Preparation and Characterization of Polypropylene Nanocomposites Containing Polystyrene-grafted Alumina Nanoparticles

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Abstract: After surface modification of γ-Al₂O₃ nanoparticles with a silane coupling agent, styrene was graft-copolymerized onto γ-Al₂O₃ nanoparticles using a simultaneous γ-ray irradiation technique. The influence of the irradiation dose and the grafting kinetics were investigated in detail. Polypropylene nanocomposites were fabricated by blending polypropylene, polystyrene-grafted γ-Al₂O₃ (γ-Al₂O₃-g-PS), and a small amount of 1,4-butandiol dimethacrylate (1,4-BDDA) as a crosslinker, followed by e-beam irradiation. The polystyrene-grafted γ-Al₂O₃ and polypropylene nanocomposites were characterized by TGA, FT-IR spectroscopy, SEM, and UTM analyses. The polystyrene graft yield onto γ-Al₂O₃ increased with the absorbed dose. The graft yield was higher at 50 vol% of the styrene solution than at 70 vol%. The nanocomposite fabricated with 5 phr of γ-Al₂O₃-g-PS and 3 phr of 1,4-BDDA showed the highest tensile strength. The homogeneous dispersion of γ-Al₂O₃-g-PS into the polypropylene matrix and the crosslinking through e-beam irradiation improved the mechanical properties of the nanocomposites.

Keywords: polypropylene, nanocomposite, nanoparticle, irradiation

Introduction

Traditional polymer nanocomposites have improved mechanical properties, such as toughness, as a result of the incorporation of inorganic particulate fillers [1-2]. However, high filler loadings (up to 20 % by volume) are required for such an enhancement of performance, leading to a loss of the easy processability of the polymers. Consequently, polymer-based nanocomposites are attracting considerable attention because of the unique properties that result from their nano-scale microstructures [3,4]. They are much lighter in weight, more transparent, and easier to process than conventional inorganic particulate-reinforced polymers, in addition to displaying improved mechanical properties [5-8]. However, the homogeneous distribution of inorganic nanoparticles into the polymer matrix is required to obtain the desired polymer-based nanocomposites [9-13] because agglomeration of inorganic nanoparticles caused by immiscibility between the inorganic nanoparticles and the polymer matrix leads to a reduction, rather than an improvement, of the material’s properties.

To improve the mechanical properties through uniform dispersion of inorganic nanoparticles into the matrix, we synthesized polystyrene-grafted γ-Al₂O₃ through a high-energy irradiation method after surface modification of nano-γ-Al₂O₃. The polypropylene nanocomposites were fabricated by blending surface-modified γ-Al₂O₃ nanoparticles and crosslinking agents, followed by e-beam irradiation. Their characterization is described.

Experimental

Materials
Polypropylene (PP; B310; MW: 523,000; Honam Petrochemical Co., Ltd.) was employed as a polymer matrix. Micropolished γ-Al₂O₃, possessing an average diameter of 50 nm, was purchased from Buehler.

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Table 1. Graft Polymerizations onto TMSPM-modified Al₂O₃

<table>
<thead>
<tr>
<th>Styrene Concentration (vol%)</th>
<th>Total Dose (kGy)</th>
<th>Dose Rate (kGy/h)</th>
<th>Graft Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>50</td>
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<td>2.5</td>
<td>2.1</td>
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<td>5</td>
<td>2.5</td>
<td>4.8</td>
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<td>8.1</td>
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<td>2.5</td>
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</tr>
<tr>
<td>70</td>
<td>10</td>
<td>2.5</td>
<td>7.1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Methanol used as solvent. <sup>b</sup>Weight of grafting polymer/weight of TMSPM-treated γ-Al₂O₃ measured by TGA.

Scheme 1. Surface modification of alumina particles: (a) silylation with TMSPM and (b) graft polymerization with styrene.

Company. 3-(Trimethoxysilyl)propyl methacrylate (TMSPM), xylene, methanol, and styrene were purchased from Aldrich Chemical Company and used as received. 1,4-Butanediol dimethacrylate (1,4-BDDA) and trimethylolpropane triacrylate (TMPTA) were supplied by the Aldrich Chemical Company and used as crosslinking agents without further purification.

**Graft Polymerization onto γ-Al₂O₃ Nanoparticles**

Prior to a silylation, γ-Al₂O₃ nanoparticles (10 g) were dried in a vacuum oven (195 °C) for 24 h and then dispersed in 250 mL of dry xylene with the aid of an ultrasonic probe. The nanoparticle/xylene mixture was added to a 500-mL round-bottom flask containing a stirrer a bar, and then a 10 % v/v TMSPM/xylene solution was added with stirring. The mixture was heated under reflux for 20 h under a nitrogen atmosphere. The mixture was cooled, filtered, and then dried in a vacuum oven at room temperature for 24 h. The dried TMSPM-modified γ-Al₂O₃ (0.5 g) was immersed into various concentrations of styrene in methanol. The resulting solutions were flushed for 15 min with nitrogen and then irradiated using γ-rays from a ⁶⁰Co source at a dose rate of 2.5 kGy/h at room temperature. The resulting polystyrene-grafted γ-Al₂O₃ (γ-Al₂O₃–g-PS) was washed thoroughly with hot benzene in a Soxhlet extractor to remove any residual monomer and homopolymer. The γ-Al₂O₃-γ-PS was dried in a vacuum oven at 80 °C for 24 h. The overall synthetic scheme is shown in Scheme 1. The weight loss of the grafting polymer was calculated using a TA thermogravimeter.
Preparation and Characterization of Polypropylene Nanocomposites

Polypropylene nanocomposites were fabricated by blending polypropylene pellets, γ-Al₂O₃-g-PS, and crosslinking agents using a lab-scale Brabender instrument, followed by e-beam irradiation. E-beam irradiation of the mixed samples was performed in the EB-tech using an ELV-4 electron beam accelerator with an energy of 1.0 MeV. The integral irradiation dose levels were conducted at 4 kGy. The stress-strain properties of the prepared nanocomposite were determined using an Instron model 4411 testing machine according to ASTM D 638. The test procedure was performed at a crosshead speed of 50 mm/min at room temperature. The dispersion of γ-Al₂O₃-g-PS in the nanocomposites was investigated using a scanning electron microscope (SEM; XL30S FEG, Philips Co.).

Results and Discussion

Graft Polymerization onto γ-Al₂O₃ Nanoparticles

The FT-IR spectra of neat γ-Al₂O₃, TMSPM-modified γ-Al₂O₃, and γ-Al₂O₃-g-PS are shown in Figure 1. After surface modification with TMSPM, a carbonyl peak at 1730 cm⁻¹ and an aliphatic C-H band at 2950 cm⁻¹ appeared in TMSPM. After graft polymerization, aromatic C-H bands (at 3010, 1600, and 1475 cm⁻¹) resulting from the polystyrene were newly generated. The surface modification was also confirmed by performing a floating test on water. The surface-modified γ-Al₂O₃ nanoparticles did not wet because the hydrophilic surface of the alumina particles had become hydrophobic. Quantitative results of the graft polymerization on γ-Al₂O₃ are given in Table 1. The graft yield increased upon increasing the irradiation doses. The graft yield was higher at a 50 vol% monomer concentration than at 70 vol%. The highest graft yield was obtained when 50 vol% of styrene was irradiated at 10 kGy. In addition, neat γ-Al₂O₃, TMSPM-treated γ-Al₂O₃, and Al₂O₃-g-PS were characterized using an SEM.

Characterization of Polypropylene Nanocomposites

The tensile strengths of nanocomposites prepared with different crosslinking agents and 5 phr of TMSPM-treated γ-Al₂O₃ are shown in Figure 2. The tensile strengths of pure PP and 4 kGy-irradiated PP were 2.74 and 2.78 kgf/mm², respectively. Both the 1,4-BDDA- and TMPTA-crosslinked nanocomposites displayed similar tendencies. The tensile strengths were enhanced upon increasing the content of the crosslinking agents up to 3 phr, but they gradually decreased at contents of crosslinking agents over 3 phr. At higher concentration more than 3 phr the monomers may lead to the production of homopolymers, rather than reaction with PP, because so much monomer surrounds the radicals.
Preparation and Characterization of Polypropylene Nanocomposites Containing Polystyrene-grafted Alumina Nanoparticles

The tensile strengths of the prepared nanocomposites (Figure 3) increased upon increasing the \( \gamma\text{-Al}_2\text{O}_3\text{-g-PS} \) content up to 5 phr. The nanocomposite containing 5 phr of \( \gamma\text{-Al}_2\text{O}_3\text{-g-PS} \) exhibited the highest tensile strength.

The SEM micrographs of the fracture surfaces of the composites are shown in Figure 4. \( \gamma\text{-Al}_2\text{O}_3\text{-g-PS} \) formed comparatively smaller agglomerates than did the untreated \( \gamma\text{-Al}_2\text{O}_3 \) or TMSPM-treated \( \gamma\text{-Al}_2\text{O}_3 \). The reason for this phenomenon is that the polystyrene chain grafted onto the \( \gamma\text{-Al}_2\text{O}_3 \) interfered with the agglomeration of the nanoparticles. This result is in agreement with the results of the tensile strength measurements above.

### Conclusions

In this study, we performed surface modification of neat \( \gamma\text{-Al}_2\text{O}_3 \) with TMSPM. The graft polymerization of styrene onto TMSPM-modified \( \gamma\text{-Al}_2\text{O}_3 \) was performed using the simultaneous irradiation polymerization technique under various conditions. We found that the graft yields increased upon increasing the absorbed dose; the graft yield at 50 vol% of monomer was higher than that at 70 vol%. The highest graft yield was obtained when 50 vol% of styrene was irradiated at 10 kGy. The nanocomposite fabricated with 5 phr of \( \gamma\text{-Al}_2\text{O}_3\text{-g-PS} \) and 3 phr of 1,4-BDDA showed the highest tensile strength. The homogeneous dispersion of \( \gamma\text{-Al}_2\text{O}_3\text{-g-PS} \) into the polypropylene matrix and the crosslinking by e-beam irradiation improved the mechanical properties of the nanocomposites.

Additional studies are underway to incorporate various polymergrafted \( \gamma\text{-Al}_2\text{O}_3 \) samples into polymer matrixes for the preparation of nanocomposites with improved mechanical properties.

### References


