Materials Chemistry and Physics 147 (2014) 815–822

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Sintering of nanoscale silver coated textiles, a new approach to attain conductive fabrics for electromagnetic shielding

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HIGHLIGHTS

- Assembly of highly conductive textiles capable of shielding electromagnetic radiation.
- Procedure combines *in situ* synthesis of AgNPs at the textile surface and sintering.
- AgNPs formed by precipitation of $AgNO_3$ and reduction with citrate, as observed by SEM.
- Sintering increased dramatically conductivity and shielding effectiveness.
- Treated fabrics maintained conductivity and shielding effectiveness after 8 washes.

ARTICLE INFO

Article history:
Received 26 September 2013
Received in revised form
29 May 2014
Accepted 8 June 2014
Available online 30 June 2014

Keywords:
Nanostructures
Sintering
Chemical synthesis
Electron microscopy
Electrical properties
Surface properties

ABSTRACT

The demand for conductive textiles is increasing, owing to the need for lightweight and flexible conductive materials for a variety of applications, including electromagnetic shielding of electronic equipment. Herein we propose a process that combines the *in situ* synthesis of silver nanoparticles at the textile fibre surface followed by sintering of the nanoparticles to obtain highly conductive fabrics. The formation of silver particles at the nanoscale allowed for sintering to be performed efficiently, at reduced temperature and time, bestowing fabrics with high conductivity and capability of shielding electromagnetic radiation. The nanoparticle synthesis method entailed the precipitation of 2.0 g L^{-1} silver nitrate and further reduction with citrate, with the formation of a deposit of silver nanoparticles at the fabric surface. The amount of silver deposited (up to 195 mg of silver per g of fabric) resulted in moderate electrical conductivity with sheet resistance of 803 Ω/sq. Upon sintering, this value decreased dramatically to 5.2 Ω/sq. The sintering process was monitored by SEM, which showed that sintering at 200 °C for 30 min resulted in maximal electrical conductivity with the lowest amount of silver deposited, while forming a homogenous surface. Fabrics submitted to these sintering conditions maintained their sheet resistance and shielding effectiveness values, even after eight washing cycles.

1. Introduction

Textiles capable of conducting electricity have a wide variety of potential applications, owing to their flexibility, lightweight and capability of adapting to different shapes [1]. Applications of conductive textile materials include electrostatic dissipation [2,3], electromagnetic shielding (required in many modern electronic applications) [4–6] and for technical textile applications (to conduct electricity in sensor-based materials for monitoring body functions such as heart rate [7,8], or heating devices for army personnel and elderly patients' clothes) [8,9]. Most traditional textile materials are electrical insulators or present very limited conductivity. Textiles can, however, be rendered conductive by coating with electrically conductive metallic elements or with conductive polymers. Conductive metallic elements are expensive and their brittle characteristics can damage spinning machinery over time [10]. They are also heavier than most textile fibres, making homogenous blends of conductive fibres and e.g. natural

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http://dx.doi.org/10.1016/j.matchemphys.2014.06.025
0254-0584/

fibres difficult to produce [11]. Optical fibres have the advantage of presenting high corrosion resistance but still flexibility is a problem and optical fibres thus they cannot be woven [12].

Conductive polymers, due to their high electrical conductivity, environmental stability, the ease of chemical synthesis and simple deposition on a textile surface have drawn much interest in recent years [13,14]. Their mechanical weakness, considered as one of their disadvantages, can be improved by addition of filler materials [15]. However, handling of precursors during their synthesis is difficult and/or hazardous, and little is known about long-term stability of the end product [16].

Metallic nanoparticles have been used to improve the conductivity and mechanical properties of coatings and composites due to their high surface area and high conductivity, and are applied to wide variety of substrates [17–19]. The unique properties of silver nanoparticles (AgNPs) have made them ideal for a variety of applications [17,20]. The oxidation of copper in ambient conditions and the high cost of gold prevent these materials from being a practical solution. Silver has a very high electrical conductivity [21] and presents unique static charge dissipating properties. A layer of silver particles can provide unique electromagnetic shielding properties to different materials, including textiles.

The most widely used method to synthesise spherical AgNPs consists on the reduction of a silver salt by an electron donor in the presence of a capping agent. Citrate is among the most common reducing agents used to reduce Ag^{+}, and can be simultaneously used as capping agent [22]. In a more direct approach, successful procedures for the *in situ* synthesis of AgNPs directly on cotton textiles by chemical reduction of a silver salt have been reported [23,24], but still no electrical conductivity was attained.

Due to their high surface area and reduction of binding energy per atom, metallic nanoparticles present lower melting temperatures comparing to the bulk material. Lower sintering temperature of AgNPs could lead to improved conductivity by forming continuous connectivity in deposits of nanoparticles percolated paths – as observed for other surfaces such as paper [25], glass [26] and polymers [27], and provide the lowest possible coating thickness required for conductivity.

In this article, a method based on precipitation and citrate reduction of a silver salt is proposed, combined with a sintering step, in order to obtain highly conductive cotton fabrics that provide high electromagnetic shielding, while minimizing damage to the fabric and the processing costs.

2. Materials and methods

2.1. Materials and reagents

The 100% cotton woven fabric (110 g m^{-2}, thickness of 0.197 mm) used was supplied by Devan-Portugal (the fabric was scoured, not dyed and no polymers were applied). All reagents were purchased from Sigma Aldrich, and were of analytical grade and used without further purification. The silver paste used for conductivity measurements was purchased from SPI supplies (Dotite D-550). All aqueous solutions were prepared using Mili-Q water (18 MΩ cm^{-1}) and were freshly prepared.

2.2. Methods for synthesis of nanoparticles and fabric coating

The synthesis method used initially to produce a silver nanoparticle deposit was based on the chemical reduction of a silver salt by citrate in aqueous media. Samples of cotton fabric (with 0.18 g and 4 cm by 4 cm) were immersed in a 50 mL solution of silver nitrate (concentrations between 1.25 and 3.2 g L^{-1} were tested), and the solution was heated under constant stirring. During the heating stage, 300 μL of 3 mol L^{-1} of sodium hydroxide were added stepwise until no further precipitation of silver occurred. When the solution started to boil, 1.75 mL of a fresh 10% (w/w) trisodium citrate solution was added and allowed to react for 15 min. The cotton fabric samples were then removed, rinsed in Mili-Q water and allowed to dry (Primary method).

The procedure was modified so that initially the fabric sample was placed in a solution containing 300 μL of 3 mol L^{-1} sodium hydroxide and 50 mL of 1.25 g L^{-1} silver nitrate under agitation speed of 800 rpm. When the solution started boiling, 1.75 mL of a fresh 10% (w/w) trisodium citrate solution was added. After 15 min the fabric was removed, rinsed in Mili-Q water and left to dry (Modified method).

All samples tested for resistance to washing were treated with a commercial epoxy-silane used in the textile industry before the washing procedure, in an attempt to further bind the silver nanoparticles to the fabric and prevent their release during washing. The fabric samples were immersed in 1 L of a 30 g L^{-1} of epoxy-silane solution in water and allowed to react for 15 min under agitation. The samples were removed and cured by placing in the oven for 20 min at 140 °C before the washing process.

2.3. Sintering procedure

After the initial deposition of silver particles, the fabric samples were carefully placed inside a Memmert UM100 convection oven at temperatures of 150 °C, 175 °C, 200 °C and 225 °C and left in the oven for 30, 60 or 120 min, after which they were allowed to cool down to room temperature. The oven temperature was allowed to stabilize at pre-set temperatures prior to introducing the fabric samples.

2.4. Resistance of the silver deposits to washing

Fabric samples coated with AgNP deposits after treatment with 2.0 g L^{-1} of silver nitrate (using the modified synthesis method) and subjected to sintering at different temperatures were washed with detergent to determine the resistance of silver deposits to washing.

Fabric samples were washed in 12.5 mL of Soflan® liquid detergent added to 250 mL of distilled water (at 30 °C) under agitation for 30 min using a Teflon coated magnetic bar. Each washing cycle was followed by rinsing three times with distilled water for 5 min, and the sample allowed to dry before starting the next wash. The washing cycle was repeated eight times.

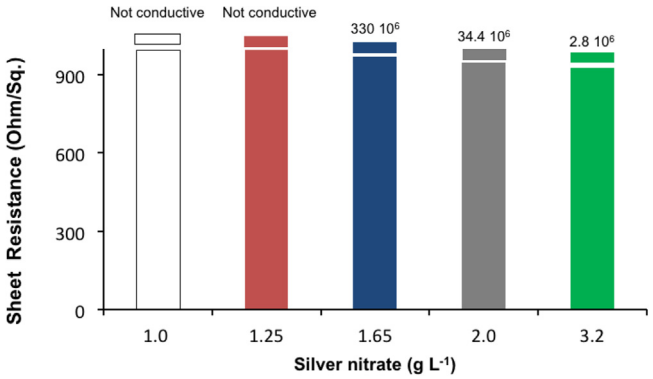

Fig. 1. Effect of silver nitrate concentration on the sheet resistance of fabrics treated using the primary method.