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# Silver ion release from antimicrobial polyamide/silver composites

Radhesh Kumar, Helmut Münstedt*

*Institute of Polymer Materials, Friedrich-Alexander-University, Erlangen-Nurnberg, Martensstr.7, 91058 Erlangen, Germany*

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**Abstract**

Silver ion ($Ag^+$) the versatile antimicrobial species was released in a steady and prolonged manner from a silver-filled polyamide composite system. Metallic silver powder having varying specific surface area (SSA) has been used as a resource of biocide in polyamide. Strong evidences are found showing the release of the antimicrobial species from the resulting composite upon soaking it in water due to the interaction of the diffused water molecules with the dispersed silver powder within the matrix. The $Ag^+$ release was observed as increasing with time and concentration of the silver powder and is found to be influenced by the SSA of the silver powder, changes in the physical state of the composite specimen as a result of the water diffusion and the composite morphology. It is observed that the $Ag^+$ release increases initially which is followed by a marginal increase between day 4 and 6. Composites containing higher amounts of silver (4 and 8 wt%) exhibit a further rise in $Ag^+$ release from the sixth day of storage in water. Composite containing silver particles with the lowest specific surface area (0.78 $m^2/g$) showed highest $Ag^+$ release. SEM shows a finer dispersion of the silver powder (4 wt%) having lowest SSA. However particles with higher (1.16 and 2.5 $m^2/g$) SSA possess an agglomerated morphology leading to lower $Ag^+$ release. The composites are found to release $Ag^+$ at a concentration level capable of rendering an antimicrobial efficacy.


*Keywords:* Silver; Antimicrobial; Plasticisation

## 1. Introduction

Nowadays the introduction of new silver-based antimicrobial polymers represents a great challenge for both academic world and industry. The silver-based thermoplastic polymer composites combine the excellent high temperature processibility of the thermoplastics with the inherent antimicrobial property of the silver. Silver-based antimicrobials capture much attention not only because of the non-toxicity of the active $Ag^+$ to human cells [1,2] but because of their novelty being a long lasting biocide with high temperature stability and low volatility. The antimicrobial activity of silver ions has been well established [3,4]. Silver ions are significant antimicrobials by virtue of their antiseptic properties [5,6] with only few bacteria being intrinsically resistant to this metal [7]. Silver is well known being a significant resource for topical therapy because of its beneficial antimicrobial properties in medical devices such as catheters, cannulae etc [8,9].

The antimicrobial activity of silver is dependent on the silver cation $Ag^+$, which binds strongly to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen. Hence the silver-based antimicrobial polymers have to release the $Ag^+$ to a pathogenic environment in order to be effective. The oxidation of the metallic silver to the active species $Ag^+$ is possible through an interaction of the silver with the water molecules. A steady and prolonged release of the silver biocide in a concentration level (0.1 ppb) capable of rendering an antimicrobial efficacy [10] is a key factor for the design of this class of materials.

The research interest in this field of material science stems from the fact that there are different methods to incorporate silver in various polymeric substrates. One conventional approach is by the deposition of metallic silver directly onto the surface of the substrate, for example by vapour coating, sputter coating, or ion beam

*Corresponding author. Tel.: +49-9131-8527604; fax: +49-9131-8528321.
*E-mail address:* polymer@ww.uni-erlangen.de (H. Münstedt).

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coating. Composites consisting of inert substrates coated with metallic silver were shown to be potentially useful as a source of silver ions for infection control [11–13]. Klueh et al. [14] investigated the usefulness of silver coated poly (ethylene terephthalate) as fabric to prevent the bacterial colonization and the subsequent biofilm formation. The authors reported that in the presence of silver coated fabric the bacterial growth was found to be substantially low indicating the inhibitory effect of $Ag^+$, which were released from the fabric. However, this technique generally suffers from many demerits, which include poor adhesion, lack of coating uniformity [13] and the need for special processing conditions and long-term activity [15]. Another method of coating silver onto a substrate involves deposition or electrochemical deposition of silver from solution. This method also has some drawbacks because of the low silver pick up onto the substrate and requirement of special technique for the surface preparation [13].

Another conventional approach to obtain antimicrobial polymer composites is by the incorporation of silver into molten polymers [16]. Also instances can be found for the use of zeolite-based silver in food packaging materials as a thin co extruded layer [17]. This work demonstrated the release of silver ions as a consequence of the entry of water to these layers, but the antimicrobial effect is reported to be unlikely because of the substantial content of amino acids in foods, which can abstract the $Ag^+$ ions. Alt et al. [18] reported on the in vitro antimicrobial activity against multiresistant bacteria MRSE and MRSA and in vitro cytotoxicity of PMMA bone cement loaded with metallic silver particles with a size 5–50 nm. The authors reported that this nanosilver filled bone cements completely prevented the bacterial proliferation in the absence of in vitro cytotoxicity.

As the antimicrobial efficacy limit [10] and concentration of the silver ions emitted by the silver filled polymer systems lie in the micro molar concentration level, it is indispensable to make use of an accurate detection device which can quantify very low concentrations of the $Ag^+$ ions in an analyte.

In our laboratory, $Ag^+$ release measurements from silver filled polyurethane using the stripping voltammetric experiments were performed concomitant with the development of the so-called "Erlanger silver catheter"[9]. The present work is concerned with the development of Ag filled polyamides by pursuing the concept that the inherent hygroscopicity of the polyamide and the intrinsic antimicrobial properties of silver can be exploited in order to accomplish a promising antimicrobial polyamide which should indubitably exhibit a wide range of antimicrobial application. The purpose of the development of these antimicrobial compositions is to make use of them for a variety of applications, which include fabrication of fishnet having antimicrobial and antifouling properties, vials, round shower mat, etc. The logic behind the use of polyamide is its hygroscopic nature, which is important for the silver ion release from the composites. The use of silver assures long-term antimicrobial property.

## 2. Materials and method

### 2.1. Materials

The thermoplastic matrix material used is an extrusion type polyamide [Ultramid C 35F of BASF, Ludwigshafen, Germany] developed for the blown film industry. It is a medium to high viscosity copolyamide 6/66 having a density of 1.12 g/cm$^3$ and a melting point of 201°C. Four different silver powders [W.C. Heraeus GmbH & Co. KG; purity 99.9%] of the specific surface areas (SSA- *nominal values*) 0.78, 1.16, 2.5 and 6.4 m$^2$/g were used.

### 2.2. Compounding

The compounding was performed at 220°C in a kneader (Poly Drive, Thermo Haake, Karlsruhe, Germany) at a rotor speed of 60 rpm. The polyamide was completely melted first for 2 min followed by the addition of silver and the mixing was continued further till the attainment of a steady torque. The total mixing time was 7 min. Various compounds with 2, 4 and 8 wt% of the silver powder with a SSA of 0.78 m$^2$/g were made. In another addition composites comprising 4 wt% of silver with SSA of 1.16 and 2.5 m$^2$/g were also produced to study the effect of SSA of the silver powder on the $Ag^+$ release capability of the PA/Ag composites.

### 2.3. Sample preparation

Rectangular specimens (20 mm × 10 mm × 1 mm) for the anode stripping voltammetric (ASV) experiments were compression molded at a temperature of 220°C. The specimens were cooled by circulating water after the moulding time while pressing. These samples were stored in flasks containing 100 ml aqueous medium (95 ml distilled water + 5 ml 0.1 N $HNO_3$) at ambient temperature. $HNO_3$ was added to protect the released $Ag^+$ ions from reducing to metallic silver.

### 2.4. ASV

The concentration of the silver ions released to the aqueous medium was measured by ASV. In order to have uniform concentration the solutions were homogenised by occasional shaking and also shaking the flasks just before the withdrawal of the analytes for the voltammetric experiments. This was done to prevent the

$Ag^+$ agglomeration in the neighbourhood of the specimen, which creates heterogeneity in $Ag^+$ concentration inside the flask. Water collected at intervals of 2, 4, 7 and 14 days from the above storages were analysed for the silver ion detection. One milli litre of the analyte was considered for the voltammetric experiments. The experimental conditions were as shown in Table 1.

ASV is a widely used electrochemical technique for trace element detection and has extensively been applied in studying the identity and concentration of anlytes in aqueous and non-aqueous media. The working principle involves applying a deposition potential that is more negative than the deposition potential of the species to be determined. In this step the electrolytic deposition of the reducible species onto an inert electrode (working electrode) surface occurs at a constant potential. The second step consists of the application of an anodic (positive-going) potential scan to oxidize (strip) the reduced metal back into solution at a potential characteristic of the species under concern. Voltammetric techniques are based on controlling the electrode potential and measuring the resulting current. A key feature in understanding the voltammetric method is the relationship between the potentials applied to an electrode and the concentration of the redox species at the electrode surface. The voltammetric set up we are using is of the Autolab/Eco Chemie; (PG STAT 10) potentiostat systems with a high resolution.

Fig. 1 shows a typical voltammogram obtained during the stripping voltammetric analysis of silver ions in one of our experiments using a PA/Ag based analyte. The potentials corresponding to the peak maximum give the value of the stripping potential. The peak height and area decreases in subsequent scans, which is an indication that the concentration of the metal on the electrode surface decreases. Also it is seen that the stripping potential distorts slightly to lower potentials with the progress of the scans. This could be due to the reduction in concentration of the silver at the electrode surface (increase in the analyte medium) with the progress of the stripping scans. It means that the stripping potential could vary depending on the concentration of the silver metal on the electrode surface. In general the stripping is observed as occurring in the potential range of 0.32–0.37 V. The base line

Table 1
Experimental conditions used for the voltammetric experiments

| | |
|---|---|
| Discharge potential (V) | −0.55 |
| Working electrode (diameter; mm) | 4, glassy carbon |
| Supporting electrolyte | 0.1 N $KNO_3$ |
| Deposition time (s) | 1000 |
| Stripping potential range (V) | 0–0.5 |
| Scan rate | 0.1 V/s |
| Analyte | 1 ml aqueous solution of $Ag^+$ |

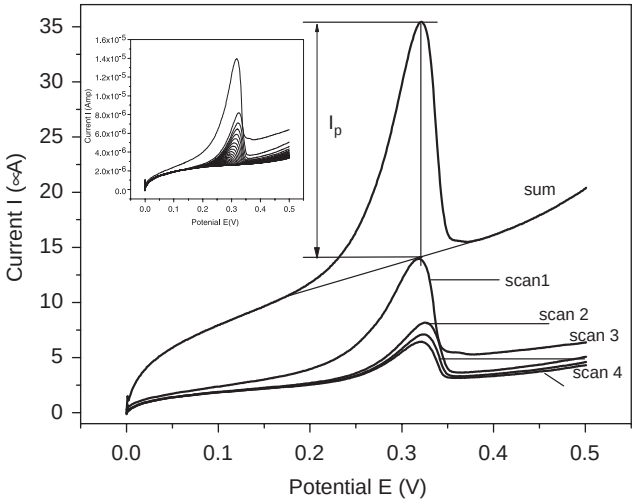



Fig. 1. Voltammogram showing the stripping of silver ions ($I_p$-means peak height).

construction and the method of evaluation of the peak heights are shown in Fig. 1. The summation of all the scans provides an addition curve whose peak height ($I_p$) is directly proportional to the total concentration of the silver ions deposited and stripped out during the redox processes according to the following relation

$$I_p \sim n^{3/2} A D^{1/2} v^{1/2} t C, \quad (1)$$

where $I_p$ is the peak current (μA), $n$ the number of electrons transferred per molecule, $A$ the electrode area ($cm^2$), $D$ the diffusion coefficient ($cm^2/s$), $v$ the scan rate (V/s), $t$ the enrichment time (s; time during which the silver ions were deposited on to the electrode from the analyte) and $C$ the concentration of the ions in the solution (g/l).

## 3. Results and discussion

### 3.1. Quantification of the $Ag^+$ release

ASV measurements of various solutions with defined silver ion concentration led to a calibration curve. The calibration curve is obtained by plotting the total peak current as a function of the silver ion concentration of the corresponding standard solution (Fig. 2). The fit of the results represents the calibration curve, which was used for the quantitative estimation of the silver ion release from various samples.

Before entering into a more detailed discussion of the voltammetric experiments the silver ion release data obtained from the ASV are compared to another independent method. Atomic absorption spectroscopy (AAS) was also used for the quantitative determination of the silver ion concentration in the analyte. Fig. 3 shows a comparison of the silver ion concentrations

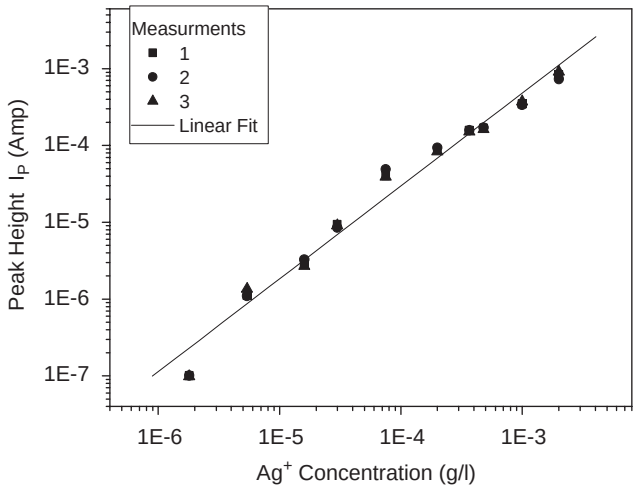



Fig. 2. Calibration curve using various standard solutions of silver.

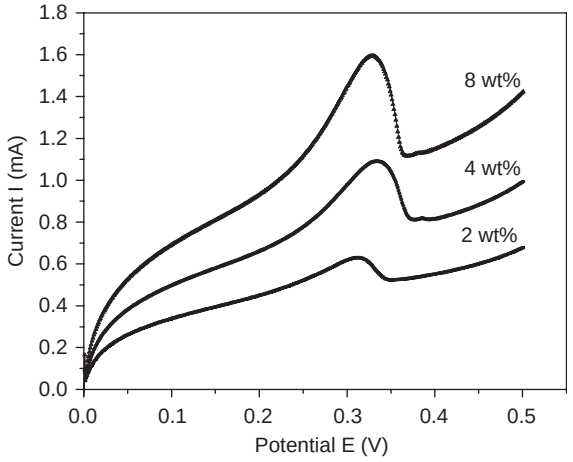



Fig. 4. Total stripping current after 14 days of immersion in water as a function of the stripping potential (silver powder used—0.78 $m^2/g$).

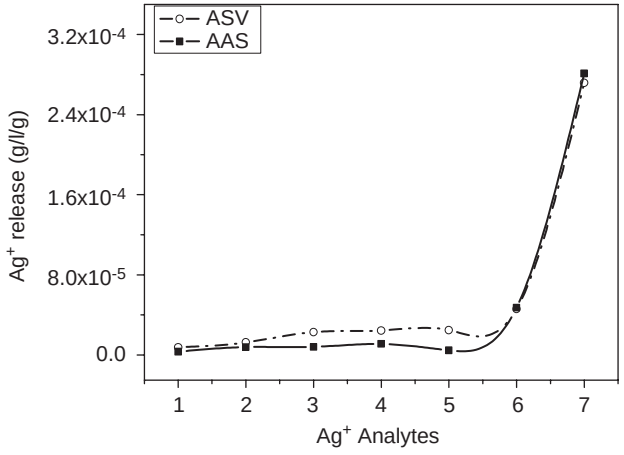



Fig. 3. Comparison between voltammetry and atomic absorption spectroscopy.

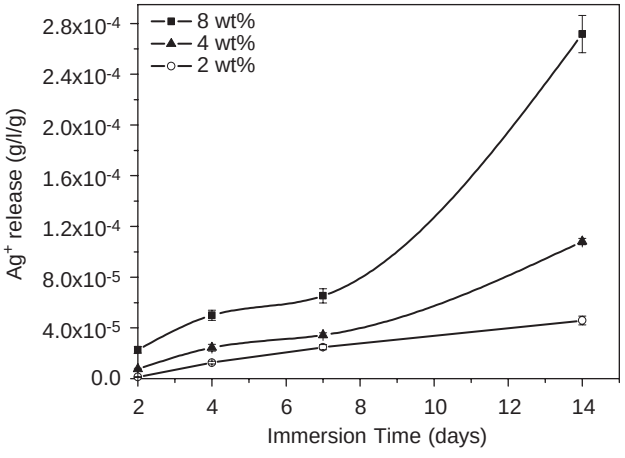



Fig. 5. $Ag^+$ release as a function of time and concentration of the silver filler.

from the same analyte quantified by means of the voltammetric and spectroscopic techniques. The comparison was made using a series of analytes having different concentrations of silver ions. It is found that a good agreement exists between the two methods of measurement. The slight differences could be attributed to the differences in the lower detection limits of the two devices.

Fig. 4 shows the characteristic nature of the PA/Ag composites as an $Ag^+$ emitter in an aqueous environment. The measurements were performed with analytes collected after 14 days of storage of the PA/Ag composites in water. From the peak potential and their heights it can be concluded that the PA/Ag composites are releasing the $Ag^+$ biocide and that its release increases with the amount of silver powder present in the specimen. Fig. 5 gives a picture about the time dependency and concentration dependency of the silver ion release for different silver concentrations in the composites. The data of the $Ag^+$ is related to the release of 1 g of the PA/Ag composites to a 100 ml aqueous environment. It is observed that the $Ag^+$ release increases as a function of time. However, the increase is found to be marginal between days 4 and 6. The reason for this observation can be explained by the following consideration: silver gets oxidized to $Ag^+$ in an aqueous medium. Therefore, the rate of water diffusion in the composite specimen is expected to control the $Ag^+$ release. The diffusion characteristics of the PA/Ag composites show that the rate of water diffusion also is lower during this period of time (Fig. 6 (a) and (b)). It is obvious that the slope of the diffusion curve during this time is almost constant (Fig. 6b). This inappreciable change in the water diffusion during this period could be the reason for the corresponding decrease in the rate of silver ion release from the

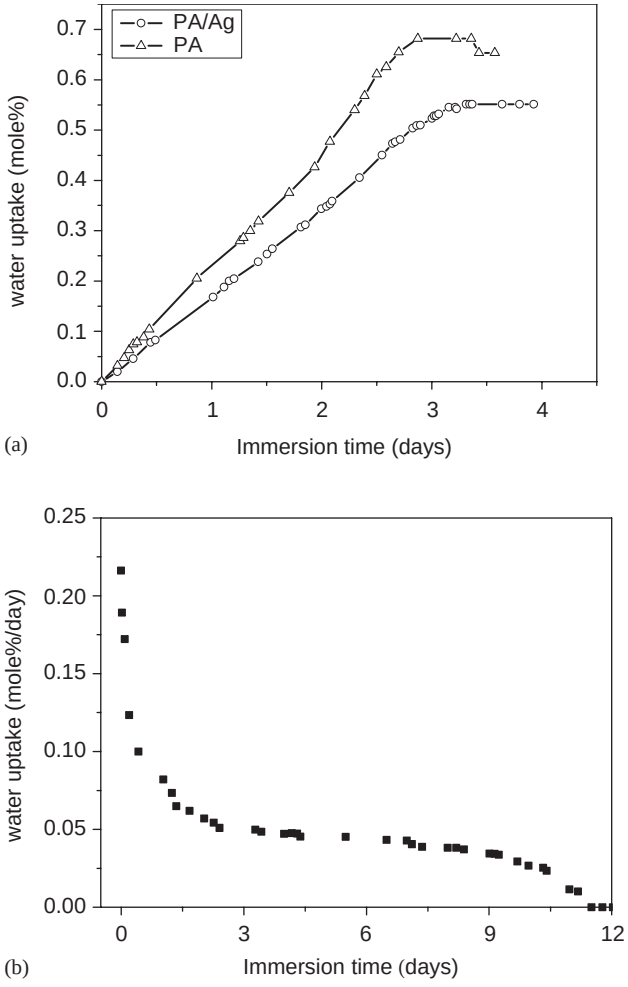



Fig. 6. Water diffusion characteristics of PA and PA/Ag composite: (a) diffusion; (b) differential curve (PA/Ag).

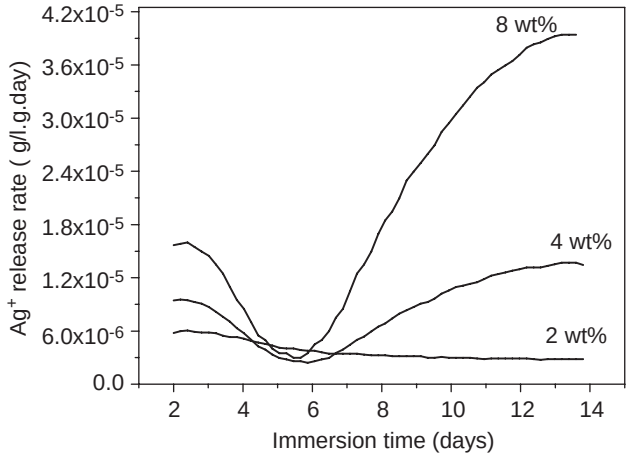



Fig. 7. Rate of $Ag^+$ release from the PA/Ag composites.

composite. Fig. 7, which is a differential curve of Fig. 5, gives a distinct picture of the rate of $Ag^+$ release for various PA/Ag compositions upon encounter with water. [To permit the changes as visible the rate has been calculated as the rate of change of concentration with respect to a day]. It can be seen that after an initial increase the rate of release shows a minimum towards the sixth day. However, the rate of release increases after the sixth day for those compositions having higher silver content. In order to give a clear explanation to this abrupt rise in silver ion release it is necessary to consider both the rate of water diffusion and the consequent physical changes to the PA/Ag specimens associated with the water diffusion.

The following considerations give a hint to the process taking place. The initial release of silver ions (for e.g. between days 2 and 4) must be from those silver particles, which are encapsulated within the surface layers of the specimen. This can be instantaneous as the migration of $Ag^+$ through the specimen is not necessary. For an oxidation and subsequent release of $Ag^+$ from the interior part of the specimen water has to cross the diffusion barrier, which could be constituted by many crystalline lamellae [19]. It is reported that in aliphatic polyamides the water molecules in the interlamellar regions can change the overall crystalline state [20]. The report says that the onset of plasticisation followed by the equilibrium sorption could provide substantial mobility to the macromolecular chains especially within the amorphous regions and some favourable changes in the crystalline regions as well. The silver fractions encapsulated well inside the specimen need to oxidise and migrate as ions ($Ag^+$) through the polyamide specimen. These silver particles are predominately responsible for the release at later times. Their oxidation and following migration as silver ions is more facilitated once the specimen is fully plasticised. In this context it is reasonable to believe that $Ag^+$ release will be influenced by the equilibrium swelling characteristics of the composite specimen. So the expulsion of the $Ag^+$ at this stage is taking place through the specimen possessing increased segmental mobility within the amorphous regions due to the disruption of the H-bonding and some consequent changes within the crystalline lamellae region [21]. With the progress of water diffusion the polar groups in the polyamide chains are separated and the water dipoles are able to interact with those of the polyamide. The structure of the polymer is then re-established with full incorporation of the plasticiser uniformly. This effect provides 'free volume' in the polymer that allows molecular flexibility.

A consideration of the dual sorption theory [22] also could explain the faster rate of $Ag^+$ release observed after the sixth day. According to the dual sorption theory there are two different physical mechanisms that affect mass transfer: diffusion and embedding (intermolecular forces between the penetrant molecules and the polymer specimen). While the diffusion process is fast the embedding process is slow. The water molecules

which initially embedding the polymeric specimen will ultimately plasticize and widen the interspace between the polymer chains [22]. At this stage the widening of the chains facilitates the ionic migration ($Ag^+$) through the water-equilibrated specimen (after 6 days) at a higher rate.

Besides this physical change, which preferably facilitates the migration of silver ions, the higher rate of $Ag^+$ release [see Fig. 7—$Ag^+$ release increases abruptly for 4 and 8 wt% of silver concentration from the sixth day] depends on its higher rate of production within the specimen. It must be considered from a kinetic point of the oxidation reaction responsible for the silver ion release at the plasticized state of the samples. It is well known that the rate of any chemical reaction depends on the concentration of the reactants according to the following fundamental equations [23].

E.g. for a chemical reaction of the type A → products, the rate of the reaction,

$$\frac{-\mathrm{d}[A]}{\mathrm{d}t} \sim [C] \tag{2}$$

where $A$ is the reactant and $[C]$ is its concentration. In the present case the reaction can be written as

$$\mathrm{Ag} \leftrightharpoons \mathrm{Ag}^+ + \mathrm{e}^- \tag{3}$$

and the reaction rate is

$$\frac{-\mathrm{d}[\mathrm{Ag}^+]}{\mathrm{d}t} \sim [\mathrm{Ag}]. \tag{4}$$

So the sudden increase in silver ion release for the 4 and 8 wt% of the silver powder based compositions from the sixth day can be explained as due to the higher rate of oxidation reaction (cf. Eq. (4)) at higher concentrations of the silver powder (reactant) present in the plasticized state of the specimen which is obviously different from the physical state of the specimen during the first few days. It means that the effect of higher concentration of the silver influences the silver ion release only when the entire system is fully plasticised.

The creditability of these composites depends on their ability to release the silver ions in a level matching to the biocidal concentration required in real conditions. Fig. 8 gives a comparison between the concentrations of the silver ions emitted from the PA/Ag composites with the biocidal concentration of silver ions reported in the literature [10]. It can be seen that the composites release $Ag^+$ in a concentration level capable of rendering antimicrobial efficacy.

### 3.2. Effect of silver SSA on the $Ag^+$ release

In order to understand the effect of the SSA of the silver powder on the silver ion release, silver powders with SSA 0.78, 1.16 and 2.5 $m^2/g$ were brought into the polyamide under the same mixing conditions discussed above. PA/Ag composites were separately prepared for each grain size by filling polyamide with 4 wt% of each type. It is important to mention here that the use of silver powder with a still higher specific surface (6.4 $m^2/g$) ended up with highly agglomerated composites. Due to the observed non-uniformity of the silver this composite was not considered for the voltammetric experiments.

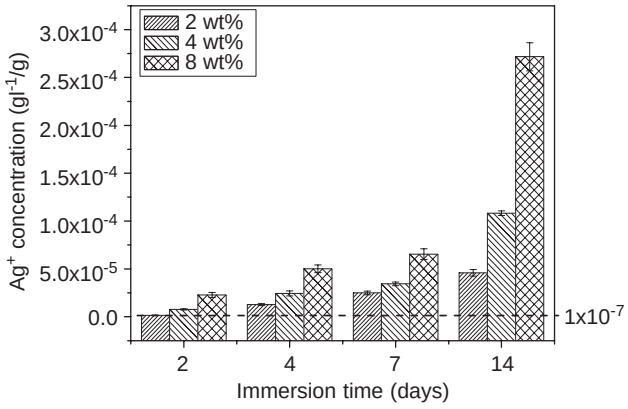
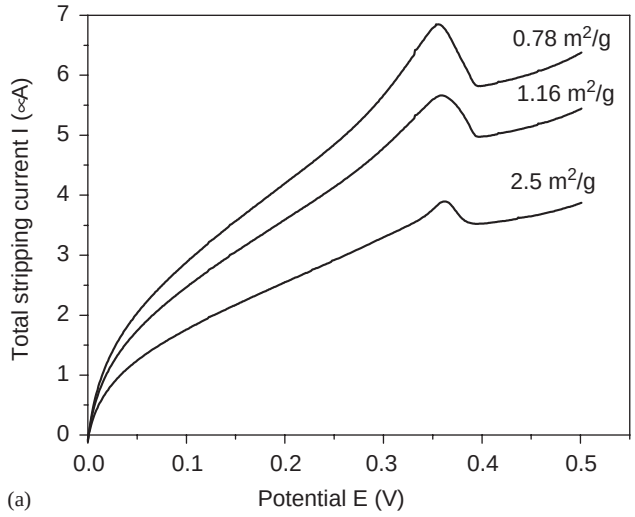



Fig. 8. $Ag^+$ release as a function of immersion time for different silver concentrations (0.78 $m^2/g$). The dashed black line shows the concentration of $Ag^+$ capable of rendering antimicrobial efficacy. ($Ag^+$ ions released by 1 g of the composite to 100 ml aqueous environment).

Fig. 9a shows the ASV results of silver ion concentration in the analyte after 4 days of immersion of composites containing 4 wt% silver with different SSAs. Contrary to what is expected the peak current is higher for those composites containing the silver powder having a specific surface of 0.78 $m^2/g$. Fig. 9b (day 7) confirms this observation. We have observed the same grains size effect on the silver ion release on day 10 also. Thus within the period of analysis (11 days) the silver ion emitting capacity of different grains of silver follows the order, $0.78 > 1.16 > 2.5\ m^2/g$. This observation could be explained by considering the nature of dispersion of the silver powder in the polyamide. The fraction with the SSA of 0.78 $m^2/g$ possesses the biggest size. Hence the degree of agglomeration in this case could be lower compared to other fractions used (recollect the agglomeration observed with a silver fraction of 6.4 $m^2/g$ during mixing process). Hence the dispersion (morphology) could be more uniform and finer due to the lesser agglomeration and hence the water molecules entering the specimen interact with more silver surface to enable the latter to undergo oxidation to the $Ag^+$ ions. A confirmation to this argument is based on the microscale morphology (SEM), which is a profound determinant of different material properties. Cryogenically fractured specimens of the PA/Ag systems containing various grains of silver were subjected to SEM analysis. Fig. 10(a) and (b) shows the nature of dispersion of the silver powder with the specific surface areas of 0.78 and



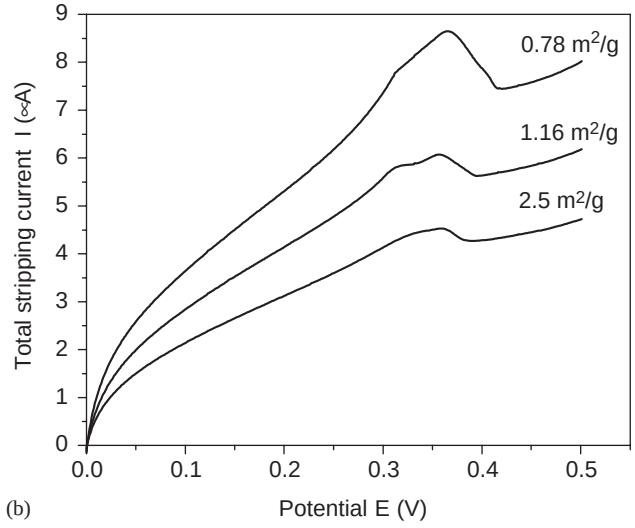
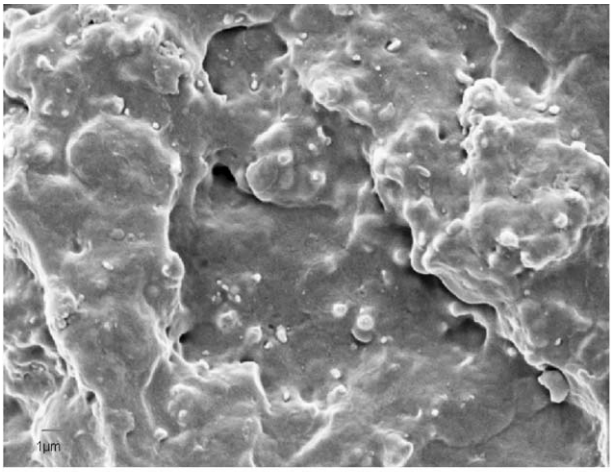




Fig. 9. Voltammogram for PA/Ag composites containing 4 wt% silver of different specific surface areas: (a) after 4 days; (b) after 7 days.



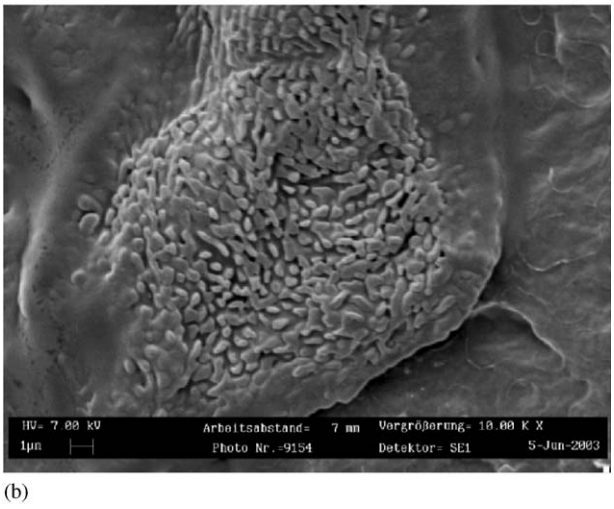




Fig. 10. SEM showing the fine dispersion: (a) 0.78 $m^2/g$ and the agglomerated dispersion; (b) 2.5 $m^2/g$ of silver powder in PA matrix.

2.5 $m^2/g$ in the polyamide. It is seen that the mode of dispersion of the silver powder is strongly dependent on the type of silver powder used. It is possible to see a fine and uniform dispersion of the silver in the case of the particles having SSA 0.78 $m^2/g$. However, the micrographs of the specimen containing particles possessing SSA of 2.5 $m^2/g$ show large-scale coalescences. Hence, it is possible to imagine that the water molecules entering the specimen can easily diffuse through the channels between the silver powder in those compositions (0.78 $m^2/g$) having a uniform and finer dispersion of the silver powder causing its oxidation and subsequent release of the $Ag^+$ ions to the aqueous environment.

For a meaningful application of this composite, $Ag^+$ release on long-term basis is essential. We have estimated the $Ag^+$ release from the PA/Ag samples (4 wt% and 0.78 $m^2/g$) after 5 months of continuous storage in water. After 5 months the sample was taken out and transferred to fresh water. Very interestingly, it was found that after 2 days in originally silver free water, the specimens release silver ions (after 5 months of continuous soaking in water) at a concentration level, which is very close to the concentration found during the first 2 days after its initial immersion in water.

### 3.3. Antimicrobial tests

The antimicrobial efficacy of the PA control and the PA/Ag composites against different types of microbes like *Escherichia coli* and *Staphylococcus aureus* was tested based on test method according to ASTM E 2149-01. The results given in Table 2 show that the composites have good efficacy against these microbes (especially after 28 days). More test results will be published soon with some important factors, which affect the silver ion release from these composites.

Table 2
Results of antimicrobial tests

| Pathogens | Log reduction PA/Ag (8% Ag) | | | |
|---|---|---|---|---|
| | 24 h | 7 d | 14 d | 28 d |
| *Escherichia coli* | — | 1 | >1 | 2 |
| *Staphylococcus aureus* | — | 1 | >1 | 3 |

## 4. Conclusion

PA/Ag systems have the potential antimicrobial efficacy by virtue of their ability to release silver ions. Soaking time, concentration of the silver powder, silver grain specific surface area, their nature of dispersion, rate of water diffusion, the changes in the physical state of the composite etc are discovered as controlling the $Ag^+$ release. Composites containing higher concentrations of the silver powder possess a higher release rate when the storage time exceeds 6 days. It was found that fractions with a SSA of $0.78\,m^2/g$ release highest concentration of the $Ag^+$ within the period of analysis. The silver fractions with relatively higher specific surfaces are observed to agglomerate at the adopted processing conditions. It was found that the silver powder showing the highest release possesses a finer distribution of the silver powder. Antimicrobial tests prove the composites are active against the pathogens.

## Acknowledgements

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