Polypropylene-Based Nanocomposite with Enhanced Aging Stability by Surface Grafting of Silica Nanofillers with a Silane Coupling Agent Containing an Antioxidant

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ABSTRACT: Simultaneous improvement in the mechanical properties and lifetime of polymer nanocomposites is crucially significant to further extend the versatility of polymer materials and reduce environmental impact. In this study, we fabricated reinforced polypropylene (PP)-based nanocomposites with improved aging stability by the addition of surface-modified well-ordered silica nanospheres with a silane coupling agent (SCA) containing hindered phenol antioxidant as a filler. Uniform grafting of the SCA on the filler surface contributed to homogeneous dispersion of the filler into the matrix, leading to improved properties (e.g., stiffness and ductility) and uniform distribution of the antioxidant component into the entire nanocomposite by filler dispersion. The grafting of SCA also likely provides an inhibitory effect on antioxidant migration, which leads to loss of polymer stability during the aging process. This novel idea for the material design of PP-based nanocomposites, which simultaneously enhances their mechanical properties and lifetime, is promising for application in the fabrication of various types of polymer nanocomposites.

INTRODUCTION

Improving the properties of polypropylene (PP)-based materials and extending their lifetime are highly effective means of reducing product thickness and further increasing its versatility, which contributes to weight saving in automotive components. The addition of inorganic nanofillers to the PP matrix has resulted in improved mechanical strength,1–9 gas barrier properties,10 and thermal conductivity11 over ordinary PP. The oxidation reaction of PP materials by exposure to heat, light, and so forth normally leads to serious destruction of chemical structures, a decrease in their properties, and a shorter lifetime of PP materials.12 The addition of antioxidants with hindered phenol groups is a common way of suppressing the oxidation of PP which leads to the loss of structure and desirable properties during the aging process.3,13 However, antioxidant components are often physically lost, such as by volatilization and migration, leading to loss of polymer stability.14–18 To overcome these drawbacks, grafting antioxidants on the surface of inorganic fillers is an efficient way.19,20 In this study, a silane coupling agent (SCA) containing a reactive antioxidant is grafted onto the nanofiller surface. We aimed to fabricate a PP-based nanocomposite that simultaneously enhances the mechanical properties and provides aging stability by dispersing the surface-modified nanofiller into the matrix.

Platinum-catalyzed hydrosilylation of olefins is a common and straightforward method of obtaining various SCAs. However, these protocols sometimes suffer from limited functional group compatibility of conventional Pt catalysts in the synthesis of SCA with various functional groups such as halogen, oxygen, nitrogen, and sulfur atoms.21 This prompted us to address the question of how to develop efficient transition metal catalysts for hydrosilylation of functionalized olefins.22–25 Using our synthetic techniques, the target SCAs to extend the lifetime of PP would be obtained starting from olefins containing antioxidant components (e.g., a hindered phenol-type antioxidant).

Nano fillers, because of their large relative surface area, can act as efficient solid supports for grafting large amounts of SCA containing antioxidant components. If the nanofillers grafted with the SCA-containing antioxidant component can be finely dispersed into PP materials, it is possible that the antioxidant...
Scheme 1. Synthesis of SCA Containing a Hindered Phenol Moiety

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would be uniformly transported throughout the materials. This uniform distribution of the antioxidant would likely contribute to effective enhancement of the polymer’s stability. In most cases, however, such nanofillers do not disperse well in the PP matrix, owing to the extreme inertness of PP, which has no functional groups. A method for improving the dispersibility of the fillers is therefore needed.

One strategy to improve the poor dispersion of nanofillers into a polymer matrix is enhancement of matrix-filler affinity using functionalized polymer matrices. We have developed a PP-based nanocomposite with monodisperse silica nanospheres (SNSs) as a filler using functionalized PP containing hydroxyl groups (PPOH) as a matrix. The close affinity between hydroxyl groups in PPOH molecules and surface silanol groups of SNS leads to a uniform dispersion of SNS in the matrix, and thus provides effectively improved mechanical properties, such as stiffness and yield strength of the nanocomposite, without significantly reducing its ductility.

The PP-based nanocomposite with improved mechanical properties and lifetime was, herein, developed by taking advantage of SCA containing the antioxidant components SNS and PPOH. The nanocomposite was prepared using following procedures: (i) synthesis of SCA containing hindered phenol-type antioxidant, (ii) grafting of the SCA onto the surface of SNS denoted as AOxSNS, and (iii) melt-mixing of PPOH with AOxSNS denoted as PPOH/AOxSNS. The variation of mechanical properties and the chemical structure of PPOH nanocomposites with AOxSNS during the thermal aging process was elucidated by tensile testing and Fourier-transform infrared (FTIR) microscopic analysis. To prove the superior performances of PPOH/AOxSNS, we also evaluated the influence of the aging process on PPOH/SNS physically mixed with a commonly used antioxidant, dibutylhydroxytoluene (BHT), as a control experiment.

| RESULTS AND DISCUSSION |

Synthesis and Characterization of SCA Containing the Antioxidant. We conducted synthesis of the target SCA using a two-step process starting from commercially available 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (Scheme 1). We initially performed condensation between carboxylic acid and 3-butene-1-ol with the nanocomposite, without significantly reducing its ductility.

Preparation of AOxSNS. Before fabrication of the PPOH/AOxSNS nanocomposite, we confirmed that the grafting reaction of the SCA with the silica surface would proceed as intended. To estimate the content of grafted SCA, Thermogravimetric/differential thermal analysis (TG-DTA) of AOxSNS was carried out in an air atmosphere (Figure 1). The weight loss arising from combustion of SCA, which occurs at 200–385 °C, as shown in Figure S2, reveals that AOxSNS contains 3.8% SCA. TG-DTA curves of unmodified SNS shows that the moderate weight loss at over 350 °C in the TG curve of AOxSNS is possibly due to dihydroxylation by condensation of silanol groups in silica, which is also observed in the TG curve of an unmodified SNS (Figure S3).

The state of the SCA in the AOxSNS surface was further investigated by evolved gas analysis-mass spectroscopy (EGA-MS) in a helium atmosphere (Figure 2). The intensities of the total ion current (TIC) and extracted ion monitoring (EIM) curves were normalized by integrating the intensity of the entire TIC curves. TIC curves of SCA in AOxSNS and the original SCA exhibit continuous thermal degradation between 150 and 600 °C (Figure 2a). In addition, SCA in AOxSNS shows a specific peak in the TIC curve at higher temperatures of 500–550 °C, unlike the original SCA.

To investigate the degradation process in greater detail, the evolution behaviors of the products were examined in the EIM mode. Figure 2b,c shows EIM curves at m/z 77 and 91, corresponding to benzene and toluene ions, respectively, which are rarely evolved during ordinary degradation of SCA. The aromatic compounds are notably evolved only from the SCA in AOxSNS at higher temperatures of 500–550 °C. Aromatic compounds such as this can be generated by scission of tert-butyl and hydroxyl groups in the hindered phenol moiety. Figure 2d shows the EIM curve at m/z 219 corresponding to the dibutylhydroxytoluene ion that is derived from the hindered phenol moiety without further degradation. The intensity in the EIM curve at m/z 219 of SCA in AOxSNS is much lower than that of the original SCA. These results indicate that the degradation process of SCA in AOxSNS is different from that of the original SCA, possibly because of the effects of grafting conditions. It is likely that stabilization by grafting on the AOxSNS surface suppresses volatilization of SCA until further degradation of the hindered phenol moiety.
takes place. Strong adhesion between organic compounds and silica surface often inhibits degradation of the organic compounds, resulting in further degradation into smaller products at higher temperature.33

The morphologies of SNS and AOxSNS were confirmed by field-emission scanning electron microscopy (FE-SEM) (Figure 3). The FE-SEM image of SNS shows the formation of uniformly-sized nanoparticles with a diameter of 115 nm (Figure 3a). AOxSNS maintained a uniform particle size and well-ordered arrangement, revealing that each nanospheres possesses a uniform surface state even after grafting with SCA (Figure 3b). Therefore, the morphology observation indicates that the SCA molecules are uniformly grafted onto the surface of AOxSNS.

**Dispersion State of Fillers.** As a control experiment to demonstrate the superior performance of PPOH/AOxSNS, we prepared PPOH nanocomposites simply melt-mixed with 10 wt % of SNS and BHT at the same molar ratio as SCA in AOxSNS, which we denote as PPOH/SNS + BHT. The structures of the nanocomposites were analyzed by cross-sectional FE-SEM observation of the sample sheets (Figure 4). Note that AOxSNS is homogeneously dispersed without any aggregation in the PPOH matrix (Figure 4a). On the other hand, some aggregates of SNS are observed in PPOH/SNS + BHT as well as uniformly dispersed SNS (Figure 4b). This indicates that the dispersibility of AOxSNS in PPOH is higher than that of SNS presumably because the large SCA molecules contribute to reducing the cohesive energy of the nanofiller by inhibiting the attractive interparticle interaction.

The glass transition temperatures ($T_g$) of PPOH/AOxSNS and PPOH/SNS + BHT are 55.1 and 53.6 °C, respectively, examined by Differential scanning calorimetry (DSC) measurements (Figure S4). $T_g$ is related to the interfacial interaction between the matrix and filler. Strong interaction increase $T_g$ while weak interaction decrease $T_g$.35 The enhancement in $T_g$ of PPOH/AOxSNS implies that the AOxSNS shows better dispersibility in the PPOH matrix than SNS with strong interfacial adhesion between PPOH and AOxSNS.

**Mechanical Properties.** The nanocomposite samples were aged by statically heating the fresh samples in air at 110 °C for 12, 24, and 80 h. The changes in the mechanical properties of the original PPOH, PPOH/SNS, PPOH/AOxSNS, and PPOH/SNS + BHT caused by the aging process were...
examined by tensile testing (Figure 5). The stress–strain curves suggest that the mechanical properties of PPOH/AOxSNS and PPOH/SNS + BHT vary as a function of sample composition and aging time (Figure 5a,b). The maximum tensile strength and elongation at break of original PPOH, PPOH/SNS, PPOH/AOxSNS, and PPOH/SNS + BHT.

Figure 5. Mechanical properties of the original PPOH, PPOH/SNS, PPOH/AOxSNS, and PPOH/SNS + BHT. Representative stress–strain curves for (a) PPOH/AOxSNS and (b) PPOH/SNS + BHT; insets show the expansion in the initial strain area. (c) Maximum tensile strength and (d) elongation at break of original PPOH, PPOH/SNS, PPOH/AOxSNS, and PPOH/SNS + BHT.

Figure 6. FTIR spectra of (a,b) PPOH/AOxSNS and (c,d) PPOH/SNS + BHT over (a,c) 1400–1340 and (b,d) 1750–1670 cm⁻¹. The samples are aged for 0, 12, and 24 h.
tensile strength and elongation at break (EB) estimated from the stress–strain curves are shown in Figure 5c,d, respectively. When compared with the fresh sample before the aging process, PPOH/AOxSNS show higher tensile strength and EB than the original PPOH, PPOH/SNS, and PPOH/SNS + BHT. The superior mechanical properties of PPOH/AOxSNS are likely due to the homogeneous dispersion of AOxSNS in the PPOH matrix (Figure 4a). The aggregation of filler particles in PPOH/SNS + BHT could also trigger breakage, resulting in poor ductility (Figure 4b). The tensile strength and EB of the original PPOH and PPOH/SNS are significantly decreased during the aging process. After aging for 24 h, both of the PPOH and PPOH/SNS without any antioxidants are immediately broken as soon as tensile load is applied. Lengthening the aging time to 24 h slightly increases the tensile strength of PPOH/AOxSNS, which remains almost constant even after aging for 80 h. However, the tensile strength of PPOH/SNS + BHT markedly decreases after aging for 80 h. The EB of both PPOH/AOxSNS and PPOH/SNS + BHT tends to decrease on lengthening the aging process, despite the EB for PPOH/SNS + BHT being smaller than PPOH/AOxSNS during the entire aging process. A cross-sectional FE-SEM image of a sample sheet of PPOH/AOxSNS after aging for 24 h indicates that dispersion state of AOxSNS in the matrix is unchanged by the aging process (Figure S5). Therefore, the migration of fillers is not the main cause of the decrease in EB of PPOH/AOxSNS by the aging process. DSC measurements reveal that the polymer crystallinity in PPOH/AOxSNS increases from 27.7 to 34.6% during the aging process, which possibly leads to the decrease in the EB of PPOH/AOxSNS. These results clearly indicate that the addition of AOxSNS to the polymer not only contributes to enhanced strength and ductility but also effectively suppresses the loss of mechanical properties during the aging process.

**Structural Changes during the Aging Process.**
Changes in the chemical structures of PPOH/AOxSNS during the aging process were examined by FTIR measurements to provide a better understanding of the mechanism by which AOxSNS suppresses the reduction in mechanical properties. Figure 6 illustrates extracted FTIR spectra of PPOH/AOxSNS and PPOH/SNS + BHT over the 1400–1340 and 1750–1675 cm⁻¹ regions. In Figure 6a, peaks at 1376 and 1359 cm⁻¹ assigned to the CH₃ and CH bending vibration of the PPOH molecules are observed. There is no obvious change in the peak intensity during the aging process.

If the reaction over the PPOH matrix proceeds through the aging process, IR absorption essentially occurs in the region of 1750–1675 cm⁻¹, which corresponds to carbonyl groups. In other words, IR absorbance derived from the carbonyl groups can be used as an index related to the oxidation progress of PP. It is interesting to note that no clear peak is observed in PPOH/AOxSNS, even after aging for 24 h (Figure 6b). In contrast, the intensity of the peak centered at 1712 cm⁻¹ that arises from carbonyl groups increases in PPOH/SNS + BHT as the aging time lengthens (Figure 6d). These results suggest that the oxidation of the polymer matrix is more effectively inhibited in PPOH/AOxSNS than in PPOH/SNS + BHT.

We further analyzed the distribution of carbonyl compounds in the nanocomposites by FTIR microscopic analysis to gain better understanding of the localized changes in the PPOH molecules during the aging process. Cross-sectional optical images and corresponding FTIR images of the sample sheet of PPOH/AOxSNS are shown in Figure 7. The FTIR images are generated by integrating the absorbance at 1400–1340 and 1750–1675 cm⁻¹ in PPOH. Bright colors in the figures indicate the predominance of the components in that spatial region. IR absorbance at 1400–1340 cm⁻¹ arising from the PPOH molecules tends to be roughly consistent with the matrix thickness. The FTIR image constructed from the absorbances in the 1400–1340 cm⁻¹ range region reveals the section thickness to be almost uniform. The FTIR images constructed from the total absorbance at 1750–1675 cm⁻¹ (C=O) clearly indicate that very few oxidation products are generated during the aging process.

FTIR microscopic analyses were also performed for PPOH/SNS + BHT (Figure 8). According to the FTIR image constructed from the absorbances in the 1400–1340 cm⁻¹ range region, the section’s thickness is close to being uniform, in a similar manner to PPOH/AOxSNS. The FTIR image constructed from the absorbances at 1750–1675 cm⁻¹ (C=O) reveals that the content of carbonyl compositions is enhanced on increasing the aging time because of continuing oxidation reactions. Furthermore, the uneven distribution of the carbonyl components in PPOH/SNS + BHT after the aging process suggests an inhomogeneous distribution of BHT molecules in the nanocomposite and the migration of BHT molecules during aging. The results of tensile testing and FTIR microscopic analyses thus suggest the oxidation stability of PPOH/AOxSNS to be much higher than that of PPOH/SNS + BHT. The good dispersion of AOxSNS into the polymer matrix is likely to contribute to the uniform distribution of the antioxidant throughout the nanocomposites. It is also likely that the grafting onto the filler surface with SCA improves in

| Aging Time | Optical Image | FTIR Image |
|------------|---------------|------------|
| 0 h        | ![Optical Image](https://example.com/image1) | ![FTIR Image](https://example.com/image2) |
| 12 h       | ![Optical Image](https://example.com/image3) | ![FTIR Image](https://example.com/image4) |
| 24 h       | ![Optical Image](https://example.com/image5) | ![FTIR Image](https://example.com/image6) |
types of polymer nanocomposites characterized by both longer lifetime and improved mechanical properties.

## EXPERIMENTAL SECTION

### Sample Preparation. Polymer Matrix. PPOH was synthesized using previously reported methods. Poly(5-hexen-1-co-propylene) containing 1.3 mol % of comonomer ($M_w = 503,000, M_n/M_w = 1.90, mm = 98.0\%$) was used as the polymer matrix.

**SCA Containing Antioxidant.** The target SCA was prepared using a two-step synthesis, as shown in Scheme 1. A 100 mL Schlenk flask was equipped with a stir bar, 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (1.39 g, 5.0 mmol, Combi-Blocks, >98%), 3-buten-1-ol (0.52 mL, 6.0 mmol, Tokyo Chemical Industry, >98%), 4-dimethylaminopyridine (DMAP, 61.1 mg, 0.5 mmol, Wako, >99%), and dry dichloromethane (20 mL, Wako). N,N′-dicyclohexylcarbodiimide (DCC, 1.13 g, 5.5 mmol, Sigma-Aldrich, >99%) was then added to the stirred solution at 0 °C. The mixture was warmed to room temperature and kept at stirring for 12 h at the same temperature. The resultant white suspension was filtered and then washed with dry THF. The filtrate was concentrated to dryness under vacuum. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (50/1) to afford 3-(3,5,1-buteryl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate) (1.56 g, 4.7 mmol) in 94% yield.

Next, a 50 mL Schlenk tube, equipped with a stir bar, was filled with the obtained ester (1.50 g, 4.5 mmol), triethoxysilane (1.24 mL, 6.8 mmol, Tokyo Chemical Industry, >99%), and dry toluene (5 mL, Wako). Karstedt’s catalyst (50 µL, 2% solution in xylene, Sigma-Aldrich) was then added dropwise to the stirred solution at 80 °C and kept at stirring for 24 h at the same temperature. After having cooled to room temperature, the reaction mixture was concentrated to dryness under vacuum. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (25/1) to afford the SCA in question (1.64 g, 3.3 mmol) in 74% yield.

**Filler.** SNS 100 nm in size were synthesized using previously reported methods. First, 0.17 g of l-arginine (Arg, Sigma-Aldrich, >98%) and 174 g of ionized water were added to a 250 mL PP bottle and stirred at room temperature. Tetraethyl orthosilicate (TEOS, 10.41 g, Tokyo Chemical Industry, >96%) was rapidly added to the Arg-H2O solution, whereas PPOH/SNS + BHT decreased after aging for 24 h. FTIR imaging analyses were performed to elucidate the influence of the aging process of the chemical structure of the nanocomposites. Variation of the FTIR spectra during the aging process indicates that the formation of carbonyl compounds derived from oxidative aging is effective in PPOH/AOxSNS, unlike in PPOH/SNS + BHT. FTIR imaging of PPOH/SNS + BHT revealed an uneven distribution of the carbonyl components, suggesting inhomogeneous distribution of BHT molecules in the nanocomposite by simple melt mixing and the migration of BHT molecules during aging. Thus, in the case of PPOH/AOxSNS, the extensive dispersion of AOxSNS into the polymer matrix leads to uniform distribution of the antioxidant into the entire nanocomposite. It is also likely that the grafting onto the filler surface with SCA improves in the migration stability of SCA, possibly resulting in the effective improvement seen in the oxidation stability of PPOH/AOxSNS. We believe that this novel idea for fabricating PP-based nanocomposites is promising for applications to the manufacture of various types of polymer nanocomposites characterized by both longer lifetime and improved mechanical properties.
The SNS grafted with SCA containing an antioxidant agent (AOxSNS) was synthesized using a modified regrowth method (Scheme 2).32 SCA (0.25 g) was added to the dispersed liquid of SNS 100 nm in size, and the resulting mixture was placed in an oven at 70 °C for 10 h. A white precipitate was collected using centrifugation for 60 min at 4000 rpm. The precipitate was washed twice with excess ethanol and ionized water. AOxSNS was obtained after drying in an oven (EO-300B, ASONE, Japan) at 110 °C for 3 h.

**Compounding Procedures.** The composites were prepared by melt-mixing using a Labo-Plastmill kneading machine (Toyo Seiki Seisakusho, Japan) equipped with a KF6 twin roller, was 3 g. Sample sheets (50 × 50 × 0.5 mm) for mechanical tests were prepared using 2 g of melt-mixed samples by hot pressing at 180 °C under 5 MPa for 3 min, and then under 10 MPa for 10 min, using a Nafion sheet (Nichias), a stainless steel window frame (0.5 mm thick), and stainless steel plates. The hot-pressed samples were then quickly quenched to room temperature. The sheet samples were aged in an oven (EO-300B, ASONE, Japan) at 110 °C for 12 and 24 h in air.

**Characterization.** The morphology of the fillers and filler dispersion in nanocomposites were evaluated using FE-SEM (S-4800, Hitachi High-Tech Science Corporation, Japan) operated at 1 kV. TG/DTA was performed using an EXSTAR 6000 TG/DTA 6200 (Hitachi High-Tech Science Corporation, Tokyo, Japan). A given sample (approximately 10 mg) was placed in an aluminum pan and heated from 100 to 500 °C at a heating rate of 10 °C/min under air. DSC measurements were performed using an EXSTAR DSC7000X (Hitachi High-Tech Science Corporation, Japan) at a heating rate of 10 °C/min under nitrogen. EGA-MS and DSC curves of PPOH/AOxSNS and PPOH/SNS+BHT; cross-sectional FE-SEM image of PPOH/AOxSNS after aging (PDF).

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01198.

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The authors declare no competing financial interest.

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