Plasma Surface Modification of Polypropylene for Durable Antistatic Finishing

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Abstract
Plasma surface modification of the polypropylene (PP) woven fabric was carried out using helium and oxygen gasses. Change in surface hydrophilicity after plasma treatment was measured by the wicking height measurement. Nano-Graphene was used to introduce antistatic functionality on the PP fabric. The effectiveness of the applied finish was studied by measurement of static charge development and half decay time. Change in surface morphology and chemistry was analyzed by SEM and FT-IR respectively. ISO 105- C10 (A 1) test method was adapted to assess the wash durability of the developed antistatic PP samples.

Keywords
Antistatic, Graphene, Plasma, Polypropylene (PP)

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1.0 Introduction:

The use of polypropylene is incensing in various fields like automotive, packaging, medical etc. However due to the static charge generation, low surface free energy, absence of functional groups on the polymer surface limits its application in sports and apparel next to skin garments. PP is also difficult to dye and chemical bond to any nano materials without any structural modification. Modification of the PP to conquer those problems has been tried in various ways like UV radiation grafting and electron beam irradiation[1–3], plasma surface modification and grafting[4], and application of various additives like antistatic, antioxidant, organic and inorganic fillers during melt spinning. In recent years, the use of graphene for the modification of fibre properties is gaining importance worldwide due to the extraordinary property of graphene. Graphene has found applications in electronics, data storage, supercapacitors, solar cells, wearable electronics, sensors etc [5–7.] Researchers have applied graphene on various textile fibres and studied its electrical properties. Cotton is the most studied textile fibre for graphene application followed by polyester and nylon. However, polypropylene is the least studied. Recently, modification of PP polymer with graphene oxide during met spinning has been reported. The extrusion technique is the most widely used. However, the major drawback of this technique is the aggregation and non-uniform dispersion of graphene. Therefore, there is a necessity to develop a technique to modify the PP with graphene using a suitable approach[8]. As the plasma surface treatments are known for improving the wettability or hydrophilicity of the material depending on the gas type used S. Palaskar et al. [9] have reported the change in wetting properties of the different types of PP fabric after helium plasma treatment. The surface free energy of the PP tape samples was measured by the contact angle (CA) method using different test liquids. The untreated PP tape samples showed a surface energy of 23.59 mJ/m^2 which was then increased to 33.26 mJ/m^2 after plasma exposure of 15sec at 3.5kW discharge power. Further, it was reduced to 32.87 mJ/m^2 after 28 days of ageing. It must be noted that even after 28 days of ageing the surface energy of the plasma treated sample is very high than that of the untreated samples. This shows the durability of the plasma treated samples. Likewise, other researchers have also reported the durability of the plasma modified polymeric material[10].

In the present study, we have reported the surface modification of PP woven fabric using plasma treatment and the application of nano-graphene for the development of antistatic PP fabric.

2. Materials and Methods:

2.1 Materials :

Polypropylene (PP) fabric – multifilament with 130GSM was procured from Kiran Threads Surat, Gujrat. Graphene

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nano particles were procured from Ad Nano Labs Bangalore, India. Other reagents were of laboratory grade. Plasma gasses were from INOX India Pvt. Ltd.

2.2 Plasma Treatment:

An atmospheric pressure plasma system working on the dielectric barrier discharge (DBD) principle was used for the plasma treatment of PP fabric. 50cm wide PP fabric sample was passed through the plasma zone to get treated. The plasma was generated from a mixture of helium and oxygen gasses and total plasma exposure was 30sec. at plasma generation power of 2.5kW.

2.3 Preparation of graphene solution:

Dimethylformamide (DMF) was used for making graphene solutions. 50ml of ethanol was mixed with 50ml of DMF and 0.5gm of graphene nanoparticles were added to this mixture. Dispersion of the graphene nanoparticles was done through an ultrasonication process for 60min at room temperature. The prepared solution was applied to the PP fabric by padding and curing repeated times. After the application of the graphene solution samples were washed to remove the unfixed graphene particles and prepared samples were tested for change in static charge decay using a static honestometer.

3. Results and discussion:

3.1 Wicking properties:

The wettability of the untreated and plasma treated samples was measured by the vertical capillary rise method according to ISO 9076-6:2000. Figure 1 shows the wicking heights of the untreated and plasma treated samples. As can be seen from the figure, after plasma treatment of 30sec the wicking height of the PP samples was increased from 70mm to 120mm. The increase in wetting properties can be attributed to the generation of hydrophilic functional groups after plasma treatment 11.

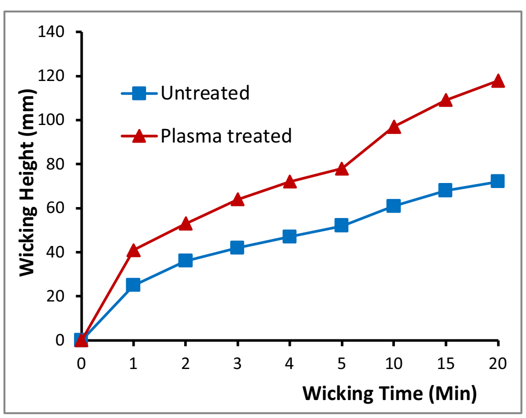

Figure 1 Wicking weight of untreated and plasma treated PP samples

3.2 Static charge measurement:

Static change developed on the untreated, graphene treated and plasma + graphene samples was measured using a static honestometer. 10kV charge was applied to the fabric and impressed peak voltage and time required for half decay was measured and shown in figure 2. As can be seen from Figure 2, the impressed peak voltage for the untreated sample was around 2500V and the time required for half decay was more than 120sec. The hydrophobic nature of the PP sample is responsible for high charge generation and holding it for a long time. However, only after plasma treatment without graphene, the impressed peak voltage was reduced to 2200V.

It was observed that for graphene treated samples the impressed peak voltage was reduced significantly. Further, it can be seen from Figure 2 that the samples treated with plasma + graphene have the lowest impressed peak voltage. This may be due to better impregnation of the graphene inside the sample.

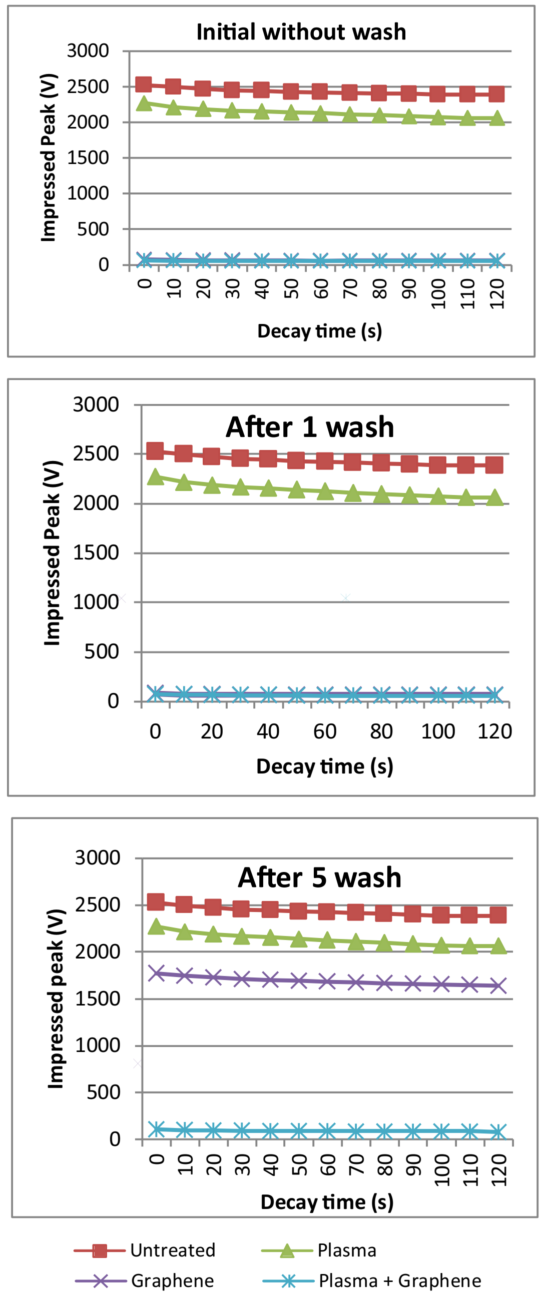

Figure 2. Static decay charge of the untreated and plasma treated PP samples. Durability to washing.

Washing of the plasma + graphene treated samples was carried out as per ISO 105 standard test method at 40°C for 30 min and after drying the samples overnight static charge was measured again. It can be seen from Figure 2, that after 1 washing graphene treated as well as plasma+ graphene treated samples are showing the same results and good resistance to washing. However, after 5 washing cycles, the graphene treated sample showed an impressed peak voltage of around 1700V and lost its antistatic properties. On the other hand, plasma+ graphene treated samples showed no change in impressed peak voltage and it was very low even after 5 washing cycles. This could be attributed to better adhesion of graphene nanoparticles on the plasma treated samples. Plasma treatment can improve the adhesion and increase the durability as reported in the published literature[12].

3.3 Surface Morphology by Scanning Electron Microscopy (SEM)

The surface morphology of the treated samples was studied by scanning electron microscopy. Figure 3 demonstrates SEM micrographs of the graphene (3-A) and Plasma+ graphene (3-B) treated PP samples. It can be observed that more graphene nanoparticles have adhered to plasma treated sample than that of the only graphene treated sample. This could be due to the improved wettability of the plasma treated samples as shown by the wicking measurements. This higher adsorption of the graphene nanoparticles is mainly responsible for reduced impressed peak voltage and improved antistatic properties.

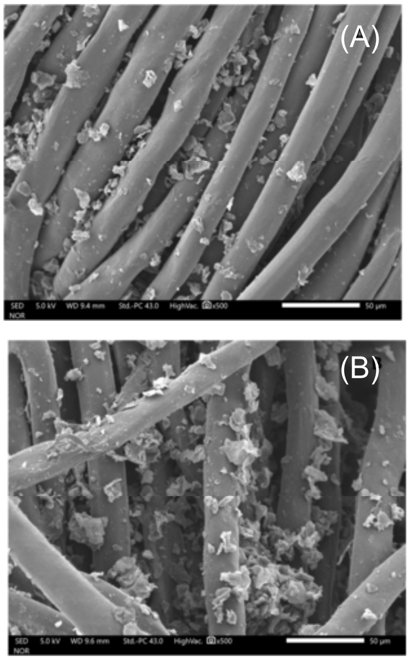

Figure 3. SEM images of the graphene (A), Plasma +Graphene (B) treated samples

3.4 Fourier transform infrared spectroscopy study (FTIR)

Perkin- Elmer FTIR spectrometer was used for recording the ATR-FTIR spectra of the untreated and plasma treated PP samples. Characteristic peaks of PP polymer can be seen at peak positions 2950, 2918, 2868,2839, 1454 and 1375 cm^{-1} for untreated as well as for plasma treated samples as depicted in Figure 4. Apart from the characteristic peaks, addition peaks at 1734 and 1103 cm^{-1} can be seen for plasma treated samples in Figure 4. Symmetrical vibrations of the C=O carbonyl group are responsible for peak at 1734cm^{-1}, which shows the surface oxidation after plasma treatment and hence improved wettability [13].

The peak at 1103cm^{-1} is attributed to ester C–O–C bond stretchings [14].

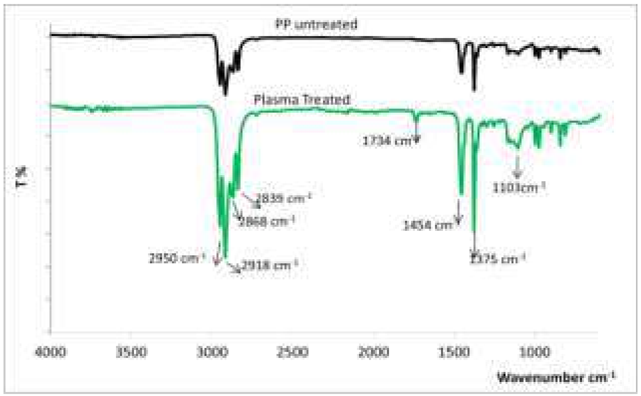

Figure 4. ATR- FTIR spectra of the untreated and plasma treated PP samples

4.0 Conclusions:

Antistatic finishing of the plasma surface modified PP fabric was carried out using graphene nanoparticles. The wettability of the PP samples was found to be increased after plasma treatment with helium and oxygen. The impressed peak voltage of the graphene treated as well as plasma + graphene treated samples was found to be reduced significantly before washing. Plasma + graphene treated samples showed durability to washing up to 5 washing cycles. Further, SEM results proved more deposition of the graphene nanoparticles on the plasma treated sample. ATR-FTIR results showed the additional peak at 1734 and 1103cm^{-1} which is mainly responsible for improved wettability and adhesion of graphene nanoparticles onto the surface of plasma treated PP sample.

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