J Mater Sci (2007) 42:6067–6073
DOI 10.1007/s10853-006-1158-5

Long-term antimicrobial polyamide 6/silver-nanocomposites

Cornelia Damm · Helmut Münstedt · Alfons Rösch

Received: 13 July 2006 / Accepted: 17 October 2006 / Published online: 16 April 2007

Abstract Elemental silver nanoparticles were generated in polyamide 6 (PA6) by the thermal reduction of silver ions during the melt processing of a PA6/silver acetate mixture. The silver ion release from PA6 filled with 2 wt% nanosilver obeys a zero-order rate law for at least 100 days. During this time about 17 μg silver per day, per litre immersion liquid and per cm^2 sample surface are released. The PA6/Ag-nanocomposite was shown to be active against *Escherichia coli* whereas the pure PA6 did not show any antimicrobial efficacy. Immersion of a nanocomposite containing 2 wt% silver in water for 100 days does not reduce its antimicrobial efficacy against *Escherichia coli*. Thus PA6 filled with 2 wt% nanosilver is an effective antimicrobial material for long-term applications.

Introduction

In medicine, hygiene and food packaging technology there is an increasing demand for polymer materials possessing antimicrobial properties.

C. Damm (✉) · H. Münstedt
Friedrich-Alexander-University Erlangen-Nuremberg, Institute of Polymer Materials, Martensstrasse 7, 91058 Erlangen, Germany
e-mail: Cornelia.damm@ww.uni-erlangen.de

H. Münstedt
e-mail: Helmut.muenstedt@ww.uni-erlangen.de

A. Rösch
Friedrich-Alexander-University Erlangen-Nuremberg, Institute of Microbiology, Staudtstrasse 5, 91058 Erlangen, Germany
e-mail: aroesch@biologie.uni-erlangen.de

Antibiotics [1], organic [2] and inorganic biocides [3] are used for the preparation of antimicrobial medical devices. The use of antibiotics for the prevention of infections is critical, however, because a frequent application of these materials facilitates the development of bacterial resistances.

As biocides often organic chlorocompounds are used, but these materials have the disadvantage of a rather high human and eco toxicity. Thus inorganic biocides are a favourable alternative to organic antimicrobial compounds. Amongst the heavy metal ions, which are principally suitable for this purpose silver exhibits the highest antimicrobial efficacy in combination with a fairly low toxicity against human tissue [4].

Silver ions form complexes with the sulfur-, nitrogen- or oxygen-containing functional groups of bacterial enzymes. This leads to a destabilization of the bacterial cell wall as well as to a disturbance of the metabolism (bactericidal action) [5, 6]. Moreover, silver ions interact with the bacterial DNA preventing the reproduction of the cells (bacteriostatic action) [5, 6]. Because silver ions attack microbial cells in a such complex manner, the risk of resistance development is much smaller in comparison to antibiotics.

Moreover, silver is effective against a broad spectrum of gram-negative and gram-positive bacteria as well as fungi.

Thus elemental silver or silver compounds are used as antimicrobial coating materials or fillers for catheters [7–10], wound dressings [11–13], heart valve sewing cuffs [14, 15] and bone cement [16].

Catheters coated with silver sulfadiazine and wound dressings coated with elemental silver nanoparticles are already on the market. In most cases coated devices are suitable only for short-term applications because the silver reservoir in the coating is rather small. Silver-filled poly-

mer materials should have the potential to provide antimicrobial devices for long-term applications. As fillers silver ions on inorganic carriers like zeolites (''Agion'') are already commercially available. In Ref. [17] it was shown that PA6 filled with ionic silver compounds exhibited a strong and fast silver ion release, which limited its efficacy to short-term applications, only.

In contrast, elemental silver particles can provide a large reservoir of antimicrobial silver ions, because in contact with water and dissolved oxygen ($O_{2(aq.)}$) they release small amounts of silver ions according to Eq. 1 [18].

$$O_{2(aq.)} + 4H_3O^+ + 4Ag_{(s)} \rightarrow 4Ag^+_{(aq.)} + 6H_2O \quad (1)$$

Thus polymer materials filled with elemental silver should well be suitable as long-term antimicrobials. Indeed, the last generation of the ''Erlanger silver catheter'' consisting of thermoplastic polyurethane filled with silver nanoparticles on $BaSO_4$ microparticles as carriers exhibited an efficient silver ion release and an antimicrobial efficacy over at least one year [10].

The oxidation of elemental silver into ions according to Eq. 1 occurs on the surface of the particles, only. For that reason, the concentration and rate of the silver ion release can be controlled by the surface to volume ratio of the silver particles that means by the particle size.

In previous works it was shown, that polymers filled with elemental silver nanoparticles release silver ions much more effectively than materials filled with conventional silver particles having sizes in the μm-range [10, 19].

Polymers can be filled with elemental silver microparticles by simple thermoplastic processing methods [20]. The preparation of polymer/silver-nanocomposites is much more complicated, because nanoparticles form large aggregates and agglomerates very easily. Solution processing methods are frequently used for the preparation of polymer/silver-nanocomposites with well-dispersed silver particles [19, 21]. Residuals of the solvent remaining in the polymer matrix can be critical for applications in the medical field. Moreover, the solvents can act as plasticizers and change the mechanical properties of the materials.

Another synthesis route for polymer/silver-nanocomposites is a precipitation of silver nanoparticles on microparticles as carriers [10]. The silver nanoparticles distributed on the carrier surfaces can well be dispersed in a polymer matrix by thermoplastic processing [10]. This method has the advantage to be solvent free in the last step, but the preparation of the fillers is a rather complicated and time-consuming procedure.

In this work we present a simple single step method for the preparation of polyamide 6/silver-nanocomposites without the use of a solvent or a carrier for the silver particles. We prove that these materials are well suitable as long-term antimicrobials.

Experimental

Preparation of polyamide 6/silver-nanocomposites

For the preparation of a PA6/Ag-nanocomposite containing 2 wt% of silver, 784 g of polyamide 6 pellets (Ultramid B3SK, M_n = 18 kg/mol, from BASF) were premixed with 25 g of silver acetate powder (Merck). The mixture was processed in a co-rotating twin-screw extruder at 230 °C. The length over diameter ratio of the screw was 30, the screw had a diameter of 34 mm.

During processing a thermal reduction of the silver salt into elemental silver nanoparticles occurs causing a yellow-brownish colour of the extruded strands. From the extruded strands rectangular specimens having dimensions of 2 cm × 1 cm × 0.1 cm were prepared by compression moulding at 230 °C and at a pressure of 300 bars using a heated press.

Morphology investigations

A transmission electron microscope (TEM) type ''EFTEM LEO 912'' (Leo Co.) was used to check the morphology of the silver particles in the PA6 matrix. The TEM investigations were performed on microtome cuts having a layer thickness in the range between 70 nm and 100 nm.

Anodic stripping voltammetry

To investigate the silver ion release from the PA6/Ag-nanocomposite six of the rectangular specimens mentioned in section ''Preparation of polyamide 6/silver-nanocomposites'' having a total surface area of 27.6 cm^2 were immersed in 15 mL of distilled water. At defined times the immersion liquid was exchanged completely. The concentration of silver ions in the immersion liquid was measured by anodic stripping voltammetry. This method is briefly discussed below and described more in detail elsewhere [19, 20]. A device consisting of a glassy carbon-working electrode, a silver/silver chloride reference electrode and a platinum wire counter electrode was used. The electrolyte was a 0.1 M aqueous KNO_3 solution. In the first step of the experiment a potential was applied to the working electrode, which is more negative than the reduction potential of silver ions. During this first stage of the experiment the silver from the electrolyte is deposited on the working electrode. In the second stage of the measurement a potential scan is

performed and the current is measured as a function of the potential. During the scan the potential becomes more positive than the oxidation potential of silver leading to a stripping of the silver from the working electrode into the electrolyte. The silver ions released from the working electrode give rise to a peak of the current in the voltammogram. By means of a baseline correction the area of the peak in the voltammogram is calculated. In a previous paper [20] it was shown, that there is a linear relationship between the peak area and the silver ion concentration in solution. Thus, the silver ion concentration in the electrolyte can be determined from a calibration line.

All the silver ion concentrations presented in this paper are the mean values of three voltammetric measurements.

Antimicrobial efficacy tests

Escherichia coli strain DH5α (Invitrogen Corp.) was used as a test organism to check the antimicrobial efficacy of pure and silver filled PA6. This strain is known to be sensitive against silver ions.

The bacteria were grown over night in Luria-Broth at 37 °C. The resulting suspension of bacteria was diluted to a concentration in the range from 1×10^5 to 2×10^5 CFU/mL. In a second set of experiments the suspension was diluted to about 10^6 CFU/mL. The exact initial concentration of bacteria was determined by the solid agar plate method as described below.

For the antimicrobial efficacy tests rectangular specimens mentioned in section ''Preparation of polyamide 6/silver-nanocomposites'' were used. The PA6-specimens sterilized with chloroform were transferred into the wells of a sterile microtitre tray. Each specimen was incubated with 1 mL of the diluted bacterial suspension, that means with $1–2 \times 10^5$ or with 10^6 bacteria. The microtitre tray was gently shaken for 24 h at room temperature. After 24 h incubation the concentration of living bacterial cells in the suspension was determined as follows: From each well 10 μL of the suspension were taken off and distributed on a Luria-Broth solid agar plate. The suspensions from the control well (without sample) and the well containing pure PA6 were diluted before distribution on a solid agar.

The agar plates were incubated for 24 h at 37 °C. During this time each living bacterial cell grows to a colony having a diameter between 1 mm and 2 mm. These colonies were counted. From the number of colonies and the dilution factor the concentration of bacteria having survived after being 24 h in contact with the sample was calculated.

The concentrations of bacteria mentioned in this paper are the mean values of two determinations.

Results and discussion

Morphology

The TEM micrograph of a PA6/Ag-composite containing 2 wt% silver displayed in Fig. 1 shows that the diameters of the silver particles are below 100 nm. The particles are well distributed in the polymer matrix and most of the particles are spherical.

Most particles have a diameter of about 20 nm. Some larger aggregates and agglomerates can also be seen in Fig. 1. But their diameters are below 100 nm. Thus Fig. 1 proves that the simple preparation method described in section ''Preparation of polyamide 6/silver-nanocomposites'' yields PA6/Ag-nanocomposites. The reasons for the good distribution are strong interactions between the polar amide groups of the polymer and the silver particles. This leads to a good adsorption of the PA6 chains on the silver particles. This means the silver particles are nearly completely covered by the PA6 chains preventing the growth or agglomeration of the silver particles.

Silver ion release

In contact with water the PA6 specimens filled with 2 wt% nanosilver release silver ions over a longer period of time due to the involved process of oxidation of the elementary silver nanoparticles to silver ions and a subsequent diffusion of the silver ions to the sample surface (cf. Fig. 2).

The amounts of silver ions released per cm^2 of PA6/Ag are in a range in which an antimicobial efficacy has been found according to [7].

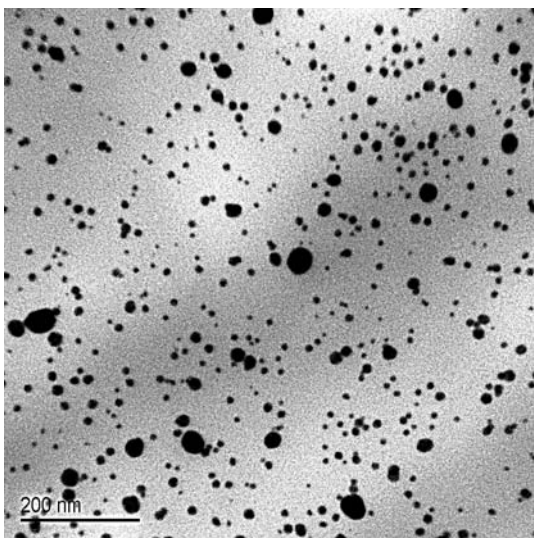

Fig. 1 TEM micrograph of a PA6/silver-nanocomposite containing 2 wt% silver

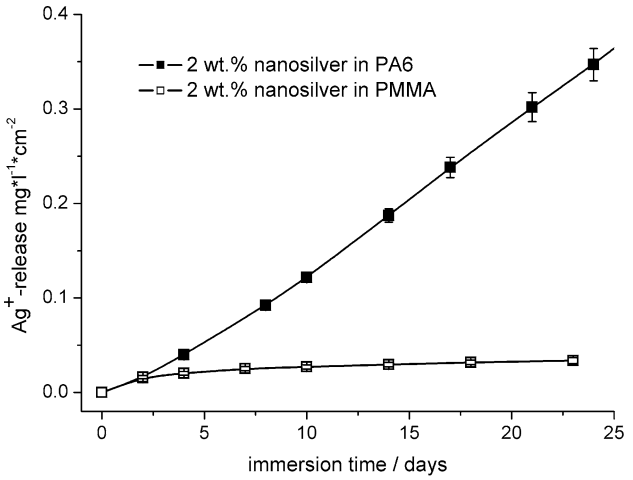

Fig. 2 Cumulative silver ion release from a PA6/silver- and a PMMA/Ag-nanocomposite. The filler content is 2 wt% for both polymers

For comparison in Fig. 2 the kinetics of the silver ion release from a PMMA/Ag-nanocomposite is shown, too. The PMMA is filled with 2 wt% spherical elemental silver nanoparticles, too, having diameters from 10 nm to 50 nm. For more details about the properties of the PMMA/Ag-nanocomposite see ref. [19]. The silver ion release of this nanocomposite is very small. This result throws some light into the release mechanism.

If only the filler content and the morphology of the silver particles would govern the silver ion release from polymers, then for the PA6/Ag- and the PMMA/Ag-nanocomposite the kinetics of silver ion release should be comparable. Indeed, after an immersion time of 2 days both materials release a comparable amount of silver ions (cf. Fig. 2).

But for longer immersion times the kinetics of the silver ion release from the two nanocomposites differs strongly, proving that the properties of the matrix polymer play an important role for the release processes.

The PMMA/Ag-nanocomposite releases much fewer silver ions than the PA6/Ag-nanocomposite. Moreover, the silver ion concentration in the immersion liquid surrounding the PMMA/Ag samples increases up to a saturation value with growing immersion time (cf. Fig. 2). The plateau value is reached after about 10 days. As in Fig. 2 the cumulative silver ion release is plotted versus time, a plateau value does mean, that the composite does not release remarkable amounts of silver ions any more. Thus, from Fig. 2 it becomes obvious that a PMMA/Ag-nanocomposite containing 2 wt% silver is not suitable as a long-term antimicrobial material.

In contrast, the silver ion concentration in the immersion liquid increases continuously with growing immersion time of the PA6/Ag-nanocomposite. That means the PA6/Ag-nanocomposite releases silver ions over a longer period of time very efficiently. The amount of silver ions released by the PA6/Ag-nanocomposite after short immersion times is about two orders of magnitude higher than that released from a conventional PA6/Ag-composite containing 2 wt% elemental silver [20].

To check whether the PA6/Ag-nanocomposite has potential long-term antimicrobial properties, the silver ion release from this material was investigated over 100 days (cf. Fig. 3).

According to Fig. 3 the silver ion concentration in the immersion liquid increases proportional to the immersion time of the PA6/Ag-nanocomposite. That means a zero-order silver ion release kinetics is observed. About 17 µg of silver per day, per cm^2 specimen surface and per litre immersion liquid are released over 100 days. From the cumulative silver ion release within about 100 days, the filler content, the specimen mass and the volume of the immersion liquid was calculated, that only about 3% of the silver available in the PA6/Ag-nanocomposite was released after 100 days of immersion in water. Thus, it can be expected that a zero-order silver ion release from PA6/Ag will occur over a much longer timescale than 100 days. From the results presented in Fig. 3 it is expected that PA6 filled with 2 wt% nanosilver is a suitable antimicrobial material for long-term applications.

For short immersion times a small deviation from a linear dependence of the cumulative silver ion release from PA6/Ag on the immersion time is observed (cf. Fig. 3). This becomes more obvious if the silver ion release rate instead of the cumulative silver ion release, which was determined by differentiating the curve shown in Fig. 3, is plotted versus the immersion time (cf. Fig. 4).

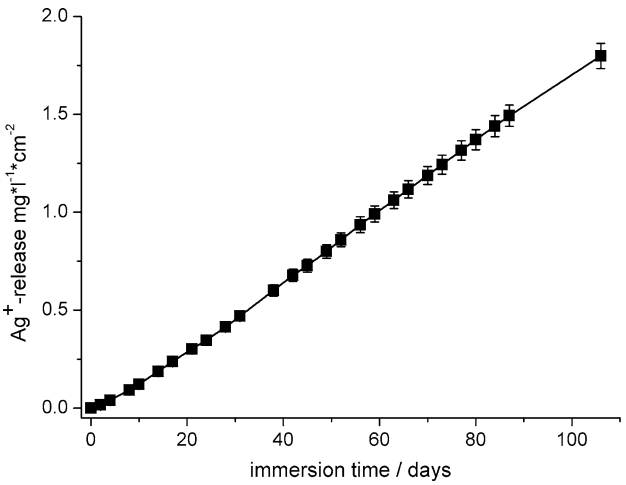

Fig. 3 Long-term silver ion release from a PA6/silver-nanocomposite containing 2 wt% silver

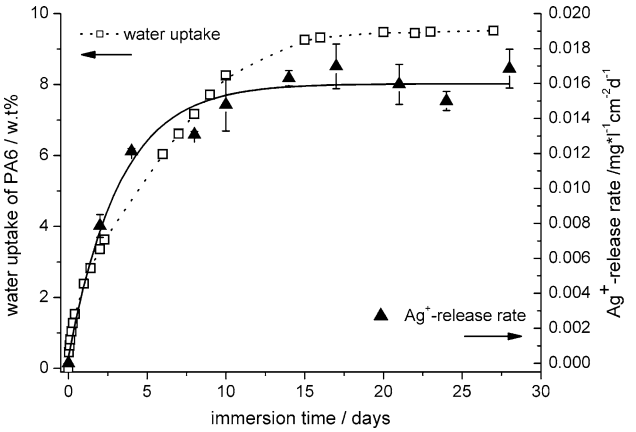

Fig. 4 Silver ion release rate from a PA6/silver-nanocomposite containing 2 wt% silver (right axis) and kinetics of the water uptake of PA6 (left axis)

The release rate increases with growing immersion time and becomes constant after about 15 days. This behaviour can be explained by the kinetics of the water uptake by the PA6 matrix (cf. Fig. 4).

According to Eq. 1 elemental silver particles release silver ions only in the presence of water. Thus the water uptake of the polymer matrix is decisive for the silver ion release [22].

PA6 is a very hydrophilic polymer taking up 9.5 wt% water at the maximum. From Fig. 4 it becomes obvious that the sorption of water is a function of time. It takes about 15 days until the sample is completely soaked with water. Comparing the two graphs in Fig. 4 it is obvious that the time dependence of the silver ion release rate from a PA6/Ag-nanocomposite coincides well with the kinetics of the water uptake of the polymer matrix. Thus it can be concluded that immediately after immersion in water only silver particles situated at the surface of the specimen contribute to the silver ion release. During the first 15 days of immersion the water diffuses from the surface into the bulk of the sample. That means that the number of silver particles being able to take part in the silver ion release process increases with time. After 15 days of immersion in water the whole sample is soaked with water. Thus, it can be imagined that after 15 days all the silver particles present in the sample contribute to the silver ion release.

Moreover, the water plasticizes the PA6 matrix. That means the water molecules are located between the polymer chains. The resulting enlarged distance between the polymer molecules facilitates the diffusion of silver ions through the polymer.

The different silver ion release properties of PMMA/Ag and PA6/Ag presented in Fig. 2 can also be explained by the water uptake of the matrix.

In comparison to PA6, PMMA is a rather hydrophobic polymer, its water uptake amounts to 1.7 wt% at the maximum. In a previous work it was shown that this water uptake is not sufficient for a silver ion release from particles situated in the bulk of the sample [19]. Thus, in PMMA only silver particles located at or near the sample surface contribute to the silver ion release [19]. After the dissolution of these particles there is no silver ion release any more.

The comparable amount of silver ions released from PA6/Ag and PMMA/Ag after 2 days of immersion in water can be understood as follows: After this short immersion time in both materials only the particles near the sample surface contribute to the silver ion release. Thus, the released amount of silver ions should increase with a growing number of particles situated at the sample surface. Because the specimen geometry is the same and both polymers have the same filler content (2 wt%) and a comparable morphology of the silver nanoparticles, the number of silver particles located at or near the specimen surface should be similar for the two materials resulting in comparable initial release rates.

Antimicrobial efficacy

From the high silver ion release rate of the PA6/Ag-nanocomposite a good antimicrobial efficacy should be expected. In order to check this the antimicrobial efficacy of the samples against *Escherichia coli* was investigated in two independent sets of experiments using an initial concentration of about 10^5 CFU/mL. For the tests in addition to the unmodified PA6 two silver filled PA6 samples having a different prehistory were used: one sample was never immersed in water before the antimicrobial efficacy test, the other one was immersed in water for 100 days before the test. That means one of the two silver filled samples had already released 3% of the available amount of silver. The results of these tests are summarized in Table 1.

In both test series the same trend was observed (cf. Table 1): In the absence of PA6 and/or silver (control sample) the concentration of bacteria in the suspension remains nearly unchanged after 24 h. That means that the bacteria survive in the suspension under the conditions used and that they do not adhere noticeably to the walls of the microtitre tray wells.

In the suspension, which was in contact with neat PA6 for 24 h, a concentration of bacteria was found which was significantly lower than that for the control sample.

No bacteria could be detected in the suspensions, however, which had been in contact with the silver filled PA6 for 24 h. The same result was found for a PA6/Ag-nanocomposite, which was immersed in water for 100 days before the test.

The test method used is able to record bacterial cells in suspension only. For that reason, adherence of the cells to

Table 1 Initial concentration of *Escherichia coli* and concentrations of the bacteria in suspension after 24 h contact with the differently modified samples

Test serial no.	C_0^a (CFU*ml^{-1})	C_1^b (CFU*ml^{-1})	C_2^c (CFU*ml^{-1})	C_3^d (CFU*ml^{-1})	C_4^e (CFU*ml^{-1})
1	$(1.2 \pm 0.1)*10^5$	$(9.6 \pm 1.0)*10^4$	$(4.2 \pm 0.4)*10^4$	0	0
2	$(1.6 \pm 0.2)*10^5$	$(1.5 \pm 0.2)*10^5$	$(2.7 \pm 0.3)*10^4$	0	0
3	$(1.6 \pm 0.3)*10^6$	$(1.7 \pm 0.4)*10^6$	$(1.8 \pm 0.4)*10^6$	0	0
4	$(1.1 \pm 0.1)*10^6$	$(1.1 \pm 0.1)*10^6$	$(2.6 \pm 0.1)*10^6$	0	0

[a] Initial concentration of bacteria

[b] Concentration of bacteria after 24 h in the absence of PA6 and Ag (control)

[c] Concentration of bacteria after 24 h contact with neat PA6

[d] Concentration of bacteria after 24 h contact with PA6 filled with 2 wt% Ag, polymer sample not immersed in water before the test

[e] Concentration of bacteria after 24 h contact with PA6 filled with 2 wt% Ag, polymer sample immersed in water for 100 days before the test

the PA6 specimens or death of the bacteria due to a bactericidal efficacy of the samples could be the cause for the disappearance of the bacteria from the suspension.

Moreover it must be taken into account that the suspensions taken from wells contain silver ions released from the PA6 samples. Thus the bacteria could have survived, but the growth of colonies on the agar plates could be prevented by a bacteriostatic effect of the silver ions.

According to the composition of the Luria-Broth (LB) agar a growth prevention by a bacteriostatic action of the suspensions should be very unlikely: The LB agar mainly consists of trypton, that means it contains a plenty of amino acids being able to form complexes with silver ions. Amino acids containing SH-groups are also present in the agar. The SH-groups interact strongly with silver ions and inactivate them by a formation of S–Ag-bonds. Moreover LB agar contains sodium chloride in a concentration of 10 g/L. Chloride ions precipitate silver ions as silver chloride leading to an inactivating of silver ions.

Thus, if no colonies are detected on the agar plates that means that the bacteria are dead or that the cells adhere to the PA6 specimens.

To find out the reasons, the colonization of the specimen was checked qualitatively by the following test: After 24 h the polymer samples were removed from the bacterial suspensions. Then the samples were rinsed carefully with sterile water to remove loosely bound bacteria. The samples as well as the rinsings were then incubated on a Luria-Broth solid agar at 37 °C for 24 h.

No bacterial colonies could be detected on, under or besides the silver filled PA6 samples as well as in the rinsing solutions. That means these samples were not colonized and the disappearance of the bacteria in the suspension was solely caused by the antimicrobial efficacy of the materials. Hundred days immersion of the PA6/Ag-nanocomposite in water before the test did not decrease its antimicrobial efficacy.

An initial concentration of about 10^5 CFU/mL is not so much of challenge for the specimen. Thus, in a second set of experiments the PA6 samples were inoculated by a suspension containing about 10^6 CFU/mL. After having been in contact with the silver containing PA6 samples for 24 h, no bacteria could be detected in the suspensions, see Table 1.

Generally, the biological tests confirm that the PA6/Ag-nanocomposite exhibits a good antimicrobial efficacy over a longer period of time, as expected from the results of the silver ion release tests.

A comparison with ref. [20] shows, that the antimicrobial efficacy of the nanocomposite is much higher than that of a conventional PA6/Ag-composite: A suspension of *Escherichia coli* must be brought into contact with a conventional composite containing 8 wt% silver for at least 7 days until a remarkable reduction of bacterial cells is observed. A comparison of the results of the silver ion release tests presented in this work and in ref. [20], respectively, shows, that the reason for the lower antimicrobial efficacy of the conventional composite is a much lower silver ion release rate.

In contrast, on and besides the neat PA6 sample and in the rinsing solution of this sample a large amount of bacterial colonies could be detected proving that this sample was heavily colonized by the bacteria after having been 24 h in contact with the bacterial suspension. In that case the decrease of the concentration of bacterial cells in suspension was caused by a simple adsorption effect.

If the initial concentration of bacteria is around 10^6 CFU/mL no loss of bacteria in the suspensions is observed after having been in contact with pure PA6 for 24 h. Thus, it can be concluded, that neat PA6 does not show any antimicrobial efficacy.

Conclusions and outlook

PA6/Ag-nanocomposites can be prepared by the simple processing operation of mixing silver acetate into molten PA6 without the aid of a solvent or a carrier for the silver particles.

PA6 filled with 2 wt% elemental silver nanoparticles releases silver ions over at least 100 days according to a zero-order rate law. Within this time about 17 μg Ag^+/d cm^2 L are released. In comparison to PA6 filled with 2 wt% conventional elemental silver microparticles [20] the rate of the silver ion release from a PA6/Ag-nanocomposite is about two orders of magnitude higher. This excellent silver ion release behaviour of PA6/Ag can be explained by the high surface to bulk ratio of the silver nanoparticles as well as by the strong hydrophilic properties of the PA6 matrix.

As expected from the silver ion release studies, PA6 filled with 2 wt% nanosilver exhibits a convincing antimicrobial efficacy: If *Escherichia coli* are brought into contact with the PA6/Ag-nanocomposite, they are killed completely within 24 h. An immersion of the PA6/Ag-nanocomposite in water for 100 days does not reduce its antimicrobial efficacy against *Escherichia coli*.

From the results of the silver ion release studies and the antimicrobial efficacy tests it can be concluded, that PA6 filled with 2 wt% nanosilver is a suitable antimicrobial material for long-term applications.

In future work the minimum filler content necessary for an antimicrobial efficacy of PA6 against *Escherichia coli* will be determined. Moreover, the efficacy of PA6/silver-nanocomposites against other bacteria will be checked.

Acknowledgement The authors are grateful for financial support from the German Research Foundation (DFG). Many thanks to Dr. E. Ingolic and Dr. H. Schröttner from the Research Center of Electron Microscopy in Graz (Austria) for performing TEM investigations.

References

1. Malassney P, Goeau-Brissonniere O, Coggia M, Pechere JC (1996) J Antimicrob Chemoth 37:121
2. Kalyon BD, Olgun U (2001) J Infection Control 29:124
3. Stickler DJ (2000) Curr Opin Infect Dis 13:389
4. Golubovich VN, Rabotnova IL (1974) Microbiology 43:948
5. Russel AD, Hugo WB (1994) Prog Med Chem 31:351
6. Feng QL, Wu J, Chen GQ, Cui FZ, Kim TN, Kim JOA (2000) J Biomed Mater Res 52:662
7. (a) Schierholz JM, Lucas LJ, Rump AFE, Pulverer G (1998) J Hosp Infect 40:257; (b) Schierholz JM, Beuth J, Rump AFE, König DP, Pulverer G (1999) Mat-wiss Werkstofftech 30:869; (c) Schierholz, JM, Seyfert UT, Rump AFE, Beuth J, Pulverer G (1999) Infusion Th Trans Med 26:278
8. Darouiche RO (1999) Clin Infect Dis 29:1371
9. Guggenbichler J-P (guest editor) (1998) Infection 26(Suppl. 1) (german edition):1
10. Guggenbichler J-P (2003) Mat-wiss Werktofftech 34(12):1145
11. Dunn K (2004) Burns 30(Suppl 1):1
12. Holder IA, Durkee P, Supp AP, Boyce ST (2003) Burns 29:445
13. Ovington LG (2004) Ostomy/Wound Management 50(9A Suppl):1
14. Klueh U, Wagner V, Kelly S, Johnson A, Bryers JD (2000) J Biomed Mater Res (Appl Biomater) 53:621
15. Tweden KS, Cameron JD, Razzouk AJ, Bianco RW, Holmberg WR, Bricault RJ, Barry JE, Tobin E (1997) Am Soc Art Int Org J 43:M475
16. Alt V, Bechert T, Steinrücke P, Wagener M, Seidel P, Dingeldein E, Domann E, Schnettler R (2004) Biomaterials 25:4383
17. Kumar R, Howdle S, Münstedt H (2005) J Biomed Mater Res Part B: Appl Biomater 75B:311
18. Hoskins JS, Karanfil T, Serkiz SM (2002) Environ Sci Technol 36:784
19. Damm C (2005) Polym & Polym Comp 13(7):649
20. Kumar R, Münstedt H (2005) Biomaterials 26(14):2081
21. Aymonier C, Schlotterbeck U, Antonietti L, Zacharias P, Thomann R, Tiller JC, Mecking S (2002) Chem Comm 24:3018
22. Joyce-Wöhrmann RM, Hentschel T, Münstedt H (2000) Adv Eng Mat 2(6):380