#### (19) World Intellectual Property Organization

International Bureau



# . I DERTE ENTREMENT DE ENTRE ENT

(43) International Publication Date 15 September 2005 (15.09.2005)

PCT

# (10) International Publication Number WO 2005/085339 A1

(51) International Patent Classification<sup>7</sup>: B82B 3/00

C08K 3/08,

(21) International Application Number:

PCT/KR2005/000576

(22) International Filing Date: 2 March 2005 (02.03.2005)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data: 10-2004-0016124 10 March 2004 (10.03.2004) KR

(71) Applicant and

(72) Inventor: LEE, Jeong-Hun [KR/KR]; Saebyul-Hanyang Apt 206-1501, Dalan-dong, Dongan-gu, Anyang-shi, Kyunggi-do 431-050 (KR).

(72) Inventor; and

(75) Inventor/Applicant (for US only): CHOI, Gil-Bae [KR/KR]; Daechi-Samsung Apt 110-404, Daechi-1-dong, Kangnam-gu, Seoul 135-968 (KR).

(74) Common Representative: CHOI, Gil-Bae; Daechi-Samsung Apt 110-404, Daechi-1-dong, Kangnam-gu, Seoul 135-968 (KR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

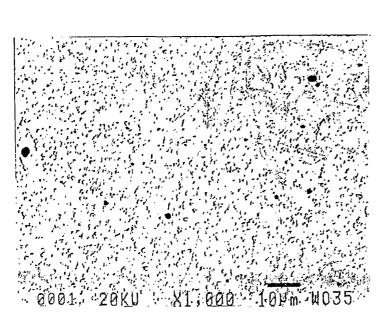
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### **Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR THE PREPARATION OF SILVER NANOPARTICLES-POLYMER COMPOSITE



(57) Abstract: It is desired to develop a new composite composed of silver nanoparticles and a polymer in which nanoparticles are uniformly incorporated without coagulation in a polymer in order to maximize the antibacterial effect of silver without deteriorating the properties and functions of the polymer. According to the invention, a method for the preparation of silver nanoparticles-polymer composite comprising introducing silver nanoparticle colloid solution to a preheated polymer, rotating the resulted mixture at the same temperature to remove water, kneading and extruding the resulted mixture in a suitable The silver nanoparticle-polymer composite thus prepared can be used as a master batch or a functional chip for extrusion, injection, spinning to prepare molding article, film, sheet, fiber or the

1

# METHODE FOR THE PREPARATION OF SILVER NANOPARTICLES-POLYMER COMPOSITE

#### **Technical Field**

5

The present invention relates to a method for the preparation of silver nanoparticle-polymer composite. More particularly, the present invention relates to a method for the preparation of a silver nanoparticle-polymer composite by dispersing silver nanoparticle in a polymer without coagulation and a silver nanoparticle-polymer composite prepared thereby.

10

#### **Background Art**

In recent, the advance of nanotechnology makes it easy to prepare many inorganic or metallic particles having a nano-size. It has been reported that, due to their extremely increased surface area and quantum size effect, nanoparticles can give much more physical and chemical effects than bulk material even when used in much less amount than the bulk material, as well as they may show properties significantly different from the bulk material.

20

15

As stated above, since nanoparticles are used in an extremely small amount, they shows the equivalent or better effect than micro-particles or bulk material, nanoparticles can be used in an extremely small amount, and thus they shows less toxicity to the human body and the environment. As a result, nanoparticles are considered as being stable to the environment and benefit to human body and the environmental and many studies have been made on nanoparticles.

In case where nanoparticles are incorporated in a polymer to prepare composites such as synthetic fiber, plastic molding article, film, paint, ink, etc., it is also reported that it

is difficult to obtain the effects which are desired to achieve via employing nano-sized particles since there are problems that the properties of the resulted composite may be deteriorated due to the low compatibility of inorganic or metallic nanoparticles with polymer, the coagulation, the uneven distribution, etc., or that the polymer may become opaque. In order to solve the problems such as the incompatibility, the coagulation and the uneven distribution, there have been proposed several methods such as a method of functionalizing nanoparticles, a method of using a compatibilizer such as a dispersant, a method for polymerization in the presence of nanoparticles, etc. However, a satisfactory method has not yet been developed.

10

5

Meanwhile, silver is a conductive metal and it is known from ancient times that silver has various effects such as antibacterial effect, germicidal effect, antifungal effect, deodorant effect, antistatic effects, and the like. Since silver is a precious metal, it is used in the form of particulate, coating or plating, or after carrying on a porous materials such as silica or zeolite.

15

Silver nanoparticles which have been made into nano-sized particulate are expected to have more excellent properties than bulk silver and there have been made many studies on nanotechnology about methods of preparing silver nanoparticles in the form of powder or solution. Further, several studies using thus prepared silver nanoparticles have reported that silver nanoparticles show extremely improved antibacterial, germicidal, antifungal effects with relative to bulk silver, for example, more than 99 % of germicidal effect even within several seconds against many bacteria.

20

Many documents have proposed to incorporate silver nanoparticles into a polymer to prepare antibacterial articles such as fibers (for example, see Korean Patent Laid-open publication Nos. 2003-0055197 and 2003-0091574), films (for example, see Korean Patent

Laid-open publication No. 2003-0036491), or the like.

5

10

15

20

When silver nanoparticles prepared in the form of colloid solution are dried for use, the nanoparticles coagulate and grow to a micro-particles, and it is difficult to divide thus resulted micro-particles into nanoparticles to uniformly incorporate in a polymer. Further, when silver nanoparticles prepared in the form of powder are employed, the nanoparticles have a low compatibility with the polymer and thus coagulate with each other to grow to particles having a micro size.

Such coarsening or coagulation of nanoparticles will essentially reduce the excellent effects of nanosized particles, deteriorate the properties of the polymer, and particularly, make it impossible to prepare the composite in the form of fiber or film.

Meanwhile, methods of incorporating silver nanoparticles into a polymer matrix via a polymerization of a solution containing silver nanoparticles and monomers have been proposed (for example, see Korean Patent Laid-open Publication Nos. 2003-0049007 and 2003-0031090). The above polymerization methods make it possible to uniformly disperse silver nanoparticles in polymer matrix. However, there are also problems that the method can be applied only to a solution polymerization and the polymerization reaction may be affected by additives such as silver nanoparticles, their solvent or any dispersant which has been used to uniformly disperse silver nanoparticles.

A process to directly incorporate silver nanoparticles or their colloid solution into a polymer is proposed using a dispersant. Although a dispersant may suppress the coagulation of nanoparticles or enhance the dispersion of particles, the antibacterial ability or physical properties of the composite are deteriorated.

#### **Description of Drawings**

4

Figure 1 is a photograph (magnification x1000) showing the distribution of silver nanoparticles on a sectioned surface of a silver nanoparticle-polymer composite prepared according the present invention.

Figure 2 is a photograph (magnification x2000) showing the distribution of silver nanoparticles on a sectioned surface of a silver nanoparticle-polymer composite prepared according the present invention.

#### Disclosure

#### **Technical Problem**

10

15

20

5

Under such circumstances, it have been desired to develop new composite composed of silver nanoparticles and a polymer in which silver nanoparticles are uniformly incorporated without coagulation in a polymer in order to maximize the antibacterial effect of silver without deteriorating the properties and functions of the polymer.

The inventors of the present invention have extensively studied in order to uniformly disperse silver nanoparticles issued from a silver nanoparticle colloid solution without coagulation in a polymer, and finally found that silver nanoparticles can be uniformly disperse without coagulation in a polymer by preheating the polymer to a temperature of 50 ~ 90 °C, introducing a silver nanoparticle colloid solution to the polymer together with an optional dispersant, rotating at a high speed the resulted mixture at the above temperature range to remove a sufficient amount of water to adsorb the silver nanoparticles on the polymer, and kneading and extruding the resulted mixture at a suitable temperature. Further, the silver nanoparticle-polymer composite thus prepared can be used as a master batch or a functional chip for extrusion, injection, spinning.

#### **Technical Solution**

5

10

15

20

The object of the present invention is to provide a method for the preparation of silver nanoparticles-polymer composite comprising:

- (1) introducing a silver nanoparticle colloid solution to a polymer preheated to a temperature of  $45 \sim 85$  °C,
  - (2) rotating the resulted mixture at the above temperature to remove water,
  - (3) kneading and extruding the resulted mixture in a suitable form.

Another object of the present invention is to provide a silver nanoparticle-polymer composite prepared by the above method, in which silver nanoparticles are uniformly dispersed.

The still another object of the present invention is to provide a use of a silver nanoparticle-polymer composite thus prepared according to the above method as a master batch or a functional chip.

In below, the present invention will be illustrated in more details.

In the context of the present invention, the silver nanoparticle colloid solution means a water solution in which silver particles having a nanometer size exist as a colloid. The silver nanoparticle colloid solution which can be used in the present invention may be prepared according to documents [See, for example, Nature 1985, 317, 344; Material Letters 1993, 17, 314; Korean Patent Laid-open Publication No. 2003-0082065] or any nanoparticles sold in a market may be employed.

The silver nanoparticles of the present invention can generally have a mean diameter between several nanometers (nm) to several microns ( $\mu$ m), for example, 1 nm  $\sim$  1000 nm, preferably 2  $\sim$  100 nm, particularly 4  $\sim$  70 nm.

5

10

15

20

The silver nanoparticle colloid solution can contain silver nanoparticles in a concentration of more than 10,000 ppm, preferably more than 20,000 ppm, more preferably more than 30,000 ppm, particularly more than 50,000 ppm. If the content of silver nanoparticles is too low, for example not more than 5,000 ppm, the removal of water is difficult and expensive. Although there is no upper limit of the concentration of silver nanoparticles in a colloid solution, it may have a concentration of not more than 500,000 ppm, preferably not more than 300,000 ppm, more preferably not more than 200,000 ppm in the view of economy and process efficiency.

Polymers which can be used in the present invention are not particularly restricted and may include, for examples:

- Polyethylenes, for example, low density polyethylene (LDPE), very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), ethylene-vinyl acetate (EVA), their copolymers;
- Polypropylenes, for example, homo polypropylene, random polypropylene, their copolymers;
- Polystyrene, for example, HIPS (High Impact Polystyrene), GPPS (General Purpose Polystyrene), SAN (Poly(Styrene Acrylonitrile)), etc.;
  - Transparent or general ABS (acrylonitrile-butadiene-styrene terpolymer),
  - Hard PVC,

- Engineering plastics, for example, nylon, PBT (Polybutylene terephthalate), PET (polyethylene terephthalate), POM (Polyoxid Methylene), PC (Polycarbonate), urethane, powder resin, PMMA (Polymethyl methacrylate), PES (Polyethersulfone), or the like.

It will be clearly understood that the present invention will not be restricted to the above polymers and can be applied to any natural or artificial polymers, their mixtures or

7

blends may be employed.

5

10

15

20

In the first step of the present invention, the preheating temperature of polymer in a mixer is  $45 \sim 85$  °C, preferably  $50 \sim 80$  °C, more preferably  $55 \sim 70$  °C. If the preheating temperature is lower than 45 °C, the removal of water is slow and inefficient and silver nanoparticles will not be well adsorbed on polymers. If the preheating temperature is higher than 85 °C, the removal of water is too fast or will be excess and thus it is difficult to achieve a uniform adsorption and/or blending.

According to one preferred embodiment of the present invention, the preheating of polymers can be carried out for  $10 \text{ min} \sim 150 \text{ min}$ , preferably  $20 \text{ min} \sim 100 \text{ min}$ , more preferably  $30 \text{ min} \sim 70 \text{ min}$  under rotation. In such case, the rotation speed is not particularly restricted, but may be generally not more than 1000 rpm, preferably  $10 \sim 700 \text{ rpm}$ , more preferably  $20 \sim 500 \text{ rpm}$ . It is thought that such rotation will generate static electricity on the surface of polymer, which attracts and adsorbs silver nanoparticles in a static electricity manner on the surface of polymer to prevent the coagulation of silver nanoparticles.

It is also understood that it is necessary to adjust the preheating temperature, the preheating time and the rotation speed of a polymer in a suitable manner on the basis of the amount of water to be removed, the removal rate of water, and/or the softening point (or melting point) of polymer used. A skilled person in this field can find a suitable or optimal preheating temperature, preheating time and rotation speed of polymer within the above ranges via several experiments on the basis of the type of polymer used and the concentration of silver nanoparticles of the colloid solution.

According to the present invention, polymer and colloid solution are introduced in

8

order. If polymer and colloid solution are introduced simultaneously, the separation of the colloid solution and polymer occurs and the silver nanoparticles can not be blended with the polymer in a desired state. At this time, the addition of a dispersant such as polyethylene wax fails to blend them due to the incompatibility of water and polymer.

5

In the present invention, it is preferable to adjust the content of silver nanoarticles in a polymer so as that 1 kg of end products have  $10 \sim 500$  ppm, preferably  $50 \sim 200$  ppm of silver nanoparticles in order to obtain the optimal antibacterial effect (more than 99.9%) with minimal cost. However, the present invention is not limited to the above range.

10

In the second step, the water evaporating speed and the amount of water to be removed is not strictly limited if silver nanoparticles can uniformly adsorbed on the surface of polymer without coagulation. It is possible to remove more than 80%, preferably more than 90 %, more preferably more than 95% of water present in the mixture of the polymer and the colloid solution before transferring the polymer on which silver nanoparticles are adsorbed to an extrude.

15

20

The second step of the present invention constitutes an important characteristics and advantage of the process of the present invention. Polymers have an inherent property that, if they are heated, they attract surrounding particles. The second step utilizes such inherent property of polymers to uniformly disperse silver nanoparticles in a polymer without using any dispersant or compatibilizer. The other reason that the present invention would not employs any dispersant or compatibilizer which may help the uniform dispersion of silver nanoparticles is that such dispersant or compatibilizer may deteriorate the properties of polymer or may offset the effect of nano-sized particles. In order to investigate the condition to maximize the ability of attracting surrounding particles, therefore, many experiments have been performed by controlling the temperature and rotation speed of

9

polymers in a mixer or extruder.

In one experiment, a polymer (LDPE5321) had been treated at a condition of 200 rpm and 90 °C for 30 min under rotation in a mixer and then a silver nanoparticle colloid solution had been added. As a result, the colloid solution had mixed with the polymer but had not uniformly dispersed in the polymer. In other words, silver nanoparticles did not uniformly disperse in the polymer due to phase separation. It is assumed that the reason of the above result is an excessive and rapid evaporation of water due to the high temperature and rapid rotation of the polymer in the mixer.

Similarly, the suitable ranges of process conditions enabling silver nanoparticles to uniformly disperse in polymers had been determined via many experiments carried out under many combinations of temperature and rotation speed (rpm) of polymer in a mixer.

In the second step of the present invention, it is assumed that the coagulation of silver nanoparticles can be prevented since silver nanoparticles are fixed on the surface of polymers by adsorption and/or sealing.

15

10

5

In the second step of the present invention, polymers on which silver nanoparticles are adsorbed are transferred into an extruder and then kneaded and extruded. Thus, a silver nanoparticle-polymer composite in which silver nanoparticles are uniformly dispersed without coagulation can be obtained. The kneading and extrusion can be made under common conditions known in the pertinent field.

20

According to one embodiment of the present invention, the silver nanoparticles-adsorbed polymer obtained at the above second step is directly introduced to an extruder. Since it is preferable to maintain the silver nanoparticles-adsorbed polymer at the process temperature of the second step, it is possible to adjust the temperature of the input portion of an extruder to a temperature similar to the above process temperature of the

10

second step.

The temperatures of barrel and dies of the extruder are not strictly limited and can be suitable determined by a skilled person in this field according to the type of polymer used. For example, if polymer is polypropylene, the temperatures of the extruder are adjusted to  $160 \sim 200 \,^{\circ}\mathrm{C} \, (\pm 5 \,^{\circ}\mathrm{C})$  at cylinder barrel portion and to  $150 \sim 190 \,^{\circ}\mathrm{C} \, (\pm 5 \,^{\circ}\mathrm{C})$  at dies portion, and if polymer is polyethylene terephthalate (PET) or nylon, the temperatures of the extruder are adjusted to  $220 \sim 260 \,^{\circ}\mathrm{C} \, (\pm 5 \,^{\circ}\mathrm{C})$  at cylinder barrel portion and to  $220 \sim 260 \,^{\circ}\mathrm{C} \, (\pm 5 \,^{\circ}\mathrm{C})$  at dies portion.

The type of mixer or extruder is not strictly limited in the present invention, a mixer and/or extruder sold in the market may be employed.

#### Advantageous Effect

The silver nanoparticle-polymer composite prepared according to the method of the present invention may be used as a master batch or functional chip for the preparation of a molding article, film, sheet, fiber or the like. The silver nanoparticles are uniformly dispersed without coagulation in the silver nanoparticle-polymer composite prepared according to the method of the present invention. Therefore, when the composite is formed in a thin film or microfiber with less than 1 denier, the silver nanoparticles do not deteriorate or lower the physical properties of the resulted articles.

20

5

10

15

The silver nanoparticle-polymer composite prepared according to the method of the present invention has advantages that the uniform dispersion state of the nanoparticles can be maintained without coagulation of the particles for a long time or nearly permanently, that a good or excellent antibacterial effect can be achieved even with relatively small

11

amount of silver due to maximized antibacterial effect of silver nanoparticles, that the friction fastness is permanent because the nanoparticles are incorporated within the polymer matrix, that the one-step process can lower the cost, that very thin or fine articles such as fiber or film can be prepared, and that, when a fiber is formed, it is possible to make a mixed textile with natural fibers with little or no deterioration of their properties.

The silver nanoparticle-polymer composite according to the method of the present invention is stable to the human body and the environment since silver nanoparticles are sealed on the surface or inside the polymer to minimize the loss or scattering of the silver nanoparticles into the environment.

10

5

#### **Best Mode**

Hereinafter, the present invention will be described more in detail by reference of several specific examples, which do not restrict the invention in any way. In addition, it is obvious that those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the present invention. Thus, the invention is intended to cover alternatives, modifications, and equivalents, which may be included within the spirit and scope of the invention as defined by the claims.

# Example 1: Preparation of silver nanoparticle-LDPE composite

20

15

1) To a super mixer (Model: Super Mixer 300L AC 75HP 4P; made by DAECHANG Precision Co., Ltd, Korea), 100 kg of low-density polyethylene (LDPE) (Model: LDPE5321; made by HANWHA Chemical Corp., Korea) was introduced and then rotated for about 40 minutes in a high speed (about 100 RPM), during which the temperature was increased to 55  $^{\circ}$ C  $^{\circ}$ C.

12

2) To the mixer, 2 kg of a silver nanoparticle colloid solution in water having a concentration of 100,000 ppm/kg (Trade name: NanoSilver; sold by Nanotek Ltd, Korea) was introduced and then rotated for 20 ~ 30 minutes in a high speed (about 100 RPM) to sufficiently remove water, by which the silver nanoparticles were adsorbed on the polymer beads.

- 3) After sufficiently mixing, the mixture of the polymer beads and silver nanoparticles was introduced into a twin-screwed extruder (Model: DCM 70 Twin Extruder Machine; made by DAECHANG Precision Co., Ltd, Korea). The extruder had maintained the temperatures of 70  $^{\circ}$ C ( $\pm$  5  $^{\circ}$ C) at the input portion, 180  $^{\circ}$ C ( $\pm$  5  $^{\circ}$ C) at the cylinder barrel portion, and 170  $^{\circ}$ C ( $\pm$  5  $^{\circ}$ C) at the dies p ortion.
- 4) The mixture was kneaded and extruded in the extruder to give silver nanoparticle-polymer composite in the form of pellet. The concentration of silver was about 2,000 ppm/kg.

Figures 1 and 2 are the photographs (Magnification of 1000 times and 2000 times, respectively) showing the distribution of silver nanoparticles on the surface of silver nanoparticle-polymer composite thus prepared.

## Comparative Example 1:

5

10

15

20

The same procedure was repeated as in Example 1 except that the polymer was treated with a colloid solution in a room temperature without preheating of the polymer. The silver nanoparticle colloid solution was introduced at an interval after introducing the polymer. The silver nanoparticle colloid solution could be blended with the polymer. However, the silver nanoparticles coagulated to large particles and did not uniformly

13

disperse on the polymer.

The observation of thus prepared composite with an electron microscope revealed that the silver nanoparticles had coagulated to more than 10-times particles in the polymer composite.

5

10

15

#### Comparative Example 2:

The same procedure was repeated as in Example 1 except that a dispersant was incorporated and the polymer was treated with a colloid solution in a room temperature without preheating of the polymer. As the dispersant, a wax (trade name: X861; sold by Bayer), which is usually employed as an additive (dispersant) in the preparation of a color master batch (color M/B), was employed to prevent the nanoparticles from coagulating and from not uniformly dispersing.

In a resulted composite, the dispersion of the silver nanoparticles in the polymer was stabilized, but the antibacterial ability which is the essential function of silver nanoparticles was remarkably reduced.

Example 2: Preparation of silver nanoparticle-PP composite

1) To a super mixer of the same type as used in Example 1, 100 kg of polypropylene (PP) (Trade name : PPJ700; made by HYOSUNG Corp., Korea) was introduced and then rotated for about 40 minutes in a high speed (about 100 rpm), during which the temperature was increased to  $55 \sim 65$  °C.

20

2) To the mixer 2 kg of a silver nanoparticle colloid solution in water having a concentration of 100,000 ppm/kg was introduced and then rotated for about  $20 \sim 30$ 

14

minutes in a high speed (100 RPM) to sufficiently remove water.

5

15

20

- 3) Since the surface of polypropylene was very slippery (maybe due to the presence of wax in the raw polymer beads), 500 g of wax (Trade name: X861; sold by Bayer) was introduced as a dispersant and then rotated for  $5 \sim 10$  min, by which the silver nanoparticles were uniformly adsorbed on the polymer beads.
- 10 5) The mixture was kneaded and extruded in the extruder to give silver nanoparticle-polypropylene composite in the form of pellet.

# Example 3: Preparation of silver nanoparticle-PET composite

The same procedure was repeated as in Example 1 except that polyethylene terephthalate (PET) (Trade name: K177Y; made by KOLON Ind. Inc., Korea) was employed and preheated to  $60 \sim 70$  °C. The extruder had maintained the temperatures of 70 °C ( $\pm 5$  °C) at the input portion, 240 °C ( $\pm 5$  °C) at the cylinder barrel portion, and 240 °C ( $\pm 5$  °C) at the di es portion.

A silver nanoparticle-PET composite in which silver nanoparticles were uniformly dispersed in the PET polymer without coagulation was obtained in the form of pellet.

# Example 4: Preparation of silver nanoparticle-Nylon composite

The same procedure was repeated as in Example 1 except that nylon (Nylon 6 or 66;

15

made by KOLON Ind. Inc., Korea) was employed and preheated to  $60 \sim 70 \,^{\circ}\text{C}$ . The extruder had maintained the temperatures of  $70 \,^{\circ}\text{C}$  (±5  $^{\circ}\text{C}$ ) at the input portion, 240  $^{\circ}\text{C}$  (±5  $^{\circ}\text{C}$ ) at the c ylinder barrel portion, and 240  $^{\circ}\text{C}$  (±5  $^{\circ}\text{C}$ ) at the dies portion.

A silver nanoparticle-Nylon composite in which silver nanoparticles were uniformly dispersed in Nylon polymer without coagulation was obtained in the form of pellet.

# Example 5: Preparation of silver nanoparticle-PC composite

5

10

15

20

The same procedure was repeated as in Example 1 except that polycarbonate (PC) (Trade name: PC; made by SAMYANG Corp., Korea) was employed and preheated to  $60 \sim 70 \,^{\circ}\mathrm{C}$ . The extruder had maintained the temperatures of  $70 \,^{\circ}\mathrm{C}$  ( $\pm 5 \,^{\circ}\mathrm{C}$ ) at the input portion,  $260 \sim 270 \,^{\circ}\mathrm{C}$  ( $\pm 5 \,^{\circ}\mathrm{C}$ ) at the cylinder barrel portion, and  $260 \sim 270 \,^{\circ}\mathrm{C}$  ( $\pm 5 \,^{\circ}\mathrm{C}$ ) at the dies portion.

A silver nanoparticle-PC composite in which silver nanoparticles were uniformly dispersed in PC polymer without coagulation was obtained in the form of pellet.

Example 6: Preparation of silver nanoparticle-ABS composite

The same procedure was repeated as in Example 1 except that acrylonitrile-butadien-styren (ABS) terpolymer (Trade name: ABS380; sold by KUMHO Petrochemical Co., Ltd., Korea) was employed and preheated to  $60 \sim 70~$ °C. The extruder had maintained the temperatures of 70~°C ( $\pm 5~$ °C) at the input portion,  $260 \sim 270~$ °C ( $\pm 5~$ °C) at the dies portion.

A silver nanoparticle-ABS composite in which silver nanoparticles were uniformly dispersed in ABS polymer without coagulation was obtained in the form of pellet.

16

## Example 7: Preparation of a nonwoven fabric by using a melt blown method

In a mixer rotating in a speed of about 800 rpm, 5 kg of silver nanoparticle-polypropylene composite having a concentration of 2000 ppm/kg prepared in Example 2 and 95 kg of polypropylene (Trade name PPJ700; made by HYOSUNG Corp., Korea) were added and mixed for about 3 min at a temperature of about 150 °C. The mixture was introduced in a hopper cooled to 15 °C and then introduced in an extrude having an inner temperature of 280 °C, of which cylinder screw was rotating in the speed of 52 rpm. Silver nanoparticle-containing fiber of  $0.3 \sim 0.6$  deniers was spun from the outlet of the cylinder screw. The resulted fiber had a silver concentration of  $80 \sim 100$  ppm/kg. Before the fiber was hardened, it is subjected to thermosetting to prepare a nonwoven fabric, which has uniform micro-spaces and can filter more than 99.9 % of fine particulate having a size of more than 0.3 micron. Thus prepared nonwoven fabric of microfiber level has a silver concentration of  $80 \sim 100$  ppm/kg.

15

20

10

5

#### Test Example 1: Antibacterial test

By using the silver nanoparticle-containing unwoven fabric prepared in Example 7, an antibacterial test was performed as follows:

The unwoven fabric was cut into a disc (diameter 4.8 cm), inoculated with test strains described in Table 1 and incubated for 24 hours under shaking (150 times/min). The resulted disc is immersed and shaken in a predetermined amount buffer solution (pH  $7.0\pm0.2$ ) of phosphoric acid to extract the incubated bacteria. The number of bacteria in the resulted solution was counted to determine the change of number.

17

The results obtained as a mean value from two tests are shown in the following Table 1.

Table 1

Strains	Number of bacteria	Blank	This invention			
		(Bacteria/ml)	(Bacteria/mℓ)			
Staphylococcus aureus	Initial	1.6x10 <sup>5</sup>	$1.6 \times 10^5$			
ATCC 6538	After 24 hours	$7.2 \times 10^6$	<10			
	Ratio	45-times increase	99.9% Reduction			
Escherichia coli	Initial	1.3x10 <sup>5</sup>	$1.3 \times 10^5$			
ATTC 25922	After 24 hours	6.1x10 <sup>6</sup>	<10			
	Ratio	47-times increase	99.9% Reduction			
Candida albicans	Initial .	5x10 <sup>5</sup>	1.5x10 <sup>5</sup>			
ATCC 14053	After 24 hours	6.6x10 <sup>6</sup>	<10			
	Ratio	44-times increase	99.9% Reduction			

# 5

10

### **Industrial Applicability**

According to the present invention, it is possible to uniformly disperse silver nanoparticles without coagulation into a polymer to provide new silver nanoparticle-polymer composite which can give a maximized antibacterial effect of silver without deteriorating physical properties and performance of the polymer. Thus prepared silver nanoparticle-polymer composite can be used as a master batch or a functional chip for extrusion, injection, spinning and then formed in various articles such as molding article, fiber, sheet, film, etc.

#### Claims:

5

10

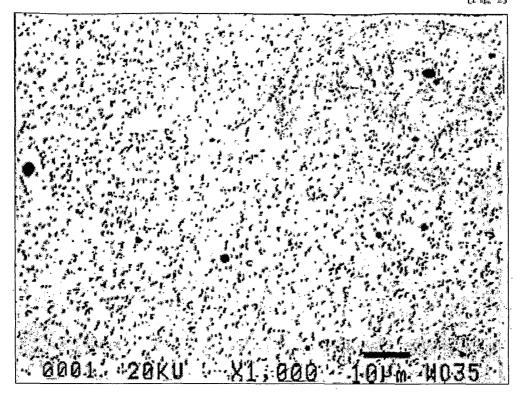
15

20

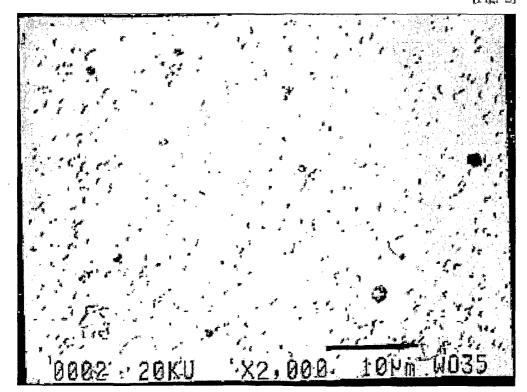
- 1. A method for the preparation of silver nanoparticles-polymer composite comprising:
- (1) introducing silver nanoparticle colloid solution to a polymer preheated to a temperature of  $45 \sim 85$  °C,
  - (2) rotating the resulted mixture at the above temperature to remove water,
  - (3) kneading and extruding the resulted mixture.
- 2. The method according to claim 1, wherein in the step (1), said polymer is preheated to a temperature of  $55 \sim 70 \,^{\circ}\text{C}$ .
- 3. The method according to claim 1, wherein in the step (1), said polymer is preheated under rotation.
- 4. The method according to any one of claims 1 to 3, wherein said polymer is selected form a group consisting of polyethylene, polypropylene, polystyrene, ABS, PVC, engineering plastics, their copolymer or mixture thereof.
- 5. The method according to claim 1, wherein in the step (2), more than 80% of water is removed.
  - 6. The method ac cording to claim 1, wherein a dispersant is further added.
- 7. A silver nanoparticle-polymer composite prepared by the method of claim 1, in which silver nanoparticles are uniformly dispersed.

1/1

(Fg 1)



[Fig. 2]



**SUBSTITUTE SHEET (RULE 26)** 

#### INTERNATIONAL SEARCH REPORT

International application No. PCT/KR2005/000576

#### A. CLASSIFICATION OF SUBJECT MATTER

# IPC7 C08K 3/08, B82B 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08K 3/08, B82B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean Patents and applications for inventions since 1975

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and application for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used) KIPASS, PAJ

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X.	KR 2002-74913 A (Kangju Institute of Science and Technology) 04 October 2002 See the whole document	1 - 7
A	KR 2003-38585 A (Ihn, Kyo Jin) 16 May 2003 See the whole document	1 7
A	KR 2002-43363 A (Korea Institute of Science and Technology) 10 June 2002 See the whole document	1 - 7
A	KR 2003-31090 A (Ihn, Kyo Jin) 18 April 2003 See the whole document	1 - 7

1	1 1	r ui	mer	uocuii	ichts	are	nsieu	ш	uie	COIII	mua	uon	01	BOX	U.
	_														

- Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority

See patent family annex.

- date and not in conflict with the application but cited to understand the principle or theory underlying the invention

  "X" document of particular relevance; the claimed invention cannot be
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

12 JULY 2005 (12.07.2005)

Date of mailing of the international search report

12 JULY 2005 (12.07.2005)

Name and mailing address of the ISA/KR



Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

HONG, SUNG RAN

Telephone No. 82-42-481-8146

