Chiara Pavan

**ATMOSPHERIC PRESSURE PLASMA SOURCES AND SYSTEMS – CASE STUDIES**
GRINP PLASMA TECHNOLOGY

- Italian SME grounded in 2001, located in Torino.
- Developed proprietary Atmospheric Pressure Plasma Technology

Mission

Implementation of atmospheric plasma processes

Laboratory

Customized Industrial APP equipments

Production
GRINP: From Lab to Production

EnviPark, Italy

Swerea IVF, Sweden

BTRA, India

Loro Piana, Italy

Sefar AG, Switzerland
**Industrial Applications – Surface Treatments**

- **Custom Plasma sources & equipments**
- **Different processes & applications**

**Sectors**

- Textile (Woven & Non-Woven)
- Composites
- Plastic Film & Sheets (Adhesion, Multi-Functional layers, …)
- Wood, cellulose, …
- Decontamination
Plasma:
• generated in an electrical field
• composed by excited species
• DBD layout
GRINP PLASMA TECHNOLOGY: How it works

Cathode
Precursor Injection
Spray Unit
Generator Unit

Gas
Substrate
## Characteristic of GRINP System

### Electronic System:
- **Core of the system**
- composed by a generator and a matching box
- completely in-house designed and realized
- Complete **control of the parameters**: power, frequency, temperature, gas flow

### Precursor Management:
- Spray
- Injection in plasma phase

### Multi-Cathode System → High Versatility
- Treatment time can be modulated
- Each cathode can be fed with a different mixture of gas or monomer → subsequent continuous treatments on the same substrate
Characteristics of the GRINP System

Atmospheric Pressure Glow Discharge (APGD)

- Dielectric Barrier Discharge
- Superficial Discharge
- Continuous or pulsed, with independent control on $T_{\text{off}}$ and $T_{\text{on}}$
Plasma = Chemical Reactor

Hydrophilicity

Adhesion

Self-Cleaning

Play with chemistry → tailored surfaces → match market needs
Gas & Precursors

Organic Gases

- HMDSO
- CH₄
- Allylic Monomers

Inorganic Gases

- O₂
- N₂
- He
- Ar
- …

...or a mixture of them!

- Directly in Plasma phase
- Atomizer/Vaporizer
Effects of Plasma: Tuning Parameters...

- **Etching**
  - OH
  - O
  - COOH
  - NH$_2$

- **Chemical Modification**

- **Deposition**

- **Graft-Polymerization/Cross-Linking**

- **Plasma Etching**
  - OH
  - O
  - COOH
  - NH$_2$

- **Plasma Chemical Modification**

- **Plasma Deposition**

- **Plasma Graft-Polymerization/Cross-Linking**
CASE STUDIES
From the Lab to Production
Plasma is a primary technology for the treatment of fabrics and fibres, because it can confer functional properties to materials, leaving intact the specific characteristics, such as softness, elasticity, transpiration, ...
Plasma represents a Green Solution for several finishing processes, reducing water and energy consumption (dry process) and avoiding use of chemical products.

### Functional Properties:
- Wettability Enhancement for synthetic fibres
- Adhesion for lamination processes
- Anti-Shrinkage for wool fabrics and fibers
- Water-repellant and anti-stain for clothing and home textiles
- Adhesion for carbon and glass fibers.
Polyester

Effects

Etching

Untreated

Treated $\rightarrow$ Nanoroughness

SEM Analysis

Chemical Modification

He/Ar

He/O$_2$

Untreated

XPS Analysis

+20% in O content
Polyester

Hydrophilicity

<table>
<thead>
<tr>
<th></th>
<th>$\theta_a$</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>89</td>
</tr>
<tr>
<td>Ar</td>
<td>49</td>
</tr>
<tr>
<td>He/Ar</td>
<td>59</td>
</tr>
<tr>
<td>He</td>
<td>58</td>
</tr>
<tr>
<td>He/O$_2$</td>
<td>65</td>
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</tbody>
</table>

Adhesion

Applications

- Facilitates impregnation of water-based Resins and Finishing Products

DEVELOPMENT OF A NEW PRODUCT

- PET mesh with enhanced properties for screen-printing application: controlled wettability and adhesion
R&D of a new Process/Product

- PET mesh with enhanced properties for screen-printing application
- First trials by Grinp on A4 samples and 60cm rolls
- Satisfactory Results

- Rent-a-Machine for 5 months
- 20,000 meters pre-production
- Purchase of 4,2 mt wide machine
- March 2009: Installation of the machine
Wool

**Effects**

- Etching
  - Untreated
  - Treated → Removal of scales

**SEM Analysis**

**Chemical Modification**

**Oxidation Products of S-S Bridges:**

- Bunte's Salt and Cysteic Acid → Polar Surface
- Cystine Monoxide and Cystine dioxide → Increased Reactivity

**Determined by ATR-FTIR**
Wool

Applications

- Anti-Felting
- Fibers
  - Textiles
  - Non-wovens
- Non-wovens

Dyeability

- Dyeing Enhancement:
  - +60% with reactive dyes
  - +20% premetallized dyes

Anti-Felting

- Basolan
- Super wash
- Total Easy Care
- 5x5A with Tumbler (test method 31)

No Chlorination Process
Wool

Anti-Felting treatment on fabrics and fibres (tops)

Carding line with plasma unit

Plasma equipment 2mt wide
Oil & water-repellent textiles

Fluorocarbon resins

- Applied by foulard + thermal treatment
- Plasma pre-treatment improves fastness & performances: superior abrasion resistant (3 times standard FC process)

Deposition of FLUOROPOLYMER thin layer on textiles:
- Water Repellency
- Oil Repellency
- Avoid wet fluorocarbon resin chemistry (water, foulard,...)
Oil & water-repellent textiles

Atmospheric Pressure Plasma Vapour Deposition

- Fluorocarbon Monomer vaporized directly in plasma zone
- Plasma Polymerization & Deposition of Fluoro-containing thin layer

One-step dry process!
Oil & water-repellent textiles

Chemical-Physical Properties

- Crosslinking → Stability
- FC Chains oriented outwards
- FC Chains parallel to surface

Lotus Effect

- Etching
- Surface Nano-Roughness increases CA
Oil & water-repellent textiles

**Performances**
- Contact Angle > 150°
- AATCC TM 193: Repellency = 6-7 (10 home laundrings)
- AATCC TM 118: Repellency = 5

**Advantages**
- Strong adhesion to substrate → Fastness to washings
  - Unmodified textile touch
  - One-side treatment → Dual Effect
- Water & Energy consumption reduction
  - Environmentally clean process
Glass fiber reinforced composite materials: high strength glass fiber embedded in a concrete matrix. Fiber /Matrix adhesion enhances performances by:

- **Etching**
- **Chemical Modification**

- **Nano-Roughness**
- **Size Removal (Starch)**

+ 40% Resistance in concrete after 28 days (alkaline conditions)
Composites: Carbonfiber

**Uses**

Reinforcement in composite materials:
- Automotive industry (ongoing Project with FIAT)
- Structural engineering applications

**Effects & Applications**

- Impregnation and performances of epoxy resins for prepreg production

**Adhesion**

- Treatment of PAN (polyacrylonitrile) precursor to reduce carbonfiber production cycle

**ETCHING**

- Functional Groups
Zipper

- Water-proofing
- Combination of plasma & spray (nanoparticles)
- Speed up to 10 mt/min
- Pre-production: 500 mt
Industrial Applications: Plastic Sheets

Multiwall Polycarbonate Sheets

APP for the treatment of 2mt wide polycarbonate sheets for anti-fog effect

- Installed after polymer extruder
- Speed up to 2 mt/min
- Deposition of SiO$_2$-like thin layer

Industrial Applications: Plastic Sheets

Multiwall Polycarbonate Sheets

- High plasticity
- Good adhesion
- 65°C Vapor Test: 300h lasting performance
Industrial Applications: Plastic Sheets

Multiwall Polycarbonate Sheets

Even layer up to 600nm thickness!
Industrial Applications: Plastic Sheets

Effects

- Wettability
- Adhesion
- Anti-Fogging

Multiwall Polycarbonate Sheets

Light transmission
Industrial Applications: Plastic Films

- Permanent corona effect
- Surface Energy >46 dyn/cm²
- High speed > 100 mt/min
- No size limit
- Single/Double side
- PECVD (GD)
- Non-Woven substrates
Industrial Applications: Plastic Films

Fluoropolymer Films for Composites Lamination

- Strong adhesion towards Carbon & Glass Fibers composites
- Hydro- & Oleo-repellant surface
- UV-Stable → protects resins from light degradation
- Multifunctional → structural and aesthetic elements for building, automotiv and aerospace industry.
Grinp strongly believes in research. Research means future. Collaboration with international research center is of primary importance.

- THE BOMBAY TEXTILE RESEARCH ASSOCIATION
  Mumbai - India

- HOGESCHOOL GENT TO2C – Uni Gent – Belgium

- LEITAT Technological Center
  Barcelona – Spain

- VARESE – ITALY

- SWEREAA swedish research
  Gothenburg - Sweden

- UNIVERSITÀ DEGLI STUDI DI TORINO
  Turin - Italy
e-mail: grinp@grinp.com
Website: www.grinp.com
## Technical Data

<table>
<thead>
<tr>
<th>Plasma Type</th>
<th>DBD – Glow Discharge - SD</th>
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<tbody>
<tr>
<td>Power</td>
<td>15-20 kW</td>
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<tr>
<td>Maximum width</td>
<td>4 m</td>
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<tr>
<td>Maximum thickness</td>
<td>n.d.</td>
</tr>
<tr>
<td>Consumption - Costs</td>
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<tr>
<td>Energy 10-50 m/min</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy</th>
<th>20 kWh (15kWh plasma + 5 kWh refrigeration)</th>
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<tbody>
<tr>
<td>Water</td>
<td>Ca. 200 L (0,2 m³)</td>
</tr>
<tr>
<td>Gas</td>
<td>20 l/min (Carrier gas + reactive gas)</td>
</tr>
<tr>
<td>Total (Italy)</td>
<td>0.03-0.06 euro/m² (20 m/min)</td>
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</tbody>
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