Two-Step Polyimide Curing Technique for Flexible Plastic Liquid Crystal Devices

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An intriguing and simple method, a two-step polyimide (PI) curing technique, was proposed for the fabrication of flexible plastic liquid crystal (LC) devices. This technique is based on the concept that PI interfaces contacted through the columnar spacers act as adhesive for the secure attachment of two plastic substrates via the curing process in poly(amic acid)'s (PAA) conversion to PI. A preliminary version of a flexible LC display employing this concept was fabricated, and was confirmed as useful for such applications. The electro-optical reproducibility of the flexible LC device fabricated in this study showed remarkable endurance against external perturbation when compared with a device fabricated by the conventional method. © 2009 The Japan Society of Applied Physics

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Recently, a great deal of attention has been focused on the development of flexible plastic displays.[1–10] This type of display has several advantages over the conventional displays fabricated with rigid glass substrates, such as increased bending capability, lighter weight, increased portability, thinner packaging requirements, increased durability, and lower cost.[4] These features are suitable for future applications in personal digital assistants (PDAs), smart cards, electronic books, wearable displays, and so on. Several prototypes of flexible displays using organic light emitting materials,[1,2] electro-phoretic materials,[3] and liquid crystals (LCs)[4–10] have been previously proposed and demonstrated.

Among the prototypes mentioned, LC-type flexible displays have a crucial weak point. The electro-optical properties of LC-type devices easily degrade after repeated external perturbation, diminishing the reliability of the device. Nevertheless, LC-type flexible displays are currently promising, as the relevant infrastructures have been well-established.[5]

Several approaches have been explored to overcome the above-mentioned crucial weak point. Some research groups have proposed fabrication of flexible LC displays with polymer walls, polymer networks, or pixel-encapsulated techniques.[4–9] However, these suggested techniques suffer from unavoidable drawbacks; additional processes are required in their implementation, resulting in increased manufacturing cost. Therefore, the development of a novel technique consisting of simple structure and low cost is necessary. In this paper, a two-step polyimide (PI) curing technique for fabricating flexible LC devices is proposed. A preliminary version of a flexible plastic LC display was fabricated employing this two-step PI curing concept, and the electro-optical reproducibility was confirmed to be remarkably enhanced against external perturbation when compared with the display made by the conventional method.

Figure 1 illustrates the general LC display cell-making processes. As shown, the processes include: 1) cleaning the two substrates, 2) coating the alignment layer on the substrates, 3) curing at a high temperature, 4) rubbing, 5) assembling the two substrates under hot pressure, and 6) filling the LCs. In process 2, a polymer of poly(amic acid) (PAA) is commercially employed as an alignment layer [see Fig. 2(a)]. The coated PAA layer forms a PI layer via the curing process because of a close ring reaction of the PAA, and the imidization ratio of the PI increases as the curing temperature and time increase. The proposed concept of the two-step PI curing technique is described as follows: first, in process 3, the chemically active PI layers (residual PAA layers) are intentionally prepared with an insufficient imidization ratio by means of controlling the curing conditions (1st PI curing) [see Fig. 2(b)]. Then, in process 5, the residual PAA is sufficiently imidized (2nd PI curing), which causes fixed adhesion between the top and bottom substrates through the columnar spacers, as shown in Fig. 2(c). That is, during the 2nd PI curing process, the residual active PAA exhausts so fully that PI-bonding can spontaneously form between the two substrates through the columnar spacers without additional processes. This PI-bonding within the flexible LC display allows for improvement of mechanical stability and electro-optical reproducibility against external perturbation.

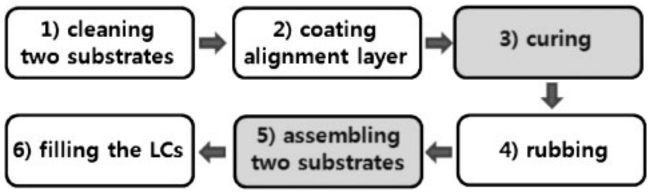

Fig. 1. The general LC display cell-making processes. Among these processes, thermal treatment is generally treated at process 3, and process 5.

The imidization ratio of the alignment layer used here was monitored with a Fourier transform infrared (FTIR) spectrophotometer. Figure 3(a) shows the IR absorption spectra of the alignment layer according to curing intervals; 0, 135, 270, and 540 s. (The curing temperature was fixed at 180 °C.) The adsorption band at 1370 cm^{-1} (C–N stretching vibration of the imide) was employed for the determination of the imidization ratio. As shown, the 1370 cm^{-1} peak increased as the curing interval increased, which indicates that the extent of imidized conversion increased. The

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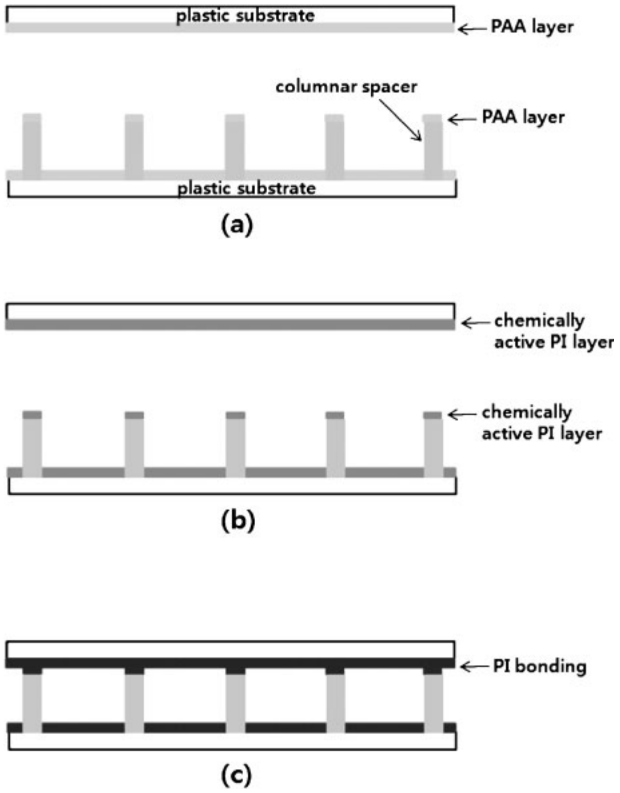

Fig. 2. A schematic processes of fabricating flexible LC display employing two-step curing PI technique. (a) A polymer of PAA type is coated on the substrates as an alignment layer. Then, (b) the chemically active PI layers (residual PAA layers) are intentionally prepared with an insufficient imidization ratio (1st PI curing). Finally, (c) the residual PAA is sufficiently imidized (2nd PI curing), which causes fixed adhesion between the top and bottom substrates through the columnar.

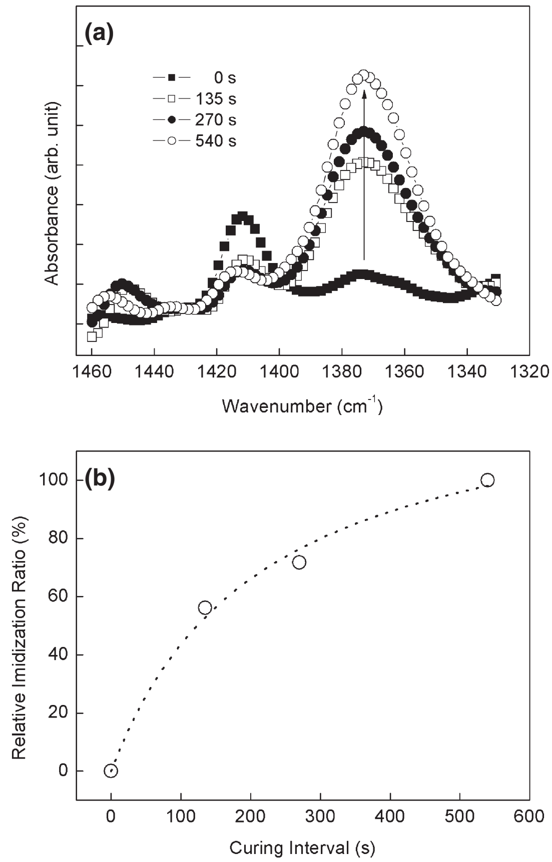

Fig. 3. (a) The IR absorption spectra of alignment layer according to curing intervals; 0, 135, 270, and 540 s. (b) The relative imidization ratio calculated using eq. (1).

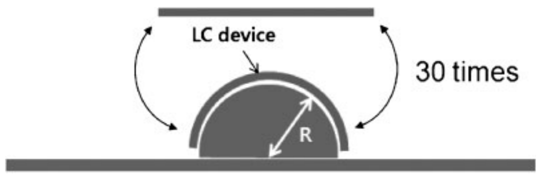

Fig. 4. Homemade equipment for applying the repetitive mechanical bending stress to the flexible LC displays.

relative imidization ratio was calculated using the adsorption band at 1510 cm^{-1} (C–C stretching of the p-substituted benzene) as an internal reference. The conversion to PI during the thermal imidization at curing interval T was determined by the following equation:[11–13)]

$$\text{Imidization ratio (\%)} = \frac{(D_{1370\,cm^{-1}}/D_{1510\,cm^{-1}})_T}{(D_{1370\,cm^{-1}}/D_{1510\,cm^{-1}})_{540\,s}} \times 100, \quad (1)$$

where D is the optical density of each absorption. The determined imidization ratio is depicted in Fig. 3(b). In this experiment, it was assumed that a 100% imidization ratio was obtained by thermal curing at 180 °C for 540 s.

A preliminary version of a flexible LC display was fabricated using the proposed concept. Poly(ether sulfone) (PES) films coated indium–tin-oxide (ITO) were used as flexible plastic substrates. The PES substrates used here have small birefringence and a high softening temperature (200 °C) with 200 μm thickness. The columnar spacers formed on the bottom substrate are 20 μm thick and 5 μm high on average. The PAA-type alignment layer (supplied by Nissan Chemical) was coated on the inner sides of both top and bottom substrates using spin coating, followed by thermal curing at 180 °C for 270 s (1st PI curing). This 1st curing condition corresponded to approximately 70% of the imidization ratio from Fig. 3(b). The substrate surfaces were rubbed with a rubbing machine, and the two substrates were assembled with a twisted nematic (TN) configuration under hot pressure (180 °C for 270 s). During this process (the 2nd PI curing step), the conversion of the chemically active residual PAA was accelerated into PI, resulting in spontaneous PI-bonding between the two substrates through the columnar spacers. Finally, a mixture of nematic LCs was injected by capillary action.

The device performances of the flexible LC displays, fabricated employing the two-step PI curing technique, were then examined against repetitive mechanical bending stress. In this experiment, the test of the mechanical stability of the flexible LC display was performed with the homemade equipment, shown in Fig. 4, where the geometrical curvature was defined as radius R on a round stage. The prepared flexible displays were exposed to repetitive mechanical bending stress (the 30-times bending deformation of R varied from $R = \infty$ to 21 mm). Figures 5(a) and 5(b) show typical electro-optical switching curves of the flexible LC displays fabricated by the conventional method and by the

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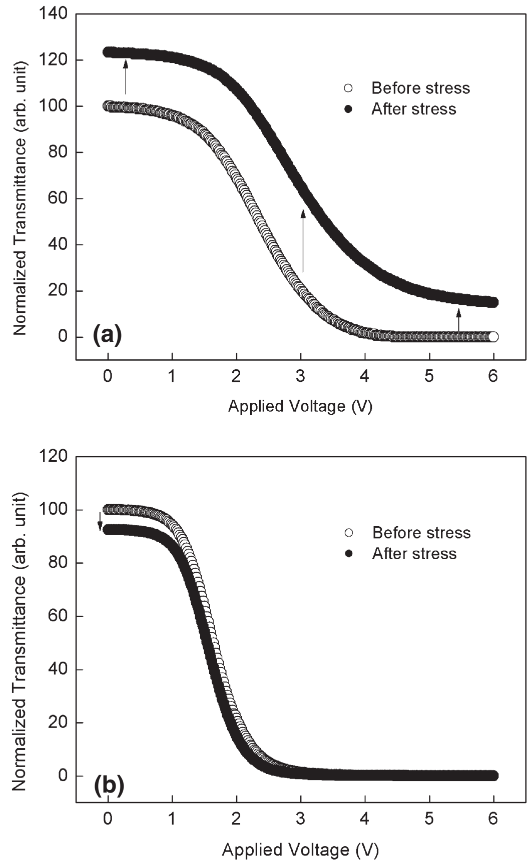

Fig. 5. Typical electro-optical switching curves of the flexible LC displays fabricated (a) by the conventional method and (b) by the two-step PI curing technique, respectively, after repetitive bending deformation.

two-step PI curing technique, respectively, after repetitive bending deformation. These TN LC displays were set to be normally white under crossed polarizers. As shown in Fig. 5(a), the black and white levels were extremely changed after the bending stresses. In the case of the conventional flexible LC display with plastic substrates, as the bending perturbation increased, the electro-optical switching curve became worse due to two major problems;[14] (1) plastic substrates cannot give a solid support for the molecular alignment of LCs between them, and (ii) two plastic substrates are easily detached by bending. Namely, this could give rise to the variation of cell gap and a certain disorder of the initial LC alignment when the LC display was bent. This problem could be overcome by means of the two-step PI curing technique. As shown in Fig. 5(b), although the bright state changed slightly, the switching curves were almost the same before and after the repetitive bending distortion. The electro-optical switching profiles for different panel-points were also shown same trend. Namely, the flexible LC display fabricated using the two-step PI curing technique was able to nearly recover from the bent state without critical damage because of the enhanced mechanical stability of the LC display originating from the adhesive structures on both the top and bottom substrates. In other words, spontaneous PI bonding prevents the detachment of the two plastic substrates in this flexible LC display, resulting in improvement of reproducibility against mechanical bending deformation.

In conclusion, an intriguing and simple two-step PI curing technique for fabrication of flexible plastic LC devices was presented, and a preliminary version of a flexible LC display employing this concept was actually fabricated. The concept of this technique was based on the spontaneous formation of adhesive structures between the two plastic substrates through columnar spacers, using the conversion from PAA to PI via the PI curing processes. In other words, the PI-bonding acts as an adhesive for the secure attachment of the two plastic substrates. The electro-optical reproducibility of the fabricated flexible LC device was remarkably enhanced against external perturbation when compared with the conventionally-fabricated device, as the adhesive structure between the two substrates improved the cell gap uniformity and mechanical stability against bending deformation.

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