Electrorheological response of polyindene/colemalite conducting composite

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Abstract. In this study, electrorheological (ER) responses of colemanite and polyindene (PIn)/colemanite conducting composite dispersions in silicone oil (SO) were investigated. Antisedimentation ratios of the dispersions were determined. Some parameters which affect the ER properties of the dispersions such as electric field strength (E), shear rate, frequency and temperature were investigated. The rather unusual behavior known as “negative ER effect” was observed for colemanite/SO above \( E = 1.5 \) kV/mm and for PIn/colemanite/SO under all the values of electric field strength at volume fraction of 25%. This negative ER response was converted to positive with the addition of non-ionic surfactant.

1. Introduction
Electrorheological (ER) fluids are colloidal dispersions that commonly compose of polarizable powders dispersed in insulating liquids such as silicone oil (SO). ER fluids exhibit reversible changes (liquid-like to solid like) in their rheological properties as a function of the electric field strength (E). To enhance the ER effect and the stability of the suspension, sometimes, ER fluids require small amounts of additives such as polar compounds or surfactants. If the electric field induced viscous properties increase with the application of electric field, this phenomenon is termed positive ER effect. On the other hand, if the electric field induced viscosity of the ER fluid decreases as the applied electric field increases, this refers to negative ER effect [1].

Colemanite (2CaO.3B2O5.5H2O) is the most important calcium and boron containing commercial borate mineral. The basic structure of colemanite contains endless chains of interlocking BO2(OH) triangles and BO3(OH) tetrahedrons with the calcium, crystalline water molecules and extra hydroxides interspersed between the chains. The sheets are held together by weak hydrogen bonds involving both water molecules and hydroxyl groups [2].

Polyindene (PIn) is one of the conducting polymers and because of its cyclic structure, phenyl rings of PIn are arranged horizontally along the main chain; hence, the repeating unit of PIn forms a nearly planar structure. This unique structure renders PIn having a high glass-transition temperature and special optical properties [3]. In the literature, it was reported that the viscosities of PIn/CaCO3 [4] and PIn/kaolinite [5] composites showed positive ER effect and the ER activities of these system rose with PIn content.

In this study, colemanite and PIn/colemanite composites were used as ER active materials. Antisedimentation stabilities of these systems in non-aqueous medium (SO) were determined. The
parameters which affect the ER properties of colemanite/SO and Pln/colemanite/SO systems were investigated such as electrical field strength, shear rate, frequency, temperature and surfactant. Full details of the study is given in our previous publication [6].

2. Experimental

2.1. Materials
Colemanite (2CaO.3B₂O₃.5H₂O) was kindly supplied by ETI Mining Co. (Turkey) and all the other chemicals were Aldrich products and used as received. Indene was used after distillation.

2.2. Synthesis and characterization of Pln/colemanite composite
Pln was in-situ polymerized in the presence of colemanite using FeCl₃ as oxidizing agent taking the monomer to initiator ratio as 2:1 in CHCl₃ and the obtained Pln/colemanite composite was subjected to various characterization techniques. The full details of the synthesis and characterization of Pln and Pln/colemanite composite are given in our previous publication [7].

2.3. Preparation of dispersions
Dispersions of colemanite and Pln/colemanite composite were prepared at a volume fractions of 25% by dispersing definite amount of solid particles in SO (\(\rho = 0.965 \text{ g/cm}^3\), \(\eta = 1.0 \text{ Pa s}\), \(\varepsilon = 2.61\), Aldrich, Germany), which were both vacuum dried before mixing in an oven for overnight to remove any moisture present. The ionic-surfactant examined was Triton X-100 (\(t\)-octylphenoxypolyethoxyethanol) and the concentration of Triton-X in the dispersions was 5 wt.%. These surfactant containing dispersions were coded as T-colemanite and T-Pln/colemanite. All the prepared dispersions were allowed to equilibrate for overnight before ER measurements.

2.4. Antisedimentation ratio measurements
Antisedimentation stabilities against gravitational forces of the colemanite/SO and Pln/colemanite/SO dispersions were determined at \(T = 25\pm0.1^\circ C\). Glass tubes containing the above dispersions were immersed into a constant temperature water bath and formation of the first precipitates was recorded to be the indication of colloidal instability. During the neat eye observations, the height of phase separation between the particle-rich phase and the relatively clear oil-rich phase was recorded as a function of time by using a digital composing stick. The antisedimentation ratio was defined as the height of the particle-rich phase divided to the total height of dispersion.

2.5. Electrorheological measurements
ER properties of the dispersions were determined with a Thermo-Haake RS600 parallel plate torque electrorheometer (Karlsruhe, Germany). The gap between the parallel plates was 1.0 mm and the diameters of the upper and lower plates were 35 mm. The potential used in these experiments was supplied by a 0–12.5 kV (with 0.5 kV increments) dc electric field generator (Fug Electronics, HCL 14, Germany), which enabled resistivity to be created during the experiments.

3. Results and discussion

3.1. Antisedimentation stabilities of the dispersions
The antisedimentation stability of ER materials is one of the main criteria because the ER fluids are supposed to be homogeneously dispersed before applying external electric field strength.

The effects of dispersed particles on the antisedimentation ratios of the materials used in this study were examined. For the particle volume fraction of 25%, antisedimentation ratios at the end of 25 days were determined as 72% for colemanite/SO and 92% for Pln/colemanite/SO systems. It was observed that Pln/colemanite/SO dispersion system was significantly stable against gravitational sedimentation than colemanite/SO. Furthermore, increasing antisedimentation ratios were recorded with increasing
average hydrodynamic particle sizes \(d_{0.5}\) of samples \(d_{0.5}(\text{PIn/colemanite}) \) (2.2 \(\mu\)m)\(>\) \(d_{0.5}\) (colemanite) (1.2 \(\mu\)m)\) and decreasing apparent densities of the samples \(\rho_{\text{colemanite}}(1.69)\)\(>\) \(\rho_{\text{PIn/colemanite}}(1.02)\). It was observed that the PIn/colemanite/SO dispersion system had higher antisedimentation ratio than 
colemanite/SO, although particle size of PIn/colemanite was bigger than colemanite. On the other hand, the density of PIn/colemanite was lower than colemanite and closer to the density of SO. Furthermore, in composite structure PIn chains form steric hindrance that holds the particles in suspended positions against agglomeration.

3.2. Electrorheological studies

3.2.1 Viscometry results. The colemanite particles dispersed in SO were distributed randomly without applying \(E\) (Figure 1). When an electric field was applied, the particles became polarized and tended to attract each other, and consequently the fibril-like structures aligned to the direction of electric field were formed, which provide additional resistance against flow. For colemanite/SO system, this occurs under low electric field values and the formation of fibril-like structures could be weak (Figure 2). After \(E = 1.5\) kV/mm, weak fibrillar structures between the electrodes broke-down because of the enhancement in electrophoretic mobility of particles with increasing applied electric field, and the colemanite particles moved towards the positive electrode, resulting in phase separation and decrease in viscosity (Figure 1). Similar migration of particles to one of the electrodes was reported for Teflon/SO system, which was attributed to the interactions between the oil and the Teflon particles [8].

![Figure 1. The ER response of colemanite/SO and T-colemanite/SO \((\varphi = 25\%)\).](image1)

![Figure 2. Change in viscosity of the materials with \(E\) \((\varphi = 25\%, T = 25^\circ C)\) [6].](image2)

Sigma bonds between the hexagonal rings in colemanite structure facilitate the rotation of the rings, and this rotation prevents the formation of stronger fibrillar structures under electric field and also polyanion structure of colemanite contribute to the dispersed particles to migrate to one of the electrodes.

The PIn/colemanite/SO system showed slight changes in viscosity with increasing electric field. But, the mean apparent viscosity showed to be lower than that of the viscosity at \(E = 0\) kV/mm condition which is an indication of negative ER behavior. In the presence of an electric field, structure of dispersion was destroyed by electrostatic forces acting on polarized particles, reorganizing them into fibrillar chains parallel to the electric field, whose resistance against the flow was lower than that
of the structure of dispersion with the absence of electric field. Consequently, the negative ER effect was occurred.

After observing negative ER effect for the materials studied, especially at high electric field strengths, the effects of non-ionic surfactant (Triton-X) on ER behaviors of the materials were investigated. Significant increases in the electric field viscosities were observed with the addition of Triton-X. The presence of Triton-X surfactant observed to cause dramatic changes on the ER responses and the viscosities of T-colemanite/SO and T-PIn/colemanite/SO systems increased with increasing electric field, in contrast to pure colemanite/SO and pure PIn/colemanite/SO systems. It is believed that Triton-X interacted with colemanite and PIn/colemanite with the secondary forces, and prevented the particle migration to one of the electrodes. Triton-X surfactant provoked the modification of the interfacial properties of the dispersed particles and formed a kind of bridge between the adjacent particle surfaces. Thus, the formation of stronger fiber structure was provided and also fibrillar structures were observed easily by neat eyes for T-colemanite/SO dispersion system (Figure 1). Furthermore, the electric field viscosity enhancement of PIn/colemanite/SO system was higher than colemanite/SO system with the addition of Triton-X into these systems. This is due to the interaction between hydrophobic chains of Triton-X and polyindene chains in PIn/colemanite composite structure. Virtually, these interactions reversed the observed negative ER behavior of the materials to positive, as targeted.

3.2.2. Effect of shear rate on shear stress and viscosity. The effects of shear rate ($\dot{\gamma}$) on shear stress and viscosity for colemanite/SO and T-colemanite/SO systems were depicted in Figure 3(a, b), and for PIn/colemanite/SO and T-PIn/colemanite/SO systems were shown in Figure 4(a, b) for $E = 0$ kV/mm and $E = 1.5$ kV/mm conditions. The viscosities of the systems were observed to decrease exponentially at lower shear rate regions with typical curves of shear thinning non-Newtonian viscoelastic behaviors both under $E = 0$ kV/mm and $E = 1.5$ kV/mm conditions.

Non-Newtonian shear stress increments were observed with increasing shear rate for all the materials examined. But it was clearly seen that PIn/colemanite/SO system showed weaker structure with the presence of electric field than the absence against to the shearing forces as a results of negative ER effect (Figure 4a). On the other hand, with the application of electric field, Triton-X provoked the formation of chain-like structures in the dispersions which resulted in a resistance to flow with an abrupt enhancement of electric field induced viscosity at low shear rate regions. It can be concluded that Triton-X enhanced the formation of electric field induced fibrillar structures in dispersions as targeted.

Yield stress ($\tau_y$) values of all the materials examined were calculated from the shear stress-shear rate curves obtained at control rate (CR) mode of the electrorheometer by extrapolating the flow curve to $\dot{\gamma} = 0$ s$^{-1}$. Yield stresses of the samples at $E = 3.5$ kV/mm are calculated to be as following: $\tau_y$ (T-PIn/colemanite) 408 Pa > $\tau_y$ (T-colemanite) 91 Pa > $\tau_y$ (colemanite) 6 Pa > $\tau_y$ (PIn/colemanite) 4 Pa. A tremendous yield stress increase was obtained for T-PIn/colemanite/SO system as targeted. It was concluded that, the interactions between the surfactant molecules and the dispersed particles caused the reduction of surface tension of the dispersion system; and also the surfactant molecules promoted the colloidal stability of the dispersed particles. This situation is in accordance with “water/surfactant bridge” model [9]. Besides, the surfactant molecules may overcome the negative ER effect via stabilizing the particles and preventing electromigration of the particles due to the charge injection at the electrodes [10] and preventing a possible phase separation between the upper and lower plates of the electrorheometer.

3.2.3. Effect of frequency on storage modulus and loss modulus. It is well known that the relationship between storage modulus ($G'$) and loss modulus ($G''$) indicates whether the material is solid-like ($G'>G''$), gel-like ($G'$≈$G''$) or liquid-like ($G''>G'$) in the whole frequency range measured [11].
Figure 3. The effect of shear rate on shear stress and viscosity of (a) colemanite/SO and (b) T-colemanite/SO (T=25°C, ϕ = 25%) [6].

Figure 4. The effect of shear rate on shear stress and viscosity of (a) PIn/colemanite/SO and (b) T-PIn/colemanite/SO (T=25°C, ϕ = 25%) [6].

Figure 5 shows G' and G'' as a function of frequency for colemanite/SO, T-colemanite/SO, PIn/colemanite/SO and T-PIn/colemanite/SO dispersion systems at $E = 1.5$ kV/mm. Stress sweep was first carried out to determine the proper stress values to ensure collecting data in the linear viscoelastic regime for the samples. It was observed that G’ values of all the dispersions except PIn/colemanite/SO were higher than G” values and showed slight increments in the whole frequency sweep range and owing to not providing fully elastic solid-like structure in the dispersions. However, G’ values of PIn/colemanite/SO were closer to G” values at moderate frequency values and also increased notably with increasing frequency. At lower frequencies the viscous behavior reflected by G” was dominant whereas, at the higher frequencies the elastic behavior reflected by G’ was outweighing. This suggests that fibrillar structure between the electrodes could not occur at lower frequencies. Similar increment in G’ were reported for goethite/SO suspension system at both lower volume fractions and electric field strengths [12].

3.2.4. The effect of temperature on shear stress. It is known that the temperature affects on various physical properties of the particles and dispersant liquid, such as the dielectric constant, conductivity and current density. Moreover, thermal motion and colloidal stability are influenced by change of temperature. The ultimate ER behavior depends on the balance attained among these factors [13].

To investigate the behavior of materials at elevated temperatures, temperature sweeps were carried out between 15°C and 75°C for all the materials studied (Figure 6). The shear stresses of all the samples, except colemanite/SO system, were recorded to decrease with increasing temperature. The overall shear stress losses ($Δτ = τ_{15°C}−τ_{75°C}$) were in the order of: $Δτ_{T-PIn/colemanite}$ (160 Pa)$>Δτ_{PIn/colemanite}$ (15 Pa)$>Δτ_{T-colemanite}$ (14 Pa) and shear stress increment for colemanite was calculated to be 3 Pa. With increasing temperature the thermal motions of the dispersed particles were enhanced; as a result the
mobility of the particles raised and formation of stripes along the direction of the electric field got relatively difficult. Colemanite/SO system showed slight increment with raising temperature which was believed to cause by its crystal water.

On the other hand, the temperature effect on ER behavior became more complicated with the addition of Triton-X surfactant. As the temperature varies, beside change in the electrical properties of the dispersion, the adsorption and desorption behaviors of the surfactant molecules contribute to the ER behavior. From the results, it can be clearly seen that surfactant molecules caused to decrease of the ER performance of T-colemanite and T-PIn/colemanite dispersions significantly. A possible explanation to this behavior may be the formation of weaker chains as a result of desorption of the surfactant molecules between the adjacent particles that act as a bridge or aggregation of the surfactant molecules between the electrodes via phase separation.

Figure 5. The effect of the frequency on the storage modulus and loss modulus of the samples (\(\phi = 25\%\), \(T = 25^\circ\text{C}\)) [6].

Figure 6. The effect of the temperature on the shear stress of the samples (\(\phi = 25\%\), \(T = 25^\circ\text{C}\)) [6].

4. Conclusions
Colemanite/SO dispersion observed to show positive ER effect until \(E = 1.5\) kV/mm and became negative ER active material when \(E > 1.5\) kV/mm was applied. On the other hand, PIn/colemanite/SO system showed negative ER activity under all the electric field conditions. Both behaviors were attributed to the migration of the dispersed particles to one of the electrodes. The use of Triton-X non-ionic surfactant in the dispersions observed to convert the negative ER effect to positive one by also enhancing the ER activity, which was explained by the water/surfactant-bridge formation model.

Acknowledgement
The authors thank to the Gazi University Research Fund (Grant No: 05/2011-05, 05/2012-34) and Turkish Scientific and Technological Research Council (Grant No: 111T637) and COST Action CM1101 for the financial support to this work.

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