

Study of utilizing thin polymer surface coating on the nanoparticles for melt compounding of polycarbonate/alumina nanocomposites and their optical properties

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Abstract

This paper presents a thin polymer surface coating approach to facilitate dispersion of poly(styrene-maleic anhydride) (SMA) copolymer-coated alumina (Al₂O₃) nanoparticles in polycarbonate (PC) using a high intensity thermokinetic mixer (K-mixer) and the optical properties of the resultant nanocomposites. Electron spectroscopy for chemical analyses (ESCA), energy filtered transmission electron microscopy (EFTEM), thermogravimetric analysis (TGA), and field emission scanning electron microscopy (FESEM) were used to investigate the covalent bonding of polymer coating on the nanoparticles and the nanoparticle dispersion. The light transmittance of the PC/alumina nanocomposites was measured and compared with that of the transparent neat resin.

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1. Introduction

Polymer nanocomposites, which consist of a polymer matrix filled with nanosize particles, represent a new class of lightweight, high performance materials that exhibit improved tensile strength, heat resistance, barrier properties, and/or flame retardation, and have found commercial application. However, despite the substantial expansion of the field of nanocomposites (most notably with layered silicate clay), there has been little focus on transparent optical nanocomposites. While a number of studies have been performed on the synthesis of high light transmittance nano-

composites, such nanocomposites were produced via the sol-gel methods [1–6]. These sol-gel methods require the use of organic solvents and are less suitable for mass production compared to the melt compounding method. Accordingly, this study focuses on the feasibility of producing optical nanocomposites via melt compounding, that could potentially impact a broad range of industrial sectors including aerospace, automotive, construction, consumer electronic, electrical, food packaging, health, medical, military, ophthalmic, optical, optoelectronic, and photonic industries [7–11]. The idea is to incorporate chemically treated spherical nanoparticles of proper size and attributes into the polymer matrix and disperse them at the nanoscale to minimize light scattering and attain high transmittance while realizing retention or improvements in some of the material and optical properties.

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Compared to conventional micron-sized particles, nanoparticles have a much higher surface-to-volume ratio. As the particle size decreases, the percentage of molecules/atoms present on the surface is increased tremendously [12,13]. As a result, interparticle forces such as van der Waals and electrostatic forces, as well as magnetic attraction, become stronger. Without proper chemical treatment to reduce the surface energy, it is very common for nanoparticles to form clusters or agglomerates, which makes it challenging to disperse them individually and uniformly in the polymer matrix, thus resulting in opaque nanocomposites akin to conventional composites.

One method to facilitate dispersion of nanoparticles is to coat the nanoparticle with a thin layer of polymer to introduce steric stabilization [14]. By coating the nanoparticle with a thin layer of polymer, the van der Waals influence from the nanoparticles can be masked and the compatibility between the organic polymer host and inorganic nanoparticles can be improved, thereby facilitating better nanoparticle dispersion and increased loading content. The resulting core/shell nanohybrids can then be easily compounded with the host polymer to produce nanocomposites. The interface between the nanoparticles and the polymer coating is important, and the best strategy for this would be to have covalent bonding on the nanoparticle surface to ensure proper and well adhered coating on the nanoparticle surface.

Poly(styrene-maleic anhydride) copolymer (SMA) was selected for such coatings as its maleic anhydride groups can react with primary amines commonly available in aminosilane coupling agents. Furthermore, because it is transparent to visible light and its refractive index of 1.583 is in the proximity of PC (1.585), it will not hamper the overall transparency of the host PC. Low molecular weight SMA has also been used as a compatibilizer in PC blends with acrylonitrile-butadiene-styrene (ABS) or styrene-co-acrylonitrile (SAN) copolymers with glass fiber, suggesting its compatibility with PC [15,16]. In this study, alumina nanoparticles were surface treated with an aminosilane coupling agent and coated with SMA, followed by compounding with optical grade PC using a high intensity thermokinetic mixer. The material preparation, degree of nanoparticle treatment and dispersion as well as the resulting light transmittance of the nanocomposites are reported.

2. Experimental

2.1. Materials

Optical grade Panlite AD-5503 (MFI: 64.8 g/10 min, T_g : 144 °C, M_w : 15,000 g/mol) polycarbonate (PC) resin, made available by Teijin Kasei America Inc., was used as the matrix polymer. Poly(styrene-maleic anhydride) copolymers, SMA[®] EF-80 (M_w : 14,400, T_g : 104 °C), were obtained from Sartomer. The SMA used in this study is a low molecular weight copolymer commonly used as an additive with an 8:1 molar ratio between the styrene and

the maleic anhydride. The alumina nanoparticles were purchased from Nanotechnologies, Inc. with an average particle size D_{50} of 96 nm and an average specific surface area (SSA) of 50.4 m²/g (based on the static light scattering, SLS, method). Finally, fluorescamine and the coupling agent 3-aminopropyltriethoxysilane (M_w : 221.4 g/mol, SSA: 353 m²/g) were purchased from Sigma-Aldrich and Gelest Inc., respectively. All chemicals were used as received without further purification. Whenever necessary, drying of nanoparticles as well as polymer resins and composites prior to treatment/molding was performed to remove the moisture.

2.2. Preparation of nanoparticles

2.2.1. Coupling agent treatment

The alumina nanoparticles were dried at 100 °C under vacuum overnight to remove any moisture prior to surface treatment. After drying, 5 wt% alumina nanoparticles in tetrahydrofuran (THF) were dispersed using ultrasonic vibration for 10 min to break up any agglomerates. At the same time, the required coupling agent was calculated based on the specific surface areas of both the nanoparticles and the coupling agent, and 30 wt% excess of the aminosilane coupling agent was pre-hydrolyzed with a 1:3 molar ratio of deionized water (such that there were 3 mol of water for every mole of aminosilane) in a small amount of THF for 3 min. The pre-hydrolyzed coupling agent was then added dropwise to the alumina nanoparticle solution in a water bath at room temperature under constant ultrasonic vibration for 15 min. Afterwards, the nanoparticle solution was quenched with an equal amount of THF to slow the reaction, and the nanoparticles were separated by centrifugation at 1000 rpm for 6 min. After removing the supernatant, fresh THF was added to the separated nanoparticles to remove any excess coupling agent and this washing process was repeated twice. Finally, fresh THF was added to the treated nanoparticles to reach a 5 wt% concentration, and the solution was refluxed overnight.

2.2.2. Polymer coating

The THF from the refluxed nanoparticle solution was removed by centrifugation and fresh THF was added. Separately, 0.1% (w/v) of SMA was first dissolved in THF and the aminosilane treated nanoparticles were added dropwise into the polymer solution under rigorous stirring to 1% (w/v) concentration, followed by sonication of the solution for 15 min. After the sonication process, the solution was refluxed for 3 h to complete the reaction between the primary amines and the maleic anhydrides. Similar washing by the centrifugation process at 3500 rpm for 20 min was performed three times on the coated nanoparticles to remove any excess unbound SMA. The final supernatant from the washed nanoparticles was tested for any remaining polymer by mixing it with water. The coated alumina nanoparticles were collected only when there was no excess

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