode, while the static yield stress is measured directly using controlled shear stress (CSS) mode by increasing the shear stress to a critical value at which the sample begins to flow. In this study, the static yield stress was also examined using the CSS mode in which the test begins from the rest state. **Figure 2.2** shows the changes of shear viscosity as a function of the shear stress. While the shear viscosity has a constant value at a low shear rate region, the shear viscosity abruptly decreased at a particular value which is considered to be a static yield stress. The static yield stresses at magnetic field strengths of 86, 171, and 343 kA/m were extrapolated to be approximately 1.39, 4.50, and 10.80 kPa, respectively. These values which are the static yield stress developed below which there was no real macroscopic flow [39]. It indicates that the sufficiently small strain in this stage deforms the particle chain structures under magnetic field, and it is expected to rearrange and stabilize the chain structure until breakage of them with higher strain followed.

The oscillatory test was also carried out under different magnetic field in order to examine the viscoelastic properties of MR fluid. **Figure 2.3** represents an amplitude sweep measurement which describes the changes of the storage modulus (G’) and loss modulus (G”) as a function of strain for MR fluid, in
which the $G'$ and $G''$ are the measurement of elasticity and viscous behavior of the MR fluid, respectively. Without a magnetic field, the storage modulus and loss modulus are similar to each other. But, the storage modulus is considerably greater than the loss modulus in a most strain region when the magnetic field is present. It is determinable that the MR fluid has a very strong solid-like structure rather than a liquid-like structure in the magnetic field [23].

**Figure 2.3** Amplitude sweep dependence of storage modulus, $G'$ (close symbol) and loss modulus, $G''$ (open symbol) for CI-PIB/PB based MR viscoelastic fluid under various magnetic field strength.

Moreover, as shown in **Figure 2.4**, the storage modulus ($G'$) of the MR fluid
was enhanced with increasing the applied magnetic field, similarly for the flow curve. It is because the chains were reinforced via a strong dipole-dipole interaction between the adjacent magnetic particles with increasing external magnetic field strength [40]. In addition, it is apparent that at a fixed magnetic strength, the storage modulus (G’) demonstrates constant value over a long frequency range. The storage modulus does not rely on angular frequency, implying that the MR fluid changes from liquid-like to solid-like under an applied external magnetic field [41-43].

**Figure 2.4** Frequency dependence of the storage modulus, G’ for CI-PIB/PB based MR viscoelastic fluid under various magnetic field strength.
Finally, sedimentation of CI-PIB/PB based MR viscoelastic fluid was examined by putting it on a flat table for 1 month. Image of Figure 2.5 shows that the CI-PIB/PB based MR viscoelastic fluid does not have sedimentation. Even after long time, CI particles were still suspended in the PIB/PB matrix, in which PIB/PB plays an important role as a highly elastic matrix. Note that commonly used medium oil of MR fluid often causes serious sedimentation problem. From this study, we find that the PIB/PB viscoelastic matrix not only helps CI particles to form stable chains in a magnetic field but also minimizes the sedimentation drawback of the typical MR fluids.

Figure 2.5 Snapshot image of CI dispersed in PIB/PB (a) before (b) after 1 month.
3.2 CARBONYL IRON (CI) DISPERSED IN MIXTURE OF GREASE AND KEROSENE

Figure 2.6 indicates the shear-thinning phenomenon of two MR fluids, with a kerosene concentration of 5 wt% and without kerosene oil, as a function of shear rate [44]. It is clear that the shear viscosity of both systems decreases with increasing shear rate ranging from 0.1 to 1000 s⁻¹. Furthermore, we confirm that the shear viscosity with a kerosene concentration of 5 wt% decreases a little more than pure grease MR fluid. It means that we can adjust and facilitate the shear viscosity of grease by using kerosene oil for helping better dispersed CI suspension.

Figure 2.6 Viscosity of pure grease and grease added with 5 wt% kerosene oil at no external magnetic field. (open symbol: pure grease, closed symbol: grease added with 5 wt% kerosene oil)
We can confirm the shear stress of two MR fluids as a function of shear rate under various magnetic field strengths from 0 to 342 kA/m. As shown in Figure 2.7, shear stress in case of grease with 5 wt% kerosene decreased more than that of grease in all magnetic field strengths. Generally, MR fluids indicate solid-like behavior with yield stress under applied magnetic field strengths. The yield stress, depending on the applied magnetic field strengths, reaches to a magnetically saturated maximum point which has no further effect by increase in magnetic flux density. Since grease has its own peculiar property and formation of chain-like structure at a gap of 1 mm between two poles, two MR fluids present this solid-like yield stress. We calculated the yield stress by extrapolating the obtained each flow curve to zero shear rate and drawing the line to vertical axis using the Bingham plastic model as given Eq. (2.1) and Eq. (2.2). The behavior of MR fluid is as follows.

\[
\tau = \tau_y(H), \quad \text{for} \quad \tau \leq \tau_y \tag{2.1}
\]

\[
\tau = \tau_y(H) + \eta \dot{\gamma}, \quad \text{for} \quad \tau \geq \tau_y \tag{2.2}
\]

Here, \(\tau, \tau_y\) are the shear stress and the yield stress, respectively. \(H\) indicates the magnetic field strength and \(\dot{\gamma}\) is the shear rate. In order to deform both CI based MR grease, it is required a certain degree of yield stress. The reason why shear
stress increases more strongly with increasing applied magnetic field strengths is dipole-dipole interaction between soft magnetic carbonyl irons creating the chain structure perpendicular to the direction of MR fluid flow [45, 46].

![Graph showing shear stress vs. shear rate for two types of MR grease at different magnetic field strengths.](image)

**Figure 2.7** Shear stress of two CI based MR grease at various applied magnetic field strengths. (open symbol: pure grease, closed symbol: grease added with 5 wt% kerosene oil)

**Figure 2.8** depicts the shear viscosity of two CI based MR fluids with variations of applied magnetic field strengths. It is clear that the shear-thinning behavior of both CI based MR fluids shows up obviously in all magnetic field strengths. As expected, in case of addition of 5 wt% oil, the viscosity of the CI
based MR fluid decreased as a function of shear rate from 0.1 to 1000 s\(^{-1}\) in all magnetic fields.

![Graph showing shear viscosity of two CI based MR grease with increasing applied magnetic field strengths.](image)

**Figure 2.8** Shear viscosity of two CI based MR grease with increasing applied magnetic field strengths. (open symbol: pure grease, closed symbol: grease added with 5 wt% kerosene oil)

This phenomenon of reduction of viscosity means that we can control and adjust medium of the CI based MR grease for obtaining better dispersed CI systems. And we can make the CI based MR grease system a little easier by adding small amount of kerosene oil. When magnetic field strength is applied between two poles at a gap, the particles formed the chain or cluster structure
owing to dipole-dipole interactions of carbonyl iron (CI) magnetic particles. At low shear rate, the CI magnetic particles form chain structure more dominantly than the velocity of deformation under applied magnetic field strengths. But, at high shear rate, the viscosity of both CI based MR fluids decreases with increasing shear rate due to the strong and fast deformation than forming the chain-like structure between two poles at a gap of 1 mm.

Ginder et al. divided the range of yield stress ($\tau_y$) into two different regimes based on the applied magnetic field strengths ($H_0$). At very low fields, the yield stress ($\tau_y$) is proportional to $H^2$ because of the local saturation of the magnetized particles. At intermediate magnetic field strengths, the yield stress ($\tau_y$) is expected to change with $H^{3/2}$. At large magnetic field strengths enough to achieve complete saturation, magnetic particles can be treated as a simple dipole with stress and modulus independent on magnetic field strength and scale as saturation magnetization ($M_s$). Note that in the case of MR fluid, there may exist a critical magnetic field strength ($H_c$) with $\tau_y \propto H_0^{3/2}$ ($H < H_c$) and $\tau_y \propto H_0^2$ ($H > H_c$). Therefore, we carefully hypothesize that a universal hybrid yield stress equation of electrorheological (ER) fluids can be adopted for MR fluids, considering the existence of a critical magnetic field strength ($H_c$), to examine dynamic yield stress of MR fluids under external magnetic field strengths by presuming the similarity between ER and MR fluids. So, we propose the following new equation [23, 47-48]:
\[ \tau_y(H_0) = \alpha H_0 \frac{2}{3} \left( \tanh \sqrt{\frac{H_0}{H_c}} \right) = \alpha H_0^{3/2} H_c^{1/2} \tanh \sqrt{\frac{H_0}{H_c}} \] (2.3)

Here, \( \alpha \) is related to the susceptibility of the fluid and volume fraction or other analogous physical parameters. \( \tau_y \) possesses two limiting behaviors around a critical magnetic field strength \( (H_c) \) with respect to \( H_0 \),

\[ \tau_y = \alpha \sqrt{H_c H_0^{3/2}} \quad \text{for} \quad H_0 \ll H_c \] (2.4)

\[ \tau_y = \alpha \sqrt{H_c H_0^{3/2}} \quad \text{for} \quad H_0 \gg H_c \] (2.5)

Eq. (2.4) and (2.5) depict that the dynamic yield stress \( \tau_y \) is proportional to \( H_0^2 \) at low magnetic field strength and becomes proportional to \( H_0^{3/2} \) when \( H_0 \) passes through the critical magnetic field strength. From the above explanation, Figure 2.9 shows that we can calculate the dynamic yield stress \( \tau_y \) for two CI based MR fluids which fit almost perfect agreement with Eq. (2.5) under various magnetic field strengths \( H \). Comparing two systems, the CI based MR fluids with 5 wt% kerosene is smaller than that of without kerosene in all magnetic fields. And, we can say that both systems follow the intermediate region dependence of Ginder et al [49].
Figure 2.9 Re-plotted dynamic yield stress under various magnetic field strengths. (open symbol: pure grease, closed symbol: grease added with 5 wt% kerosene oil)

Figure 2.10 indicates that the storage modulus ($G'$) and loss modulus ($G''$) steadily go up with increasing angular frequency ($\omega$) for both MR fluids under different magnetic field strengths ranging from 0 to 342 kA/m. It is evident that the frequency sweep of the CI based MR grease, in which both $G'$ and $G''$ exhibit stable plateau region over a broad frequency range under all measured magnetic field strengths, implies that both CI based MR grease possess a very strong solid-like property than a liquid-like property because the value of $G'$
shows more dominant than that of \( G'' \) all over the magnetic field strengths. Oscillation test allows us to confirm viscoelastic behaviors of CI based MR grease because both the storage and loss modulus tell elasticity and viscous properties. Surely, in the event that addition of 5 wt\% kerosene, reduction of both storage and loss modulus happen at all magnetic field strengths ranging from 1 to 100 rad/s. As increase magnetic fields, rise of both modulus values is shown because a dipole-dipole interaction between two poles at a gap of 1mm becomes stronger in both CI based MR grease.
The stress relaxation modulus \(G(t)\) of two CI based MR grease confirming the solid-like state of MR fluids can be calculated by using the values of both \(G'(\omega)\) and \(G''(\omega)\) from the Schwarzl relation given in Eq. (2.6) [37]. In Fig. 6, we confirm almost plateau region of the stress modulus \(G(t)\) with no relaxation feature as a function of time with increasing magnetic field strengths. Therefore, we can think that the chain structure of the two CI based MR
greases indicate very solid-like behavior due to their strong interactions between magnetic carbonyl iron particles under external magnetic field. As expected, the relaxation modulus of MR grease without kerosene is also higher as a function of time in all magnetic fields due to more elastic property indicating higher storage modulus.

\[
G(t) \approx G'(\omega) - 0.560G''(\omega/2) + 0.200G''(\omega)
\]  

(2.6)

**Figure 2.11** Relaxation modulus (G(t)) of pure grease (open symbol) and other grease added 5 wt% kerosene oil (closed symbol) calculated from G'(\omega) and G''(\omega) values.
4. CONCLUSIONS

4.1 CARBONYL IRON (CI) DISPERSED IN POLYISOBUTYLENE/ POLYBUTENE (PIB/PB) SOLUTION
MR viscoelastic fluid sample have been prepared from soft magnetic CI micron sized particles and PIB/PB medium matrix which is known as a Boger fluid. Rheological properties of the CI-PIB/PB based MR viscoelastic fluid were observed by static and dynamic tests using a rotational rheometer under external magnetic fields. The MR viscoelastic fluid represented typical MR features which is higher yield behaviors and higher shear stresses in applied magnetic fields. In addition, the CI-PIB/PB based MR viscoelastic fluid was found to overcome the serious sedimentation problem, demonstrating that the system which consists with a Boger fluid has a potential to be used as a MR fluid without sedimentation.

4.2 CARBONYL IRON (CI) DISPERSED IN MIXTURE OF GREASE AND KEROSENE
In this work, the characteristics of two CI based MR greases were investigated by a rheometer equipped with the MR equipment. Kerosene was used to decrease the viscosity of the MR grease with soft magnetic carbonyl iron (CI) particles for approaching commercial applications and obtaining well dispersed
suspension. The two MR greases exhibited a Bingham plastic behavior for requiring the yield stress to flow under magnetic field strengths, implying the formation of strong chain-like structure between two poles at a gap of 1mm. And the CI based MR grease contained kerosene oil takes advantage of its peculiar shear-thinning characteristic for using as a lubricator at high frequency range. Finally, the MR fluids for this study have almost no sedimentation behavior compared with other MR fluids due to unique property of grease at all magnetic fields.
5. REFERENCES


