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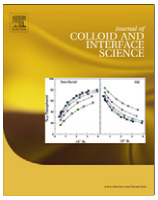

Contrasting roles of layered structures in the molecular assembly of liquid crystal matrices on the viscoelastic properties of microparticle/liquid crystal composite gels leading to rigidification and destabilization

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ABSTRACT

We investigated the effects of the nematic and smectic A (SmA) phase structures of liquid crystalline matrices on the viscoelastic properties of microparticle/liquid-crystal composite gels. The storage (G') and loss (G'') moduli of the gels were largely increased in gels containing SmA matrices with a layered molecular assembly. However, the critical strain at which the gel state transformed into the sol state by the application of mechanical strain showed no significant changes with variation in the liquid crystal phase of the matrix. These results indicate that the introduction of a layered molecular assembly could be effective for rigidification of composite gels, while maintaining their critical strains. However, the composite gels tended to show a metastable state when SmA matrices were used because G' and G'' of the gels were close to each other in the entire frequency region. This behavior was in contrast to the gels with nematic matrices, which showed a larger value in G' than that in G''. The metastable state of gels with SmA matrices was also reflected in the frequency dependence of G' and in the deterioration of the recovery of the gel state after mechanical breakdown.

1. Introduction

Colloidal materials in which small substances are dispersed in continuous phases are ubiquitous and have gained considerable importance in various industrial fields [1]. In fact, many familiar systems including milks, paints, foams, and gels are colloidal systems. Recently, colloidal composites containing liquid crystals (LCs) as the matrix have been recognized as a new class of soft materials and have been extensively explored [2]. For instance, from a technological point of view, nematic LCs containing dispersed inorganic or polymeric nanoparticles were initially investigated as light scattering materials for application in electro-optical devices [3–8]. Subsequently, microparticle or nanoparticle/LC composites have received increasing attention because they present a unique collective behavior leading to the formation of diverse self-organized colloidal structures [9]. In these composite materials, intriguing colloidal behaviors characterized by boundary conditions between the LC matrices and the dispersed particles can be identified. For example, if the surface anchoring of the dispersed particles is sufficiently strong to induce a specific molecular arrangement on the particles, the proximity of the director field of the particle can conflict with the uniform orientation of the bulk LC. As a result, topological defects of the LC alignment can be created in the vicinity of the dispersed particles [10]. When multiple particles with topological defects exist in the system, the orientation dependent elasticity of the LCs can induce repulsive and attractive interactions between the particles. As a result, the dispersed particles can self-organize into ordered microstructures such as one-dimensional chains, two-dimensional hexagonal structures [11–16], and even three-dimensional networks exhibiting a quasi-solid gel state [17–27]. Recently, a variety of applications of microparticle/LC composite gels have been proposed. For instance, the microparticle/LC composite gels have been applied to cell culture media and chemical sensing devices [23,24]. The self-organized structures obtained with particles have also been reported to be analogous to the vortex glass state in type II superconductors [26]. In addition, we have very recently proposed that microparticle/LC composite gels can be used as photohealable materials by the site-selective control of the gel–sol transition based on the photochemical phase transition of the LC matrix via the *cis–trans* isomerization of an azobenzene dopant [28].

Previous studies have demonstrated that the viscoelastic properties of the microparticle or nanoparticle/LC composite gels can be tuned by changing the diameters and the concentrations of the dispersed articles or the phase transition temperatures of the LC matrix [19–23,25,26]. In addition, the viscoelastic properties of the composite gels have mostly been investigated using nematic LCs [18,20–26]. To the best of our knowledge, reports on the effects

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of the phase structures of the LC matrix on the viscoelastic properties of the composite gels are absent in the literature. In addition to the nematic phase, LCs exhibit a variety of phases such as cholesteric and smectic phases [29]. For instance, the smectic A (SmA) phase is one of the distinct mesophases of LC materials. This system can be viewed as a set of two-dimensional liquid layers stacked on each other with well-defined spacings. The direction of molecular alignment is parallel to the layer-normal of each layer, and specific positional order of the LC molecules is hardly present. The motion of the LC molecules is restricted within the layer, and the smectic layers can slide over each other similar to those present in soap. Generally, the SmA phase is more solid-like than the nematic phase due to the layer compression modulus, although the fluidic nature is maintained. The structures and dynamics of silica and gold nanoparticles dispersed in an SmA phase have previously been discussed [30–32]. However, the effects of varying the phase structures of the LC matrix on the viscoelastic properties of the composite gels are yet to be investigated. In this paper, we report the influences of the layered structures present in the molecular assembly of the LC matrix on the frequency and strain dependency of storage and loss moduli and the recovery of the gel state from the sol state after large-amplitude oscillatory breakdown.

2. Materials and methods

2.1. Materials

LC matrices (7CB: 4-heptyl-4′-cyanobiphenyl and 8CB: 4-octyl-4′-cyanobiphenyl) were purchased from Merck and used as supplied (Fig. 1). 7CB shows only the nematic phase, while 8CB shows both SmA and nematic phases. The nematic–isotropic phase transition points of both the LCs are similar (42 and 40 °C for 7CB and 8CB, respectively). Therefore, the effects of the variation in the phase structures on the viscoelastic properties of the composite gels can be reasonably discussed, without interference from the effects of temperature dependence of the elasticity of the LC phases. Monodisperse polymer microparticles (diameter: 3.6 μm) consisting of polymerized divinylbenzene core with surface anchoring properties were purchased from Sekisui Chemicals. The mean particle diameter was estimated using the Coulter counter. The particle surfaces were treated to induce homeotropic alignment of the LC matrix molecules. Therefore, hedgehog or Saturn ring defects could be formed around the particles.

2.2. Sample preparation

The polymer microparticles were weighed and suspended in each LC sample in a glass vial. The particle concentration was adjusted to 30 wt.%. The composites were subsequently heated in the isotropic phase of each LC on a hot plate and vigorously mixed to ensure the homogeneous dispersion of the microparticles. The resultant suspensions were then cooled down (at the rate of approximately 5 °C/min) to 25 °C after which, gel formation was induced in each sample. The composite gels were maintained at 25 °C overnight before being subjected to various experiments (listed in the sections below). A self-standing sample of the microparticle/8CB composite gel was prepared on a glass plate using a procedure similar to the protocol described above, and the sample was cut into the pieces (with width × height × depth = 13 mm × 8 mm × 3 mm).

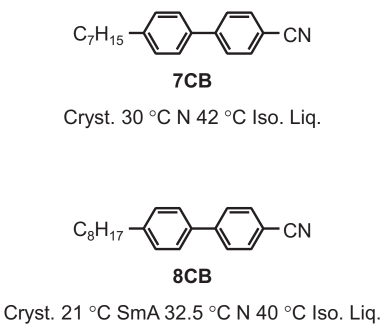

Fig. 1. Chemical structures and phase transition points in a heating process of the LCs (7CB and 8CB) used as matrices in this study. N and SmA indicate nematic and smectic A phases, respectively.

2.3. Rheology

An advanced rheometric expansion system (ARES, TA Instruments, Rheometric Scientific) with a parallel-plate-type geometry (plate diameter = 25 mm) was used to measure the dynamic viscoelastic properties of the microparticle/LC composite gels. Dynamic frequency and strain sweep tests were conducted at 25 °C at which 8CB and 7CB show SmA and nematic phases, respectively. The frequency and temperature sweep tests were carried out in a strain-controlled mode (strain = 0.1%). The microparticle/LC composite gels were placed appropriately between the plates and any excess composite extending beyond the plates was removed before each measurement. During a temperature sweep test, a cooling process was carried out at the rate of 2 °C/min. A gap of 0.75 mm was left between the plates to be filled with the composite.

2.4. Polarizing optical microscopy

The optical textures of the microparticle/8CB composite gel were observed with a polarized optical microscope (Olympus, BX51). The observations were carried out using commercially available evaluation cells (cell gap = 10 μm) without surface coating (purchased from E.H.C. Co., Ltd., Japan). The sample temperature was adjusted using a temperature controller (LK-600PH, LCP94/2, Linkam).

3. Results and discussion

Fig. 2 shows the dynamic storage (*G*′) and loss (*G*″) moduli profiles of the microparticle/nematic 7CB composite gel (Fig. 2a) and microparticle/SmA and nematic 8CB composite gel (results from gel with the SmA phase shown in Fig. 2b) (both containing particles at a concentration of 30 wt.%) during a dynamic frequency sweep test under 0.1% strain at 25 °C. In the case of the microparticle/nematic 7CB composite gel (Fig. 2a), the frequency sweep test produced *G*′ values with a substantial elastic response that were always higher than the *G*″ values over the entire range of the measured frequency, although the two values became close at higher frequencies. A similar viscoelastic profile was observed also for the microparticle/nematic 8CB composite gel at 37 °C (see Fig. S1 in the Supporting information). In contrast, in the case of the microparticle/SmA 8CB composite gel (Fig. 2b), a crossover frequency between *G*′ and *G*″ was observed eventually at around 3 Hz, and a certain level of non-linear viscoelastic nature was exhibited even at 0.1% strain. When the scanning frequency was higher than the crossover frequency, *G*′ was found to be lower than *G*″, indicating the predominance of the viscous property. When the scanning frequency was lower than the crossover frequency, *G*′ was higher than *G*″, and the elastic property dominated. A similar frequency dependence of the viscoelastic properties suggesting a non-linear viscoelasticity has been previously reported in microparticle/nematic LC composite gels, without any explanation for