Synthetic Metals 202 (2015) 110–122

Contents lists available at ScienceDirect

Synthetic Metals

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

Plasma treatment of polyester fabrics to increase the adhesion of reduced graphene oxide

J. Molina [a,b], J. Fernández [a], M. Fernandes [b], A.P. Souto [b], M.F. Esteves [b], J. Bonastre [a], F. Cases [a,*]

[a] Departamento de Ingeniería Textil y Papelera, EPS de Alcoy, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell s/n, 03801 Alcoy,Spain
[b] Department of Textile Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

ARTICLE INFO

Article history:
Received 20 October 2014
Received in revised form 14 January 2015
Accepted 19 January 2015
Available online 10 February 2015

Keywords:
Dielectric barrier discharge (DBD)
Adhesion
Polyester
Reduced graphene oxide
Conductive fabrics

ABSTRACT

Polyester (PES) fabrics were treated with plasma to enhance the adhesion of reduced graphene oxide (RGO) and produce conductive fabrics. The surface energy of the plasma treated fabrics was measured using contact angle measurements and showed a stabilization of this parameter with plasma dosages of 3000 W min m^{-2}. The surface roughness measured by atomic force microscopy (AFM) also showed a stabilization with the same plasma dosage value. The plasma treatment induced negative charges on the surface of the fibers and graphene oxide (GO) also presented negative charges – and so deposition of GO on the surface of the PES fibers was not possible. For this reason, bovine serum albumin (BSA) was employed as an intermediate coating that acquired a positive charge and enabled the self-assembly of GO on plasma treated PES fibers. Electrochemical impedance spectroscopy (EIS) was employed to measure the resistance of the conductive fabrics. The plasma treatment and BSA coating improved the coating level of the samples and hence the conductivity of the fabrics was improved with the application of fewer RGO layers. RGO adhesion on fabrics was also improved as shown in rubbing fastness tests.

1. Introduction

In the field of textiles there is increasing interest in the development of fabrics with new properties such as: flame resistance [1]; self-cleaning [2]; thermal regulation [3]; electrical conduction [4]; or even catalysis [5]. Among these properties, electrical conductivity has attracted particular attention. Conductive fabrics can be employed for the production of smart textiles with the integration of sensors or various electronic devices [6,7]. Various approaches can be used to produce conductive fabrics. For instance, the use of metallic fibers inserted in the fabric has been reported; however, the continuous bending and stretching that take place in fabrics produce breakages in the fibers [4]. This is why other approaches have been investigated: the extrusion of fibers with conductive particles such as carbon derivatives [8], or the synthesis of conducting polymer films on the fabrics [9–11].

The discovery of graphene and its derivatives has opened a new era in the field of physics and materials science [12]. The outstanding optical, electronic, thermal and mechanical properties shown by this material have created expectations regarding various possible applications [12–19]. Different methods have been employed for the production of graphene and its derivatives [18–20]. Mechanical exfoliation of graphite crystals was the first method reported by Novoselov et al. [12]. Although the quality of graphene produced in this way is excellent; the quantity of graphene that can be obtained is minimal and can only be used for fundamental studies. This is why other methods such as chemical vapor deposition or chemical methods have been continuously developed in response to the increasing demand for graphene materials. Chemical methods have been proposed as a cheaper alternative and with higher production capacity than chemical vapor deposition. One of these methods is the production of graphene oxide (GO) by the oxidation of graphite. The oxidation of graphite allows the exfoliation of graphene oxide layers. However, a reduction step is necessary to convert the insulating GO into conducting reduced graphene oxide (RGO) [20].

Regarding the application of graphene and derivatives to produce conductive fabrics, the most widely employed method has been the adsorption of GO on the fabric or fibers and its posterior

* Corresponding author. Tel.: +34 966528412; fax: +34 966528438.
E-mail addresses: jamopue@doctor.upv.es (J. Molina), jaferse1@posgrado.upv.es (J. Fernández), marta.fernandes@det.uminho.pt (M. Fernandes), souto@det.uminho.pt (A.P. Souto), festeves@det.uminho.pt (M.F. Esteves), joboca@txp.upv.es (J. Bonastre), fjcases@txp.upv.es (F. Cases).

http://dx.doi.org/10.1016/j.synthmet.2015.01.023
0379-6779/

reduction to produce RGO [21–28]. Graphene oxide sheets are adsorbed on the surface of the fabrics due to the attraction forces between the oxidized groups of GO and the functional groups of the fabrics. The direct deposition of graphene on fabrics has also been reported by Yu et al. [29]. In the present paper the adsorption/reduction strategy has been employed to produce RGO coated polyester fabrics. Plasma techniques have been widely used to increase the adhesion between different materials, including polymers [30]. Plasma treatment produces reactive groups and radicals on the surface of treated fabrics. In the case of polyester, plasma treatment can oxidize the polyester surface by breaking the ester bonds and creating radicals [31]. These radicals are able to react with the plasma gas generated and create hydroxyl, carbonyl, and carboxyl groups. These polar groups form dipolar interactions, van der Waals forces or hydrogen bonds between the fabric and the coating, thereby increasing the adhesion of the coating to the surface of the fabric [30,32]. In addition to the creation of functional groups, an increase in roughness on the surface of the fabrics takes place due to the removal of material. The rougher surface allows a better contact between the fibers and the coating and enhances its adhesion [30,31]. The novelty of the paper is the increase in the adhesion of RGO sheets to the surface of the fabrics after applying a plasma technique. The plasma treatment was combined with a bovine serum albumin (BSA) intermediate layer that converted the negative charges generated by plasma treatment on the fabric surface into positive charges, this allowed self-assembly with GO sheets that possess a negative charge before the reduction to RGO. The effect of this treatment on the electrical resistance of the modified fabrics will also be explored.

There are various plasma methods available. In the present work we have used dielectric barrier discharge (DBD). This technique is a type of cold plasma generated by an electric discharge in atmospheric conditions. Electrical discharge takes place between two electrodes separated by a small gap where the fabric is continuously treated at a controlled speed. Fabric modification by plasma methods has the advantage that no water or other chemical products are needed. The low temperature produced by DBD also allows little deterioration of organic samples [33].

2. Experimental

2.1. Reagents and materials

All the reagents used were of analytical grade.

For the synthesis: monolayer graphene oxide (GO) powders were acquired from Nanoinnova Technologies SL (Spain); sodium dithionite ($Na_2S_2O_4$) was acquired from Merck; and bovine serum albumin (BSA) was acquired from Sigma–Aldrich. The polyester fabric characteristics were: fabric surface density, 100 g m^{-2}; warp threads per cm, 55; weft threads per cm, 29. These are specific terms used in the textile industry and their meaning can be consulted in a textile glossary [34].

For the characterization: sulfuric acid (H_2SO_4) and potassium chloride (KCl) were purchased from Merck. $K_3Fe(CN)_6$ 99% was used as received from Acrōs Organics.

When needed, solutions were deoxygenated by bubbling nitrogen (N_2 premier X50S). Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q Advantage A10 system with a resistivity of nearly 18.2 MΩ cm.

2.2. Dielectric barrier discharge (DBD) treatment

Plasma treatment of polyester was carried out at atmospheric pressure with the dielectric barrier discharge modality (DBD) (Softal/University of Minho patented prototype) [35]. The laboratorial prototype machine used in this work has a width of 50 cm and consisted of the following components: a metallic electrode coated with ceramic; a metallic counter electrode coated with silicone; an electric generator and a high tension transformer. The velocity (v) and power (P) are variable and the fabric passed through the electrodes continuously. The plasma dosage was defined by the Eq. (1) [35]:

$$\text{Dosage} = \frac{N \times P}{v \times w} \quad (1)$$

where N (number of passages); P (power, W); v (velocity, m min^{-1}); and w (width, 0.5 m). For the treatment of polyester fabrics, velocity and power were maintained constant and the number of passages was varied. Table 1 shows the conditions created for the treatments.

2.3. Contact angle measurements

For measuring the contact angles of the water drops in untreated and plasma treated polyester fabrics we used Goniometer Dataphysics equipment and OCA software with a video system for the caption of images in static and dynamic modes. A drop of 5 μl of distilled water was placed on the fabric surface with a microliter syringe and observed with a special CCD camera. At least ten measurements at different places were taken for each fabric. The camera takes an image every 0.04 s.

To calculate the surface energy (γ) and its polar (γ^P) and dispersive components (γ^D) the Wu method (harmonic-mean) was used [36]. The surface energy (γ) is considered to be composed of polar and dispersive components. In particular, the polar component results from three different intermolecular forces due to permanent and induced dipoles and hydrogen bonding, whereas the dispersion (non-polar) component is due to instantaneous dipole moments. For polar solids or liquids, the total γ is a sum of the always-existing London dispersion forces (γ^D) with intermolecular interactions that depend on the chemical nature of the material, compiled as polar forces (γ^P):

$$\gamma = \gamma^D + \gamma^P \quad (2)$$

The polar and dispersive components of the surface energy (γ^D and γ^P, respectively) were calculated using the Wu method (harmonic mean) in Eq. (3):

$$\gamma_{sl} = \gamma_s + \gamma_l - 4\left[\frac{\gamma_s^D \gamma_l^D}{\gamma_s^D + \gamma_l^D} + \frac{\gamma_s^P \gamma_l^P}{\gamma_s^P + \gamma_l^P}\right] \quad (3)$$

Three liquids with known surface energy and surface energy components were used in this study to calculate the surface energy components of the fabrics: distilled water (γ: 72.8; γ^D: 29.1; γ^P: 43.7); polyethylene glycol 200 (PEG) (γ: 43.5; γ^D: 29.9; γ^P: 13.6); and glycerol (γ: 63.4; γ^D: 37.4; γ^P: 26.0). The units used are mJ m^{-2}.

Table 1
Conditions and plasma dosages applied to polyester fabrics.

Sample	Velocity (m min^{-1})	Power (W)	N° passages	Dosage (W min m^{-2})
1	0	0	0	0
2	4	1000	1	500
3	4	1000	3	1500
4	4	1000	6	3000
5	4	1000	9	4500
6	4	1000	12	6000
7	4	1000	15	7500