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Morphology and mechanical properties of antimicrobial polyamide/silver composites

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Abstract

Silver filled antimicrobial polymers were produced from composites comprising polyamide and elementary silver powder possessing various specific surface area (SSA) by melt compounding. Different concentrations (2%, 4% and 8%) of the silver powder were incorporated in the polyamide to investigate the effect of silver loading on the mechanical properties. As the water uptake imparts antimicrobial properties, the influence of the diffused water on the mechanical properties of the composites is discussed. Scanning electron microscopy (SEM) is employed to investigate the morphology of the composites. The composite morphology found to be dependent on the SSA of the silver powder employed within the polyamide matrix. DMTA measurements were performed to follow the visco elastic behaviour of the composites. The crystallinities of the composites were evaluated using Differential Scanning Calorimetry (DSC).

Keywords: Silver; Polyamide; Mechanical properties; Morphology; Antimicrobial

1. Introduction

Silver filled polymers are well known antimicrobial materials by virtue of their ability to release the biocidal species, viz. Ag^+ ions in an aqueous environment [1–5]. Silver is unique in certain features pertaining to its spectrum of activity, durability of action and the thermal stability. The mechanism of inhibitory action of silver ions on microbes is partially known. It is believed that DNA loses its replication ability and cellular proteins become inactivated upon Ag^+ encounter [6]. Besides this, the silver ions attack some functional groups in the proteins, causing its danaturation [7]. Thermoplastic composites produced from metal powder filled polymers represent an important class of materials especially when the metal has potential properties like the antimicrobial activity. Apart from the antimicrobial properties, for a useful application the materials have to possess excellent mechanical properties depending on the type of application. In certain cases, the non-uniformity of composite properties owing to poor dispersion of the dispersed phase in the polymer is detrimental to the mechanical and other desirable properties.

The antimicrobial activity is decided by the ability of the emerging composites to release silver ions in a pathogenic environment [8]. The polyamide/silver composite system generated mainly with the purpose of producing antimicrobial polymers has been recognised as capable of releasing the silver ions [9]. The development of this composite material is with the purpose of fabricating them into a number of applications like vials, garments, fishnets, etc. For such applications, the mechanical properties are to be very profound having the same importance as the antimicrobial efficacy. Thermoplastic composites produced by incorporating silver in polyamide tailor the intrinsic antimicrobial properties of silver and the easy processibility of plastics and offer cost effectiveness and rapid fabrication possibilities. The silver ion release properties were tested

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using stripping voltammetric experiments by subjecting the analytes collected from the storages of the composites in water. The silver ion release properties and the antimicrobial properties of this composite system were discussed in an earlier report [9].

The PA/Ag composites were subjected to different mechanical properties assessment to follow the stress–strain behaviour and viscoelastic behaviour. The morphology of the system was also observed as it has relevance to both antimicrobial and the mechanical properties. In this report, the morphological and mechanical properties of the antimicrobial materials from PA/Ag composites are discussed.

2. Experimental

2.1. Preparation of PA/Ag composites

The PA/Ag composites were produced by melt compounding in an internal mixer (Polydrive 600 Haake) at 230 °C at a rotor speed of 60 rpm. The mixing was performed for 7 min as this time ensured a steady torque. The polyamide used is ultramid C35 F of BASF, Ludwigshafen, Germany and the elementary silver powder was procured form the W.C. Heraeus GmbH and Co. KG (purity 99.9% and the specific surface area of 0.78, 1.16 and 2.5 m^2/g). Different proportions (2, 4 and 8 wt.%) of the silver were used for the composite preparation.

2.2. Morphology and mechanical properties

The mechanical properties were tested using universal testing machine (Zwick Z050). The testing was done at a crosshead speed of 10 mm/min (DIN 53455). The stress–strain behaviour was monitored using dumb bell shaped specimens prepared by compression molding. In a separate attempt the stress–strain behaviour of water soaked dumb bell specimens were also tested to understand the influence of water diffusion on the mechanical properties. Dynamic Mechanical Thermal Analysis was performed (DMTA *Mk* IV, Rheometric scientific, USA) using rectangular specimens ($2\times1\times0.2$ cm^3) in three point bending mode. The morphology of cryogenically fractured PA/Ag composites was observed to follow the nature of dispersion of the silver powder in the polyamide matrix. Scanning electron microscopy was used for the characterisation of the surface morphology of cryogenically broken composite specimens.

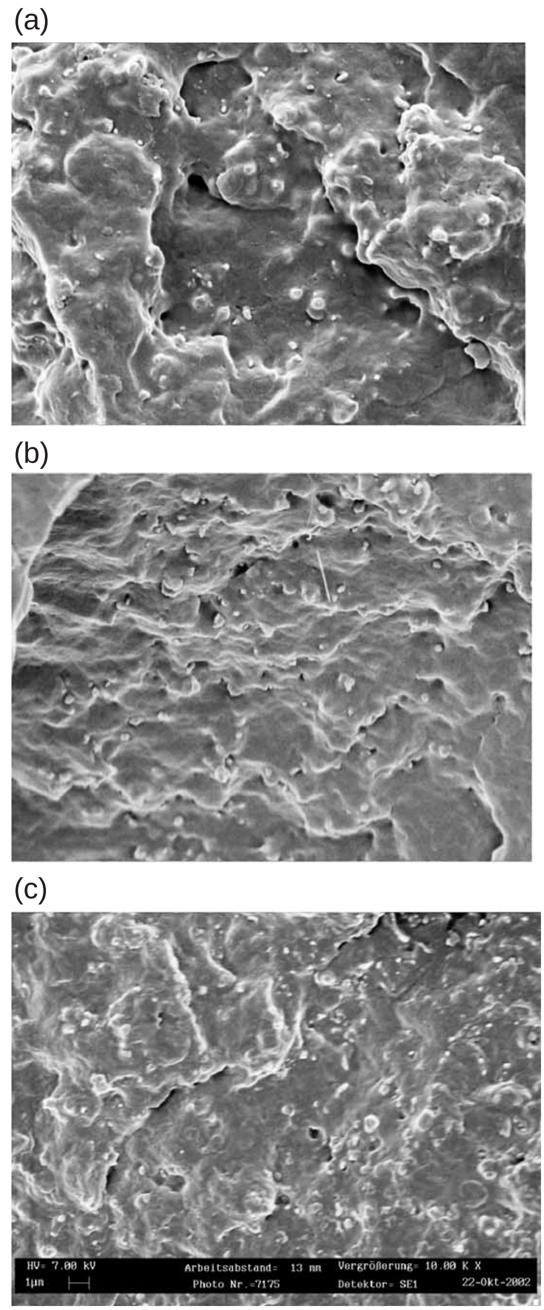

Fig. 1. Scanning electron micrographs of PA/Ag composites, 2 wt.% (a), 4 wt.% (b), and 8 wt.% (c) silver in polyamide matrix. Magnification—10,000 (Ag-SSA 0.78 m^2/g).

3. Results and discussion

3.1. Morphology

Fig. 1a–c shows the morphology of PA/Ag composites containing 2, 4 and 8 wt.% of silver powder having a SSA of 0.78 m^2/g. It is possible to see fine dispersion of silver powder in the PA matrix. It is seen that independent of the silver powder concentration, all the composites show a finely dispersed morphology of the silver powder having the specific surface area of 0.78 m^2/g. In order to see the effect of SSA of the silver powder on the morphology of the emerging systems, silver powder having specific surface area of 1.16 and 2.5 m^2/g also was used to produce the composites. In these cases the composites show an agglomerated morphology where the silver entities coalesce in the polyamide matrix. Fig. 2a,b shows the scanning electron micrographs of the composites containing silver

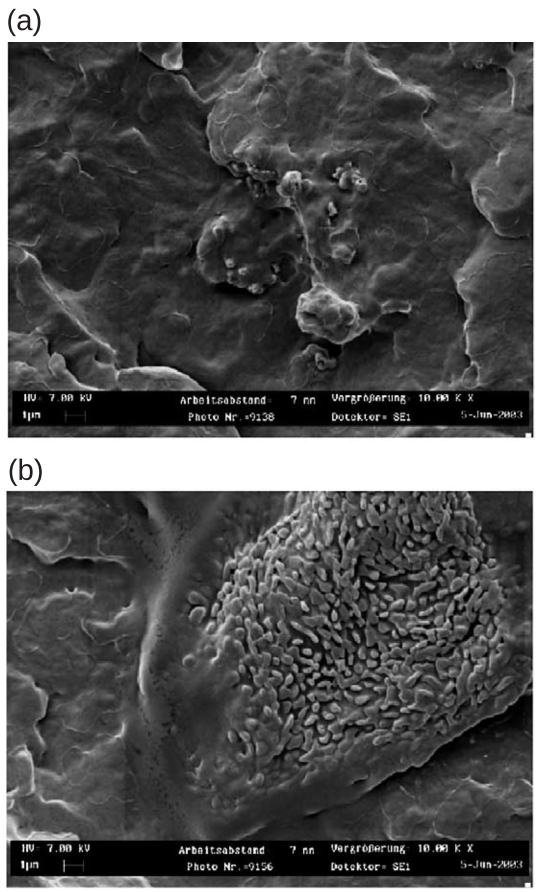

Fig. 2. Scanning electron micrographs of polyamide composites containing silver particles with SSA, 1.16 m^2/g (a), 2.5 m^2/g (b). Magnification—10,000 (Ag—4 wt.%).

powder with specific surface area of 1.16 and 2.5 m^2/g. This agglomerated morphology reflected in their silver ion release properties [9]. It was seen that these composites release lesser concentration of silver ions compared to composites containing silver powder with SSA 0.78 m^2/g. A detailed discussion of the silver ion release experiments can be seen in a previous report [9].

3.2. Stress–strain behaviour

Fig. 3 shows the stress–strain curves of various PA/Ag composites containing 2, 4 and 8 wt.% of elementary silver powder. The pure polyamide used in the tensile test as reference was subjected to the same sample preparation (kneader, compression molding) conditions as the composites. From the figure it is possible to understand that the addition of silver causes a reduction in the tensile strength of the polyamides. The composites containing lower proportions of silver exhibited cold drawing behaviour preceded by the fracture. The stress at break also reduced with an increasing concentration of the silver. The elongation at break (ϵ_b) values reduced with an increase in concentration of the silver powder in the composites. Composite with 2 wt.% silver powder shows more toughness as can be seen in the figure. However with increases in filler loading the material loses its strength and toughness enormously. In metal filled polymer composites generally sharp metal particles tend to create cavities due to the debonding of the polymer from the filler surface [10]. Fig. 4 shows the Young's modulus of PA and PA/Ag composites as a function of Ag powder concentration. No significant changes in tensile modulus were found. However the modulus of toughness (area under stress–strain curve) decreased with increase in concentration of the silver powder. The decrease in elongation and the toughness with increase in filler loading shows the existence of weak structure in the composite. In particulate filled composites debonding of the polymer from the filler surface creates stress concentrations that in turn generate discontinuities in the structure, making it weak.

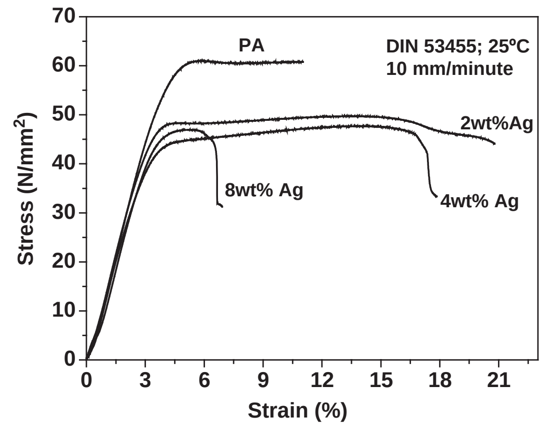

Fig. 3. Stress–strain curves of PA/Ag (dry) composites containing different concentrations of silver powder (SSA—0.78 m^2/g).

The antimicrobial property is a subject of discussion when the PA/Ag composites are in an aqueous environment [11,12]. Antimicrobial efficacy is ensured by the Ag^+ ions, which are releasing from the composites. The oxidation of Ag particles to Ag^+ ions is facilitated by the concentration of the diffused water molecules inside the specimens [9]. In

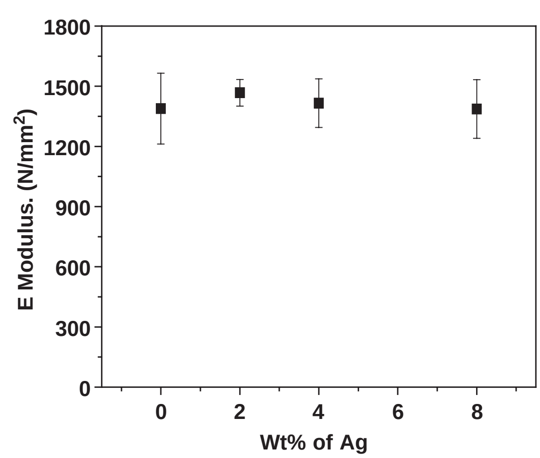

Fig. 4. Modulus of elasticity as a function of concentration of silver powder (Ag used 0.78 m^2/g—SSA).

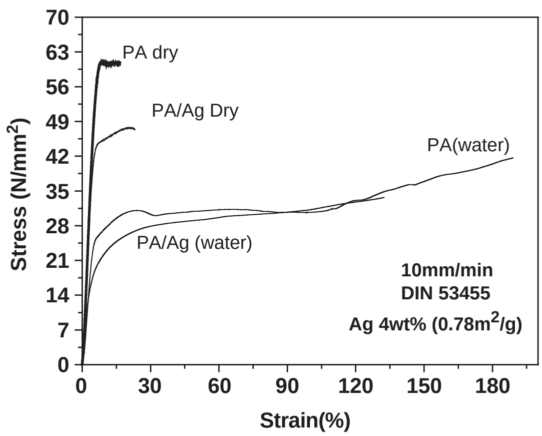

Fig. 5. Stress–strain curves of PA and PA/Ag (water sorbed) composites (time of soaking—4 days).

view of this, the stress–strain behaviour of the composites soaked in water has been investigated. Fig. 5 depicts the stress–strain tests conducted on the water soaked specimens. The composite containing 4 wt.% of Ag powder having a specific surface of 0.78 m^2/g was used for the investigations. It is obvious from the figure that pure PA matrix and PA/Ag composite achieved better toughness in water. The tensile strength is reduced (from 47.6 to 33.6 N/mm^2) due to the plasticising action of water. The elongation at break increased by 600% for the silver filled composites compared to dry PA/Ag composites. It is possible to see increased stress values for pure PA and PA/Ag specimens (water soaked) after 100% elongation. This phenomenon can be attributed to strain-induced crystallisation. The increased modulus of toughness in water is typical for polyamides [13] and the observation is very promising for the PA/Ag composites considering its application like fishnet fabrication.

3.3. DMTA spectra

Figs. 6 and 7 show the results of the DMTA studies conducted on dry PA/Ag composite specimens having the dimension $2\times1\times0.2$ cm^3 containing various weight percentages of the silver powder (specific surface area -0.78 m^2/g) measured in the three-point bending mode at a heating rate of 1 K/min. It is possible to see from Fig. 6 that the storage moduli of the Ag filled systems are higher than that of PA in the glassy, transition and the viscous regions. All the samples show a decrease in storage modulus above 20 °C indicating the glass rubber transition of the amorphous regions in the PA. The storage modulus was found to increase with the addition of silver powder in general. Apart from pure PA, the composite containing 2 wt.% of the Ag powder shows higher E' values above 25 °C in particular. This observation is very much supporting the stress–strain behaviour of this composition (Fig. 3; 2 wt.% Ag powder). This composition exhibited also higher crystallinity compared to pure PA and the rest of the PA/Ag composites. Fig. 8 is the results of the DSC experiments performed on the PA/Ag composites. The samples containing various concentrations of the silver powder were cooled at different cooling rates to monitor their crystallisation behaviour. It can be seen that the crystallinity is slightly higher for the composites containing 2 wt.% of silver powder. The reason can be that the silver particles act as heterogeneous nucleating sites facilitating crystalline growth. However at higher concentration this behaviour was not observed.

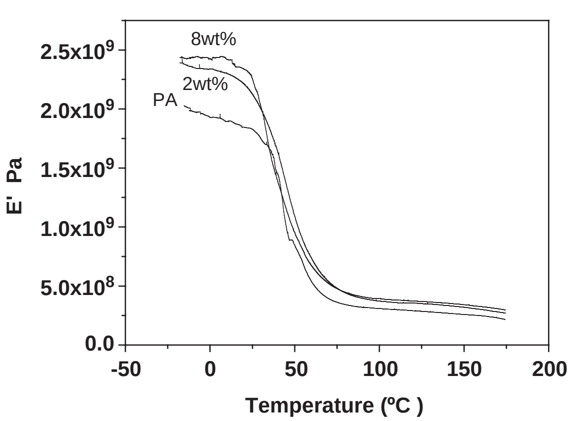

Fig. 6. Storage modulus (E') as a function of temperature.

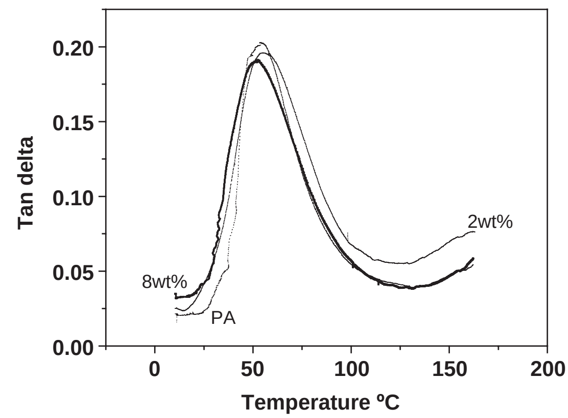

Fig. 7. Damping characteristics as a function of temperature.

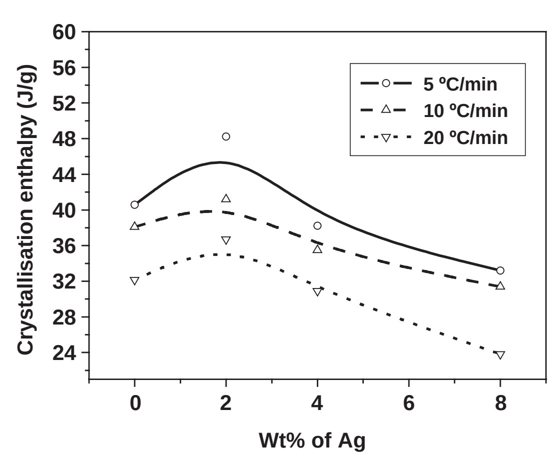

Fig. 8. Crystallisation enthalpy of various PA/Ag composites at different cooling rates.

Reduction of crystallinity at higher filler concentration was also previously reported in polypropylene based composites [14]. Interestingly, this composition (2 wt.% Ag) was observed as capable of releasing silver ions above the biocidal concentration required for the antimicrobial efficacy [9].

Fig. 7 depicts the damping characteristics as shown by the tan δ of the PA/Ag composites. As expected, no change in the glass transition temperature (T_g) with the addition of the silver powder was seen. Fig. 7 shows that damping decreases slightly with the addition of silver to polyamide. The peak width at half height, which is a measure of the interfacial strength, is found to be the highest for the 2 wt.% based PA/Ag composite system.

4. Conclusion

Polyamide/silver composites containing silver particles with a specific surface area of 0.78 m^2/g exhibit a finer and uniform morphology. With the increase of silver particle SSA agglomeration occurred. The mechanical properties evaluation showed the composites as possessing lower toughness and elongation at break with the increase of silver content. Composites containing 2 wt.% of silver powder found promising as it has higher elongation, elasticity, crystallinity and storage modulus compared to compositions containing higher concentration of the filler. The modulus of toughness and elongation data of the dry PA/Ag composites indicate that the increased addition of silver powder into polyamide create a weak structure in the composite. However water diffusion provided interesting improvements in the toughness and the elongation values compared to dry specimens, which fits well with the condition (water diffusion) of antimicrobial activity.

Acknowledgements

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