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Lyotropic mesophase formation in PVA/imogolite mixture

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SUMMARY

The mesophase formation was observed in the ternary system consisting of a solvent, a rigid rod solute (imogolite), and a randomly coiled polymer chain (poly(vinyl alcohol) ; PVA). Although the mesophase formation in this system seems to follow qualitatively the scheme presented by Flory, no marked segregation of the two solute component was confirmed. The physical properties of the composite film prepared from this ternary system were also examined.

INTRODUCTION

Imogolite is a natural product in the clay fraction of Japanese soil. It consists of hydrated aluminium silicate and has a characteristic geometrical profile of the hollowed cylindrical shape of 25.2 Å in diameter and several thousands Å in length as schematically shown in Fig.1. Here twelve gibbsite units form the cylinder of an imogolite unit which is 8.4 Å in length. The chemical composition of a gibbsite unit is given as $(Al_2O_3{\bullet}SiO_2{\bullet}2H_2O)_2$, so that the molecular weight of an imogolite unit is equal to 4754[1,2].

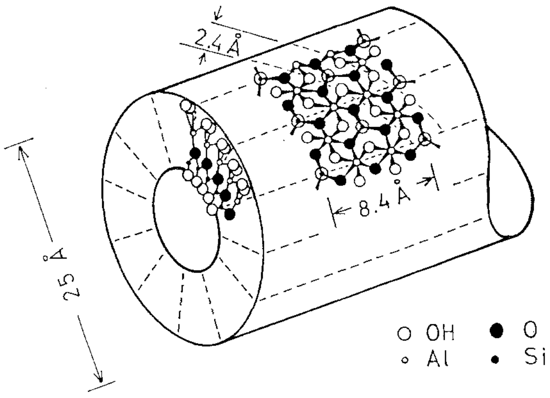

Fig.1 Schematic view of an imogolite cylinder.

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Imogolite can be dispersed molecularly in acidic aqueous solution by ultrasonic wave treatments and its molecule in solution is approximated as a completely rigid rod from the analysis of the dilute solution properties1). Imogolite forms lyotropic mesophase2-4) as predicted by Onsager5) and Flory6) for a rigid rod when its concentration exceeds a certain limit.

Imogolite possesses hydroxy (OH) groups on its cylindrical surface (see Fig.1), so that it is expected to compose a molecular composite with other polymers which also possess OH groups such as hydroxypropylcellulose (HPC) or poly(vinyl alcohol) (PVA). The former molecule is rigid and forms the lyotropic (and thermotropic) mesophase by itself. Indeed the mixed solutions of imogolite and HPC form the lyotropic co-mesophase where the imogolite concentration is lower than in the single imogolite solution at the threshold concentration of the transition from the anisotropic/isotropic biphase to a single anisotropic phase7,8). Young's modulus and tensile strength of its composite films cast from the solutions were also improved with increasing imogolite contents7). On the contrary, PVA is a flexible macromolecule and shows no tendency to form mesophase. Since PVA is expected to be compatible with imogolite through its OH groups, the interest for the characteristics of the ternary system of PVA/imogolite is in two points; (i) the role of PVA in the process of the mesophase formation in the mixed solution of PVA/imogolite, and (ii) the composite effect of imogolite on the properties of the blended film of PVA/imogolite.

In this report, we examine the co-operation process in the PVA/imogolite system, where PVA is flexible and imogolite is rigid.

EXPERIMENTAL PART

Sample preparation

Raw materials of imogolite gel were collected from the pumice bed in Murasakino, Iwate, Japan. They were purified by washing thoroughly, and dispersed in aqueous solution of acetic acid. The detail of imogolite preparation is already reported in previous papers1,2). The molecular weight of imogolite sample was estimated from it's intrinsic viscosity [η] (dl/g) through the following equation1):

$$[\eta]=(9.35\times10^{-12})M_w^2/\ln M_w \quad \text{(in water at 30°C)} \qquad (1)$$

Since the measured intrinsic viscosity was equal to 0.85 dl/g, the molecular weight (M_w) of the imogolite sample was calculated as 1.1×10^6 which is equivalent to 1944 Å and 77 in terms of the rod length and the axial ratio, respectively.

The three kinds of PVA sample were purchased from Tokyo Kasei, Co., Ltd. (Tokyo, Japan). The degrees of saponification were found to be 98, 97, 97% from the titration using NaOH aq. and the degrees of polymerization were 400, 2500, 4500, respectively, which were estimated from the intrinsic viscosity using the following equation11):

$$[\eta] = (42.8\times10^{-3})M_w^{0.64} \text{ (in water at 30°C)} \qquad (2)$$

The stock solutions of PVA (5.0 wt.%) and of imogolite (0.64 wt.%) were prepared separately, where the concentration of imogolite was sufficiently lower than that to form the lyotropic mesophase. Then solutions of imogolite/PVA were prepared by mixing the two stock solutions with varying the imogolite composition from 3 to 40 wt.% with respect to PVA component. The A and B points were estimated by eye inspection through on a polarized microscope in the course of concentrating the solution by gradual evaporation of solvent until the partial anisotropic domain in the isotropic phase was first observed (referred to as the A point) and further until the transition from the biphase to the total anisotropic phase (referred to as the B point). Here a special attention was paid to maintain the pH value of solution to 3.0 by occasional dialysis, because imogolite molecules may flocculate at higher pH's than the value of 4.5.

The composite films of imogolite/PVA (having D.P. of 2500) were prepared by evaporating solvent from the mixed solution at room temperature. The evaporation was started from an initial concentration lower than that of the A point.

Measurements

Morphological study of composite films was carried out by wide angle X-ray scattering (WAXS) and laser light scattering (LS) using a He-Ne laser. The WAXS was recorded on photo films with the incident beam being parallel and vertical to the film surface. The LS from composite films was observed on a Polaroid camera.

The cracked surface of composite films was observed by scanning electron microscope (SEM). The composite films were immersed in liquid nitrogen for a few seconds, taken out, cracked, and coated with gold by vacuum-evaporation technique. The surface of these fragments was observed by SEM (S-800, Hitachi Co., Ltd. Tokyo, Japan) with various magnifications.

Each composite film prepared was cut in 4 rectangular pieces of 2.5×0.3 cm. They were used as specimens for tensile measurements at room temperature on a tensile tester (CATY-500BH, Yonekura Co., Ltd., Osaka, Japan). The sample length subject to elongation was fixed to 1.5 cm.

RESULTS AND DISCUSSION

Lyotropic mesophase in PVA/imogolite mixed solution

It is already known that when the concentration of the single solution of imogolite exceeds a certain limiting point (A point), the solution separates to two phases, the isotropic and the anisotropic phases. The entire solution becomes anisotropic above a higher imogolite concentration (B point). Those mesophase formation processes were found3) to follow quantitatively the scheme presented by Onsager5).

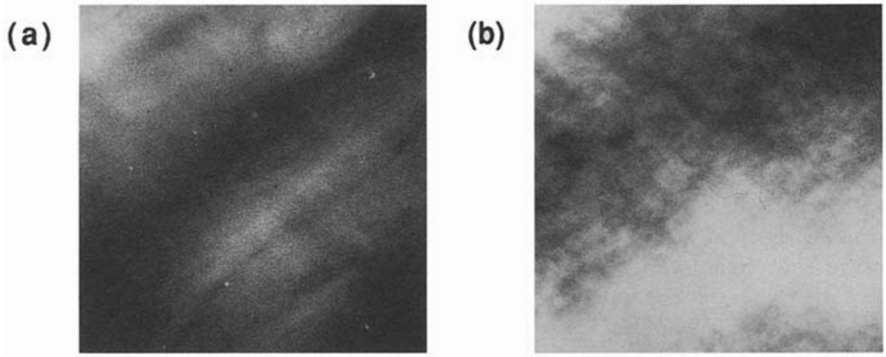

Fig.2 Polarized microscopic observation of the lyotropic mesophase close to the B point in the mixed solution of imogolite and PVA. The imogolite content is 10 wt% (a), or 25 wt% (b) of the total solute.

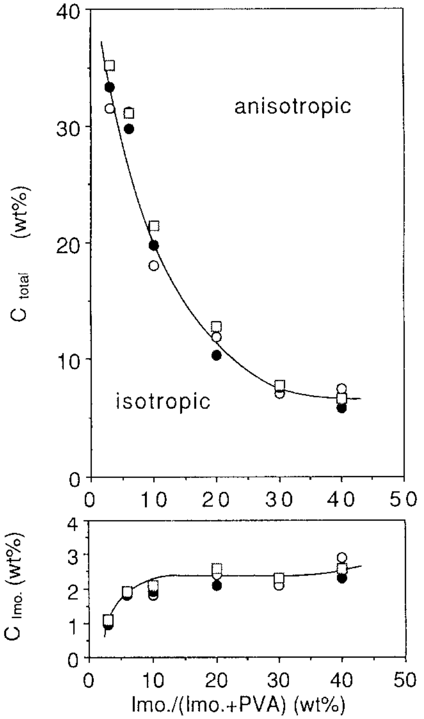

Fig. 3 Phase diagram of acetic aqueous solution of imogolite and PVA mixtures. The D.P. of PVA is 400(○), 2500(●), or 4500(□), respectively.

Imogolite is expected to be compatible with PVA through the interaction between respective OH groups. In fact, the composite film of PVA/imogolite is transparent, and looks homogeneous. The mixed solution of any imogolite/PVA ratio is also transparent and exhibits no tendency of phase separation in its dilute region. When the total solute concentration is increased, the solution starts forming mesophase. Fig.2 shows polarized microscopic photographs of the mixed imogolite/PVA solutions under crossed polarizers, where the concentration of imogolite/PVA was close to the B point. The anisotropic phase was clearly recognized. The mixed system of PVA/imogolite is able to form the anisotropic mesophase, while the single-component system of PVA shows no mesophase formation. The phase diagram specifying the transition from the isotropic to the anisotropic phase (B point) of the mixed solutions of imogolite/PVA is given in Fig.3. Here, the mixed solutions did not exhibit clear A point (the onset of the biphasic region) because of the high viscosity of the solutions and the restricted visible area under the polarized microscope. The sole imogolite concentrations C_{imo} at B points in respective mixed solutions were also plotted in the lower part of Fig.3. As shown in the figure, the total polymer concentration C_{total} at the B point decreased sharply with increasing relative imogolite concentrations. C_{imo} is constant over the observed concentration range from 10 to 35 wt.% imogolite content, and its value is 2.4 wt.%. The value is considerably lower than 6.8 wt.%, which is the estimated B point in the single solution of imogolite. C_{imo} tends to increase when the relative imogolite content exceeds 40 wt.%, and to decrease below 7 wt.% of the relative imogolite content. A similar tendency of C_{imo} was observed in the HPC/imogolite system[8]. These results indicate the predominant role of imogolite molecules to form the mesophase in the mixed systems. It is interesting to note that both C_{imo} and C_{total} at B point are independent of the degree of polymerization of PVA. This result implies that PVA constitutes the medium of the mesophase and the mesophase formation is solely due to imogolite. Thus the structure of the PVA/imogolite mesophase is similar to that of the imogolite mesophase$^{9)}$. Here PVA is considered to act as a promoter for the mesophase formation of imogolite.

The mesophase formation seems to follow the scheme presented by Flory$^{10)}$ for the ternary system consisting of a solvent, a rigid rod molecule and a randomly coiled polymer chain. No expected segregation of two solute components was confirmed. The solute concentration dependence of C_{imo} (Fig.3) is as predicted by Flory$^{10)}$. Since no PVA contour length dependence was observed, Flory's theory$^{10)}$ fails to describe the mesophase formation of the ternary system quantitatively. The reason for this failure is probably ascribed the non-athermal interaction between imogolite and PVA. The thermodynamic behavior of the system seems to be determined not only by the hard core repulsion of imogolite but also by the other type of the intermolecular interaction between two components.

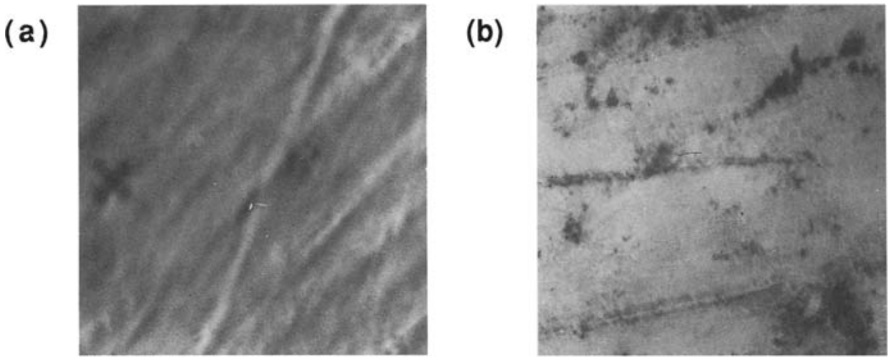

Fig.4 Polarized microscopic observation of composite films of imogolite/PVA=10/90 (a), and 25/75 (b).

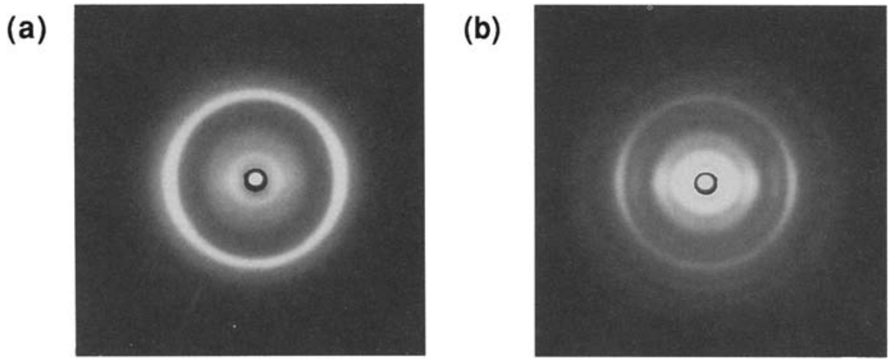

Fig.5 WAXS photographs from composite films of imogolite/PVA=0/100 (a), and 30/70 (b). The incident beam is parallel to the film surface.

Properties of composite films

The composite films of PVA/imogolite were subjected to the morphological studies by polarized microscope, WAXS, LS and SEM. The results are summarized in Figs.4-8. Fig.4 shows that these composite films still maintain their anisotropic structure observed in solutions. WAXS's (see Fig.5) were taken parallel to the film surface. The reflection pattern from the single PVA film showed homogeneous Debye-Scherrer (DS) rings. In the case of composite films, the DS rings from PVA showed higher intensity in the equator direction with the increase of imogolite content, suggesting that PVA molecules are oriented parallel to the film surface by imogolite molecules.

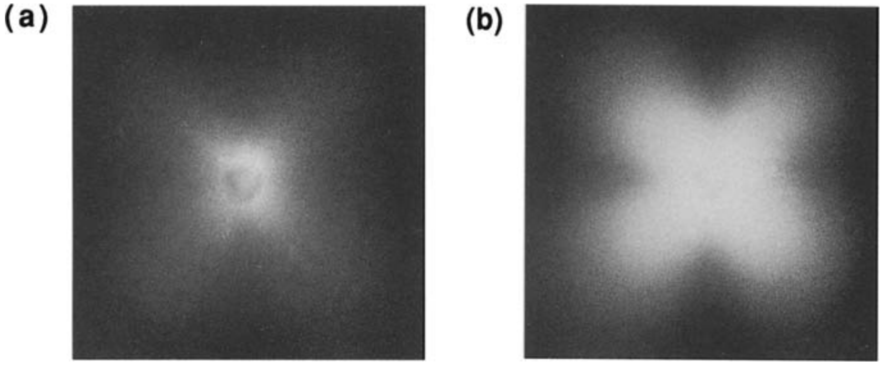

Fig.6 Hv laser scattering patterns from composite films of imogolite/PVA=6/94 (a), and 30/70 (b). The D.P. of PVA is 2500.

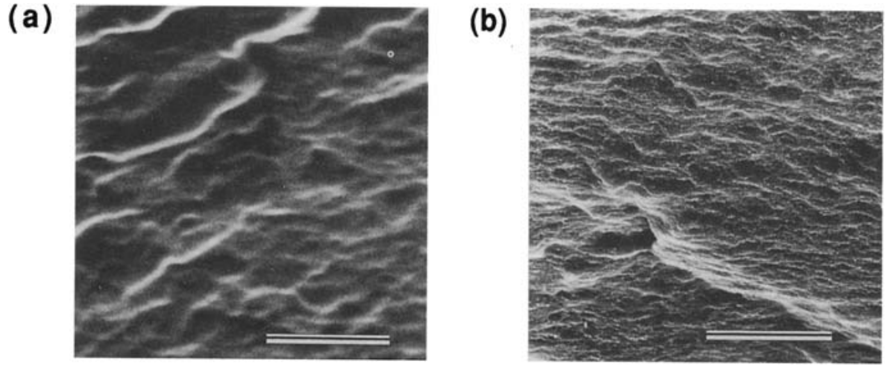

Fig.7 Scanning electron micrographs of cracked surfaces of composite films of imogolite/PVA=0/100 (a), and 20/80 (b). The D.P. of PVA is 2500. A scale bar in each photograph represents 2μm.

Fig.6 displays the Hv light scattering (LS) pattern obtained for the PVA/imogolite system. Here the LS pattern consists of lobes at 45° from the polarization direction of the incident laser light over all contents of imogolite. The SEM of the cracked surface reveals the layered sheet structure characteristic of imogolite in the composite film of imogolite/PVA (see Fig.7). Both results of LS pattern and SEM are consistent, and confirm the growth of sheet structure by introducing in PVA.

The mechanical properties of the composite films are shown in Fig.8. Despite of a remarkable structural change induced by imogolite, its composite effect on the mechanical properties of the PVA/imogolite film is rather small in the present condition of film preparation. The increase of Young's modulus is ascribed to a filling effect of imogolite, and a plane-orientation of PVA chain due to imogolite has no influence on the mechanical properties of the composite film. In the case of the composite film cast from HPC/imogolite solution[7)], Young's modulus and tensile strength were drastically increased in the presence of imogolite. Both HPC and imogolite form the lyotropic mesophase for themselves and the mixed solution of HPC/imogolite system formed the co-mesophase. PVA and imogolite are however non-cooperative in the mechanical properties. PVA chains are flexible and coiled, while imogolite molecules are dispersed in the matrix of coiled PVA chain.

CONCLUDING REMARKS

The composite effect of imogolite was found less remarkable in the PVA/imogolite film prepared from isotropic solution. Since the PVA/imogolite mixed system is able to form a lyotropic mosophase at the concentrations lower than the critical boundary concentrations (the A and B points) of a single component solution of imogolite, the ordering of component molecules seems to be promoted by mutual interaction.

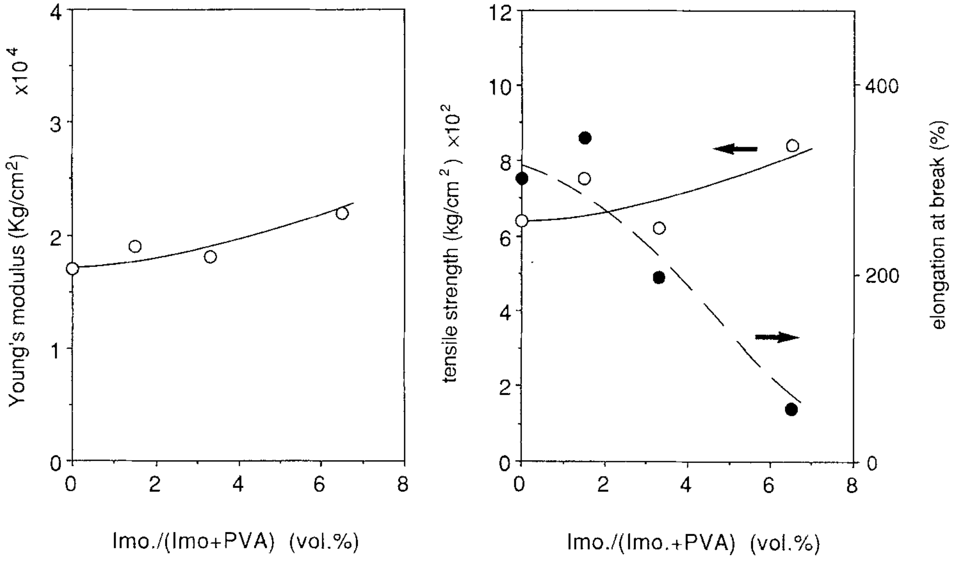

Fig.8 Mechanical properties of composite films of imogolite/PVA. The D.P. of PVA is 2500.

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