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Enhancement of the thermal stability and mechanical properties of a PMMA/aluminum trihydroxide composite synthesized via bead milling

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ABSTRACT

The use of aluminum trihydroxide (ATH) fillers as non-halogen flame retardants for polymethylmethacrylates (PMMA) creates a conflict between the mechanical properties and heat resistance of the composites. Therefore, to ensure that the PMMA mechanical properties remain satisfactory, improvements in both the filler–polymer interactions and the ability to control the size and size distribution, morphology and dispersion of the fillers are required. Thus, in the present study, bead milling was used to control both the size distribution and dispersion of ATH fillers in MMA, which had an initial average size of 0.75 μm. The dispersion was obtained by alteration of the surface characteristics of ATH fillers using a silane-based dispersing agent, (3-acryloxypropyl) trimethoxysilane (APTMS). Bead milling successfully comminuted the ATH particles and prevented the formation of ATH agglomerates. The smallest average size of the ATH particles after bead milling was 300 nm. Highly dispersed ATH filler particles were observed in the TEM images of the PMMA/ATH composites. The filler–polymer interaction, i.e. the interaction parameter (B), was calculated. The effects of volume fraction, particle size distribution, and surface modification of the fillers on the results of dynamic mechanical analysis (DMA) are discussed. The thermal stability of the PMMA/ATH composites was also investigated using thermal gravimetric analysis (TGA).

1. Introduction

Polymethylmethacrylates (PMMAs) are most commonly used as a shatterproof replacement for glass. PMMA is also a key ingredient in the production of casts, extruded acrylic sheets, acrylic emulsions, molding powders and extrusion resins. Polymers and copolymers of methyl methacrylate are also used in undissolved surface coatings, adhesives, sealants, impact modifiers, emulsion polymers, surgical bone cements, packaging applications, vinyl siding and other construction materials. The flame retardancy of PMMA should be improved for some applications. Polymer-based composites of organic and inorganic filler components are widely used in flame retardants. The use of finer filler particles (i.e. nano- or sub-micrometer in size) as reinforcements in composites is an important area of research. Unlike larger reinforcement particles, the effects of the smaller particles on composites are unpredictable — sometimes enhancing the composite properties, but other times diminishing them [1–6]. Non-halogen flame retardants, such as aluminum trihydroxide (ATH), have recently been promoted as alternatives to halogen-based flame retardants, which give off heavy smoke and hazardous gases during combustion [7–9]. However, because composites have many microscopic interfaces, the surface properties of the fillers have a significant effect on the microscopic interfaces [10–14]. Thus, enhancement of the flame retardancy of a PMMA/ATH composite must not interfere with retention of the satisfactory mechanical properties of the PMMA matrix.

The interfacial interactions between inorganic compounds and polymer matrices are key determinants of the overall properties of composites. Unfortunately, high loading with inorganic fillers has detrimental effects on the mechanical properties of composites due to either poor dispersion of fillers or incompatibility between the fillers and polymers. Consequently, the mechanical properties of composites are dynamic; they are dramatically altered by changes in temperature or stress, which impacts the nature of the interfacial interactions. Therefore, processing methods that allow for controlled particle size distribution, dispersion and interfacial interactions are critical to obtain inorganic–organic composites that have novel properties due to finer particle size [9–11,15]. Nano- and sub-micrometer-sized composite fillers require processing technologies that differ from those used for composites with micrometer-sized fillers. Thus, new developments in composite processing are required for the production of finer composite fillers.

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Previously, we reported successful comminution of various micro-sized particles into nano-sized particles, as well as de-agglomeration of nano-sized particles with high-dispersion stability for use as a nanocomposite in optical applications [16,17]. Composites can be prepared by synthesizing particles within a polymer matrix [18]. Alternatively, composites can be prepared by dispersion of particles in a monomer and by polymerization of the monomer in the presence of the particles [19–22]. The former method has several drawbacks that result from relatively weak interaction forces between the polymer and the particles. In addition, the attractive force between finer particles in liquid suspensions is often strong enough [23,24] to result in particle agglomeration in most monomers. Poorly dispersed particles in monomer solutions cause poor interface interactions within particle–polymer composites [10,25,26]. Thus, the surface properties of the fillers influence both the dispersion of the filler and the elastic modulus and composite strength [10–14,27,28]. Gao et al. [11] investigated the dynamic mechanical properties and calculated the interaction parameter of micro-sized alumina in EPDMA. However, nano- and submicron-sized fillers have different effects on the interaction between the filler and the polymer matrix. Thus, the purpose of the present study was to investigate the relationship between the mechanical properties and the microstructure of submicron-sized ATH particles in PMMA.

In the present study, a bead mill was used to comminute micro-sized aluminum trihydroxide (ATH) particles suspended in MMA into finer particles. The ATH fillers were adequately dispersed by surface modification with a suitable silane coupling agent. The filler–polymer interactions of the PMMA/ATH composite were investigated by measurement of the effects of different filler volume fractions, particle size distribution, and surface state on the dynamic mechanical properties. The relationships between the mechanical properties, microstructure, and thermal properties assessed using thermal gravimetric analysis (TGA) of the PMMA/ATH composites are discussed. In addition, the optical properties such as haze, luminous transmittance, diffuse luminous transmittance and parallel transmittance of PMMA/ATH composites with different compositions were also obtained.

2. Experimental procedures

2.1. Materials

Commercially produced, surface unmodified, micro-sized ATH particles, which had a primary particle size of 0.75 μm (Showa Denko, Co. Ltd., Japan), were used in the experiments. A silane-based coupling agent, (3-acryl-oxypropyl)trimethoxysilane (Shin Etsu, Kagaku Co. Ltd, Japan) was used for surface modification of the ATH particle suspensions. The typical chemical structure of these compounds is $(XO)_3SiCH_2CH_2CH_2$-R. Silicone (Si) is the center of the silane molecule which contains an inorganic functional group ($R=CH_3$). The functional group (R) will attach to an organic (MMA) while the functional group ($X=CH_3$) attaches to an inorganic material (ATH) to achieve a "coupling" effect. The beads used were 50-μm ZrO_2 (zirconia) beads (Neturen Co. Ltd., Tokyo, Japan). ATH particles were dispersed in MMA (Kuraray, Co. Ltd., Japan). In this study, the chain addition polymerization method was used. In the chain addition polymerization, the chain reaction involves four steps: initiations, propagation, termination, and transfer. In this investigation, the polymerization was initiated by 2, 2′-azobis(4-methoxy-2, 4-dimethylvalero-nitrile) (V-70, Wako Co. Ltd. Japan) and lauroyl peroxide (LPO, NOF Co. Ltd., Japan). The V-70 has a lower decomposition temperature than LPO. Thus, it allowed the V-70 as an active initiator in the early stage of polymerization.

2.2. Bead milling and polymerization

A detailed description of the bead mill was reported previously [21,22]. Briefly, the bead mill (Kotobuki Co. Ltd., Japan) was composed of a 170-mL vessel, a pump and a mixing tank. The vessel was filled to 70% of capacity with beads. The ATH particle suspension was pumped into the vessel, which contained zirconia beads and a centrifugation rotor operated at a speed of 73.8 Hz (6095 rpm). The beads were agitated in the lower portion of the vessel (dispersing section) to break-up the aggregated and agglomerated ATH particles. After dispersion, the suspension was pumped from the dispersing section to the upper region (centrifugation section) where centrifugal force was used to separate the zirconia beads from the particle suspension. The particle suspension was then recycled back to the dispersing section. To keep the temperature of the system constant, the vessel was cooled in a water jacket and was completely sealed from the outside environment. Suspensions of ATH particles in MMA with various ATH concentrations, i.e. 1, 5 or 10 wt.%, were pumped through the bead mill at an optimized recirculation mass flow rate of 10–20 kg/h.

The solution for the casting plate of the composite was prepared by the addition of the initiators V-70 (0.5 g/kg) and LPO (1.0 g/kg) to the dispersion of ATH particles in MMA, followed by mixing for 10 min using a magnetic stirrer. Bubbles were removed by subjecting the solution to low pressure (−740 mm Hg) for 5 min. The solution was then poured into a cell that consisted of two glass plates sealed with a PVC tube with a diameter of 3 mm and a thickness of 1 mm. The cell was pressed between two sealed glass plates (60 mm × 60 mm × 5 mm) and heated in a 50 °C water bath for 1.5 h. The first and second polymerizations were performed by increasing the temperature to 70 °C for 1 h and to 120 °C for 1.5 h, respectively, using a temperature-controlled air chamber.

2.3. Characterization

The particle size distribution after various predetermined milling times was measured by dynamic light scattering using an HPPS-5001 Malvern Instrument. Initial ATH particles were observed using a field emission scanning electron microscope (FE-SEM, S-5000, Hitachi Ltd., Tokyo, Japan). The crystallinity of the ATH particles before and after bead milling was characterized by X-ray diffractometry (XRD, RINT 2200 V, Rigaku, Japan) using nickel-filtered CuK_α radiation ($\lambda=1.54$ A°) at 40 kV and 30 mA. The XRD step and scanning rates were 0.020° and 4°/min, respectively. An XRD of the ATH particles after bead milling was performed on a dispersion of ATH particles (10 wt.%) with APTMS (1 wt.%). Particle morphology and dispersion of the ATH fillers inside the composite were visually examined using transmission electron microscopy (TEM, JEM-3000F Japan Electron Optics Laboratory Ltd., Tokyo, Japan). To investigate surface modification of the ATH particles, the samples that contained only APTMS-covered ATH particles were prepared. Thus, prior to FTIR, the dispersed ATH sample was diluted with water and centrifuged at 15,000 rpm for 1 h at room temperature four times to remove the MMA. Subsequently, the solid precipitates were dried at 60 °C for 2 h for evaporation of water and homocondensates of APTMS. Samples of unmodified or APTMS-modified ATH were analyzed using Fourier transform infrared spectroscopy (FTIR) in the range of 600–4000 cm^{-1} (PerkinElmer, Spectrum One System).

The dynamic mechanical properties of the casting plates of the composite specimens (with dimensions of 3.0 mm × 2.0 mm × 20 mm) were measured with a dynamic viscoelasticity measuring instrument (Rheogel E4000, UBM Co. Ltd., Japan). These measurements were performed as the temperature was increased from 25 to 250 °C at a rate of 3 °C/min. In addition, the following measurement parameters were used: tension mode, basic frequency of 11 Hz, an undulating strain pattern of a sine wave, a strain control of 3 μm, and a distress distance of 10 mm. Viscoelastic properties, such as the storage modulus (E') and mechanical loss factors ($\tan\,\delta=E'/E''$), were recorded as a function of temperature. The thermal properties of the composites also were analyzed using thermal gravimetric analysis