Tunning the surface wettability of graphene-coated polymeric substrate by plasma treatment

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Non thermal plasma[1] proposes a dry, clean, and safe method for modifying the surface of different materials[2] without changing their bulk properties[3]. This is particularly advantageous for heat-sensitive polymers commonly used in textiles, as non-thermal plasmas can be applied without to thermal damaging materials[4]. Plasma processing includes grafting[5] of reactive functional species, deposition of inorganic or organic[6] thin films and cleaning and etching. The different plasma processing can be tailored in order to engineering the polymeric surfaces. The adhesion and efficiency of a coating can be influenced by the surface's level of its wettability[7]. By the treatment of plasma, the chemical composition[8,9], and physical structure[10] of a material's surface will change, which in turn can affect its ability to facilitate the adhesion of resin coatings as well as nanoparticle inclusion.

In this work polymers are plasma treated to facilitate graphene coatings on their surfaces with the aim to control its thermal properties such as thermal conductivity and heat transfer, in view of applications in the textile sector. In details the experiments concern the plasma treatment of polymers, in a reactive oxygen gas, to enhance the surface wettability and the deposition of graphene oxide (GO) and graphite on the polymeric surfaces. Scanning electron microscope (SEM) on the polymeric surfaces for structural information, Raman spectroscopy for the control of graphene and substrate wettability analyses prior and after the graphene deposition are performed.

Equipment Setup and Methodology

Plasma treatments were carried out to check the hydrophilicity of the fabric. The experiment was performed on polyester (PET) fabric material. The sample was cut into small pieces of 6 × 6 cm^2. The Oxygen-Plasma was built with a capacitively coupled generator with an output power of 100W. The pressure was assessed by a vacuum gauge of 1.5×10^{-1} bar, and the power is supplied by a 13.56 MHz power generator. The samples were placed in the discharge tube and treated for 2 min and 4 min.

SEM has been performed for samples to investigate the structure of the polymeric substrates. We used Zeiss 500 instrument for SEM analysis. SEM analysis, which allows sample observations at different magnitudes**.**

The hydrophilicity was measured after plasma treatment by determining the water contact angle by using a demineralized water droplet of 3µl volume. An apparatus equipped with PC software SCa20 was used for taking measurements. For each sample, 5 measurements were taken in order to lower the statistical error. The droplet was dispensed on the surface of the sample. Seven samples were measured P (untreated), P2 (2 mins oxygen-plasma treated), and P4 (4 mins oxygen-plasma treated), P (untreated) coated with Graphite powder, P4 coated with graphite powder, P (untreated) with GO, P4 coated with GO.

For Graphene oxide formation, the modified hummers method was used[11]. For deposition**,** 0.05 g of Graphene Oxide and Graphite powder were dispersed in the deionized water and sonicated the solution for 30 minutes. 2 × 2 cm^2 PET fabrics (P and P4) were dipped in the solution of GO and Graphite powder for 30 mins and then dried in an oven at 40 °C for 30 minutes. This process is repeated three times to increase the deposition rate of GO and Graphite powder. After deposition, the fabrics were washed to remove the excess GO and Graphite powder and then dried again in the oven.

Results and Discussion

Raman spectroscopy was also performed on Graphite powder and GO to identify the formation of GO from graphite powder and to analyze the vibrational bands. The Raman spectrum of Graphite powder and GO is shown in Fig 1. The D and G band is observed in Fig 1 a) at 1350 cm^{-1} and 1580 cm^{-1} respectively. While the D and G bands Fig 1 b) showed at 1350 cm^{-1} and 1598 cm^{-1} respectively. The intensity of the D band of both spectrums is different. The I_D/I_G ratio of graphite powder is 0.29 and for GO is 0.9.

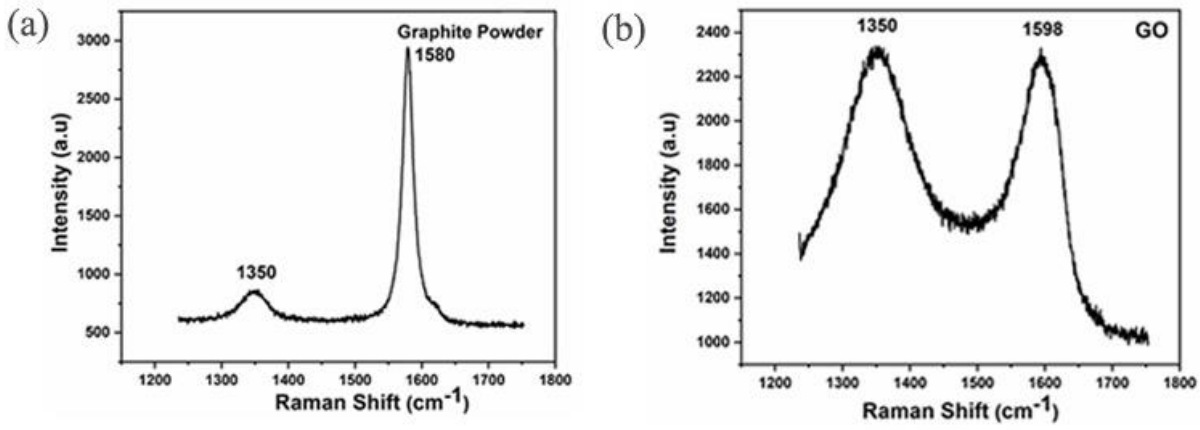

Fig 1. Raman spectra of a) Graphite Powder b) Graphene Oxide

The SEM was used to investigate the change in the surface morphology of untreated polyester fabric and oxygen-plasma treated polyester fabric at 2 mins and 4 mins. It's evident that the untreated polyester surface in Figure 2 (a-c) is smooth aside from a few dust particles. However, the 2 min oxygen- plasma treated polyester Figure 2 (d) shows a desperate change in the polyester surface. The small pores and voids can be seen on the surface of the polyester surface, these may be due to the etching effect of the oxygen plasma on the surface of the polyester. With the increase of plasma treatment time on the surface, the structure can be changed more prominently, Figure 2 (e). Thus, this roughness caused by the plasma treatment is directed to the hydrophilic nature of the polyester fabric.

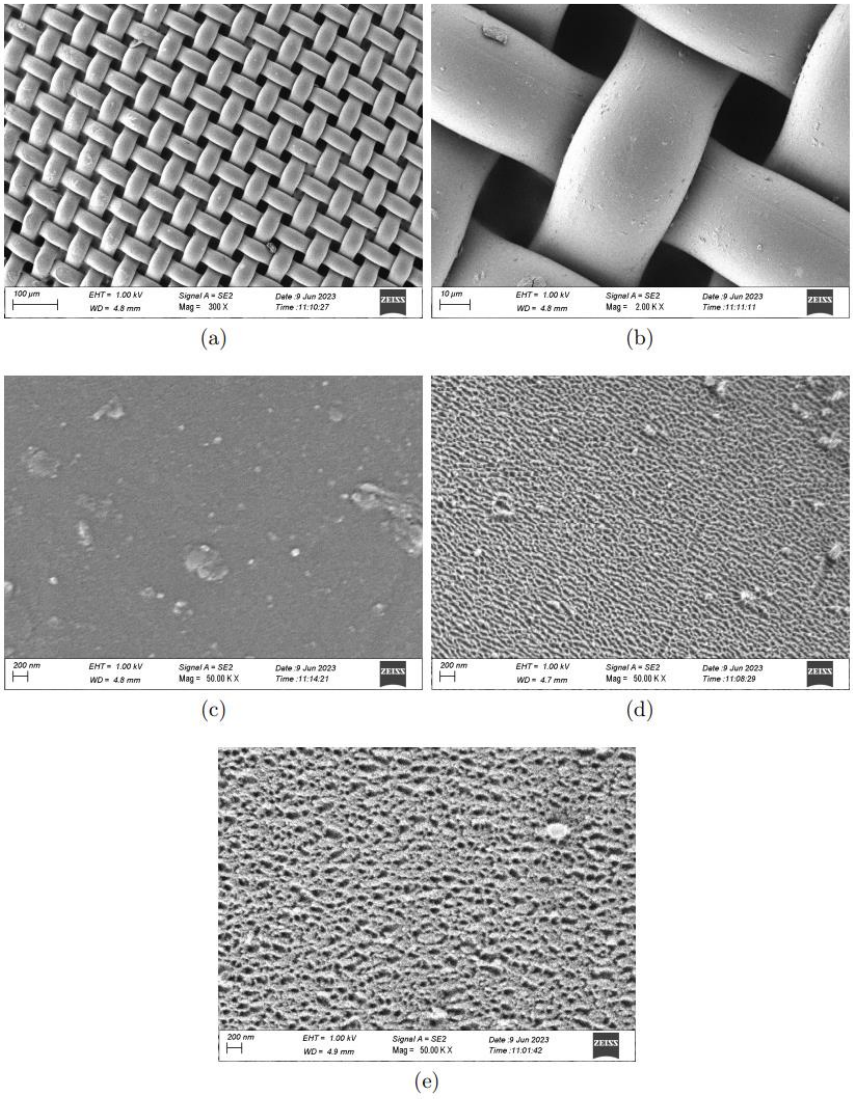

Fig 2. SEM images of (a) P (untreated) with 100 µm (b) P (untreated) with 10 µm (c) P (untreated) with 200 nm, P2 (treated 2min) with 200nm, P4 (treated 4min) with 200nm

Contact angle measurements show a decrease in angles after the plasma treatment with oxygen. The contact angle of P was 113.38˚. This is the untreated sample, and it was clearly hydrophobic. The