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Preparation and characterization of UV-cured polyurethane acrylate/ZnO nanocomposite films based on surface modified ZnO

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ABSTRACT

A series of polyurethane acrylate (PUA)/ZnO nanocomposite films with different ZnO contents were prepared via a UV-curing system. To ensure good dispersion in the PUA matrix, ZnO nanoparticles were modified with a silane coupling agent and confirmed by FT-IR analysis. The morphological structures, thermal properties, mechanical properties and water transfer properties of the prepared films were investigated as a function of their ZnO concentration. WAXD and SEM analyses showed that the surface-modified ZnO nanoparticles were homogeneously dispersed in the PUA matrix and the molecular ordering increased with increasing ZnO content. Compared with neat PUA, the hardness and elastic modulus in films increased from 0.03 to 0.056 GPa and from 2.75 to 3.55 GPa, respectively. Additionally, the water uptake and WVTR in the PUA/ZnO nanocomposite films decreased as the ZnO content nanoparticles increased, which may come from enhanced molecular ordering and hydrophobicity in films. UV light below approximately 450 nm can be efficiently absorbed by incorporating ZnO nanoparticles into a PUA matrix, indicating that these composite films exhibit good weather ability and UV-shielding effects. The enhanced physical properties achieved by incorporating modified ZnO nanoparticles can be advantageous in various applications, whereas the thermal stability of the composite films should be increased.

1. Introduction

Recently, the design and synthesis of new polymer/nanosized-inorganic composite materials have been widely investigated in order to combine the properties of inorganic fillers and polymer matrices [1–4]. Incorporating nanosized-inorganic particles can afford the resulting nanocomposites excellent electrical and mechanical properties. In the process of preparing these nanocomposite materials, it is very important to control the dispersion homogeneity of the nanosized particles over the entire matrix, because composition greatly influences many functions of the nanohybrid materials. Due to the nanoscale sizes and the large specific surface areas of nanosized fillers, the interfacial interaction between the filler and the polymer is strong, resulting in a large improvement in the physical properties of the polymer [5–7].

Among the various types of nanoparticles, nanosized zinc oxide (ZnO) has attained an increased interest and is widely used in a variety of applications including functional devices, catalysts, pigments, optical materials, cosmetics, UV-absorbers, and additives in many industrial products [5,7–9]. Recently, the antimicrobial activity of ZnO nanoparticles with sizes less than 100 nm has been reported; this originates from their small particle size and large surface area [10,11].

Crosslinked polymers offer very intriguing properties, such as high solubility and reactivity, which have great potential value for applications [12]. One possible application of highly crosslinked polymers is in coating technologies, to make low viscosity and high functionality coatings. UV-curable coatings are one of the most promising fields of application of highly crosslinked polymers. As is well known, polyurethane acrylates (PUA) are widely used for UV coatings due to their excellent physical properties, such as impact strength, flexibility at low temperature, abrasion resistance, controllable hardness and transparency [13,14]. UV-curable coatings have few or no volatile organic compounds. In addition, compared to thermally cured coatings, UV-curable coatings offer some advantages, such as instant drying, a broad formulating range, reduced energy consumption, and low space and capital requirements for

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curing equipment. Low viscosity and high curing speed are two important properties pursued in UV-curable oligomers. Acrylate oligomers are some of the most important UV-curable resins. Various efforts have been devoted to improving PUA's properties by chemical modification to the molecular structure and/or by addition organic or inorganic fillers, e.g. rice husk and polyethylene glycol, natural-fiber, mineral, SiO_2, Al_2O_3, ZnO, carbon nanotubes, and so on [5,6,15,16].

In this work, a series of highly crosslinked UV-cured PUA/ZnO nanocomposite films were prepared from a trifunctional polyol and different concentration of ZnO nanoparticles. Here, the ZnO nanoparticles were modified with a silane coupling agent and characterized using Fourier transform infrared (FTIR) spectroscopy. For the prepared PUA/ZnO nanocomposite films, their morphological structure, mechanical properties, thermal properties, and optical properties were investigated as a function of the ZnO concentration.

2. Experimental

2.1. Materials

Polycaprolactone triol (PCLT, average Mn: 900 g/mol, CAS No: 37625-56-2) as a polyol, 2-hydroxyethyl acrylate (HEA, Mw: 116.12 g/mol, CAS No: 818-61-1) as a reactive monomer and dibutyltin dilaurate (DBT, Mw: 631.56 g/mol, CAS No: 77-58-7) as a reaction catalyst were purchased from Aldrich Chemical Co. Isophorone diisocyanate (IPDI, Mw: 222.28 g/mol, CAS No: 4098-71-9) as a diisocyanate was purchased from TCI Korea. Trimethylolpropane triacrylate (TMPTA, Mw: 296.32 g/mol, CAS No: 15625-89-5) and methyl methacrylate (MMA, Mw: 100.12 g/mol, CAS No: 80-62-6) as reactive diluents were purchased from Miwon Commercial Co. Ltd (Anyang City, Korea) and Aldrich Chemical Co, respectively. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184D, Mw: 204.26 g/mol, CAS No: 947-19-3), purchased from Ciba Specialty Chemicals Co., was used as a photoinitiator. For the surface modification of ZnO nanoparticles, 3-(trimethoxysilyl)propyl methacrylate(TPM, Mw: 248.35 g/mol, CAS No: 2530-85-0) as a silane coupling agent and absolute ethanol as solvent were purchased from Aldrich Chemical Co. All reagents were used as received without further purification. Inorganic ZnO nanoparticles with an average size of 50 nm were supplied by Sukgyung AT Co. (Ansan City, Korea).

2.2. Methods

2.2.1. Preparation of TPM-modified ZnO nanoparticles

ZnO nanoparticles were modified by introducing reactive groups, using the reaction of silane coupling agent (TPM) with the hydroxyl groups of the ZnO surface. The typical procedure was given as follows:3.0 g of ZnO nanoparticles, 15 g of TPM, and 150 ml of absolute ethanol were poured into a 250 ml three-neck flask. Then it was refluxed at 70 °C for 5 h under magnetic stirring and nitrogen atmosphere. Are action can take place for each Si-OCH_3 group which has hydroxyl groups on the nanoparticle surface; the anticipated mechanism is illustrated in Fig. 1. After centrifuging to separate it from the suspension using a multipurpose centrifuge(Hanil Co., Korea) at 5000 rpm for 15 min, white precipitate was collected. The precipitate (TPM-modified ZnO nanoparticles) was purged with alcohol for 12 h using a Soxhlet extractor to remove the excess silane absorbed on the ZnO nanoparticles. Finally, the precipitate was dried in vacuum at room temperature for 12 h.

2.2.2. Preparation of urethane acrylateoligomer

Our method for preparing crosslinkable urethane acrylate oligomer PCLT-IPDI was described in our previous studies [16,17]: PCLT and IPDI (1:2.5 by mole) were mixed in a 500 mL four-necked flask in an oil bath equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser with a drying tube, and thoroughly mixed. Then, approximately 200 ppm of DBT was added. After the urethane forming reaction proceeded at 80 °C for over 3 h, the reaction mixture was cooled down to 60 °C and HEA was added dropwise. Tipping the NCO-terminated prepolymer with HEA was done for 1 h at a temperature below 60 °C.

2.2.3. Preparation of PUA/ZnO nanocomposite films

A series of UV-cured PUA/ZnO nanocomposite films with different TPM-modified ZnO contents were prepared according to the compositions listed in Table 1. At first, oligomer, TMPTA and MMA solutions put into the vial glass and the mixture solutions were stirred with ultrasonication (Ultra-cell vcx750, power: 750 W; work-frequency: 20 Hz) for 30 min. And then, TPM-modified ZnO was added and stirred with ultrasonication for 30 min to ensure that the ZnO nanoparticles dispersed well. Lastly, photoinitiator was put into the mixture solutions and stirred with ultrasonication for 10 min.Then, each mixture solution was bar-coated on a glass substrate. The coated films were then exposed to UV radiation from a medium-pressure 1.2 kW mercury lamp for 5 min. The film thickness was kept at about 30 μm to aid in evaluating the physical properties.

2.3. Characterization

Fourier transform infrared spectra (FTIR) were recorded on an Excalibur Series Varian 4100 FTIR spectrometer (Digilab Co., MA, USA) in transmission mode. FTIR was used to characterize the functional groups of each film: the unmodified nano-ZnO, TPM-modified ZnO, and the UV-cured PUA/ZnO nanocomposite films with different ZnO contents. UV–visible spectra of the UV-cured PUA/ZnO nanocomposite films were recorded with a single beam OPTIZEN 2120UVspectrometer (Mecasys Co., Daejeon, Korea) in the range of 200–800 nm and a blank glass plate was employed as a reference.

To analyze the morphology of the UV-cured PUA/ZnO nanocomposite films, wide-angle X-ray diffraction (WAXD) patterns were obtained using a high resolution X-ray diffractometer (Bruker AXS GmBH, Model Bruker D8 DISCOVER, Karlsruhe, Germany) with a monochromator (flat crystal type). The CuKα (α = 1.5406 Å) radiation source was operated at 40 kV and 40 mA; all measurements were carried out in $\theta/2\theta$ mode. Data were collected in the range of 13–60° at 0.02° intervals with a scan speed of 2.0°/min. The scanning electron microscope (FEI Co., Model Nova 200, Hillsboro, OR, USA) was employed to examine the morphology of ZnO and TPM-modified ZnO nanoparticles. In addition, SEM images of the fractured surfaces of the UV-cured PUA/ZnO nanocomposite films were observed to investigate the dispersion of TPM-modified ZnO nanoparticle. For the fractured surface measurements, the films were first frozen in liquid nitrogen and then broken to produce a cross section. Prior to the examination, the samples were coated with a thin layer of gold.

Additionally, the modulus and hardness of the UV-cured PUA/ZnO nanocomposite films were measured by using a MTS XP nanohardness tester (MTS Co., USA) and a Berkovich (three-side pyramid) diamond indenter. Multiple indentations were made at five different locations on each film surface at fixed and applied loads. At different locations, the load-displacement curve was recorded, from which the effective modulus and hardness could be calculated with standard formulas [18].

The extent of water sorption of the UV-cured PUA/ZnO nanocomposite films was determined gravimetrically. Before testing, each sample was dried in a vacuum oven at 60 °C for 24 h. First the weight of each completely dried sample (W_d) was measured