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# Synthesis and characterization of new electrorheological fluids by carboxymethyl starch nanocomposites

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ABSTRACT

Electrorheological fluids are new materials with good properties such as dielectric constant, dielectric loss or conductivity. These materials find practical applications in various industries. In this paper have been studied a ternary nanocomposite as rheological fluid based on Carboxymethyl starch and dimethylsulfoxide with feldspar particles. These nano composite was prepared by the two-step composite method. Firstly, the polar DMSO compound was directly intercalated into the interlayer of nano ferric oxide and then the intercalated complex was composite with CMS by the solution method. The composites, thus synthesized have been characterized by Fourier transfer infrared (FT-IR) spectrophotometer and X-ray diffraction. The morphology of these composites was studied by scanning electron microscopy.


## 1. Introduction

Electrorheological fluids are typical materials from a micro-sized particles with dielectrical good properties. The characterization of electrorheological fluids such as viscosity, yield stress and shear modulus can change in the different media (BrØndsted & Kopeček, 1990). This characterizations find practical applications in many fields, e.g. shock absorbers, active devices, human muscle simulators, photonic crystal and various control systems (Giammona, Pitarresi, Cavallora, & Spadaro, 1999).

Feldspar comprises a group of minerals containing potassium, sodium, calcium and aluminium silicates (Krogars et al., 2000). They are the most common rock-forming minerals. The common feldspar is potassium feldspar, namely, orthoclase ($K_2O$, $Al_2O_3$, $6SiO_2$). Sodium feldspar is albite ($Na_2O$, $Al_2O_3$, $6SiO_2$) and calcium feldspar is anorthite (CaO, $Al_2O_3$, $2SiO_2$). A variety of crossed, hatched, twinned orthoclase (to be seen under the petrological microscope only) is called microcline (Chiu, Hsiue, Lee, & Huang, 1999). Sodium and calcium feldspars form an isomorphous mixture known as plagioclase feldspars (Jabbari & Nozari, 2000). In between sodium and calcium, the other feldspars of the plagioclase series are oligoclase, andesine, labradorite and bytownite (Fanta & Doane, 1986). They are composed of suitable proportions of sodium and calcium with an increasing percentage of calcium beginning from mineral oligoclase to bytownite, turning completely into calcium feldspar (anorthite) Athawale & Rathi, 1997. A rock containing only plagioclase feldspars is called anorthosite. The commercial feldspar is orthoclase. The potassium molecule is replaced by sodium to some extent and hence, orthoclase feldspar usually contains a small percentage of sodium (Saboktakin, Maharramov, & Ramazanov, 2007). The composition range of the commercial feldspar varies within the limits of potash, soda and up to oligoclase. Potash and soda feldspar occur as essential constituents of granite, syenite and gneisses (Peppas, 1987). However, workable deposits are found in pegmatite veins consisting mainly of feldspar, quartz-feldspar veins and also occur with mica pegmatites. Feldspar is of widespread occurrence and is mined in almost all countries (Honghua & Tiejing, 2005).

The choice of intercalation feldspar with dimethylsulfoxide (dielectric constant is about 47) is aimed at modifying the dielectric and polarization properties of feldspar, so as to improve its electrorheological activity, reduce cost and attain the high cost performance (Jabbari & Nozari, 2000). In this study, the feldspar/dimethyl sulfoxide/carboxymethyl starch nanocomposite is fabricated according to the physical and chemical design of the electrorheological fluid material (Ratner, 1989). The polar liquid (DMSO) is directly intercalated into the interlayer of feldspar and then the intercalated complex is interacted with carboxymethyl starch by the solution method (Mahfouz, Hamm, & Taupitz, 1997; Thierry, Winnik, Mehri, & Tabrizian, 2003). The dielectric and conductivity properties of these nanocomposites are improved enormously. The experimental results show that by the design and control of the molecular chemical structure, the physical design for dielectric properties is achieved and thus the characterization of nanocomposite is optimized (Bloembergen & Pershan, 1967; Schmitz et al., 2000).

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## 2. Materials and methods

### 2.1. Materials

The feldspar sample employed in this work was obtained from Geological Survey of Iran and was used to prepare the nanocomposites without further purification. The cornstarch was purchased from Merck Co., Germany. Dimethylsulfoxide (DMSO), sodium hydroxide, chloroacetic acid were used as received.

### 2.2. Instruments

The Fourier transfer infrared (FT-IR) spectrum of the nanoparticles were recorded on Perkin 810 spectrometer in KBr medium at room temperature, in the region 4000–450 $cm^{-1}$ and Perkin spectrometer, that it was referenced to tetramethylsilane, respectively. X-ray diffraction patterns of the nanoparticles were taken with Philips X-ray diffractometer using CuKα radiation ($\lambda$ = 1.5406 Å). The powder morphology of samples in the form of pellets (to measure grain size) was investigated using Philips XL-30 E SEM scanning electron microscope (SEM). There was carried out in chemistry Department of Tarbiat Modares University.

#### 2.2.1. Preparation of carboxymethyl starch (CMS)

Firstly, the 0.5 g cornstarch and 120 ml 2-propanol were placed in a 500 ml vessel and stirred for 2 h. The 5 g sodium hydroxide was added and reacted for 1 h at 78–80 °C. After that, the 10 g chloroacetic acid was added to the vessel and stirred for another 2 h at 50 °C. The product was filtered and washed several times with ethanol, then dried under vacuum. The resulting carboxymethyl starch (CMS) was crushed in a mortar [degree of substitution (DS) = 0.49].

#### 2.2.2. Preparation of feldspar/DMSO intercalate

Feldspar (3 g) was dispersed in 40 ml ethanol and stirred for 3 h. Then 2.25 g sodium acetate (mass ratio feldspar:DMSO is 1:0.75) were added drop by drop into the feldspar suspension. When sodium acetate solution was dropped, the temperature was increased to 50 °C for the purpose of evaporation of ethanol. The sample was sealed in a weighting bottle and placed in an oven for 14 h at 80 °C and the resulting material was got.

#### 2.2.3. Preparation of feldspar/DMSO/carboxymethyl starch nanocomposite

1.8 g CMS and 50 ml distilled water were mixed and stirred for 10 h in a 100 ml vessel, then the appropriate amount of feldspar/DMSO intercalation was added slowly into the vessel and stirred for 12 h at room temperature. After approximately 180 min, the product was sprayed into a liquid nitrogen bath cooled down to 77 K, resulting in frozen droplets. These frozen droplets were then put into the chamber of the freeze-dryer. In the freeze-drying process, the products are dried by a sublimation of the water component in an iced solution. The ternary nanocomposite was crushed in a mortar.

## 3. Results and discussion

Fig. 1 is the X-ray diffraction pattern of feldspar/0.75 DMSO/0.60 CMS. The maximal peaks of with DMSO intercalation, as expected, we can observe that the X-ray diffraction pattern of original feldspar modifies dramatically. When the content of CMS is fixed, the relevant nanocomposite with different DMSO contents can be got. As shown in Fig. 1, the intercalation for nanocomposite is measured as 44.8%. So when the mass rate of nanocomposite is adjusted, the nanocomposite possessing different intercalation should be got and the electrorheological effect of feldspar/DMSO/CMS nanocomposite will be varied.

The morphology of feldspar/DMSO/CMS nanocomposite is shown in Fig. 2. It can be seen that feldspar is composed of small platelets. However, the morphology of feldspar/DMSO/CMS nanocomposite reveals significant differences. The passivating and rounding edges of the feldspar caused by the coating of CMS and the particle size are increased. Fig. 3 shows the SEM of the transaction for sample cylinder. The difference is distinctive between nanocomposite. From the cross-section of feldspar, it can be seen that the stack of the curly thin flake is distinctive. However, this figure shows that the stack disappears and the edge of feldspar is unclear due to the coating of CMS. Furthermore, the surface distri-

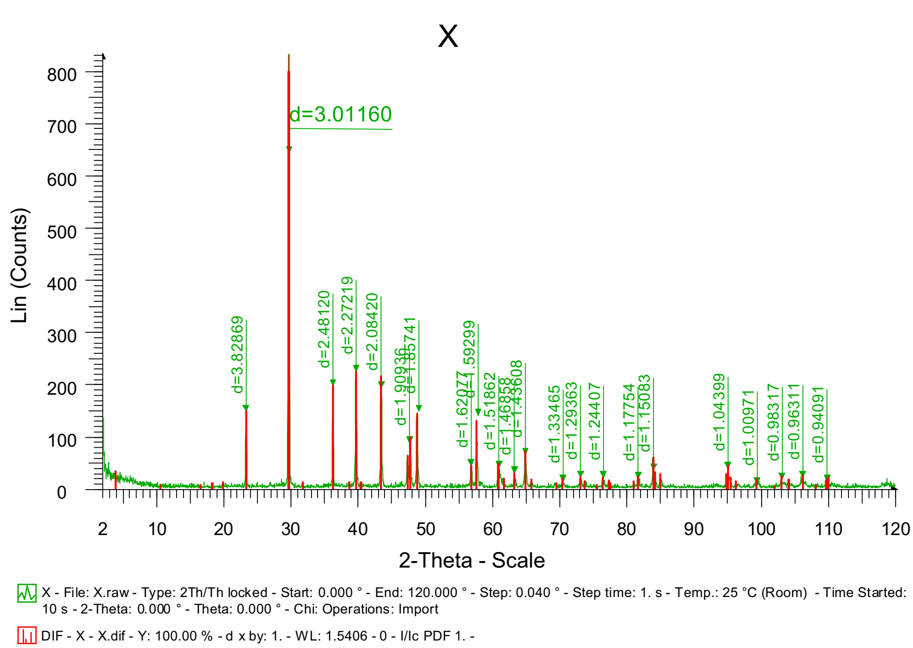


**Fig. 1.** XRD pattern of feldspar/0.75DMSO/0.60CMS.

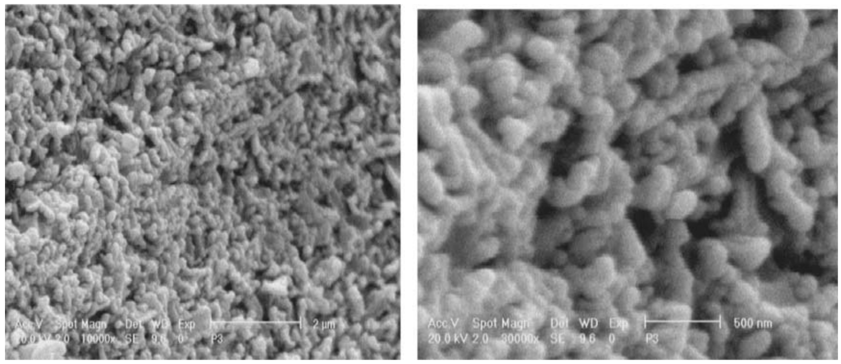


**Fig. 2.** SEM image of the feldspar/DMSO/CMS nanocomposite.

bution of the Na element in the cross-section of feldspar/DMSO/CMS nanocomposite is obtained. It also that Na element is dispersing at nano-scale and CMS as nanoparticle coated on the surface of intercalate.

Fig. 3a shows the Fourier transfer infrared (FT-IR) spectrum of carboxymethyl starch (CMS), where the% of transmittance is plotted as a function of wave number ($cm^{-1}$). The wide peak around 3411 $cm^{-1}$ is attributing to the O–H stretching vibrations of CMS. The peaks at 1597 and 1417 $cm^{-1}$ attribute to the $COO^-$ unsymmetrical and symmetrical stretching vibrations, respectively. The FT-IR spectrum of nanocomposite in Fig. 3b shows that those peaks associated with intercalation have a small change. But the peaks of the $COO^-$ unsymmetrical and symmetrical stretching vibrations are moved to 1582 and 1424 $cm^{-1}$, respectively, and the results show that the $COO^-$ groups of CMS have a strong interaction with the group of feldspar particles.

For the different feldspar/DMSO/CMS nanocomposites, the dielectric constant ($\varepsilon$), conductivity ($\sigma$) and dielectric loss ($\tan\delta$)

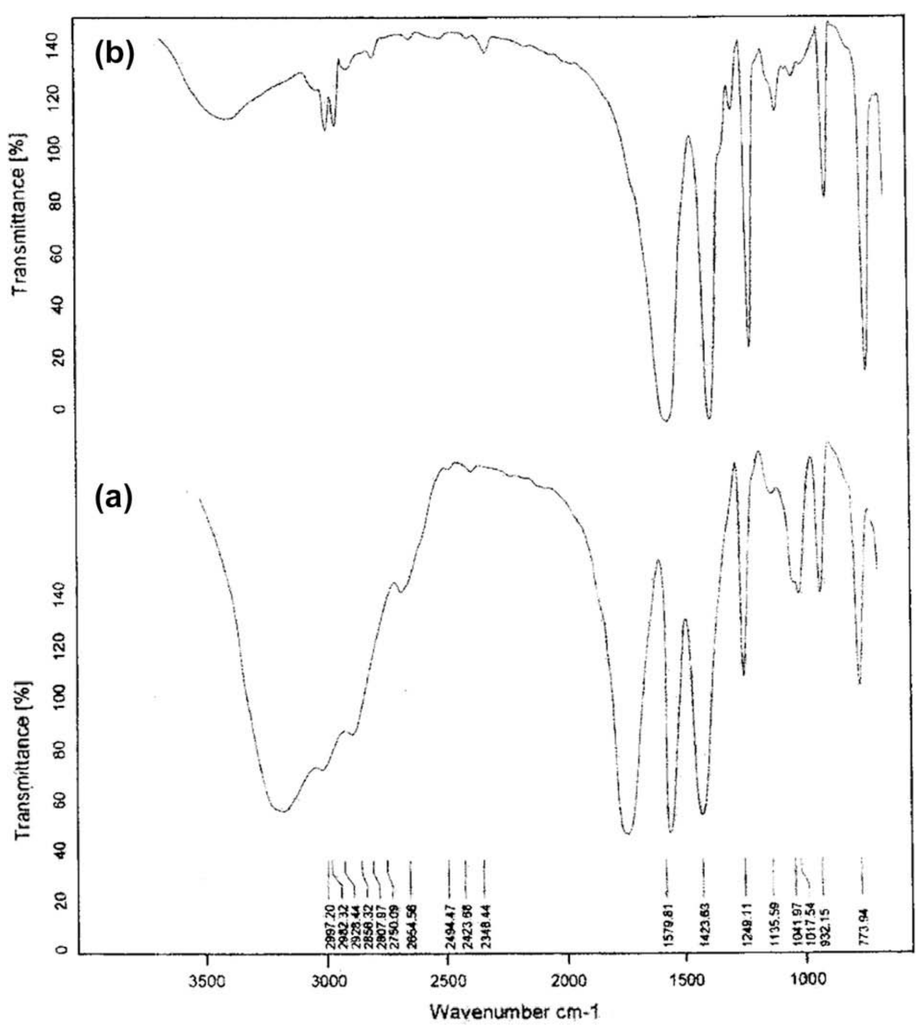


**Fig. 3.** FT-IR spectra of (a) pure CMS (b) feldspar/DMSO/CMS nanocomposite.

**Table 1**
The dielectric data of electrorheological fluid in $T = 25\ °C$.

| | | CMS | Feldspar | Nanocomposite |
|---|---|---|---|---|
| $\varepsilon$ | 100 Hz | 4.940 | 6.887 | 17.245 |
| | 1 kHz | 4.710 | 5.986 | 10.547 |
| | 10 kHz | 4.640 | 5.698 | 8.547 |
| $\sigma \times 10^{-8}$ S/m | 100 Hz | 0.250 | 0.547 | 2.987 |
| | 1 kHz | 0.290 | 3.851 | 18.236 |
| | 10 kHz | 2.064 | 28.564 | 96.547 |
| $\tan\delta$ | 100 Hz | 0.098 | 0.150 | 0.247 |
| | 1 kHz | 0.011 | 0.095 | 0.254 |
| | 10 kHz | 0.007 | 0.098 | 0.157 |

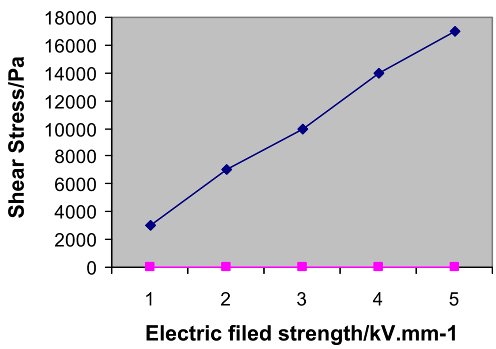


**Fig. 4.** Change in shear stress with varying electric field for electrorheological fluid.

were measured and shown in Table 1, respectively. $\varepsilon$, $\sigma$ and $\tan\delta$ play an important role for high performance electrorheological materials. The dielectric constant is connected to the polar strength, while dielectric loss and conductivity are associated with stability of polar response and interaction between particles. It is well known that a high dielectric constant and dielectric loss and proper conductivity are the physical base to obtain the optimum electrorheological effect. Report that the particles with a conductivity of around $10^{-7}$ S/cm usually show the largest electrorheological effect, because in this case, the strength of interfacial polarization for particles can reach a maximum. The dielectric constant of pure feldspar is much lower and intercalation of DMSO. The results show that the dielectric properties of nanocomposite are increased by the intercalation of DMSO.

Fig. 4 shows the shear stress of feldspar/DMSO/CMS (mass rate 1:0.75:0.60) nanocomposite electrorheological fluid with an increase of DC electric field under a fixed shear rate. In order to contrast the mechanical component electrorheological fluid are prepared at the same volume fraction 30$\varphi$%. It can be seen from the curves that the shear stress of the nanocomposite electrorheological fluid is much higher than of a pure feldspar electrorheological fluid. The feldspar-based nanocomposite, the dielectric properties are improved and the polarizability of particle is strengthened, which is suitable to the enhancement of the electrorheological effect.

## 4. Conclusions

We synthesized the two-step nanocomposite by organic/inorganic materials. The results showed that the polar species such as DMSO intercalated in the interlayer of feldspar with different DMSO content. The feldspar/DMSO/CMS nanocomposite is fabricated according to the physical and chemical design of the electrorheological material. The polar compound (DMSO) is directly intercalated into the interlayer of feldspar, and then the intercalated complex is interacted with CMS by solution method. The experiment results show that by the design and control of the molecular chemical structure, the physical design for dielectric properties is achieved and thus the characterization of nanocomposite is optimized.

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