



Calcium carbonate mineralization in chiral mesomorphic order-retaining ethyl cellulose/poly(acrylic acid) composite films



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ABSTRACT

A CaCO_3 mineralization was carried out using a mesomorphic network system composed of ethyl cellulose (EC) and poly(acrylic acid) (PAA), to realize a polymer–inorganic hybrid invested with a chiroptical functionality and thermal and mechanical high-performances. The EC/PAA samples were prepared in colored film form from chiral nematic liquid crystals of EC in acrylic acid (AA) by polymerization and cross-linking of the solvent monomer AA. The mineralization was allowed to proceed in a batchwise operation by immersing and swelling the liquid-crystalline polymer films in an aqueous salt solution providing Ca^{2+} , HCO_3^- , and additional Mg^{2+} ions. By varying the ionic condition (i.e., pH and Mg/Ca ratio) of the employed salt solution, calcite (Cal), aragonite (Ara), and solely amorphous CaCO_3 (ACC) were separately deposited inside the EC/PAA matrices. Irrespective of the polymorphs of the incorporated CaCO_3 , the mineralized EC/PAA films (weight gain, ca. 20–28%) retained the original left-handed chiral nematic arrangement and exhibited a reflective color that was shifted to the red side relative to that of the corresponding nonmineralized films. It was also confirmed that the inorganic hybridization remarkably enhanced the thermal and thermomechanical properties of the optically functionalized EC/PAA films. In thermogravimetric analysis data above 300 °C, however, a significant difference was observed between the three sorts of hybrids with Cal, Ara, and ACC, respectively.

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1. Introduction

A recently grown research field on polymer-based materials is the design and fabrication of polymer–inorganic nanocomposites showing mechanical and thermal high-performances or optical, electrical, magnetic, and other specific functionalities. A diversity of inorganics such as layered clays [1,2], silica [3], magnetic iron oxides [4,5], and calcic biominerals [6,7] can be the component to be hybridized in nanosize with polymers. As a matter of course, the matrix polymers involve natural polymeric resources represented by cellulose and related polysaccharides [8–13]. Cellulose derivatives as macromolecules and also cellulose nanocrystals (CNCs) as fragmented microfibrils form a liquid crystalline phase in a suitable solvent under adequate conditions [11,14–16]; the mesogenic arrangement in the phase is mostly chiral nematic, synonymous with cholesteric here. Chiral nematic mesophases often impart a vivid color due to selective light reflection, when the supramolecular helical periodicity (i.e., pitch P) is comparable to

wavelengths of visible light. This mesomorphic ordered structure in the cellulose's lyotropics can be carried over into the solid materials [11,17] by casting the solutions (or suspensions) [18–20] and also by polymerizing monomers (including alkoxy silane) as the solvent component [21–24]. In this context, the use of such a mesomorphic assembly should expand the variety of cellulose-based functional composites. This is well exemplified by recent works [9,12] on the hybridization of inorganics (e.g., silica and metal oxides) using a chiral nematic CNC liquid-crystalline template for development of photonic and electronic materials.

Biomimetic calcific mineralization in a chiral nematic layered polymer matrix can also be a challenging assignment. Many natural organisms possess an ability to mineralize calcic ingredients under mild aqueous surrounding conditions in association with structured proteins and/or polysaccharides [25–27]. In a preceding study, the authors' group has carried out a calcium phosphate mineralization using chiral nematic liquid-crystalline gels of ethyl cellulose (EC)/poly(acrylic acid) (PAA) and hydroxypropyl cellulose (HPC)/PAA [28]. The EC/PAA and HPC/PAA samples were made into colored films from EC and HPC lyotropics of left-handed and right-handed chiral nematics, respectively, by polymerization and cross-

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linking of the solvent, acrylic acid (AA). The mineralization was conducted in a batchwise process by soaking of the films in an aqueous salt solution containing the relevant ions, Ca^{2+} and HPO_4^{2-} , under an adequate pH condition, so that the ions were selectively taken in the swollen gel films working as a kind of Donnan membrane. The calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$ or hydroxyapatite)-incorporated cellulosic/PAA composites retained the chiral nematic organization of the respective original handedness and imparted cholesteric colorations; besides, the inorganic hybridization led to a remarkable enhancement in thermal and mechanical properties relative to those of the initial binary polymer films.

As an extensional work, the present paper deals with another mineralization producing calcium carbonate in the chiral mesomorphic networks of EC stabilized with PAA. Calcium carbonate is a pivotal biomineral involved in the CO_2 cycle in nature. The carbonate CaCO_3 as biomineral is known to take two major crystal forms, calcite and aragonite [29,30]; thermodynamically, calcite is more stable than aragonite. According to the past investigations into the polymorphs and crystal growth of calcium carbonate [31,32], the metastable aragonite crystal can precipitate from aqueous salt solutions containing Ca^{2+} and CO_3^{2-} (or HCO_3^-) with the addition of another metallic ion (e.g., Mg^{2+} and Sr^{2+}). It is suggested that the additive ions would inhibit calcite crystal growth and facilitate aragonite formation [31–34].

In this present study, first, we aimed at realizing aragonite mineralization as well as calcite mineralization in the liquid-crystalline EC/PAA gelatinous films by controlling ionic conditions of the surrounding salt solutions. Then, we examined the chiroptical characteristics and thermal and thermomechanical performances of the EC/PAA films mineralized with CaCO_3 under various conditions, with the ultimate aim of demonstrating a colored, hard, and heat-resistant polymer–inorganic hybrid. As an example of related work, Kato et al. have recently synthesized helically structured chitin– CaCO_3 (calcite) hybrids using a liquid crystalline template of chitin whiskers stabilized with PAA [35]. The hybrid products (uncolored) retained a chiral nematic periodic arrangement of longer pitch (several micrometers). The calcite formation was attained by soaking the template in a colloidal suspension of amorphous CaCO_3 , unlike the method of *in-situ* ionic reaction adopted in our present study.

2. Experimental

2.1. Materials

The EC sample used was purchased from Tokyo Kasei Kogyo Co., Ltd. (nominal viscosity, 90–110 cps for 5% solution in 80:20 toluene/ethanol at 25 °C); weight-average and number-average molar masses, $M_w = 1.4 \times 10^5$ and $M_n = 4.2 \times 10^5$, respectively (from GPC measurements); degree of substitution, $\text{DS} = 2.50$ (from ^1H NMR measurement). AA monomer (Nacalai Tesque, Inc.) was purified by distillation (14 Torr, 40 °C) before use. A photopolymerization initiator, 2-hydroxy-2-methylpropiophenone (HMPPH; Sigma-Aldrich), and a cross-linking agent, ethylene dimethacrylate (EDM; Wako Pure Chemical Ind., Ltd.), were used without further purification. Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), and ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) were purchased from Nacalai Tesque, Inc. and used as ion sources for mineralization. A low-molecular-weight PAA (Sigma-Aldrich; average degree of polymerization (DP), ~25) was used as a precipitation inhibitor in the salt solution of ion server [28,36,37]. Other conventional reagents were purchased from Nacalai Tesque, Inc. and used as received.

2.2. Preparation of samples

Lytotropic liquid crystals of EC in AA were prepared in a polymer concentration range of 42–55 wt% by mixing weighed amounts of EC and AA in a light-blocked glass vial. The monomer AA contained HMPPH and EDM at 1.0 and 0.5 wt%, respectively, with respect to this solvent part. EC/PAA films (ca. $40 \times 30 \times 0.25 \text{ mm}^3$) showing a reflective coloration were made in a similar way to that described in the preceding paper [28]. In brief, an aliquot of each lyotropic EC/AA solution was sealed between a Teflon plate and a transparent PET film by using another Teflon film as spacer. The sandwiched sample was conditioned in a dark room at 23 °C for 5 days, and then allowed to solidify via polymerization of AA by 2 h irradiation of UV light (~350 nm). A 10 W UV lamp FL10BLB-A (Toshiba Lighting and Technology Corp.) was used and the sample was placed at a distance of ~50 mm from the light source in an atmosphere of N_2 gas. The EC/PAA films thus synthesized were washed with distilled water, then dried at 40 °C under reduced pressure.

Strips about $10 \times 10 \text{ mm}^2$ (or $20 \times 5 \text{ mm}^2$ for DMA measurements) cut from the as-prepared EC/PAA films were employed for mineralization experiments. Salt solutions containing 10 mM CaCl_2 , y mM MgCl_2 , 10 mM $(\text{NH}_4)_2\text{CO}_3$, and 0.5 mM PAA (DP = 25) in the monomer unit were prepared at ~23 °C in basic pH conditions of 7.5–9.5 (using NaOH). The amount of MgCl_2 was varied between $y = 0$ (Mg/Ca = 0) and 60 mM (Mg/Ca = 6); this magnesium addition was done for possible control of the polymorphs of calcium carbonate precipitates [31,32]. A few strips of EC/PAA films were immersed in 200 mL of a salt solution whose initial pH and Mg/Ca were adjusted properly, and the system whole was thermostated at 30 °C in an incubator for 5 days; however, the salt solution as ion supplier was exchanged for fresh one at intervals of 24 h. After the mineralization treatment, the film samples were rinsed in distilled water for 10 min, then air-dried, and subsequently vacuum-dried at <10 mmHg and 40 °C for more than 12 h.

2.3. Measurements

Wide-angle X-ray diffraction (WAXD) measurements were made on a Rigaku Ultima IV diffractometer, to examine calcium carbonate polymorphs for mineralized EC/PAA films. Nickel-filtered $\text{CuK}\alpha$ (0.154 nm) radiation was used at 40 kV and 40 mA. Diffraction intensity profiles were collected in a range of $2\theta = 5\text{--}60^\circ$.

Selective light-reflection of mesomorphic samples were examined by measurements of reflection bands with a UV–vis. spectrometer (Hitachi U-4100) and a circular dichroism (CD) spectropolarimeter (Jasco J-820DH). These spectral measurements were conducted in an optical alignment of the normal incidence of light beam to the surface plane of each filmy sample. Refractive index measurements were carried out using an Abbé refractometer (Atago Co., Ltd., Type 2T) equipped with a rotatable polarizer mounted over the eyepiece.

Morphological observations were made for mineralized EC/PAA films by using a field emission scanning electron microscope (FE-SEM), Hitachi S-4800; the samples were fractured at liquid nitrogen temperature and sputter-coated with platinum before the observation. For some of the fractured samples, energy-dispersive X-ray (EDX) analysis was made using an EDAX Genesis XM2 to see the distribution profile of elements C, O, Ca, and Mg in the inside of the hybrid films.

Dynamic mechanical analysis (DMA) was carried out using a Seiko DMS6100/EXSTAR6000 apparatus. Film specimens of rectangular shape ($20 \times 5 \text{ mm}^2$) were used for measuring the temperature dependence of the dynamic storage modulus E' , loss modulus E'' , and loss tangent $\tan\delta$ at an oscillatory frequency of 10 Hz. The temperature was raised at a rate of 2°C min^{-1} from 25 to 240 °C.

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