Helical-structure-induced softening of particle/liquid-crystal composite gels

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We investigated the effects of the introduction of helical structures into a host liquid crystal on the viscoelastic properties of particle/liquid-crystal composite gels. A composite gel using a cholesteric liquid crystal as a host matrix was found to become soft compared to that using a nematic liquid crystal. With reducing the half-pitch length of a helical structure of cholesteric liquid crystals, a storage modulus of the composite gels showed a linear decrease. On the other hand, a crossover point which is a mechanical quasi-solid–quasi-liquid transition point exhibited no significant changes when the half-pitch length was larger than the radius of a particle used in this study. However, a decrease of the crossover points was observed when the half-pitch length was shorter than the particle radius. We qualitatively discussed the origin of helical-structure-induced softening of particle/liquid-crystal composite gels based on the differences in self-organization behavior of particles in nematic and cholesteric liquid crystals.

Key words: liquid crystal, composite, gel, nematic phase, cholesteric phase

1. INTRODUCTION

Particle/liquid-crystal (LC) composite gels are a kind of liquid-crystalline physical gels and have recently attracted an increasing attention due to their scientific and technological interests [1-12]. In particle/LC composite gels, micro- and nano-sized particles act as a sort of gelators and form three-dimensional networks in host LCs [4, 5]. So far, a few applications of particle/LC composite gels have been proposed, such as chemical sensors and cell culture media [11, 12]. Recently, we reported the development of novel photo-healable materials consisting of particle/LC composite gels doped with an azobenzene derivative [9]. By means of the gel–sol transition induced by *trans-cis* photoisomerization of an azo-dye, we achieved light-assisted mending of surface cracks on the particle/LC composite gels. In addition, we previously investigated effects of the phase structures (nematic and smectic A phases) of host LCs on the viscoelastic properties of particle/LC composite gels [10]. By the introduction of a layer structure of molecular organization into a host LC matrix, we found that a storage modulus indicating the rigidity of the composite gels showed an increase of approximately one order of magnitude with no significant reduction of a crossover point which denotes the toughness of the composite gels. In this study, we investigated effects of the introduction of a helical structure of molecular alignment into the host matrix using cholesteric LCs on the viscoelastic properties of particle/LC composite gels.

2. EXPERIMENTAL SECTION

2.1 Materials

Fig. 1 shows the chemical structures of a nematic LC mixture (ZLI-1083) and chiral dopants (S811 and R811). Cholesteric LCs were prepared by doping ZLI-1083 with the mixtures of S811 and R811 having the different enantiomeric excess (*e. e.*) values. The concentrations of the mixtures of S811 and R811 in cholesteric LCs were

adjusted at 5 or 15 wt%. The *e. e.* value was calculated using a following equation (Eq. 1). The *e. e.* value = 100% means that ZLI-1083 contains only S811. A half-pitch length (pitch/2) of cholesteric LCs was measured by a conventional wedge cell method at 25 °C.

$$e. e. (\%) = \frac{([S811] - [R811])}{([S811] + [R811])} \times 100 \quad (\text{Eq. 1})$$

Monodisperse polymeric particles (Micropearl, EX-0036-AC6, radius = 1.8 μm) consisting of polymerized styrene and divinylbenzene were purchased from Sekisui Chemical Co. Ltd. The particles were the same as the previous studies [9, 10].

2.2 Sample preparation

The polymeric particles were weighed and suspended in each host cholesteric LC in a glass vial. The

Fig.1 Chemical structures of liquid-crystalline mixture (ZLI-1083) and chiral dopants (S811 and R811) used in this study.

concentration of the polymeric particle to cholesteric LCs was 33 wt %. In this study, in order to allow discuss the effects of phase structures of LCs, we employed almost the same particle concentration as the previous study [10]. The suspension was heated above the clearing temperature of the host cholesteric LCs on a hot plate and vigorously mixed to ensure the homogeneous dispersion of the particles. The suspension was then cooled to 25 °C at a fixed rate of about 10 °C/min. At the phase-transition point from an isotropic phase to a cholesteric one, the gel formation was induced. Each sample was kept overnight at 25 °C before each experiment was performed.

2.3 Measurements

Viscoelastic properties of particle/LC composite gels were investigated using an Advanced Rheometric Expansion System (ARES-RFS, TA Instruments, Rheometric Scientific) with a parallel-plate type geometry (plate diameter: 25 mm). Dynamic frequency and strain sweep tests were conducted at 25 °C. A frequency sweep test was performed in a strain-controlled mode (strain: 0.1%). A strain sweep test was conducted at the frequency of 1 Hz. A gap of 0.75 mm was left between the plates to be filled with the composite gels.

Fig. 2 Clearing temperatures (A) and half-pitch length (pitch/2) values (B) of host cholesteric LCs as a function of *e. e.* values. The concentrations of the mixture of the chiral dopants were 0 (▲), 5 (●), and 15 (■) wt%.

Fig. 3 Frequency dependency of storage (G' , ●) and loss (G'' , ○) moduli of particle/LC composite gels with different *e. e.* values: (A) 0% (nematic phase); (B) 100% (cholesteric phase, pitch/2 = 0.88 μm). The concentration of the chiral dopants was 5 wt% for both composite gels. Experiments were conducted at 25 °C.

3. RESULTS AND DISCUSSION

3.1 Physical properties of cholesteric host LCs

Fig. 2 shows the clearing temperatures of host cholesteric LCs and pitch/2 values of helical structures as a function of *e. e.* values. Although, the addition of the non-liquid-crystalline chiral dopants (S811 and R811) simply induced a reduction of the clearing temperatures of ZLI-1083 from 52 (▲, 0 wt%) to 48.5 (●, 5 wt%) and 43.3 (■, 15 wt%) °C at *e. e.* = 0% (nematic phase), the clearing temperature of cholesteric LCs (*e. e.* > 0%) did not show any significant changes even if the *e. e.* value changed at each dopant concentration (Fig. 2 (A)). Meanwhile, the pitch/2 values of the helical structure became shorter with increasing the *e. e.* value (Fig. 2 (B)). Therefore, in this study, we can discuss the effects of (i) the introduction of a helical structure and (ii) pitch lengths of a helical structure on the viscoelastic properties of the composite gels at each dopant concentration.

3.2 Effects of helical structures on the viscoelastic properties of particle/LC composite

Fig. 4 Storage (G' , filled symbols) and loss (G'' , open symbols) moduli of particle/LC composite gels as a function of pitch/2 of cholesteric LCs. The concentrations of chiral dopants were 5 ($\bullet$, $\circ$) and 15 ($\blacksquare$, $\square$) wt%. Experiments were carried out at 25 °C.

gels

Fig. 3 shows the frequency dependence of viscoelastic properties (storage and loss moduli) of particle/LC composite gels (the concentration of the mixture of the dopants was 5 wt% and $e.e. = 0$ or 100%). In this frequency region, we confirmed that both composite gels exhibited quasi-solid nature ($G' > G''$) similarly to the previous reports [9, 10]. As a representative value, at a frequency of 1 Hz, the values of the storage modulus which indicate the rigidity of the composite gels are 2.9×10^4 and 0.5×10^4 Pa at $e.e. = 0$ and 100%, respectively. We therefore found that the storage modulus was reduced by the introduction of a helical structure into a LC matrix even though the clearing temperatures of both composite gels were almost the same as shown in Fig. 2(A) ($T_c = 48.5$ °C). As opposed to the case of the introduction of a layer structure into a host LC [10], these results clearly indicate that helical structures make the composite gels soft. Similar results were also observed in the composite gels containing the chiral dopants of 15 wt % (data not shown). Fig. 4 shows the effect of pitch/2 values on the storage and loss moduli of the particle/LC composite gels. In both concentrations of the chiral dopants, the composite gels became softer as the pitch/2 values became smaller. In addition, we found that both moduli of the composite gels can be continuously tuned by changing the pitch length of a helical structure in each composite gel. This would be a novel manner of the control of the viscoelastic properties of particle/LC composite gels.

Next, we investigated effects of helical structure on a crossover point at which a mechanical quasi-solid–quasi-liquid transition occurred, in other words, the crossover point indicates the toughness of the composite gels against mechanical strain. Fig. 5 shows the results of strain sweep tests of the composite gels containing the chiral dopants of 5 wt%. The crossover point was slightly reduced from 11.9 (Fig. 5A, $e.e. = 0\%$) to 9.1% (Fig. 5B, $e.e. = 100\%$) by the introduction of a helical structure into the host matrix. However, the

reduction of the crossover point strongly depended on the pitch/2. Fig. 6 shows the effect of pitch/2 values on the crossover points of the composite gels containing the chiral dopants of 5 and 15 wt%. When the pitch/2 value was larger than approximately 1.8 μm , the crossover points did not show significant changes. However, the crossover points exhibited a clear decrease when the pitch/2 values were smaller than approximately 1.8 μm . Interestingly, this pitch/2 value is almost the same as the radius of particles used in this study.

Self-organizing behavior of particles in nematic and cholesteric LCs was previously investigated [6]. In that study, the authors reported that particles tended to form one-dimensional chains in nematic LCs. One-dimensional chains could easily propagate to all direction in a nematic matrix. Therefore, we expect that the three-dimensional networks would be easily constructed with particles in nematic LCs. On the other hand, in cholesteric LCs, two-dimensional plates were predominantly formed with particles. The authors revealed that two-dimensional plates propagated preferentially within the same plane. In such a situation, we infer that the formation of firm three-dimensional

Fig. 5 Strain sweep tests of storage (G' , $\bullet$) and loss (G'' , $\circ$) moduli of particle/liquid-crystal composite gels with different $e.e.$ values: (A) 0% (nematic phase); (B) 100% (cholesteric phase, pitch/2 = 0.88 μm). The concentration of the chiral dopants was 5 wt% for the both composite gels. Experiments were conducted at 25 °C and a constant frequency of oscillation (1 Hz).

Fig. 6 Plots of crossover points of storage and loss moduli particle/LC composite gels as a function of pitch/2 values of cholesteric LCs. The concentrations of dopant mixture were 5 (●) and 15 (■) wt%. Experiments were carried out at 25 °C.

network structures of particles would be difficult in cholesteric LCs. In addition, the authors pointed out two important features: (i) the size of the two-dimensional plate clusters in cholesteric LCs became remarkably larger at the point where the pitch of a helical structure was significantly smaller than the particle size and (ii) a particle-particle distance slightly grew as the pitch of a helical structure became shorter. From these features, we qualitatively speculate here the origins of the softening of the particle/LC composite gels induced by the helical structures. By the introduction of the helical structure into a host LC, particles could not form networks efficiently due to the predominant formation of two-dimensional plate clusters. As a result, the composite gel became soft. Then, as the pitch of a helical structure became shorter with increasing the *e. e.* value, the composite gel exhibited a further softening. This would be due to the increase of a particle-particle distance. Furthermore, as the pitch of a helical structure was shorter than the particle size, the networks became fragile. The reduction of the toughness of the composite gels would be caused by a significant enhancement of the formation of two-dimensional plates in host LCs.

4. CONCLUSIONS

In this study, we found that the phase structures (nematic and cholesteric phases) of a host matrix had significant effects on the viscoelastic properties of particle/LC composite gels. The composite gel became soft by the introduction of a helical structure into a host LC. Storage modulus indicating the rigidness of the composite gels decreased as pitch/2 values of a helical structure became smaller. Crossover points which denoted the toughness of the composite gels exhibited no significant changes when the pitch/2 values were larger than approximately 1.8 μm which was coincided with the radius of particle used in this study. When the pitch/2 values were smaller than 1.8 μm, the toughness of the composite gels was significantly decreased. The differences in self-organization behavior of particles in

nematic and cholesteric LCs will strongly affect the network formation of particles in host LCs and the viscoelastic properties of particle/LC composite gels.

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