

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 March 2007 (22.03.2007)

PCT

(10) International Publication Number
WO 2007/032001 A2

(51) International Patent Classification:
B32B 27/14 (2006.01)

(74) Agent: **BEN-AMI, Paulina**; Ben-Ami & Associates, P.O.
Box 94, 76100 Rehovot (IL).

(21) International Application Number:
PCT/IL2006/001066

(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, HN, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT,
LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ,
NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU,
SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
12 September 2006 (12.09.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/715,609 12 September 2005 (12.09.2005) US

(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, LV, 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).

(71) Applicants (for all designated States except US):
BAR-ILAN UNIVERSITY [IL/IL]; Bar-Ilan University,
52900 Ramat Gan (IL). **NILIT LTD.** [IL/IL]; P.O. Box
276, 23102 Migdal HaEmek (IL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GEDANKEN,**
Aharon [IL/IL]; 29 Nitzana Street, 53465 Givataim (IL).
PERKAS, Nina [IL/IL]; 18/22 Borochoy Street, 49632
Petach Tikva (IL). **DUBINSKY, Stanislav** [IL/CA]; 300
Antibes Drive, Apt. 1502, Toronto, Ontario M2R 3N8
(CA). **GAZIT, Samuel** [IL/IL]; 6 Halrusim Street, 15227
Givat Avni (IL). **ROTEM, Ran** [IL/IL]; 49 HaOren Street,
30095 Ramat Yishay (IL).

Published:

— without international search report and to be republished
upon receipt of that report

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

(54) Title: METHOD FOR PREPARATION OF SILVER-POLYMER COMPOSITES BY SONOCHEMICAL DEPOSITION

(57) Abstract: The invention relates to a method for the preparation of silver-polymer composites, which comprises sonochemical deposition of silver nanoparticles onto the polymer, preferably by ultrasonic irradiation of a polyol solution of a silver salt containing the polymer. The invention further relates to Ag-polymers, preferably Ag-nylon, composites obtained by the method of the invention; to antibacterial Ag-polymers, preferably Ag-nylon, yarns spun therefrom; and to fabrics knitted from said yarns.



WO 2007/032001 A2

METHOD FOR PREPARATION OF SILVER-POLYMER COMPOSITES BY SONOCHEMICAL DEPOSITION

FIELD OF THE INVENTION

5 The present invention relates to silver-polymer composites and, particularly, to their preparation by sonochemical deposition.

BACKGROUND OF THE INVENTION

 The anti-microbial effects of metallic ions such as Ag, Au, Pt, Pd, Ir (i.e. the noble metals), Cu, Sn, Sb, Bi and Zn are known for a long time. Of the metallic ions
10 with anti-microbial properties, silver is perhaps the best known due to its unusually good bioactivity at low concentrations. In modern medical practice both inorganic and organic soluble salts of silver are used to prevent and treat microbial infections. These compounds are effective as soluble salts, but they do not provide prolonged protection due to loss through removal or complexation of the free silver ions and
15 thus must be reapplied at frequent intervals to overcome this problem. In order to slow the release of silver ions during treatment, silver-containing complexes which have a lower level of solubility have been proposed. For example, US 2,785,153 discloses colloidal silver protein for this purpose.

 The development of nanotechnology techniques opened a new opportunity
20 for silver delivery by formation of organic-inorganic nanocomposites combining various properties of polymers with the antibacterial activity of silver. Coating of silver nanoparticles onto polymers is of great interest because of the wide application of these materials in various fields, e.g., food processing, medical equipment, agriculture, biochemistry and textile industries.

25 US 5,681,575 discloses antimicrobial coatings and method of forming same on medical devices. The coatings are formed by depositing a biocompatible metal by vapor deposition techniques to produce atomic disorder in the coating such that a sustained release of metal ions sufficient to produce an anti-microbial effect is achieved. The medical device may be made of any suitable material, for example

metals, including steel, aluminum and its alloys, latex, nylon, silicone, polyester, glass, ceramic, paper, cloth and other plastics and rubbers, and the coating is formed by physical vapour deposition, for example, coating of one or more antimicrobial metals on the medical device by vacuum evaporation, sputtering, magnetron sputtering or ion plating.

A considerable amount of work has been conducted in the field of silver metal treatment of bacterial infections. A variety of silver-coated nylon cloths and fibers have been investigated (Deitch *et al.*, 1983 and 1987; Mackeen *et al.*, 1987). Silver-coated nylon fibers with antibacterial properties are available commercially such as Mipan Bano Magic Silver™ (Hyosung, Korea), Livefresh N-NEO™ (Kanebo, Japan). Examples of commercially available yarns containing silver as an antimicrobial agent include a sheath-core yarn having silver particles in the sheath, FossFiber™ with AgION™ (Foss Manufacturing Company, Inc., N.H., US), that protects against a broad spectrum of odor-causing and destructive bacteria, mold and mildew, using the proven antimicrobial properties of silver and is said to maintain the efficacy of its antimicrobial protection for the longevity of the product, even withstanding multiple launderings.

In order to achieve the optimum antibacterial effect of silver-containing nanocomposite fibers, a proper concentration of silver ions must be available in the solution. The number of silver ions released from silver nanocrystals is about 30 times less than the number of silver ions released from silver complexes, but silver nanocrystals exhibit a better antimicrobial performance with a faster bacterial killing curve. Pure silver is known to have a positive influence on wound healing, while silver complexes show a negative effect on the wound healing process.

The principal requirements for silver-polymer composites are small dimension of silver nanoparticles, their regular shape, and uniform size distribution. One example of silver available at present for this purpose is in the form of silver powder (particle size about 20 micron) and colloidal silver (particle size 30 nano).

Different methods for incorporation of pure silver into polymers have been disclosed and include in situ polymerization (Aymonier *et al.*, 2002; Choi *et al.*,

2003), sol-gel technique (Chen and Iroh, 1999), and laser ablation (Zeng *et al.*, 2002). However, for insertion into commercially available industrial polymers, most of the nanocomposites derived from polymerization-based techniques should be exposed to a melt-processing stage, during which significant morphological changes
5 such as aggregation and growth of the nanoparticles occur.

Sonochemistry is the application of ultrasound to chemical reactions and processes. Ultrasound is the part of the sonic spectrum which ranges from about 20 kHz to 10 MHz: the range from 20 kHz to around 1 MHz is used in sonochemistry whereas frequencies far above 1 MHz are used as medical and diagnostic
10 ultrasound.

The origin of sonochemical effects in liquids is the phenomenon of acoustic cavitation. Acoustical energy is mechanical energy i.e. it is not absorbed by molecules. Ultrasound is transmitted through a medium via pressure waves by inducing vibrational motion of the molecules which alternately compress and
15 stretch the molecular structure of the medium due to a time-varying pressure. Therefore, the distance among the molecules vary as the molecules oscillate around their mean position. If the intensity of ultrasound in a liquid is increased, a point is reached at which the intramolecular forces are not able to hold the molecular structure intact and, consequently, it breaks down and a cavity is formed. This
20 cavity is called cavitation bubble as this process is called cavitation and the point where it starts cavitation threshold. A bubble responds to the sound field in the liquid by expanding and contracting, i.e. it is excited by a time-varying pressure.

Sonochemical irradiation has been proven as an effective method for synthesis of nanophased materials as well as for deposition and insertion of
25 nanoparticles on/into mesoporous and ceramic supports. The reasons that chemical bonds are ruptured when ultrasound radiation passes through a liquid are the high temperature (5000°K) and pressures (600 atm) developed when the acoustic bubble collapses.

One of the many advantages of sonochemistry is its ability to coat or dope
30 various nanoparticles onto or into ceramics and polymers. By this technique, a

homogeneous dispersion of the nanoparticles on the substrate is achieved in one step. In this step, nanoparticles of the desired product are formed and accelerated at a very high speed onto/into the surface or body of the polymer or ceramics via microjets or shock waves created when the bubble collapses near solid surfaces.

5 In the laboratory of the present inventors, a large variety of nanoparticles have been coated and doped onto and into polymers using sonochemical method/ultrasound irradiation. The deposition was conducted using materials which were either dissolved or dispersed (not dissolved) in the irradiated solution. In this way, were prepared Co- and Fe-polymer composites (Wizel *et al.*, 1999), Fe-
10 polystyrene composites (Wizel *et al.*, 2000), Ag₂S/PVA and CuS/PVA nanocomposites (Vijayakumar *et al.*, 2002), ZnO/PVA nanocomposites (Vijaya Kumar *et al.*, 2003), EuO/silica microspheres (Ramesh *et al.*, 1999), magnetite/PVA (Vijaya Kumar *et al.*, 2000), CuO/PVA (Vijaya Kumar *et al.*, 2001), Ag nanoparticles on silica spheres (Pol *et al.*, 2002).

15 SUMMARY OF THE INVENTION

It has been found, in accordance with the present invention, that sonochemical deposition can be utilized for coating silver nanoparticles onto polymers.

20 Thus, in one aspect, the present invention provides a method for preparation of silver-polymer composites, which comprises sonochemical deposition of silver nanoparticles onto the polymer. In a preferred embodiment, the method is carried out by ultrasonic irradiation of a polyol solution of a silver salt containing the polymer.

25 The polymer that can be coated with silver nanoparticles according to the invention may be any water insoluble polymer such as, without being limited to, nylon, polyester, polycarbonate (PC), polymethyl methacrylate (PMMA), or polypropylene. In one preferred embodiment, the polymer is nylon.

30 The Ag-polymer composites of the invention can be characterized as polymer pellets coated by Ag nanoparticles. The concentration of the silver nanoparticles in the Ag-coated polymer pellets is at least one order of magnitude

higher than the concentration needed for an antibacterial effect. The Ag-coated polymer pellets can be used as a “master-batch” for the production of antibacterial yarns, for example, by melt spinning processes. In particular, the “master batch” obtained may be metered into an extruder alongside the main polymer stream at a controlled ratio, whereby the silver nanoparticles get thoroughly mixed with the main polymer stream to form a diluted Ag-polymer composite, containing the required concentration of Ag-based particles needed for an antibacterial effect. The diluted Ag-polymer may then be used for the production of yarns which are then knitted into fabrics.

The Ag/nylon composite of the invention was unexpectedly found to be stable to many washing cycles, and thus the antimicrobial properties of the fabrics knitted from these Ag-nylon yarns will be maintained through the washings of the garments for a long period of time.

Thus, in other aspects, the present invention relates to Ag-polymers, preferably Ag-nylon, composites obtained by the method of the invention; to antibacterial Ag-polymers, preferably Ag-nylon, yarns spun therefrom; and to fabrics knitted from said yarns.

The antibacterial fibers/yarns manufactured from the Ag-polymer composites prepared by the method of the present invention may be used for any of the known uses for such antibacterial fibers/yarns.

In particular, the antibacterial fibers/yarns manufactured from the Ag-nylon composites can be used for different purposes such as, but not limited to, performance apparel, medical textiles, uniforms, home furnishings, bedding, baby diapers, underwear, socks, hats, table cloth, carpet, floor mat, cleaning products, blanket, bed sheet, automotive textiles, tooth brush, shoes., etc. All of the above examples may be in the form of knitted, woven or non-woven fabrics.

BRIEF DESCRIPTION OF THE FIGURE

Fig. 1 is a photo depicting nylon chips before and after sonochemical coating with silver, and Ag/nylon fibers spun from the Ag/nylon composite.

DETAILED DESCRIPTION OF THE INVENTION

Using the sonochemical deposition method according to the present invention, Ag-polymer composites are obtained with the main desired requirements, namely, a small dimension, a regular shape, and a uniform size distribution of silver nanoparticles.

The advantages of using ultrasonic irradiation over other methods is due to the microjets that are created in the irradiated solution when the acoustic bubbles collapse near solid surfaces, as described in the background section hereinabove. These microjets throw the silver nanoparticles onto the nylon surface at such a speed that the collision, according to our interpretation, causes the melting of the substrate guaranteeing the imbedding of the silver nanoparticles in the polymer surface.

As used herein, the terms "Ag-polymer composites" and "Ag-coated polymer pellets" are used interchangeably to define polymer pellets coated with silver nanoparticles, prepared according to the method of the present invention.

The polyol that can be used according to the method of the present invention may be any suitable alcohol containing at least two hydroxyl groups, such as a diol, a triol, and the like. In a preferred embodiment, the polyol is a diol that may be a small molecule such as ethylene glycol or propylene glycol or a polymer such as polyethylene glycol (PEG) 400. In a more preferred embodiment, the polyol is ethylene glycol.

The polyol solution may be a pure polyol solution as well as a solution of said polyol in any suitable polar solvent. In preferred embodiments, the polyol solution is an aqueous polyol solution wherein the water : polyol ratio is in a range of 10:1 (v:v) to 1:5 (v:v), preferably 9:1 (v:v).

The silver salt used in the method of the present invention may be any suitable silver salt such as, without limitation, silver nitrate, silver acetate or silver perchlorate. The concentration of silver ions in the polyol solution determines the final silver amount in the silver-nylon composites prepared; however, by increasing the silver ions concentration, larger and more aggregated silver nanoparticles are

obtained. In preferred embodiments, the concentration of Ag ions is in a range of 0.02 M to 0.1 M, most preferably 0.02 M.

The temperature of the polyol solution during the method of the invention may be in a range of 15°C to 60°C, preferably 20°C to 40°C, most preferably about 30°C.

The duration of the ultrasonic irradiation according to the present invention may be up to 4 hours, preferably in a range of 1 hour to 3 hours, most preferably about 2 hours. The efficiency of the ultrasonic irradiation may be in the range of 50% to 80%, preferably 70%.

In one preferred embodiment, the present invention relates to a method for the preparation of silver-nylon composites comprising placing nylon pellets in a solution of a silver salt in an aqueous solution of a polyol, irradiating the mixture with a high intensity ultrasound horn for about 2 hours, and washing and drying the resulting product to obtain the desired silver-nylon composite. The silver salt may be silver nitrate, silver acetate or silver perchlorate and the polyol solution is preferably an aqueous solution of ethylene glycol.

The invention further relates to silver-polymer composites obtained by the method of the invention, particularly to silver-nylon composites obtained by the method as described above and to antibacterial silver-nylon yarns spun from said silver-nylon composites.

In one preferred embodiment of the invention, sonochemistry was employed for coating nanosilver particles on Nylon 6,6 chips, as shown in Example 1 hereinafter. The nanocrystals of pure silver, 50-100 nm in size, were finely dispersed on the polymer surface without damaging the Nylon 6,6 structure. As mentioned hereinabove, this Ag/nylon composite was stable to many washing cycles. It is worth mentioning that 80 'laundering' cycles did not reduce the amount of silver on the nylon surface, thus demonstrating the efficient deposition of the silver nanoparticles by the ultrasonic irradiation according to the invention. The fabric knitted from this yarn showed excellent antimicrobial properties. It worked on both gram positive and gram negative bacteria, while not all commercially

available additives work on both types of bacteria. Also the amount of this Ag/nylon composite required to achieve the bactericidal effect was small (concentration of 0.1% wt.), while commercial products that we tested, such as Alphasan (Japan) master batch, required a higher amount (up to 1%) to achieve the same effect. These results indicate that this Ag/nylon composite can be used as a master batch for the production of nylon yarn with outstanding properties by melting and spinning processes.

The invention will now be illustrated by the following non-limiting Examples.

EXAMPLES

Example 1. Preparation of Ag-nylon composite by sonochemical deposition

Nylon 66 pellets of average grain size of about 2 mm in diameter were placed in a 0.02 M solution of AgNO_3 in water : ethylene glycol (10:1). The reaction mixture was then purged with argon for 1 hour in order to remove traces of O_2 /air, and irradiated for 2 hours with a high intensity ultrasonic horn (Ti-horn, 20 kHz, 1.5 kW, Sonics and Materials INC, USA) at 70% efficiency under a flow of argon at 30°C. An aqueous ammonia solution (molar ratio $\text{NH}_4\text{OH} : \text{AgNO}_3 = 1 : 1$) was added to the reaction slurry during the first 10 minutes of the sonication. After the sonication process was completed, the color of the polymer changed from white to bright grey. The product was washed thoroughly, first with water to remove traces of ammonia and then with ethanol, and dried under vacuum. The Ag-Nylon composite obtained contained 1.0% wt of $\text{Ag}^{(0)}$. The silver nanoparticles of 50-100 nm were homogeneously distributed in the polymer.

Similar results were obtained using different water-soluble silver salts - silver acetate and silver perchlorate. By increasing the silver ions concentration in the reaction solution, a higher concentration of silver in the polymer can be achieved. Thus, the molar concentrations of AgNO_3 was increased by intervals of 0.01 M up to 0.1 M, and the silver concentration in the Ag-nylon composite obtained increased up to 5% wt.

Additional experiments were conducted with other polyols, namely, propylene glycol and polyethylene glycol 400, instead of ethylene glycol. The volume ratios of water : polyol were changed from 10 : 1 to 1 : 5; different reaction temperatures in the range of 15-60°C were used; and the reaction time was 1, 2, 3 or 4 hours. The power of the sonicator used in all experiments was 1.5 kW, but the sonication efficiency was 60, 65, 70 or 75%. The results obtained indicate that the optimal sonication efficiency was 70% and that a reaction duration longer than 2 hours did not increase the silver concentration in the Ag-nylon composite.

Example 2. Antibacterial activity of silver-coated nylon yarns spun from Ag-nylon composites of the present invention

Ag-Nylon composites prepared as described in Example 1 hereinabove were used as a master-batch for the preparation of antibacterial silver-coated nylon fibers.

Nylon 6,6 27/7 (decitex/filaments) yarns, containing 0.1% wt of Ag, were spun at a partially oriented yarns (POY) pilot-plant (Nilit Ltd, Israel), and their antibacterial activity was tested (by Aminolab Ltd, Israel), according to the American Association of Textile Chemists and Colorists (AATCC) Test Method 100-1993. The Log Reduction test showed a reduction of bacterial counts by 4 logs after 18 hours, both for gram positive (*Staphylococcus aureus*) and for gram negative (*Pseudomonas aeruginosa*) bacteria.

Fig. 1 is a photo depicting nylon chips before (left) and after sonochemical coating with silver (middle), and Ag/nylon fibers spun from the Ag/nylon composite (right).

REFERENCES

- Aymonier, C. Schlotterbeck, U. Antonietti, L. Zacharias, P. Thomann, R. Tiller, J.C. Mecking, S., Hybrids of silver nanoparticles with amphiphilic hyperbranched macromolecules exhibiting antimicrobial properties, *Chem. Comm.*,
5 **2002**, 3018-3019
- Chen, Y. Iroh, J.O., Synthesis and characterization of polyimide silica hybrid composites, *Chem. Mater.*, **1999**, 11, 1218-1222
- Choi, S.H. Lee, K.P. Park, S.B., Preparation and characterization of poly(ester)-silver and nylon-silver nanocomposites, *Nanotechnol. in Mesostruc. Mater. Stud. In Sur. Sci. And Catal.*, **2003**, 146, 93-96
10
- Deitch, EA, Marino, AA, Gillespie, TE, Albright, JA., "Silver-Nylon" a New Antimicrobial Agent, *Antimicrobial Agents and Chemotherapy*, **1983**, 356-359
- Deitch, EA, Marino, AA, Malaleonok, V, Albright, JA, Silver Nylon Cloth: In vitro and in vivo Evaluation of Antimicrobial Activity, *J. Trauma*, **1987**, 27301
15
- MacKeen, PC, Person, S, Warner, SC, Snipes, and SE Stevens Jr., Silver-Coated Nylon Fiber as an Antibacterial Agent, *Antimicrobial Agents and Chemotherapy*, **1987**, 93-99
- Pol, V.G. Srivastava, D.N. Palchik, O. Palchik, V. Slifkin, M.A. Weiss, A.M. Gedanken, A., Sonochemical deposition of silver nanoparticles on silica spheres,
20 *Langmuir*, **2002**, 18, 3352-3357
- Ramesh, S. Minti, H. Reisfeld, R. Gedanken, A., Synthesis and optical properties of europium oxide nanoparticles immobilized on morphous silica microspheres, *Optical Materials*, **1999**, 13, 67-70
- Vijaya Kumar, R. Koltypin, Yu. Cohen, Y.S. Cohen, Y. Aurbach, D. Palchik,
25 O. Felner, I. Gedanken, A., Preparation of amorphous magnetite nanoparticles embedded in polyvinylalcohol using ultrasound radiation, *J. Mater. Chem.*, **2000**, 10, 1125
- Vijaya Kumar, R. Mastai, Y. Diamant, Y. Gedanken, A., Sonochemical synthesis of amorphous copper and nanocrystalline copper(I) oxide embedded in
30 polyaniline matrix, *J. Mater. Chem.*, **2001**, 11, 1219

Vijayakumar, R. Palchik, O. Koltypin, Yu. Diamant, Y. Gedanken, A., Sonochemical synthesis and characterization of Ag₂S/PVA and CuS/PVA nanocomposite, *Ultrasonic Sonochemistry*, **2002**, 9, 65-70

5 Vijaya Kumar, R. Elgamiel, R. Palchik, O. Gedanken, A. Norwig, J., Synthesis and characterization of Zinc oxide-PVA nanocomposite by ultrasound irradiation and the effect of nanocomposite on the crystal growth of Zinc oxide, *J. Crystal Growth.*, **2003**, 250, 409

10 Wizel, S. Prozorov, R. Cohen, Y. Aurbach, D. Margel S. Gedanken, A., The preparation of metal-polymer composite materials using ultrasound radiation, *J. Mater. Res.*, **1998**, 13, 211-216

15 Wizel, S. Margel, S. Gedanken, A. Rojas, T.C. Fernandez, A. Prozorov, R., The preparation of metal-polymer composite materials using ultrasound radiation: Part II. Differences in physical properties of cobalt-polymer and iron-polymer composites prepared by a sonochemical method, *J. Mater. Res.*, **1999**, 14, 3913-3920

Wizel, S. Margel, S. Gedanken, A., The preparation of a polystyrene-iron composite by using ultrasound radiation, *Polymer International.*, **2000**, 49, 445

Zeng, R. Rong, M.Z. Zhang, M.Q. Liang, H.C. Zeng, H.M., Laser ablation of polymer-based silver nanocomposites, *Appl. Sur. Sci.*, **2002**, 187, 239

20

CLAIMS

1. A method for preparation of silver-polymer composites, which comprises sonochemical deposition of silver nanoparticles onto the polymer.
2. The method of claim 1, comprising ultrasonic irradiation of a polyol solution
5 of a silver salt containing pellets of the polymer.
3. The method of claim 2, wherein said polyol is a diol selected from ethylene glycol, propylene glycol or polyethylene glycol 400.
4. The method of claims 3, wherein said diol is ethylene glycol.
5. The method of claim 2, wherein said polyol solution is an aqueous polyol
10 solution wherein the water : polyol ratio is in a range of 10:1 (v:v) to 1:5 (v:v), preferably 9:1.
6. The method of claim 2, wherein said silver salt is silver nitrate, silver acetate or silver perchlorate, and the concentration of Ag ions in said polyol solution is in a range of 0.02 M to 0.1 M, preferably 0.02 M.
- 15 7. The method of claim 2, wherein the temperature of said polyol solution is in a range of 15°C to 60°C, preferably 20°C to 40°C, most preferably about 30°C.
8. The method of claim 2, wherein the duration of said ultrasonic irradiation is up to 4 hours, preferably in a range of 1 hour to 3 hours, most preferably about 2 hours.
- 20 9. The method of any one of claims 1 to 8, wherein said polymer is selected from the group consisting of nylon, polyester, polycarbonate, polymethyl metacrylate and polypropylene.
10. The method of claim 9, wherein said polymer is nylon.

11. A method for the preparation of silver-nylon composites comprising placing nylon pellets in a solution of a silver salt selected from silver nitrate, silver acetate or silver perchlorate in an aqueous solution of a polyol, irradiating the mixture with a high intensity ultrasound horn for about 2 hours, washing and drying the resulting product to obtain the desired silver-nylon composite.
12. The method of claim 11, wherein said silver is silver nitrate, silver acetate or silver perchlorate and said polyol solution is an aqueous solution of ethylene glycol.
13. Silver-polymer composites obtained by the method of any of claims 1 to 10.
14. Silver-nylon composites obtained by the method of any of claims 10 to 12.
15. Antibacterial silver-polymer yarns spun from silver-polymer composites according to claim 13.
16. Antibacterial silver-nylon yarns spun from silver-nylon composites according to claim 14.

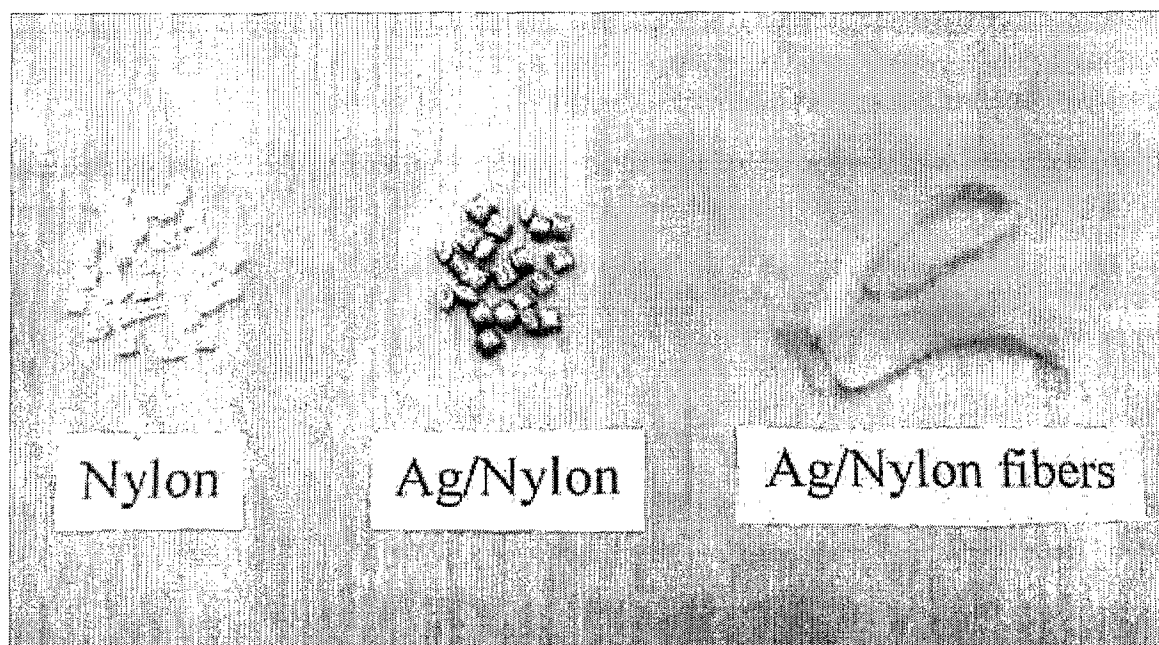


Fig. 1