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The effect of filler particle size on the antibacterial properties of compounded polymer/silver fibers

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Antibacterial activity has become a significant property of textiles used in applications such as medicine, clothing, and household products. In this study, we compounded polypropylene with either micro- or nano-sized silver powders. These polypropylene/silver compounds were prepared by direct melt-compounding using a conventional twin-screw mixer. We analyzed the characteristics of the compounds using wide-angle X-ray diffractometry (WAXS), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The DSC and WAXS results indicated that the crystallinity of the polypropylene component decreased slightly when compared with that of the pure polymer. The SEM micrographs indicated that the silver particles had good dispersibility in the matrix. We measured the mechanical properties of these materials using a universal tensile tester and evaluated the antibacterial activities of these compounds by performing quantitative antibacterial tests using the AATCC-100 test method. From these evaluations of antibacterial activity, we conclude that the compounds incorporating the silver nanoparticles exhibited superior antibacterial activity relative to the samples containing micron-sized particles.

1. Introduction

Interest in developing technologies related to creating comfortable living environments has increased because of pollution caused by various sources. For instance, research on antibacterial finishing has been investigated actively in the textile industry [1–3]. There are two main methods by which antibacterial finishing occurs during processing of textiles: one in which the antibacterial agent is mixed directly with fiber or polymer during the spinning process and the other in which the agent is treated on the textiles during a finishing process, such as dyeing. Generally, some type of organic agent, such as a quaternary ammonium salt, is used in the second of these methods. Since it was discovered that some organic antibacterial agents, included aromatic halogen compounds, have a harmful effect on the body, there was a rapid reduction in the quantity of these compounds utilized industrially.

Recently, the number of studies of natural or inorganic compounds for antibacterial finishing has increased because of the perceived lack of safety when using some organic agents [4, 5]. Silver is a non-toxic inorganic metal that is a safe antibacterial agent; it has been reported that silver is a strong agent that is capable of killing ca. 650 disease-causing organisms in the body. Thus, silver has the potential to be an excellent antibacterial agent [6–10]. The silver that has been mainly used for antibacterial finishing during the past few decades has been in the form of chemical compounds because of technical difficulties dealing with the elemental form. As technologies for producing nanoparticles have developed to a high-degree recently, attempts have been made to apply them to antibacterial finishing. As the size of the silver particles decreases, down to the nano-scale regime, their antibacterial efficacy increases because of their larger total surface area per unit volume [11, 12].

Polypropylene (PP) is one of the most widely used polymer resins in the textile and plastics industry because it can be applied in various forms, e.g., nonwoven, filaments, and films [13–15], and because it does not contain any polar groups in its backbone. While it might be expected that synthetic fibers do not require antibacterial activity, because their resistance to bacteria is generally stronger than that of natural fibers, it is easy for a microorganism to attack the main chains of most commercial polymers, such as PP, because they comprise methyl chains. Moreover, because polypropylene is primarily used for sanitary applications, e.g., in filters, diapers, and surgical masks, there is in need to impart it with antibacterial activity.

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To study the antibacterial effect as it relates to the size of the silver particles, we mixed polypropylene chips and two silver powders, that have different silver contents, by melt compounding and characterized these compounds by DSC, XRD, and SEM. We used a tensile tester to investigate the mechanical properties of the polymer/silver compounds and evaluated the antibacterial activity of the compounds by performing quantitative antibacterial tests using the AATCC 100–1999 method.

2. Experimental

2.1. Materials

Two silver powders, which comprised sphere-shaped silver particles, were supplied by NP-Tech Co., Ltd., Korea. The average diameter of the first silver powder (Silver I) was ca. 100 nm and the second (Silver II) was 1 μm (Fig. 1). The silver powders were dried from silver colloidal solutions, which we prepared by the reduction of an $AgNO_3$ solution using hydrazine solution in both the presence and absence of a surfactant. The silver particles formed according to the following reaction:

$$N_2H_4 + 4Ag^+ + 4OH^- \rightarrow 4Ag^0 + 4H_2O + N_2$$

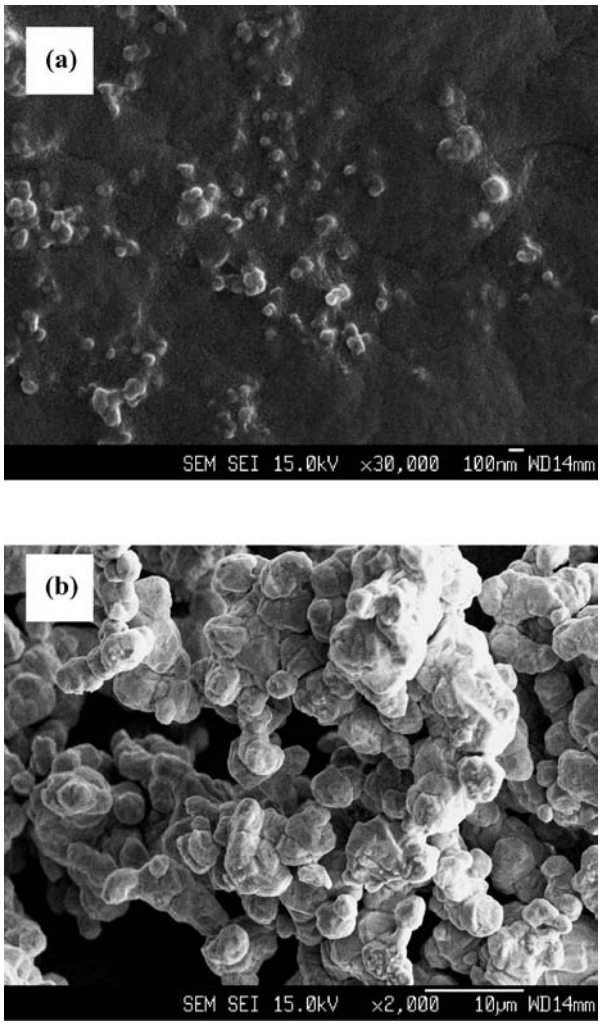

Figure 1 SEM images of silver powders: (a) Silver I; (b) Silver II.

An isotactic polypropylene (*i*-PP) was provided by Honam PetroChemical Inc., Korea. The characteristics of the PP chips are as follows: M_n, 5.2×10^4; MFI, $16.0 \times$ g 10/min; density, 0.90 g/cc; polydispersity, 4.6.

2.2. Melt compounding

Before compounding, the polypropylene chips and the silver powders were dried in a vacuum oven at 80°C for 2 h and then cooled to room temperature. The PP chips were compounded with the silver powders using a non-intermeshing counter-rotating twin-screw mixer (Haake Rheomix 600); the rotor speed was 60 rpm, the mixing temperature was 250°C, and the mixing time was 5 min. Samples were prepared in which the content of silver particles in the polypropylene matrix was set to 0.1, 0.25, 0.5, 0.75, 1, and 3 wt%. Unfilled PP was also subjected to the same extrusion process to obtain similar thermal history to that of the filled samples. To perform the subsequent measurements, the composites were converted into thin films by the use of a hydraulic press (CARVER, model 2699). The polymer/silver compounds were heated in the press up to a temperature of 220°C. After the samples became entirely molten, they were kept at that temperature for 5 min to eliminate the heat history; a load was then applied onto the press to form the thin films that were then quickly removed from press and quenched in liquid nitrogen. The thickness of each film was ca. 0.5 mm.

2.3. Measurements

To identify the silver particles dispersed in the polypropylene matrix, the morphology of each sample was observed, after coating with Pt for 5 min, using a scanning electron microscope (SEM, JEOL JSM 6330F) operating at 15 kV and employing magnifications of up to 30000.

Antibacterial tests are generally classified into two methods: either quantitative or qualitative analysis. In this study, we performed our evaluation of the antibacterial activity of the silver particles in compounds by using a quantitative antibacterial test method: the AATCC 100 1999 test. We present the degree of the antibacterial effect as the ratio of reduction of a bacteria colony. The equation for quantitative antibacterial evaluation is given by

$$R(\%) = \frac{B - A}{B} \times 100$$

where $\boldsymbol{R}$ is the percentage of reduction, $\boldsymbol{A}$ is the number of bacteria in the colony recovered from the inoculated film swatches in a jar incubated for 24 h, and $\boldsymbol{B}$ is the number of bacteria in the colony recovered from the inoculated film swatches in the jar immediately after inoculation.

For thermodynamic experiments, we used a differential scanning calorimeter (DSC, Perkin Elmer DSC-7) equipped with a cooler and operated under a nitrogen atmosphere. The samples were heated from –50 to 225°C at 10°C/min, held at that temperature for 2 min to remove their thermal history, and then cooled to –50°C

at 10°C min. Using this procedure, the melting temperature (T_m) and the crystallization temperature (T_c) were obtained from the thermodynamic curves and the apparent enthalpies of fusion were calculated from the area of the endothermic peak. The percentage of crystallinity of the polypropylene samples was evaluated using the following equation:

$$Crystallinity\,(\%) = \frac{\Delta H_f}{\Delta H_f^0 \cdot w_f} \times 100$$

where ΔH_f is the heat of fusion of PP, w_f is the weight fraction of PP in the composites, and $\Delta H^0{}_f$ is the extrapolated value of the enthalpy corresponding to the heat of fusion of 100% crystalline PP, which we obtained from the literature (209kJ/kg) [16].

The antibacterial polymer compounds were analyzed by the use of a wide-angle X-ray diffractometer (XRD, Rigaku X-ray diffraction system) using Cu-Kα radiation and operating at 40-kV and 100 mA. The diffraction angles (2θ) of each sample were measured from 5 to 90° at a scan speed of 5 °/min. The static mechanical tensile tests were conducted using a tensile testing machine (Instron-4465, Instron Corp.) equipped with a 1-kN cell at room temperature. The specimen bars (ASTM D638 type) were made using a Cutting Press (RAY-RAN TEST EQUIPMENT. LTD.). The crosshead speed was 5 mm/min and the gauge length was 30 mm. 10 specimens for each compound composition were tested and the average values were used as the result data.

3. Results and discussion

3.1. Surface observation

Fig. 2 presents SEM micrographs of the polypropylene/silver compounds. Most of the silver particles having an average diameter of ca. 30 nm had relatively good dispersibility, but some of these nanoparticles had agglomerated into clusters because of attractive interaction forces between them. The particles sizes of Silver I and Silver II in the matrices were smaller than they were in their powder states. This finding implies that the silver particles in the polypropylene were fragmented into smaller pieces by the action of the twin helical screw during the melt-compounding process. This phenomenon resulted in the uniform appearance of the Silver I particles in the matrix.

3.2. Antibacterial evaluation

We performed antibacterial tests using two types of bacteria: a Gram-positive microbe (*Staphylococcus aureus,* ATCC 6538) and a Gram-negative microbe (*Escherichia coli,* ATCC 25922). The initial number of cultured bacteria was 1.6×10^5 for the Gram-positive microbe and 1.2×10^5 for the Gram-negative microbe. The cultured bacteria were inoculated with both the control polypropylene sample and the samples incorporating the various silver contents. The compounds containing very small amounts of silver nanoparticles exhibited almost perfect reduction against both kinds of bacilli.

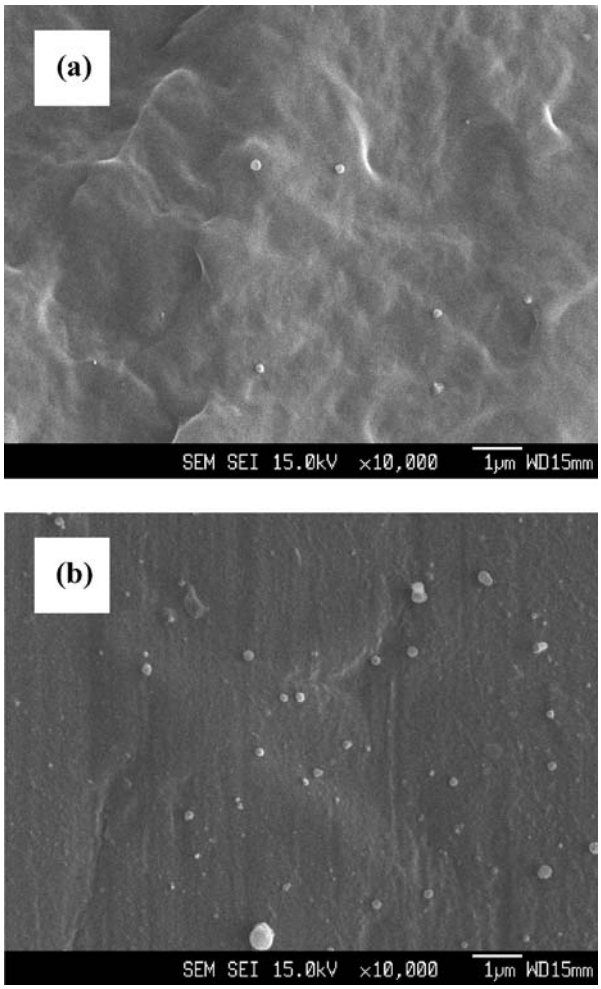

Figure 2 SEM images of polypropylene/silver compounds: (a) Silver I; (b) Silver II.

For the silver nanoparticles (Silver I), we found that the compound having a 0.1% silver content displayed excellent antibacterial effect (bacterial reduction of 99.9%), but the micron-sized silver (Silver II) required a silver content > 0.5 before exhibiting good antibacterial activity. Therefore, the polymer compounds that contain the smaller silver particles have the stronger antibacterial activity, regardless of the Gram class.

3.3. Thermal analysis

Fig. 3 displays DSC thermogram curves of the polymer/metal composites obtained after heating. We used the heating scans to determine the melting behavior of the components in the blend or compound, such as the temperature of melting (T_m) and the heat of fusion (ΔH_f). Both T_m and T_c decreased, although inappreciably, upon increasing the silver content, and the heat of fusion in the range of the melting temperature decreased slightly. The degree of supercooling (ΔT) of the PP composites was slightly higher than that of the control, which suggests that the silver powders did not act as nucleating agents in the polymer matrix and decelerated the crystallization rate of the polymer. Fig. 4 presents the variation in the crystallinity of the polypropylene composites as a function of the silver content. The crystallinities of polypropylene in the melted compounds were close to that of the control.

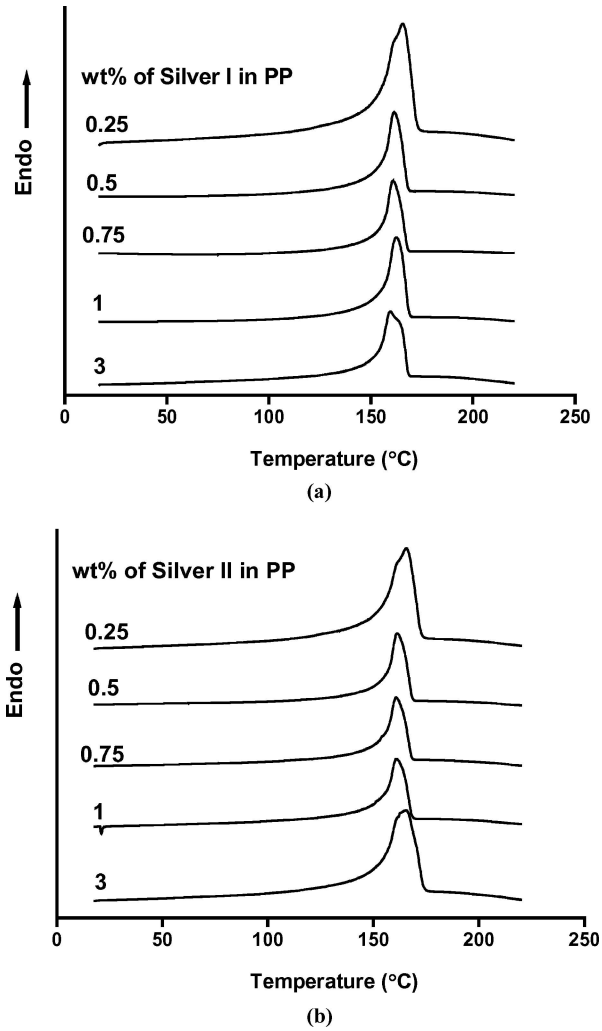

Figure 3 DSC thermogram curves of polypropylene compounds: (a) Silver I; (b) Silver II.

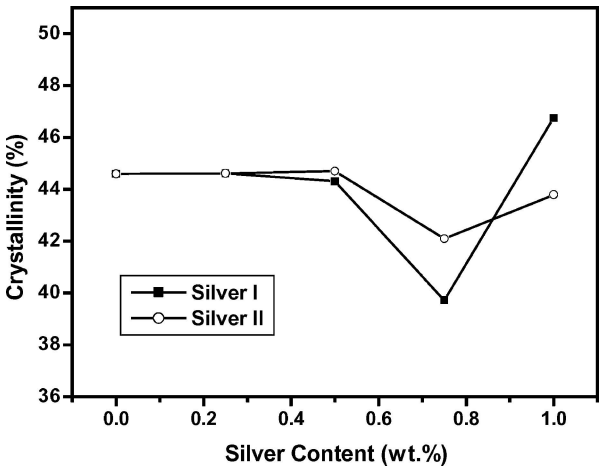

Figure 4 The crystallinity of polypropylenes filled with silver powders.

This result reveals that the silver nanoparticles exerted hardly any acceleration effect on the crystallization of polypropylene.

3.4. Structural analysis

Fig. 5 presents the WAXS patterns of the polypropylene compounded with 1 wt% of silver powder. The diffraction peaks of the PP crystal, which range from

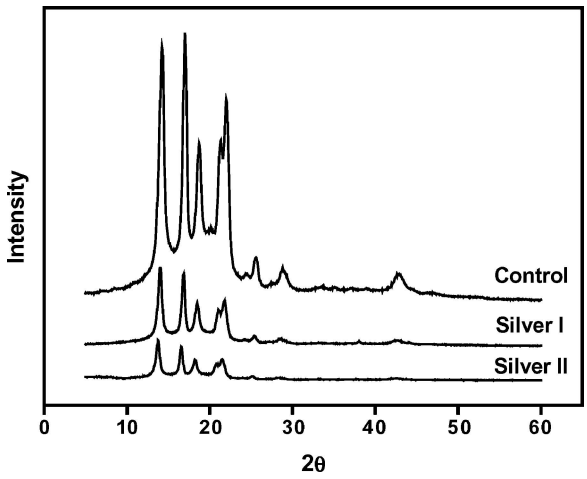

Figure 5 XRD patterns for the polypropylene containing 1 wt% of silver.

10 to 30°, indicate a typical α crystallite form of PP. The diffraction patterns of PP crystals in the two compounds did not indicate any significant change in their crystallinity, but the magnitude of the diffraction peaks of the PP crystallites decreased significantly [17, 18]. In addition, we observe some other peaks beside the PP crystal peaks (2θ = 38.0, 44.6, 64.8, and 77.6°); these peaks correspond to the diffraction of silver metal [19]. The XRD peaks of the silver crystals became clearer and increased in size upon increasing the silver nanoparticle content in the polypropylene matrix. It has

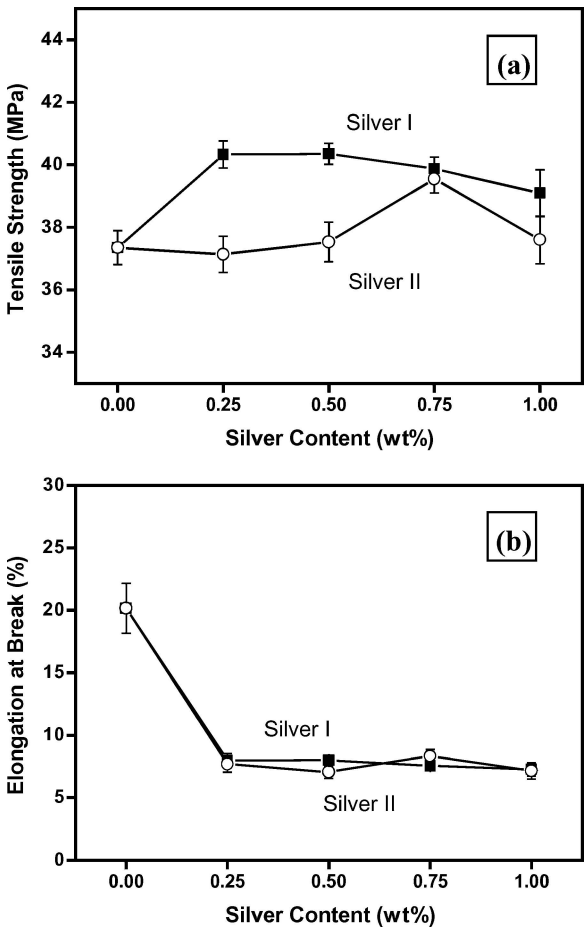

Figure 6 Mechanical properties of the PP/Ag composites as a function of their silver content: (a) tensile strength; (b) elongation at break.

TABLE I Bacteria reduction ratio of polypropylene/silver compounds against *Staphylococcus aureus*

Conc. (%)	0	0.1	0.25	0.5	1	3
Silver I	26.3 (10.8)*	99.9	99.9 84.5	99.9	99.9	99.9
Silver II		–	(82.8)*	99.9	99.9	99.9

(X)*: against Escherichia coli.

been reported that if the nanoparticles are perfectly exfoliated in the matrix, the inherent crystal diffraction peaks of these particles are not detected in XRD patterns [20, 21]. Thus, our XRD results indicate that the silver particles were not completely exfoliated in the polypropylene matrix.

3.5. Mechanical properties

We measured the tensile properties of the films, such as their yield strength and strain at break, to evaluate the effect of mixing in the fillers. Paul et al. [12, 21–23] observed systematic effects on the tensile properties of matrix polymer—increased yield strength and modulus sequential—upon addition of a nano-filler. Fig. 6 displays the mechanical properties of the PP/Ag composites as a function of silver content. The yield strength did not undergo any significant change as the amount of silver increased; the initial values were nearly maintained after compounding with the fillers. We believe that there are no significant interactions between the silver particles and the PP matrix because polypropylene does not possess any reactive functional groups. In contrast, the elongation at break decreased rapidly in response to a very small amount of filler (0.25wt%), but the value was maintained thereafter.

4. Conclusions

We prepared polypropylene/silver compounds by melt compounding using a general counter-rotating twin-screw mixer. From the DSC results, we observed that the heat of fusion and the crystallization temperature both decreased appreciably, but the crystallinity of polypropylene in the composites was nearly maintained, upon increasing the content of silver particles in the polymer matrix. The X-ray diffraction peaks of the silver crystals enlarged considerably upon increasing the silver content. With regard to the mechanical properties, we found that there was a negligible relationship between the strength and the silver content, but the elongation at break decreased rapidly upon adding the silver particles. When we observed the films' surfaces by SEM, we found that the silver particles in general displayed good dispersibility in the matrix. All of the compounds incorporating Silver I exhibited perfect antibacterial behavior, but only the compounds containing > 0.5 Silver II possessed good antibacterial activity. Therefore, for the production of compounds having antibacterial activity, the nano-sized silver is superior to micro-sized silver at the same weight.

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