Magnetic Alignment of Rhodamine B Intercalated in Synthetic Mica

Tsunehisa Kimura,* Taichi Uemura, Takumasa Kimura, Shinsuke Takagi, Haruo Inoue

Summary: Rhodamine B was intercalated in interlayer spaces of Somasif Me-100, a synthetic mica, and the obtained rhodamine B/Somasif hybrid was suspended in a UV-curable resin precursor. Then, the suspension was subjected to an applied rotating magnetic field to align the hybrid particles, followed by solidification of the medium by UV irradiation to fix the alignment. The hybrid particles were aligned so that the Somasif layer lay perpendicular to the axis of rotation of the applied rotating magnetic field. UV/vis measurement indicated that the transition moment of xanthene ring of rhodamine B lay inclined to the layer of Somasif.

Keywords: clay; magnetic alignment; rhodamine B; rotating magnetic field; Somasif

Introduction

Recently, attention has been paid to magnetic alignment of feeble magnetic materials in the field of Magneto-Science, an emerging field of science and technology. Because most materials, including biological, organic, and inorganic materials, are feeble magnetic materials, the technique of magnetic alignment has a wide range of applications. In the area of polymer science and technology, this technique is applied to the alignment of crystalline polymers and the alignment of filler particles in polymer composites.[1–12]

The size of particle is an important factor for the magnetic alignment. The alignment is achieved when the magnetic energy of a particle exceeds the thermal energy. Since the magnetic energy is proportional to the volume of the particle, the particle should be large enough to undergo magnetic alignment. The critical size is estimated as about sub-micrometer order, though the detail depends on the strength of the applied magnetic field and the anisotorpic magnetic susceptibility of the particle. If we wish to align a single molecule, we would need very high magnetic fields that cannot be achieved currently even with a pulsed high magnetic field.

Many studies have been reported on organic-clay hybrid materials.[13–17] Organic compounds intercalated in the interlayer spaces of the clay can exhibit interesting properties. If the orientation of the clay is controlled in a thin film or in a composite with polymer, the properties of the hybrid could be greatly enhanced or we could even expect new properties. Magnetic alignment of clay and inorganic materials has been reported by Uyeda et al.,[18–23] but few papers have been reported on the use of this phenomenon to the processing of polymer-clay composites. Very few have been reported on the alignment of the clay in which organic molecules are intercalated.

In this paper, we report a method of magnetic alignment at a molecular level: the molecules intercalated in the interlayer spaces of the clay are aligned indirectly through the magnetic alignment of the clay. The alignment is fixed by solidifying the suspending medium and spectroscopic measurements are performed.

Experimental

Clay Particles

Some clay particles were subjected to the examination of magnetic alignment. Five

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grams of each of Somasif Me-100 (CO-OP Chemical Co., Ltd.), Lucentite (CO-OP Chemical Co., Ltd.), Sumecton SA (Kunimine Industries Co., Ltd.), and Laponite (Rookwood Additives Ltd.) was mixed with 95 g of a UV-curable resin precursor (Kyoritsu W/R No. XFL-06L) under ultrasonication to prepare a suspension. Each suspension was placed in electromagnet of 2 T for 1 h, followed by UV irradiation to solidify the resin precursor.

Intercalation of Rhodamine B

0.5 g Somasif Me-100 was mixed with 100 g water and agitated with stirrer for 1h to obtain a suspension. 0.288 g rhodamine B dissolved in 100 g water was added to the suspension and agitated with stirrer for 24 h. The suspension was then centrifuged and the precipitate was washed with water ten times and dried to obtain red powder. One hundred milligrams of this powder was dispersed in 19.9 g UV-curable resin precursor under ultrasonication. The resin dispersion was sandwiched between two slide glasses (gap of 100 μm), and exposed to a magnetic field. The alignment was fixed by UV irradiation (365 nm, 6000 mJ/cm^2).

Rotating Magnetic Field

An electromagnet generating a static 2-T magnetic field was used. A rotating magnetic field was generated by rotating the sample in the static magnetic field at 20 rpm instead of rotating the field.

Results and Discussion

Magnetic Alignment

A particle acquires anisotropic diamagnetic energy when it is placed in an external magnetic field:

$$E_{mag} = -(1/2\mu_0)V\chi_a B^2 \cos^2\theta \tag{1}$$

where μ_0 is the magnetic permeability of vacuum; B, the applied magnetic field; V, the volume of the particle. Here we assume uniaxial anisotropy, and χ_a represents the anisotropic diamagnetic susceptibility defined as $\chi_a = \chi_{//} - \chi_\perp$ with the suffices indicating the directions parallel and perpendicular to the magnetic axis (uniaxial direction) of the particle. θ is the angle between the magnetic field and the magnetic axis. If the magnetic energy is larger than the thermal energy, i.e., $E_{mag} > k_B T$, an appreciable change of alignment can be observed. This condition is expressed in terms of the minimum size l of the particle:

$$l = (2\mu_0 k_B T/|\chi_a|B^2)^{1/3} \tag{2}$$

Here we assumed $\theta = 0$. This relation is shown in Figure 1. It is understood from this

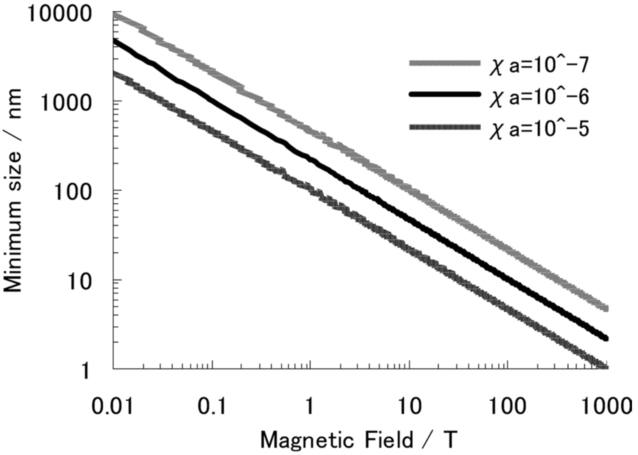

Figure 1.
Minimum size of particle necessary for magnetic alignment plotted as a function of applied magnetic field.

figure that several thousands of tesla is needed to align a molecule of 1 nm in size. We find that the molecular alignment is impossible because the highest static magnetic field currently available is about 40 T. On the other hand, particles of micrometer sizes can easily align under moderate magnetic fields (1 to 2 T) generated by an electromagnet. The strategy that we took in this work for the molecular alignment is that molecules and/or molecular aggregates are intercalated in or adsorbed on a substrate particle of a host particle of a larger size, then the host particle is subjected to the magnetic alignment, resulting in the indirect magnetic alignment of the guest molecules.

The alignment manner of the guest molecules depends on their orientation in the host particle in which they are intercalated. A number of studies of the stacking manner of guest molecules and aggregates have been reported.[24–30] The alignment manner also depends on the orientation of the host particle with respect to the applied magnetic field. It is reported recently that particles with biaxial magnetic anisotropy, which has three different diamagnetic susceptibility axes, can be aligned three-dimensionally using a dynamic elliptic magnetic field.[31,32] Therefore, if a host is biaxial and the stacking manner of the guest is well defined, then, the alignment manner of the guest molecules are precisely determined with respect to the laboratory frame.

In a static magnetic field, the easy magnetization axis aligns parallel to the applied magnetic field, while the other two axes remain unfixed. On the other hand, in a rotating magnetic field, the hard magnetization axis aligns perpendicular to the rotating plane of the magnetic field,[33] while the other two axes remain unfixed. In many cases, the hard magnetization axis of a clay particle lies approximately perpendicular to the layer planes, or in other words, approximately parallel to the crystallographic c-axis. Therefore, the layer planes of the clay particles cannot be aligned parallel to each other if we use a static magnetic field as shown in Figure 2. On the other hand, the parallel alignment of the layer planes is achieved if we use a rotating magnetic field (Figure 2). Though the parallel alignment of the layer planes is achieved using a rotating magnetic field, the other two axes on the layer plane are still unfixed. In order to align these two axes with respect to the laboratory frame, we need to use an elliptic magnetic field. The use of the elliptic magnetic field is beyond the scope of this paper.

Magnetic Alignment of Clay Particles

As described in the previous section, the ability of the magnetic alignment of a particle is determined by the anisotropic diamagnetic susceptibility χ_a and volume V of the particle. However, a good dispersion of particles in a liquid medium is a

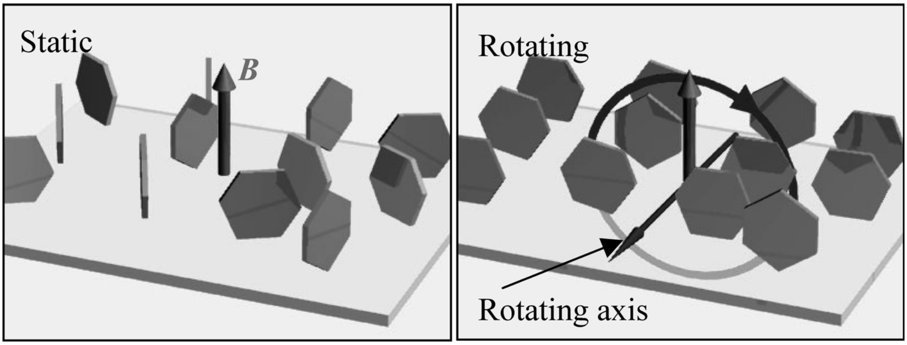

Figure 2.
Crystallographic c-axis, which is assumed normal to the clay layer and corresponding to the hard magnetization axis, aligns perpendicular to the applied static magnetic field (left) and parallel to the rotation axis of the applied rotating magnetic field (right).

Table 1.
Test of magnetic alignment.

Sample Name	Composition	Magnetic alignment
Somasif ME-100	$NaMg_{2.5}(Si_4O_{10})F_2$	good
Lucentite	$Na_{0.33}(Mg_{2.67}Li_{0.3})Si_4O_{10}\ (OH)_2$	fair
Sumecton SA	$[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.33}) \cdot O_{20} \cdot OH_4]^{-0.77} \cdot [Na_{0.49}Mg_{0.14}]^{+0.77}$	fair
Laponite	$Na_{0.68}[Si_8(Mg_{5.34},\ Li_{0.66}) \cdot O_{20} \cdot (OH)_4]$	NA
Hydrotalsite	$Mg_6Al_2(OH)_{16}CO_3$	NA

dominant factor in the actual experiment. The particles cannot undergo alignment if they form a random aggregate in which the average of the magnetic anisotropy of the individual particles becomes zero. We examined several different kinds of clay samples to know whether they align or not. The alignment was carried out under a rotating magnetic field. Table 1 shows the results of the alignment test. Among five clay samples, Somasif exhibited high alignment. This is mainly because Somasif has a large particle size and well dispersed in the resin precursor. Thus, we chose Somasif as a sample in which rhodamine B is intercalated.

Figure 3 shows microphotographs of the cross section of the film sample obtained by UV curing after magnetic alignment. It is clearly observed that the plane of Somasif is aligned perpendicular to the rotation axis of the applied rotating magnetic field. This alignment manner is observed both for the experimental setups of (a) and (b) irrespective of the mutual orientation of the rotation axis with respect to the glass substrate. The substrate affects little on the alignment.

Rhodamine B Alignment through Magnetic Alignment of Somasif

Somasif in which rhodamine B is intercalated is subjected to magnetic alignment. After the magnetic alignment, the film sample was subjected to the microscope observation between crossed polars. Extinction was observed every 90° during one revolution, clearly indicating the alignment. The observation with the color plate indicated that the alignment manner is the same as shown in Figure 3, i.e., the plane of Somasif is aligned perpendicular to the

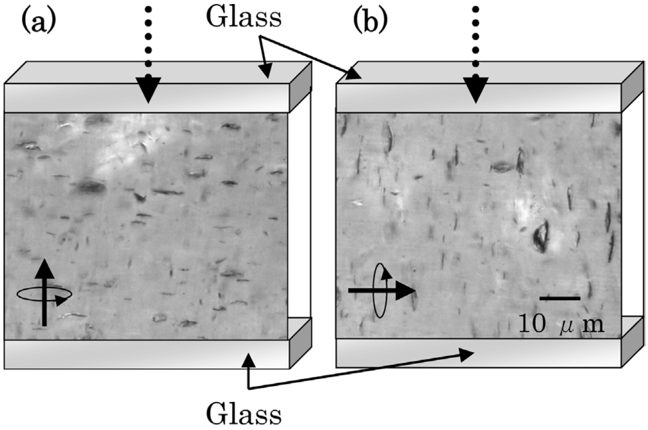

Figure 3.
Microphotograph of the cross section of magnetically aligned Somasif taken after solidification of the medium by UV irradiation. The applied field was a rotating magnetic field whose rotating axis is indicated by solid arrow. A broken arrow indicates the direction of the incident light in the UV/vis measurement. The sample (a) and (b) are defined as perpendicular and parallel, respectively.

rotation axis of the applied rotating magnetic field. This result is reasonable because it is expected that the intercalation of rhodamine B hardly affects the magnetic property of Somasif due to a small volume ratio of the guest (rhodamine B) to the host (Somashif).

Figure 4 shows UV/vis absorption spectra of the samples. The light source is not polarized. The main band at around 550 nm is assigned to the absorption due to the optical transition moment of xanthene ring of rhodamine B. In the present study, we do not know whether this band is the contribution of the monomer or aggregate of rhodamine B intercalated in Somasif or the contribution of both of them. The intensity of the band at around 550 nm is higher for the parallel sample than for the perpendicular sample. Here, ''parallel'' and ''perpendicular'' indicate that the layer of Somasif is parallel and perpendicular, respectively, to the incidnet light beam in the UV/vis measurement. The term, ''parallel'' and ''perpendicular'', also corresponds to Figure 3b and 3a, respectively. Since the concentration of Somasif is the same for both parallel and perpendicular samples and also the sample thickness is the same, the difference in band intensity between these two samples should be attributed to the orientation of the transition moment of xanthene ring with respect to the light beam. Because the absorption is the largest when the transition moment lies perpendicular to the light beam and the smallest (zero) when it lies parallel to the light beam, a higher absorbance for the parallel sample indicates that the transition moment is inclined with respect to the layer plane of Somasif.

In Figure 4b, an enlargement of the spectra around 425 nm is shown. It should be noted that the absorbance is higher for the perpendicular sample than for the parallel sample, which is opposite to the observation for the band at around 550 nm. This observation means that there is another transition moment that has a different direction from that contributing to 550-nm band with respect to the Somasif interlayer spaces. The origin of the transition moment giving rise to the band around 425 nm is not identified at present time.

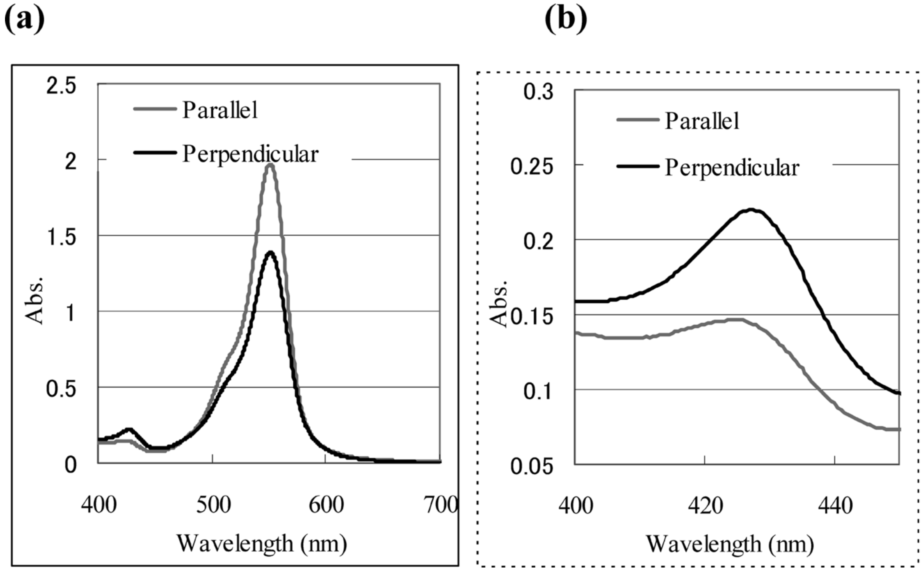

Figure 4.
UV/vis absorption spectra measured for parallel and perpendicular samples shown in Figure 3. (a) the range of wavelength is 400 to 700 nm and (b) the enlargement the range between 400 and 450 nm.

Conclusion

Particles of Somasif (a synthetic mica) in which rhodamine B molecules were intercalated were aligned using a rotating magnetic field. The Somasif layer planes were aligned perpendicular to the axis of rotation of the applied magnetic field, indicating that the crystallographic *c*-axis of Somasif is close to the hard magnetization axis. The UV/vis measurements of the aligned samples indicated that the intercalated rhodamine B molecules lie inclined with respect to the layer plane. The technique presented in this work is useful in various ways. (i) Alignment of the guest molecules is achieved through the magnetic alignment of the host clay particles. This indicates that the magnetic alignment at the molecular level is indirectly realized. (ii) Since the alignment of the clay particles is three-dimensionally controlled (if their crystal type belongs to the biaxial system) using a more advanced magnetic method, the alignment of the intercalated molecules are also three-dimensionally controlled if the packing manner of the guest in the host is well defined. If the packing manner of the guest molecules is unknown, the precision alignment of the host clay particle might greatly facilitate the analysis of the packing manner. (iii) Polymer/(clay/organic molecules hybrid) composites, in which the functional organic molecules are precisely aligned, can be fabricated by using the technique proposed in this paper.

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