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Low-temperature solution processible, solventless and transparent silica nanoparticle-dispersed epoxy hybrid materials

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Low-temperature solution processible and solventless silica-epoxy hybrid materials composed of organically modified silica nanoparticles and epoxy monomers were successfully fabricated through simple sol-gel process and solvent evaporation. These silica-epoxy hybrid materials exhibited the homogeneous dispersion without any phase separation, aggregation, and gelation in the solventless environment due to the good surface modification of various organosilanes upon silica nanoparticles. The homogeneous dispersion between silica nanoparticles and epoxy monomers was confirmed by TEM. These homogeneously dispersed silica-epoxy hybrid materials can be formed into the films through the simple low-temperature solution coating and thermal-curing process for 30 min at 150 °C. The silica-epoxy hybrid materials showed high transmittance of above 90% in the visible wavelength regions regardless of the embedded content of silica nanoparticles. In particular, these solventless silica-epoxy hybrid materials exhibited the film formation ability with thick film thickness of several hundred μ m without any cracks and the incorporated silica nanoparticles in mechanical hardness, adhesion, and thermal stability in proportion to the embedded content of silica nanoparticles of below 1 nm.

Key words: Silica nanoparticle, Epoxy, Hybrid materials, Thermal curability, Solventless.

Introduction

Epoxy materials have been variously applied as the main matrixes due to their good mechanical, electrical, and chemical properties in the industrial fields such as insulation, protection coatings, and moldings, etc [1-5]. However, the much better properties of applied materials are required, as the industry has been developed speedily and variously. To satisfy these requirements, nowadays, hybrid materials have been widely studied due to the synergetic effect of the organic and inorganic materials through the hybridization of two materials [6-14]. Moreover, the weak properties of the hybrid materials can be compensated through the controlled incorporation of inorganic nanoparticles and organic components. These materials can be also applied to the solution process, which lead to the effective low-cost process. However, the incorporation of inorganic nanoparticles into organic matrix or other solutions can cause problems such as phase separation, precipitation, aggregation and gelation. These problems cause to the decrease of the properties of the materials such as optical, mechanical and electrical, etc. In particular, the dispersion of inorganic nanoparticles is much harder due to the difficulty in controlling viscosity and high hydrophobisity in the

solventless typed matrix or solution, which is even required in various fields by the thick film formation. Thus, the intensive studies for successful incorporation of inorganic nanoparticles into solutions are required and in particular, the dispersion of inorganic nanoparticles in solventless solution is very crucible.

In this study, we attempted to produce solventless typed hybrid materials with colloidal silica nanoparticles homogeneously dispersed in epoxy matrix. We sought to enhance the dispersion stability of the colloidal silica nanoparticles in epoxy matrix by organically grafting using organosilanes and increase the solution processability in the solventless system. In addition, we fabricated organosilane-modified silica-epoxy hybrid films with different thickness, which had high transmittance, good mechanical properties such as hardness and adhesion, high thermal stability, and low RMS roughness by using a solution-coating process with solventless silicaepoxy hybrid solution.

Experimental details

Fabrication of Organically Modified Colloidal-Silica Nanoparticles

The organically modified colloidal-silica (CS) nanoparticles (NPs) were prepared with CS in water (12 nm diameter, 30 wt% solids in water, pH 4.3, Grace co.) and organosilanes such as methyltrimethoxysilane (MTMS, Aldrich), phenyltrimethoxysilane (PTMS, Aldrich) and glycidoxypropyltrimethoxysilane (GPTMS, Aldrich).

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The surfaces of CS NPs were firstly modified with MTMS for 5 hrs under a stirring rate of 400 rpm, using a magnetic stirrer, at room temperature (RT). The weight ratio of MTMS to CS NPs was 1:6. After the 5 hrs reaction to the fabrication of the MTMS-treated CS NPs, Water and any residual product such as alcohol were replaced with ethylene glycol (EG, Aldrich) at 30 °C, using an evaporator. Then, PTMS and GPTMS were reacted with the MTMS-treated CS NPs under magnetic stirring for 20 hrs, with a stirring rate of 400 rpm at RT, for well dispersion and chemical polymerization with epoxy monomers. The weight ratio of PTMS and GPTMS to CS NPs were 0.5:6, respectively. After the reaction to the fabrication of the MTMS, PTMS and GPTMS-treated CS NPs, any residual product (such as alcohol and water) was replaced with EG at 30 °C, using an evaporator, for the hybridization of the organically modified CS NPs with epoxy monomers. Finally, the PTMS and GPTMS-treated CS MTMS, NPs homogeneously dispersed in EG could be fabricated and their solid content in EG was 30 wt%.

Fabrication of Solventless Colloidal Silica Nanoparticle Dispersed Epoxy Hybrid Materials and Films

For the synthesis of solventless CS NPs dispersed epoxy hybrid materials (HMs), EG was replaced with trimethlypropanetriglycidylether (TMPTGE, Aldrich) as an epoxy monomer at 40 °C, using an evaporator. Then, solventless CS NPs dispersed epoxy HMs were fabricated. The 0- to 30-wt% organically modified CS NPs that were stabilized through surface modification were homogeneously embedded in epoxy monomer without any solvents. These thermalcurable and solventless HMs with CS NPs and epoxy monomers were filtered and were spin-coated onto clean glass substrates and wafers. The coated solventless silica-epoxy hybrid (SEH) films were then thermally cured at 150 °C for 30 min under an air atmosphere. Consequently, thermally cured SHE (TCSHE) films were fabricated.

Characterization

Transmission electron microscopy (TEM, 300 kV, JEM 3010 of JEOL) was employed for the analysis of the size and dispersion of the organically modified CN NPs. The dispersion of CS NPs in hybrid films and their film thickness were analyzed by scanning electron microscope (SEM, S-4800, Hitachi) and optical transparency of the TCSEH films were examined through ultraviolet visible near-infrared (UV/Vis/NIR) spectroscopy. In addition, the influence of the CS NPs on the mechanical properties and thermal stabilities of films were determined through the TCSEH thermogravimetric analysis (TGA), a pencil hardness test (501 pencil hardness tester, Elcometer) and a adhesion tape test (ASTM D3359-02) and the surface properties of the TCSEH films were examined through atomic-force measurement (AFM, NanoWizard II, JPK).

Results and discussion

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Fig. 1 shows the TEM image of the CS NPs with diameters of around 12 nm, indicating the monosized and homogeneous dispersion with surface modification of the functional silanes on the CS NPs. Such monosized and homogeneous dispersion of the CS NPs is due to the surface modification of the methyl, phenyl and glycidyl silanes on the CS NPs through the sol-gel technique. The organically modified CS NPs were not agglomerated and phase-separated even upon exposure to a high-energy electron beam (i.e., 200 kV TEM), as shown in Fig. 1. Moreover, the CS NPs could be homogeneously mixed with epoxy monomers even in solventless condition, and the mixed hybrid solutions remained transparent and stable, without phase separation and precipitation, within all the composition ranges of $0 \sim 30$ wt% CS NPs in epoxy monomers.

The hybrid materials consisting of organically modified CS NPs in epoxy monomer can be cured through thermal induced polymerization due to their thermally curable epoxy groups. The silica-epoxy hybrid films can be simply fabricated through low







Fig. 2. (a) the control of TCSHE film thicknesses depending on the RPM of spinning speed, (b) SEM cross section view of the thermally cured SEH film with a thickness of around 233 μ m, (c) around 12 μ m, and (d) SEM internal perspective view of SEH film fabricated by using thermally curable SEHMs with 7 : 3 weight ratio in hybrid composition of epoxy and CS NPs.



Fig. 3. Optical transparency of the TCSEH films with 0- to 30wt% organically modified CS NPs in epoxy matrix.



Fig. 4. (a) the hardness and (b) the adhesion of the TCSEH films coated on glass substrates as a function of organically modified CS NPs contents in epoxy matrix.

temperature curing process at 150 °C for 30 min. More importantly, the thin films with a thickness of several or ten µm as well as the highly thick films with a thickness of above 200 µm could be efficiently formed by using the solventless SEHMs without any cracks and separations. Fig. 2 shows (a) the control of TCSHE film thicknesses depending on the RPM of spinning speed, SEM cross section view of the TCSEH film with a thickness of (b) around 233 µm, (c) around 12 µm, and (d) SEM internal perspective view of SEH film fabricated by using thermally curable SEHMs with 7:3 weight ratio in hybrid composition of epoxy and CS NPs. As shown in Fig. 2, the SHE films with various thicknesses could be fabricated by using solventless SEHMs by simple thermal curing process without any crack and the CS NPs in epoxy matrix were homogeneously dispersed.

Fig. 3 shows the optical transparency of the TCSEH films with 0- to 30-wt% organically modified CS NPs in epoxy matrix. The analysis of the optical transmission of the TCSEH films that had been used to coat the quartz substrate was carried out at visible wavelengths of 400-800 nm, using UV/Vis/NIR spectroscopy. All TCSEH films were optically transparent despite the incorporation therein of CS NPs in epoxy monomer. The spectra show that the TCSEH films within all the composition ranges are highly transparent with above 95% transmittance in the visible spectrum regions of 400-800 nm. This is due to the homogeneous dispersion of



Fig. 5. Thermal stabilities in the TCSEHMs depending on the organically modified CS NP contents, compared with that of epoxy matrix.



Fig. 6. 2- and 3-D AFM image of TCSEH films with 7 : 3 weight ratio in hybrid composition of epoxy and CS NPs.

the organically modified CS NPs in epoxy matrix without phase separation during thermal curing process.

Fig. 4 shows (a) the hardness and (b) the adhesion of the TCSEH films coated on glass substrates as a function of organically modified CS NPs contents in epoxy matrix. The hardness and adhesion of the TCSEH films within $0 \sim 30$ wt% of organically modified CS NPs in epoxy monomer was measured via pencil hardness tester and adhesion tape tester and were compared with that of epoxy films fabricated with base epoxy monomer without organically modified CS NPs, as shown in Fig. 4(a). The hardness of the TCSEH films was enhanced by increasing their CS NP contents, and it was almost 3 times higher than that of the epoxy-monomer-coated film under the same curing conditions. Also, the film adhesion remained the highest value of 5B regardless of incorporation contents of organically modified CS NPs. This means that the mechanical property such as hardness of TCSEH films can be efficiently enhanced without any decrease of film adhesion through the homogenous dispersion and thermal-induced chemical networking of the organically modified CS NPs with higher hardness than organic epoxy monomers.

Fig. 5 shows the thermal stabilities in the TCSEHMs depending on the organically modified CS NP contents, compared with that of epoxy matrix. The dynamic thermogravimetric curves exhibited the different inorganic residual weight losses of the TCSEHMs as a function

of CS NP content. The 5-wt% weight loss temperature in the TCSEHMs was around 280-290 °C, and it increased in proportion to the incorporated CS NP content in epoxy matrix, as shown in Fig. 5.

Fig. 6 shows 2- and 3-D AFM image of TCSEH films with 7:3 weight ratio in hybrid composition of epoxy and CS NPs. The TCSEH films exhibited a low root-mean-square (RMS) roughness of below 1 nm. This is because the incorporation and thermally induced chemical networking of the organically modified CS NPs with epoxy matrix could reduce the fluctuation due to the shrinkage the hybrid films during thermal curing process. This good RMS roughness of TCSEH films is able to make an important role in coating applications.

Conclusion

Low-temperature solution processible and solventless SEHMs composed of organically modified CS NPs and epoxy monomers were successfully fabricated through simple sol-gel process and solvent evaporation. These SEHMs exhibited the homogeneous dispersion without any phase separation, aggregation, and gelation in the environment of solventless and highly dispersed CS NPs. The good hybridization in solventless environment is due to the good surface modification of various organosilanes upon silica nanoparticles. The homogeneous dispersion between CS NPs and epoxy monomers was confirmed by TEM. These homogeneously dispersed SEHMs can be formed into the films through the simple low-temperature solution coating and thermalcuring process for 30 min at 150 °C. The SEHMs showed high transmittance of above 95% in the visible wavelength regions and good thermal curability by simple low temperature curing process regardless of the embedded content of CS NPs. In particular, these solventless SEHMs exhibited the film formation ability with thick film thickness of several hundred µm without any cracks and the incorporated CS NPs in SEH films were homogeneously dispersed without any aggregation. In addition, these SEHMs enhanced properties in mechanical hardness, thermal stability and surface roughness in proportion to the embedded content of CS NPs. Therefore, these SEHMs with these good performances can be good potential candidates for the applications in functional coatings of the field in electronics, optics, electro-optics and energy.

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