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Fabrication of poly(methyl methacrylate) microsphere added pressure-sensitive adhesives and their physical characteristics

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Abstract Pressure-sensitive adhesives (PSAs), which prevent an optical film being shrank under high temperature and high humidity conditions thus protecting light-leakage phenomenon resulting from the stress induced, were synthesized in this study. Such phenomenon occurs in the edge of an LCD panel because the stress is concentrated on its edge and distorts the absorbance axis of a polarizer. To enhance performance of the PSAs, spherical PMMA microbeads were synthesized and added into the acrylic-based polymeric PSAs in this study and then light-leakage properties of each PSAs with spherical microbeads were evaluated by the light-leakage pictures of the samples. Dynamic storage modulus (G′) of the samples was also measured by a rotational rheometer and then correlated with light-leakage characteristics.

Introduction

Pressure-sensitive adhesives (PSAs), which effectively adhere to various substrates and are relatively easy to re-peel, have been widely applied in various engineering areas of the construction field and the manufacture of household goods, automotive and stationary goods because they adhere to a substrate in a short time with a little pressure [1–3]. The PSAs are classified by either primary material of which they are composed: rubber, acrylic polymer, and silicone, or the solvents being used: organic solvent, waterborne emulsion, and hot melt. Rubber and acrylic polymer based PSAs were widely used in the past, but the amount of waterborne emulsion or hot-melt PSAs has been increasing gradually due to environmental issues.

The PSAs have been also widely used in the liquid crystal displays (LCDs) industry. The LCDs, being used in TVs, computer monitors, notebook computers, and cellular phones have gained immense popularity in recent years due to their unique properties: they are thin, consume low power, and display pictures and video at a high resolution with low cost. In general, LCD has a cell containing liquid crystals, and it is sandwiched between two crossed absorption-type sheet linear polarizing films. The basic structure of a polarizing film for an LCD module is illustrated in Fig. 1a. The linear polarizer is usually made of a stretched poly(vinyl alcohol) (PVA) film containing dichroic dyes with two protective triacetyl cellulose (TAC) films, whose total thickness is about 200 μm. Such a linear polarizer has strong absorption over the entire visible wavelengths along the stretched direction, in which the iodine-PVA complexes are functioned as dichroic dyes, and they selectively absorb a part of light oscillating in the same direction of the stretched PVA film. The PSAs are generally used in order to fix polarizing film on the both side of LC cell, thus playing an important role in aspect of optical properties and the manufacturing process of LCD panel. Nowadays, the main roles of PSA become multi-functional with such as light control performance, electrostatic discharge performance, and anti-glittering performance so as to satisfy each characteristics and each applications. Especially in the case of small-sized LCD application, the resolution of LCD becomes very important. Therefore the polarizing film with an anti-glare film (AG) has to control the glittering.

Figure 2 demonstrates the glittering phenomenon of high resolution LCD. However it is not easy to satisfy anti-glittering performance by optimizing the AG film itself. Therefore, some approaches to develop diffusive PSA in the

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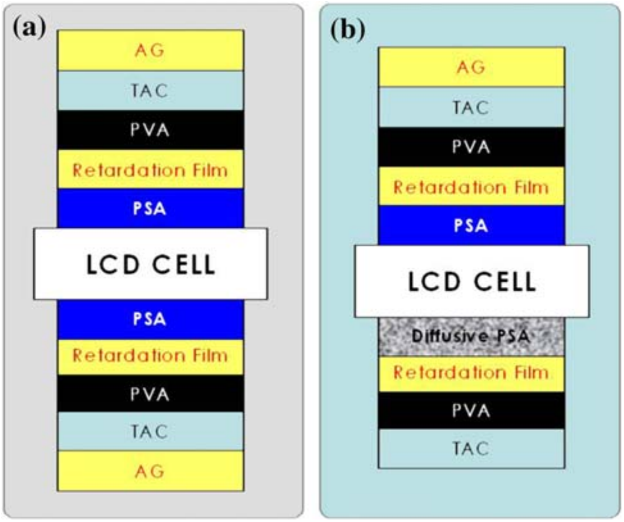

Fig. 1 Basic structures of LCD modules using **a** general type polarizing film and **b** polarizing film with diffusive PSA

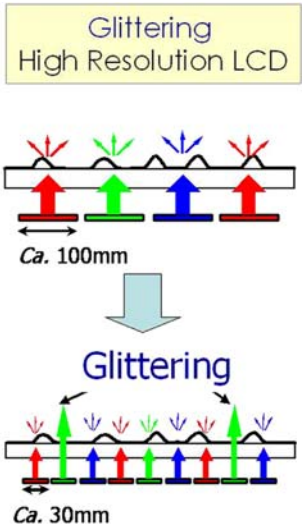

Fig. 2 Glittering phenomenon of LCD

polarizing film itself were attempted as shown in Fig. 1b. With respect to reducing glittering phenomenon, applying a diffusive function in the PSA is one of the effective approaches. Therefore, polymeric microbeads were added into the PSAs based on effect of particle size and composition of the emulsion [4] such as particle size and particle size distribution effect on the latex produced by miniemulsion system [5]. Effects of polymer molecular weight and cross-linking reactions on the end-use properties of the microsphere added water-based acrylic pressure-sensitive adhesives were also investigated [6]. Furthermore, durability of the LCD polarizer was found to be related with the stress relaxation of the pressure-sensitive adhesive system [7]. However the diffusive PSA might decrease its polarization efficiency. Therefore, PSA for the polarizing film must have a good reliability at high temperature and high humidity as well as at extremely low temperature for the stable durability of LCD applications [8–11].

In this paper, among various PSAs such as urethane-based, silicone-based, and acrylic-based polymer, the efficiency of diffusive acrylic-based polymer PSA for the improvement of light leakage was investigated. Especially, the effect of adding microbeads in PSAs on improvement of light leakage was examined by the light-leakage pictures of the samples and then their dynamic storage modulus (G′) was measured by a rotational rheometer to be correlated with light-leakage characteristics regarding the hardness of PSA as the storage modulus increases.

Experimental

Poly(methyl methacrylate) (PMMA) microbeads [12–14] were prepared by a dispersion polymerization method [15–17], one of the most popular methods for synthesizing monodisperse polymer microparticles [15–18]. The purified 10 wt% of methyl methacrylate monomer (MMA, Aldrich, USA) and a 0.1 wt% of a radical initiator of 2,2′-azobisisobutyronitrile (AIBN, Aldrich, USA) were dissolved in methanol containing 4 wt% of poly(vinyl pyrrolidone) (PVP, ISP, USA) as a stabilizer at room temperature. After removing oxygen by purging nitrogen, the reaction mixture was heated to 55 °C and then kept for 24 h. The synthesized spherical microparticles were sufficiently washed by methanol and then dried in vacuum oven at 80 °C for 24 h. Surface morphology of the fabricated spherical microbeads was examined by scanning electron microscopy (SEM, S-4300SE, Hitachi, Japan) as shown in Fig. 3a with a size of approximately 4.54 μm and a narrow size distribution as confirmed from Fig. 3b.

Using a reaction vessel consisted with a cooling tube, a nitrogen introducing tube, a thermometer and an agitator, 98.5 parts of butyl acrylate (BA), 0.5 part of acrylic acid (AA), and 1.0 part of hydroxy ethyl acrylate (HEA) were added together with toluene. The mixture was subjected to a reaction at 60 °C in a nitrogen gas stream for 4 h. After that, toluene was again added into the reaction liquid to obtain a solution (with a solid matter concentration of 30%) containing an acrylic-based polymer with a weight average molecular weight of 1,100,000 g/mol (measured by GPC). Mixed into the acrylic-based polymer solution were 0.15 part of a cross-linker, a kind of TDI-type isocyanate, 0.2 part of a silane-coupling agent; and four different amounts of 0, 5, 15, and 25 parts of PMMA spherical microbeads for each sample. Finally, four different PSA samples relative to 100 parts of a solid matter of the acrylic-based polymer solution with and without PMMA microbeads were prepared as shown in Table 1.

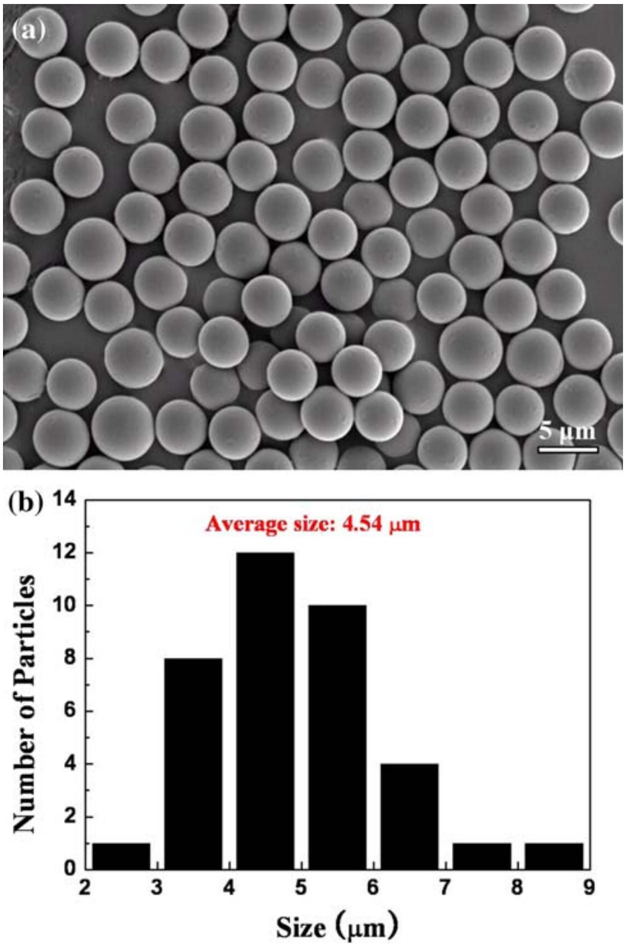

Fig. 3 **a** SEM image of spherical PMMA microbeads and **b** particle size distribution of the PMMA microbeads

A PSA layer with a thickness of 25 μm was obtained by coating the PSA on a separator constituted of a polyester film surface treated with a silicone-based release agent. The PSA layer was transferred onto one surface of a polarizing plate from the separator on which the PSA layer was formed to thereby fabricate a pressure-sensitive adhesion-type polarizing plate. Previously, we fabricated a thickness of 25 μm the PSA layer onto the release film. In order to measure dynamic rheological characteristics of the PSAs especially from a temperature-sweep test, each PSA layer was laminated for making the film of 0.5 mm thickness. Dynamic rheological characteristics such as time-sweep test and temperature-sweep test were measured by a rotational rheometer (MCR300, Physica, Germany) with a parallel-plate geometry (diameter: 25 mm). Measurements were conducted with 0.5 mm gap distance of parallel plate. Prior to both time sweep and temperature sweep measurements, an amplitude-sweep test was carried out under a constant angular frequency of 10 s^{-1} in order to find a linear viscoelastic region. The time-sweep test was performed using uncross-linked PSA samples, that is, unfabricated onto the release film in order to investigate the time-dependent rheological properties of PMMA microbeads-dispersed PSA. The time-sweep test was performed at room temperature with constant strain (0.1%) for 7 days. In addition, the temperature-sweep test was performed using the 100% cross-linked PSA samples which were fabricated onto the release film and laminated for the film of 0.5 mm thickness. The prepared 100% cross-linked PSA samples were investigated at temperature range of 20–80 °C with constant strain of 0.1% [19–21].

To evaluate the light leakage, the pressure-sensitive adhesion-type polarizing films (each size was 100 mm in length and 100 mm in width) were used. The various samples were adhered to both surfaces of a 0.7 mm thick non-alkali glass plate. The composites were then treated in an autoclave at 50 °C under 5 atm for 20 min so as to achieve perfect adherence. After the samples were treated at 80 °C for 100 h, they were placed on a backlight with 10,000 cd and light leakage was visually observed considering the evaluation criteria. As shown in Fig. 4, a CCD camera is located in front of a sample and takes full pictures of the samples to compare the light-leakage conditions.

Results and discussion

Figure 5 shows the time-sweep test for the PSAs as a function of temperature, in which the storage modulus (G′)

Table 1 Compositions of PSA samples

	Composition of PSA				Polymeric beads			Cross-linker
	BA [pbw][a]	AA [pbw][a]	HEA [pbw][a]	Refractive index[b]	Shape	Refractive index[b]	Weight fraction [pbw][a]	
PSA1	98.5	0.5	1.0	1.42	Spherical	1.43	0	0.15
PSA2	98.5	0.5	1.0	1.42	Spherical	1.43	5	0.15
PSA3	98.5	0.5	1.0	1.42	Spherical	1.43	15	0.15
PSA4	98.5	0.5	1.0	1.42	Spherical	1.43	25	0.15

[a] [pbw]: part by weight

[b] Refractive index: measured by Abbe refractometers

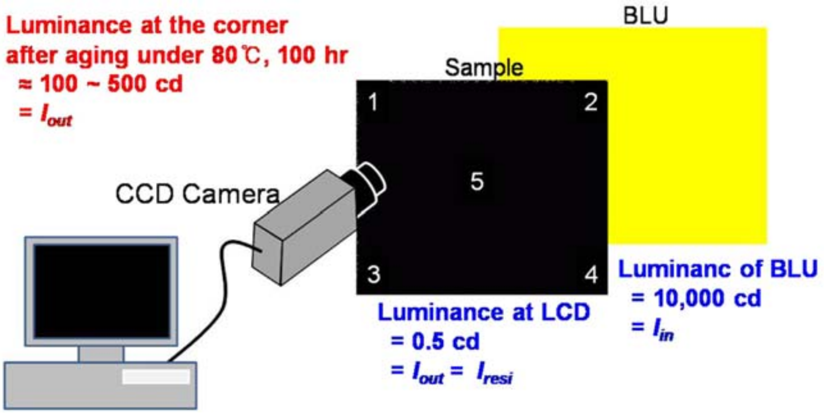

Fig. 4 CCD camera for measuring light-leakage phenomena

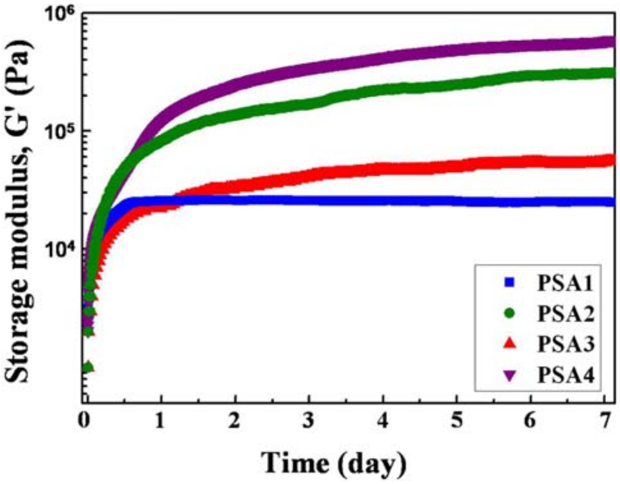

Fig. 5 Storage modulus (G′) as a function of time of polymeric beads-dispersed PSAs

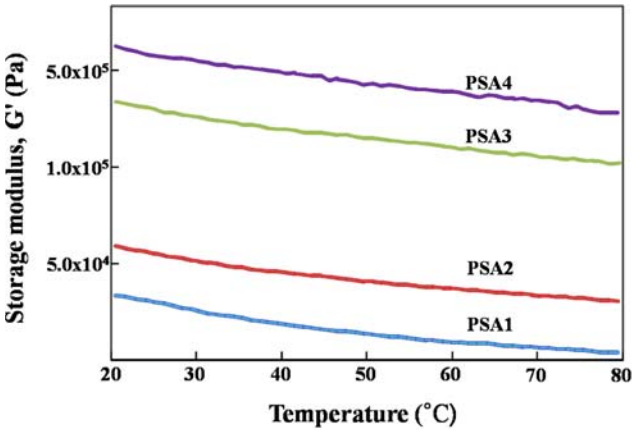

Fig. 6 Storage modulus (G′) vs. temperature of polymeric beads-dispersed PSAs

of the PSAs was found to be enhanced with increased PMMA bead contents. The PMMA beads behaved like reinforcing fillers in the PSA matrix, indicating that contribution of the PMMA beads is one of the main factors affecting the modulus of the PSAs [22, 23]. In addition, the storage modulus (G′) of the PSA1 sharply increased compared with other PSA samples and then maintained constant storage modulus (G′) value. It represented that as we increased the PMMA bead contents, the PMMA beads disturbed cross-linking behavior of the PSA while increasing the G′. Therefore, based on the time-sweep rheological test, we can conclude that the PMMA microbeads are enhancing the hardness (G′) of the PSA while retarding the time for perfect cross-linking of the PSA.

Furthermore, as shown in Fig. 6, storage modulus (G′) of the samples measured by the rotational rheometer exhibits monotonic decrease in the region of the measured temperature because polymer chain mobility becomes larger with the increase of temperature [24–27]. Storage modulus of the PSA was also found to increase as a function of the amount of PMMA microbeads. Due to the reinforcing effect of the PMMA particles to a composite system with partially cross-linked polymer of the PSA, the composite PSA shows more solid-like characteristics by increasing particle content [28–30]. Especially, the solid-like behavior of PSA should be related to the light-leakage properties in the LCD application. It has been known that the stiffer PSA shows the stronger resistibility in the dimensional stability of polarizer [31–33]. Furthermore, because the PMMA microbeads used [34] here have similar refractive index of 1.43 compared with the PSA matrix of 1.42, there is little light scattering in the composite PSA layer. It can contribute to minimize a loss of light coming from the back-light unit (BLU) in the LCD system [35].

Our work was carried out that the amount of light leaked on the LCD panel decreases as the hardness (related to storage modulus) of the PSA matrix increases [36, 37]. Figure 7 shows the light-leakage phenomena of the polymeric microbead-dispersed PSA in which the full pictures of light leakage on the samples were taken to compare with which the one was better. The light-leakage phenomena were controlled by the increasing weight fraction of

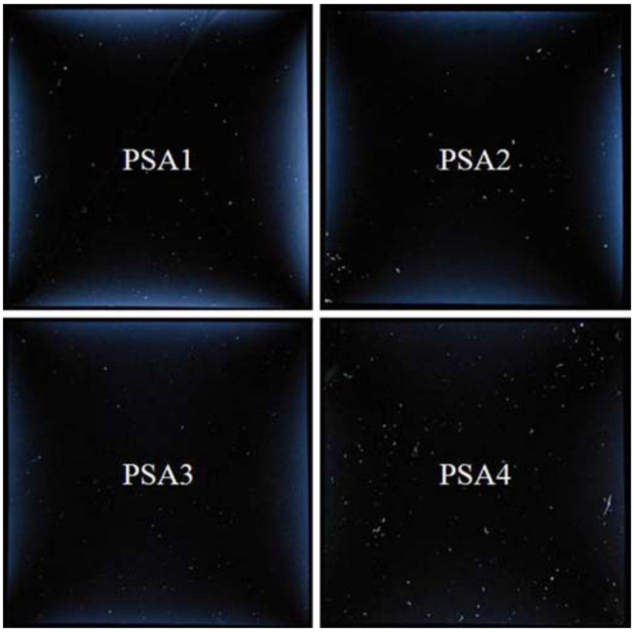

Fig. 7 Light-leakage phenomena of the polymeric beads-dispersed PSA

polymeric beads in the PSA matrix. It seems that the one of major role of polymeric beads in the PSA interferes the mobility of the matrix polymer of PSA [38–40]. Therefore it is not easier to shrink the film of polymeric beads-dispersed PSA rather than that of PSA without polymeric bead. Consequently, light leakage got improved as we increased the weight fraction of polymeric microbeads. At a fixed PMMA microbead weight fraction of 25 wt%, we can expect particle size will influence the improvement of glittering problem. As the particle size becomes smaller, number of particle content along with surface areas will increase, thus improves glittering problem; however, smaller particles will deteriorate optical properties (depolarization) due to the scattering of small particles. Therefore the proper size of PMMA is important. Furthermore, even though we do not examine the PSA with over 25% of PMMA (max. content) beads contents, we can predict that the PSA with higher contents of PMMA beads will decrease both optical performance (depolarization) and adhesion strength.

Conclusion

Micron-sized PMMA beads were synthesized by a dispersion polymerization method, and then mixed together in the PSA with different weight fraction. Two different dynamic rheological tests of time sweep and temperature sweep were investigated in linear region for the PMMA beads-dispersed PSA samples. Storage modulus (G') of the polymeric beads-dispersed PSA was found to be dependent on the weight fraction of polymeric beads, representing the relationship between hardness of the PSA and the light-leakage phenomena. In addition, light-leakage phenomena of polymeric microbeads-dispersed PSA showed the effective performance by increasing weight fraction of polymeric beads. However, adding polymer beads were increased the hardness and became less show the light leakage but it took long time for cross-linking PSA. The light-leakage phenomena distinctly improved even though the cross-linking time was delayed. Consequently, the polymeric microbead-dispersed PSAs are harder than PSAs without polymeric beads, thus improving the light-leakage phenomena.

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