



Improvement of thermal stability of UV curable pressure sensitive adhesive by surface modified silica nanoparticles



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ABSTRACT

Pressure sensitive adhesives (PSAs) with higher thermal stability were successfully prepared by forming composite with the silica nanoparticles modified via reaction with 3-methacryloxypropyltrimethoxysilane. The acrylic copolymer was synthesized as a base resin for PSAs by solution polymerization of 2-EHA, EA, and AA with AIBN as an initiator. The acrylic copolymer was further modified with GMA to have the vinyl groups available for UV curing. The peel strength decreased with the increase of gel content which was dependent on both silica content and UV dose. Thermal stability of the composite PSAs was improved noticeably with increasing silica content and UV dose mainly due to the strong and extensive interfacial bonding between the organic polymer matrix and silica.

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1. Introduction

Pressure sensitive adhesives (PSAs) are semi-solid phase materials with viscoelastic properties and adhesion strength on solid substrates after applying a light contact pressure in a short contact time. PSAs are generally used in a wide range of fields including medical products, electronic devices, and the construction and automobile industries [1]. The use of acrylic polymers in PSAs is growing because of their resistance to oxidation and transparency under exposure to sunlight [2,3]. The PSA films for silicon wafer require both higher reliability and thermal stability to adapt the rapid development of integrated semiconductor technology.

The linear acrylic chains in PSAs are not generally crosslinked with chemical bonds but connected physically by the hydrogen bonding interactions with the carboxylic groups. The reversible hydrogen bonding of acrylic PSAs results in the relatively poor thermal stability [2,4]. Therefore, the mobility of molecular chains in PSA has to be restricted intentionally in order to improve the thermal stability. One of the effective methods to restrict the molecular mobility is to crosslink the acrylic chains in PSAs.

Compared to the traditional thermal curing method, UV curing method has various advantages such as faster curing speed, lower power consumption, and lower curing temperature, resulting in the proper application to thermally sensitive substrate. The UV curable materials are widely used in the fields such as coatings,

adhesives, paper, microelectronics, three-dimensional precision molding processing, and laser recording materials [5–7]. Acrylic copolymer, epoxy resin, and polyurethane are usually employed as important main components in the UV curing system. In addition, the properties of the UV-cured acrylic copolymer could be further improved in many aspects [8].

The combination of both organic polymers and inorganic fillers into nanocomposites has attracted considerable attention in recent years, as these materials offer the prospect of new synergetic properties that originate from their organic and inorganic components [9–12]. The silica/polymer nanocomposites have attracted considerable interest among various organic/inorganic nanocomposites because of the potential uses as aerospace materials, structural materials in electronics, sensors, and materials in other various industries [13–20]. The shape-memory polyurethane-silica nanocomposites prepared with fumed silica and hydrolyzed 3-amino-propyltriethoxysilane showed the increase in both modulus and tensile strength although some aggregation of fumed silica particles in the polyurethane matrix was found [21,22].

Many preparation methods for nanoparticles/polymer composites via UV curing have been studied recently. The in situ synthesis of noble metal nanoparticles in a polymer matrix has been performed by the simultaneous photopolymerization and photoinduced electron transfer triggered by UV irradiation resulting in the unique properties and structural characteristics [23–26]. Another approach to prepare the nanoparticle/polymer composite involves the uniform dispersion of inorganic nanoparticles in the liquid monomer formulation followed by photopolymerization in order to trap the nanoparticles in the photocrosslinked network

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and thus to avoid their macroscopic agglomeration. A variety of hybrid polymer composites have been thus prepared by photoinduced polymerization of multifunctional acrylic monomers in the presence of various nanoparticles with spherical, rod or plate-like shapes for the highly potential applications in advanced technologies [27–29]. Photopolymerizable silane coupling agent $R'Si(OR)_3$, where R' included an unsaturated carbon double bond susceptible to UV polymerization, was employed as precursors for the sol–gel reactions to prepare hybrid polymer composites. The polysiloxane network was formed inside the polymer matrix after a preliminary sol–gel stage implying a series of hydrolysis and condensation reactions. The crosslinked organic/inorganic hybrid composites were finally formed by UV irradiation [30–33].

Despite of the many researches performed on the preparation of silica/polymer nanocomposites, acrylic copolymer/silica nanocomposites have not been studied in depth yet for the PSA applications in terms of thermal stability and adhesive property improvement to our best knowledge. The improvement in thermal stability of temporary bonding PSAs is needed strongly in the thin wafer handling and fabrication processes especially for the multichip packaging. In this study, silica nanoparticles were surface modified to have unsaturated carbon double bonds for the possible UV curing with acrylic copolymers as presented schematically in Fig. 1. The improvement in properties of acrylic copolymer/silica composite PSAs was evaluated depending on the dispersion of silica, silica content, and UV dose.

2. Experimental

2.1. Materials

Ethyl acrylate (EA, Samchun Pure Chemical, Korea), 2-ethylhexyl acrylate (2-EHA, Samchun Pure Chemical, Korea), and acrylic acid (AA, Samchun Pure Chemical, Korea) were used as monomers for radical polymerization to synthesize the acrylic copolymer. N,N'-azobisisobutyronitrile (AIBN, Daejung Chemicals & Metals, Korea) and ethyl acetate (Junsei Chemicals, Japan) were used as a radical initiator and a solvent, respectively. Glycidyl methacrylate (GMA, Mitsubishi Rayon, Japan) bearing a reactive vinyl group was employed to modify the acrylic copolymer to have UV curable sites. 2-Methylimidazole (2-MZ, Sigma–Aldrich, USA) was used as catalyst for the reaction between epoxy group in GMA and carboxylic groups in acrylic copolymer. Nano-sized fumed silica powder (Sigma–Aldrich, USA) had the average particle size in the range from 5 to 15 nm. γ -Methacryloxypropyl trimethoxysilane (MPS, Kukdo Chemical, Korea) was used to modify the silica nanoparticles to have vinyl groups on surface. 1-Hydroxycyclohexylphenyl ketone (CP-4, Miwon Chemical, Korea) was used as the photoinitiator.

2.2. Preparation of acrylic copolymer

The acrylic copolymer base resin was synthesized with the fixed composition of 2-EHA, EA, and AA in 41.7 wt%, 41.7 wt%, and 16.6 wt%, respectively. Optimum cohesive and adhesive properties of the copolymers are usually attained by a proper balance of its molecular weight, polarity, and glass transition temperature. In this study, three different monomers were selected for the synthesis of base polymer in PSA. 2-EHA contributed the good tack property due to the lower glass transition temperature. EA contributed the higher cohesiveness of PSA due to the higher mechanical property. AA worked as the function site, which was able to react further with another chemical such as GMA.

The acrylic copolymer was synthesized by solution radical polymerization with 1.5 wt% AIBN in ethyl acetate at the solid content of

32.5 wt% in a 500-ml, four-necked, round-bottomed flask equipped with a thermometer, condenser, dropping funnel, and mechanical stirrer. The flask was charged with 50% of the monomer and solvent mixture, and then polymerization was carried out at 80 °C for 0.5 h followed by the addition of the remaining 50% of the monomer and solvent mixture over 1.5 h and the further reaction at 80 °C for 3 h under the N_2 purging. The acrylic copolymer base resin was subsequently reacted with GMA at 50 °C for 10 h to prepare the UV curable acrylic copolymer.

2.3. Preparation of modified silica

10.4 g MPS was added into the dispersion of 2 g silica nanoparticles in 78.9 g ethanol followed by immediate addition of 9 g ammonia solution (28%). The excess MPS was beneficial to the higher extent of condensation reaction between hydroxyl groups on silica nanoparticles and methoxysilane groups of MPS. The reaction solution was then stirred at 300 rpm for 24 h at room temperature. After washing with ethanol three times, the modified silica nanoparticles were dried at 60 °C for 24 h.

2.4. Preparation of UV curable acrylic copolymer/silica composite PSA film

UV curable acrylic copolymer, CP-4 (3 wt% of PSA fraction), and modified silica nanoparticles (0–10 phr of PSA fraction) were mixed intensively in a ball mill containing ZrO_2 balls at room temperature for 3 days. The mixture was casted onto a poly(ethylene terephthalate) (PET) film of 56 μm in thickness. The mixture was coated on PET to have a uniform thickness with Baker applicator (YBA-5) and then dried at 80 °C to remove the solvent. The thickness of acrylic copolymer/silica composite PSA layers after drying was about 20 μm . After removal of solvent, the acrylic copolymer/silica composite PSA film samples were placed under UV light source of various UV doses (HM1500, UMCK, Korea) in an atmosphere of air. The distance between the PSA film and the center of UV lamp was fixed at 20 cm.

2.5. Characterization

The characteristic properties of both silica and modified silica were studied with X-ray photoelectron spectroscopy (XPS, Axis-Nova, Kratos, UK) and Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, USA).

The gel contents of the UV-cured acrylic copolymer/silica composite PSAs were measured gravimetrically. The initial weight of sample (W_0) was measured before the immersion in ethyl acetate at room temperature. The sample was filtered through a 200 mesh wire net after immersion for 3 days at 60 °C followed by drying at 70 °C for 24 h and then the weight of dried sample (W_t) was measured at room temperature. The gel contents of UV-cured PSAs were calculated using the following equation:

$$\text{Gel content (\%)} = \frac{W_t}{W_0} \times 100\%$$

Thermogravimetric analyses (TGA) were done in a thermobalance (TA Instruments, TASDT Q600, Mettler-Toledo, USA) with approximately 5 mg of sample weighed in a standard alumina crucible. The temperature was raised from 25 to 500 °C at a rate of 10 °C/min under a nitrogen flow to investigate the main decomposition behavior. In addition, the samples were separately kept at 250 °C for 2 h under a nitrogen flow to investigate the thermal stability at 250 °C.

Transmission electronic microscopy (TEM) images were recorded on Tecnai F30 S-Twin (FEI, USA) at the acceleration

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