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Plastic Surface Modification:
Cleaning, Adhesion and Functionalization

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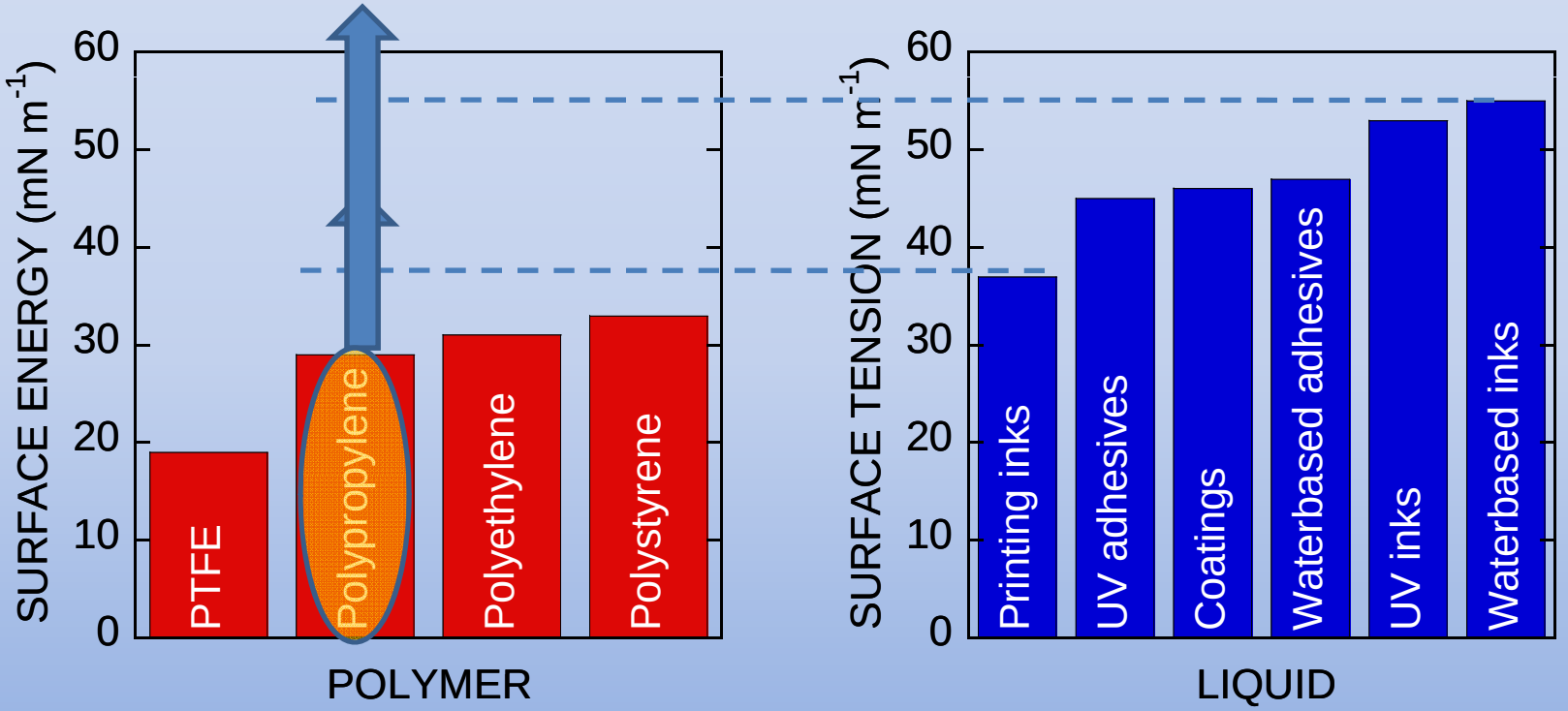
Webinar Discussion

- Surface Energy and Functionality of Polymers
- Plasma Reaction Mechanisms
- Plasma Surface Modification Effect on Polymers
- Plasma Functionalization of a PP Surface
- Comparison of Atmospheric Plasmas for Polymer Surface Modification
- Treatment Recommendations

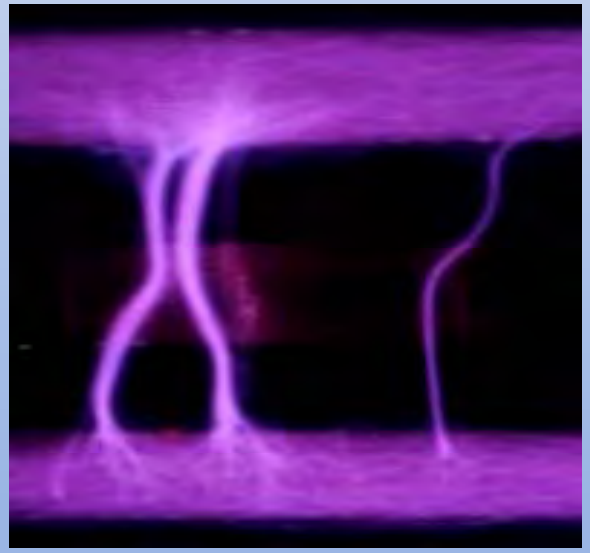
Surface Energy and Functionality of Polymers

- Most polymers, having low surface energy, are hydrophobic.
- For good adhesion and wettability, the surface energy of the polymer should exceed of the interface by ≈ 10 mN/m^{-1}.

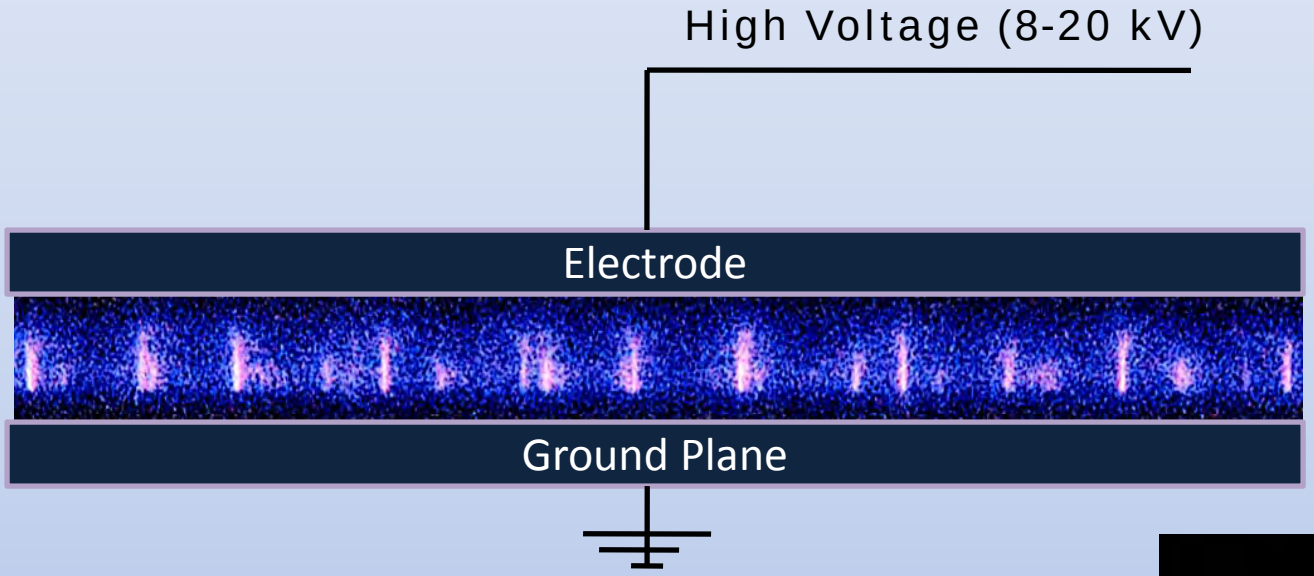


Air Plasma

- Improved adhesion of the functional layers is due to physical interactions and chemical bonds.
- Transient micro-discharges (duration ca. 10 ns, diameter of 10-100 microns)
- Temperature of free electrons in the discharge is a few thousand degrees, however discharge canals are slightly higher than ambient.
- Energy density of the micro-discharge is about $10 mJ/cm^3$.



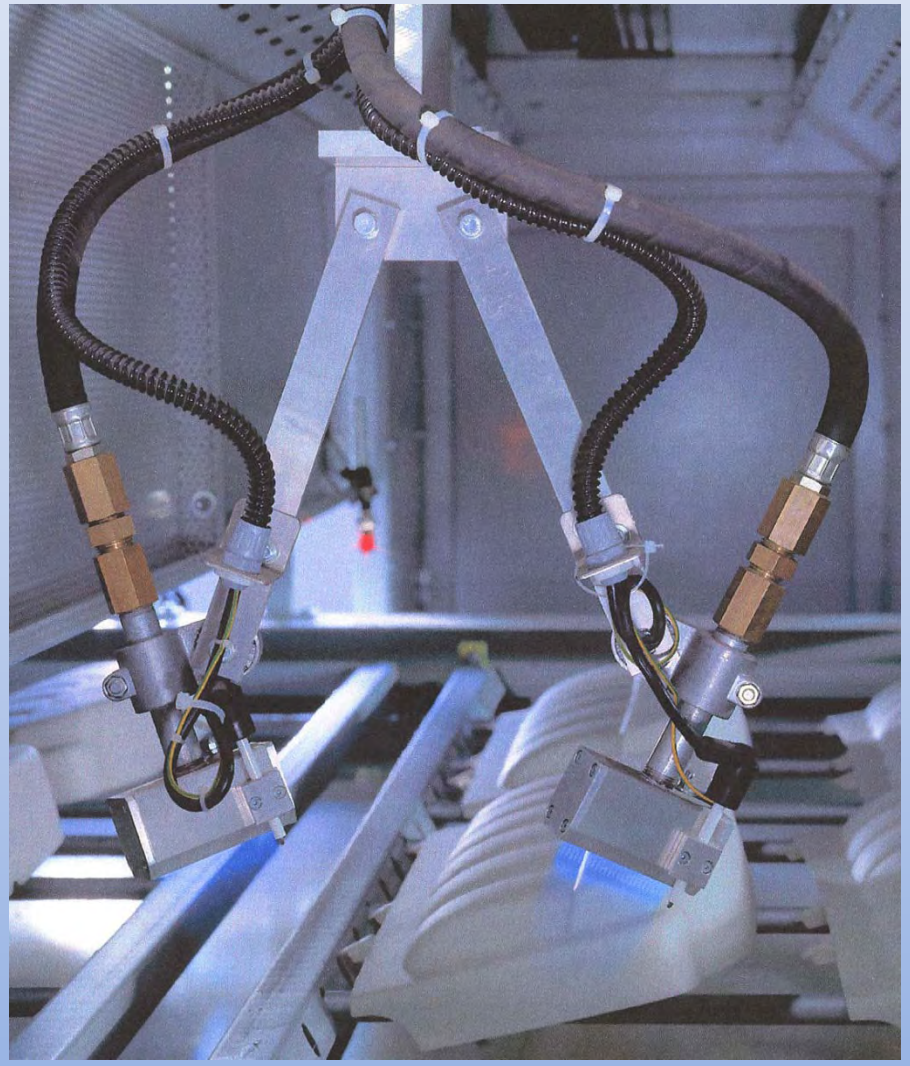
Air Plasma



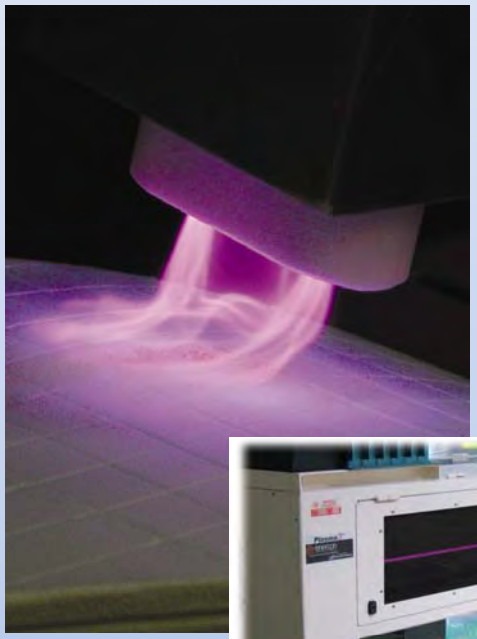
- An air plasma is a high voltage arc in air.
- When air is ionized, electrons collide with polymer surfaces to break molecular bonds, creating free radicals which react in the presence of reactive oxygen species (ROS) to form high polarity functional groups.

Flame Plasma

- A flame plasma is the ionization of a gas mixture typically comprised of 10:1 air to hydrocarbon gas.
- Surface concentration after treatment of hydroxyl, carbonyl and carboxyl groups.
- Water-soluble low molecular weight oxidized materials (LMWOM) generated as products of oxidation and chain scission of the polymer surface, agglomerated into small topographical mounds

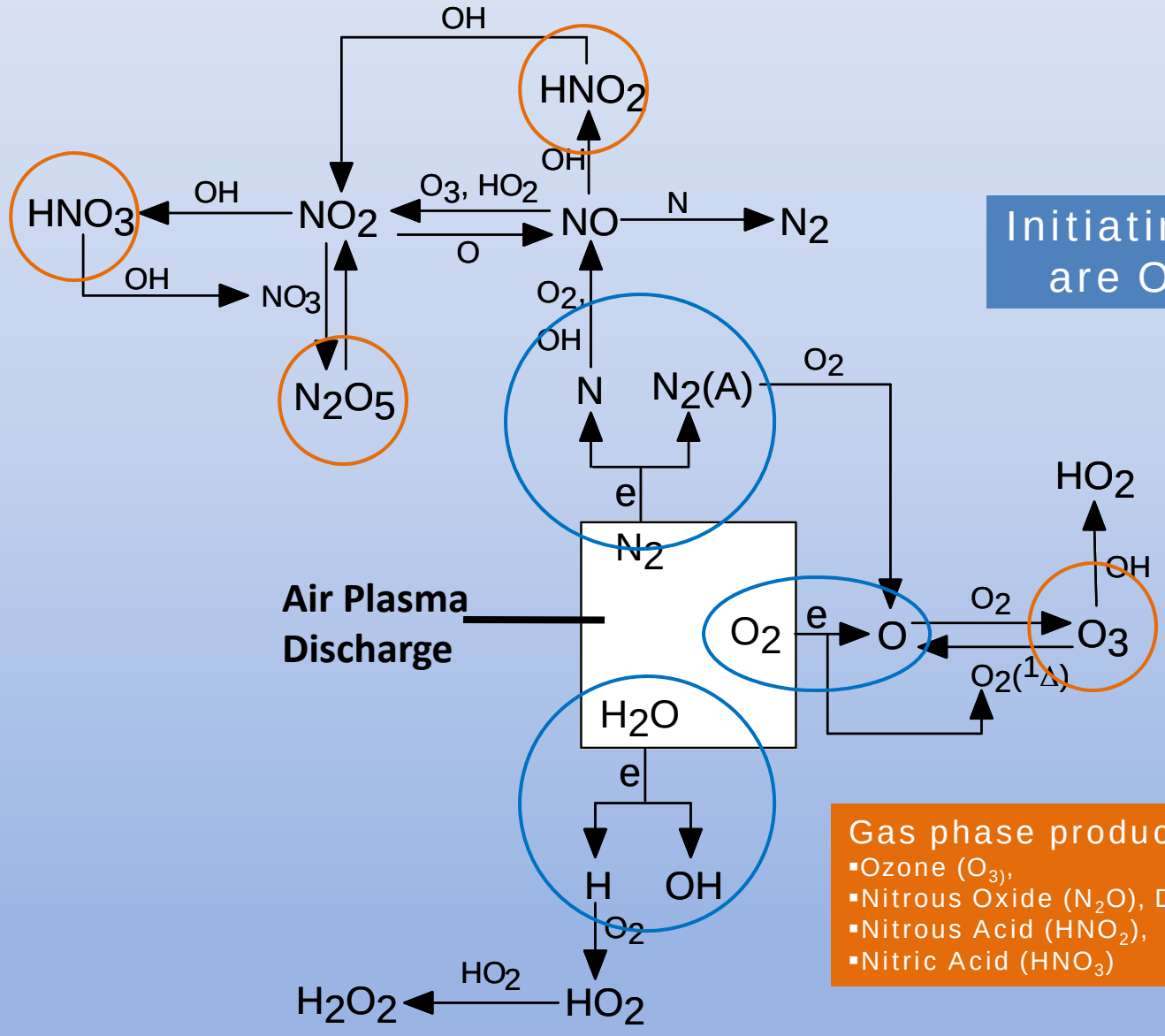


Variable Chemistry Gas-Phase Plasma



- A gas-phase plasma is the ionization of various gas mixtures at low temperature, low voltage, and high frequency.
- Ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small.
- Non-thermal plasma. Have ions and neutrals at a much lower temperature, (normally room temperature), whereas electrons are hotter.
- Very high density discharge

Reaction Mechanism for Air Plasma-based Discharge (white box)

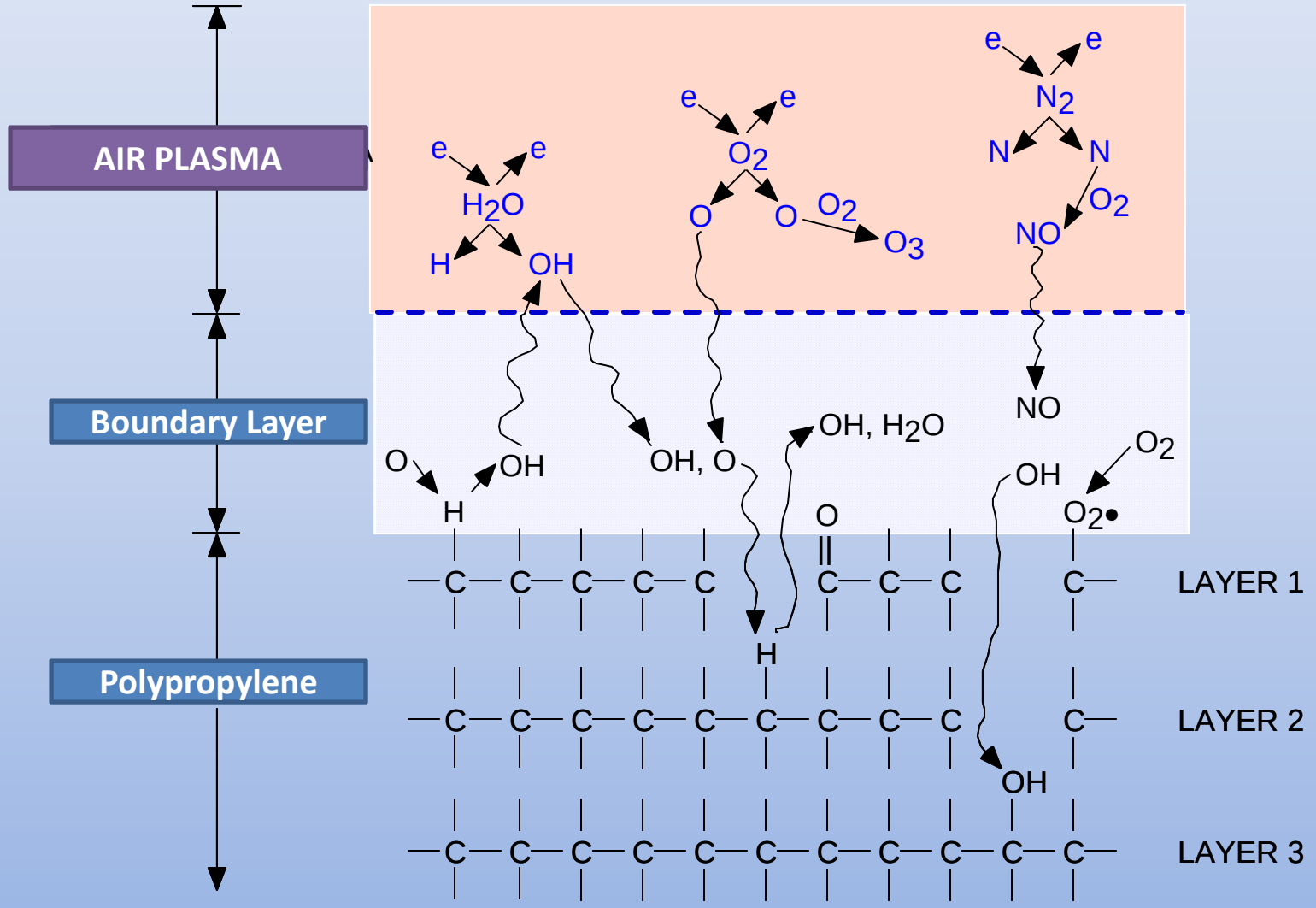


Initiating radicals are O, N, OH, H

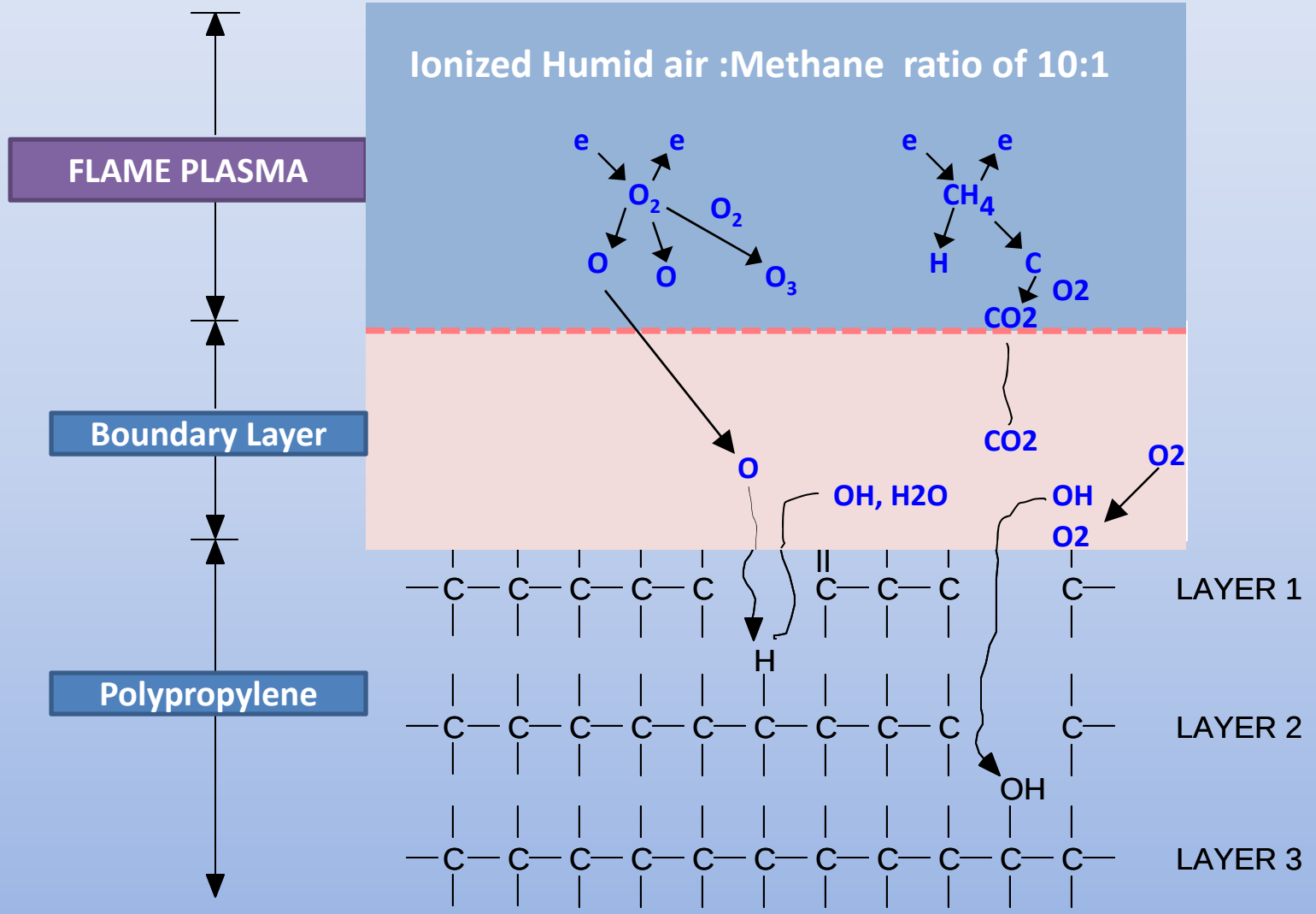
Gas phase products include:

- Ozone (O_3),
- Nitrous Oxide (N_2O), Di-nitrogen Pentoxide (N_2O_5),
- Nitrous Acid (HNO_2),
- Nitric Acid (HNO_3)

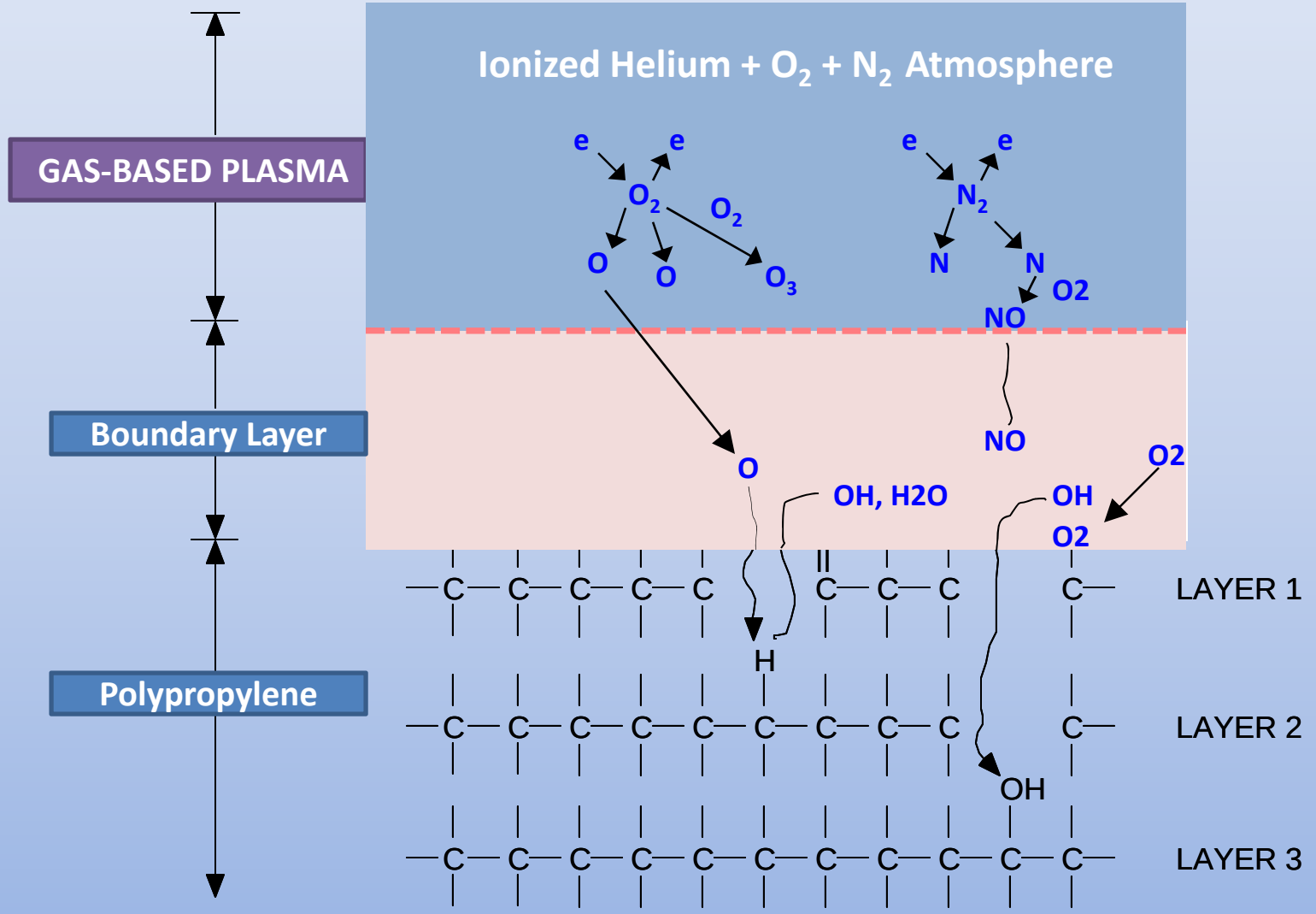
Air Plasma Reaction Pathway



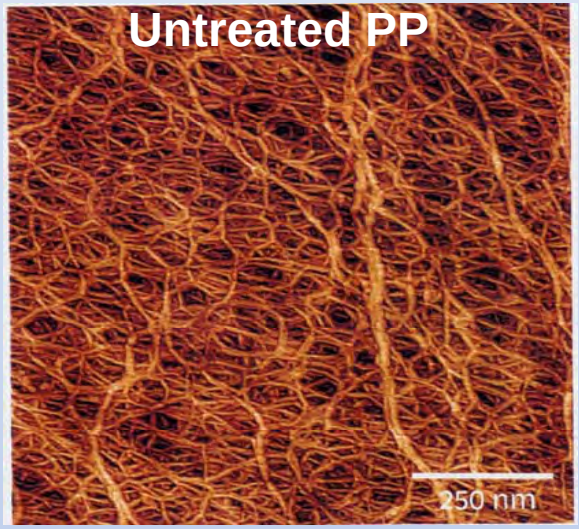
Variable Chemistry Plasma Reaction Pathway

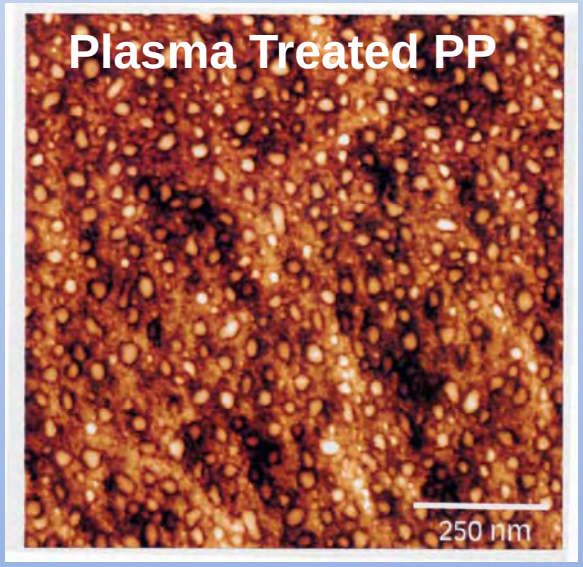


Variable Chemistry Plasma Reaction Pathway



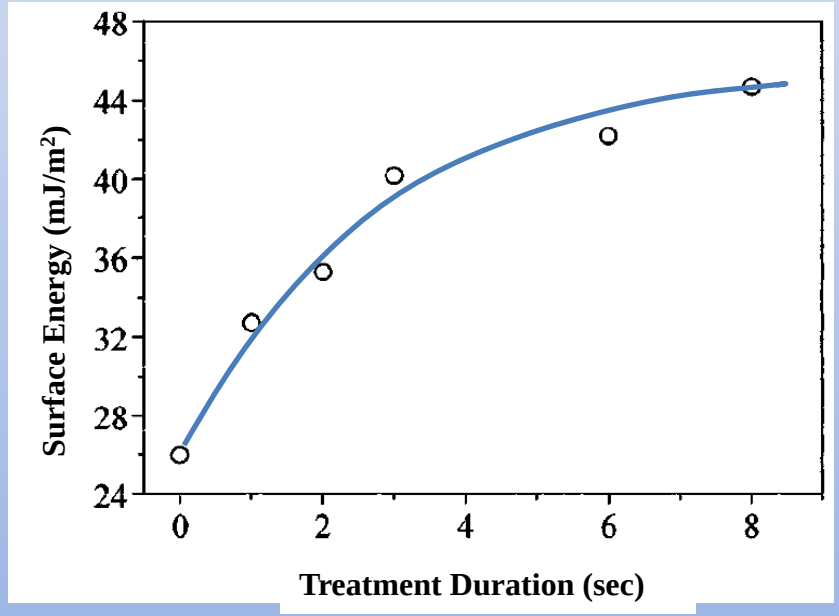
Plasma Surface Modification of Polymers





- To improve wetting and adhesion of polymers, atmospheric plasmas are used to generate radicals to functionalize surfaces.

Polypropylene (PP)



Hydrophilic

↑

Hydrophobic

Massines *et al.* J. Phys. D 31, 3411

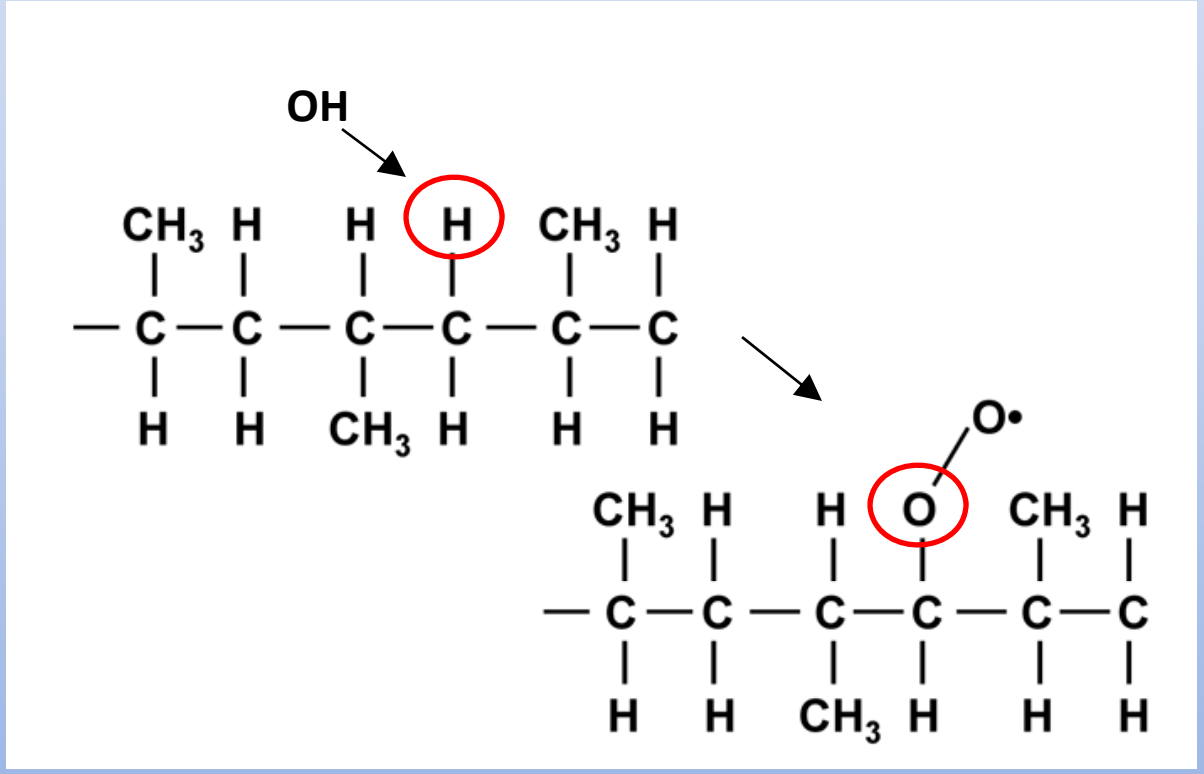
- M. Strobel, 3M

Plasma Functionalization of a PP Surface

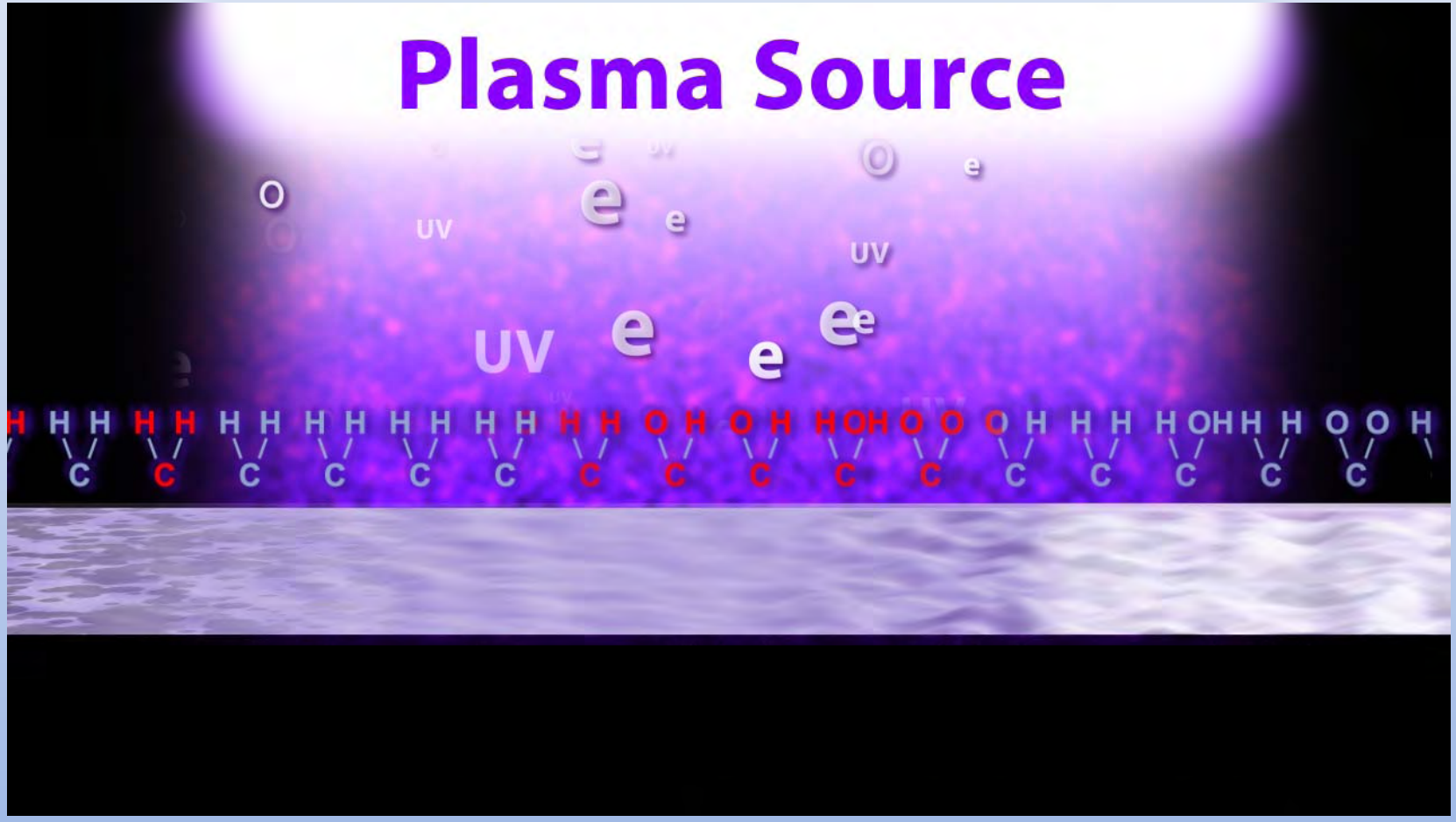
- Untreated PP is hydrophobic.
- Increases in surface energy by plasma treatment are attributed to the functionalization of the surface with hydrophilic groups. Examples:
  - Carbonyl (-C=O)
  - Carboxyl (-COOH)
  - Hydroxyl (-OH)
  - Amine (-N-)
- The degree of functionalization depends primarily upon gas used and energy density.

Polypropylene Polymer Structure

- The surface energy of polypropylene $[C_2H_3(CH_3)]_n$ is increased by hydrogen abstraction (ions, radicals photons) followed by passivation by O atoms, in this case forming peroxy groups.



Atmospheric Plasma Surface Effects



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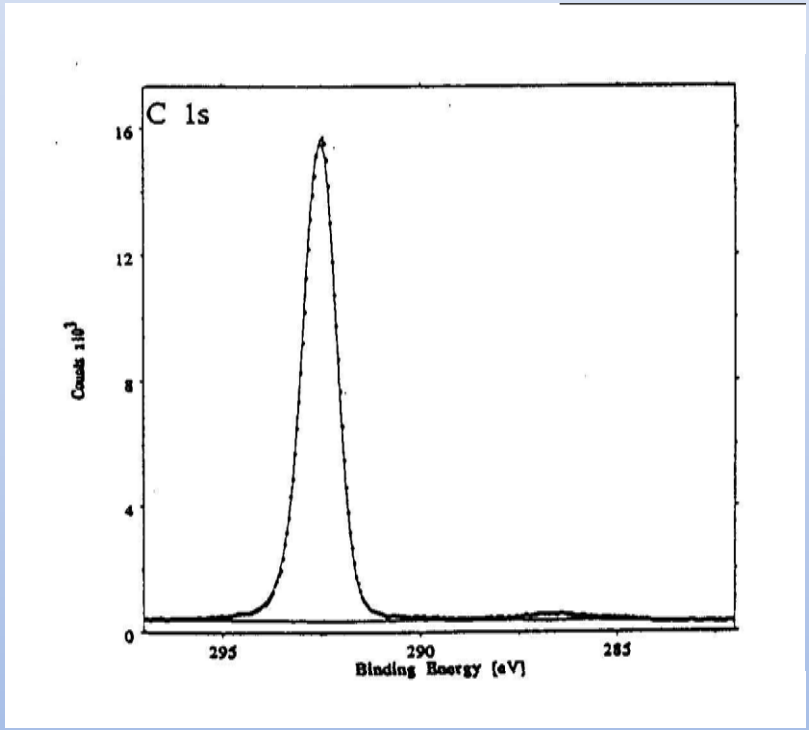
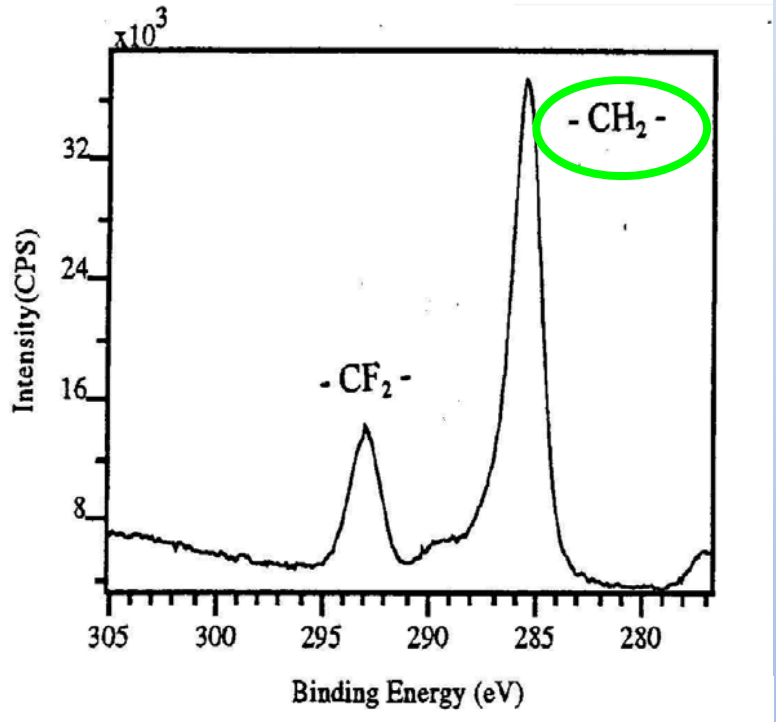


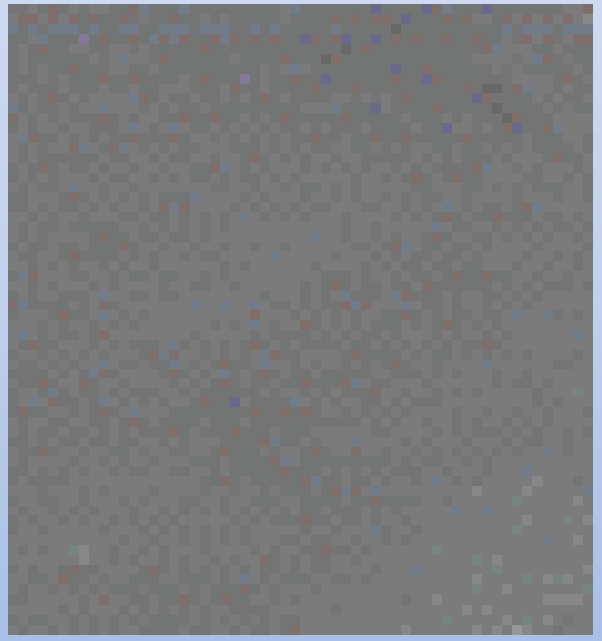
XPS spectrum results of untreated PTFE sample



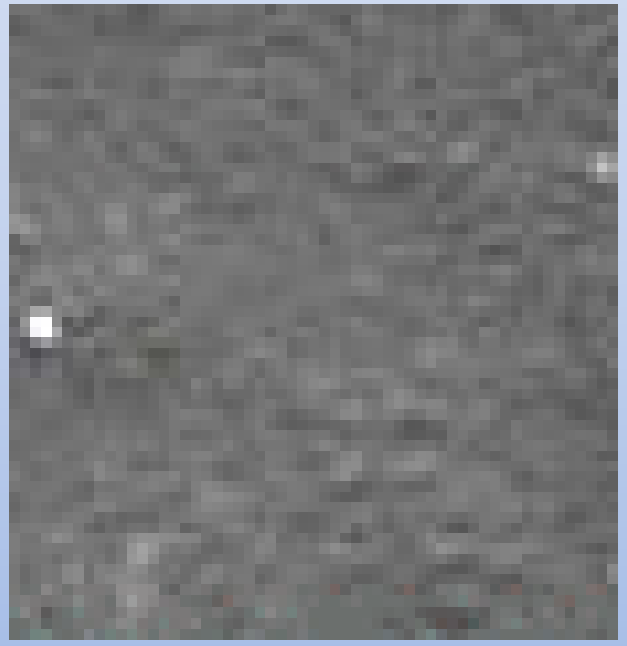
XPS spectrum results of treated PTFE sample

Atmospheric Plasma Surface Effects

PE Film (30,000 SEM magnification)



Original Film



Plasma-Treated

Comparison of Atmospheric Plasmas

Type of Discharge	Plasma Density (electrons/cm $^{-3}$)	O Atom Density (electrons/cm $^{-3}$)

Comparison of Atmospheric Plasmas

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Plasma Torch	10^{16}	10^{17} - 10^{18}

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Air Plasma Discharge	10^{9}	10^{12}

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Plasma Torch	10^{16}	10^{17} - 10^{18}
Air Plasma Discharge	10^{9}	10^{12}
Flame Plasma Discharge	10^{16}- 10^{17}	10^{17} - 10^{18}

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Dielectric Barrier Discharge	10^{9}	10^{13}

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Low Pressure (Vacuum) Glow Discharge	10^{-1} – 10^{-5}	n/a

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Dielectric Barrier Discharge	10^{9}	10^{13}
Low Pressure (Vacuum) Glow Discharge	10^{-1} – 10^{-5}	n/a
RF Atmospheric Pressure, High Density Discharge	10^{12}	10^{14} - 10^{16}

Achievable Plasma Treatment Levels by Material Class

Materials	Surface Energy (dynes/cm)		DI Water Contact Angle (degrees)	
	before	*after*	*before*	*after*
Hydrocarbons				
Polypropylene	29	>72	87	22
Polyethylene	31	>72	87	42
Polystyrene	38	>72	72.5	15
ABS	35	>72	82	26
Polyamide	<36	>72	63	17
Epoxy	<36	>72	59	12.5
Polyester	41	>72	71	18
Rigid PVC	39	>72	90	35
Phenolic	None	>72	59	36.5
Fluorocarbons				
Polytetrafluoroethylene	37	72	92	53
Polyvinylidene	25	>72	78.5	36

Materials	Surface Energy (dynes/cm)		DI Water Contact Angle (degrees)	
	before	*after*	*before*	*after*
Elastomers				
Silicone	24	>72	96	53
Natural rubber	24	>72	None	None
Latex	None	>72	None	None
Polyurethane	None	>72	None	None
Styrene but. rubber	48	>72	None	None
Fluoroelastomers				
Fluorocarbon copolymer elastomer	<36	>72	87	51.1
Engineering Thermoplastics				
PET	41	>72	76.5	17.5
Polycarbonate	46	>72	75	33
Polyaryl ether ketone	<36	>72	92.5	3.5
Polyacetal	<36	>72	None	None
Polyphenylene oxide	47	>72	75	38
PBT	32	>72	None	None
Polysulfone	41	>72	76.6	16.5
Polyethersulfone	50	>72	92	9

Composite Surface Tensions

Reinforcements	Dynes/cm	Matrices	Dynes/cm	Composite Dynes/cm
Carbon (PAN)	30	PEEK	34	34
Carbon (PAN)	30	Epoxy	47	45
Carbon (Graphite)	32	Epoxy	47	45
Glass	40	PEEK	34	35
Glass	40	Phenolic	47	46
Glass	40	Thermoset PET	43	43
Glass	40	ABS	42	42
Glass	40	Epoxy	47	46
Kevlar	27	Epoxy	47	45

Adhesion Impediments

- Low Surface Tension
- Presence & Migration of Formulation Components (processing additives such as erucimide, stearates)
- Mold Release Agents
- Low temperature
- UV light
- Mechanical Stresses
- Design and Fabrication Issues

Adhesion Impediments

... and other surface anomalies on molded and formed parts can impede adhesion performance dramatically if they are not addressed with surface pretreatments.

- Oxygen plasma is excellent for removing organics
- When exposed to the RF energy field, oxygen (O2) is broken down into monatomic oxygen (O), O+ and O-
- Resultant combination is water vapor, CO and CO2, which is carried away in exhaust stream.

Treatment Recommendations

Thermoplastics	Key Characteristic; Recommended Treatment Technique
Acetal (POM)	Highly chemically; Variable Chemistry Plasma
Acrylic (PMMA)	Air Plasma
Cellulostics (CAL, CAB)	Acid surface residues; Air Plasma
Fluoroplastics (PTFE)	Very low polarity; Varibale Chemistry Plasma
Ketones (PEEK)	High toughness; Variable Chemistry Plasma
Polyamides (Nylon 6)	Moderate toughness; Air Plasma, Flame Plasma
Polyamideimides (PAIS)	High temperature resistance; Air Plasma, Flame Plasma
Polyarylate	Heat resistance; Air Plasma
Polybutylene (PB)	Semi-crystalline; Flame Plasma
Polycarbonate (PC)	Surface sensitivity; Variable Chemistry Plasma
Polyester Thermoplastic (PBT)	Chemical resistance; Air Plasma
Polyethylene (PE)	Non-polar; Flame Plasma, Variable Chemistry Plasma
Polyphenylene Oxide (PPO)	Impact resistance; Air Plasma
Polyphenylene Sulfide (PPS)	Very inert; Variable Chemistry Plasma
Polypropylene (PP)	Heat resistance; Air Plasma, Flame Plasma
Styrenic resins (ABS, PS, SAN)	Heat resistance; Air Plasma
Sulfone-based resins (Polysulfone)	Heat resistance; Air Plasma
Thermoplastic Elastomers (TPO, TPU)	Low density; Air Plasma, Flame Plasma
Vinyl based resins (PVC)	Include plasticizers, stabilizers; Variable Chemistry Plasma

Thermosets	Key Characteristic; Recommended Treatment Technique
Allyl	Chemical resistance; Air Plasma
Bismaleimides (BMI)	Heat resistance; Air Plasma
Epoxy	Reactive surface; Air Plasma
Phenolic	Crosslinked structure; Air Plasma
Polyester	Polar; Air Plasma
Polyurethanes (PUR)	Polar; Air Plasma
Polyurea	Amino groups; Air Plasma

Concluding Remarks

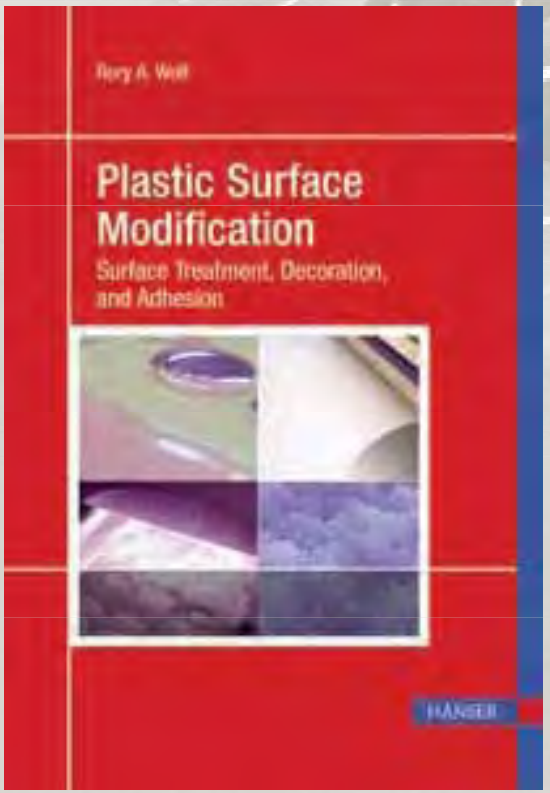
- Surface energy of any polymer surface should exceed of the interface (paint, coating, ink, adhesive) by ≈ 10 mN/m^{-1}
- Improved adhesion of interfaces is due to physical interactions and chemical bonds.
- Primary adhesion impediments are low surface tension, low surface area, polymer polarity, and surface processing residues.
- ROS, treatment power density, and treatment chemistry are key to promoting surface adhesion to polymers.

Concluding Remarks

- Air plasma, flame plasma and variable chemistry plasma individually prescribable to specific polymers.
- Environmentally friendly, consuming little energy, requiring no drying, and presenting no waste-disposal issues.
- Depending upon process, can provide high degree of activation and long shelf life.
- Causes no substrate damage or bulk property changes.
- Can be applied to an extensive range of substrates in practically all geometries—small or large, simple or complex.

"Plastic Surface Modification: Surface Treatment, Decoration, and Adhesion"

(Hardcover-English version)



North America: **www.amazon.com**
http://www.amazon.com/Plastic-Surface-Modification-Treatment-Adhesion/dp/1569904472/ref=sr_1_1?ie=UTF8&s=books&qid=1270759852&sr=1-1

Europe (UK): **www.amazon.co.uk**
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Thank you for attending!

Plastic Surface Modification:

Cleaning, Adhesion and Functionalization

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