Thermomechanical analysis of a polymer dispersed liquid crystal containing a thermoplastic elastomer

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Bulk samples of polymer dispersed liquid crystals (PDLCs) containing polystyrene (PS) and a thermoelastic elastomer as polymer matrices, have been prepared by a thermally-induced phase separation method. Thermomechanical analysis measurements revealed that the PDLC containing the thermoplastic elastomer possessed rubber-like elasticity even in the mesomorphic temperature range of the LC while the PDLC based on PS showed plastic deformation during the measurement.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) have attracted great interest because of their potential applications [1–4]; their physical properties have been extensively studied in the thin film state, as also for other materials based on phase-separated structures containing LCs [5–9], largely due to their application to flat panel displays. To our knowledge, however, few investigations on the bulk state, such as the determination of mechanical properties, have been carried out. The investigation of the mechanical properties of blended systems such as PDLCs is indispensable for identifying the strength of various types of material and optimizing methods of processing and moulding. The mechanical properties depend to a large extent on the miscibility of components and microstructures of blends. Therefore, it is of particular interest to study the mechanical properties of PDLCs, since they are composed of polymers and fluid LCs, and have phase-separated structures consisting of LC droplets surrounded by polymer networks. The mechanical properties of PDLCs are of additional importance since it has been found that the geometry of the droplets and the orientation of the LCs (which significantly affect the performance of PDLCs) can be transformed by stretching the PDLCs mechanically [10].

There are three main methods for preparation of PDLCs, which are associated with a phase separation process: the solvent-induced, polymerization-induced, and thermally-induced methods. The solvent-induced phase separation method involves the evaporation of

solvent from a solution containing a polymer and an LC [11, 12]. In the polymerization-induced phase separation method, UV irradiation is usually employed for polymerization [13, 14]. A combination of a polymer and an LC which shows an upper critical solution temperature is used in the thermally-induced phase separation method [15, 16]. The first and second methods are suitable for thin film samples rather than bulk samples. In contrast, the thermally-induced phase separation method is considered to be suitable for obtaining a bulk sample as well as a film sample of the PDLC. The thermally-induced phase separation method would therefore be preferred for preparation of a bulk PDLC sample; however, the polymer matrix of the PDLC prepared by this method is often plasticized by the LC rendering mechanical analyses difficult.

In this study, we have examined polystyrene (PS) and a thermoplastic elastomer, styrene-ethylene/butylene-styrene block copolymer (SEBS), as polymer matrices and employed a thermally-induced phase separation method to prepare bulk samples from these polymers and a LC. We intended to overcome plasticization problem by using SEBS which has physical crosslinking and itself shows rubber-like elasticity. We investigated the temperature dependence of mechanical properties such as Young's modulus and the stress–strain (S-S) curve for the resulting bulk samples of PDLCs.

2. Experiment and results

The SEBS used in this study was supplied by Shell Japan Co. Ltd., under the trade name of Kraton G 1652. 4-Cyano-4′-hexylbiphenyl (6CB) was purchased from Merk Co. Ltd. It shows an enantiotropic nematic phase

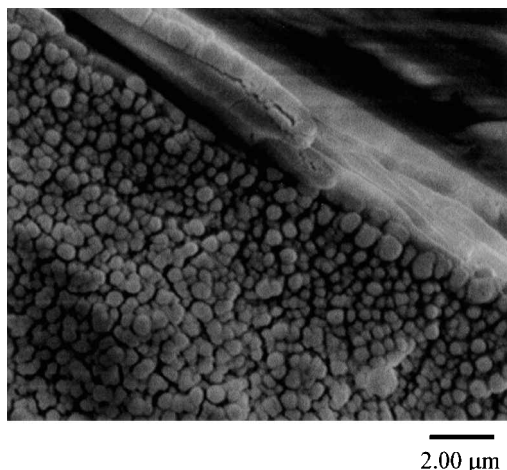*Author for correspondence; h-kihara@aist.go.jp

2.00 μm

Figure 1. CryoSEM image of the cross section of the PDLC consisting of SEBS and 6CB.

(Cr 14.5°C N 29.0°C I), on heating. A sample tube containing SEBS and 6CB, in weight ratio 30/70, was heated on an oil bath at 180°C. The mixture was stirred with a spatula until it became homogeneous and transparent, and then cooled to room temperature yielding an opaque PDLC bulk sample.

A cryoSEM image of the PDLC was taken by a TOPCON DS-720 instrument equipped with a Polar-Prep 2000 Cryo Transfer System. In order to preserve the structure, the PDLC was quenched in liquid nitrogen, transferred into the cooling chamber, and cut with a blade.

Figure 1 shows a cryoSEM image of the cross section of the PDLC. Many particles with the diameter of *c.* 500 nm, whose distribution was relatively small, were packed together; they were the crystals of 6CB. We assume that the polymer matrix peeled off when the PDLC was cut in the cooling chamber. The cryoSEM image indicates that the PDLC had a phase-separated structure with liquid crystalline droplets surrounded by the polymer matrix.

Thermomechanical analysis (TMA) on the PDLC was performed using a Seiko Instruments Inc. TMA/SS120C. A schematic illustration of the TMA measurements is shown in figure 2. The force given to the sample and the variation in its length can be simultaneously detected
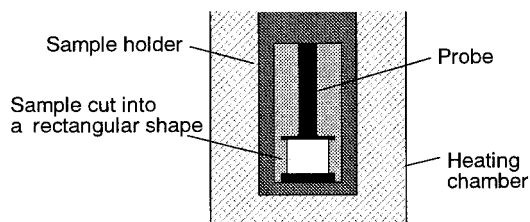

Figure 2. Schematic illustration of the arrangement for TMA measurements.

by the TMA apparatus. In addition, the temperature can be controlled by the heating chamber. In this study, the variation in length of the sample was measured while the temperature was kept constant and an oscillating force directing downward given to the sample. When the stress estimated from the force and the strain calculated from the variation in the length are taken as ordinate and abscissa, respectively, stress–strain (S-S) curves are obtained. If a sample measured by this method has complete elasticity, the S-S curve becomes a linear line. In contrast, if a soft material having viscoelasticity like a rubber is used, and it exhibits no plastic deformation during the TMA measurement, the S-S curve forms an ellipse. This is because the S-S curve pursues different courses depending on the increasing or decreasing force and returns to the start point after one cycle due to restoration of the shape. A bulge of the ellipse is deeply associated with viscoelasticity. The Young's modulus is derived from a tangential line to the ellipse. If plastic deformation occurs in a sample during the TMA measurement, the S-S curve does not return to the same point after one cycle, so that it is unable to form an ellipse.

The SEBS-containing PDLC was cut into a rectangular shape with $2.35 \times 2.10 \, mm^2 \times 1.85 \, mm$ thick such that the area of the upper surface of the sample was smaller than that of the tip of the probe. An oscillational stress with maximum load 1.5 g, minimum load 0.5 g, and a frequency of 0.05 Hz was applied to the sample at a controlled temperature. The S-S curves of the PDLC obtained from TMA measurement at 21.6 and 5.1°C are shown in figure 3, and compared with that of a pure SEBS sample at 21.2°C. 6CB is liquid crystalline and solid at 21.6 and 5.1°C, respectively. The strain value at which the 1.0 g load was applied to the sample, was taken as 0%. An elliptical S-S curve, characteristic of a rubber, was observed for pure SEBS, figure 3 (*a*). As shown in figure 3 (*b*), the S-S curve of the PDLC also showed an elliptical shape at 21.6°C, although it became more round and the elongation was slightly larger than for SEBS. This result indicates that the PDLC still showed rubber elasticity without plastic deformation, while the viscosity increased. At 5.1°C, the elasticity of the PDLC has significantly increased so that the ellipse of the S-S curve has become fairly flat and the elongation considerably decreased, figure 3 (*c*).

We also prepared a PDLC consisting of PS with M_w 280 000 and 6CB of weight ratio 30/70, and performed a TMA measurement at 23.0°C at which 6CB exhibits a nematic phase. This bulk sample was also obtained from PS and 6CB by a thermally-induced phase separation method. However, this PDLC containing PS did not maintain its original shape during the TMA measurement due to significant plastic deformation. The resultant
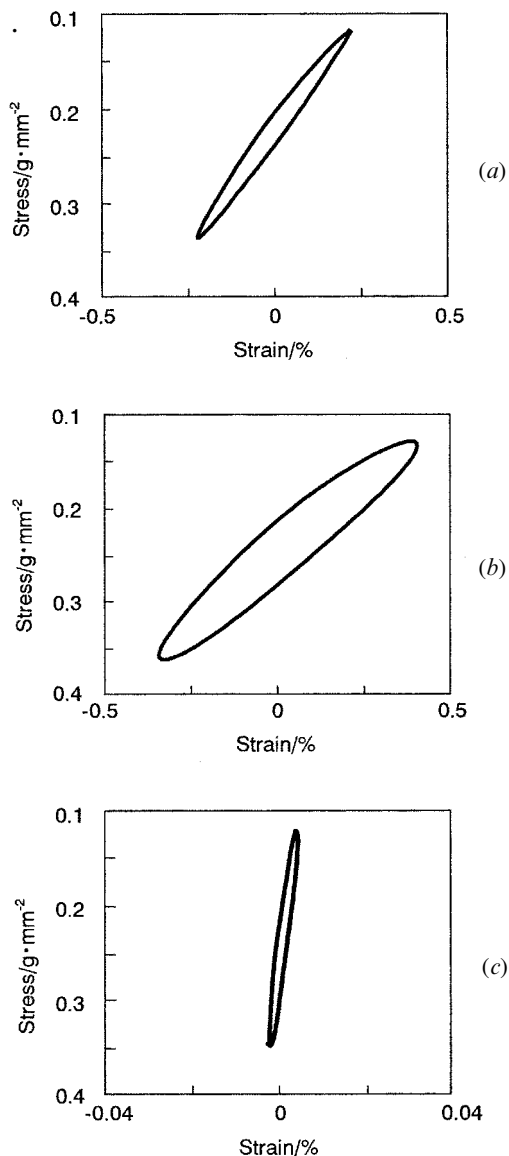
Figure 3. Stress–strain curves of pure SEBS (*a*), and for the PDLC consisting of SEBS and 6CB at 21.6°C (*b*) and at 5.1°C (*c*).

Figure 4. Stress–strain curve of a PDLC consisting of PS and 6CB at 23.0°C.

S-S curve. The temperature dependence of the Young's modulus of this PDLC is shown in figure 5, and compared with that of pure SEBS. The value of the Young's modulus of pure SEBS showed no significant change in the experimental temperature range, whereas that of the PDLC decreased from 1.6×10^7 to 5.0×10^5 Pa as the temperature increased from 11.0 to 17.0°C. This decrease of the Young's modulus is associated with the phase transition of the 6CB component from crystal to LC. Subsequently, the PDLC Young's modulus value recovered achieving 1.8×10^7 Pa on reducing the temperature to 7.1°C. While a hysteresis existed in this cycle, a thermoreversible transition of the bulk modulus was observed for the PDLC.

The loss tangent, tan δ, of the PDLC and pure SEBS were also determined from the shape of the S-S curves and are depicted in figure 5. The results indicate that the LC component strongly affects the viscoelasticity of

S-S curve did not form an ellipse but exhibited a spiral line, as shown in figure 4. Although plastic deformation appeared even in the SEBS-containing PDLC as the temperature increased beyond the clearing point of 6CB, it is noteworthy that it showed rubber-like elasticity in the mesomorphic temperature range of 6CB; this was not observed for the PS-containing PDLC. This phenomenon is thought to be caused by physical cross-linking in SEBS; the effect might, however, be attributed to the presence of slight crystallinity [17].

TMA measurement on the SEBS-containing PDLC was performed at various temperatures and its Young's modulus for compression was determined from the
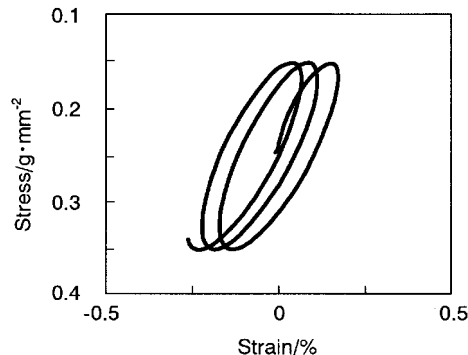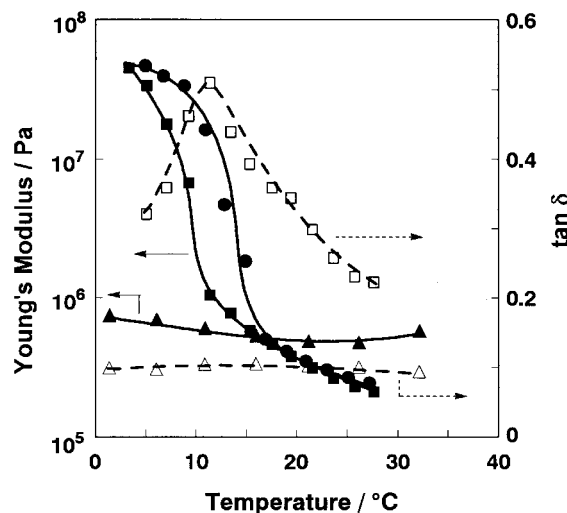

Figure 5. Temperature dependence of the Young's moduli of the PDLC consisting of SEBS and 6CB on heating (●) and cooling (■), and that of SEBS (▲); and the temperature dependence of tan δ of the PDLC on cooling (□), and that of SEBS (△).

the PDLC. In the mesomorphic temperature range of 6CB, the value of $\tan \delta$ of the PDLC was larger than that of SEBS. This is probably due to energy loss associated with the viscosity of the LC component. As the temperature decreased, the viscosity of the LC increased, resulting in the increase of $\tan \delta$ of the PDLC. After crystallization of the LC component, $\tan \delta$ rapidly decreased because of disappearance of LC viscosity.

3. Summary

A bulk PDLC sample consisting of SEBS and 6CB, prepared by a thermally-induced phase separation method, was submitted to TMA measurement. The PDLC showed rubber-like elasticity in the temperature range in which 6CB was in the LC state. The plastic deformation problem was resolved by using a thermo-plastic elastomer as polymer matrix. We anticipate that the Young's modulus of the PDLC may be controlled by external stimuli such as an electric field, which may lead to interesting new applications. Other properties of the PDLC containing a thermoplastic elastomer are now under investigation.

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