Antimicrobial polymers from polypropylene/silver composites—Ag$^+$ release measured by anode stripping voltammetry

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Abstract

Polypropylene/silver composites were subjected to silver ion release experiments in order to investigate their Ag$^+$ release capabilities, a pertinent condition for antimicrobial efficacy. Polypropylene containing elementary silver powder having a specific surface area of 0.78 m^2/g was considered as the principal antimicrobial filler. In addition the effectiveness of other commercial antimicrobials based on silver were also examined. Evidence is presented for the release of silver ions from these composites in an aqueous environment. The silver ion release depends on the nature of the antimicrobial filler and the polymer matrix. Scanning electron microscopy has been employed to investigate the morphology of the composite and they were found to be active against the microbes. An excellent correlation between the silver ion release experiments and the antimicrobial efficacy was found. Multifilament yarns produced from polypropylene containing elementary silver powder show excellent long term Ag$^+$ release properties.
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1. Introduction

Antimicrobials gain interest from research and industry due to their potential to provide quality and safety benefits to various materials and environments depending on the type of applications. There are different antimicrobial materials based on either organic or inorganic additives with good efficiency. There are numerous ways by which antimicrobial properties can be accomplished in a polymer matrix. Incorporation of volatile and non-volatile antimicrobial agents directly into polymers [1,2], coating or adsorbing antimicrobials onto polymer surfaces [3,4], immobilisation of antimicrobials to polymers by ion or covalent linkages [5,6] and the use of polymers that are inherently antimicrobial [7]. Among all these, silver based compositions deserve special attention due to some unique properties, which differentiate silver from other antimicrobial additives. This class of antimicrobial materials constitute both

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elementary silver (colloidal form) and silver in some carrier materials like zeolites. Silver substituted zeolites are incorporated into polymers like polyethylene, polypropylene, polyamides at levels of 1–3 wt% [1] by melt blending or by solvent compounding. Because of the thermal stability (up to 800 °C) of silver, extrusion and injection molding may be used in such instances. Antimicrobials that cannot withstand the processing temperatures of the polymers are often coated onto the materials, which require surface functionalisation to improve the adhesion of the coatings [4]. Surface immobilisation requires the presence of functional groups on both the antimicrobial and the polymer and also spacer molecules that link the polymer surface to the active agent [6].

Among the various antimicrobials silver is unique because of its inherent properties of high thermal stability and long-term activity [8]. Silver has been one of the most versatile antimicrobial agents due to its intense antimicrobial properties and little toxicity to mammalian cells and tissues [9,10]. Because of these unique properties, its incorporation into different materials often leads to the generation of antimicrobial materials having activity against a broad spectrum of microbes.

The silver filled materials have to release the silver ions to a pathogenic environment in order to be efficacious [11]. This necessary condition is accomplishable in aqueous medium where the interaction between the water molecules and silver produces the active biocidal species i.e. the silver ions. In this context polymers, which are hygroscopic in nature, have the potential for the fabrication of articles like catheters, cannulae, ophthalmic vials, fishnets, garments etc. So the selection of a matrix polymer for the production of silver filled polymers needs to consider the hygrophilicity of the polymer. Polar polymers like polyamides are excellent candidates in this context [12]. Despite this, there is special research interest in obtaining antimicrobial polymeric products from commercial polymers such as polypropylene [13].

Some of the recent reports describe the action of certain additives to matrix polymer thereby enhancing the water uptake properties resulting in an increase in silver ion release [14]. Instances can be found where zeolites used as carrier materials for silver; provide channels for the water molecules to enter the polymer matrix thereby improving the water diffusion characteristics [15]. In such instances, the silver substituted zeolites act as an

ion pump providing controlled time release of silver ions to an aqueous environment.

The entire process of silver ion release from silver filled material is composed of three elementary processes [12]. The diffusion of water into the composite specimen, the reaction between the silver and water molecules leading to the formation of silver ions and the migration of silver ions through the composite specimen leading to the release from the composite specimen to the aqueous environment. The carrier materials can be effective in accelerating the diffusion of water molecules and the migration of silver ions through the matrix polymer. Among them the production of silver ions is faster compared to the water diffusion and the Ag^+ migration processes. Having slower rates these physical processes can be the rate determining stages of the entire release mechanisms. So material properties like the crystallinity and matrix polarity, which constitute the diffusion barrier to water molecules and the Ag^+ ions during their propagation through the specimens, can influence the rate of release. Silver in polypropylene is less promising because of its nonpolar and crystalline nature but interesting when considering its commercial importance. Silver filled polypropylenes would have a perspective in a variety of applications, which include the fabrication of antimicrobial ophthalmic vials, packaging materials [16] and multifilament yarns.

This paper deals with the understanding of the Ag^+ release capabilities of unmodified silver filled polypropylene and the influence of various filler types (commercially available silver antimicrobials) on the Ag^+ release properties. An understanding of the release characteristics of unmodified PP/Ag could be useful in finding new ways to modify the matrix polymer in such a way that the Ag^+ release properties are improved.

2. Experimental

2.1. Materials and sample preparation

PP/Ag composites (polypropylene—Moplen HP 462 R from Basell) were prepared in a kneader. Elementary silver powder having a specific surface area of 0.78 m^2/g was added to molten polypropylene (200 °C). In a separate attempt different commercial silver based antimicrobials were incorporated in polypropylene in order to compare their release efficiencies with the elementary silver powder under the same compounding conditions.

The composites were compression molded at 200 °C into rectangular specimens having $20 \times 10 \times 1$ mm^3 size for the silver ion release experiments using Anode Stripping Voltammetry (ASV). After the molding time (5 min), the specimens were cooled by passing water through the press. These samples were stored in flasks containing 100 ml aqueous medium (93 ml distilled water + 7 ml 0.1 N HNO$_3$) at ambient temperature. HNO$_3$ was added to protect the released Ag$^+$ ions from reducing to metallic silver.

2.2. Antimicrobial tests

The antimicrobial tests were performed using ASTM E 2149-01 (shake flask) method. The working bacterial solution containing the microbes (*Staphylococcus aureus* and *Escherichia coli*) in sterile ringer solutions grown at optimal growth conditions having a final concentration (after dilution) of 10^7–10^8 CFU/ml. One gram of the silver filled polypropylene was admitted into three sterile wide mouth bottles used for the antimicrobial tests. In each bottle containing the silver biocide sample, 1 ml from each bacterial inoculum having concentration 10^7–10^8 CFU/ml was added. The samples (the bottles with materials and each inoculum) were maintained at room temperature and protected from light. The bottles containing the samples were shaken. 1 ml from each sample was withdrawn at different contact periods (3 h, 24 h, 7 days, 28 days), and decimal dilutions (until 10^7) were prepared in sterile ringer solutions. Hundred microliters of the decimal solutions were spread onto agar media (tryptona soya) and the plates were incubated at 37 °C. The colonies were counted (in CFU/ml). The activity values are expressed as log reduction (difference between the logarithms of viable cells on control and the silver filled specimen). An alternate antimicrobial test method viz. Japanese Industrial Standard (JIS Z 2801) was also performed in order to ascertain the biocidal activity of the composites.

2.3. Anode stripping voltammetry

Anode stripping voltammetry (ASV) is widely used for the determination of trace amounts of metal ions in aqueous media of various origin [17]. ASV is a highly competitive technique to neutron activation analysis regarding sensitivity and reliability [18]. Electrodes made of carbon are most commonly used as working electrode for the determination of silver

ions. These electrodes differ from the mercury electrode by a wider range of working potentials, which makes it possible to determine metal ions, whose electrooxidation potentials are more positive than the oxidation potentials of mercury, including silver. Experiments were carried out in a three-electrode cell with an external silver–silver chloride reference electrode and a platinum auxiliary electrode using an Autolab/Eco Chemie; (PG STAT 10) potentiostat. The Ag/AgCl reference electrode was connected to the electrolytic cell through a liquid junction filled with 0.1 N KNO$_3$, which is also the supporting electrolyte used for the analysis.

The voltammetric principle involves applying a preconcentration 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 (Ag$^+$) onto an inert electrode (working electrode-carbon) surface occurs at a constant potential. The second step consists of the oxidation (stripping) of the reduced metal (Ag) by applying an anodic potential to bring the metal back into solution (Ag$^+$) at a potential characteristic of the species under concern. Voltammetric techniques are based on controlling the electrode potential and measuring the resulting current. The resultant current involved during the stripping of the metal from the electrode surface is proportional to the concentration of the redox species at the electrode surface according to the Ilkovik equation [19] given below

$$I_p \sim n^{3/2}AD^{1/2}v^{1/2}tC \qquad (1)$$

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

More details of the experimental procedure and method of evaluation of the concentration of the analytes from the peak heights (stripping current) are described in reference [12,14].

3. Results and discussion

3.1. Method of evaluation of silver ion release

Stripping voltammetric experiments with standard solutions of silver led to a calibration curve shown in Fig. 1. The analytes collected at various

intervals from the storages (silver filled specimens in water) were subjected to the voltammetric experiments in order to estimate the Ag^+ ion concentration. Using the calibration curve the silver ion concentrations of various analytes were estimated after an evaluation of the peak heights of the summation curve of all the stripping scans obtained during a voltammetric experiment. In an ASV experiment, the stripping process ends up with several scans (having peaks whose heights are proportional to the concentrations of the Ag^+ ions produced in every scan) whose height decreases with the progress of the scans due to the reduction in concentration of the silver metal on the electrode surface. As mentioned earlier the peak height of the summation curve (from all the stripping scans) is proportional to the concentration of the silver ions in that analyte.

3.2. Silver ion release from polypropylene/silver powder composites

Fig. 2 shows the results of the voltammetric experiment with the analyte collected from the storages of the PP/Ag composites on day 3. The composite specimens contain 8 wt% of silver powder having a specific surface area of 0.78 m^2/g. Very surprisingly, silver ion release was observed as the voltammogram consists of several peaks corresponding to the progressive silver stripping from the electrode surface. Based on the hypothesis that water uptake is one of the conditions for the release of silver ions out of polymer/Ag systems, the observation would imply water permeation through the PP specimens. Due to its non-polar nature the water uptake in PP is much less compared to PA. This fact implies that silver particles on the surface get oxidised while
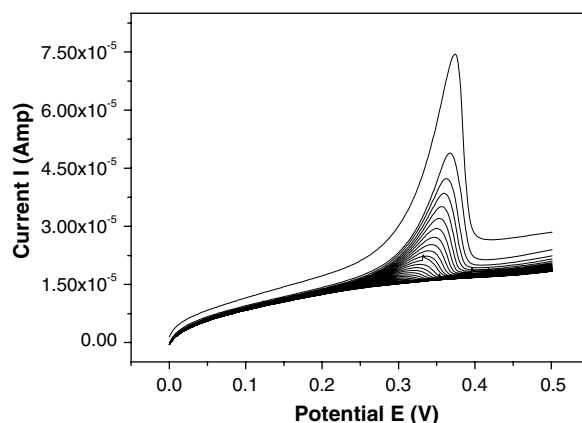

Fig. 2. Voltammogram showing the silver ion release from PP/Ag composites (silver used –8% having SSA 0.78 m^2/g).

soaking. However, there was no visible protrusion of the metallic particles from the surface of the composite specimen.

In an effort to understand the latent facts behind the release, the silver ion release characteristics of the PP/Ag composites were examined after providing a coating of pure polypropylene to the PP/Ag composites. This was done to prove that silver ion release is not only from the surface layers but from the bulk of the PP/Ag composite specimen as well. The PP/Ag composites were impregnated with molten PP so that a coating of pure polypropylene was put on the specimens. These coated samples were soaked in water and voltammetric experiments were performed for the estimation of silver ion concentration. Very interestingly, silver ion release from the coated samples was monitored from the third day onwards but at a much lower concentration level (Fig. 3). Although very faint, this observation points to a water permeation and silver ion migration across the thin layers ($\cong$50 μm) of the coated polypropylene. From this observation it is reasonable to believe that for the silver ion release from a PP/Ag composite, the silver particles from the interior of the filled specimens also could contribute to the total release. This is supported by the finding reported in literature that water can permeate through the transcrystalline layers of polypropylene [20,21]. A filler in a semi-crystalline polymer melt may act as a preferred nucleating site for the growth of crystalline spherulites. Provided there is a high density of nucleating sites, and specific thermal conditions are met, the resulting spherulitic growth will be restricted in the lateral direction, normal to the fiber surface, so that a columnar layer, known as
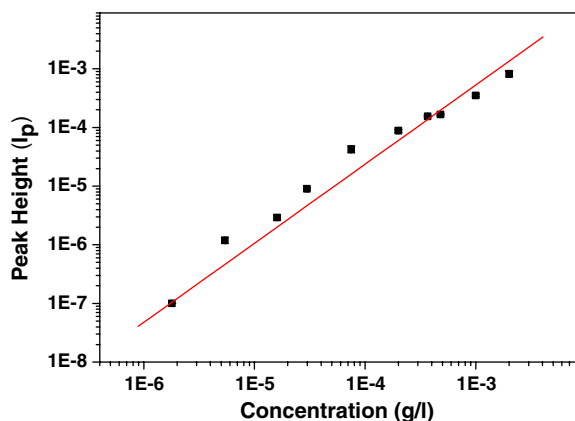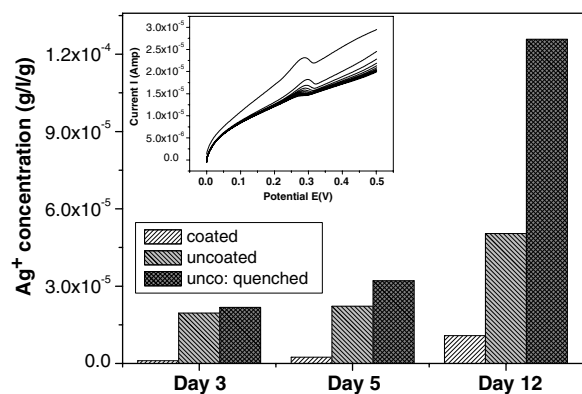

Fig. 1. Calibration curve.

Fig. 3. Comparative efficiency of Ag^+ release between coated and uncoated PP/Ag specimens. Inset: Voltammogram corresponding to silver stripping from coated samples (day 5).

transcrystallinity will develop. The transcrystallinity arises in filled system especially at higher filler loading.

The Ag^+ release from the PP/Ag composites was monitored on the 3rd, 5th, 10th and the 15th day of soaking respectively, in order to quantitatively estimate the silver ion release. The analytes collected after the intervals mentioned above were subjected to voltammetric experiments. Fig. 4 shows the results. The silver ion release increased with increasing soaking time. It is seen that the PP/Ag composites quenched after molding are capable of releasing higher concentrations of the Ag^+ compared to the samples cooled by passing water through the press. This can be attributed to the reduced crystallinity of the specimens due to the quenching. Fig. 5 depicts the melting behaviour of the quenched and non-quenched PP/Ag specimens. The melting enthalpies
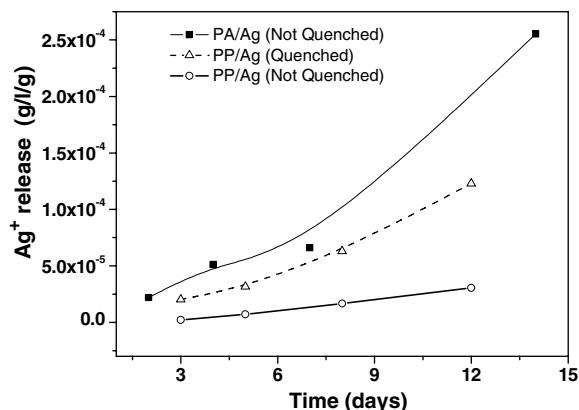

Fig. 4. Total Ag^+ concentrations as a function of time released by various polymer silver composites (silver content 8%; SSA-0.78 m²/g).
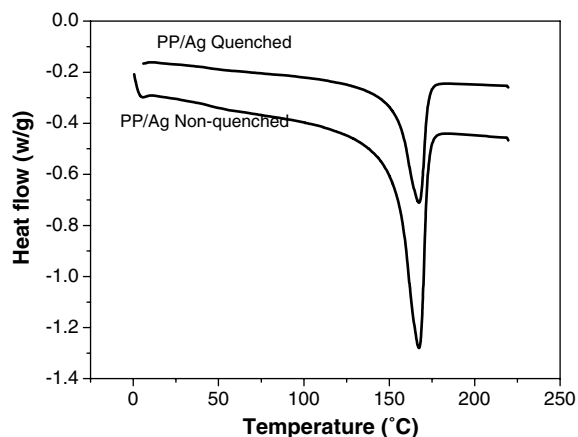

Fig. 5. Melting behavior of quenched and non-quenched PP/Ag composites (Ag content 4 wt%; 10 °C/min).

(measure of crystallinity) were 7.1 and 12.8 J/g respectively for the quenched and non-quenched specimens. The susceptibility of the less crystalline specimens towards water sorption is reflected in their increased silver ion release characteristics (the mole % water uptake of the quenched and non-quenched specimens are respectively 0.0291and 0.0093). This finding throws some light on the silver ion release mechanisms as depending on the water diffusion characteristics of the composites. The amorphous layers near the surface are able to accommodate more water resulting in a higher Ag^+ release. The released concentrations from PP/Ag composites are much lower than the PA/Ag systems. But compared to the PA/Ag composites there is no sudden increase in concentrations from the 7th day onwards. This could be due to the poor water uptake (hence poor plasticisation of the matrix) of the PP/Ag composites compared to the PA/Ag systems [12].

3.3. Effect of filler types on the Ag^+ release characteristics

The voltammetric experiments using the analytes from the PP/Ag composites revealed that they are capable of rendering Ag^+ ions in an aqueous medium. However, the release is much lower than the release from the PA/Ag composites. This is reflected in the antimicrobial efficacies (active after 14 days—*reported later*) of these specimens. However the PA/Ag composites, which released higher concentrations of the silver ions, were found to be active after 7 days [12]. The poor efficacy of PP/Ag composite could be attributed to its poor Ag^+ release property,

which owes to the poor water affinity of the PP matrix in comparison with the PA matrix.

The observation of the higher release of silver ions by less crystalline specimens observed in the case of PA/Ag systems [22] and the performance of the quenched PP/Ag composites point towards the water diffusion rate as decisive in the ion release. In order to investigate whether this condition (higher water intake) is accomplishable by changing the filler type and to substantiate this as a pertinent condition for Ag^+ release, a series of silver based antimicrobial materials were incorporated in polypropylene to monitor their Ag^+ release characteristics.

In an effort to investigate the effects of various types of silver based antimicrobial materials on the silver ion release properties, a few commercial silver based antimicrobials were also employed in PP besides the elementary silver powder. These commercial materials contain titanium dioxide or sodium hydrogen zirconium phosphate or zeolites used as carriers of silver. Table 1 provides some information about these materials. The silver content in most of the non-elementary silver fillers is less than 20 wt%. More exact data are not known. Four weight percentage of each filler (so that actual silver content is 0.8 wt%) is compounded with polypropylene in a kneader. In order to compare their performance with the composites containing elementary silver powder, PP/Ag composites containing 0.8 wt% of silver powder also were produced and studied to quantify the release properties. The mixes were then compression molded to produce rectangular specimens having dimension as mentioned earlier, for the voltammetric experiments. All the composites were prepared and processed under the same procedures and experimental conditions. The composites were stored in aqueous (0.1 N HNO_3 + water) medium taken in separate flasks to monitor their Ag^+ release characteristics. The analytes from these storages were collected and anode stripping voltammetric experiments were performed after 2, 4, 7, 10 and 14 days of storage. Fig. 6 shows the results of the voltammetric studies.

Composites containing JMAC and AM 91455 masterbatches showed a silver ion release, which is significantly higher than that from the composites containing elementary silver powder. The composites containing other fillers did not show appreciable release within the time considered for the analysis. It is possible that the filler, which shows a higher rate in the beginning, can become less efficient on a long-term basis. Earlier works [23] proved that those composites showing an early dominance in release become inefficient on a long-term basis due to the exhaustion of the silver ion owing to the higher rate of initial release.

The highest release is exhibited by the samples containing the masterbatch AM 91455. Besides the presence of higher silver in this masterbatch, their higher initial rate of silver ion release could be due to the improved water diffusion characteristics possessed by the specimens containing these fillers, which would have facilitated the water transport towards the interior part of the composite specimens. Fig. 7(a–c) shows the scanning electron micrographs of the composites containing elementary, JMAC and AM 91455 additives. The dispersion of the silver power could be seen in Fig. 7a. It is worth mentioning here that during the scanning of the specimens containing JMAC and AM 91455 many regions having the features similar to Fig. 7b and c were confronted in those specimens. It is possible to find many tiny pores in Figs. 7b and c (unlike in a), which would have permitted the entry of water molecules and the migration of

Table 1
Details of the various silver fillers used for the preparation of the composites using PP

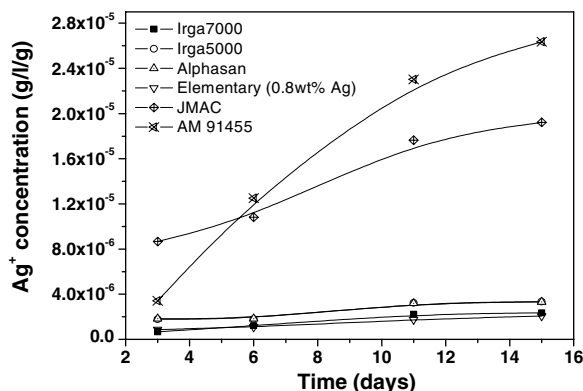| Antimicrobials	Suppliers	Silver content
Elementary silver	W. C Heraeus GmbH & Co. KG	100 wt%
Alphasan RC 2000	Milliken Chemical	10 wt%
JMAC composites PG	Clariant	15 wt%
Irgaguard B 5000	Ciba	Proprietary
Irgaguard B 7000	Ciba	Proprietary
AM 91455 (PP Masterbatch)	Wells Plastics Ltd	25 wt%

Fig. 6. Total Ag^+ release from PP/Ag composites containing various commercial silver based antimicrobials (filler content 4 wt%).
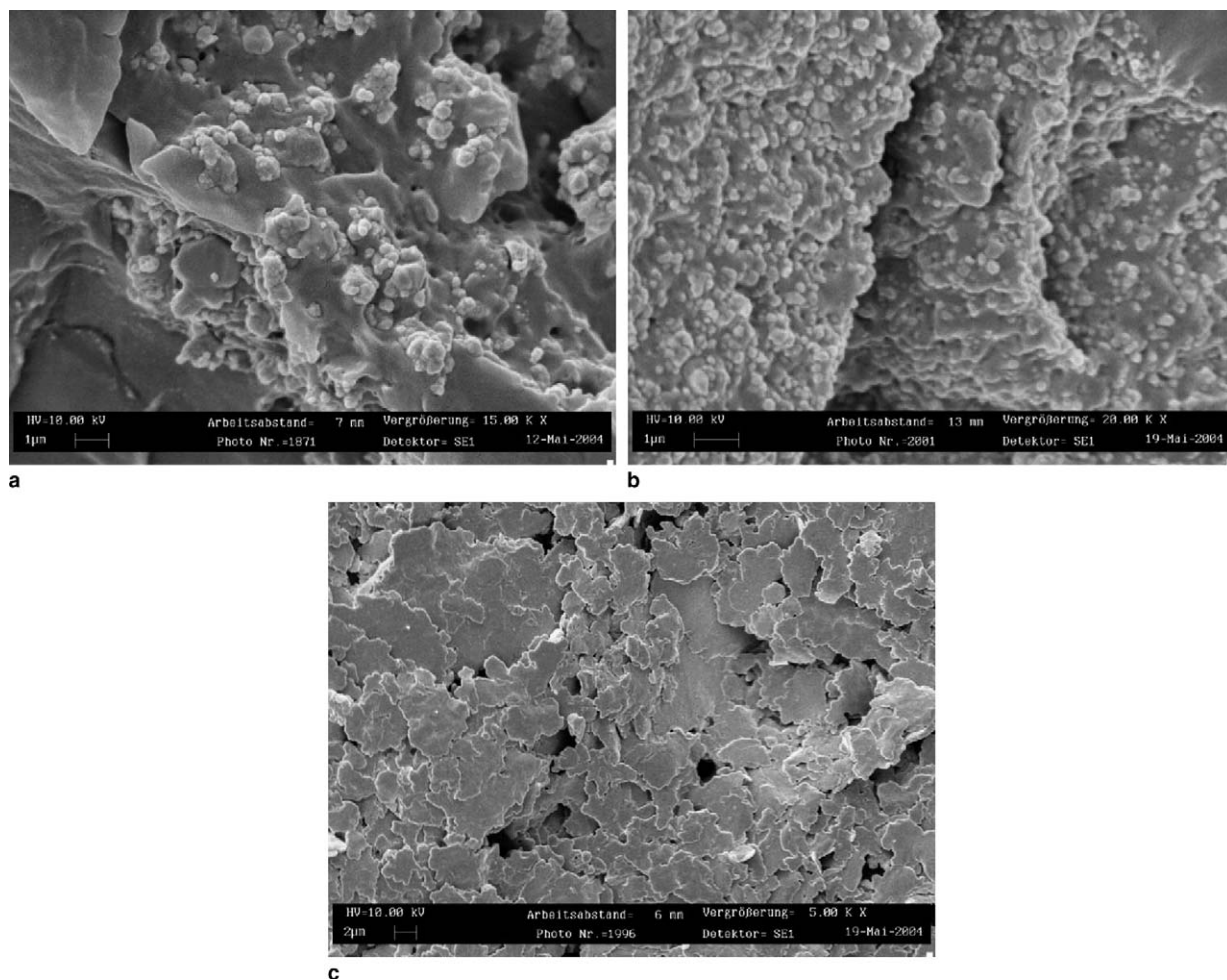
Fig. 7. SEM of composites containing elementary silver powder: (a) JMAC (b) AM 91455 and (c) fillers in polypropylene.

silver ions through the material. The water uptake of all these samples was monitored after 14 days of continuous soaking. The results are given in Fig. 8. It can be seen that the elementary composition shows a very low uptake compared to composites containing commercial materials. AM 91455, which showed the highest silver ion release exhibited the highest water uptake among all the composites. The illustrated experimental results strongly support water diffusion and matrix crystallinity as two important decisive parameters for the silver ion release characteristics of silver based antimicrobial polymers.

The purpose of investigating the silver ion release properties of the silver filled PP composites was to check the applicability of these materials for the fabrication of multifilament yarns. The PP/Ag composites containing elementary silver powder were made into multifilament yarns having a silver concentration of 0.3%. These yarns were soaked in tap water to monitor the silver ion release characteristics. It was found that they are capable of releasing the silver ions in an aqueous medium. Fig. 9 shows the results of the voltammetric experiments after the third day of storage. It can be seen that a release occurred although the content of silver in the yarns is rather low. Silver ion release was monitored even after 5 months of continuous soaking which proved the long-term Ag^+ release capabilities of elementary silver.

3.4. Antimicrobial tests

The PP/Ag composites containing elementary silver powder and AM 91455 were subjected to an evaluation of their antimicrobial efficacy according
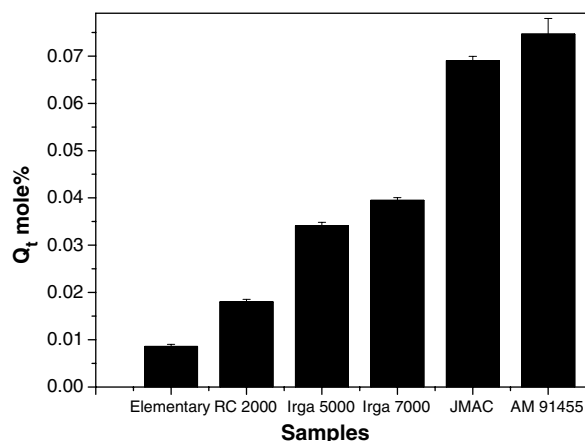
Fig. 8. Water uptake (in mole%) by various PP/Ag composite specimens (after 14 days).
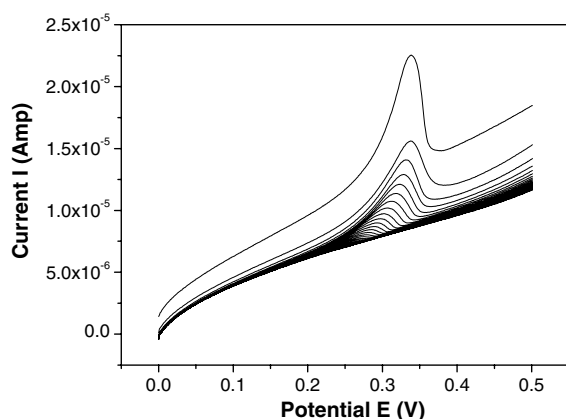

Fig. 9. Voltammogram showing the silver stripping in an experiment with the analytes from the PP/Ag yarns (silver content: 0.3%; size: 0.78 m^2/g).

to the test methods ASTM E 2149-01 and Japanese Industrial Standard (JIS Z 2801). The efficacy of the composites against *E. coli* and *St. aureus* was proven by both test methods (cf. Table 2). The ASTM test results indicate a log reduction of '1' for the PP/Ag specimens after 28 days. However, the results are more obvious in the case of the JIS method. JIS has been observed as more reliable in cases where the antimicrobial agents are not confined to the matrix surface but are released to the medium [24]. Table 2 shows the results of the antimicrobial tests performed according to both methods. The results indicate the composites are efficacious against the microbes considered. The antimicrobial test results shows the agreement between the silver ion release properties and the antimicrobial efficacies of the PP/elementary and the PP/AM 91455 composites.

4. Conclusions

Polypropylene containing elementary silver powder proved to be capable of rendering the antimicrobial species (Ag$^+$) in an aqueous environment. The release potential was found to be lower compared to the quenched PP/Ag and PA/Ag composites. The release of silver ions from PP/Ag$_{elem}$ composites can be regarded as not only a surface phenomenon but contributed by the silver entities embedded within the inner layers as well. The Ag$^+$ release characteristics depend on the nature of the silver antimicrobial employed and the polymer matrix. Some of the commercial silver based antimicrobials are more efficient than the elementary silver powder owing to the presence of certain porous materials used as carriers of silver. Crystallinity and water uptake found to be very decisive for the biocidal release. There exists a good agreement between the observed silver ion release potential and the antimicrobial properties of the emerging composites. Composites possessing higher water uptake characteristics showed early antimicrobial activity. Polypropylene containing elementary silver powder showed excellent long-term silver ion release behaviour.

Table 2
Results of the antimicrobial tests (log reduction)

Microbes	PP control				PP/Ag (elementary)				PP/Am 91455			
Time (h/days)	24 h	7 d	14 d	28 d	24 h	7 d	14 d	28 d	24 h	7 d	14 d	28 d
ASTM method												
E. coli								>1		1	>1	2
St. aureus								1			2	2
JIS Z 2801 method												
E. coli						1	2	3				
St. aureus						2	2	3				

Acknowledgements

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