NANOTEXTURING OF HIGH-PERFORMANCE WOVEN FABRICS FOR NOVEL COMPOSITE APPLICATIONS

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ABSTRACT

Nanotechnology offers the ability to create new material systems as well as dramatically improve the performance of existing systems through the introduction of new physical mechanisms not found in the original material. Nanomaterial modification of fibers and textiles has been used to increase fabric performance in areas ranging from biocidal capability to stain resistance and water repellency. In this study we use scalable methods to modify nanoscale features on organic materials to probe the potential for increased impact energy absorption and mechanical properties in composite applications. Specifically atmospheric plasma treatment and wet-chemistry methods were utilized to create nanoscale chemical scaffolding and surface textures on model polyethylene films and fibers. This approach was successful at modifying the surfaces of these fibers and scaling to high speed web manufacturing is easily envisioned.

1. INTRODUCTION

Organic fibers, due to their inherently low surface energy and chemical inertness, have generally required elaborate surface modification schemes to optimize favorable fiber-matrix interactions (Brown et al., 1991). However, their more widespread use is limited by poor interfacial adhesion to some polymer matrix materials, relative low thermal resistance, and low mechanical strength. Fiber-matrix adhesion in advanced composites depends on the physical and chemical interactions at their interface and efforts have been made to fully characterize the surface energetics of fibers to identify the relationship between wetting behavior and interfacial bond strengths. Polymer films also have poor adhesion properties but they are easier to modify due to their geometric uniformity compared to fabrics.

Low pressure plasma methods have been studied as a technique to modify polymeric surface properties. Plasma is a quasi-neutral gas, consisting of a single gas or a mixture of different gases, which emits light under the presence of an external electric field. A material exposed to such an environment will sustain the attack of plasma reactive species, such as ions, electrons, excited atoms and molecules and neutrals. Plasma modification results in tailoring fiber-matrix strength (Park et al., 2003) without affecting the bulk properties of the fiber. It is a technique employed to modify their surfaces and enhance properties such as the following; adhesive bonding, durability, wettability, biocompatibility, and adhesion of dyes. At the same time the glow discharge assists in the removal of a weak boundary layer (WBL) residing on the surface serving as a cleaning process as well. It is an alternative method to wet chemical treatments providing a uniform modification, is not environmentally hazardous, requires short process times, and avoids some of the complexities of low pressure (vacuum) plasma.

These methods can increase polymer surface roughness (plasma etching), introduce chemical functional groups, polymerize or cross-link, deposit coatings, and promote adhesion in fiber composites. The requirement for high vacuum presents some challenges for high-throughput applications. To overcome these possible limitations atmospheric plasma treatment has been gaining more popularity and is the subject of the present research.

An atmospheric plasma system for surface treatments was used here. The gases, He and He-O_2 in this case, were used to form a dielectric barrier discharge (DBD). The films and fibers were exposed to the plasma created between this electrode and a second electrode covered by a dielectric layer. The plasma modified surfaces were subsequently coated with nanoscale inorganic-organic coatings containing colloidal silica and to covalently bond and texture the surface of the fibers.

In this paper, we discuss the physicochemical modification of on polyethylene (PE) textiles and films exposed to atmospheric pressure plasmas, a field that is still poorly understood and we attempt to scale up the process by using an industrial type system, designed to plasma treat polymer films and woven fabrics up to 0.5 m wide at an average speed of 5 m/min.

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2. EXPERIMENTAL

The atmospheric plasma system used for the surface treatments was a Sigma Technologies large scale plasma system. The gases, He and He-O_2 in this case, were injected into the electrode at atmospheric pressure and allowed to diffuse, forming a filamentary glow discharge. Helium is typically used to initiate and generate the plasma at atmospheric pressure before another gas is introduced to the system. The operating frequency was 90 kHz with an operating power of 1050 W.

Ultra High Modulus Polyethylene fibers (UHMPE), having an average diameter of 100 μm and Ultra High Molecular Weight (UHMW) Polyethylene films (Goodfellow, 75 μm thick) were exposed to the plasma created between the above described electrode and a second electrode covered by an alumina layer.

Near surface compositional depth profiling was performed using the Kratos Axis Ultra 165 X-ray photoelectron spectroscopy system, equipped with a hemispherical analyzer. A 100 W monochromatic A1 Ka (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area and the take-off angle was 90°. Elemental high resolution scans for C1s, O1s, N1s, and Si2p were taken at the pass energy of 20 eV.

The morphological changes of plasma treated polyethylene surfaces were observed using scanning electron miscroscopy (SEM). A field emission scanning electron microscope (Hitachi, model S4700) was used in secondary electron mode, using mixed of upper and lower detectors. The magnification ranged from 2500x up to 100,000x and the working distance varied from 3mm to 9mm. Accelerating voltage could not be greater than 2 keV as damage to the substrate surface was observed. Approximately 1cm^2 polyethylene samples were cut and adhered to aluminum posts with carbon tape. Samples were stored in a dry box in order to limit exposure to moisture and other contaminants. Several areas on each sample were investigated in order to discern the uniformity of the untreated and plasma treated surfaces.

ATR-FTIR spectra were obtained using a Thermo Electron Nicolet 380 FT-IR spectrometer, using a single bounce SmartOrbit diamond ATR fixture. A spectral window of 525 – 4000 cm^{-1} was analyzed for each film sample, using 32 scans with 4cm^{-1} resolution. Quantification of silica content was determined as a ratio of CH_2 peak symmetric and asymmetric stretches (2800-3000 cm^{-1}), compared to the signal arising from the silica component (1010 – 1370 cm^{-1}). The value of this ratio for each film was compared, to provide relative levels of silica attachment.

Plasma treated substrates were functionalized with silica according to the following two-stage procedure. In the first stage, a 1% solution of glycidoxypropyltrimethoxy silane (GPS, Alfa Aesar) in methanol was prepared, and the plasma treated films were immersed for one minute. After air drying, the films were placed into an oven to dry and fully cure at 70 °C for 60 minutes.

The second stage of treatment required the preparation of a solution of colloidal silica (Ludox, Aldrich). A 1% solids solution was prepared, using a 90/10 ethanol/water solution with a pH adjusted to 4.5 as the solvent. The GPS-treated films were immersed in the colloidal silica solution for one minute, and were then allowed to air dry. The films were then dried and fully cured in an oven at 70 °C for 60 minutes.

RBS measurements were done using a 1.2 MeV He+ ion beam from a National Electrostatics 5SDH-2 tandem positive ion accelerator. The backscattering angle was 170 degrees, and the solid angle of the surface barrier detector was approximately 4 millisteradians. All spectra were fit and interpreted using the program RUMP (Doolittle, 1986). The areal densities of the coatings measured by RBS were converted to physical thicknesses assuming a typical density for the film studied (2.65 g/cm^3 for silica).

3. RESULTS AND DISCUSSION

3.1 Plasma treatment and surface characterization of polyethylene films

At atmospheric pressure, due to the high collision rates between the plasma species a growing electron avalanche can generate high charge density at its tip, a phenomenon known as streamer formation. The difference in drift velocities of electrons and ions, due to their mobility, is superimposed on the applied local electric field. Collisional ionization in the high-field region of the streamer leads to a fast propagation of the ionization path and the formation of an intense plasma channel.

The SEM micrographs shown below (figures 1a and 1b), taken at a 5000x magnification while the working distance was 3 mm, are a representation of these electron avalanches, similar to the Lichtenberg figures used to footprint the filamentary discharge (Kogelschatz, 2002). The untreated PE film is fairly smooth, with no particular features, as seen in picture 1a, compared to the plasma treated under He-O_2 for 9 seconds, film. The latter exhibits the formation of micropits having an average size of 5 μm, cause by the plasma exposure. The formation of these crater-like features is evident even when the samples were exposed to the discharge for limited time, as

short as 3 seconds. The increased roughness of the plasma modified sample (McCord et al., 2002) proposes that it could be an ideal candidate in composite applications, as a larger area is now available to react.

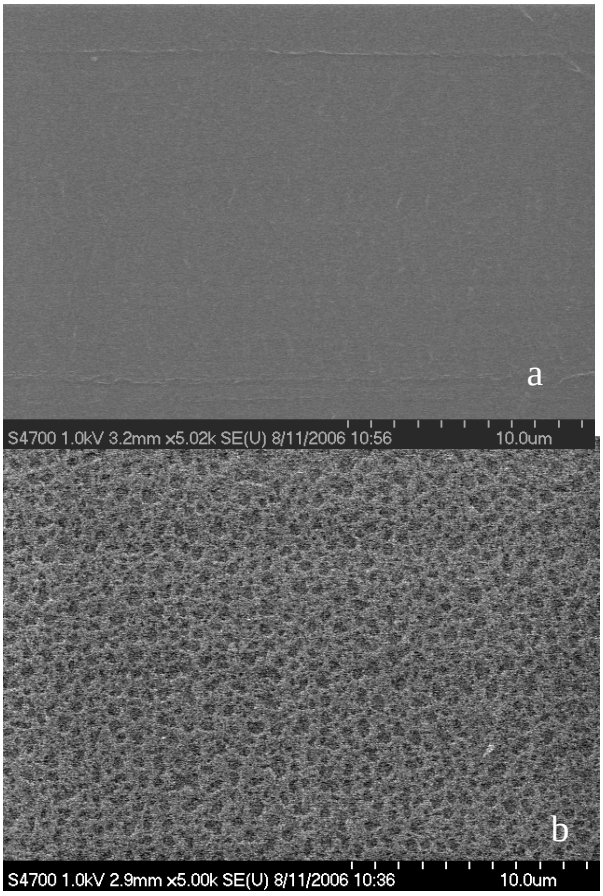


Figure 1a and b. Top: SEM micrograph of control PE film; bottom: plasma treated PE under He-O_2 plasma for 9 seconds (O_2/He=0.6%).

The formation of the craters seen in figure 1b cannot be solely attributed to the streamers impact. We expect an activation process and mild surface etching due to plasma exposure. Atomic oxygen is known to cause etching of polymer surface when present in the discharge (Yip et al., 2004). The role of helium is to remove any surface residing impurities and through energy transfer mechanisms to cause chain scission and the formation of crosslinked layers on the polymer surfaces. These layers provide stability to the material and act as a barrier to surface changes. Moreover, helium is expected to impose Penning ionization to other molecules present –mainly O_2 (Arefi-Khonsari et al., 1998). Therefore, the combined action of helium and oxygen results in cleaning, etching and activation of the surface.

XPS results reveal that the modified surfaces exhibit a surface rich in oxygen containing groups. It is suggested that the plasma treatment induced the formation of carboxylic species on the surface, which finally enhances the hydrophilicity of the polymer. The oxygen uptake can be attributed to either/or both the presence of atomic oxygen during the process, resulting from the reactions in the bulk plasma area O_2, and/or the reaction of the resulting "active" surface obtained after the plasma modification. It is known that the plasma treatment is responsible for chain scission on the polymer surface and thus, during the post treatment process, can react with the environment prior to reaching equilibrium.

The graph below (Figure 2a and b) is the XPS survey spectrum showing the increase of the oxygen concentration on the polyethylene film surface, due to the plasma treatment. The control film contained traces of oxygen-probably obtained from the cleaning process prior to plasma exposure- of less than 1%, observed at 532 eV, as demonstrated in figure 1b. It shows the survey spectrum of a polyethylene film treated under He-O_2, where the oxygen percentage was only 0.6% in the gas mixture.

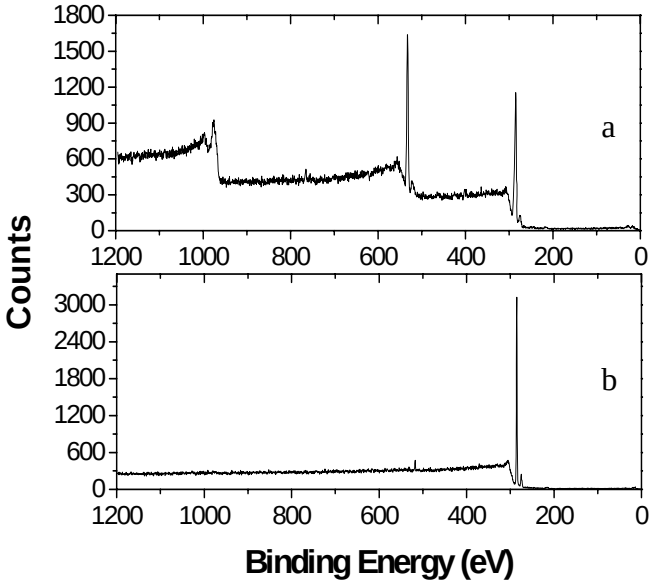
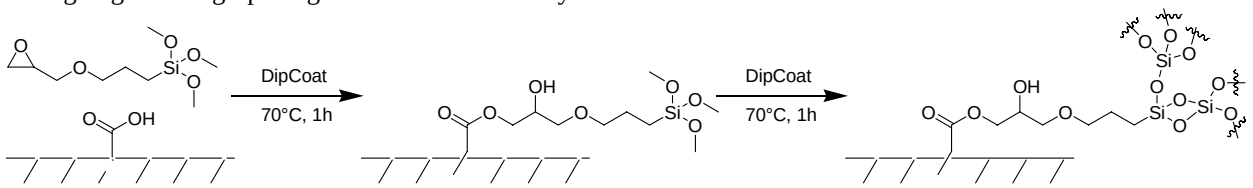


Figure 2. XPS survey spectra for the control PE film (lower graph) and a He-O_2 plasma treated film (upper graph) for 81 sec.

After the plasma treatment the carbon content of the surface decreases, giving rise to the increased oxygen content. We observed a dependence of the oxygen concentration on the treatment time; the longer the plasma exposure, the greater the degree of surface oxidation. A saturation point is reached when the substrate material is treated for times longer than 81 s; further treatment does not increase the intensity of the O1s peak. This result is not surprising, as there is a limited number of sites on the polymer backbone where oxygen functionalities can be grafted. Therefore, a further increase of the oxygen feed

in the gas mixture or longer treatment times will no longer have an impact on the surface chemistry.

Subsequently, as plasma treatment of the films installed many oxygen containing functional groups on the film surface, an attempt was made to coat the films with silica, something that could not be done before, due to the inertness of the untreated films. The films were immersed in a 1% solution of glycidoxypropyltrimethoxy silane (GPS) in methanol and then dried for one hour. The GPS reacted with the available acid groups, undergoing a ring-opening reaction driven by the dissociation of the proton from the surface-bound acids (Scheme 1, first step). The films, now functionalized with the methoxy silane groups, were immersed in a 1% suspension of colloidal silica in 90:10 EtOH:H_2O, with a pH of 4.5. The mildly acidic conditions began hydrolysis of the GPS methoxy groups, and allowed for the covalent attachment of the colloidal silica to the film surface. The hydrolytic exchange was driven to completion during a one hour heat treatment at 70 °C, resulting in a film functionalized with covalently attached colloidal particles.



Scheme 1: Attachment of silane coupling agent and silica on PE films after plasma treatment.

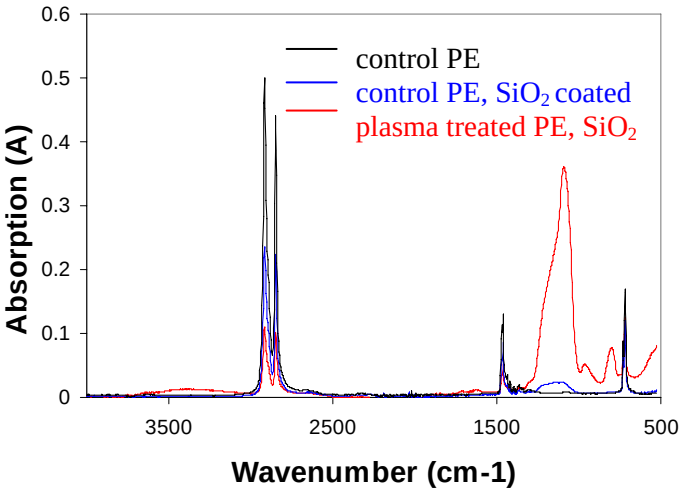


Figure 3. ATR-FTIR spectrum of control PE (black), control coated with silica (blue) and plasma treated under He-O_2 for 9 seconds (red).

The successful attachment of SiO_2 was confirmed by infrared spectroscopy. The results from representative ATR-FTIR spectra are shown in Figure 3, including those for unmodified PE, PE + silica/GPS without plasma treatment, and PE+silica/GPS after plasma treatment. The symmetric and asymmetric stretches arising from the methylene groups of the PE backbone are clearly observed at 2848 and 2915 cm^{-1}, respectively. The base PE material also demonstrates no absorption in the broad region around 1100 cm^{-1} where the signal for silica-based material is observed (Hikita et al., 2005). By using the summation of the two strong methylene stretches as an internal standard, the amount of bound silica to the surface has been quantified in relative terms. Comparing the non-plasma treated sample, which underwent the same wet chemistry treatments used to install the colloidal silica, an enhancement of ca. 18-fold was observed for the plasma treated sample.

Rutherford backscattering spectroscopy was used in this study to measure the relative concentration of silicon (Dennler et al., 2002) with respect to the lighter elements, carbon and oxygen in our case, composing the substrate after the plasma treatment. We have chosen to work with 1.2 MeV ions, because this allowed us to have a large enough gap between silicon and oxygen peaks and avoid their overlapping in case of thicker layers.

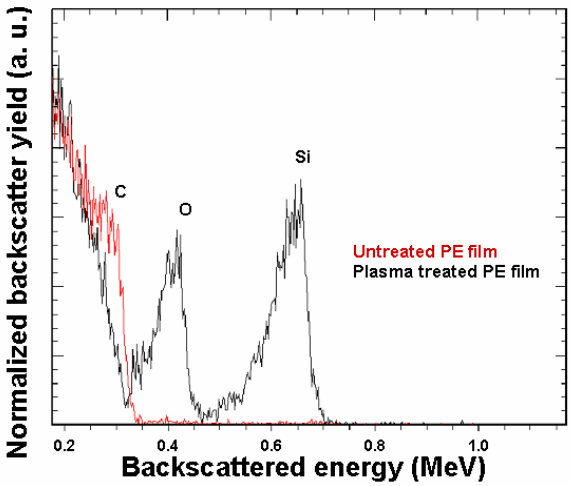


Figure 4. RBS spectrum of control PE (red) coated with silica, and plasma treated under He-O_2 for 9 seconds and coated with SiO_2 (black).

There are no signs of silica attachment of the non plasma treated PE films, as expected. The RBS spectrum of the sample that was plasma modified under He-O_2 plasma for a treatment time of 9 s and then reacted with the silane coupling agent and the silica solution, shown in black in figure 4, shows the presence of silicon and oxygen on the surface. The calculation reveals that a 100 nm thick layer of silica is deposited on the surface of the substrate material.

The SEM micrographs of the silica coated PE films that were plasma modified prior to the coating process agree with the RBS and FTIR observations. As seen in picture 5a, the substrate is coated with SiO_2, while the craters formed due to plasma exposure still exist.

Figure 5a when compared to figure 1b exhibits a greater coverage with silica, of the film surface. The crater–like features of figure 5a have a diameter ranging from 500 nm up to 30 μm, while those in figure 1b have a more uniform size distribution.

The area between the craters (figure 5b) appears to be fully covered with the silica nanoparticles, having an average diameter of 20 nm. The particles are grafted on the outer part of the craters, as shown in picture 5c, and not in the center, suggesting that the conditions there are unfavorable for particle attachment.

3.1 Plasma treatment and surface characterization of polyethylene fibers

UHMPE fabrics were plasma treated under the same conditions, as the PE films, and the results were similar. In the case of the control sample, seen in figure 6a, a limited number of nanoparticles is grafted on the surface, due to the absence of functional groups that would act as links between the coating and the substrate. Through plasma treatment that is achieved; therefore the attached oxygen containing functionalities covalently bond with silica and the results are depicted in figure 6b. We observed an almost full coverage of the fabrics with the silica nanoparticles.

XPS studies of the modified fabrics are in full agreement with the observations from the SEM microscopy. After plasma treatment and before the application of the coating, XPS analysis shows the attachment of polar groups such as –OH and -OOH on the fabric surface (Oh et al., 2001). The presence of a thin silica coating on the fibers is confirmed, but plasma modification prior to the coating process seems again to be necessary. The control sample exhibited a poor atomic concentration ratio of O/C and Si/C of 0.231 and 0.075, respectively.

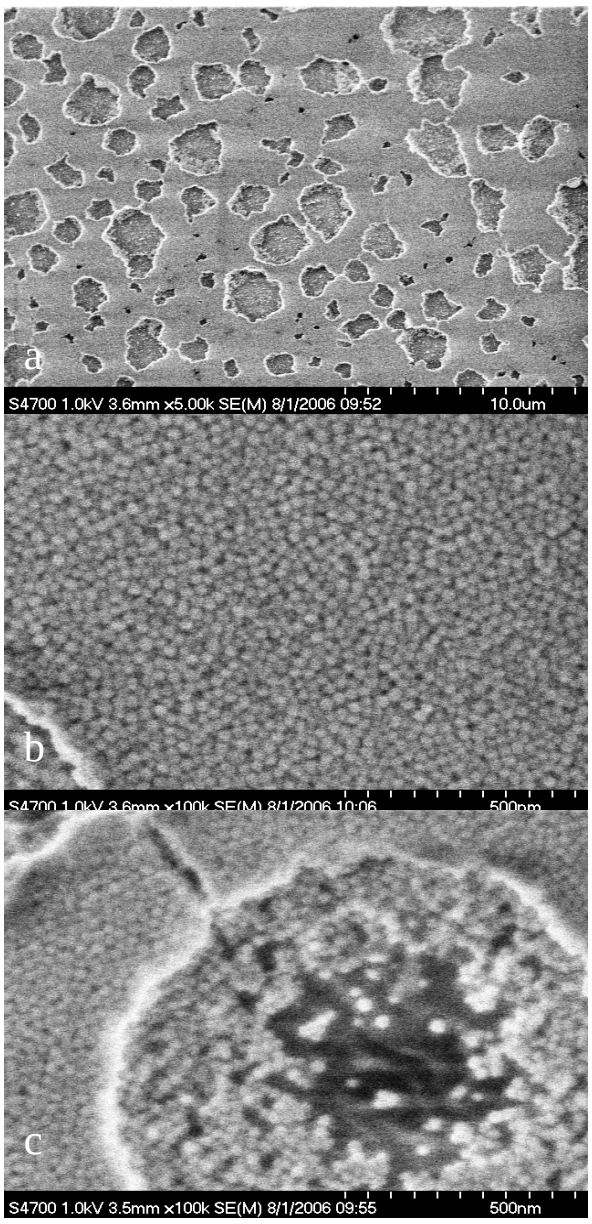


Figure 5. SEM micrograph of silica coated PE film, that was exposed to plasma before the coating was applied. a: the presence of pits, b: the area between the pits and c: detail of a nanosized crater.

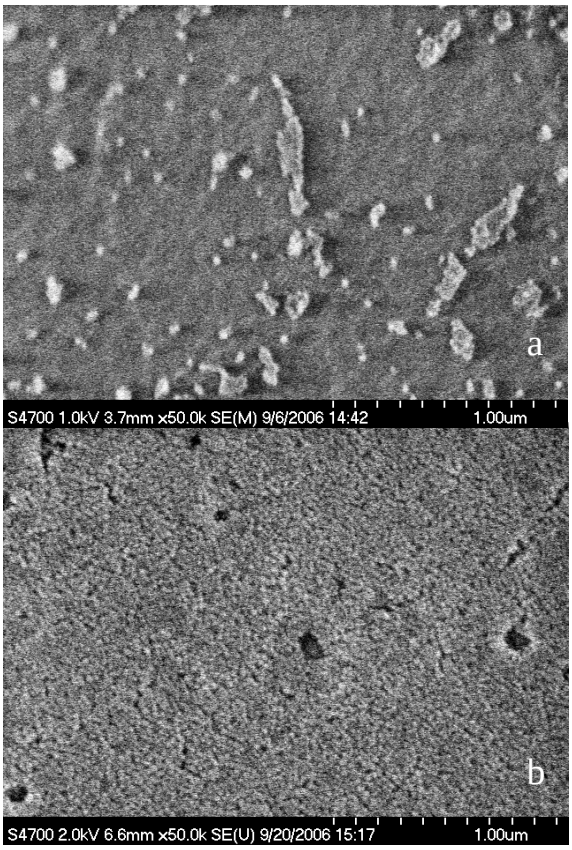


Figure 6. SEM micrograph of silica coated PE fabric, a: control, b: plasma treated under He-O_2 plasma.

In the case where the same material had undergone a treatment in a He-O_2, where the oxygen percentage was only 2% in the gas mixture, for a short treatment time of 45 seconds, a steep increase of the above described ratios is observed. The atomic concentration of oxygen on the surface showed a 4-fold increase accompanied with a 16-fold increase of the atomic silicon, as reported in Table 1.

Sample	O/C	Si/C
control PE fibers	0.231	0.075
plasma treated PE fibers	0.897	0.436

Table 1. XPS analysis results for the control and plasma exposed polyethylene fabrics.

CONCLUSIONS

A thin silica coating was successfully deposited on polyethylene fibers and films for the first time. Helium-oxygen plasmas were utilized in order to prepare and activate the surface prior to the deposition process. The grafted carbonyl functionalities enhance the chance of silica nanoparticles bound to the surface and are the key to the formation of a uniform coating.

The formed silica coating may have the potential to improve the properties of the substrate, as it is a known gas barrier coating with high mechanical strengths. Additionally, the attached silica nanoparticles may also have the potential to increase the frictional energy dissipation of the material and makes it a promising candidate for numerous Army applications, with impact and mechanical properties to be investigated.

ACKNOWLEDGEMENTS

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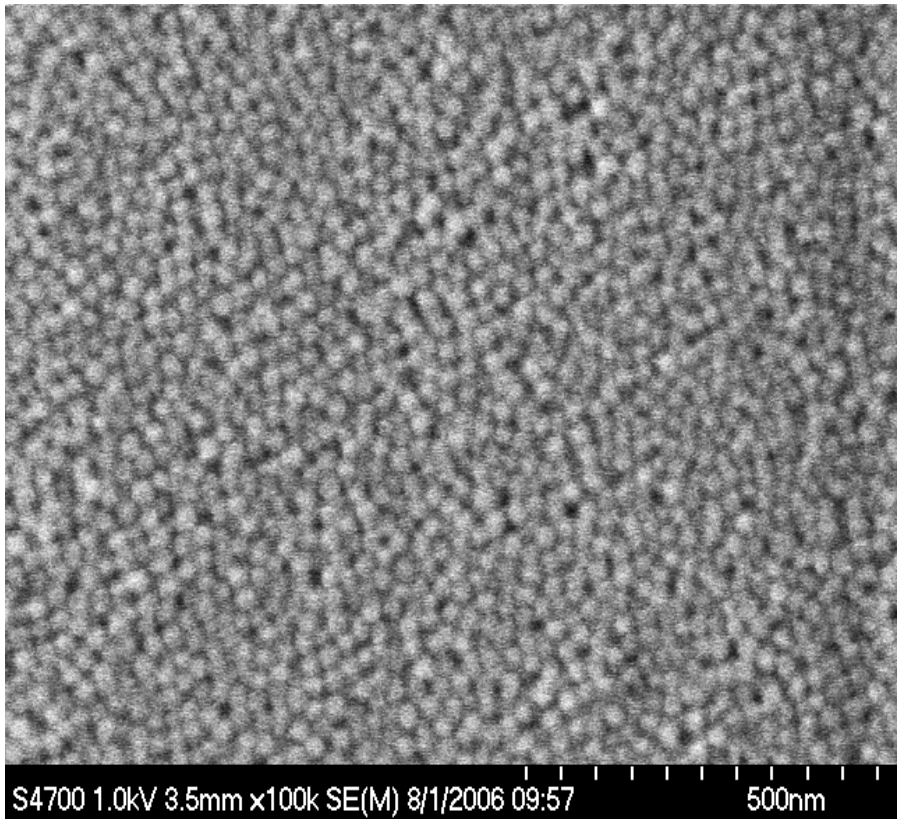

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Army Research Laboratory
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November 29, 2006

Many opportunities for surface functionalized fabrics

- Flexible body armor fabrics
- Flexible permselective membranes
- Self-sensing materials
- Self-detoxifying materials
- On-board molecular electronics

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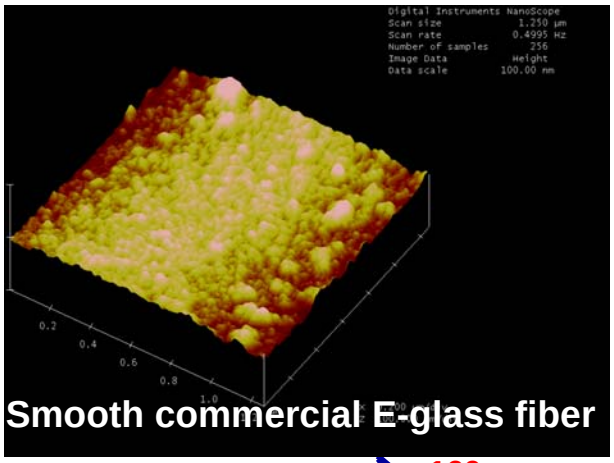
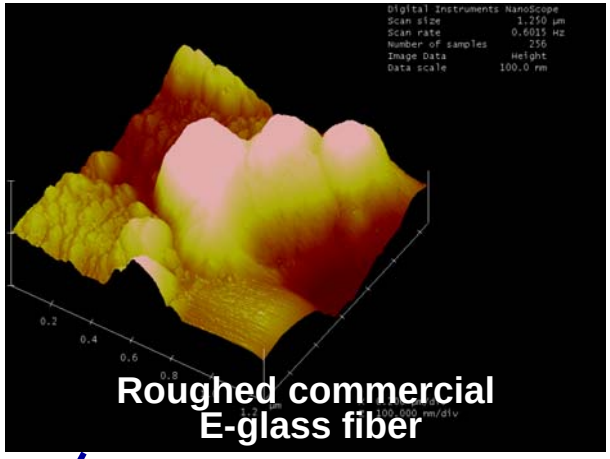
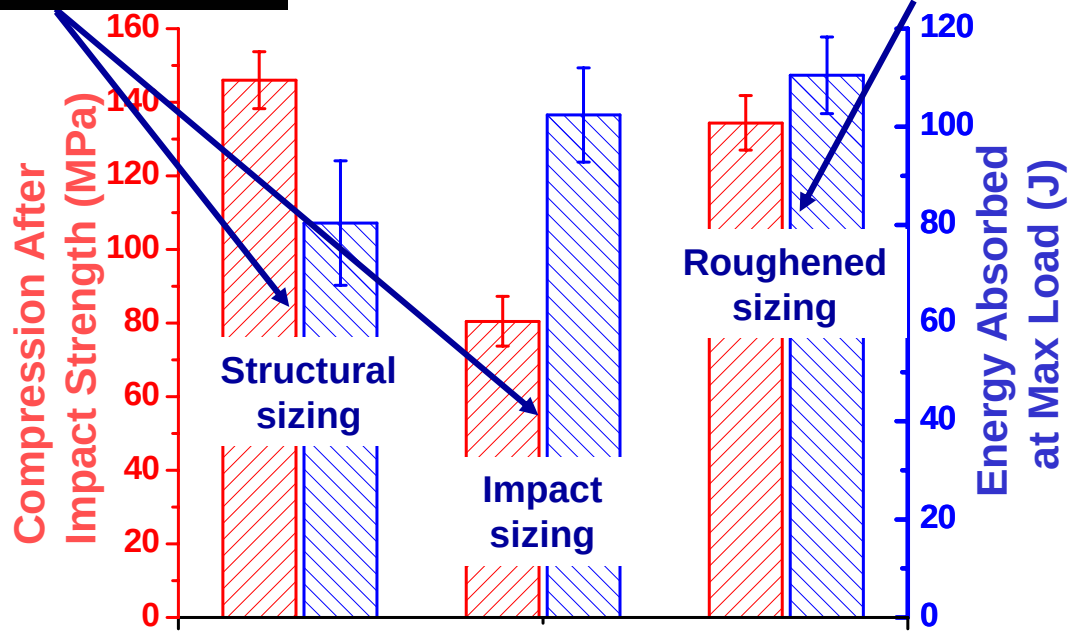
Increased surface roughness of glass fibers yields enhanced composite mechanical response



Silane chemistry

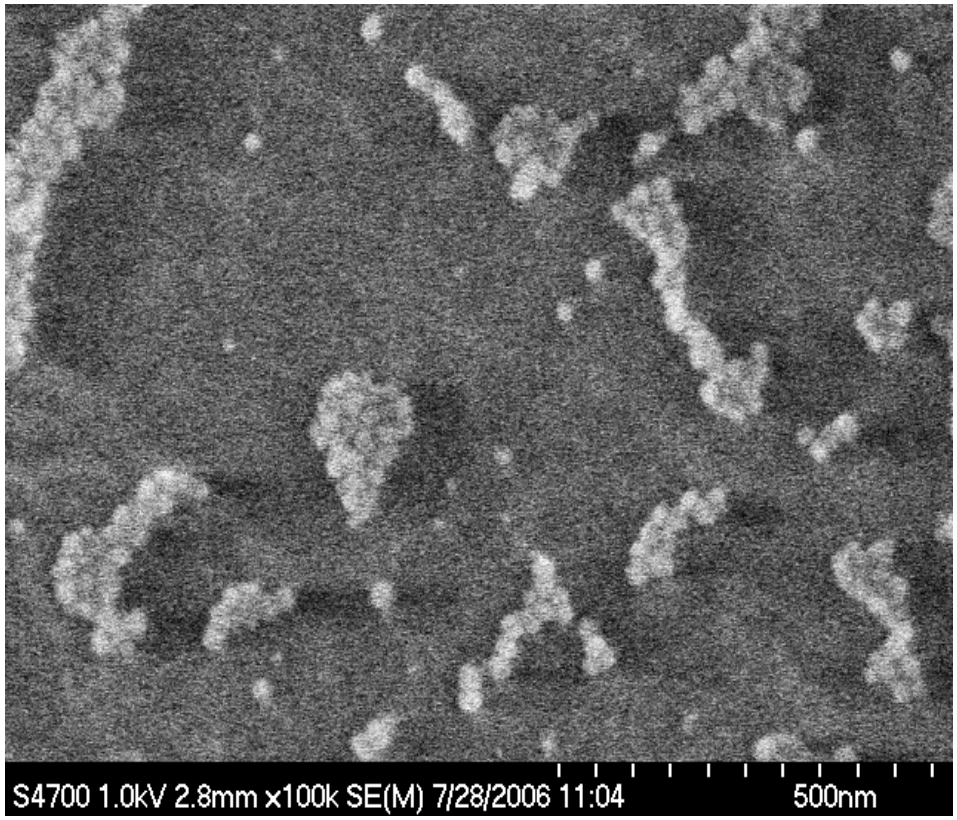
Colloidal silica





Comp Sci Tech, 66 (2006) 509-521.

Low surface free energy and low reactivity of polymer surfaces leads to poor adhesion properties



Poor adhesion of silica to untreated polyethylene film

To enhance compatibility

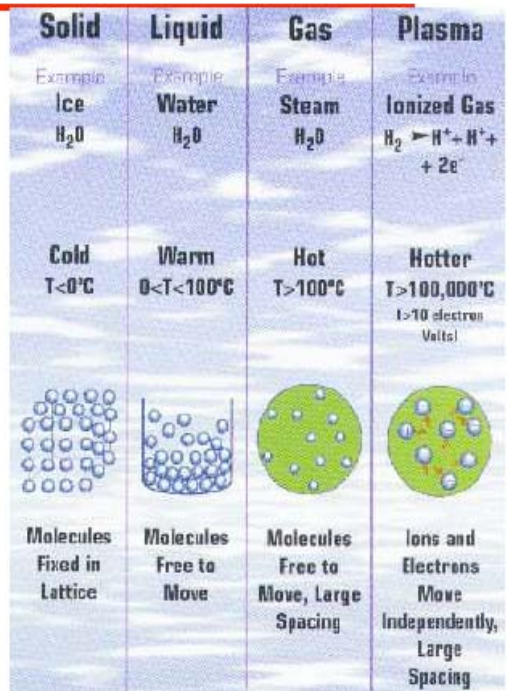
- Alter surface chemical composition
- Increase surface roughness
- Plasma processing can be employed

What is plasma?

http://www.physics.lsa.umich.edu

Plasma is the fourth state of matter

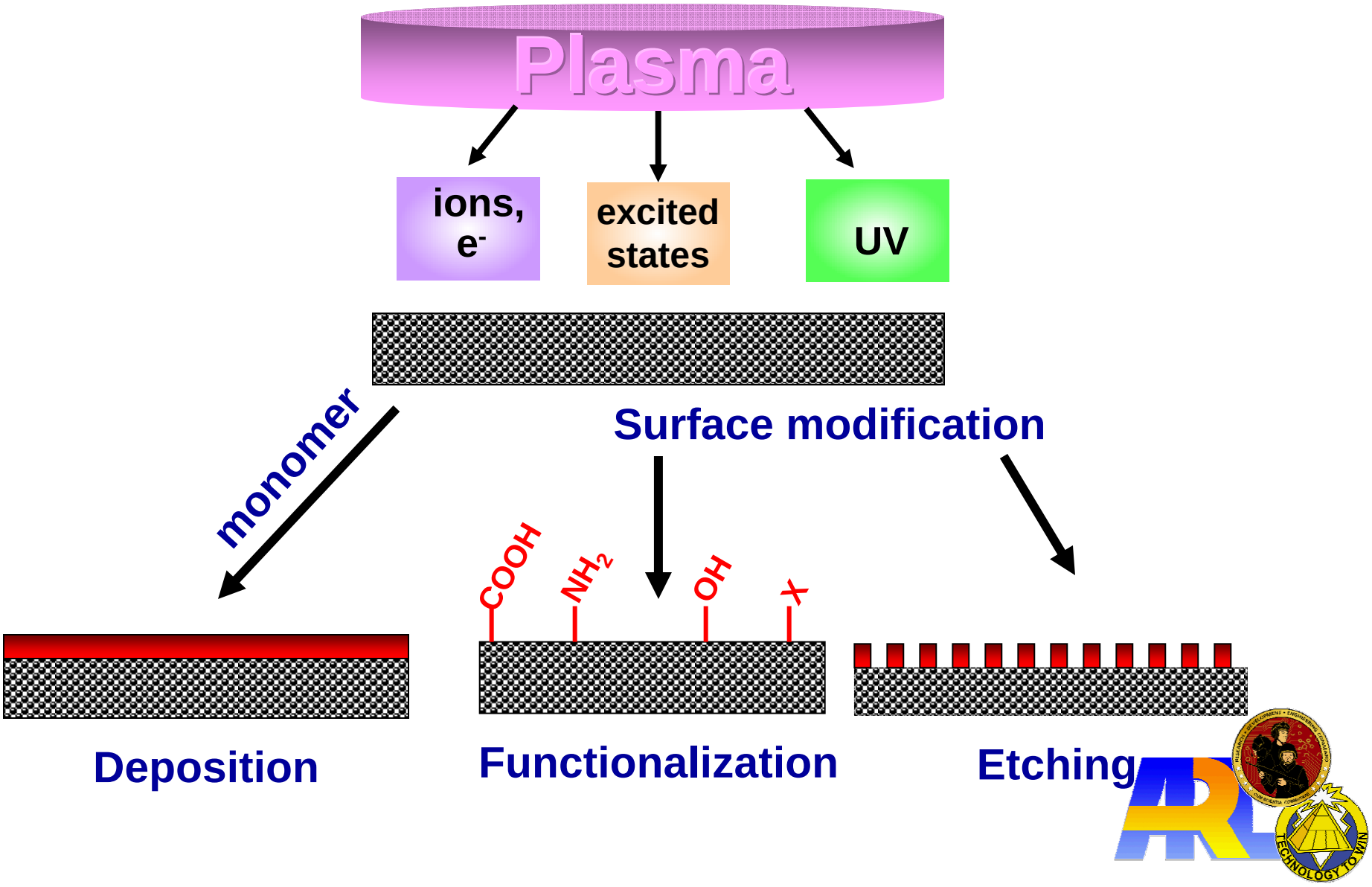
- Plasma consists of a collection of free-moving electrons and ions
- Energy is needed to strip electrons from atoms to make plasma.
- The energy can be of various origins: thermal, electrical, or light (ultraviolet light or intense visible light from a laser).
- Plasma can be accelerated and steered by electric and magnetic fields which allows it to be controlled.



www.plasmas.org

Quasineutral gas of charged and neutral particles that is produced by applying an electric field

Plasma processes can be used for a variety of surface treatments



Plasma species hold enough energy to cause chain scission

Bond	Energy (eV)
C – H	4.3
C = O	8.0
C – C	3.4
C = C	6.1
C ≡ C	8.4
C – O	3.8
O – H	4.9
O – O	1.5

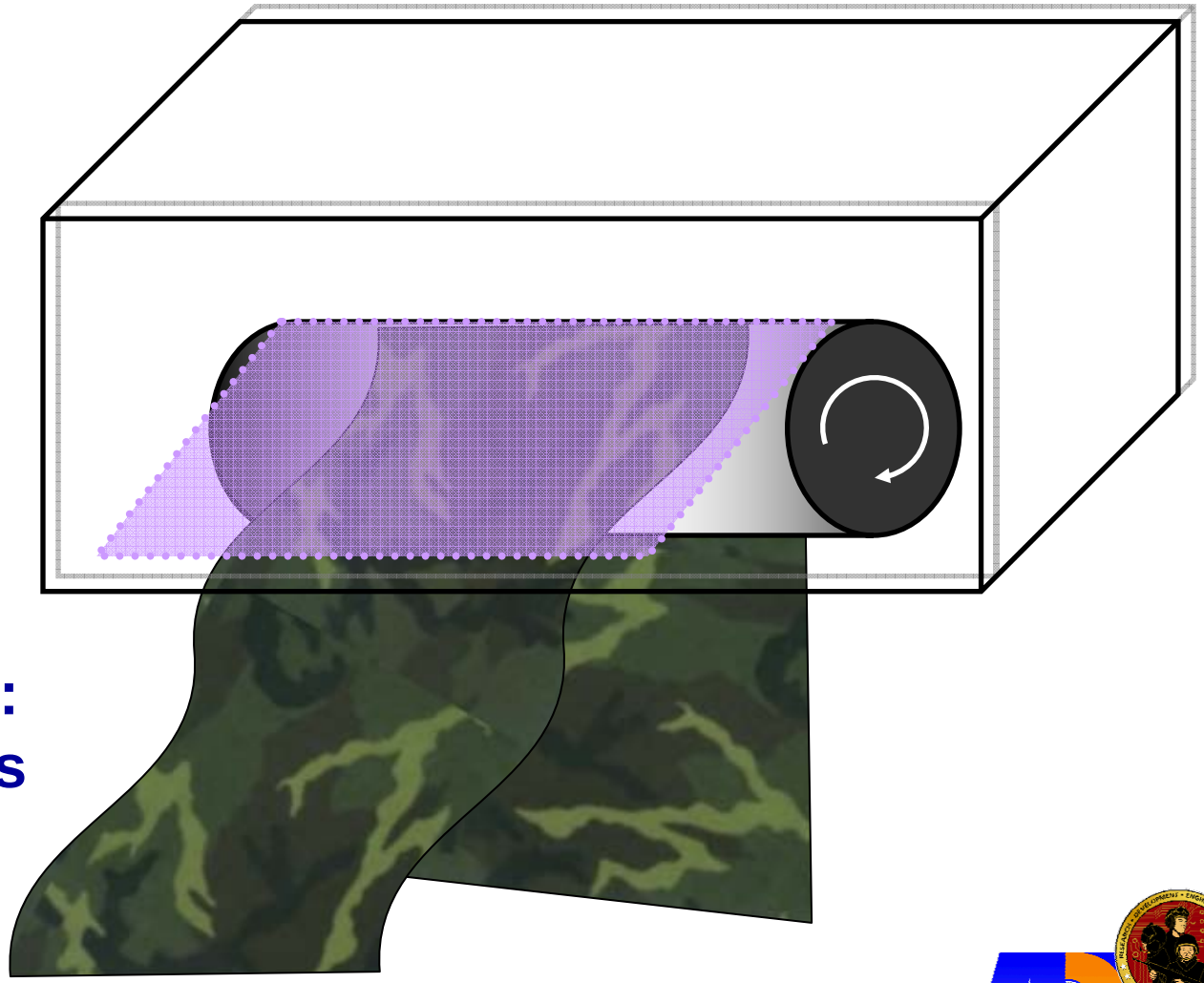
aromatic polyamides, alkyl polyamides, nylon, aralkyl polyamides, polyolefins, polyethylene (PE),polypropylene (PP), polyethylene terephthalate (PET),

poly p(-phenylenebenzobisoxazole) (PBO), polyimides, polyetherimides, carbon fibers, silk, cellulose, wool, cotton, linen, etc…

Plasma treatment of wide fabric webs is possible at atmospheric pressures

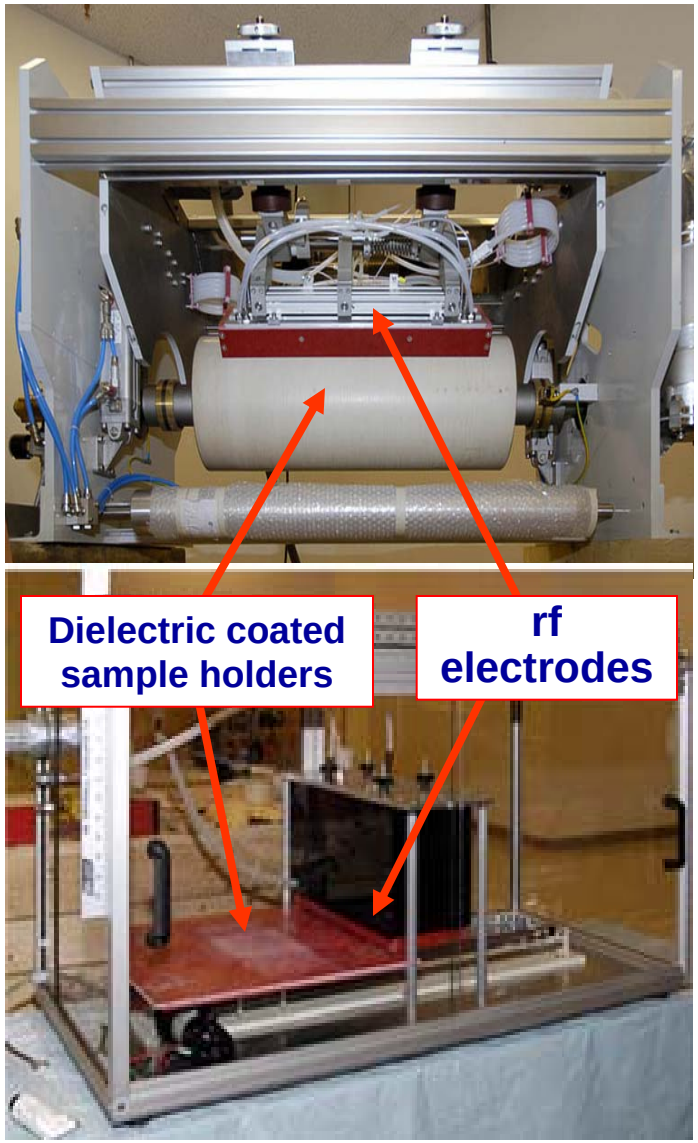
Average process speed: 15 ft/min

web width: >20 inches



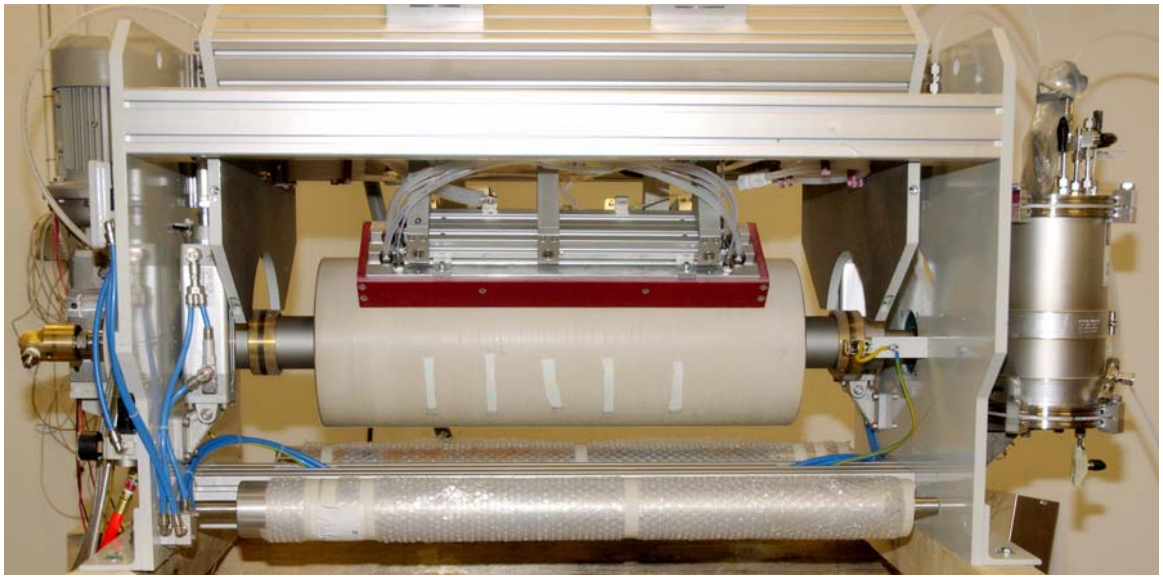
PLASMA ON

Atmospheric plasma treatment of polymer substrates has many potential advantages

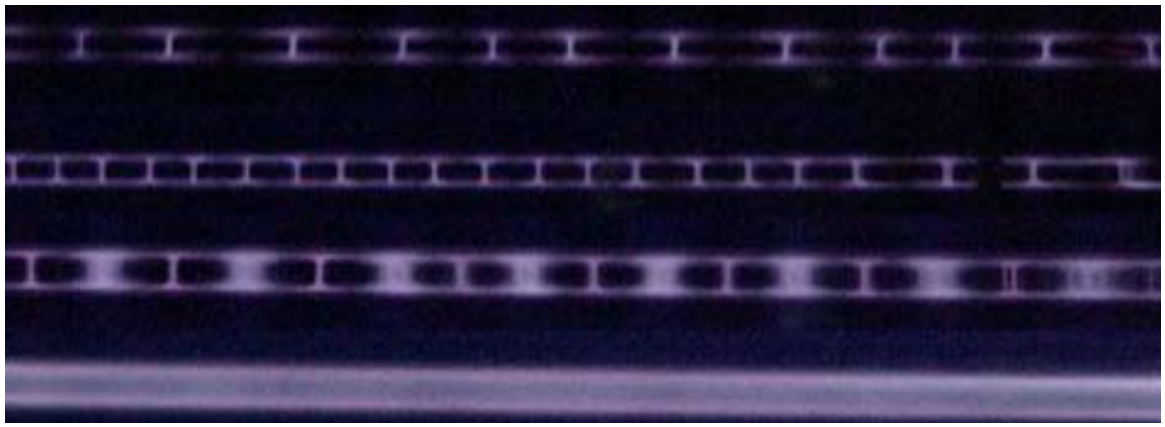


- No vacuum requirements
- Room temperature
- Environmentally friendly
- Surface modification only
- Homogenous treatment
- Industrially scalable
- Large area capability
- Fast process speed

A wide variety of experimental parameters are available



Freq: 90Khz
Exp time: 0.6 – 45 sec
1 atm – He-O_2,He-N_2
~10000 sccm He,
~ up to 1000 sccm gas

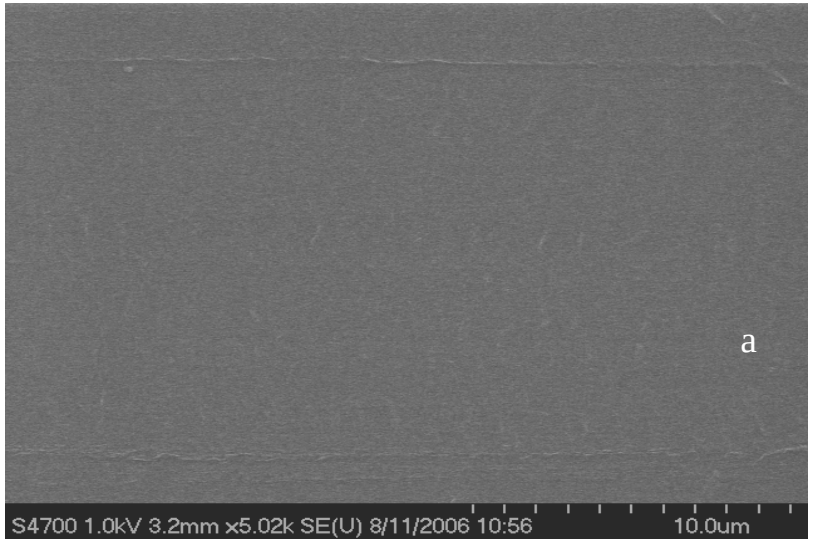


Filamentary

Range of modes possible

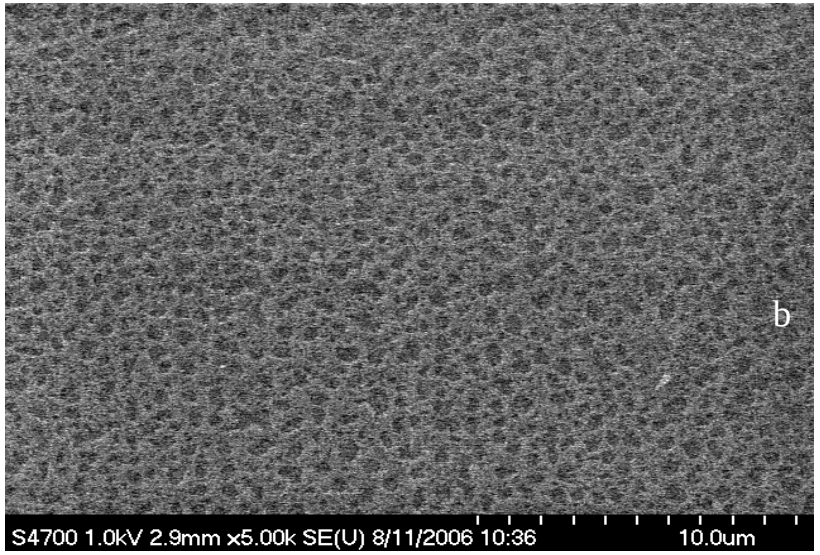
Continuous glow

SEM images show the formation of nanocraters after plasma exposure of polyethylene films



Untreated PE film

- Smooth, uniform surface

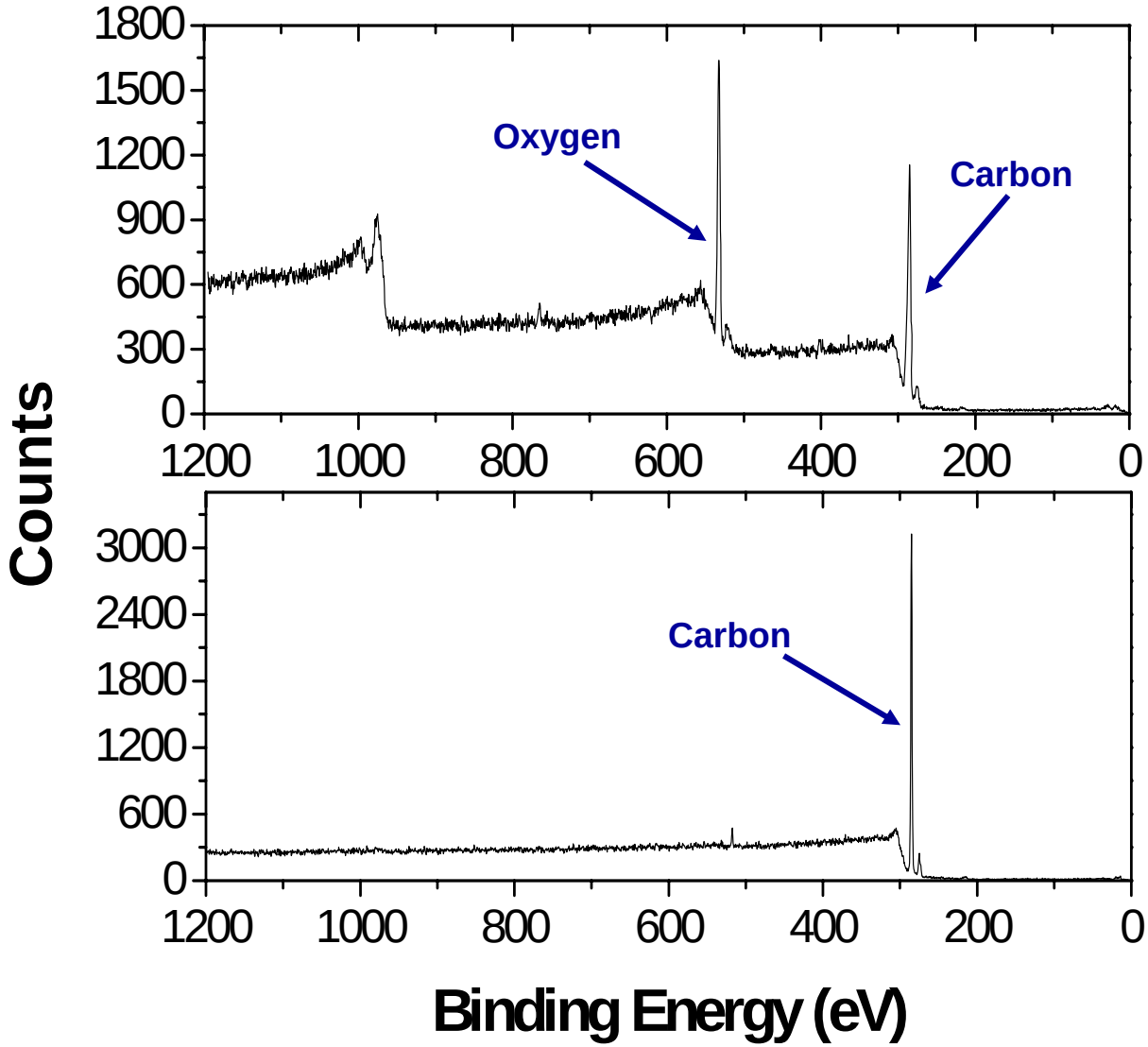


Plasma treated PE film

- Micro/nano texturing

He-O_2 plasma for 9 sec (He-O_2:0.6%)

XPS indicates plasma exposure of polyethylene films leads to an oxidized surface

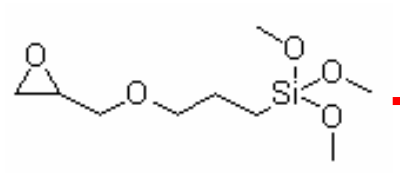


Plasma treated PE film

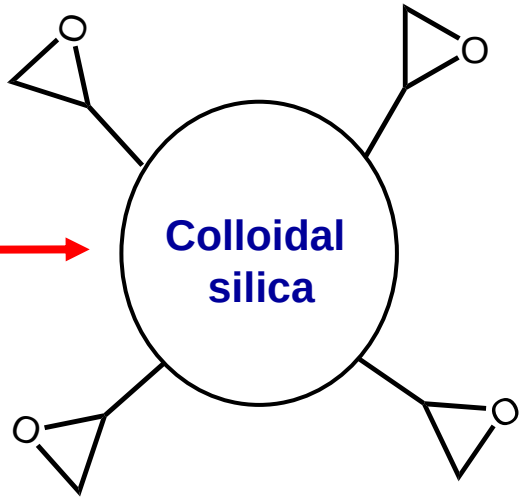
He-O_2 plasma for 81 sec (O_2/He:0.6%)

Untreated PE film

Can a plasma activated surface be used to attach chemically functionalized colloidal silica?

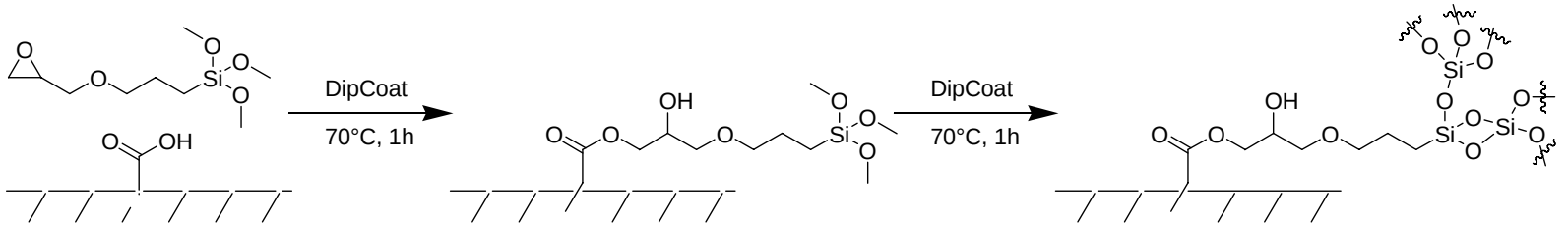


Silane coupling agent



Why SiO_2 ?

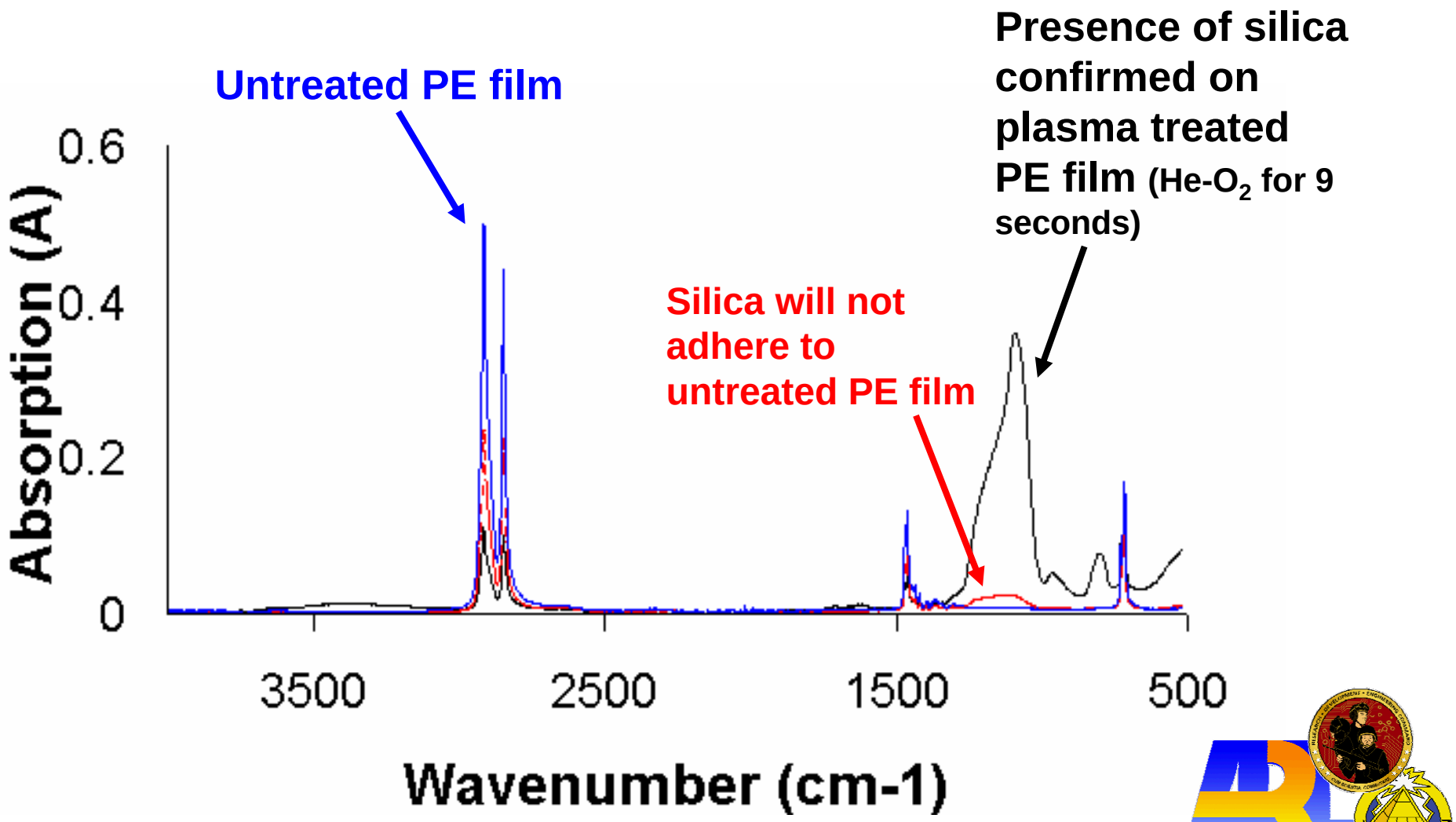
- Gas barrier layer
- Hard coating
- Increased roughness



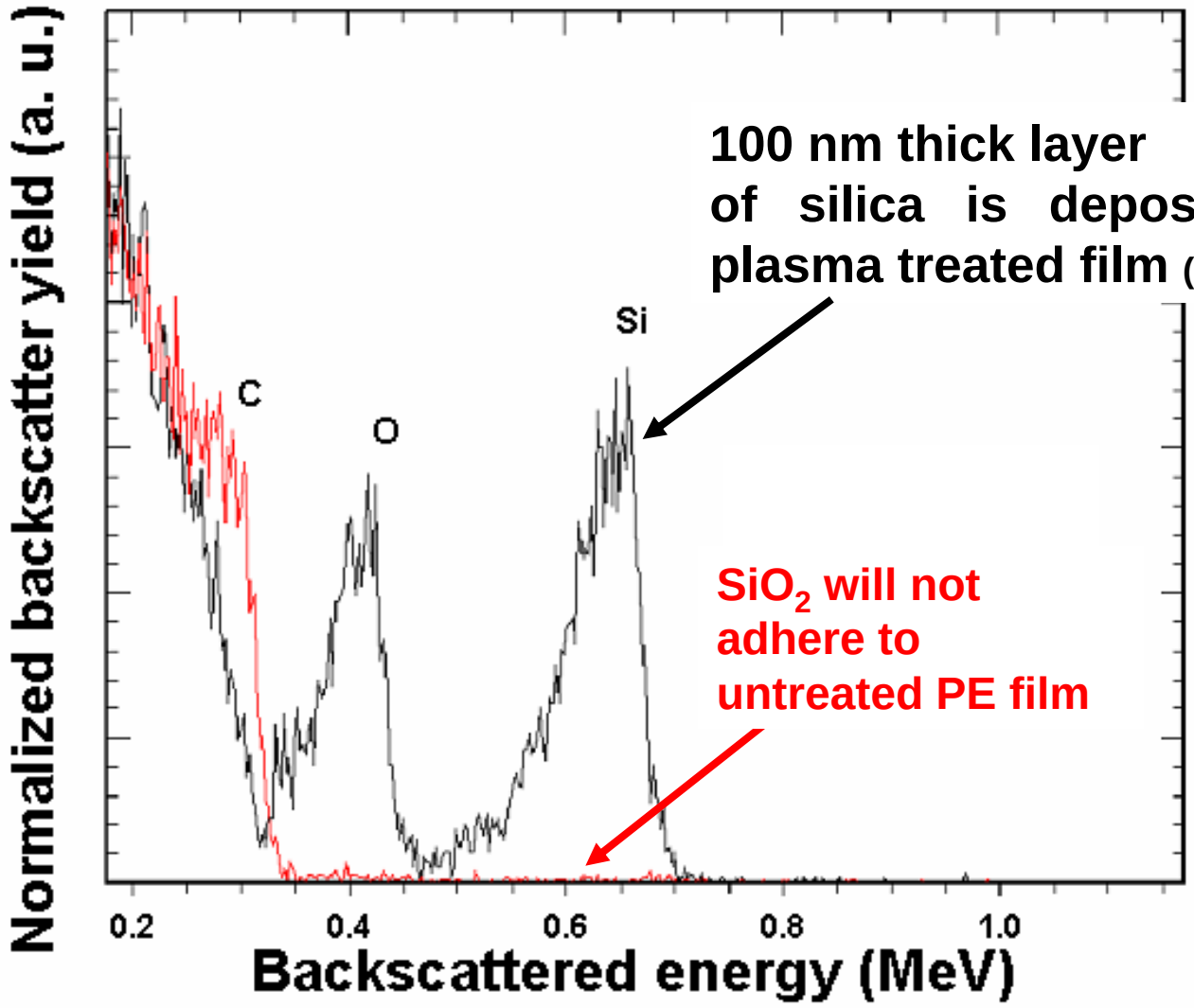
Polymer surface

Activated polymer surface

FTIR spectrum of plasma treated polyethylene film indicates the successful attachment of silica particles



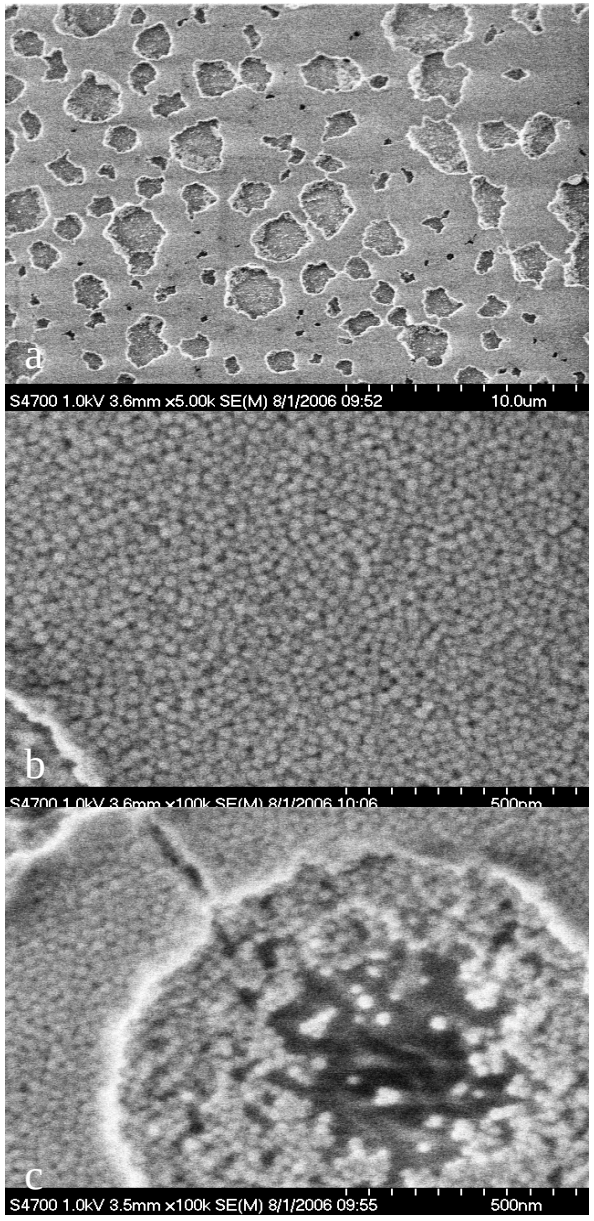
RBS Spectroscopy confirms the formation of silica coating on plasma treated surface



100 nm thick layer of silica is deposited on the plasma treated film (He-O_2 for 9 sec)

SiO_2 will not adhere to untreated PE film

Nano-sized craters seen after plasma treatments & silica coating



micropits remain

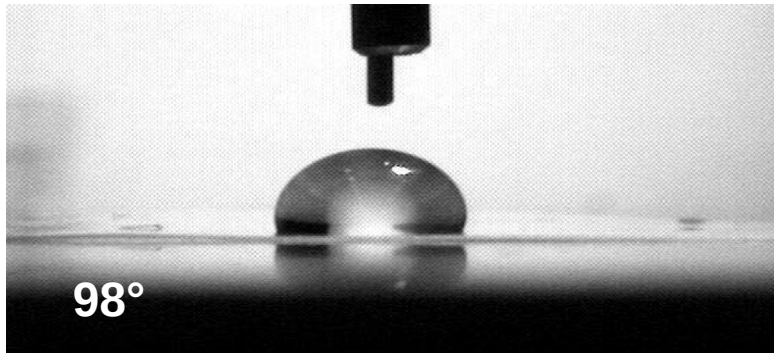
Uniform coverage

Crater profile: particles concentrated around the rim of the crater

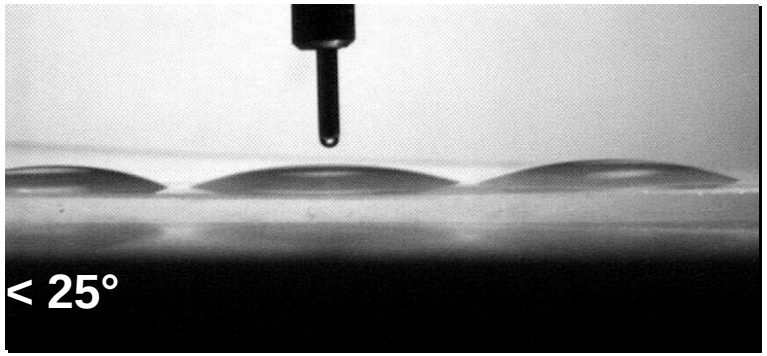
Plasma treatment of PE films is required for optimized silica deposition

XPS Atomic Concentrations (%)

	C1s	N1s	O1s	Si2p
Control with SiO_2	85.38	1.22	10.89	2.51
Plasma treated with SiO_2	33.80	0.65	53.79	11.76



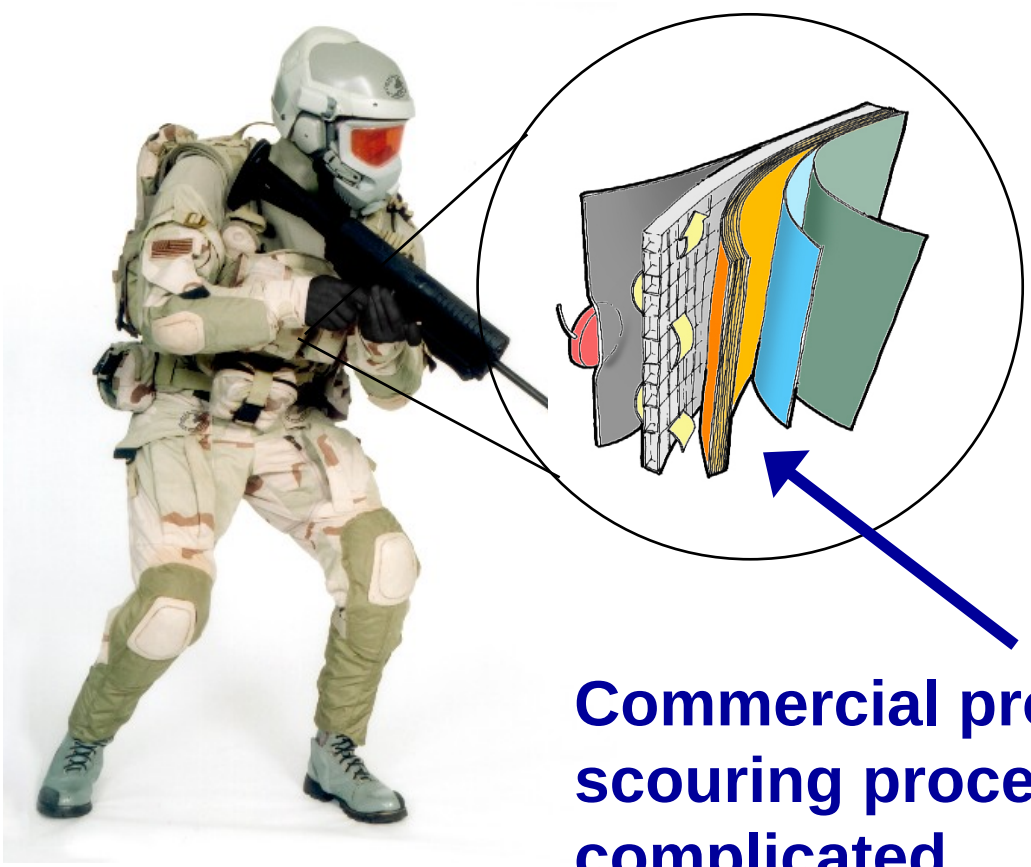
Untreated prior to silica deposition



Plasma treated prior to silica deposition

He-O_2 plasma gases, 6.0 sec.

Can we apply plasma treatment concepts towards more complex commercial fabrics?



Commercial processing aids, finishes, scouring process, etc. for fabrics is complicated

XPS analysis of PE fibers shows lower degree of silica deposition when compared to model films

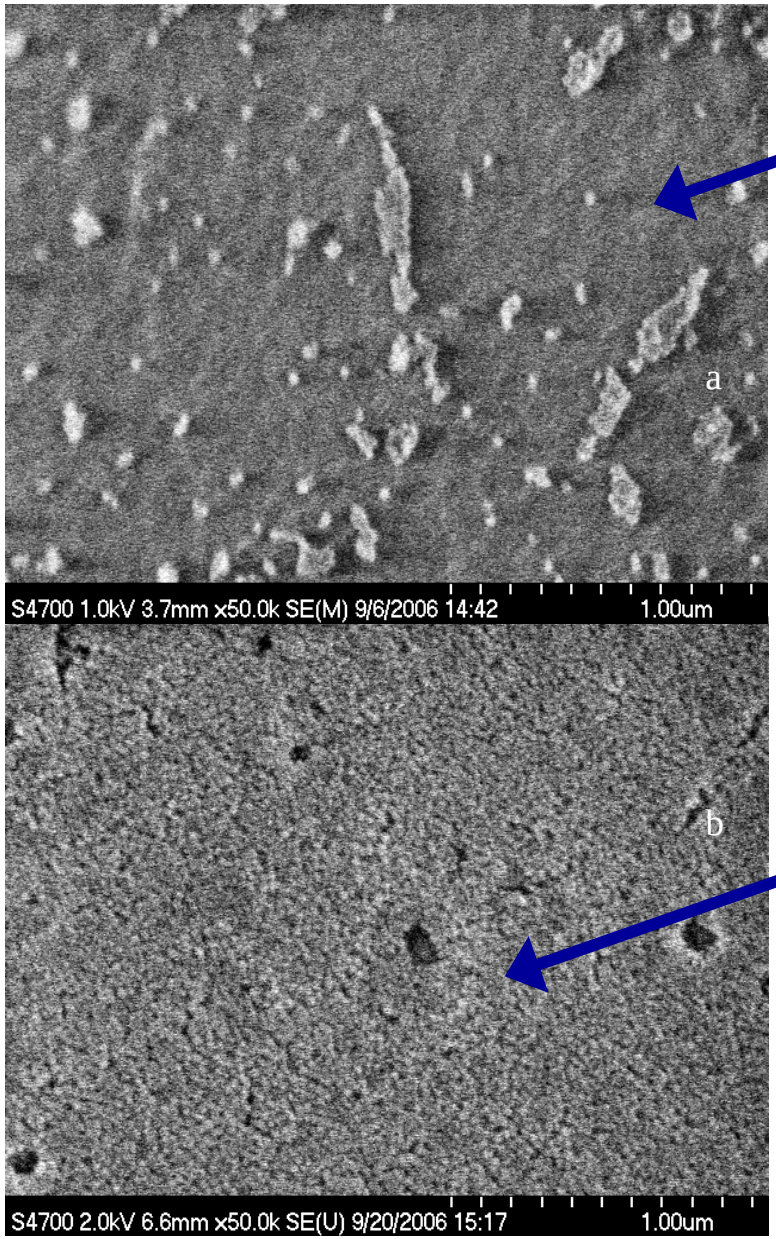
XPS Atomic Concentrations (%)

	C1s	O1s	Si2p
Plasma treated film with SiO_2	33.80	53.79	11.76
Plasma treated fabric with SiO_2	26.90	64.07	9.03

Commercial processing aids, finishes, scouring process for fabrics is complicated

He-O_2 plasma gases, 6.0 sec (film) & 60 sec (fabric)

PE fibers coated with silica after plasma treatment



Untreated

XPS Atomic Concentrations Ratios

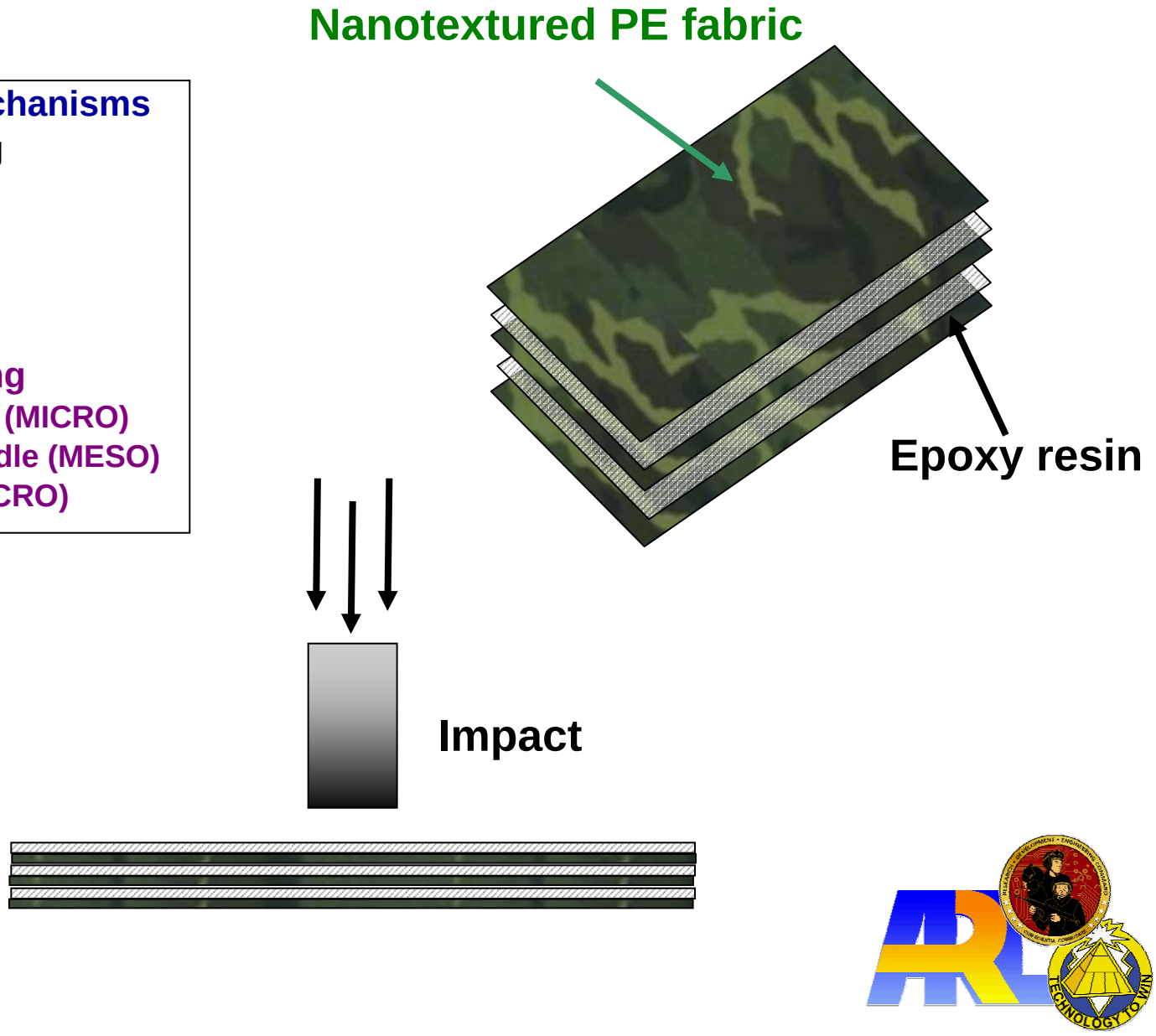
Sample	O/C	Si/C
Untreated PE fibers	**0.231**	**0.075**
Plasma treated PE fibers	**0.897**	**0.436**

Plasma treated full coverage!

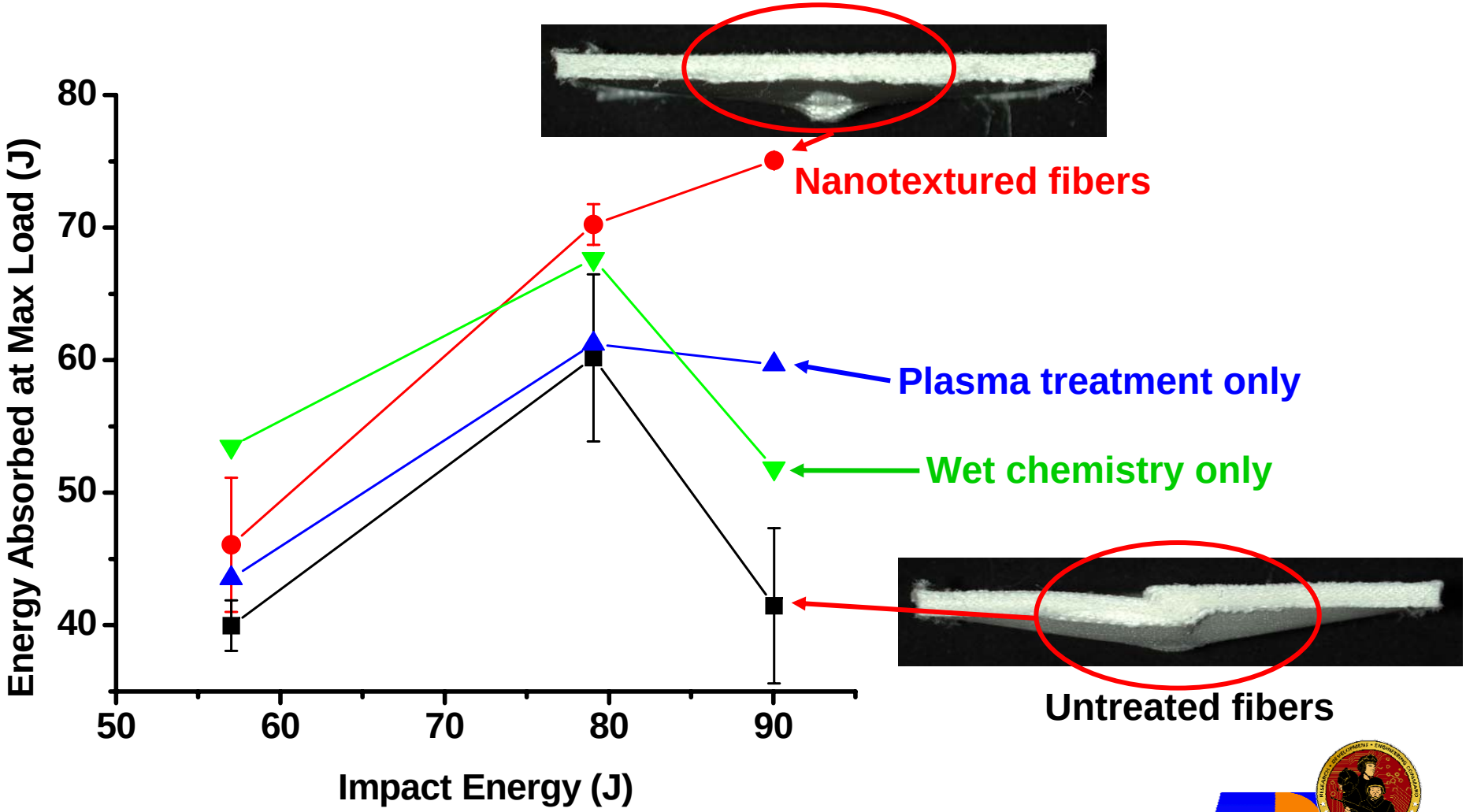
Nanotexturing of PE fibers should yield increased energy dissipation in composites

Energy Absorption Mechanisms

- Matrix Cracking
- Fiber Crushing
- Delamination
- Fiber Fracture
- Debonding
- Frictional Sliding
  - I. Fiber-Matrix (MICRO)
  - II. Bundle-Bundle (MESO)
  - III. Ply-Ply (MACRO)



Surface treatment of PE fibers alters composite damage mechanisms due to impact



Spectra S900 fiber/903 fabric, SC15 epoxy matrix, VARTM processed
Instron Dynatup 930 Drop Tower Impact Tester

Conclusions

- Atmospheric plasma modification of materials is a low cost, environmentally friendly and fast process, proven effective for treating large areas
- Plasma treated polymer films/fabrics can accept silica roughening agents
- Impact testing of showed potential for increased energy absorption of nanotextured polymer fiber reinforced composites

Acknowledgements

- ORISE

Thank you !