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Preparation of nanocomposite fibers for permanent antibacterial effect

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The polypropylene/silver nanocomposite fibers were prepared for the attainment of permanent antibacterial activity to common synthetic textile. The fibers were melt-spun by co-extrusion of polypropylene (PP) and PP/Ag master-batches using general conjugate spinning. Master-batches were made up of mixture of PP chips and nano-sized silver powder. The antibacterial efficacy of spun fibers was excellent not when the master-batch used as the core, but when used as the sheath. The antibacterial activity of nano-silver in fibers was evaluated after certain contact time and calculated by percent reduction of two kinds of bacteria; *Staphylococus aureus* and *Klebsiela pneumoniae*. For the characterization, differential scanning calorimetry (DSC) and wide-angle X-ray diffractometer (WAXD) were used for analysis of structure, thermal and crystallization behavior of the spun-fibers. Scanning electron microscopy (SEM) was carried out to observe particle distribution on the nanocomposite fibers.

1. Introduction

In these days, the use of nano-structured materials is becoming more widespread and a major advantage over either organic or inorganic nanoparticles offer many possibilities of applications in the areas of physics, chemistry, pharmacy, surface coating agents, textile sizing, agriculture, biochemistry, and so on [1–5]. In chemistry, nanoparticles are used to compartmentalize the reaction; the very large area of the particles offers new opportunities in domains like catalysis and chromatography [6].

Polypropylene (PP) is one of the most widely used synthetic fibers in textile industry, which is cheaper and stronger than the other synthetic fibers. Besides, PP is well applicable for various fields, for example, carpet, automotive interior trim, film, package, cover stock, cable, napkin, and so on. Particularly, it is used for sanitary application such as surgical mask, diaper, filter, hygienic band, etc. Then the products made up of PP need antibacterial activity, one of the important functionalities, than the others [7–9].

In the last few decades, there has been increased interest in antibacterial finishing on textile materials because of varieties environmental pollutions. By the way, using of some organic antibacterial agents has been evaded up to now, since the unsafe some halogen compounds of having aromatic group becomes a serious problem. From that point of view, silver is very good antibacterial agent because it is non-toxic and natural inorganic metal, and besides, silver can kill many harmful microorganisms against the human body [10, 11]. Such silver has a size of nano-level, the total surface area of the silver becomes larger in identity volume. Then a chance, which is antibacterial action of the nano-silver, is raised the antibacterial efficiency is consequently increased [12, 13].

In this research we designed an organic-inorganic nanocomposite fiber which have permanent antibacterial effect. For this purpose, we have prepared nanocomposite fiber of sheath-core type using PP chips and PP/Ag master-batches with varying the concentration of silver nanoparticles.

2. Experimental

2.1. Materials

Silver powder was supplied by Nano-EnC Co., Ltd., Korea. The silver powder is comprised of sphere shaped nanoparticles, which have purity of more than 99.9% and have density of 10.49 g/cc. For the size analysis of nano-silver, the particles in aqueous solution shaken by supersonic generator (Power sonic 420) for 5 min were measured using size analyzer (ELS-800, Photal otsuka electronics). The mean diameter of the silver nanoparticles was approximately 15.7 nm (SD = $\pm$ 2.6 nm) in Fig. 1. Polypropylene chips (isotactic PP) were provided from Honam PetroChemical Inc., Korea. Its characteristics commonly used for fiber spinning are as follows; M_n: 5.2×10^4, MFI: 16.0 g/10 min, Density: 0.90 g/cc, and Poly-dispersity: 4.6. For easier spinning process, PP/Ag master-batches were prepared by a conventional twin-screw extruder, were composed of PP and silver powder, and were made to two types according to the silver nanoparticles contents are 3 and 10 wt%.

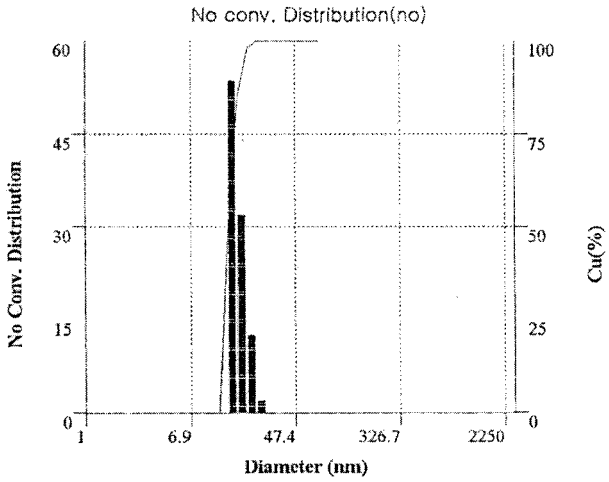

Figure 1 Analysis of size distribution of nano-silver particles.

2.2. Spinning process

The spinning machine is a general conjugate spinning machine (produced by Nanotechnics Co., Ltd. in Korea), which is composed of two extruders ($L/D = 25$, $D = 25$ mm) and gear pumps. Both PP chips and PP/Ag master-batches were dried for at least 2 hrs at 100°C in vacuum drier to secure complete moisture-free state. The spinning processes are performed by two different methods. In the first spinning, the PP/Ag master-batches were added in the core-section and the PP chips were added in the sheath-section. For the second spinning, on the contrary; the PP/Ag master-batches were put in the sheath-section and the PP chips in the core-section. Thoroughly both chips and dried master-batches were melted in both cylinders, combined in the spinneret. Then they are extruded through mono-hole nozzles, which have diameter of 0.5 ϕmm at the first spinning process and 1.0 ϕmm at second. The Melt flow rate (MFR) values of nanocomposite fibers are 3 g/min at first and 4 g/min at second, respectively. During the whole spinning processes, temperature of spinneret was maintained at 250°C and take-up speed was maintained at 1000 m/min. The melt-spun fibers are classified in Table I.

2.3. Thermal analysis

For thermodynamic experiment, dynamic scanning calorimeter (DSC, Perkin-Elmer DSC-7) equipped with a cooler was used under the nitrogen atmosphere. All the samples were heated from 0°C to 250°C at 20°C/min. From this procedure, the melting temperature (T_m) of the nanocomposite fibres was obtained and apparent enthalpies of fusion were calculated from the area of the endothermic peak. The percent crystallinity of polypropylene was evaluated using the following equation:

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

where ΔH_f is the heat of fusion of PP fibers, w_f is the weight fraction of PP in the blends, and ΔH_f^0 is the extrapolated value of the enthalpy corresponding to the heat of fusion of 100% crystalline PP taken as 209 kJ/kg from the literature [14].

2.4. Structural analysis

The fibers were analyzed by a X-ray diffractometer (XRD, Rigaku X-ray diffractometer), which was measured on RINT2000 Wide angle goniometer using Cu K_α radiation at 40 kV and 100 mA. With this procedure, the angles (2θ) of diffraction of all the samples were measured from 5° to 70° on the equatorial direction.

2.5. Morphology observation

For morphology analysis of the melt-spun fibers, samples were coated with platinum under vacuum for 5 min and these cross-section were observed with the scanning electron microscope (SEM, JEOL JSM-6330F), which was measured on 5 kV and was employed with up to 30,000 magnifications.

2.6. Antibacterial evaluation

The antibacterial properties were quantitatively evaluated against *Staphylococcus aureus* (*A. aureus*), ATCC6538, a Gram-positive bacterium and *Klebsiela pneumoniae* (*K. pneumoniae*), ATCC 4352, a Gram-negative bacterium, according to AATCC 100 test method. Fiber specimens were challenged with 1 mL of bacterial inoculum in a 250 mL container. The inoculum was a nutrient broth culture containing 1.3–1.6×10^4/mL colony forming units of bacteria. After test and control specimen had been in contact with bacteria for over 18 hrs, 100 mL of sterilized distilled water was poured into the vessel and vigorously shaken, and the supernatant was diluted to 10^1, 10^2, 10^3, and 10^4. The diluted solution aliquots were plated on a nutrient agar and incubated for 18 hrs at 37°. Viable colonies

TABLE I Classification of melt-spun fibers

Sample	Component (sheath/core)	Extruding ratio (sheath/core)	Silver content (wt%)	Melt flow rate (g/min)	Nozzle diameter (mm)
PPC-0	PP/PP	50/50	0	3.0	0.5
PPC-1.5	PP/M1[a]	50/50	1.5	3.0	0.5
PPC-5	PP/M2[b]	50/50	5.0	3.0	0.5
PPS-0	PP/PP	50/50	0	4.0	1.0
PPS-0.3	M1[a]/PP	10/90	0.3	4.0	1.0
PPS-0.9	M1[a]/PP	30/70	0.9	4.0	1.0
PPS-1.5	M1[a]/PP	50/50	1.5	4.0	1.0

[a]M1 is master-batch type 1, which contains 3 wt% silver.
[b]M2 is master-batch type 2, which contains 10 wt% silver.

of bacteria on the agar plate were counted, and the reduction in numbers of bacteria was calculated using the following equation:

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

where R is the reduction rate, A is the numbers of bacterial colonies from control, and B is the number of bacterial colonies from bicomponent melt-spun fibers.

3. Results and discussion

DSC thermograms of the fibers having nano-silver in core-part are depicted in Fig. 2. There is a negligible relationship between the melting point of fibers and the variation of nano-silver content. In this result, the heat of fusion of fibers including silver nanoparticles was decreased than that of the pure PP fibers (PPC-0), but the crystallinity of PP fibers having silver not absolutely decreased with increasing silver content (Fig. 3). The reduction of crystallinity is considered that the silver nanoparticles interfered with crystallization process of polypropylene, because they acted on a type of impurities in PP matrix. On the other hand, the silver may sometimes be a function of nuclear agent which can accelerate crystallization of PP, then its crystallinity is not always decreased.

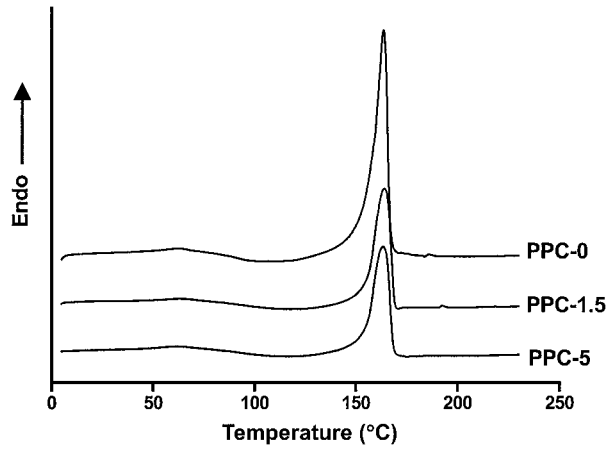

Figure 2 DSC curves of the spun fibers containing silver in core-part.

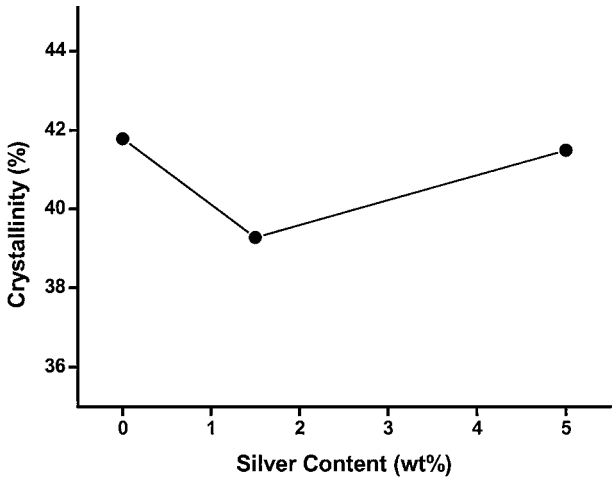

Figure 3 The variation of crystallinity of the fibers having nano-silver in core-part.

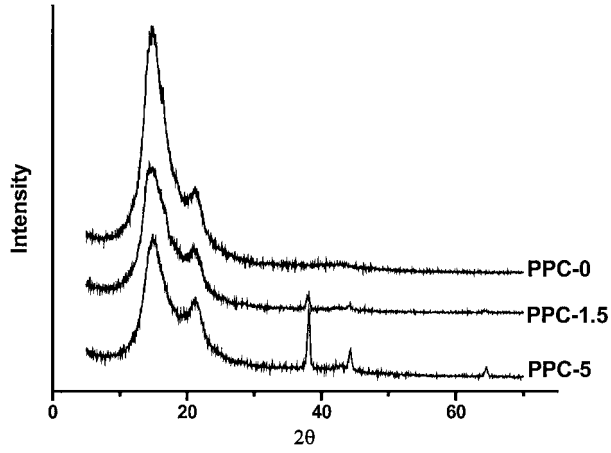

Figure 4 XRD patterns of the spun fibers containing silver in core-part.

X-ray diffraction methods of characterization represent a powerful approach to the structural analysis of nanophase materials. In fact, it must be recognized that XRD, based on wide-angle scattering, has been the single most important technique for determining the structure of materials characterized by long-range order. Fig. 4 shows the WAXS patterns of the melt-spun fibers having silver in core-part. PP is known as a crystalline polymer, and the diffraction peaks at $2\theta = 14.7^\circ$ and 21.2° (2θ: diffraction peak angle) correspond to the PP crystalline phase (110) and (131) [15, 16]. After the silver nanoparticles were added in PP fibers by the melt-spinning process at 250°C, the intensity of the PP crystalline diffraction peaks was slightly decreased. Except the diffraction peaks of PP, all the other peaks were corresponding to the silver phase ($2\theta = 38.0^\circ$, 44.3°, and 64.5°) [17]. The Peaks of silver particles were enlarged with increasing the content of silver nanoparticles in fibers.

The fibers included silver in core-part was conducted on antibacterial tests, but the fibers showed not apparently antibacterial effect as compared with virgin polypropyrene. We considered that silver in the inside fiber was not operated on the good antibacterial agent then we added nano-silver to sheath-part of fiber in second spinning (see Table I).

Figs 5, 6, and 7 indicate the DSC thermograms, the variation of PP crystallinity, and the WAXS patterns

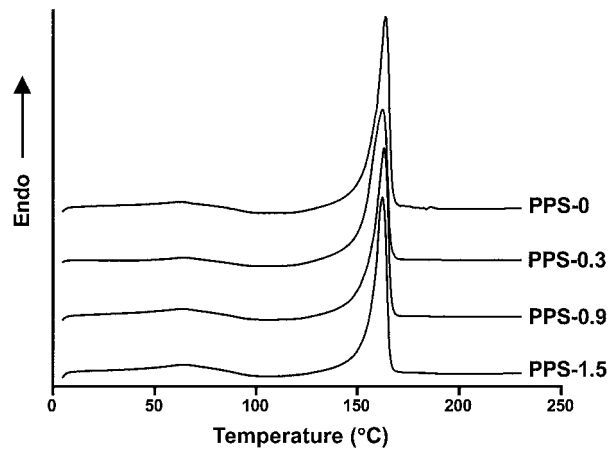

Figure 5 DSC curves of the spun fibers containing silver in sheath-part.

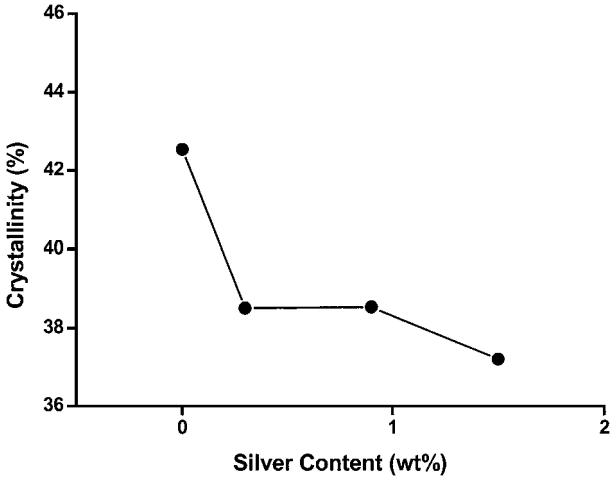

Figure 6 The variation of crystallinity of the fibers having nano-silver in sheath-part.

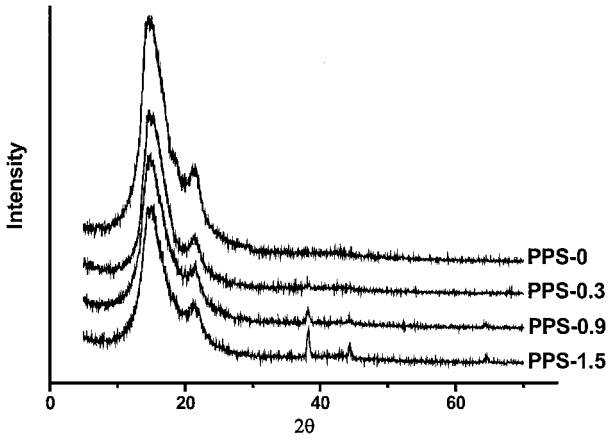

Figure 7 XRD patterns of the spun fibers containing silver in sheath-part.

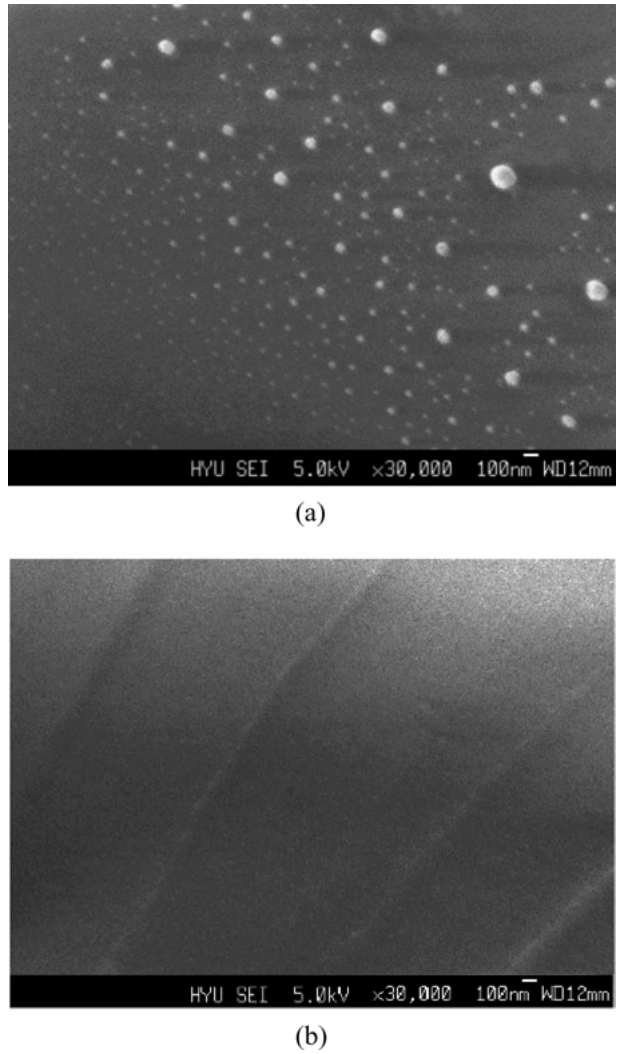

Figure 8 SEM micrographs of (a) core-part, (b) sheath-part at the cross-section of PPC-5 fiber.

of the fibers having silver in sheath-part, respectively. These results showed similar results as compared with that of the fibers having silver in core-part. But, these spun fibers in the second spinning were revealed good antibacterial effect in Table II. In other words, the silver nanoparticles placed inside fiber have a negligible relationship with antibacterial effect, but they included outside fiber contribute strongly to antibacterial action. From this result, although PPC-5 has the higher concentration of silver than the other melt-spun fibers, it show not significant antibacterial effect, just like mentioned above. However, PPS-0.3 and PPS-1.5, which have silver nanoparticles in sheath-part, are showed good antibacterial activity. The antibacterial evaluation can be closely explained as following. If a certain bacterium comes in contact with silver at the fiber surface, the bacterium is extinguished with the antibacterial activity of silver nanoparticles, then propagation of the bacteria is inhibited.

SEM is a good method to provide a real-space image of the nano-scaled particles on other material surfaces. Hence, the cross-section of nanocomposite fibers was observed on SEM. In Fig. 8, SEM micrographs show the cross-section of PPC-5, which is composed of PP/Ag in core-part and PP in sheath-part. In Fig. 8a the silver nanoparticles were observed in core-part. The other SEM micrograph, sheath-part of PPC-5, has no silver nanoparticles in Fig. 8b. In the SEM micrographs, it is demonstrated that the silver powder consists of uniform spherical nanoparticles, but some particles are aggregated by interaction force of nano-silver powder.

TABLE II Antibacterial evaluation of the spun fibers by AATCC 100 test method

	Ag content		Antibacterial evaluation (%)	
Sample	Weight (%)	Volume (%)	*Staphylococcus aureus*	*Klebsiella pneumoniae*
PPC-0	0	0	26.3	10.8
PPC-5	5.0	0.433	19.4	14.8
PPS-0.3	0.3	0.026	99.9	99.9
PPS-1.5	1.5	0.130	99.9	99.9

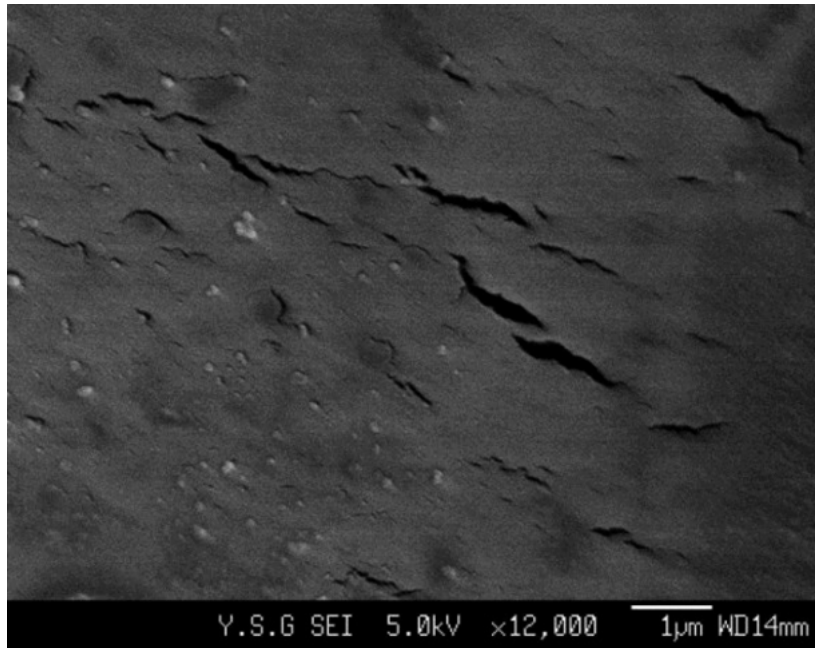

Figure 9 SEM micrographs of the boundary of sheath-part and core-part at the cross-section of PPS-1.5 fiber.

Fig. 9 shows the cross-section of the PPS-1.5 fiber, this image indicates a boundary phase of core and sheath-part.

4. Conclusions

The sheath-core bicomponent fibers of two types were melt-spun by co-extrusion of polypropylene (PP) and PP/Ag master-batch. DSC results showed crystallinity of the spun fibers added the silver nanoparticles slightly decreased or maintained as previously stated. The diffraction peaks of the silver crystal in polypropylene are grown up with increasing silver content in the two processes, the first spinning and the second spinning. The SEM results showed the silver nanoparticles in fibers have relatively good dispersibility. In the results of antibacterial test, the fibers containing silver nanoparticles in core-part had not nearly significant antibacterial activity. However, the fibers having silver in sheath-part showed excellent antibacterial effect.

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