Appl. Phys. A 91, 479–486 (2008)
DOI: 10.1007/s00339-008-4434-1

Applied Physics A
Materials Science & Processing

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Kinetic aspects of the silver ion release from antimicrobial polyamide/silver nanocomposites

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Received: 28 November 2007/Accepted: 6 February 2008

ABSTRACT Spherical silver nanoparticles were grown in situ in different polyamides by a thermal reduction of silver acetate during melt processing of the polymers. Most of the particles have a diameter of about 20 nm. The absolute amount as well as the kinetics of the silver ion release from the various polyamide/silver nanocomposites differ strongly, although the filler content in all materials is the same (1.5 wt. %) and the morphologies of the silver particles are not very different. One result of the investigations was that the absolute amount of the long-term silver ion release increases exponentially with the maximum water absorption of the polymers used as matrix materials, because silver ions are formed from elemental silver particles in the presence of water, only. Moreover, it was also found that the long-term silver ion release increases with a growing diffusion coefficient of water in the polymer. The water absorption properties of the polymers govern the kinetics of the silver ion release, too: for strong hydrophilic polyamides like PA6 or PA6.6, which are plasticized by water, the silver ion release is a zero-order process. For nanocomposites with less hydrophilic polyamides like a cycloaliphatic polyamide or a P12 modified with polytetrahydrofurane (PA12-poly-THF), the silver ion release is governed by diffusion. As expected from the efficacy of the silver ion release, PA6, PA6.6, PA12 and PA12 modified with polytetrahydrofurane and a cycloaliphatic polyamide filled with 1.5 wt. % of silver nanoparticles are active against *Escherichia coli*. But, only nanocomposites with PA6, PA6.6 and P12-poly-THF as matrix materials are suitable as long-term biocidal materials.

PACS 68.35.bm; 68.35.Fx; 68.37.Lp

1 Introduction

Polymers are widely used as a material basis for medical and life-care products. For such applications polymers should preferably possess antimicrobial efficacy to reduce the risk of device-related infections. Instead of organic biocidal agents, elemental silver can be used for the preparation of antimicrobial polymers. In the presence of humidity and oxygen from air, elemental silver particles release small amounts of silver ions that exhibit a biocidal activity against a broad spectrum of microorganisms.

The generation of silver ions occurs on the surface of the silver particles, only. Silver nanoparticles release ions quite efficiently because of their large specific surface area. For that reason silver nanoparticles are promising filler or coating materials for the preparation of antimicrobial polymers.

Many techniques have been established to incorporate silver nanoparticles into polymers. Some examples are discussed briefly below.

The reduction of silver nitrate in the presence of brush-like polymer particles with a poly(styrene) core and a poly(ethylene glycol) methacrylate or poly(acryl amide) shell yields silver nanoparticles with diameters smaller than 10 nm [1, 2]. The silver ion implantation into poly(vinyl chloride), silicon rubber, poly(urethane) or poly(ethylene) leads to the formation of silver nanoparticles in the subsurface of these polymers [3].

Antimicrobial bone cement was prepared by dispersing silver nanoparticles as powder in the liquid component of the bone cement followed by a polymerization of the mixture [4].

Polymer films with incorporated silver nanoparticles were prepared by the co-sputtering of diethylene glycol methacrylate [5] or poly(tetrafluoro ethylene) [6] and silver.

The use of supercritical carbon dioxide is a promising technique for the impregnation of polymers with silver nanoparticles because no organic solvent is necessary. In [7] an organic silver compound was incorporated into silicone using supercritical carbon dioxide as a solvent. In a second step, silver nanoparticles were formed from the silver salt by treating the polymer with hydrogen gas [7].

Processing operations based on thermoplastic properties are used for the preparation of antimicrobial polymers on a large scale. Normally, liquid suspensions of silver nanoparticles are mixed with the molten polymer. This simple method has the disadvantage that residuals of the suspension liquid can remain in the polymer. They can change the mechanical behaviour of the polymer. Moreover, residuals of solvents in the polymers are critical for applications in medicine. To avoid solvents during thermoplastic processing, the silver nanoparticles are often deposited on an inorganic carrier like barium sulphate in a first step [8]. The supported silver nanoparticles are incorporated as powders into the molten polymers.

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In this work silver nanoparticles are generated in situ in different polyamides by a thermal reduction of silver acetate during melt processing of the polymers. This method offers the opportunity to prepare polymer/silver nanocomposites on a large scale without the aid of solvents or carriers for the silver particles. The antimicrobial efficacy of polymer/silver nanocomposites against different bacteria was shown in many studies. An efficient silver ion release from the materials is essential for a good biocidal activity. The properties of the filler particles as well as those of the polymer used as the matrix govern the silver ion release. The influence of the properties of the filler particles on the silver ion release from polymers is quite well understood: as expected from the specific surface area of the filler particles, polymer/silver nanocomposites release many more silver ions than polymer/silver microcomposites [8, 9].

Traces of gold or platinum in the silver nanoparticles improve the silver ion release because the Au/Ag or Pt/Ag galvanic couple results in an enhanced oxidation of the silver [6, 10].

The role of some polymer properties for the silver ion release was investigated, too:

- Cross linking of the polymer leads to a decrease of the silver ion release rate [11].
- The silver ion release from hydrophilic polymers is much more efficient than that from more hydrophobic ones [12].
- The silver ion release from semicrystalline polymers increases with decreasing crystallinity of the matrix [13].

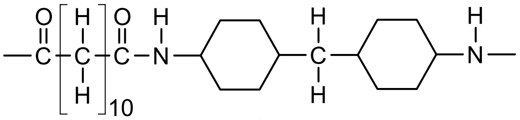
The influence of the polymer matrix on the silver ion release is much more complex than that of the filler, because many different polymer properties govern the silver ion release. For that reason, the influence of the matrix properties on the silver ion release is not well understood.

This leads to the consequence that the release mechanism involving the diffusion of water into the polymer, the oxidation of the elemental silver particles and a subsequent diffusion of silver ions from the bulk to the surface of the sample is not well understood in detail, although the silver ion release from polymers was investigated by many researchers. The goal of this work is a systematic study of the silver ion release kinetics from different polyamide/silver nanocomposites to obtain a deeper insight into the release mechanisms. Polyamides were used as matrix materials because their water absorption can be varied in a wide range by changing the chemical compositions of the materials. By using these materials relationships between the water absorption properties of the polymers and the silver ion release can be investigated. Moreover, polyamides are used for the manufacture of wound dressings and sutures as well as for artificial tendons. For these applications an antimicrobial efficacy of the polyamides would be an advantage.

2 Experimental

2.1 *Materials*

Polyamide 6 grade ‘B 3 SK’ from BASF, polyamide 6.6 grade ‘Akulon S223’ from DSM Engineering Plastics, polyamide 12 grade ‘Grilamid L 16 LM’ and polyamide 12 modified with poly-THF grade ‘Grilamid ELY 20 NZ’ from EMS-Grivory were used. The cycloaliphatic polyamide 1 (grade ‘Trogamid CX 7323’) was supplied by Degussa.



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Silver acetate was purchased from Merck.

The polymers were dried in vacuum at 80 °C for 12 h prior to use.

2.2 *Preparation of the silver-filled materials*

To prepare composites with a theoretical filler content of 2 wt. %, 980 g of the polymer pellets were premixed with 31 g of silver acetate and then processed in a co-rotating twin-screw extruder. The processing temperature was 180 °C for PA12, 170 °C for PA12-poly-THF, 230 °C for PA6 and 270 °C for PA6.6 and the cycloaliphatic polyamide 1.

2.3 *Silver ion release tests*

To investigate the silver ion release from the polyamide/Ag nanocomposites, six rectangular specimens (2 cm × 1 cm × 0.1 cm) 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 in more detail elsewhere [12, 14]. 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 that 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 cause a peak in the current–potential curve. After a baseline correction the area of the peak in the voltammogram is calculated. In a previous paper [15], 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.

The silver ion concentration in the immersion liquid is a function of the specimen surface area and the volume of the immersion liquid. The measured silver ion concentrations were normalized to 1 cm^2 specimen surface area and 1 l of immersion liquid to obtain results which are independent of these experimental parameters.

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

2.4 *Antimicrobial efficacy tests*

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

The bacteria were grown overnight in Luria Broth at 37 °C. The resulting suspension of bacteria was diluted to a concentration in the range from 2 to 3×10^6 CFU (colony forming units)/ml. The exact initial concentration of bacteria was determined by the solid agar plate method, as described below.

The rectangular film specimens sterilized with chloroform were transferred into the wells of a sterile microtitre tray. Each specimen was incubated with 1.5 ml of the diluted bacterial suspension. The microtitre tray was gently shaken for 24 h at ambient 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 was taken off and distributed on a Luria Broth solid agar plate after a suitable dilution with sterile micropore water. 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 of between 1 and 2 mm. These colonies were counted. From the number of colonies and the dilution factor the concentration of bacteria having survived after being in contact with the sample for 24 h was calculated.

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

2.5 *Layer morphology*

A transmission electron microscope (TEM) type 'EFTEM LEO 912' (Leo Co.) was used to investigate the morphology of the filler particles in the polymers. The TEM investigations were performed on 70–100 nm thick microtome cuts.

2.6 *Real filler content*

During extrusion a part of the filler may be lost. Because the silver ion release from the nanocomposites is a function of the filler content, it is important to know the real filler content of the nanocomposites.

1.2 g of dried nanocomposite pellets was heated to 600 °C in air for 2 h. Under these conditions the polymers are mineralized completely. The solid residual was dissolved in 5 ml of 32.5 vol. % nitric acid. After a suitable dilution, the silver content of the solution was measured by anodic stripping voltammetry.

2.7 *Water absorption of the polymers*

The polymer pellets were dried in vacuum at 80 °C for 24 h prior to use. Specimens having dimensions of 5 cm × 5 cm × 0.3 cm were prepared from the pellets by compression moulding. The specimens were dried in vacuum at 80 °C for 3 days. The dry specimens were weighed. Then, the specimens were immersed in distilled water and their weight was measured as a function of the immersion time until the weight remained constant. These experiments primarily yield values for the maximum water absorption in wt.%. From these values the maximum water concentration in mol/cm^3 may be calculated using the molar mass of water and the density of the polymer.

3 Results and discussion

3.1 *Composition and morphology of the composite materials*

The dissolution experiments described in Sect. 2.6 reveal that the real silver content of all materials used is 1.5 ± 0.1 wt. %. This means that independently of the polyamide used as the matrix, about 25% of the filler was lost during extrusion, probably by an adsorption at the walls and the screws of the extruder.

According to the TEM micrographs shown in Fig. 1, the thermal decomposition of silver acetate in all the polyamides used resulted in the formation of nearly spherical silver nanoparticles.

In all cases most of the particles have a diameter of about 20 nm. In PA6 and in the cycloaliphatic polyamide some larger particles are present, too. But, their diameters clearly remain below 100 nm. In all polyamides used the particles are quite well dispersed and not aggregated.

The results presented in Fig. 1 show that all of the polyamides used in this work act as good stabilizing agents for the silver particles. This finding implies that the interactions between the silver particles and the amide groups must be much stronger than the interactions between the silver particles. Consequently, the silver particles are nearly completely surrounded by the polyamide chains, preventing their growth and aggregation.

According to Fig. 1, the particle densities in the different polymers seem to be different, although the silver contents of all materials are the same. From each material at least five TEM micrographs from different places of the sample were recorded. Even for the same nanocomposite material, each TEM micrograph exhibited a different number of particles.

This finding hints to an inhomogeneous particle distribution on the microscale. A TEM micrograph reflects the particle distribution within an area of about 1 μm^2, which means that it depicts the particle distribution in the microscale. The dissolution experiment, however, yields a silver content averaged over 1.2 g of the material. Moreover, the thickness of the microtome cuts must be taken into account. The number of particles visible in the TEM micrograph increases with growing thickness of the microtome cut. Thus, differences in the layer thickness of the microtome cuts would also explain the experimental findings.

3.2 *Silver ion release*

According to Fig. 2a and b, all of the polyamide/silver nanocomposites investigated release silver ions into water. This means that an oxidation of the elemental silver particles and a subsequent transport of the silver ions to the surface of the specimens take place.

The absolute amount of silver ions released from the materials differs strongly, however, although the filler content in all materials is the same. The silver ion release increases in

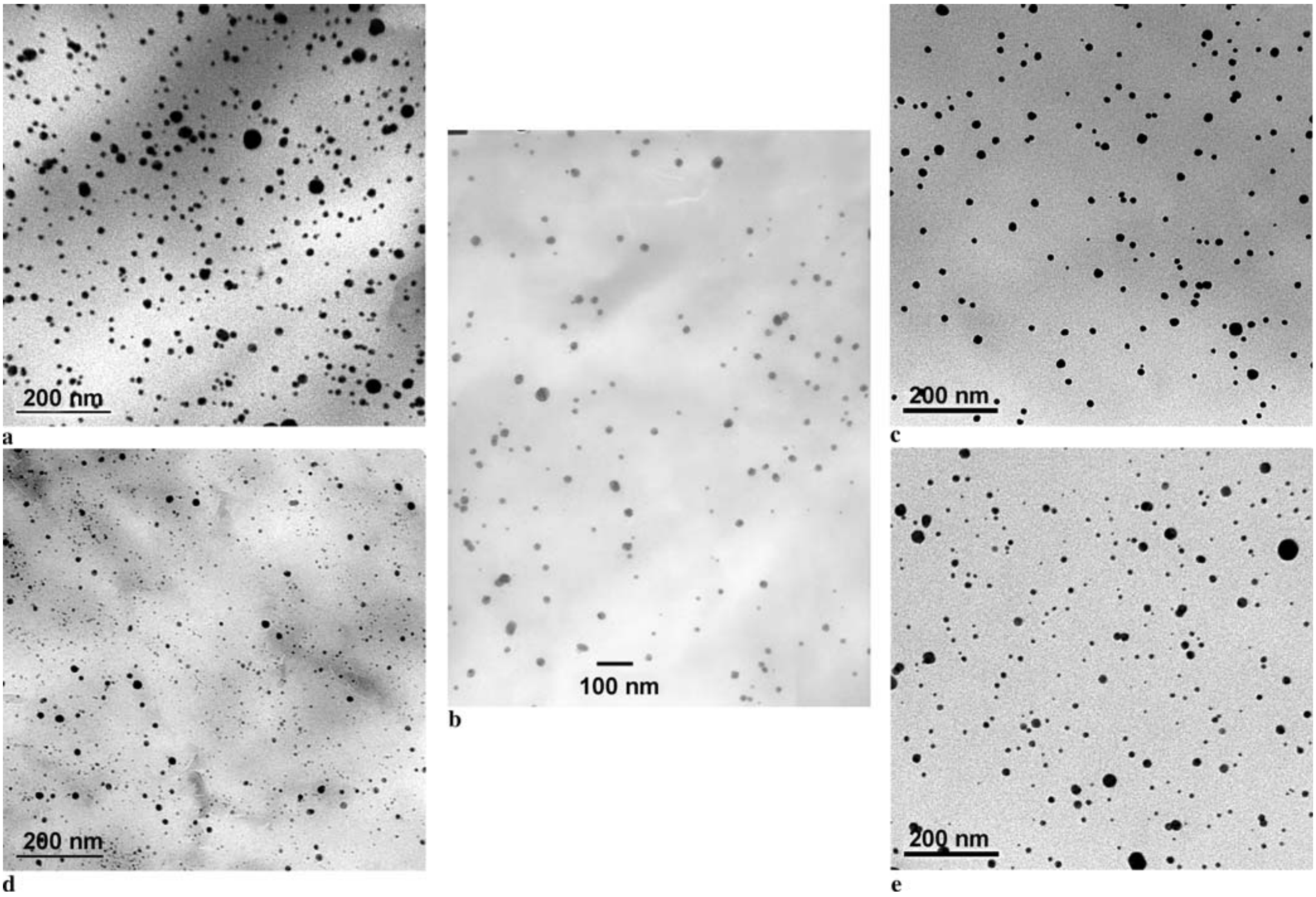

FIGURE 1 TEM micrographs of polyamide/Ag nanocomposites. (**a**) PA6, (**b**) PA6.6, (**c**) PA12, (**d**) PA12-poly-THF, (**e**) cycloaliphatic polyamide 1. The *black dots* are the silver particles

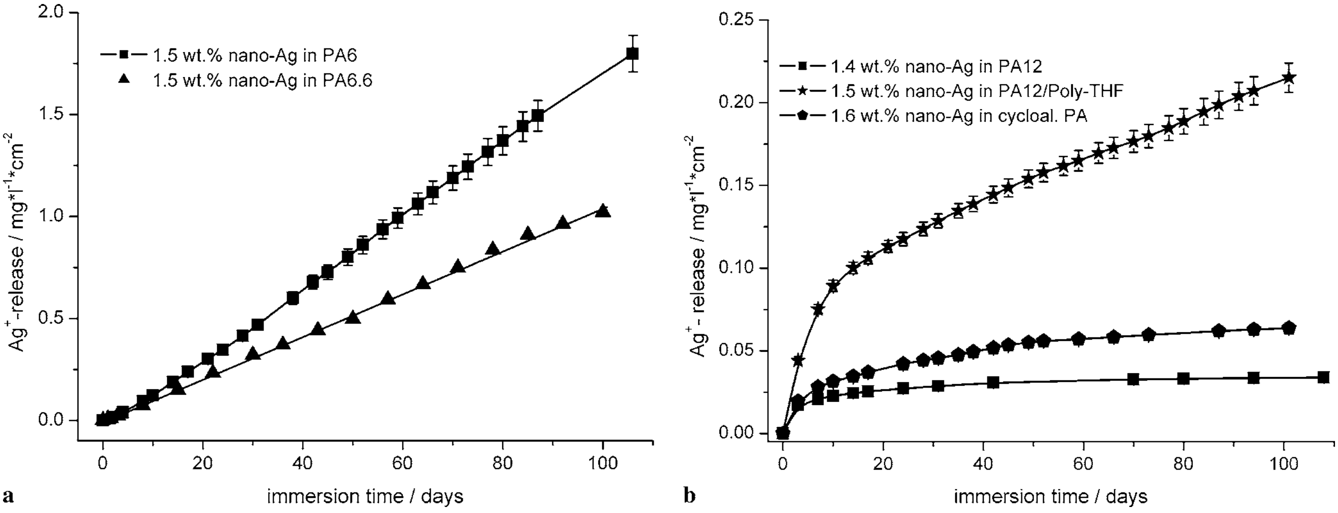

FIGURE 2 (**a**) Cumulative silver ion release from a PA6/Ag as well as a PA6.6/Ag nanocomposite as a function of the immersion time. (**b**) Cumulative silver ion release from polyamide/Ag nanocomposites with PA12 and PA12-poly-THF as well as the cycloaliphatic PA 1 as matrix materials as a function of the immersion time

the following direction: PA12 < cycloaliphatic PA < PA12-poly-THF $\ll$ PA6.6 < PA6. The silver ion release from PA6 or PA6.6 is about one order of magnitude larger than that found for PA12, PA12-poly-THF and the cycloaliphatic polyamide.

According to the TEM micrographs shown in Fig. 1, the filler morphology is not so different that it could be the reason for the differences in the silver ion release. Thus, the properties of the polymer matrix must play an important role in the silver ion release. As mentioned in the introduction, silver ions are formed from elemental silver particles in the presence of water, only. Therefore, the silver ion release is expected to increase with a growing water content of the polymer. This conclusion is confirmed by the results shown in Fig. 3.

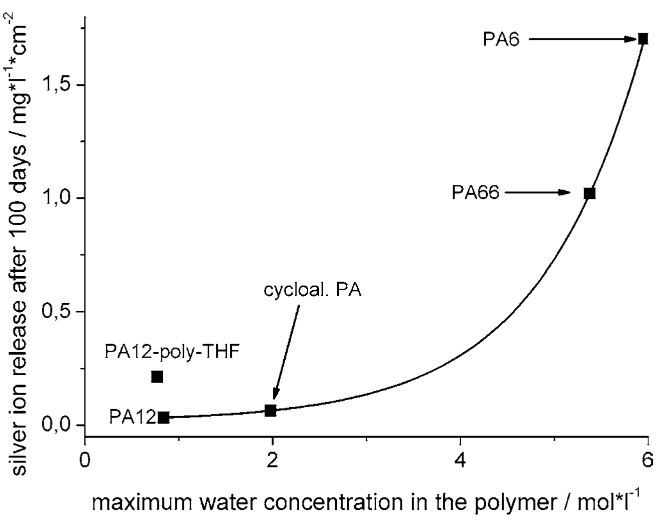

FIGURE 3 Cumulative silver ion release from the polyamide/silver nanocomposites after an immersion time of 100 days as a function of the maximum water absorption of the polymers

According to Fig. 3, the silver ion release after 100 days immersion in water increases exponentially with the maximum water absorption of the polyamides. An immersion time of 100 days was chosen because at short immersion times the silver ion release is mainly influenced by the dissolution of silver particles in the surface layer of the sample. Transport processes through the matrix influenced by the polymer properties are relevant at longer immersion times, only.

The data point for PA12-poly-THF significantly deviates from the curve in Fig. 3. If only the maximum water absorption of the polymer influenced the silver ion release, then PA12 and PA12-poly-THF should release comparable amounts of silver ions. But, according to Fig. 3, the release from PA12-poly-THF is remarkably larger than that found for the unmodified PA12.

This finding may be explained by the diffusion coefficient of water in the various polymers. The diffusion coefficients of water in the polyamides were determined from the kinetics of the water absorption. The water uptake measured at time *t* was related to the maximum water absorption and plotted vs. the square root of the immersion time. At early times a linear relationship between the normalized water uptake and the square root of the immersion time was found. From the slope of the straight line the diffusion coefficient of water was calculated using (1) (layer thickness: 0.3 cm). The values for the diffusion coefficient of water in PA12, the cycloaliphatic polyamide, PA6 and PA6.6 were found to be in the range between 3×10^{-9} and 6×10^{-9} cm^2/s. But, for P12-poly-THF the value for the diffusion coefficient of water was found to be one order of magnitude larger. This finding implies that the mobility of water molecules in the polymer also must be taken into account to explain the silver ion release.

The kinetics of the silver ion release was investigated to obtain deeper insights into the release mechanism. According to Fig. 2a, a linear relationship between the silver ion release from the PA6/Ag nanocomposite as well as from the PA6.6/Ag nanocomposite and the immersion time was found. This means that the silver ion release from these polymers is a zero-order process. The release rate amounts to $17.6\,\mu\mathrm{g\,l^{-1}\,cm^{-2}\,d^{-1}}$ for PA6/Ag and $10.5\,\mu\mathrm{g\,l^{-1}\,cm^{-2}\,d^{-1}}$ for PA6.6/Ag, respectively.

A zero-order release kinetics proves that the rate of the relaxation of the macromolecule chains due to the penetrating water dominates the transport process. This means that a zero-order release kinetics is observed if the polymer is plasticized by water. It is well known that the mechanical properties of PA6 and PA6.6 strongly depend on their water content because water plasticizes these polymers. Thus, a zero-order release kinetics was expected for PA6 and PA6.6.

In some cases the release of organic drugs from hydrogels also obeys a zero-order rate law, although in these materials the species to be released from the polymers is formed by a physical dissolution of the drug dispersed in the hydrogel [16]. In the materials used in this work, the silver ions are generated from the elemental silver particles dispersed in the polymers by a chemical process. Thus, the comparison of the silver ion release kinetics with that of the drug release shows that the nature of the generation process of the diffusing species from a dispersed precursor does not govern the rate law for the release of this species from a polymer.

According to Fig. 2b, the silver ion release from the nanocomposites based on P12, PA12-poly-THF and the cycloaliphatic polyamide as well is a nonlinear function of the immersion time. To check whether the silver ion release from these nanocomposite materials is governed by diffusion, in Fig. 4a–c the normalized silver ion release is plotted vs. the square root of the immersion time. The silver ion release from these materials was related to the complete release of silver present in the polymer. The concentration for the complete release was calculated from the specimen mass, the filler content and the volume of the immersion liquid.

According to Fig. 4a and b, at least at the beginning of the release process a linear relationship between the normalized silver ion release and the square root of the immersion time is observed for the nanocomposites with PA12-poly-THF and the cycloaliphatic polyamide as matrix materials. This means that the release from these nanocomposites is governed by diffusion. This result implies that in PA12-poly-THF and the cycloaliphatic polyamide the rate of the relaxation processes of the polymer chains is slower than the transport rates of water and silver ions.

The straight lines in Fig. 4a and b, however, do not run through the origin. The reason for that is that the transport of silver ions from the interior of the sample as well as the dissolution of silver particles situated at or near the sample surface contribute to the silver ion release. At the beginning of the silver ion release experiment the dissolution of silver particles at the surface of the specimens dominates the silver ion release. For this silver ion release process no diffusion step through the polymer is necessary.

With increasing immersion time the transport of silver ions from the bulk to the surface of the sample becomes more important, whereas the contribution of silver particles in the surface to the release of silver ions decreases because these particles are consumed faster than particles situated in the bulk of the sample.

Thus, the silver ion release becomes governed by diffusion because most of the silver ions must move from the interior of the specimen to the surface to be released.

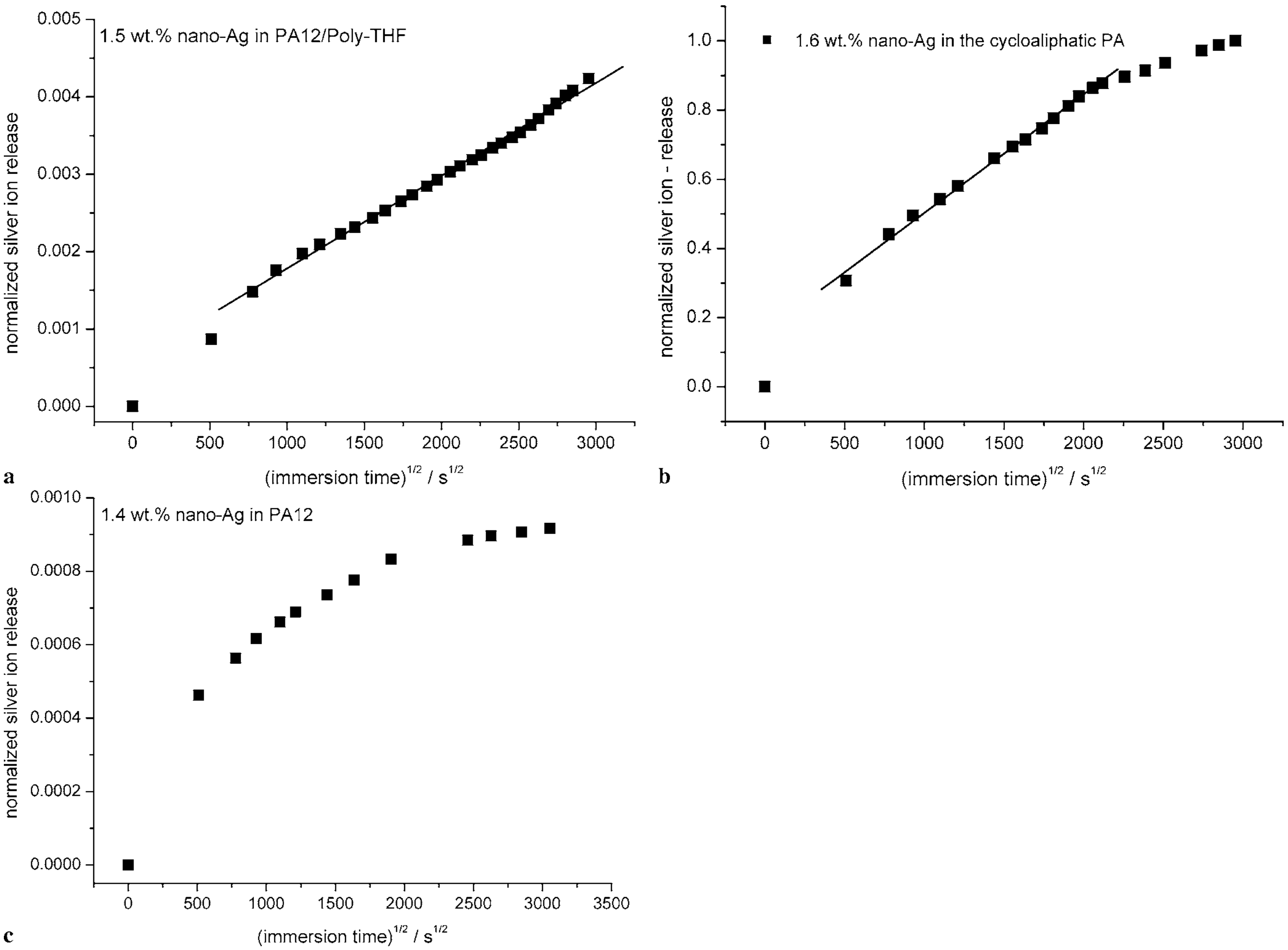

FIGURE 4 (**a**) Silver ion release from a PA12-poly-THF/Ag nanocomposite normalized to the total amount of silver in the polymer as a function of the square root of the immersion time. The slope of the straight line is $1.2 \times 10^{-6}\,\mathrm{s}^{-1/2}$. (**b**) Silver ion release from the cycloaliphatic polyamide 1 filled with 1.5 wt. % silver nanoparticles as a function of the square root of the immersion time. The silver ion release was normalized to the total amount of silver in the polymer. The slope of the straight line is $4.8 \times 10^{-7}\,\mathrm{s}^{-1/2}$. (**c**) Silver ion release from a PA12/Ag nanocomposite normalized to the total amount of silver in the polymer as a function of the square root of the immersion time

From the slopes of the straight lines in Fig. 4a and b, which amount to $1.2 \times 10^{-6}\,\mathrm{s}^{-1/2}$ for PA12-poly-THF and $4.8 \times 10^{-7}\,\mathrm{s}^{-1/2}$ for the cycloaliphatic PA, respectively, the diffusion coefficient of silver ions in the polymers can be assessed using (1) [16]:

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{Dt}{\pi d^2}}\,, \tag{1}$$

with C_t = silver ion concentration released at time t, C_∞ = silver ion concentration released at infinity, t = time, D = diffusion coefficient, and d = sample thickness (0.1 cm).

From (1) the following values for the diffusion coefficient D were calculated: $2.8 \times 10^{-15}\,\mathrm{cm}^2/\mathrm{s}$ for PA12-poly-THF and about $4.5 \times 10^{-16}\,\mathrm{cm}^2/\mathrm{s}$ for the cycloaliphatic PA. These values are about 10 and 11, respectively, orders of magnitude smaller than the diffusion coefficient of silver ions in water, which amounts to $1.77 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$ [17]. As expected, diffusion processes in these polymers are much slower than in liquids. The values found for D are in a typical size range for diffusion coefficients in solids.

As expected, the diffusion coefficient of silver ions in PA12-poly-THF is about one order of magnitude larger than the value found for the cycloaliphatic PA. PA12-poly-THF is a thermoplastic elastomer. This means that at ambient temperature it is in the rubbery state. In contrast, the glass-transition temperature of the cycloaliphatic PA is about 140 °C. This means that at ambient temperature this material is in the glassy state. For diffusion processes in polymers the free volume is important. Generally, the free volume in polymers in the rubbery state is larger than that in polymers in the glassy state. For that reason in rubbery polymers larger values for the diffusion coefficients are found.

For the PA12/Ag nanocomposite no linear relationship between the normalized silver ion release and the square root of the immersion time is observed, cf. Fig. 4c. Here, the silver ion release reaches a plateau value after an immersion time of about 14 days. Because in Fig. 2a and b and Fig. 4c the cumulative silver ion release is plotted, a plateau value does mean that after 14 days of immersion in water PA12/Ag does not release remarkable amounts of silver ions any more, although the colour of the sample, which is a function of the silver content, did not change. This finding indicates that mainly silver particles situated at or near the specimen surface are responsible for the silver ion release from PA12. After the consumption of these particles the silver ion release falls. Thus, it can be concluded that only marginal amounts of silver ions are transported from the interior of the sample to its surface because the concentration and mobility of water molecules in PA12 are not sufficient to facilitate noticeable silver ion diffusion through the polymer.

3.3 *Antimicrobial efficacy*

According to the silver ion release, it is expected that all the polyamide/silver nanocomposites investigated exhibit a good antimicrobial efficacy. Sterilized specimens of the neat polyamides as well as of the silver-filled ones were inoculated with a suspension of *E. coli* in Luria Broth to check their antimicrobial efficacy. The bacteria remained in contact with the samples for 24 h. Then, the concentration of living bacteria in the suspension was determined. The results of these tests are given in Table 1.

To check whether the nanocomposites are suitable as long-term biocidal agents, the specimens were immersed in distilled water for about 100 days prior to the antimicrobial efficacy test. This means that these samples have already released silver ions according to Fig. 2a and b before they came into contact with the bacteria. The results of these antimicrobial efficacy tests are summarized in Table 2.

In the absence of any polymer or silver (control), the concentration of bacteria in the suspensions after 24 h is comparable with the initial concentration of bacteria. This means that the test conditions are suitable for the survival of *E. coli*. In the presence of the unfilled PA12, PA12-poly-THF and the cycloaliphatic polyamide 1 the concentration of bacteria in the suspension after 24 h is comparable with that found in the control sample. In the presence of the neat PA6 and PA6.6, after 24 h the concentration of bacteria was even higher than in the control. These findings show that the neat polyamides do not exhibit any antimicrobial efficacy. PA6.6 and in particular PA6 seem to support the growth of *E. coli*. Thus, these materials could facilitate device-related infections if they were used in medicine without antimicrobial additives.

In the presence of the polyamide/silver nanocomposites no bacteria could be detected after 24 h. This means that, as expected from the silver ion release, the nanocomposites exhibit a good antimicrobial efficacy.

Even after storage in water for about 100 days prior to the antimicrobial efficacy tests the nanocomposites with PA6, PA6.6 and PA12-poly-THF as matrix materials are able to eliminate *E. coli* completely within 24 h, cf. Table 2. This result is in agreement with the good long-term release of silver ions from these materials. Thus, these materials are well suitable as long-term biocidal agents. In contrast, the PA12/Ag nanocomposite does not show any antimicrobial efficacy after 100 days storage in water, because this material does not release remarkable amounts of silver ions over such a long period of time, cf. Fig. 2b and Table 2.

After 100 days storage in water the silver-filled cycloaliphatic polyamide kills the bacteria only partially because the long-term silver ion release from this nanocomposite is weak, cf. Fig. 2b and Table 2.

Sample	Concentration of bacteria in the suspension/ CFU × ml^{-1}
Initial concentration	$(2.6 \pm 0.3) \times 10^6$
Control after 24 h	$(2.7 \pm 0.3) \times 10^6$
Neat PA6 after 24 h	$(6.5 \pm 0.7) \times 10^6$
1.5 wt. % Ag in PA6 after 24 h	0
Neat PA6.6 after 24 h	$(3.4 \pm 0.3) \times 10^6$
1.5 wt. % Ag in PA6.6 after 24 h	0
Neat PA12 after 24 h	$(2.3 \pm 0.3) \times 10^6$
1.4 wt. % Ag in PA12 after 24 h	0
Neat PA12-poly-THF after 24 h	$(2.1 \pm 0.3) \times 10^6$
1.5 wt. % Ag in PA12-poly-THF after 24 h	0
Neat cycloaliphatic PA after 24 h	$(2.7 \pm 0.3) \times 10^6$
1.6 wt. % Ag in the cycloaliphatic PA 1	0

TABLE 1 Initial concentration of *E. coli* in a Luria Broth suspension and concentrations of bacteria measured after 24 h in contact with the PA samples

Sample	Initial concentration of bacteria/ CFU × ml^{-1}	Concentration of bacteria in the suspension after 24 h/CFU × ml^{-1}
1.5 wt. % Ag in PA6	$(2.6 \pm 0.3) \times 10^6$	0
1.5 wt. % Ag in PA6.6	$(2.5 \pm 0.3) \times 10^6$	0
1.4 wt. % Ag in PA12	$(2.6 \pm 0.3) \times 10^6$	$(2.7 \pm 0.3) \times 10^6$
1.5 wt. % Ag in PA12-poly-THF	$(2.9 \pm 0.3) \times 10^6$	0
1.6 wt. % Ag in the cycloaliphatic PA 1	$(2.9 \pm 0.4) \times 10^6$	$(3.8 \pm 0.8) \times 10^5$

TABLE 2 Initial concentrations of *E. coli* in a Luria Broth suspension and concentrations of bacteria measured after 24 h in contact with the silver-filled polyamide samples. Each sample was stored in water for 100 days before the antimicrobial efficacy test

4 Conclusions

The thermal reduction of silver acetate during extrusion is an efficient and quite simple method to produce polyamide/silver nanocomposites on a large scale. The water absorption properties of the polyamides determine the silver ion release from polyamide/silver nanocomposites. The long-term silver ion release increases with growing maximum water absorption of the polymers, because silver ions are generated from elemental silver particles in the presence of water, only. Moreover, it was shown that the silver ion release from polyamide/silver nanocomposites increases with the growing diffusion coefficient of water in the polymer, too.

The kinetics and the mechanisms of the silver ion release from polyamide/silver nanocomposites are also a function of the matrix properties: for hydrophilic polymers like PA6 and P6.6, being plasticized by water, the silver ion release is a zero-order process. For more hydrophobic polyamides the silver ion release was found to be governed by diffusion. In PA12 no noticeable transport of silver ions from the interior to the surface of the sample takes place, because the concentration and mobility of water molecules in this material are too small.

As expected from the silver ion release, silver-filled PA6, PA6.6, PA12, P12-poly-THF and a cycloaliphatic polyamide exhibit a good activity against *E. coli*. Even after storage in water for 100 days the PA6/Ag, PA6.6/Ag and PA12-poly-THF/Ag nanocomposites are able to eliminate *E. coli* completely within 24 h. This property is related to the good long-term release of silver ions from these products. Thus, PA6, PA6.6 and PA12-poly-THF filled with about 1.5 wt. % of silver nanoparticles are well suitable as long-term biocidal agents.

ACKNOWLEDGEMENTS The authors are grateful to the German Research Foundation (DFG) for the financial support of this work. Many thanks are expressed to Dr.A. Rösch from the Institute of Microbiology of the University of Erlangen-Nuremberg for the opportunity to perform antimicrobial efficacy tests in his laboratory. Moreover, the authors acknowledge the support of Dr. G.-M. Kim from the Institute of Polymer Materials at the University of Halle-Wittenberg with regard to the TEM investigations.

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