Wide Angle Scattering Study of nanolayered Clay/gelatin Electrorheological Elastomer

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Abstract: In the general context of self-assembly of nanolayered clay, we have studied both kaolinite and montmorillonite guided assembly into chain-like structures in gelatin hydrogel. The electrorheological (ER) elastomers, containing clay particles which dispersed in gelatin/water matrix, were prepared with or without the applied DC electric field and cross-linked polymerized with the help of formaldehyde. The experimental techniques include synchrotron X-ray scattering, atomic force microscopy, optical microscopy. The aim is to produce a water-based, low-cost and environmentally friendly ER hydrogel. The wide-angle x-ray scattering (WAXS) patterns observed from clay/gelatin ER elastomers curing in the DC field are highly anisotropic and show differences clearly compared to that without curing in the field. Both clay nanolayers have preferential orientation in gelatine hydrogel along the direction of electric field.

1. Introduction

The physical properties of stimuli-responsive soft materials dramatically change corresponding to the external stimuli such as temperature, pH, electric and magnetic fields [1-3]. These materials are called as intelligent materials and have been harnessed in novel systems, for example, sensors, actuators, and biomedical applications [4, 5]. Electrorheological (ER) effects refer to the change of rheological properties of a material upon application of an electrical field [6-11]. When an ER fluid, a suspension of polarizable particles in an insulating medium (such as mineral oil or silicone oil), is subjected to an electric field, the particles polarize, which results in an anisotropic structure of aligned chains of particles along the direction of the uniaxial electrical field. ER fluids exhibit drastic changes in their rheological properties, including a large enhancement in apparent viscosity and yield stress under an applied electric field. An obvious problem with ER fluids is sedimentation of the particles [12-13]. Because of the fluidity, ER fluids must be sealed to prevent leakage, which can complicate the design. Another design problem with fluids is the electrodes, which must be fully supported by the container for the fluid, yet electrically insulated to resist high voltage. Recently, ER elastomers, cross-linked polymer gels with dispersed polarizable particles—have attracted attention. The dispersed phases filled with particles responsive to an applied electric or magnetic field include intercalated or exfoliated platelets obtained from clays, mica, or graphite, nanocages, nanotubes, dual fillers, porous particles, and nanocatalysts etc. Comparing with ER fluid, the liquid medium of ER elastomer is cross linked polymerized after particle alignment, so the anisotropic arrangement of polarisable particles is “frozen”. In the gel network, as matrix’s solid-like nature, particles are restricted and the congregation of particles is eliminated. Consequently, the instability of the ER effect, which is caused by the particles’ congregation in ER fluid, is improved. At the same time, the interaction among the polarized particles under the applied electric field induces the elasticity change of the ER elastomer, and then the elasticity change induces a notable ER effect. The advantages of ER elastomers over ER fluids include no leakage, no sedimentation of particles and possibility to produce custom-made ER objects of exactly the right shape and size for the application (Because the shape and size of ER elastomer can be designed for the practical requirement) [14,15]. In present work, montmorillonite (MMT) and kaolinite guided assembly into chain-like structures in gelatin hydrogel.
under the external electric field are studied using synchrotron X-ray scattering, AFM and optical microscopy. There are several green chemistry concepts in our present strategy: the choice of friendly solvent, the selection of friendly benign and non-toxic matrix, the one-step reaction. Gelatin is a water-soluble natural polymer with a long and soft polypeptide backbone and its individual monomer contains an amino acids group. It is a commercially available and inexpensive material. In our approach, firstly water is used as a based component. The second concept is the choice of the low-cost and benign clay and gelatin. The third one is the simple and reproducible syntheses. The aim is to produce a water-based, low-cost and environmentally friendly ER hydrogel.

2. Materials and characterization methods

Gelatin and formaldehyde solution (A.R. 37%, diluted to 5% when used) were purchased from Merck Schuchardt OHG, Germany. Kaolinite is a 1:1 dioctahedral clay mineral with the ideal composition of Al$_2$Si$_2$O$_5$(OH)$_4$. It was used without further purification. Montmorillonite is a typical 2:1 smectite and was purchased from Southern Clay Products, Inc. as a fine gray powder. In this study, firstly 20% gelatin of aqueous solution was prepared at 70°C for 1h. Then appropriate clay (kaolinite or montmorillonite) particles (such as 1wt%, 5wt%, 10wt% etc.) were added into the gelatin/water matrix to further stir for 6h at 70°C. The clay/gelatin/water mixture will be transferred into a custom-made casting cell (Fig.1) and cured under E=1 kV/mm DC electric field for 1 h. At the same time, the temperature will be retained at 70°C during the curing process. After that the system naturally cooled down to 25°C, the clay/gelatin physical hydrogel is obtained. Then this physical hydrogel was dipped into the chemical crosslinking agent (5wt% formaldehyde solution) over a night. The chemical crosslinking clay/gelatin ER hydrogel can be obtained. For comparison, samples with the same chemical composition but in the absence of an electric field were prepared.

![Figure 1. Schematic equipment for curing an elastomer. HV: DC power source, VM: volt meter.](image)

The reaction of the gel chemical crosslinking is described as follows:

\[
\begin{align*}
RHNCHOCOR' + 2HCHO & \rightarrow RCHOCOR' + H_2O
\end{align*}
\]

R is amino acid polypeptide macromolecule.

Relative orientations of the clay particles inside the electrorheological elastomers were determined using synchrotron X-ray scattering experiments. These experiments were performed at the Swiss-Norwegian Beamlines (SNBL) at ESRF (Grenoble, France), using the WAXS setup with a 2D mar345 detector at beamline BM01A. The X-ray beam with a wavelength of 0.72 Å and 0.3×0.3 mm$^2$ beam size were used. The AFM images were taken using a Multi Mode$^\text{TM}$ Atomic Force Microscope (nanoscope IV) from Veeco Instruments with a contact model.

3. Results and discussion

3.1. 1:1 type clay (kaolinite) assembly in gelatin

The morphology of pure kaolinite is illustrated in Figure 2. It can be seen that kaolinite is composed of stacked small platelets (1–10μm). Furthermore, kaolinite particles are sharing
morphology with well defined hexagonal edges and corner angles (120°) shown in large resolution image. Figure 3 shows the optical image of kaolinite/gelatin hydrogel without curing in the field. Solid-like or gel-like behaviour is observed. Kaolinite have hydroxyl group, which is beneficial for homogeneously dispersing in the gel network.

Solid kaolinite/gelatin ER elastomer is prepared by arranging suspended kaolinite particles in gelatin with an electric field and crosslinked the obtained structure with the help of formaldehyde to “freeze” the chain. Figure 4(a) shows the micrograph of kaolinite particles in the elastomer cured without the externally applied electric field, and Figure 4(b) shows the elastomer cured under the field with \( E = 1 \text{ kV/mm} \). It is observed that particles are randomly dispersed and aligned dispersed in Figure 4 (a) and (b), respectively. By comparing and analyzing the two elastomers, it is obvious that the particles have been assembled by the applied DC field during the curing process.

Relative orientations of the kaolinite particles inside the electrorheological elastomer were determined using synchrotron X-ray scattering experiments: chain and column formations were observed. The three-dimensional WAXS patterns obtained from kaolinite/gelatin ER elastomer are shown in figure 5.

**Figure 4.** Optical micrographs of the kaolinite/gelatin elastomers cured in the absence/presence of the applied electric field (\( E = 1 \text{kV/mm} \)).

**Figure 5.** The three Dimensional WAXS patterns obtained from 10wt% kaolinite/gelatin hydrogel curing in a DC external electric field (a) \( E = 0 \text{kV/mm} \), isotropic pattern; (b)(c)(d) \( E = 1 \text{kV/mm} \), anisotropic pattern; the distance between the detector and the sample is different as follow (b) 350mm (c) 200mm (d)110mm, which more scattering rings of kaolinite/gelatin ER hydrogel can be observed; e) pure gelatin hydrogel without curing in a field; f) pure gelatin hydrogel curing in a field \( E = 1 \text{kV/mm} \).
The 001 scattering ring of kaolinite is indicated by arrows respectively in Figure 5. Clay minerals are sheet silicates or layered silicates, whose primary particles are platelet shape. Each clay platelet is ~1 nm thick (c-direction). Kaolinite is a 1:1 dioctahedral clay mineral with the ideal composition of Al2Si2O5(OH)4. Its structure is composed of AlO2(OH)4 octahedral sheets and SiO4 tetrahedral sheets. Normally, the 001 peak of clay indicates the interlayer spacing between the two basic sheets. For the first strong peak of kaolinite in WAXS patterns represents the diffraction from the (001) crystal surface of the kaolinite, and the associated interlayer d-spacing of this peak is 0.715 nm (In figure 4) [16]. For kaolinite/gelatin hydrogel without curing in the electric field, the kaolinite particles are randomly dispersed into the gelatin matrix, so its WAXS pattern is isotropic shape due to the non-orientation of kaolinite particles (shown in figure 5a). However after curing in the electric field, kaolinite particles will polarized and assemble or orient to respond with field. Kaolinite particle have preferential orientation in gelatine hydrogel along the direction of electric field and show an anisotropic pattern after the curing of DC electric field compared with the isotropic pattern of kaolinite/gelatin hydrogel without curing in the field (shown in figure 5b, c and d). These two patterns show clearly that the kaolinite particles assemble or orient in the direction of electric field. Likewise, the electric field should be high enough such that the electric force can overcome the effect of the gravitational force acting on the dense kaolinite particles. However applying a DC field over $E=2$ kV/mm or much higher can cause the water to hydrolyze and air bubble is observed obviously. The sample will be shrunken during the curing process. The colour of sample will be changed from light gray to green for kaolinite/gelatin hydrogel. Furthermore, too weak electric field strength (below 300V/mm) is difficult to ensure particle polarized for orientation or forming chain-like structure. So we chose a medium electric field strength ($E=1$ kV/mm) to make sure clay assembling into gelatin matrix and in this case the hydrolyzation is not serious. The multipolar interactions from the highly polarizable particles undoubtedly contribute significantly to the ER response. The result indicates that the orientation of particle chain relative to the field is an important structure factor in the designing of the ER elastomers. Spatial arrangement influences the interparticle forces, especially those within the chains. Furthermore, pure gelatin samples with or without curing in an electric field is prepared and their three-Dimensional WAXS patterns are shown in figure 5 e) and f), respectively. Comparing with kaolinite/gelatin ER elastomer (figure5b), no kaolinite scattering ring, only gelatin scattering ring is shown in the pattern. Furthermore the anisotropic pattern (figure 5f) also indicates that pure gelatin hydrogel can respond with the electric field and oriented along the direction of electric field.

**Figure 6.** a) Dependence of the intensity of circular scattering rings (only integrating kaolinite 001 peak in figure 4 a and b) on the azimuthal angle for 10wt% kaolinite/gelatin composite at the different electric field; b) Dependence of the intensity of circular scattering rings (kaolinite 001 peak plus the first peak of gelatin in figure 4 c) on the azimuthal angle.

Figure 6 shows how the intensity of circular scattering rings such as those presented in figure 4 a) and b) evolve as a function of the azimuthal angle $\Phi$, between 0 and 360°. For the 10wt% kaolinite/gelatin composite, we firstly have considered the first-order Bragg peak of kaolinite (001). The scattered intensity at a given azimuthal angle is proportional to the number of particles that meet the Bragg condition for that angle, so the shapes of the scattered intensities in figure 6a provide the orientation distributions of clay particle orientations inside the chains and columnar structures. For $E$
= 0 kV/mm, the intensities are independent of $\Phi$ and the two-dimensional scattering pattern is isotropic because the kaolinite particles is randomly dispersed in gelatin hydrogel. For $E = 1$ kV/mm, the azimuthal positions of the maxima along the plots is anisotropic and this demonstrate that the preferred orientation of the kaolinite particles is with the lamellar stacking plane parallel to the direction of the electric field. Secondly, we have considered both the 001 Bragg peak of kaolinite and the first peak of gelatin evolve as a function of the azimuthal angle $\Phi$, between 0 and 360$^\circ$. From figure 6 b), we can see that the azimuthal positions of the maxima along the plots is anisotropic and have 4 maxima. So that means both the visible diffraction rings correspond to the diffraction of kaolinite and gelatin are anisotropic. The reason is probably because the macromolecules of the matrix are polymerized anisotropically under an applied dc electric field for curing. Since the clay particles are platelets with a thickness much smaller than their lateral dimension, this suggests that they are lying in the ER bundles with one of their lateral dimensions parallel to the field; i.e., on average, the clay particles have their directors aligned perpendicular to the direction of applied field [17]. Furthermore, the gelatin matrix polarizes along their macromolecules chain parallel to the direction of the electric field, and hence in figure 5b, c and d we can see that two perpendicular directions for anisotropic rings are observed for kaolinite and gelatin separately.

3.2. 2:1 type clay (MMT) assembly in gelatin

The wide angle X-ray diffraction (WAXS) patterns of a series of MMT/gelatin hydrogel are also studied. The two-dimensional WAXS patterns obtained from MMT chains of particles dispersed in gelatin hydrogel, in the presence (a) 10wt% MMT with field ($E = 1$ kV/mm); (b) 5wt% MMT with field ($E = 1$ kV/mm) or (c) absence of a DC external electric field are shown in figure 7. The 001 scattering ring of MMT is indicated by arrows respectively in figure 7. The basic structural unit of so-called 2:1 clays (such as MMT) is a 1 nm-thick platelet consisting of two tetrahedral silica sheets sandwiching one octahedral silica sheet. The interlayer d-spacing for the peak of free MMT (001 crystal surface) is near 1 nm.

Figure 7. The 2-dimensional WAXS patterns obtained from the MMT/gelatin hydrogel, in the presence (a) 10wt% MMT with field ($E = 1$ kV/mm); (b) 5wt% MMT with field ($E = 1$ kV/mm); (c) 5wt% MMT without field ($E = 0$ kV/mm).

Similarly, the isotropic pattern of 5wt% MMT absence of a DC external electric field in figure 7(c) means that MMT particles are randomly dispersed into gelatin hydrogel and no preferential orientations for the clay aggregates. The two-dimensional WAXS patterns obtained from this MMT/gelatin hydrogel elastomer (figure 7 b and c) are clearly anisotropic, reflecting the preferential orientation of the particles in the electric field. Taking advantage of the nano-layered nature of the clay crystallites, we were able to infer MMT particle orientations inside the particle bundles from the anisotropy of two-dimensional WAXS images. This study suggested that the MMT particles polarize along their silica sheets, and hence, that their directors were, on average, perpendicular to the direction of the electric field[18]. Dependence of the intensity of scattering vector for MMT/gelatin hydrogel with and without electric field for 5wt% and 10wt% MMT content are shown in figure 8, respectively. A sharp and strong peak attributable to a low degree of ordering is observed for MMT/gelatin hydrogel elastomer with electric field comparing that of MMT/gelatin hydrogel without electric field ($d_{001} = 10 \text{ Å}, d = 2\pi/q$). This is due to dipolar interaction between polarized MMT particles, which orientate and aggregate to forms chains and then column structures along the direction of applied electric field which also lead to the enhancement of MMT concentration. The intensity of 001 diffraction peak was increased, indicating an increase of MMT particles assembling along the direction of electric field. A
chain-like structure of ER composites enhances their electrostriction response to normal and shear deformations. This makes feasible application of ER composites in stand-alone sensing systems as well as implementation of electrostriction to achieve self-sensing capabilities in ER devices.

Figure 8. Dependence of the intensity of scattering vector \( q \) for 5wt\% or 10wt\% MMT/gelatin hydrogel with and without curing in an electric field.

4. Conclusions
A serial of clay/gelatin ER elastomers have been synthesized and characterized by wide angle -ray scattering. The resulting materials show different structures compared to uncuring clay/gelatin hydrogel. Two and three-dimensional WAXS images from bundles of clay inside the gelatin matrix exhibits a clear anisotropy, reflecting the preferential orientation of the clay particles in the field. The anisotropy of 2-dimesional diffractogram also provides the angular distribution of clay particles inside the clay assemble into gelatin hydrogel.

Acknowledgements: This work was supported by the Research Council of Norway (RCN) through the NANOMAT Program and the FRINAT Program.

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