Polyamide/silver antimicrobials: effect of crystallinity on the silver ion release

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Abstract: Polyamide/silver (PA/Ag) composite materials are regarded as potential antimicrobials by virtue of their efficacy to release the Ag$^+$ ions in an aqueous medium. The effects of the matrix crystallinity on the Ag$^+$ ion release characteristics of PA/Ag composites are discussed. It is found that matrix crystallinity is very decisive for the silver ion releasing properties and hence the antimicrobial efficacy of silver-based antimicrobial polyamides. The crystallinities of the composites were evaluated using differential scanning calorimetry. The silver ion release characteristics of these composites were measured by anode stripping voltammetry. Silver ion release was higher in systems possessing lower degrees of crystallinity. Water-diffusion characteristics of the composites control the silver ion release. The effect of crystallinity on silver ion release rate depends on the time of soaking of the specimens in water.
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INTRODUCTION

There is a recognized need for antimicrobial additives in plastics to maintain their integrity and longevity, especially when they find use in vital applications. Inorganic antimicrobial products based on silver ions are widely used because they protect plastic products effectively from bacterial growth for a long period of time. The main advantages of silver-based antimicrobials over organic systems in plastics are their high thermal stability in addition to health and environmental safety.[1] A steady and prolonged release of the silver biocide (Ag$^+$) upon interaction with water molecules provides the antimicrobial efficacy to a matrix polymer that contains the silver. Once silver is filled into the polymer matrix, water diffusion into the polymer decides the extent of production and release of the silver ions. This means that those polymers, which are hygroscopic, can be an excellent storehouse of silver, and such composites can release silver ions in a continuous and steady manner in an aqueous medium.

In this context polyamides represent an important class of thermoplastics, as their water uptake characteristics can be exploited for the silver ion release at a concentration level that is capable of rendering antimicrobial action. Water absorption in nylon is mainly decided by the chemical structure.[2] Polymer chains with strong polar groups are able to bind the water by hydrogen-bonding.[3] The nylon polymer contains amide functional groups (−CONH−):

they absorb the water from the aqueous environment and form hydrogen-bonded complexes with the nitrogen and oxygen of the amide linkage. All polyamides are basically hydrophilic but their water affinities are dependent on the −CONH content and crystallinity.[4] Water uptake is manifested in the silver ion release efficiency of the polyamide and hence has important technological consequences. The more polar groups there are, the higher the sorptive affinity of the polymer matrix for water. The accessibility of polar groups, the relative strength of water–water *versus* the water–polymer bonds and the degree of crystallinity of the polymer matrix are very important factors which decide the equilibrium water uptake and hence the silver ion release properties. It is worth remembering that, in polyamide, the water uptake is considerably influenced by the degree of crystallinity of the matrix polymer.[5] One of the most important characteristics of semi-crystalline polymers is the degree of crystallinity, which strongly affects many physical properties of a polymer. Being a semi-crystalline polymer with many industrial uses a knowledge of the crystallinity-dependant properties of a polyamide helps in identifying domains where this material can satisfy the required properties.

In a previous report[6] the evidence for the release of silver ions from polyamide containing various concentrations of elementary silver powder in an aqueous medium was discussed. It was found that the silver ion release increases with time of soaking

and the concentration of the silver powder, and it depends on the specific surface area of the silver powder used for the composite preparation. One of the specific observations was the drastic increase in silver ion release from the 7th day of exposure to water. In the discussion of that report we ascribed this phenomenon to the onset of plasticisation of the matrix polymer as a result of water uptake.

Among the different methods adopted for the silver incorporation into polymers, melt mixing is convenient as it can provide silver ions on a long-term basis. Compared with a surface-coated specimen, the silver embedded well inside the polymer can act as a provider of the biocide for longer periods. A disadvantage of such systems is often found with non-polar polymers because of the poor silver ion release owing to their poor water affinity. Consequently, recent efforts were oriented towards using some carrier materials for silver, like zeolites that allow easy entry of water molecules into the matrix.

In the literature, reports are found either on the silver ion release from different polymers containing a silver compound[7] or on the antimicrobial properties of the silver-filled materials.[8] Results on the dependency of the silver ion release on the matrix crystallinity have not been published in spite of its high relevance to the release properties.

Our earlier experiments have proved the PA/Ag composites to be capable of releasing the silver ions and the composites were found to possess antimicrobial and antifouling properties.[6] These composites were produced and subjected to silver ion release experiments and antifouling tests for the purpose of fabricating them to fishnet.

This paper mainly represents the results of an investigation on the role of crystallinity with respect to the silver ion release properties of the polyamide/silver composites. The conditions necessary for these investigations (ie varied crystallinity) are achieved by processing PA/Ag composites under different cooling rates. The silver ion release from these composites was monitored with an aim to correlate the crystallinity and the Ag^+ release.

EXPERIMENTAL
Sample preparation

Polyamide (Ultramid C35 F, a copolymer of PA 6 and PA 6,6 of BASF, Ludwigshafen, Germany) and elementary silver powder having a specific surface area of $0.78\,m^2\,g^{-1}$ (WC Heraeus GmbH & Co, KG) were mixed in a kneader at $230\,°C$ in an atmosphere of nitrogen gas until a steady torque was reached. The silver particles have an average particle size of $0.8\,\mu m$. The SEM micrograph of the PA/Ag composite specimen shows that silver particles disperse in a finer and uniform manner in the PA matrix (Fig 1). The composites were then compression moulded at $230\,°C$ into rectangular specimens having dimension $20 \times 10 \times 1\,mm^3$ and cooled after the
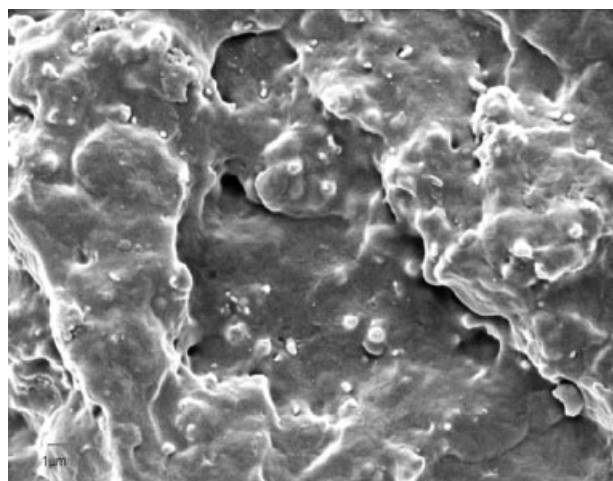

Figure 1. Scanning electron micrograph (SEM) showing the dispersion of silver particles in a PA matrix.

pressing time at various cooling rates to create different degrees of crystallinity in the samples. Four degrees of crystallinity were created by cooling the samples overnight, cooling in air, by passing water through the press, and by quenching after the pressing.

Anode stripping voltammetry (ASV)

Anode stripping voltammetry (ASV), an electro-analytical method of detecting metal ions in water, uses a two-step process of electrolysis and stripping. In the electrolysis step, metal ions in solution are deposited onto an electrode by applying a negative voltage to the electrode for a predefined period of time under convective diffusion maintained by the rotating working electrode. During the stripping step, an oxidizing current is applied to the electrode, and the metals are stripped back into solution. Metals present in the solution are identified by their characteristic oxidation potential. ASV was used for the quantitative estimation of the silver ions released from the PA/Ag specimens. A rotating glassy carbon electrode (4 mm diameter) is used as the working electrode. This method is sensitive enough to quantify biologically relevant concentrations.

The stripping voltammetric experiments give rise to voltammograms comprising several individual scans:[6] The summation of all the scans provides a 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 modified Ilkovik equation[9]

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

where I_p = peak current (μA), N = number of electrons transferred per molecule, A = electrode area (cm^2), D = diffusion coefficient ($cm^2\,s^{-1}$), v = scan rate ($V\,s^{-1}$), t = enrichment time (s; time during which the silver ions were deposited onto the electrode from the analyte), C = concentration of the ions in the solution ($g\,l^{-1}$).

ASV measurements of various solutions with defined silver ion concentration led to a calibration curve. The procedure of the construction of the calibration curve and the estimation of the concentrations of the analytes are described in a previous report:[6]

RESULTS AND DISCUSSION

Figure 2 gives results on the time and concentration dependency of the silver ion release of PA/Ag composites based on the stripping voltammetric experiments. The data for the Ag^+ are related to the release by 1 g of the PA/Ag composites to a 100 ml of aqueous environment. It can be seen that the Ag^+ release increases with time and concentration of the silver. A straightforward observation is the significant increase of the concentrations after the 7th day especially for those composites containing higher amounts of Ag. An explanation could be that, during the first 6 days, the matrix becomes plasticized and its crystallinity could have changed considerably as a consequence of the continuous water diffusion. A detailed explanation for this increase in release after the 7th day is given by a consideration of the physical changes (plasticization of the matrix) occurring within the PA/Ag specimens as result of the water diffusion and the subsequent increase in the rate of Ag^+ release.[6] A detailed illustration about the relationship between water uptake and the Ag^+ release was given in the report. It is possible that many macromolecular properties, and definitely crystallinity, would have changed as a result of the continuous water diffusion. The pursuit of this work to investigate the effect of matrix crystallinity on the silver ion release efficacies is motivated by this observation.

As a preliminary step, composites containing various concentrations of the Ag powder in PA were subjected to differential scanning calorimetry (DSC) analysis in order to understand their melting and crystallization behaviour. The experiment was performed as follows: The sample was heated to 230 °C at a heating rate of 10 K min^{-1}. After annealing the molten composite for
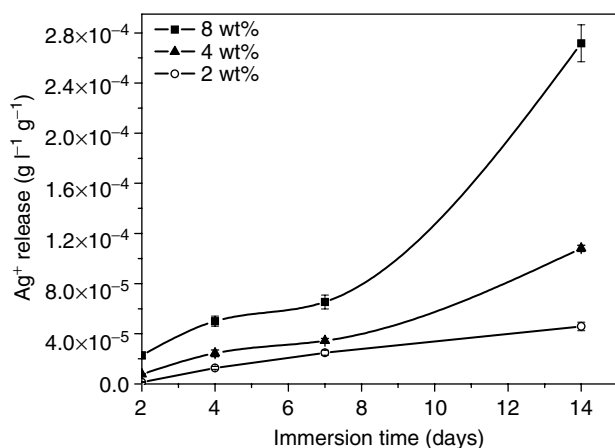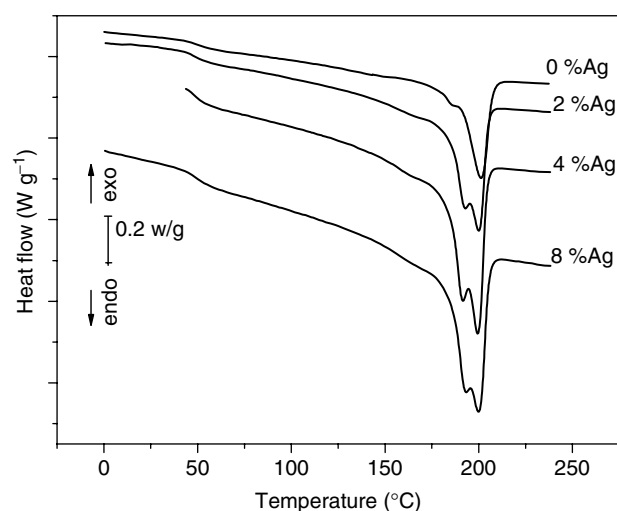
Figure 3. Second heating runs showing the melting behaviour of PA/Ag composites (10 °C min^{-1}).

about 3 min at this temperature, well above the melting temperature of 200 °C, cooling started at a rate of 10 K min^{-1}. The second heating run (10 K min^{-1}), which is not influenced by an undefined thermal history of the sample, is shown in Fig 3. It can be seen that PA exhibits double melting behaviour and this becomes more pronounced with the addition of Ag powder. This could be due to the reorganization and consequent recrystallization of polyamide crystals after the first melting. Neither the T_g nor the T_m was affected by the silver addition.

Figure 4 shows the cooling curves (10 K min^{-1}). It is seen that the crystallization temperature (T_c) shifts to higher temperatures (approximately 25 °C) with the addition of Ag. The peaks become sharper in the case of the Ag-filled systems showing a higher rate of crystallization in the presence of silver powder. This behaviour is typical of a nucleating agent. An increase of the crystallization enthalpy of polyamide, which is a measure of crystallinity, is also seen by the addition of 2 wt% of Ag. The crystallization temperature was independent of Ag concentration.
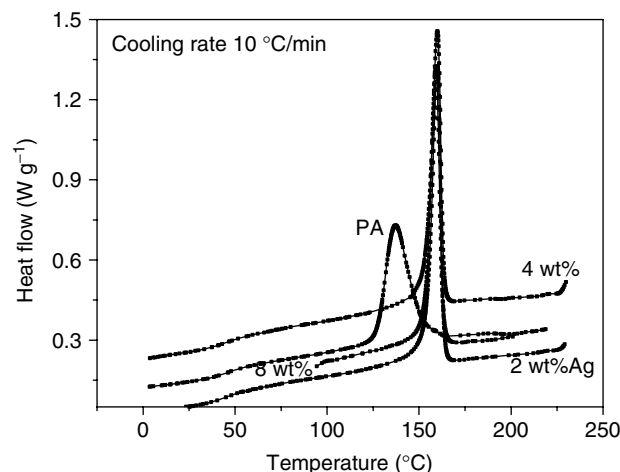
Figure 2. Ag^+ release from PA/Ag composites as a function of time and concentration of the silver powder (Ag powder 0.78 m^2 g^{-1}).

Figure 4. Cooling curves showing the crystallization behaviour of the PA/Ag composites.

In polyamides the crystallinity influences the water-diffusion characteristics. Water uptake is decisive for the Ag$^+$ release and hence it should depend on the crystallinity of the sample. The composites were cooled after the first melting at various cooling rates in order to estimate the corresponding changes in crystallization enthalpy. Figure 5 shows the changes in crystallization enthalpy (ΔH_c) as a function of the concentration of the Ag powder at various cooling rates. It is obvious from this figure that the crystallization enthalpy and hence the degree of crystallinity decreases with an increase in cooling rate. The higher crystallization enthalpies for the composites with 2 wt% Ag are attributed to the role of Ag powder acting as the site of heterogeneous nucleation, which provides higher crystallinity to the composites at this concentration. However, it is reported[4,10] that, at higher concentrations, fillers prevent the three-dimensional growth of the crystallites. These experiments were performed in order to understand the crystallization behaviour of PA in presence of Ag at various cooling rates.

Crystallinity effects on silver ion release
Determination of crystallinity
The crystallinity of the silver-filled PA composites is observed to be influenced by the rate of cooling (Fig 5). In order to evaluate the relationship between the matrix crystallinity and the Ag$^+$ release we have produced PA/Ag composites possessing various degrees of crystallinity (Ag content 4 wt%). The composites were compression moulded and were cooled to room temperature by slowly cooling overnight, cooling in air, cooling by circulating water through the press, and by quenching in cold water after pressing. The DSC experiments performed on these four PA/Ag composites containing 4 wt% Ag showed that they differ in their degrees of crystallinity (Fig 6). Crystallinities were calculated from the melting-enthalpy values. These have been calculated as the ratio of the melting enthalpy of the
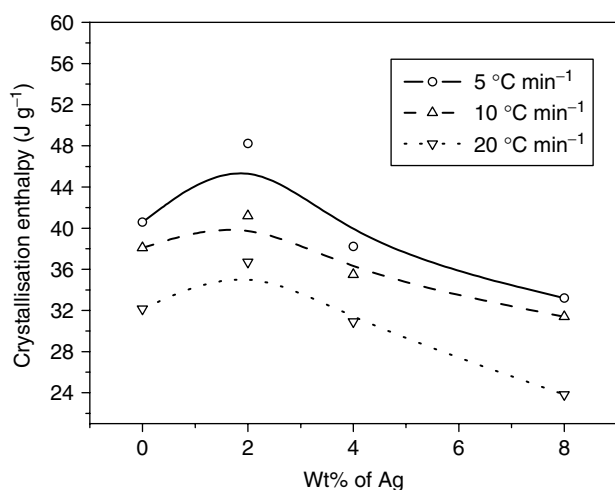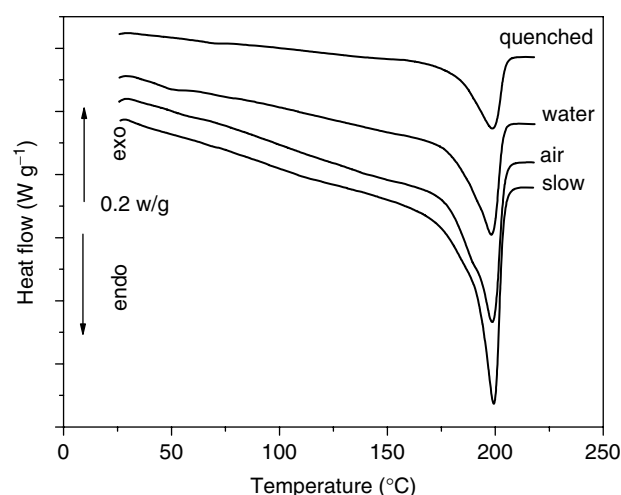
Figure 6. Melting behaviour of the PA/Ag composites processed under different cooling conditions (silver content 4 wt%).

composites to that of 100 % crystalline polyamide[11] ($\Delta H_{\text{melting}} = 240 \, \text{J g}^{-1}$). The highest crystallinity is found for the samples cooled overnight and the lowest for the quenched samples. The crystallinities were 23.7, 18.7, 17.8 and 17.1 % respectively, for the overnight cooled, air-cooled, water-cooled and the quenched samples.

Silver ion release experiments
Known masses of the PA/Ag composite specimens having the above-mentioned percentage crystallinities were stored in separate bottles containing distilled water (100 ml aqueous medium, ie 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 getting reduced to metallic Ag. One millilitre of the aqueous solutions collected from these storages were analyzed for the quantitative estimation of Ag$^+$ released by the composites specimens. All the composite specimens soaked in water contain 4 wt% of the silver powder with the specific surface area (SSA) of 0.78 m^2 g^{-1}. Voltammetric analyses were performed on days 3, 7, 10 and 14 with the analytes collected on these days to determine the concentration of Ag$^+$.

Figure 7 is a comparison of the summation curves of the stripping scans corresponding to the analytes collected from storage of samples cooled at different rates. It is possible to see that the peak heights of the summation curve vary considerably. The highest could be seen for the quenched samples and the lowest for the highly crystalline samples. Figure 8 shows the total concentration of the Ag$^+$ released in an aqueous medium by the composite specimens having the four different crystallinities mentioned above. It can be understood from Figs 7 and 8 that the crystallinity plays a vital role on the Ag$^+$ release, especially after the 3rd day. The samples having the highest crystallinity (cooled overnight) possess the lowest Ag$^+$ release efficacy while the quenched samples show the highest release over the entire time of soaking in water. This means that the processing conditions, which
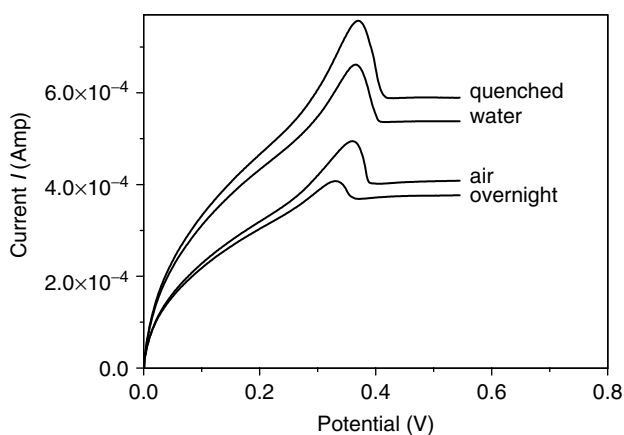
Figure 5. Crystallization enthalpy as a function of silver content at different cooling rates.

Figure 7. Total stripping current (measure of concentration of total Ag$^+$ ions) corresponding to analytes collected from samples cooled at different rates (day 10).
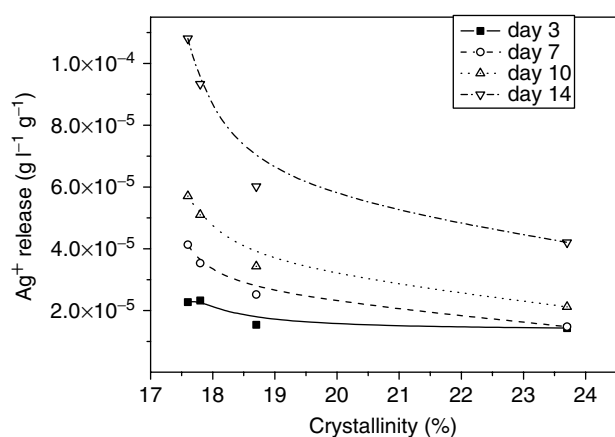

Figure 8. Ag$^+$ release as a function of percentage crystallinity (PA/Ag 4 wt% silver).

affected the crystallinity of the polymer matrix, have a substantial influence on the Ag$^+$ release properties.

The following considerations explain how a higher degree of crystallinity could reduce the Ag$^+$ release. In a semi-crystalline polyamide the absorbed water will have a preferential interaction (hydrogen-bonding) with the functional groups in the amorphous region because of the restricted ability of water to permeate the crystalline regions. It is reported that one of the important factors in the establishment of equilibrium between a polyamide and a water-containing environment is the degree of crystallinity of the polyamide.[4,5] The increase in crystallinity in the case of the samples cooled by a slower rate provides a difficulty for the water molecules to get into the voids within the samples. This increased permeation barrier affects the rate of production and migration of Ag$^+$ ions within the specimens. Water diffusion rate in polyamide is reported to retard due to the increase in crystallinity.[5,12,13] The reports describe the equilibrium water content of the amorphous polyamides (quenched) is significantly higher than that of the semi-crystalline polyamides (annealed). The density of the amorphous phase reduces in the surrounding areas where the growth

of crystallites occurs as consequences of the tension stresses (constraints) accompanying crystalline growth during the annealing process.[14,15] Hence the reduction of the density of the amorphous phase could retard the Ag$^+$ migration process within the highly crystalline samples (overnight cooled). The Ag$^+$ migration is favoured mainly by the amorphous phase as it is already seen that the Ag$^+$ release decreases with increasing degrees of crystallinity.

In every case (Fig 8) an abrupt rise in silver ion release was monitored during the second week of storage. This observation is consistent with our earlier experiments (*cf* Fig 2). This is because of the fact that the progress of water diffusion causes the disintegration of the existing intermolecular hydrogen-bonding in PA and the water molecules form their own hydrogen-bonding with the −CONH−groups. This weakens the intermolecular forces in the PA and in particular mobilizes the molecular segments, which are not fixed in the crystallites. These effects plasticize the PA matrix and permit more favourable conditions for the diffusion and migration of the water molecules and Ag$^+$ ions, respectively, into the matrix and from the matrix.

From the experiments it can be concluded that, by changing the crystallinity of the polyamide matrix in which the silver particles are embedded, it is possible to control the silver ion release to some extent. Even in the case of highly crystalline samples, the release has a sudden increase from the 7th day due to plasticization and water-induced changes in the crystal structure. Another peculiar observation is that, for longer duration, the effect of soaking with respect to Ag$^+$ release is more pronounced in composites having lower crystallinity (*cf* Fig 9). Figure 9 represents the derivative curves showing the rates of silver ion release per day from the four samples. From the shape of the differential curve, (three stages of release rates) it is possible to interpret the changes in the release rates of the samples during the period of analysis. In the beginning (up to 6 days) the release rates show a constant value for all the four types of specimens.
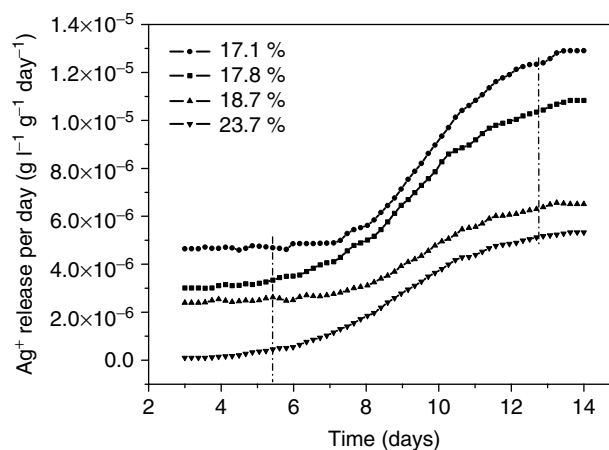

Figure 9. Derivative curves showing the rates of release (per day) of Ag$^+$ ions.

Thereafter the slopes of the curves increase, indicating an increase in the release rates between 7 and 13 days (approximately), which is followed by a levelling off. The increasing trend from 7th day can be attributed to the onset of plasticization as a result of the continuous water intake by the specimens. It can be seen that such diffusion-controlled changes in the macromolecular structure have more effects on the composites having lower crystallinity. Both for the water-cooled and the quenched specimens the silver ion release rates increase to higher values after one week of continuous water diffusion. The increased segmental mobility due to plasticization can further accelerate Ag^+ migration through these predominantly amorphous composites (quenched). The effect of crystallinity on the silver ion release depends on the time elapsed since the specimens were admitted to an aqueous environment.

The following explanations also will be useful to understand the importance of crystallinity especially for a long-term Ag^+ release behaviour. The silver particles embedded within the deeper layers of the specimens are largely providing the silver ions on a long-term basis. The restricted mobility of the water molecules within the crystallites will affect the rate of reaction between water molecules and the silver particles confined to the crystallites. In this case those particles located within the amorphous phase of the deeper layers will be the possible targets of the water molecules. Considering the silver particles role as heterogeneous nucleating sites assisting crystal growth, the slowly cooled samples will have many Ag particles embedded and blocked within the crystallites from a consideration of its high crystallinity. So the effect of plasticisation will have a lesser impact on the slowly cooled specimen possessing high crystallinity. However, for quenched specimens, most of the Ag particles in the inner layers could be located within the amorphous layers and can hence interact with the water molecules for the generation and subsequent rapid migration, especially in a plasticized specimen. The time of plasticization could be very much similar to the time at which the Ag particles and the water molecules interact within the deeper layers. The inference is that in highly crystalline specimens, the effect of long-term soaking in water and the consequent plasticization is not very productive with respect to the silver-ion generation and the release. This interpretation has excellent support from a recent report on the effect of crystallinity and water diffusion in polyamides.[15] The authors produce spectroscopic evidence for the water penetration in semi-crystalline polymers as a phenomenon occurring only for a shorter duration and reversible in crystalline lamellar regions. It means that the crystallinity is very decisive for the long-term silver ion release and the consequent antimicrobial properties.

Water diffusion behaviour

The mol% weight gain of water by these four samples after 14 days of continuous diffusion were determined.

The values are 0.40, 0.42, 0.44 and 0.45, respectively, for the overnight cooled, air-cooled, water-cooled and quenched samples. It can be seen that higher water uptake was shown by composites possessing lower degree of crystallinity, ie the quenched specimens. These samples exhibit the highest Ag^+ release among the four samples having varying degrees of crystallinity. Our very recent experiments also support this hypothesis.[6,16,17] In these studies, it was found that the use of Ag-substituted zeolites as antimicrobial additives in polyamide and polypropylene generated higher concentrations of silver ions in an aqueous medium. In these cases, the zeolites being hygroscopic, promote the water-uptake behaviour of the composites. Water-diffusion experiments on these specimens revealed that these composites also possess higher water-uptake behaviour compared to PA/Ag composites where an elementary Ag powder was used as the antimicrobial additive. These observations support the speculation that water uptake is very decisive for the Ag^+ release properties. An increased presence of water due to lower crystallinity can generate more Ag^+ ions from the PA/Ag composite specimens. The observations permit the conclusions that the composites having the lowest crystallinity, and having a high susceptibility for water diffusion,[4] lead to the highest Ag^+ release. More investigations are to be made in order to see whether the higher water uptake increases the rate of silver ion release by increasing the silver-ion production kinetics ($Ag + H_2O \rightleftharpoons Ag^+ + e^-$) or increasing the kinetics of Ag^+ migration by plasticizing the composite specimens.

Antimicrobial properties

The antimicrobial efficacy of the PA control and the PA/Ag composites against different types of microbes like *Escherichia coli* and *Staphylococcus aureus* were tested, on the basis of the ASTM E 2149-01 test method. The results given in Table 1 show that the composites have good efficacy against these microbes, especially the quenched samples. The absence of activity within a shorter duration (less than 7 days) suggests the time requirement for the water diffusion and the subsequent Ag^+ release in such a concentration level to render efficacy. An interesting observation is the notable difference in the activity of the quenched samples, which can be attributed to their highest Ag^+ release potential that is already observed (Fig 8).

Table 1. Antimicrobial properties

Pathogen	Log reduction PA/Ag			
	24 h	7 days	14 days	28 days
Escherichia coli		1[a]	>1[b] (2)[a]	2[b] (3)[a]
Staphylococcus aureus		1[a]	>1[b] (2)[a]	3[b] (3)[a]

[a] Properties of quenched PA/Ag specimens.
[b] Properties of specimens cooled by circulating water around the press.

CONCLUSIONS

Silver ion release experiments were performed on PA/Ag composites having various degrees of crystallinity in order to understand the influence of matrix crystallinity on the Ag^+ release properties. There was higher Ag^+ release from composites possessing lower crystallinity. The crystallinity affects the water uptake, which in turn controls the Ag^+ release. The measurements favour the mechanism of Ag^+ transport in the amorphous phase of the PA matrix because the Ag^+ release rate decreased with increasing crystallinity. The Ag^+ release rates of specimens possessing lower crystallinities increase significantly after the 7th day (onset of plasticization). The crystallinity effects on Ag^+ release depend on the period of soaking as the rate of Ag^+ release changes significantly as a function of time. Crystallinity is found to be very decisive and crucial for the long-term Ag^+ release and hence the long-term antimicrobial properties.

ACKNOWLEDGEMENT

REFERENCES

1 Markarian J, *Plastics Add Com* **4**:18 (2002).
2 Extrand CW, *J Colloid Interface Sci* **248**:136 (2002).
3 Nelson WE, *Nylon Plastic Technology*, The Plastics and Rubber Institute, Newnes-Butterworth, London, Chapter 4, p 116 (1976).
4 Uddin AJ, Ohkoshi Y, Gotoh Y, Nagura M and Hara T, *J Polym Sci, Polym Phys Ed* **41**:2878 (2003).
5 Kumar RC, George KE, Francis B and Thomas S, *Polym and Polym Composites* **9**:247 (2001).
6 Kumar R and Münstedt H, *Biomaterials* **26**:2081 (2004).
7 Dowling DP, Betts AJ, Popp C, McConnell ML, Eloy R and Arnoud MN, *Surf Coat Technol* **163**:637 (2003).
8 Feng QL, Kim TN, Wu J, Park ES, Kim JO, Lim DY and Cui FZ, *Thin Solid Films* **335**:214 (1998).
9 Von Fraunhofer JA and Banks CH, *Potentiostat and its Applications*. Butterworth, London, p 154 (1972).
10 Ton-That TM and Jungnickel BJ, *J App Polym Sci* **74**:3275 (1999).
11 Fornes TD and Paul DR, *Polymer* **44**:3945 (2003).
12 Van Krevelen DW, *Properties of Polymers*, Elsevier, Amsterdam (1997).
13 Lim LT, Britt IJ and Tung MA, *J App Polym Sci* **71**:197 (1999).
14 Dlubek G, Stolp M, Nagel C, Fretwell HM, Alam MA and Radusch HJ, *J Phys Condensed Matter* **10**:10 443 (1998).
15 Harrison KL and Jenkins MJ, *Polym Int* **53**:1298 (2004).
16 Kumar R, Howdle S and Munstedt H, *J Biomed Mater Res Part B: Appl Biomater* (in press).
17 Kumar R and Munstedt H, *Reactive and Functional Polymers* (in press).