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Preparation of Composite Adhesive Spacer Particles for Flexible LCD Application

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Adhesive spacer particles were fabricated to ensure the uniform cell gap between the plastic substrates for application in flexible liquid crystal display (LCD). Surface modification of rigid silica particles was performed to render adhesive polymer layer on the surface of the silica particles while maintaining the rigid properties. Methyl methacrylate (MMA) and styrene were graft-polymerized onto silica surface by UV irradiation and characterization experiments confirmed the formation of covalent bond between polymer and silica particle. FE-SEM image analysis indicated substantial increase in mean diameter of the particles after UV-induced grafting of the monomers. T-peel test value of 2.7 N/cm for PMMA film/Polyimide-PES substrate system also confirmed the applicability of these composites in flexible LCD.

Keywords: adhesive spacers; flexible LCD; PMMA; PS; silica; UV-induced grafting

1. INTRODUCTION

Conventional liquid crystal displays (LCD) typically include two opposed glass electrode substrates, spacers and a liquid crystal substance interposed between the aforementioned electrode substrates. The spacers, which have mono-dispersed size distribution, are usually randomly dispersed within the cell gap, such as by a spraying technique [1].

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These spacers are employed in order to maintain LC layer uniform and constant in thickness.

Spacers for conventional LCD panels include rigid silica particles made by the sol-gel method, the calcined product of the silica particles, styrene or divinylbenzene type polymer particles, and other organic/inorganic particles [2–4]. These spacers require certain performance characteristics, e.g., high resistance to chemical, pressure and temperature. Among the above-mentioned, rigid silica particles are one of the most commonly used spacers for their high compression resistance and less deformity during assembly.

Flexible LCD is gaining much interest as the next revolution in information technology that will enable lighter-weight, lower-power, more-rugged systems for portable and vehicle applications. However, the developments of components for such devices including high performance transparent plastic substrates [5] and spacers with more stringent requirements are the key in realizing flexible LCD. Flexible LCD requires that the spacer particles be fixed to the plastic substrates, and spacer with a highly adhesive surface will not move around in the LCD cell gap, which avoids scratching of alignment layers and uneven cell gap spacing.

Surface modified silica particles with polymer ligands will have the desired adhesive properties while maintaining the rigid properties of silica particles. The organic groups can either be grafted to preformed particles (“post-synthesis modification” method) or introduced during the particle synthesis (*in situ* method) [6]. In this study, we employed UV-induced graft polymerization of MMA and styrene monomer onto silica particles which has been proven to be an effective method in our previous work [7] to render polymer layer to rigid silica particles. This adhesive layer becomes adhered to plastic substrates when heated. Adhesive strength or binding force of silica-organic composites to polyimide alignment layer was measured [8] and compared to the values of patented adhesive spacers for peripheral sealing section of the conventional LCD.

2. EXPERIMENTAL

Materials and Reagents

Methyl methacrylate and styrene were purchased from Aldrich Chemical Co., and used after removing the inhibitor using inhibitor-remover columns (also purchased from Aldrich). Methanol, ethanol and benzophenone were purchased from Aldrich and used as received. THF was purchased from Duksan Pure Chemical Co., Korea. PMMA

powder was purchased from Aldrich. Transparent PES plastic substrates were donated from i-Components, Co., Ltd., Korea.

The spherical silica particles in micron size were prepared by sol-gel method using tetraethyl orthosilicate (TEOS) as the main reactant. The details of the silica synthesis can be found elsewhere [9].

Surface Modification of Silica Particles by UV-Irradiation

We have previously reported detail experimental procedures for UV-induced grafting of MMA onto nano-scale silica particles [7]. In this work, we applied the same procedures to graft MMA and styrene monomers onto micron-scale silica particles. In a typical graft polymerization reaction, a 150 mm Petri dish was charged with 2.5 g of silica, 25 g of ethanol and 0.05 g of benzophenone, and this reaction mixture was irradiated for 20 min, during which UV light was irradiated through a 1000 W high-pressure mercury lamp from Oriel Co. (London, UK). After 20 min, 2.5 g of monomer was charged into the reaction mixture and UV light was again irradiated for a prescribed time. Three centrifugation and redispersion cycles in ethanol and THF were used to clean the polymer-grafted silica dispersion. The particles were dried in vacuum before characterization.

Adhesion Strength Tests

To evaluate the adhesion or binding strength between the silica-organic composites prepared by UV-irradiation and polyimide film, the "Scotch-tape peel test" was performed. The PI solution was spin-coated on a glass substrate at 3,000 rpm for 30 seconds and cured at 230°C for 30 min and then, PI-coated surface of the substrate was rubbed. A batch of the composites was scattered on this PI coated-glass substrate and heat-treated at 180°C for 1 hr. It was then cooled to room temperature. An adhesive type, a poly(vinyl chloride) adhesive tape for electric insulation by Temflex™ 3M 1711, was applied to the composite-bearing surface of the PI coated-glass substrate, pressed there against under 2 g_f/cm² for three seconds, and then ripped off the film. The adhesive strength of the composites to polyimide layer was determined by counting the number of particles remaining on the film and calculating the ratio of residue by the following formula from U.S. Patent Number 5,851,605.

Adhesive strength (%)

$$= \left(\frac{\text{number of particles remaining after the test}}{\text{number of particles existing before the test}} \right) \times 100$$

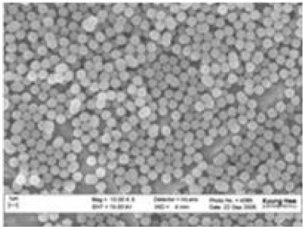
Adhesion strengths of PMMA film to PI-PES substrate are also measured by T-peel test (ASTM D1876) for better evaluation of the

applicability of these composites in flexible LCD. Thin transparent PMMA films of varied thickness were prepared by solution casting method (3 PMMA wt% in THF) and placed on the PI-glass substrate. Then, this PMMA film/PI-glass substrate system was subjected to a pressure of 50 N for 1 hour at 150°C and 180°C. 8 cm long and 2 cm wide sample were used for 90° peel test. Instron 5844 (Norwood, MA, USA) was used for the measurement of the peel strength of PMMA film to PI-glass substrate with a load cell of 10 kN at 1.5 mm/min. PMMA film/PI-PES plastic substrate system was also prepared. PI solution was spin-coated on high performance transparent PES plastic substrate (i-Components, Co., Ltd., Korea) with 300 µm thickness. And cured at 180°C for 30 min, and then the PI-coated surface of the substrate was rubbed. Then, aforementioned PMMA film was placed on this PI-coated PES plastic substrate and was subjected to the heat-press as with the PMMA film/PI-glass substrate system. 9 cm long and 1.5 cm wide sample were used for 180° peel test. The tests were carried out at ambient temperature, and at least two specimens of each thickness were tested for all samples.

3. RESULTS AND DISCUSSIONS

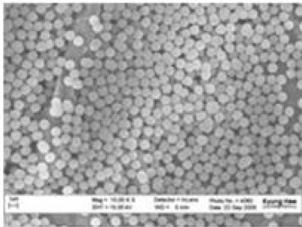
Characteristics of Silica-polymer Composites

To assess the increase in mean particle diameter after UV-irradiation, field-emission scanning electron microscopy (FE-SEM, LEO SUPRA 55, Carl Zeiss, Germany) image analysis was performed on silica and silica-polymer composite particles. Figure 1 shows the FE-SEM photographs of silica, PMMA-grafted composites for 20 and 30 min, and PS-grafted composites for 20 and 30 min. Substantial increase in mean diameter was observed for both PMMA-grafted and PS-grafted particles, resulting in 11 and 12% increase in volume of the particles, respectively. The coefficient of variation for the particles is also noted in the figure. It is an index for the accuracy of the particle diameter, and defined as the standard deviation divided by the mean particle diameter. Hisamitsu *et al.* reported that a spacer for a LCD requires the C.V. of the particle diameter to be less than 10%, preferably less than 6% [8]. If this coefficient of variation exceeds 10%, the spacer used in a LCD panel will not be able to retain the liquid crystal layer at a uniform and constant thickness, causing image unevenness. It is shown on the figure that both silica-PMMA and silica-PS composites have C.V. of less than 6%. Figure 2 shows the effect of reaction time on the grafted-polymer layer thickness for MMA and styrene monomers, respectively. The particle size gradually increases and reaches



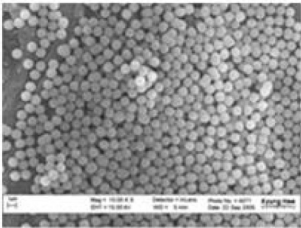
(a)

Pure Silica Particles #36
Mean: 1.175µm
C.V.: 1.45%



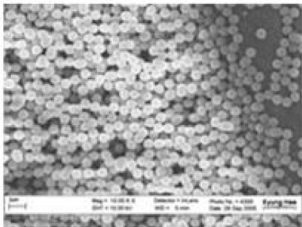
(b)

PMMA/Silica, 20min
Mean: 1.211µm
C.V.: 1.65%



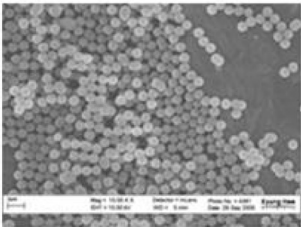
(c)

PMMA/Silica, 30 min
Mean: 1.216µm
C.V.: 2.30 %



(d)

PS/Silica, 20min
Mean: 1.204µm
C.V.: 1.50%



(e)

PS/Silica, 30 min
Mean: 1.220µm
C.V.: 1.48 %

FIGURE 1 FE-SEM photographs of (a) Pure silica particles (b) and (c) PMMA-grafted silica particles after 20 min and 30 min of irradiation, (d) and (e) PS-grafted silica particles after 20 min and 30 min of irradiation.

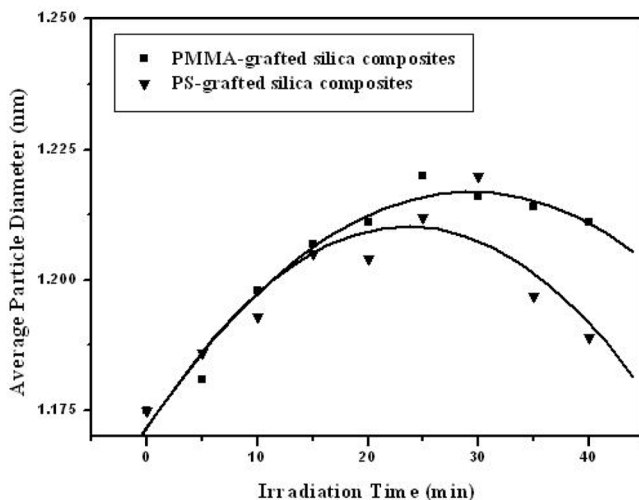


FIGURE 2 Effect of irradiation time on mean particle diameter of polymer-grafted silica composite particles.

the maximum diameter then decreases for both monomers indicating that polymer-layer thickness can be controlled and optimum thickness can be obtained.

FT-Raman Spectroscopy (RFS-100/S, Bruker, Germany) analysis was performed to confirm the successful grafting of monomers and the formation of the covalent bond between the silica surface and polymer chains as previous reported for nano-scale silica particles [7]. Figure 3 shows the spectra of PMMA-grafted and PS-grafted silica particles, respectively, along with the pure silica particles for comparison. In Figure 3(a), PMMA-grafted silica composites showed new vibration peaks at 1031 and 1003 for Si–O–C bond. In Figure 3(b), PS-grafted silica composites showed new vibration peaks 1052 and 812 cm^{-1} for asymmetric and symmetric Si–O–C stretching, respectively. The locations of these peaks are in good agreement with previously reported values [7,10].

Above experimental results confirmed the formation of adhesive polymer layer on the surface of silica particles by a covalent bond between the silica and polymer chains, resulting in the immobilization of the particles when used as the spacers in flexible LCD.

Adhesion Strength

Figure 4 shows the FE-SEM photographs of the composites before and after the Scotch-tape peel test. Three photographs were taken from a

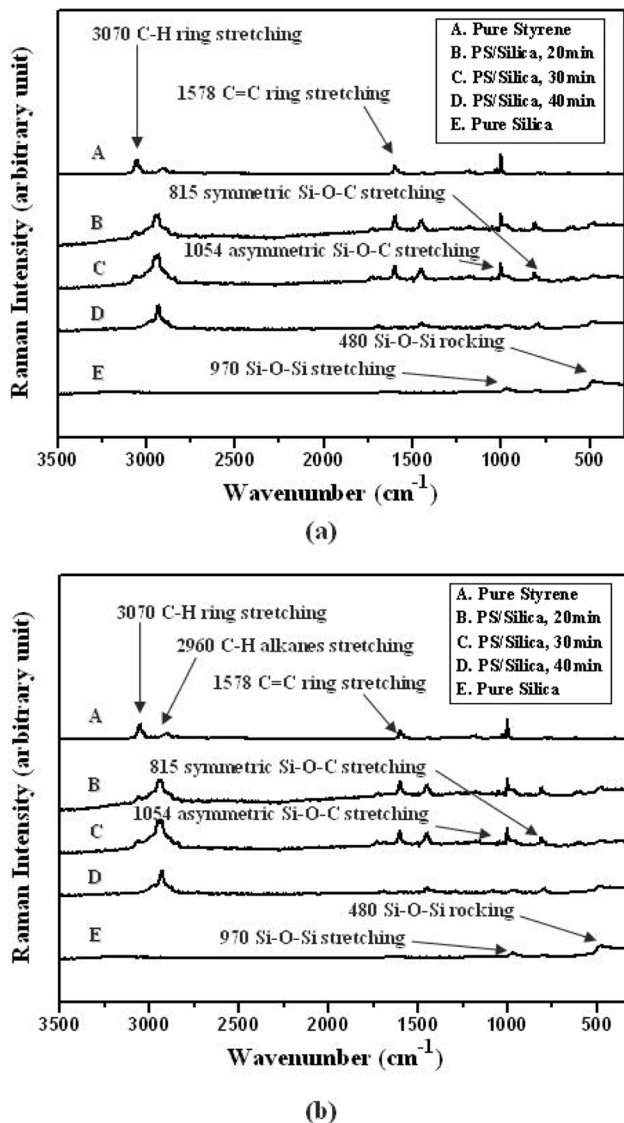


FIGURE 3 The Raman Spectra of (a) PMMA-grafted silica particles compared with pure silica and PMMA sample and (b) PS-grafted silica particles compared with pure silica and PS sample.

marked area of 0.785 mm^2 and then the number of the composites were counted and averaged. Table 1 shows the number of the particles before and after the test, and adhesive strength calculated from the

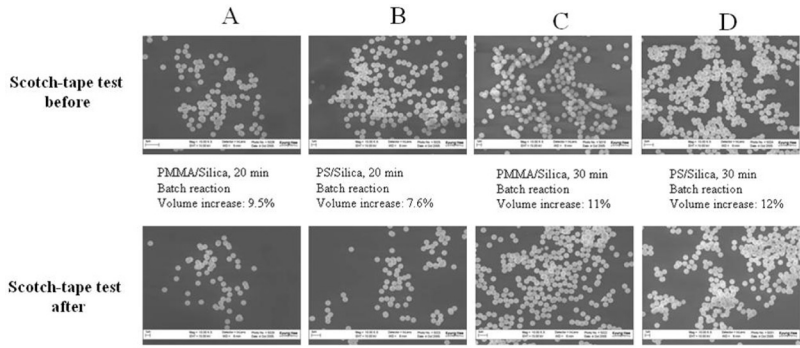


FIGURE 4 FE-SEM photographs of heat-treated polymer-grafted silica particles on PI film before and after the peel test. (dry scattered method).

formula in the experimental section. Composites A and B are PMMA-grafted silica particles, and C and D are PS-grafted silica particles. Adhesives strength of the composites to polyimide layer was above 60% except for Composite C. Adhesive strength of the PMMA-grafted silica particles was generally greater than PS-grafted silica particles. Composite B, a PMMA-grafted silica composite, showed the largest adhesive strength of 80%. Adhesive strength of patented adhesive spacers for LCD panel, synthesized by the impact method in a high-speed air current, to polyimide alignment layer has been reported. The values ranged from 72 to 79% by the same testing method [8]. Thus we can safely conclude that the adhesive strengths of our composites are very comparable to the values of currently used adhesive spacers.

For two flexible polymer films the T-peel test is the most convenient method to compare the bonding strength and has been used as a standard method [11,12]. Adhesion strengths of PMMA film/PI-glass

TABLE 1 Adhesion Strength of Four Polymer-Grafted Silica Particles to PI Film using Scotch-Tape Method

Sample description	Number of composite particles on PI film before “Scotch-tape test”	Number of composite particles left on PI film after “Scotch-tape test”	Adhesion strength (%)
A	97	58	60
B	177	92	52
C	269	219	80
D	360	268	74

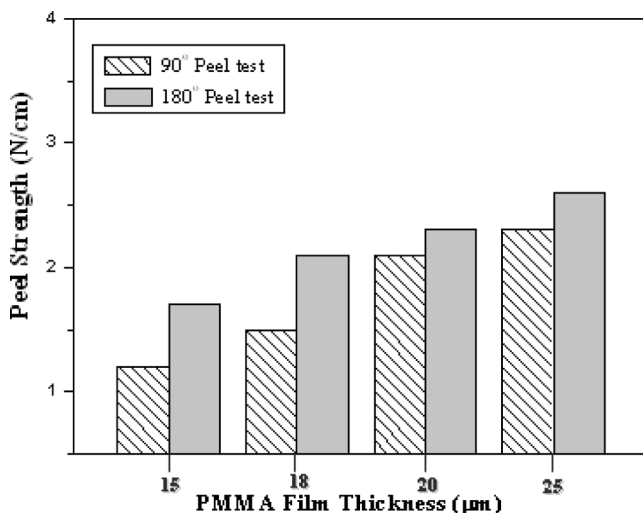


FIGURE 5 The peel strength of the laminates measured by UTM at room temp at 1.5 mm/min.

substrate and PMMA film/PI-PES substrate systems were estimated by 90° and 180° T-peel test (ASTM D1876) for better evaluation of the applicability of silica-PMMA composites in flexible LCD. For the brief notation, F/PI-G and F/PI-PES represent the PMMA film/PI-glass substrate and PMMA film/PI-PES substrate systems. Figure 5 shows the 90° and 180° peel strengths of F/PI-G systems of different PMMA film thickness. Results indicated a gradual increase in the peel strength with increase in the thickness of the PMMA film. The values ranged from 1.2 N/cm to 2.4 N/cm. The similar gradual increase with increase in the PMMA film thickness was observed as in Figure 5. The highest value obtained was 2.71 for PMMA film with 25 μm thickness. Since Lee and others reported that peel strength of around 3.0 N/cm is acceptable to most micro-electron applications, F/PI-G system with 2.4 N/cm and F/PI-PES system with 2.7 N/cm peel strength can be considered strong enough [13]. Thus, T-peel test results confirm the applicability of silica-PMMA composites as spacer in flexible LCD.

4. CONCLUSIONS

Adhesive spacer particles were fabricated by UV-irradiation of MMA and styrene monomer onto silica particles. Characterization of these PMMA and PS-grafted silica particles confirmed the successful formation of adhesive polymer layer onto silica surface by a new covalent

bond, a Si–O–C bond. Adhesion strength of the composites to polyimide alignment layer was evaluated by “Scotch-tape peel test” and T-peel test. Highest adhesion strength obtained from “Scotch-tape peel test” was 80%, which is very comparable to those of patented adhesive spacers. The applicability of these composites as spacer particles was also confirmed by the results of the T-peel test. Adhesion strength of 2.5 N/cm, obtained for PMMA film/PI-PES substrate system, can be considered strong enough for micro-electronic applications.

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