Electrorheological Properties of Environmental Friendly Modified Cellulose

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Abstract: Considerable scientific and industrial interest is currently being focused on a class of materials known as electrorheological (ER) fluids, which display remarkable rheological behaviour, being able to convert rapidly and repeatedly from a liquid to solid when an electric field (E) is applied or removed. In this study, biodegredable cellulose (Cell) was modified and converted their carboxyl salts. Modified cellulose (Cell-Li) is characterised by (FT-IR), (SEM), (EDS) and (TGA). Suspensions of native and modified cellulose are prepared in corn oil. Rheological measurements were carried out via a rotational rheometer with a high voltage generator. These suspensions are determined; effects of electric field strength, shear rate, shear stress, temperature etc. onto ER activity. The results show not only that the ER properties are enhanced by increasing the particle concentration and electric field strength, but also the cellulose-based ER fluids exhibit viscoelastic behavior under an applied electric field due to the chain formation induced by electric polarization between particles.

Introduction

The biodegradable and biocompatible polymers have caused significant attention from both ecological and biomedical perspectives in the past decaded (Ikada & Tsuji 2000).

Cellulose, as a natural polymer, has received great attention recently as a possible alternative to petroleum-based polymers and cellulose possess either branched polar groups such as hydroxy (-OH) groups (Tahiri & Vignon 2000). The polar groups may affect the ER behavior under the imposed electric field. Cellulose has the advantages of being renewable, biodegradable, abundantly available and low in costs. Considerable scientific and industrial interest is currently being focused on a class of materials known as electrorheological (ER) fluids (Winslow 1949), which display remarkable rheological behaviour, being able to convert rapidly (Block & Kelly 1988) and repeatedly from a liquid to solid when an electric field (E) is applied or removed (Trlica et al. 1996).

A wide variety of particulates or solid particles, such as cellulose, starch, flour, silica, alumina, titania, zeolite and dielectric powders dispersed in low-conductivity non-polar matrices such as silicone, hydrocarbon

oils and acrylic rubber, make up suspensions whose rheological properties can change abruptly on application of an external electric field; they are commonly known as electrorheological (ER) fluids(Tangboriboon et al. 2008). The typical characteristic of ER fluids, reversible and swift transition between the liquid state and the solid state, potentially provides the most efficient approach to controlling mechanical responses by adjusting electric field strengths. The electric field-induced interaction, arising from particle polarization, is commonly believed to be responsible for ER behavior (Otsubo et al. 1992).

In this study, we investigate cellulose and modified cellulose as a vigorous nominee for anhydrous particles in high performance dry-base systems by analysing the effect of particle concentration, electric field strength, shear rate and frequency via shear tests.

Experimental

1. Materials

All chemicals (amorphous cellulose, 2,2,6,6-Tetramethyl-1-piperidinyloxy(TEMPO), LiBr) were Acros Organics products with analytical grade and used as received. Methanol, ethanol and acetone were used as a solvent throughout the experimental procedure. Hydrochloric acid and sodium hydroxide were J.T.Baker products, sodium hypochlorite was Merck products and used as received. The host oil employed was food-grade corn oil produced by Luna and had the following physical properties at $25\,^{o}C$: density $\rho f = 0.936$ g/cc, viscosity $\eta f = 45$ mPa s, dielectric constant $K_f = 3.34$, and conductivity $(E = 1\,kV/mm) = 4X10^{-11}$ S/m.

2. Modification of cellulose

Oxidation experiments were made under the following conditions. Amorphous cellulose samples (0.648 g, 4 mmol of anhydroglucose units) were dispersed in distilled water (80 ml) for 1min with an Ultra-Turrax homogeniser. TEMPO (10 mg, 0.065 mmol) and LiBr (0.20 g, 1.9 mmol) were added in the suspension, which was maintained at $4\,^{o}C$. The sodium hypochlorite solution (13 %, 4.88 ml, 8.8 mmol) with pH adjusted to 10 by addition of 0.5 M aqueous HCl was set at $4\,^{o}C$ by means of an ice bath, and added four times (30 min each) to the suspension, which was stirred mechanically. The pH was maintained at 10 during the reaction by adding a 0.5 M NaOH solution. The temperature of the suspension was maintained at $4\,^{o}C$ by means of an ice bath during the oxidation reaction. When the solution became hazy, almost all the cellulose samples had disappeared and the reaction was stopped by adding either 10 ml of methanol or and a small amount of sodium borohydride. The reaction mixture was neutralised to pH 7 with 0.5 M HCl and centrifuged to remove the residual insoluble material. The oxidised cellulose sample in the supernatant was precipitated by adding an excess of ethanol (5–10 volumes), followed by centrifugation. The precipitate was washed with ethanol:water (9:1) and centrifuged several times and finally washed with acetone. The precipitate was then redissolved in distilled water, dialysed and freeze-dried.
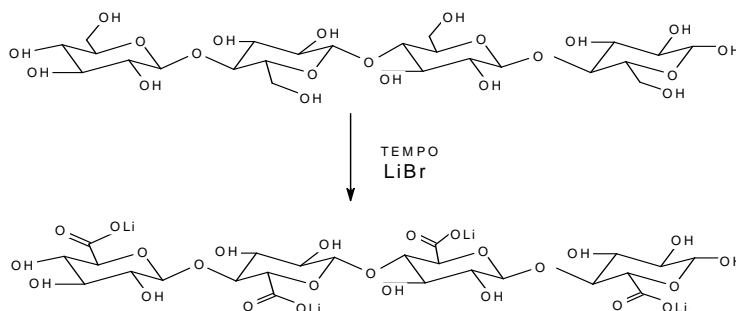

Scheme 1. Modification reaction of cellulose.

3. Electrorheological measurements

Suspensions of cellulose derivative particles were prepared in corn oil at a series of concentration (c = 5–25 % m/m). Suspensions were mechanically stirred before each measurement against sedimentation. Rheological properties of the suspensions were determined with a Termo-Haake RS600 parallel plate Electro-rheometer (Germany). The gap between the paralel plates was 1.0 mm and the diameters of the upper and lower plates were 35 mm. All the experiments were carried out at a controlled rate (CR) mode and at various temperatures (25–125

°C, with 25 °C increments.). The voltage used in these experiments was also 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.
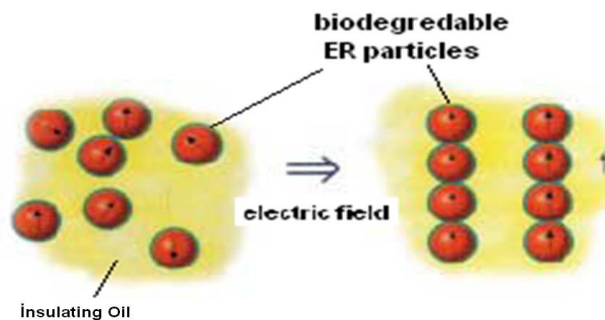
Scheme 2. Mechanism of ER behavior.

Results and Discussion

1. Characterization of native cellulose and modified cellulose

FTIR spectra of cellulose and modified cellulose were recorded on a Mattson Model 1000 instrument (UK) as KBr discs. The FTIR spectrum of native cellulose showed the expected distinctive absorptions. The absorptions at 3330 cm^{-1} (O–H stretching), 2980 cm^{-1} (aliphatic C–H stretching), 1460 cm^{-1} (aliphatic C–H bending), 1170 cm^{-1} (C–H bending), 1100 cm^{-1} (C–O–C symetric bending). Modified cellulose also gave a FTIR spectrum similar to that of cellulose. In addition this, modified cellulose gave the absorption at 1700 cm^{-1} (C=O stretching). Scanning electron micrographs (SEM-EDS) of the samples were recorded using a Jeol JSM-6360 LV scanning electron microscope (Japan). SEM-EDS photographs of native cellulose and modified cellulose are displayed in Figure 1a and 1b. The native cellulose granules appear elliptic, bread-like or irregular. After modification, cellulose granules become smaller and show more regular, homogenious and harmonious. In addition, as seen from EDS photographs, modified cellulose contains Li^+ ions (Ko et al.2007).
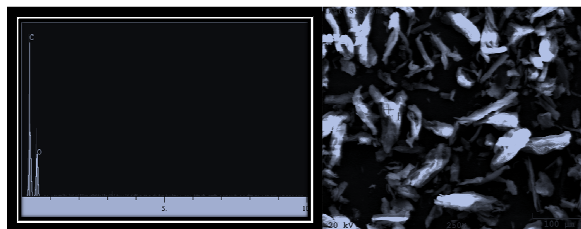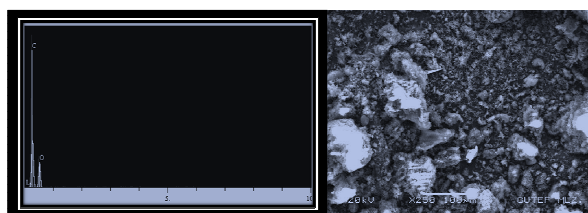

Figure 1a. SEM-EDS of cellulose.

Figure 1b. SEM-EDS of modified cellulose.

TGA analysis was carried out using a Setaram 8ET8 V8 Evolution 1760 model thermogravimetric analyzer in the presence of nitrogen atmosphere up to 600°C, at a heating rate of $10°C$ min^{-1}. The thermal stability of modified cellulose particles approached 275°C as can be seen from the TGA, shown in Figure 2. In the case of modified cellulose particles, no chemical reaction or decreasing weight was found below 275°C. The decomposition temperature of cellulose is between 290 and 330 °C. Thus it could be estimated that the modified cellulose particles dispersed in corn oil were stable below 275°C, which proved that the ER suspensions based on modified cellulose were anhydrous.
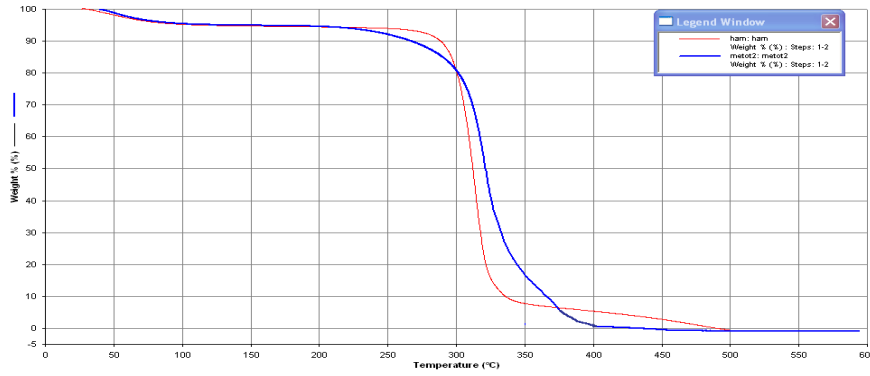
Figure 2. TGA of native cellulose and modified cellulose.

2. Electrorheology

2.1. Effect of electric field strength

Figure 3 shows the change in the electric field viscosity with electric field strength at constant conditions: $\dot{\gamma} =$ 0.2 s^{-1}, c = 15% m/m and T=20°C. As seen from the graph, electric field viscosity (η_E) increases with increasing electric field strength and nearly reaches to η_E = 5.5 kPa s for cellulose. Similar results were observed by Zhao et. al in ER studies of nano titanium oxide/silicone oil systems (Zhao et al. 2008).
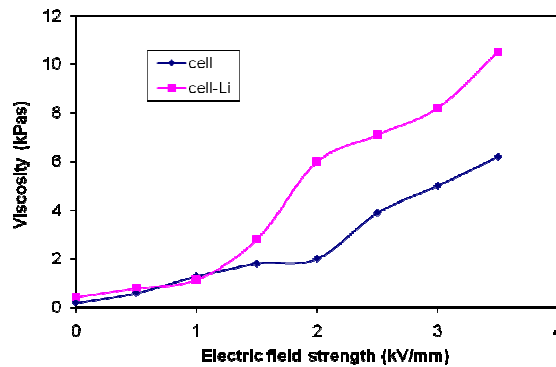

Figure 3. The change of viscosity with electric field strength.
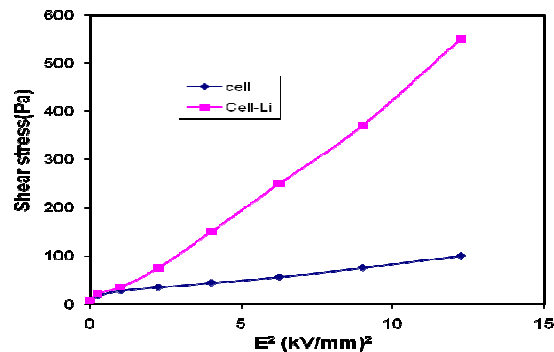T = 20° C, c = 15% m/m, $\dot{\gamma}$ = 0.2 s^{-1}.

Figure 4. The change of shear stress with electric field strength.
T = 20° C, c = 15% m/m, $\dot{\gamma}$ = 0,2s^{-1}.

Figure 4 represents the change in shear stress with electric field strength which was obtained at constant

suspension concentration (c = 15 % m/m), shear rate ($\dot{\gamma}$ = 0,2 s^{-1}) and temperature (T = 20°C). As reflected from the graph, shear stress sharply increases with increasing field strength, which indicates that the ER suspension becomes more stable under strong electric field strength. Modified cellulose suspension's shear stress is about five times higher than cellulose suspension's with electric field strength. . Similar results were observed by Yavuz and Unal (Yavuz & Unal 2004).
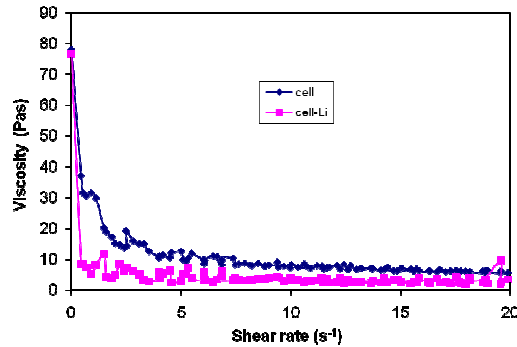
2.2. Effect of shear rate

Figure 5. The change of viscosity with shear rate.
T = 20°C, c = 15 % wt, E = 0–500 V/mm.

Change in the viscosity of the suspension with shear rate at optimum suspension concentration (15 % wt), T = 20°C, E = 0–500 V/mm is shown in Figure 5. As is evident, with and without applied electric field, the viscosity of suspensions decreases sharply with increasing shear rate, giving a typical curve of shear thinning non–Newtonian viscoelastic behavior (Ling & Keqin 2006).

2.3. Effect of temperature

Figure 6 shows the changes in the shear stress of cellulose and modified cellulose suspensions under various temperatures at constant conditions (E= 2 kV/mm, $\dot{\gamma}$ = 0.2 s^{1}, c=15 % wt). It was observed that, the shear stresses of all the suspensions examined in this work decrease with increasing temperature. Generally, the temperature has two effects on the ER fluids: one is on polarization forces and another one is on the Brownian motion. The increase of temperature results both in decreased activation energy of polarization of suspended particles, and on the polarizability of particles, which results in a decrease in shear stress. On the other hand, the Brownian motion does not contribute to chain formation of suspended particles. Although shear stress increases with increasing temperature reported in the literature by Choi (Choi et al. 1997) and Lu (Lu & Zhao 2004) Unal (Unal et al. 2006). and Liu (Liu & Shaw 2001). reported that shear stress decreases with increasing temperature. Modified cellulose is more thermal stability than native cellulose. These results were supported by TGA results.
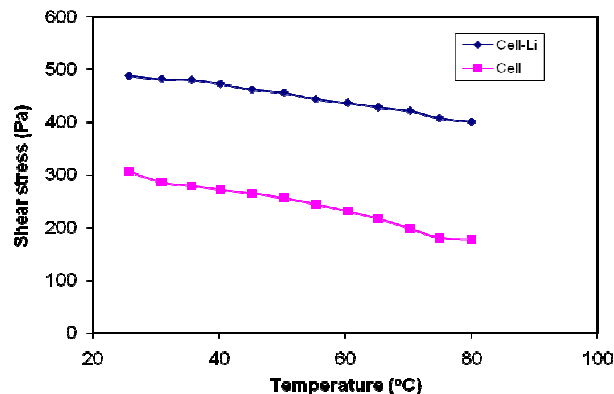

Figure 6. The change of shear stress with temperature.
c = 15 % m/m, E = 2.0 kV/mm .

2.4. Effect of frequency

For native cellulose/corn oil and modified cellulose/corn oil suspension systems, the G_E' remains unchanged at linear viscoelastic region up to f = 46.4 Hz, then a sharp increase with the further increase in frequency after f = 70 Hz was observed. As seen from Figure 7 the G_E' data obtained from the experiments, cellulose and modified cellulose suspensions show a strong vibration damping property, which is an important parameter from industrial point of view. The increase in G' with increasing external frequency was also reported in the literature (Kim et al. 2001) as the typical characteristic of a viscoelastic material (Hiamtup et al. 2006).
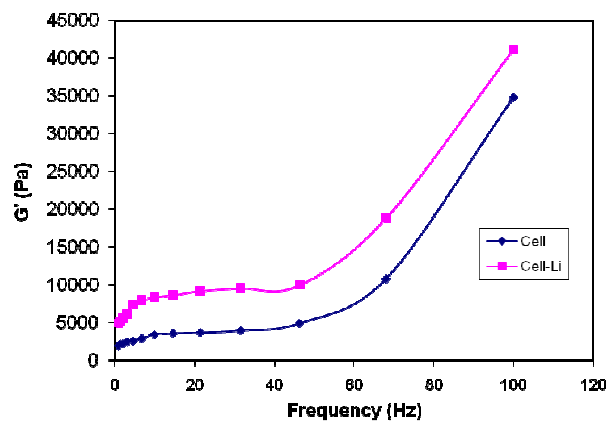
Figure 7. The change of G' with frequency.
c= 15% m/m, T=20°C, $\square$= 10 Pa, E= 2 kV/mm

Conclusions

In this paper, modified cellulose particles were prepared with TEMPO/LiBr. Modified cellulose is characterised by FT-IR, SEM-EDS and TGA. The ER properties of the native and modified cellulose/corn oil suspension were then investigated by examining the effects of electric field strength, shear rate, temperature, frequency and shear stres.

The following is a summary of the results.

We have shown that the native cellulose can be partially modified and converted to the Li$^+$ salts. Colloidal stability of polymeric salt in corn oil was found to be 56% at 15% m/m suspensions concentration. Optimum concentration was found to be 15% m/m. ER activity of suspensions increased with increasing field strength and decreasing shear rate. It was observed that the viscosity of suspensions decreased sharply with increasing shear rate, causing typical shear-thinning non-Newtonian viscoelastic behaviour. It was found that the polymeric salt system studied in the present work was a little sensitive to high temperature within the limits studied. Complex shear modulus of cellulose and modified cellulose suspensions was observed to increase with increasing external frequency and show a typical characteristic of a viscoelastic material and a potential of vibration damping.

Acknowledgements

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