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Fabrication and characterization of photocurable inorganic–organic hybrid materials using organically modified colloidal-silica nanoparticles and acryl resin

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ABSTRACT

Photocurable inorganic–organic hybrid materials were prepared from colloidal-silica nanoparticles synthesized through the sol–gel process and using acryl resin. The synthesized colloidal-silica nanoparticles had uniform diameters of around 20 nm and were organically modified, using methyl and methacryl functional silanes, for efficient hybridization with acryl resin. The organically modified and stabilized colloidal-silica nanoparticles could be homogeneously hybridized with acryl resin without phase separation. The successfully fabricated hybrid materials exhibit efficient photocurability and simple film formation due to the photopolymerization of the organically modified colloidal-silica nanoparticles and acryl resin upon UV exposure as well as an excellent optical transmission of above 90% in the visible region and an enhanced surface smoothness of around 1 nm RMS roughness. They likewise exhibit improved thermal and mechanical characteristics, much better than those of acryl resin. Lastly and most importantly, these photocurable hybrid materials fabricated through the synergistic combination of colloidal-silica nanoparticles with acryl resin are candidates for optical and electrical applications.

1. Introduction

Inorganic–organic nanohybrid materials (IONHMs) have attracted much attention of late as candidates for optical and electrical applications due to their outstanding properties, including thermal stability, mechanical strength, high transparency, and good processibility [1–6]. Thus, intensive research on the design and fabrication of IONHMs has been conducted, using a variety of methods, including a sol–gel process of organically modified silicon alkoxide, the embedment of inorganic particles in polymers, the embedment of organic dyes in sol–gel matrices, and the simultaneous formation of interpenetrating organic–inorganic networks [7–10].

In general, IONHMs can be classified into two types, depending on the strength of the bonds between the organic and the inorganic phase [8]. One type of IONHM is that with weak bonds, such as van der Waals or hydrogen bonding, fabricated through the *ex-situ* physical mixing of the inorganic and organic components. The other type of IONHM is that with strong chemical bonds, such as covalent or ionocovalent chemical bonding, between the inorganic and the organic phase, synthesized by *in-situ* chemical routes [7–15]. IONHMs with weak bonds exhibit good performance, which the respective materials cannot exhibit, through the effective combination of their inorganic and organic components. These materials appear, however, during phase separation due to the agglomeration of the inorganic particles or the organic components, and due to the interfacial defects between the two phases resulting from physical mixing, which leads not only to the degradation of the properties but also to a decrease in the stability and reproducibility of the materials. On the other hand, the IONHMs with strong chemical bonds between the two phases are uniform and stable materials. Thus, film formation is easier when these materials are used, and the overall film properties are better. The sizes of the inorganic components of the described IONHMs, however, are mostly below several nm. Thus, they cannot contribute to the enhancement of the properties shown in the results. To highlight the better properties of IONHMs, the size control of the inorganic particles with several tens of nm diameters, and their stable dispersion in organic matrices, are very important, and chemical networking between the inorganic particles and the organic components is required.

Thus, in this study, monosized colloidal-silica nanoparticles with diameters of around 20 nm were synthesized, and surface-modified, using organically modified silicon alkoxide, for the

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homogenous dispersion with acryl resin. In addition, the stable dispersion of the colloidal-silica nanoparticles in acryl resin and the degree of the chemical networking through the UV-induced polymerization of the organically modified colloidal-silica nanoparticles and acryl resin were investigated. The optical and surface characteristics of the developed IONHM films, newly formed using the synthesized colloidal-silica nanoparticles and acryl resin, were likewise examined, and the influence of the colloidal-silica nanoparticles in acryl resin on the thermal and mechanical properties was investigated.

2. Experimental section

2.1. Synthesis of the colloidal-silica nanoparticles

The colloidal-silica nanoparticles in IONHMs were synthesized using tetraethyl orthosilicate (TEOS, Aldrich), ethanol (Aldrich), concentrated ammonia (Aldrich), and distilled water as reagents. The formation of colloidal-silica nanoparticles takes place through the hydrolysis and condensation reactions, using TEOS as a starting material, in an alcoholic ethanol solution consisting of water and ammonia. Ammonia plays the role of a catalyst for hydrolysis and condensation. Furthermore, to obtain monosized colloidal-silica nanoparticles, it is important to use the following working conditions: a constant temperature reaction and appropriated molar concentrations of the reagents. Therefore, the reactions were realized at a constant room temperature and using the following molar ratio: 1 M TEOS, 3 M distilled water, 0.34 M NH_3, and 33.1 M ethanol. Ethanol, distilled water, and NH_3 were mixed and stirred for 5 min at room temperature, in a reaction flask, and were combined with TEOS. The mixture was stirred for 24 h, with a stirring rate of 800 rpm, using a magnetic stirrer. Subsequently, monosized colloidal-silica nanoparticles were obtained through hydrolysis and condensation.

2.2. Synthesis of the MTMS-MPTMS-modified colloidal-silica nanoparticles

The surfaces of the colloidal-silica nanoparticles were modified with methyltrimethoxysilane (MTMS, Aldrich, 0.2 M) for 24 h, under a stirring rate of 800 rpm and using a magnetic stirrer, at room temperature. The molar ratio of MTMS to TEOS was 1:5. Then, methacryloxypropyltrimethoxysilane (MPTMS, Aldrich, 0.2 M) was reacted with the MTMS-treated colloidal-silica nanoparticles under magnetic stirring for 24 h, with a stirring rate of 800 rpm and at room temperature, for chemical polymerization with acryl resin. The molar ratio of MPTMS to TEOS was 1:5.

2.3. Fabrication of Photocurable IONHMs using the MTMS-MPTMS-modified colloidal-silica nanoparticles and acryl resin

After the reaction to the synthesis of the methyl and the methacryl-silane-treated colloidal-silica nanoparticles, any residual product (such as alcohol and water) was replaced with propylene glycol monomethyl ether acetate (PGMEA, Aldrich) at 40 °C, using an evaporator, for the hybridization of the organically modified colloidal-silica nanoparticles with acryl resin (SK CYTEC, UP 053). The organically modified colloidal-silica nanoparticles were homogeneously dispersed in PGMEA, and their solid content in PGMEA was 30-wt%. To adequately mix and hybridize it with acryl resin, acryl resin was diluted with the PGMEA solvent, and acryl resin diluted in PGMEA with 30-wt% solid contents was fabricated. Then, the organically modified colloidal-silica nanoparticles and the diluted acryl resin with 30-wt% solid contents were efficiently mixed at a stirring speed of 800 rpm, using a magnetic stirrer, for 1 h. Finally, the homogeneous photocurable hybrid solutions in PGMEA were fabricated. The 0- to 80-wt% organically modified colloidal-silica nanoparticles that were stabilized through surface modification were homogeneously embedded in diluted acryl resin. In addition, 1-wt% solid benzyldimethylketal (BDK, Aldrich) was added as a photoinitiator to the solutions composed of organically modified colloidal-silica nanoparticles and acryl resin. After stirring the solutions for 1 h at a stirring rate of 800 rpm and at room temperature, homogeneous and photocurable IONHMs were obtained. These photocurable IONHM solutions were filtered and were spin-coated onto clean glass substrates and wafers.

2.4. Fabrication of photocurable IONHM films using UV-induced polymerization

The coated IONHM films were then subjected to UV-(500 W Hg Lamp, <365 nm, Oriel97453)-induced polymerization under a nitrogen atmosphere, after pre-drying at 90 °C for 3 min. Consequently, photocured IONHM films were fabricated.

2.5. 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 colloidal-silica nanoparticles. The changes in the chemical structure of the photocurable IONHMs were examined using Fourier transform infrared (FT-IR, JASCO 680 Plus) spectroscopy, before and after UV irradiation. The optical transparency and surface properties of the photocurable IONHM films were examined, respectively, through ultraviolet visible near-infrared (UV/Vis/NIR) spectroscopy and atomic-force measurement (AFM, SFI 3800N, SEIKO). In addition, the influence of the colloidal-silica nanoparticles on the thermal stability and mechanical properties of the photocurable IONHM films was determined through thermogravimetric analysis (TGA) and the use of a nanoindentator (Nanoindenter XP, MTS Nano Instruments).

3. Results and discussion

3.1. FT-IR spectroscopy and transmission electron microscopy of monosized and homogeneous dispersed MTMS-MPTMS-modified colloidal-silica nanoparticles

Fig. 1 shows the FT-IR spectra of the colloidal-silica nanoparticles and MTMS- and MTMS-MPTMS-modified colloidal-silica nanoparticles. As shown in Fig. 1, in the organically modified silica nanoparticles, the alkoxy groups and CH bond of the methyl groups in the 2900- to 2700-cm^{-1} regions are shown, as well as the C=C peak at 1638–1615 cm^{-1} and the C=O peak at around 1725 cm^{-1} in the methacryl groups of MPTMS. On the other hand, the unmodified colloidal-silica nanoparticles had no FT-IR spectra within the above ranges, except for the silica peaks within the 1000–1100 cm^{-1} range. Therefore, the surface modification of MTMS and MPTMS on the fabricated colloidal-silica nanoparticles was confirmed through the FT-IR spectra analysis.

Fig. 2 shows the TEM images of the colloidal-silica nanoparticles with diameters of around 20 nm, indicating (a) the monosized and homogeneous dispersion with surface modification of the functional silanes on the colloidal-silica nanoparticles, and (b) the agglomerated colloidal-silica nanoparticles due to the absence of surface modification in the functional silanes on the colloidal-silica nanoparticles. Such monosized and homogeneous dispersion of the colloidal-silica nanoparticles is due to the surface modification of the methyl and methacryl silanes on the colloidal-silica nanoparticles through the sol–gel technique. The organically modified