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Surface Modification of Polymers and Textiles by Atmospheric Pressure Argon Glow Discharge

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Abstract
The aim of the present work was the study of the surface modification of polymers and textiles in order to improve their hydrophilic properties. Atmospheric pressure argon glow discharges were applied for the surface modification of four different types of polymers: low density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalet (PET) polytetrafluoroethylene (PTFE) and three different types of protective textiles made of Ultra High Molecular Weight Polyethylene (UHMWPE). The effect of treatment time and applied power on the surface properties of these materials were investigated by contact angle measurement & scanning electron microscopy (SEM) analysis. Contact angles with water and glycerol were used to determine the surface free energy of the sample. The results indicated that few seconds of exposure time was sufficient to make significant improvement in hydrophilicity of the sample. SEM images indicated that the surface roughness significantly increases after the treatment.

Key Words: LDPE, PP, PET and PTFE polymers, DynemaSB21, DynemaSB51 and DynemaSB71 textiles, surface modification, Wettability,

1. Introduction

Polymers have a wide range of applications because of their attractive characteristics that include flexibility, transparency, softness, low density, and cost effectiveness. However, their surface properties often do not meet the demands regarding scratch resistance, wettability, gas transmission and friction. Hence surface modification is required to achieve the desired properties while maintaining the characteristics of bulk. The main purpose of surface modification of polymer used as reinforcement in composite materials is to modify chemical and physical structures of their layer, matrix bonding strength. The important advantage of using plasma for surface modification is that it alters only outermost layer of the sample and leaves the bulk properly unchanged. It offers a better uniformity, reproducibility and controllability compared to other conventional methods such as wet chemical treatment, mechanical treatment, mechanical roughing and treatment by flame etc. [1-3]. The advantage of surface treatment using non-equilibrium plasma is also the low temperature of reactive species. In this discharge, the electrons have and energy less than 1.0 eV whereas the gas temperature is much lower around 300 K.The high value of electron temperature is due to the electric field so that electron impact collisions create active species while the gas remains at a low temperature. In general at atmospheric pressure, given the high gas density, large currents can heatthe electrodes and result in a thermionic emission of electrons. Therefore thermal arcs carrying a considerable current are likely to exist. The dielectric barrier limits the current through the gas in order to avoid the thermalization and surface damages [4].

Atmospheric pressure surface treatment in open vessel has been widely studied in DBDs at 10 kHz [5-10] and in RF capacitive discharges with dielectric barrier [11]. In both cases the interaction of the plasma with the polymer surface increases its wettability. In this paper, results of surface modification of polymers and ballistic textile by APGD treatment have been reported.

2. Experimental Setup

Parallel disc electrode system was fabricated for the generation of glow discharge at atmospheric pressure. The schematic diagram of the experimental arrangement used to study the APGD is shown in Fig. 1(a).

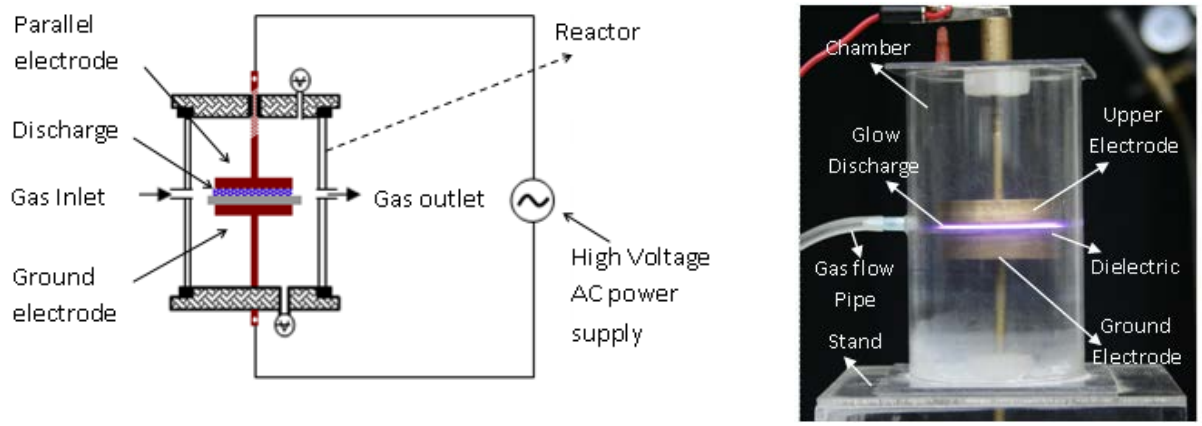


Figure 1: (a) Schematic diagram of experimental setup and (b) Discharge of parallel disc electrode system

The discharge is generated between two symmetric parallel electrodes. The electrodes are made of brass with smooth surface. They have diameter of 50 mm and thickness of 10 mm. The lower electrode is fixed and the upper one is movable with pitch of 0.5 mm. Glass plate of thickness 2 mm is used as the dielectric. A high voltage AC power supply is used and the applied voltage is in the range of 1 to 2 kV at a frequency of 30 kHz. The gap between the electrodes can be varied from 0.5 mm to 2 mm and argon gas is fed at a flow rate of 1 lit/min. A high voltage probe is used to measure the voltage applied across the electrodes while the discharge current is measured by using a shunt resistor at the earth side of the discharge tube. The signals are recorded using a Tektronix TDS2002 digital oscilloscope. The discharge obtained in the hemispherical electrode system is shown in Fig. 1(b).

3. Sample preparation

Commercially available low density polyethylene (LDPE) films of thickness 0.01 mm and with dimensions 3 cm × 2.5 cm from Good fellow Ltd., UK are used as samples for plasma treatment. Before the treatment, the samples are washed in propylene and then washed in distilled water, ultrasonicated for ten minutes, and dried at room temperature. Other polymers PP, PET and PTFE are also washed in propylene and distilled water in same way.

4. Surface Characterization

The effect of plasma treatment was studied by measuring the contact angle of the untreated and treated samples with doubly distilled water & glycerol. Sessile drops volume 4µl were made using a standard micro-syringe. The contact angle of drops with the surface of the flat polymer sheet was measured using a rame'- hart Contact Angle Goniometer model 200. This unit is equipped with standard software to analyze the drop image for the calculation of surface energy. Surface energy of the untreated and treated samples was calculated using the two liquid models.

Surface free energy can be calculated in terms of polar and dispersion componentswith the use of Fowke's equation [11]. The topography of the HDPE surface before and after the treatment was investigated by using a SEM (Leo 500 microscope) in ambient conditions.

5. Result and Discussion

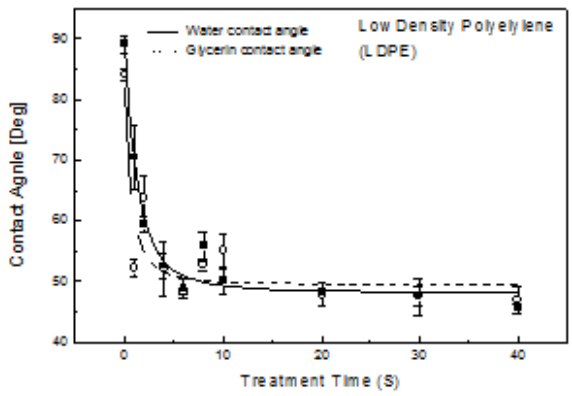
5.1 Surface Modification of Polymers by APGD in Argon

Figs., 2(a) and 2(b) show the variation of static water and glycerin contact angle on the surface of the LDPE and PET polymer film respectively with the APGD treatment time. It is seen that decrease in contact angle takes place with the treatment of 10s to 15s, which suggests that a strong increase of wettability in the samples LDPE and PET surface induced by the APGD treatment. The static contact angle found to change form 89^o for untreated samples to 48^o after the treatment for LDPE. Similarly, contact angle is found to change from 62^o to 42^o respectively in PET. When the treatment time exceeds 10s to 15s, the measured static contact angles reached a saturation state which means the physical and chemical changes induced by the plasma are also in saturation state when the plasma dose is inexcess of a certain critical value.

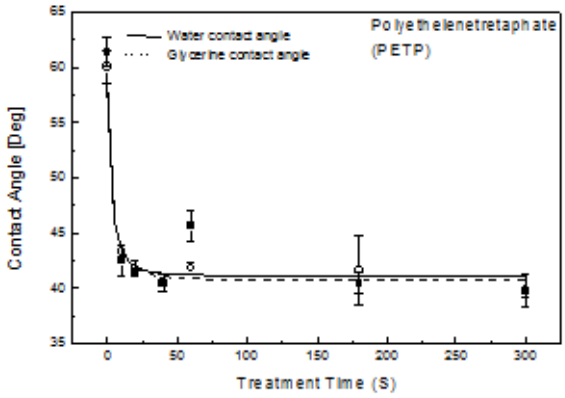
Figs. 2(c) and 2(d) show the variation of static water and glycerin contact angle onthe surface of the PP and PTFE polymer film respectively with the APGD treatment time. In case of PP and PTFE, saturation state of contact angle is after 180s and it changes from 129^o to 88^o and 112^o to 73^o respectively.

Figs. 3(a), and 3(b) show the variation of dispersive, polar and total surface free energy of LDPE and PET polymer film respectively with the APGD .treatment time. The total surface energy is increased form 19mJ/m^2 to 55 mJ/m^2, 47 mJ/m^2 to 59 mJ/m^2 in LDPE and PTFE respectively.

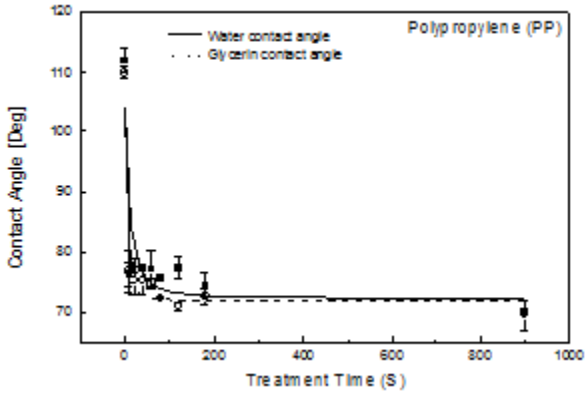
Figs. 3(c) and 3(d) show the variation of dispersive, polar and total surface free energy of PP and PTFE polymer film respectively with the APGD treatment time. In the case of PP and PTFE, total surface energy increased only 24 mJ/m^2 to 37 mJ/m^2 and 20 mJ/m^2 to 30 mJ/m^2 respectively. So, the APGD treatment is more effective in LDPE and PET in comparison to PP and PTFE.



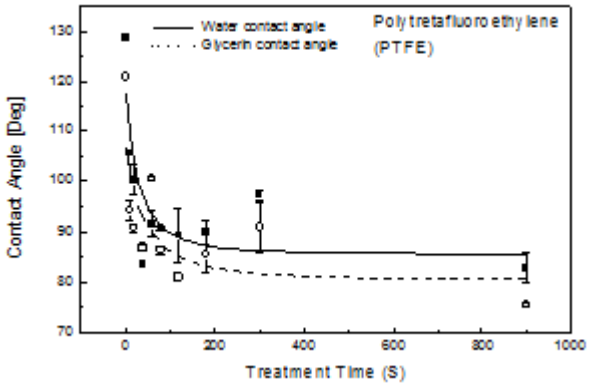
2(a)



2(b)

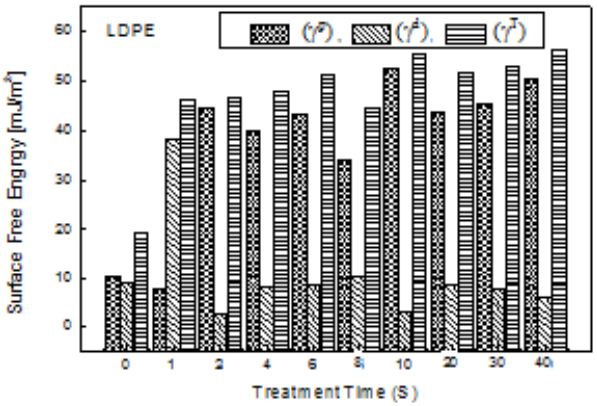


2(c)

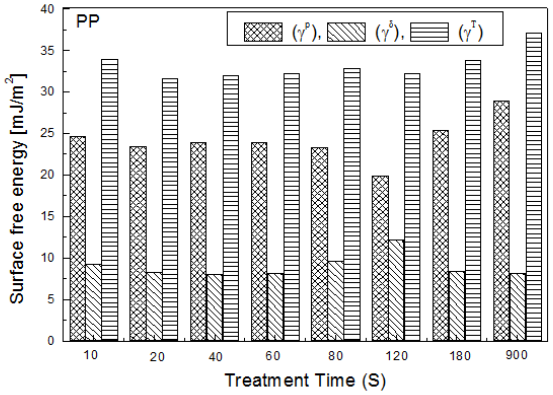


2(d)

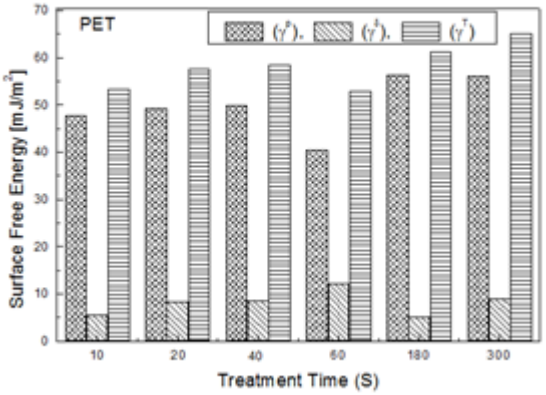
Figure 2: Water and glycerin contact angle on polymers as a function of treatment time in APGD



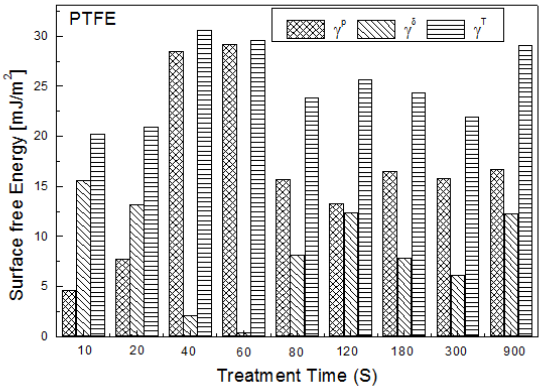
3(a)



3(b)



3(c)



3(d)

Figure 3: Polar and dispersive components of surface free energy of Polymers as a function of treatment time in APGD

5.2 Surface Morphology

SEM is simply an electron microscope that produces images of a sample by scanningit with a focused beam of electrons. The electron interact with atoms in the sample, producing various signals that can be detected and traced the image about the samplesurface topography and composition. Figs. 4(a) and 4(b) show the SEM micrographs of the LDPE and PTFE surface untreated and after APGD treatments. The topology of the untreated LDPE as Fig. 5(a) on the left side appears to be comparatively smooth. But after APGD treatment, the surface is etched uniformly and the surface roughnessis increased as Fig. (5a) on the right side. The surface roughness also increased in PTFE samples. The APGD can generate a wide range of active species includingatomic oxygen, ozone, nitrogen oxides, neutral and metastable molecules, radicals andultraviolet radiation in its discharge regimes [13-14].

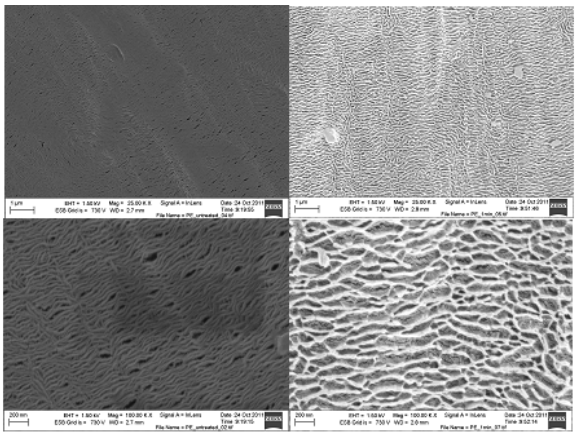


Figure 4(a) SEM image of untreated (left) and plasma treated (right) sample of LDPE

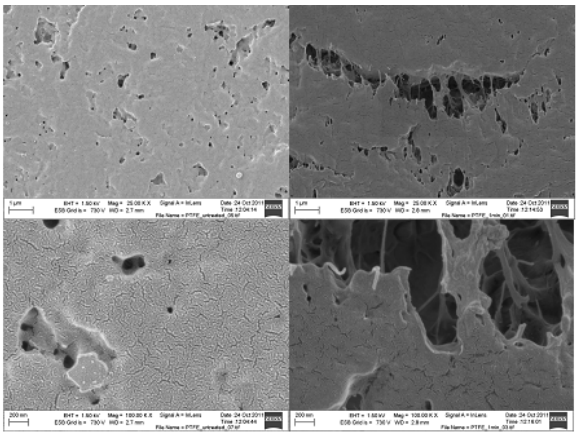
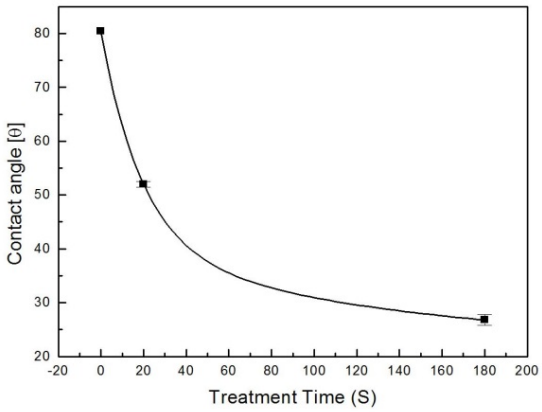


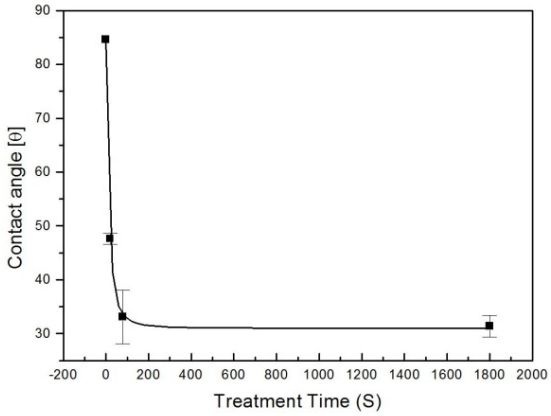
Figure 4(b) SEM image of untreated (left) and plasma treated (right) sample of PTFE

5.3 Surface Modification of Textiles by APGD

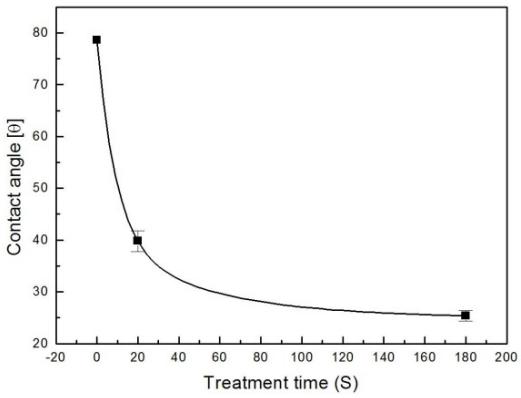
Three materials DynemaSB21, DynemaSB51, DynemaSB71 were investigated fortheir surface properties before and after the plasma treatment. These are special fabricscalled ballistic textiles. They are made of Ultra High Molecular Weight Polyethylene (UHMWPE) introduced into the binder of polyethylene with low molecular weight. Fibres are parallel arranged in one layer, the material is made of 4 layers of UHMWPE fibres, and every layer is twisted 90^{o} degree compared to previous one. The only difference between SB21, SB51, SB71 is the amount of applied binder. The influence oftreatment duration and atmosphere on materials hydrophilicity / hydrophobicity was tested. In this section, Figs. 5(a) to 5(f) show the measurement of contact angle of the DynemaSB21, DynemaSB51 and DynemaSB71 in air and argon at atmospheric pressureglow discharge.



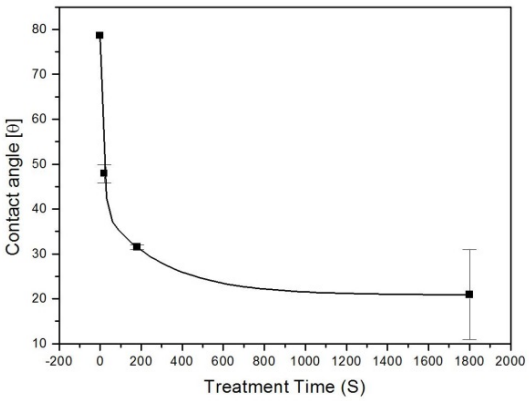
5(a) Dynema SB21treated in air



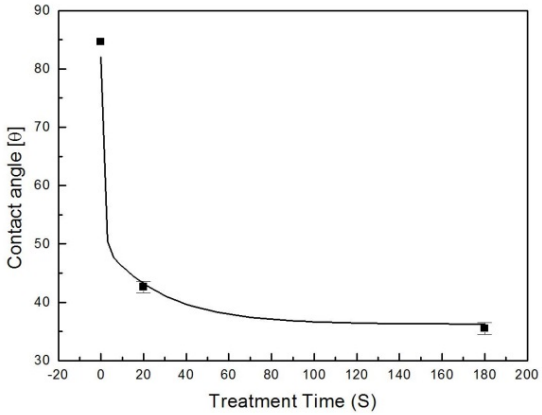
5(b) Dynema SB21 treated in air



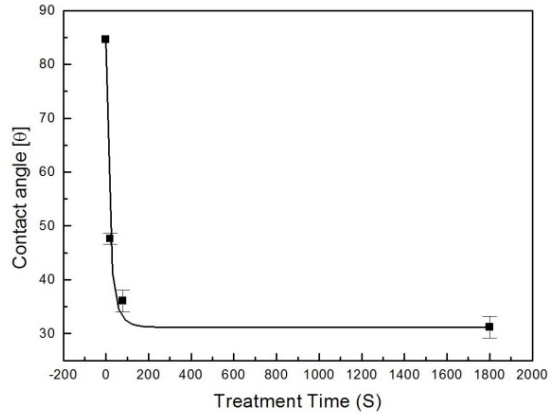
5(c) Dynema SB51treated in air



5(d) Dynema SB51treated in argon



5(e) DynemaSB71 treated in air



5(f) DynemaSB71 treated in argon

Figure 5: Water contact angle on sample as a function of treatment time

The electrode gap is 2 mm. These results clearly show that plasma treatment produces astrong effect on the hydrophilicity of polymer. In air plasma, contact angles decreased from 82^o to 28^o, 78^o to 26^o and 85^o to 37^o after three minute treatment of the samples DynemaSB21, DynemaSB51 and DynemaSB71 respectively. But, the samples were physically damaged for thirty minutes of treatment in air plasma. In case of argonplasma, the contact angles were found to decrease 34^o, 32^o and 35^o after three minutesof treatment. These results indicate that treatment in argon plasma is more homogeneousthan the treatment in air plasma.Fig. 6 presents changes of drop on the materials surface after Ar treatment in atmospheric pressure reactor. Figs. 8 show the SEM micrographs of the DynemaSB51 protective textile. Fig. 7(a) is SEM micropgraph of untreated sample and Figs. 7(b-d) are SEM micrograph of treated samples in 20s, 3min and 30min respectively. It is evident that thesurface roughness has increased after the treatment.

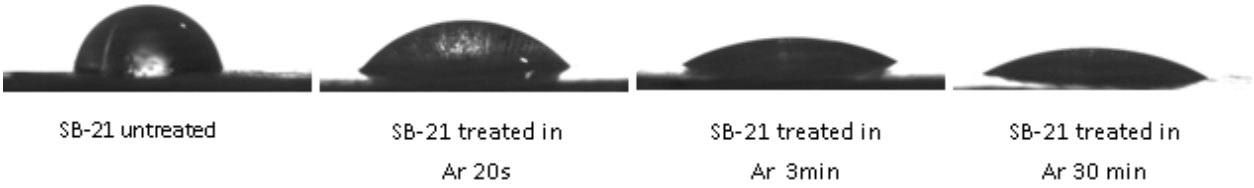


Figure 6: Water contact angle before treatment after treatment

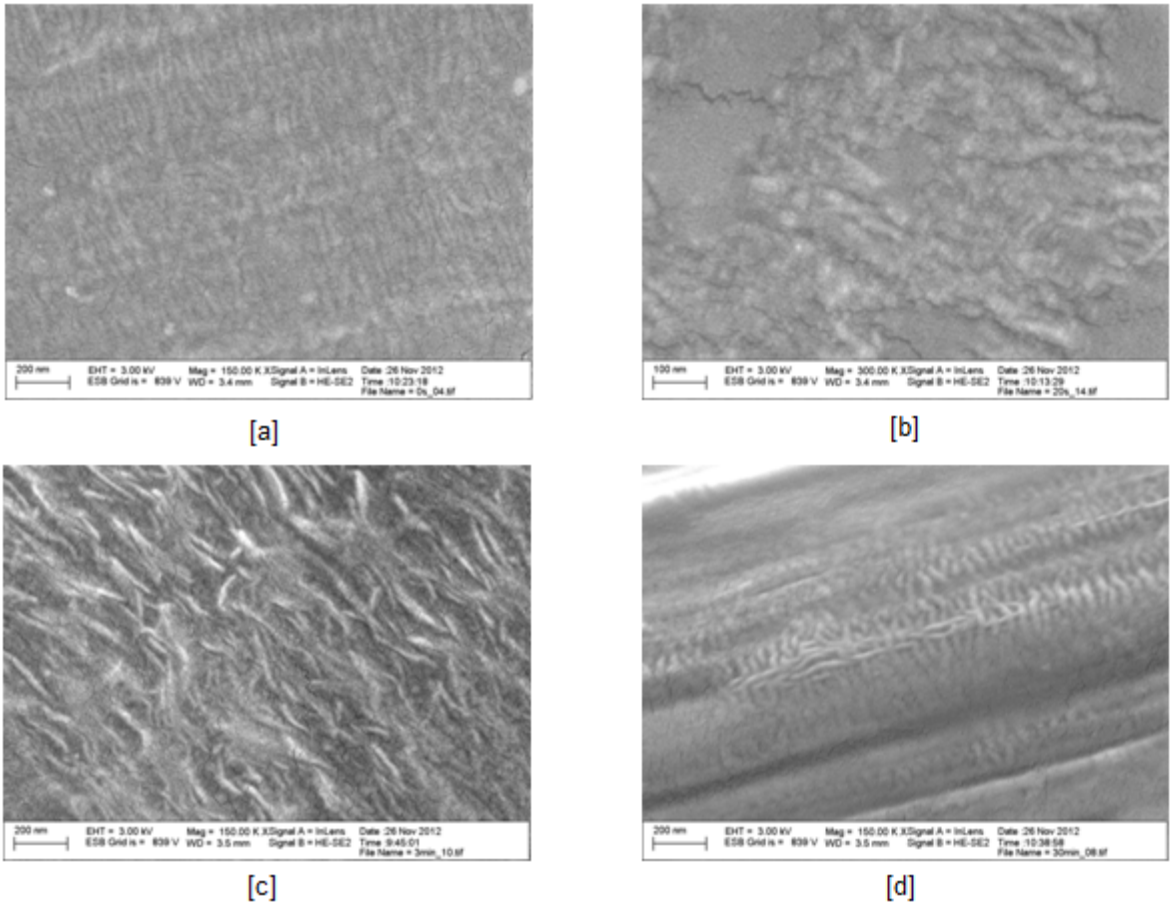


Figure 7: SEM image of DynemaSB51 (a) Untreated, (b) 20 s treatment (c) 3 min treatment and (d) 30 min treatment

6. Conclusion:

The other important aspect of the present study was the application of APGD for the surface modification of some selected polymers namely; LDPE, PP, PET, PTFE and textile DynemaSB21, DynemaSB51, DynemaSB71 in order to improve their wettability. Exposure of these polymers surface to APGD resulted a remarkable increase in surface free energy of the sample. Effect of treatment time and applied power on thewettability was investigated. It was found that few second of exposure to the dischargewas enough to ensure a significant improvement in wettability. Study of effect of appliedpower showed that surface energy increases linearly with applied power. A studyof the stability of the modified surface with respect to its wettability clearly indicated that the modified surface recovers a significant fraction of its original hydrophobicity within the first few days after treatment. Wettability of textiles was also improved after the treatment on atmospheric pressure plasma.

Acknowledgements
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