Ion Beam Treatment of Polymers (IBT)

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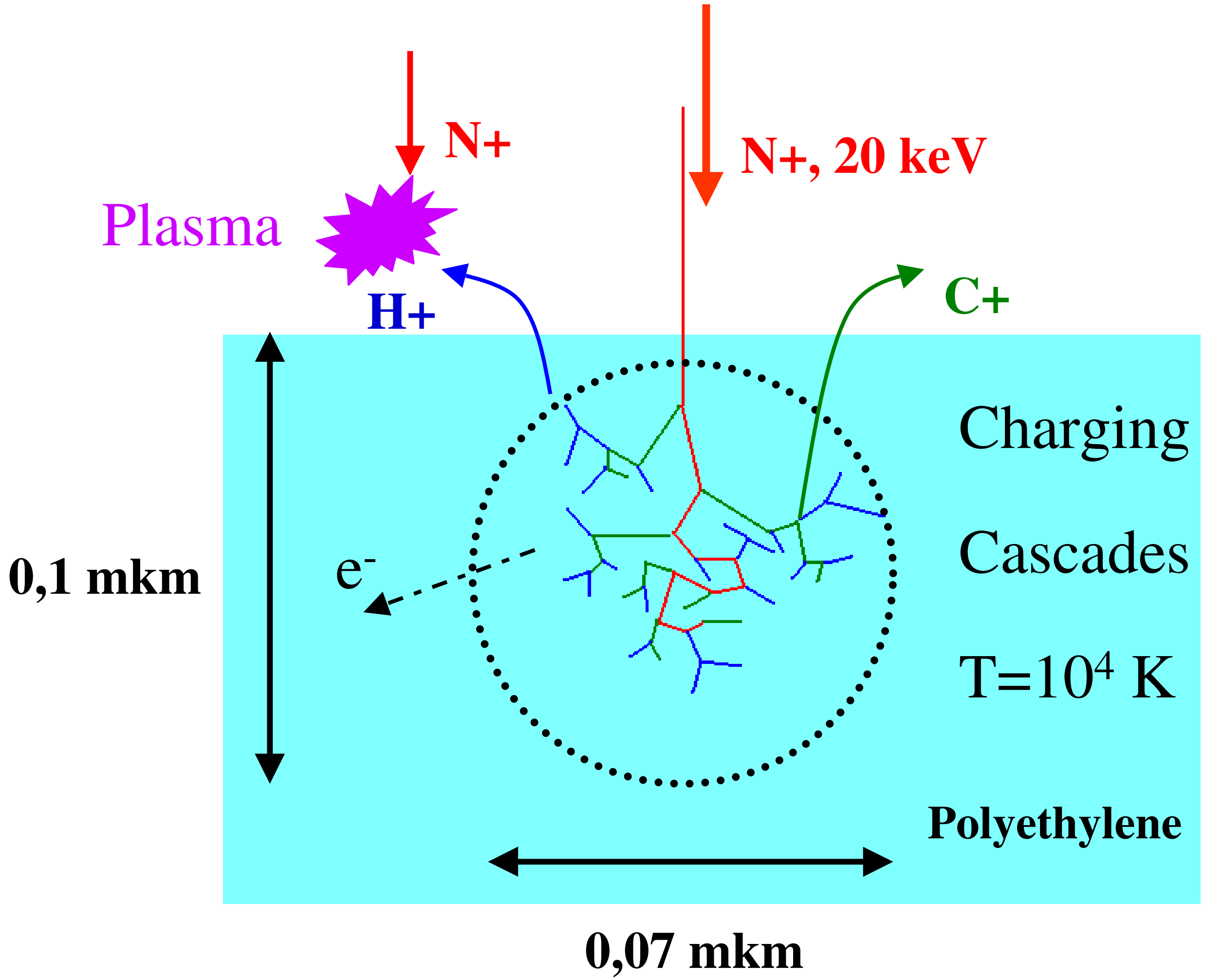
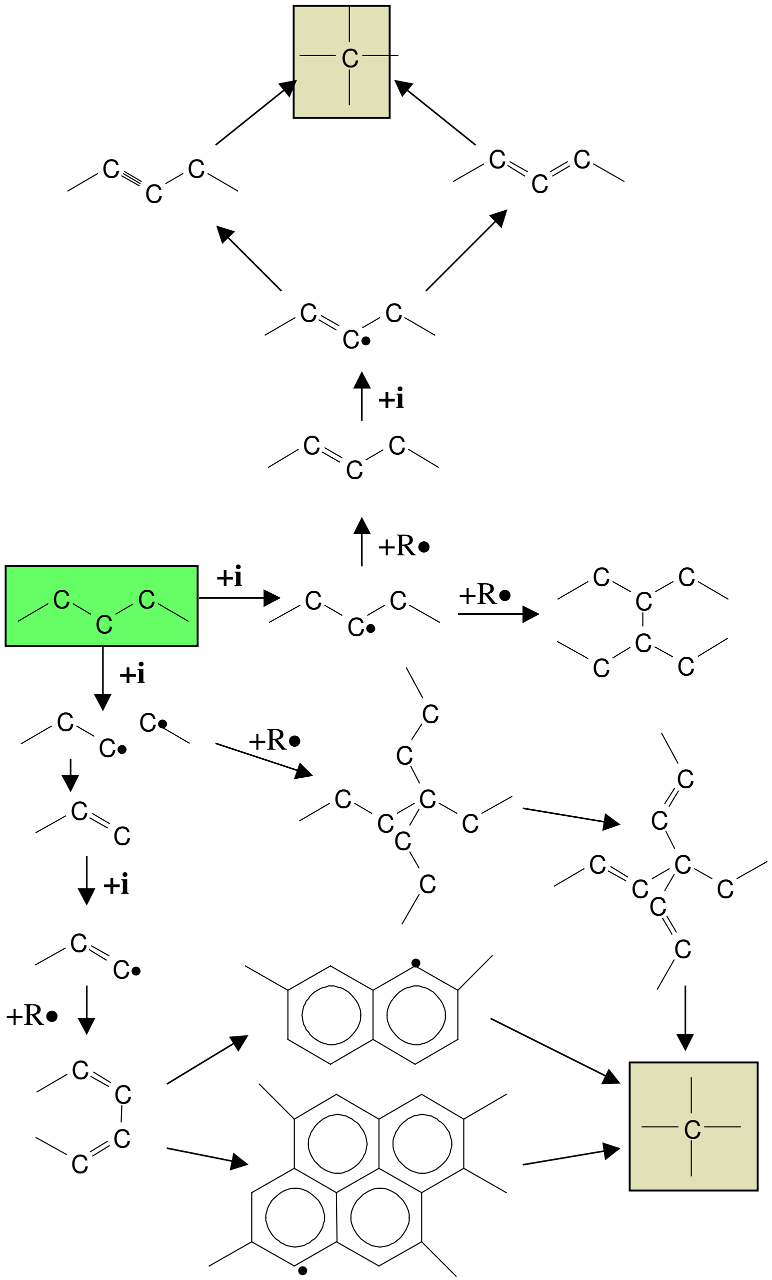
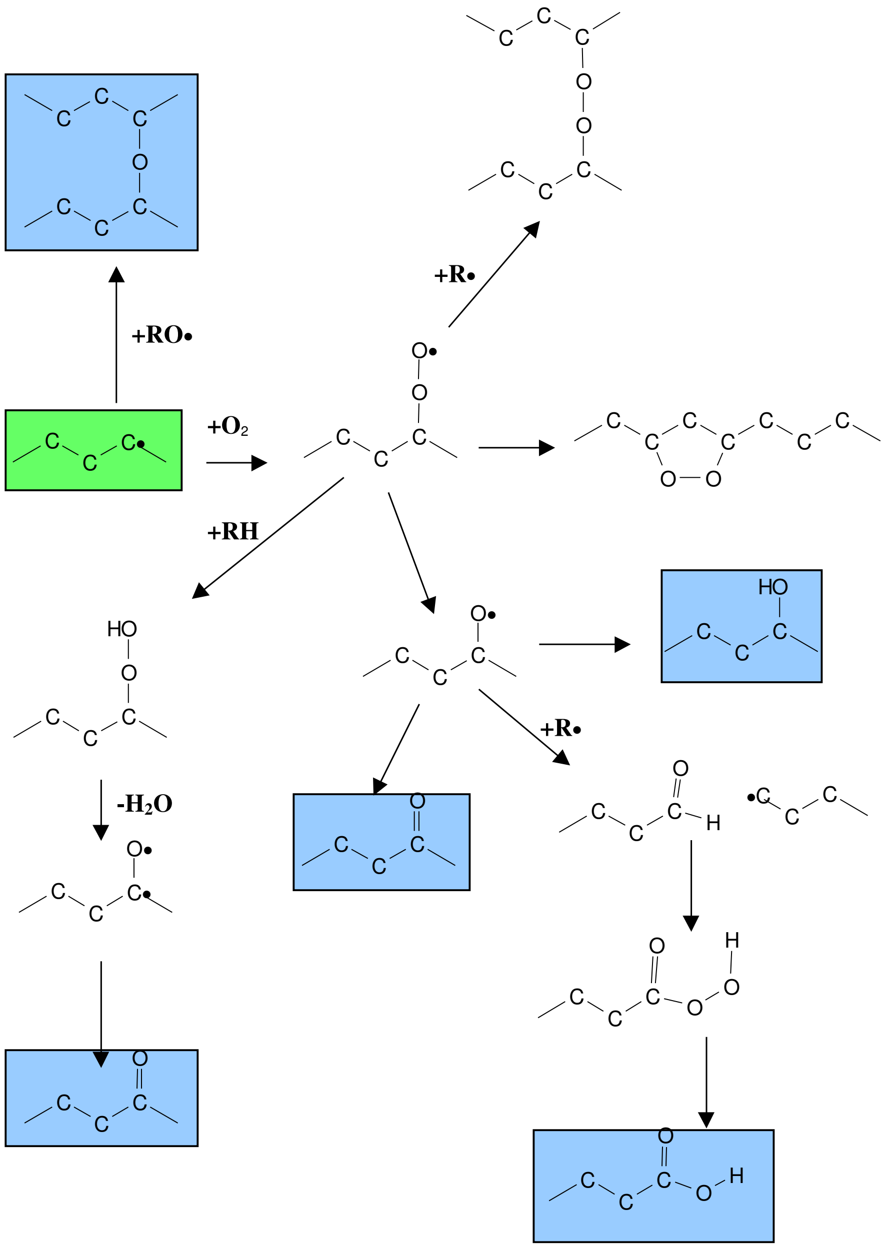
Ion Beam - Polymer interaction



Chemical Reactions of PE in vacuum



Chemical Reactions of PE in air



Goals of research

- **Structure changes in polymers**
- Structure levels, new chemical groups, layer structure
- Influence of treatment parameters and conditions
- **Comparison of different sources for treatment of polymers**
- Continuous regime, Pulse Ion beam treatment, Plasma immersion ion implantation
- **Applications**
- Adhesion, Chemical activity, Wetting, Aging, Biostability, Hardness

Polymers

- Polyethylene (PE),
- Polypropylene (PP),
- Polystyrene (PS),
- Polychlorvinyl (PVC),
- Polytetrafluorethylene (PTFE),
- Polyethyleneterephtalate (PETF),
- Polymethylmetacrylate (PMMA),
- Polyimide,
- Polycarbonate (PC),
- Epoxy resin.

- Polyisoprene rubber (PI),
- Nitryl rubber,
- Silicone rubber,
- Ethylen-Propylene rubber (EPDM),
- Butyl rubber (BR).

- <u>Polyurethanes (PU) based on:</u>
- PPG, PEG, PBG, PC
- TDI, MDI
- Aromatic Diamine,
- Aliphatic Diamine.

Equipment for IBT

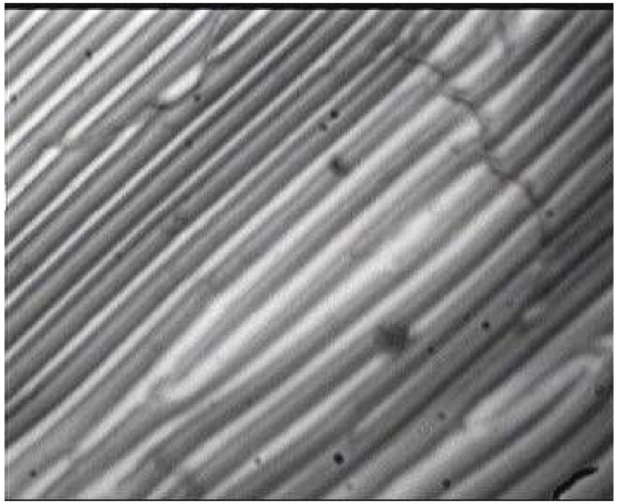
- “PULSAR”, Institute of Electrophysics
- **N^+, O^+, Ar^+, C^+(CH_4^+, CH_3^+, ...), 10-40 keV, 30-1000 mkS, 1-20 mA/cm²**
- “TEMP”, Institute of Nuclear Physics, Tomsk
- **C^+, 200 keV, 1mkS, 200 mA/cm²**
- Source of neutral atom beam, Institute of Nuclear Physics, Novosibirsk
- **N^+, 10 keV, continuous, 100 mkA/cm²**
- “ILU-4”, Produced by Kurchatov Institute
- **N^+, 20 keV; continuous, 1 mkA/cm²**
- PIII, Rossendorf Research Center
- **N^+, 20 keV, 5 mkS, 16 mA/cm²**

Methods for analysis

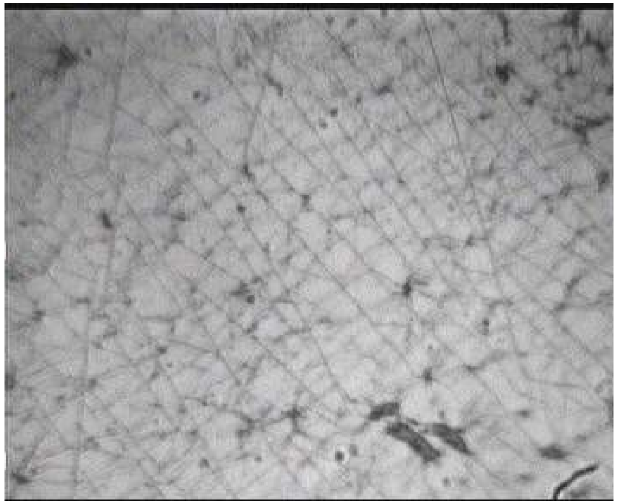
- **IR and UV spectra (Bruker, Nicolet, Bomem, Carl Zeiss Jena)**
- **XPS spectra, RBS spectra, X-ray diffraction method**
- **Wettability and surface energy calculations**
- **Microphotographs**
- **TRIM calculations**
- **Stress tests (peeling, strength, normal adhesion)**
- **Environment tests and Biodegradation in organisms**

Morphology of polymer surface

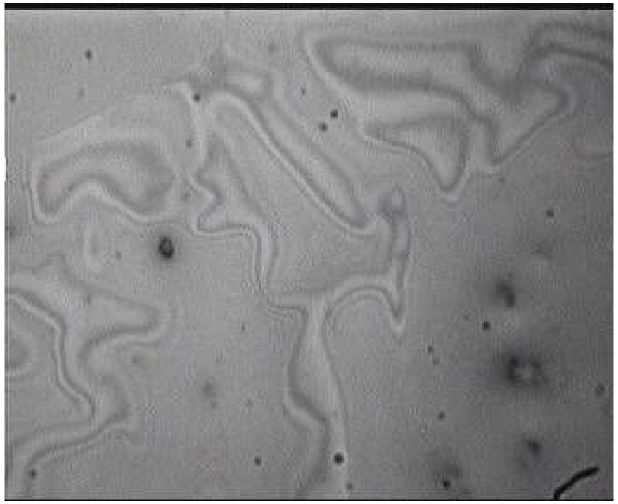
Silicon Rubber, continuous IBT, treatment of cured resin



Polyurethane, Pulse IBT

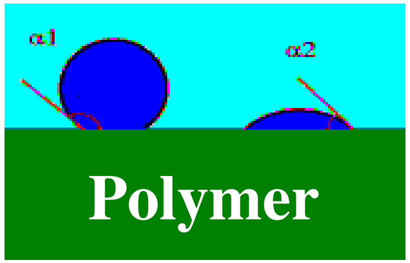


Silicon Rubber, continuous IBT, treatment of liquid resin

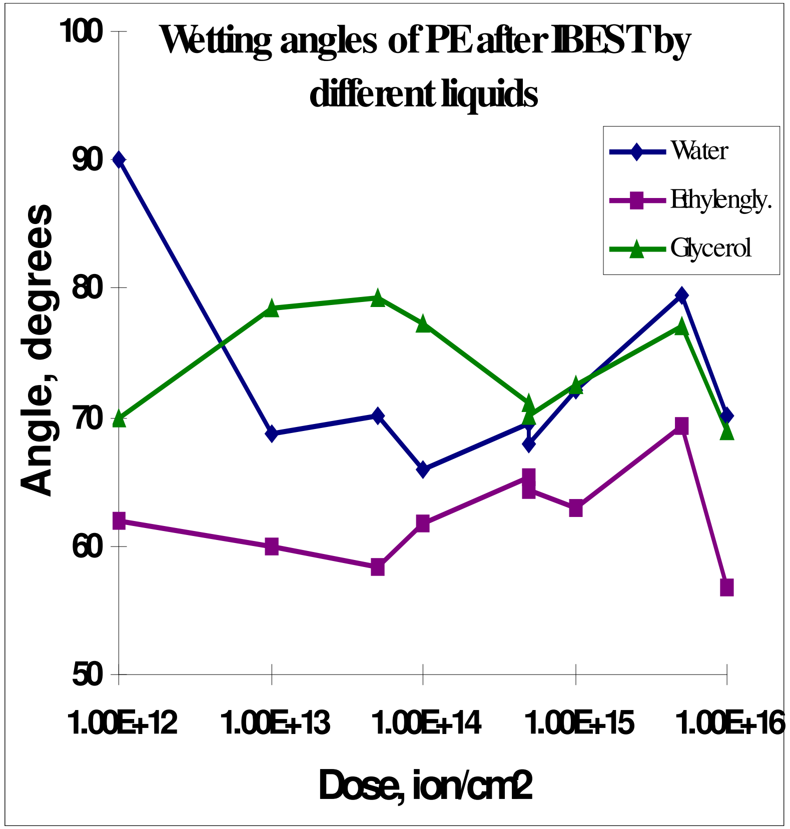


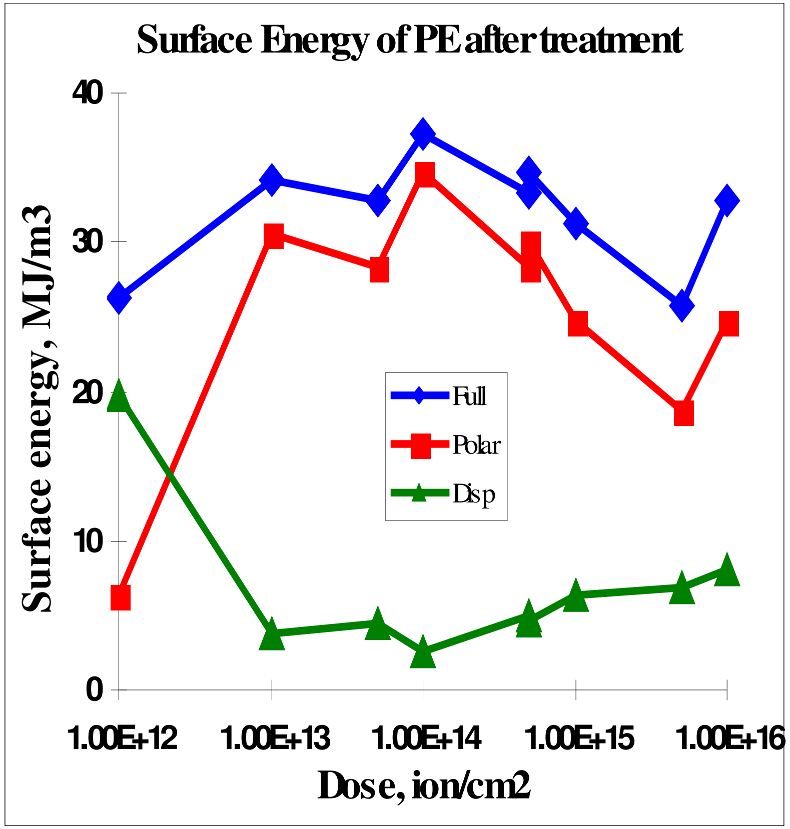
Epoxy resin, cured in Pulse IBT

Wettability of Polyethylene

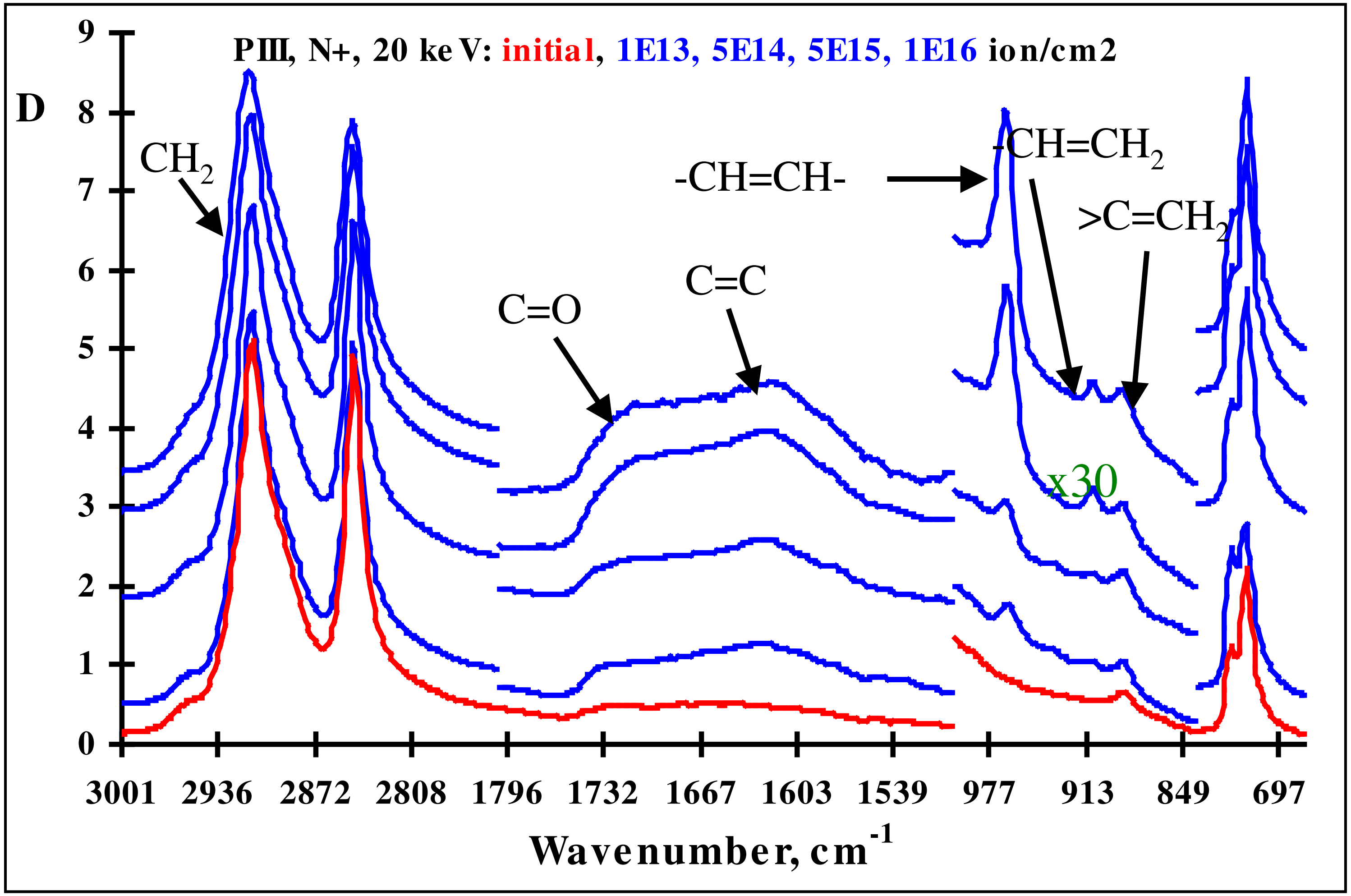


$$\sigma_2(1+\cos\theta)/\mathrm{sqr}(\sigma_2)= \mathrm{sqr}(\sigma_1^{d})+\mathrm{sqr}(\sigma_1^{p})*\mathrm{sqr}(\sigma_2^{p})/\mathrm{sqr}(\sigma_2^{d})$$

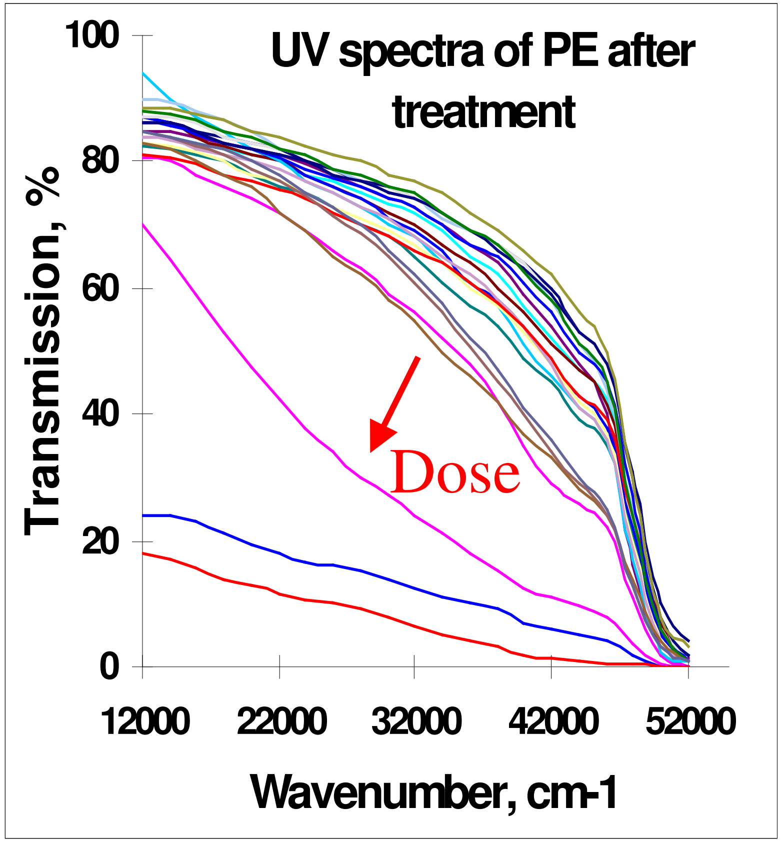


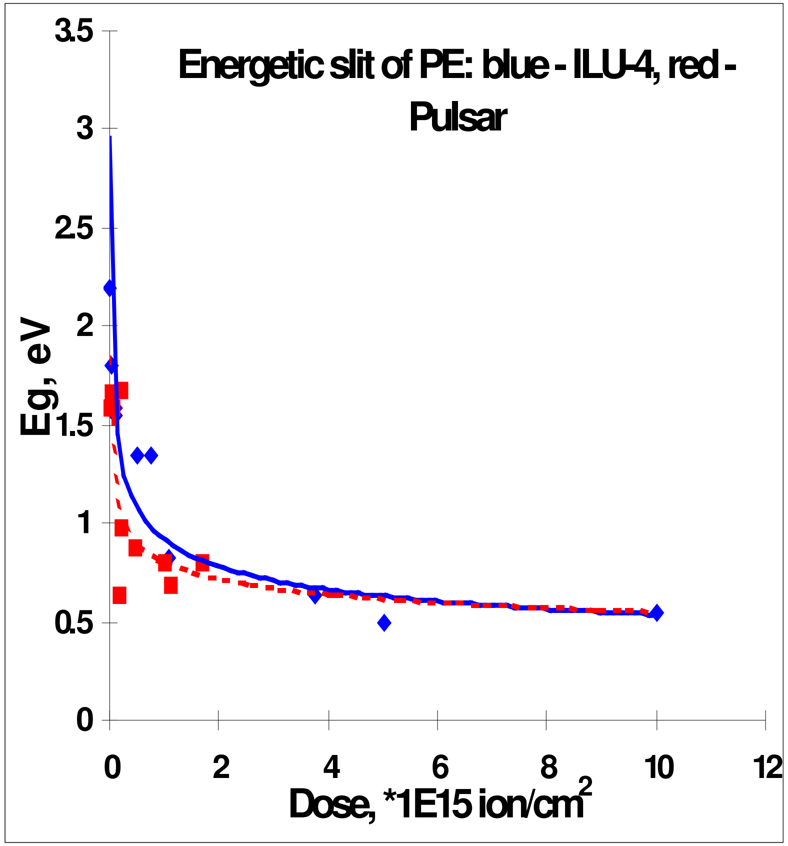


Infrared Attenuated Total Reflection spectra (IR ATR) of polyethylene surface



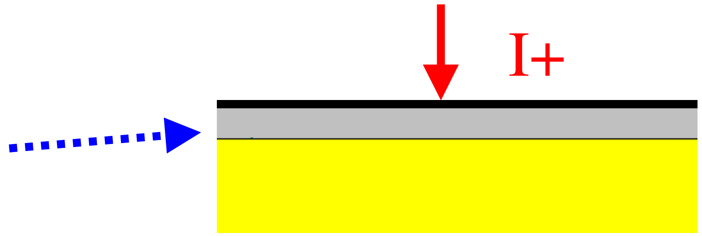
Ultraviolet and Visual Spectra of Polyethylene after IBT





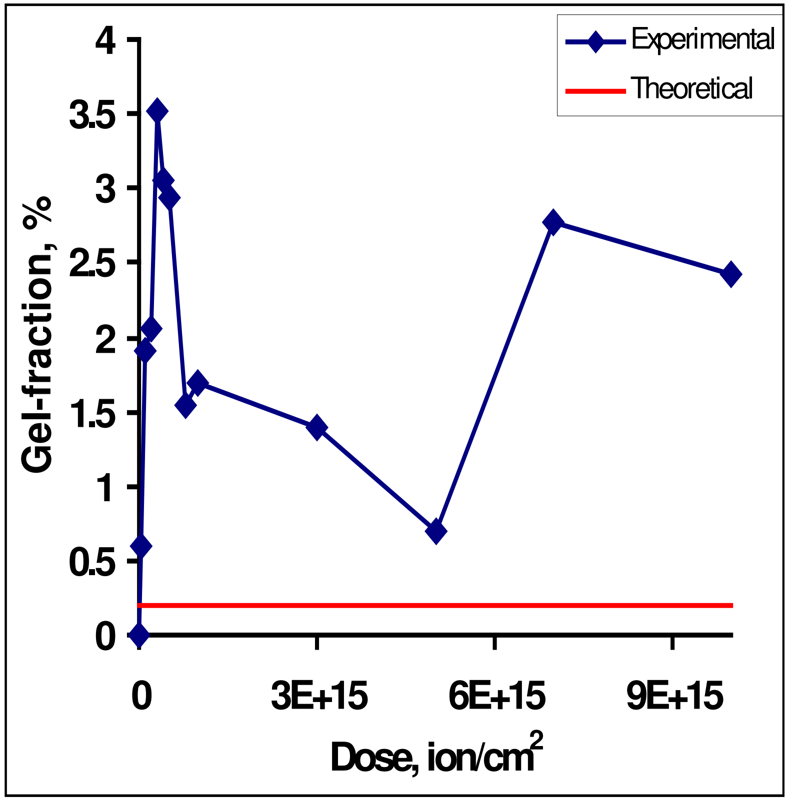
Crosslinks in Polyethylene

$$\sim CH_2\text{-}CH_2\text{-}CH_2\sim \quad \sim CH_2\text{-}CH_2\text{-}CH_2\sim \;\xrightarrow{I+}\; \sim CH_2\text{-}CH\text{-}CH_2\sim \;|\; \sim CH_2\text{-}CH\text{-}CH_2\sim$$



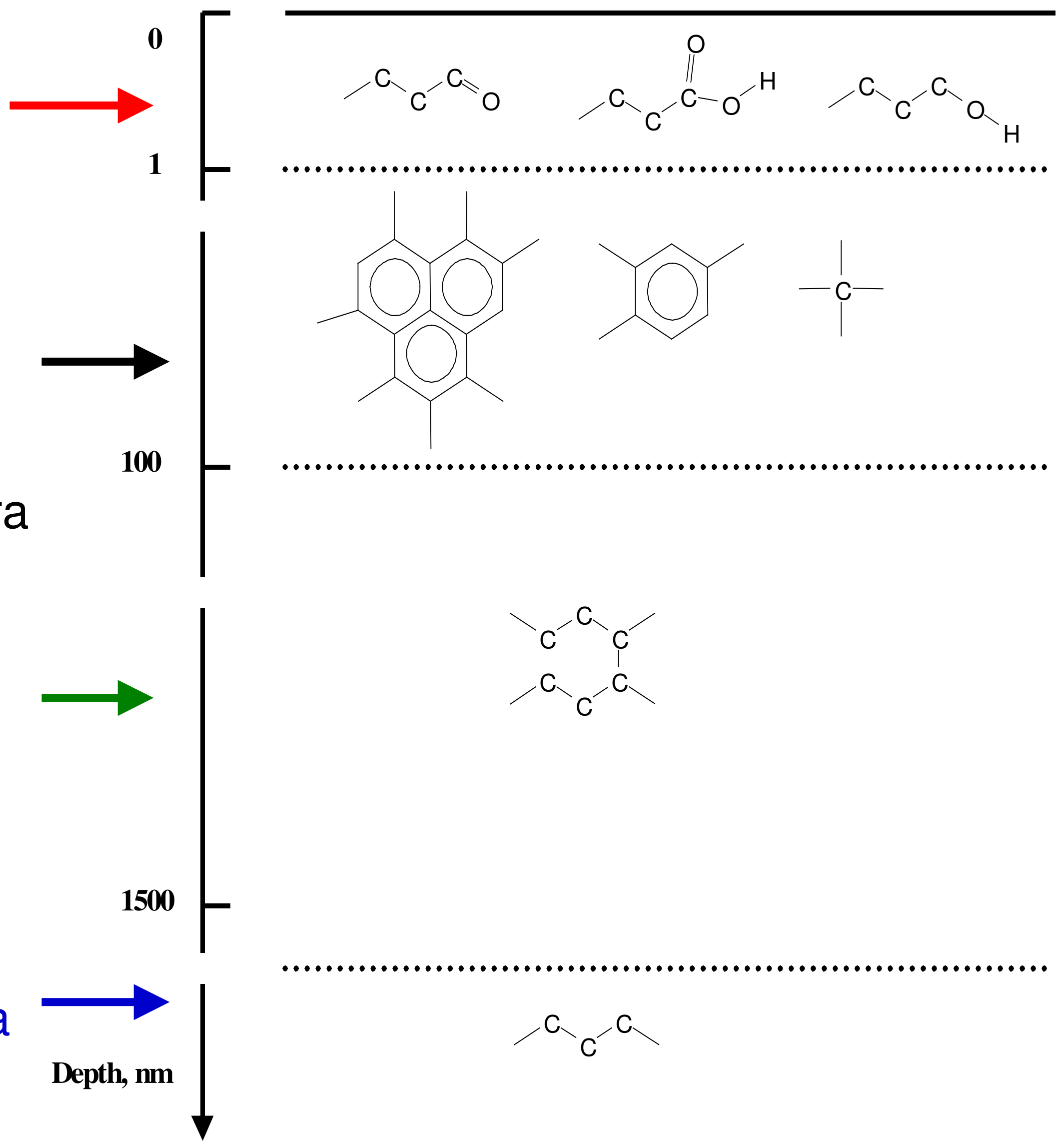
- **<u>Maximal gel-fraction:</u>**
- **Polyethylene, iiAr+, 2.09%**
- **Polyethylene, iiO+, 1.71%**
- **Polyethylene, iiC+, 1.68%**
- **Polyisopren, iiN+, 11.70%**
- **Polyisopren, iiC+, 2.40%**
- **Polyisopren, iiO+, 9.63%**
- **Polystyrene, iiO+, 4.44%**
- **Polystyrene, iiC+, 3.25%**
- **Theory - 0.2% and less**

PE, N^+ 20 keV, 5 mA/cm^2



Layer structure of Polyethylene after IBT

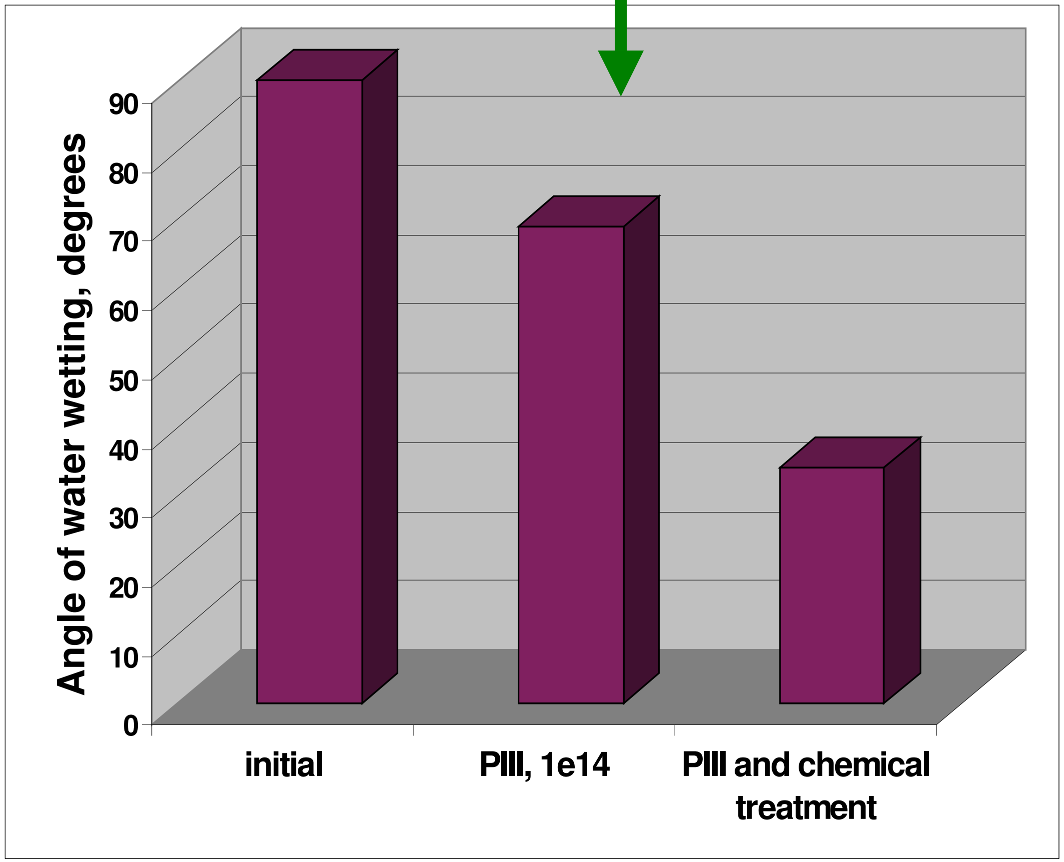
- Oxidized layer
  - Wetting angle
  - UV reflection spectra
  - XPS spectra
- Carbonised layer
  - IR ATR spectra
  - UV transmission spectra
- Crosslinked layer
  - Gel-fraction
- Unchanged layer
  - IR transmission spectra

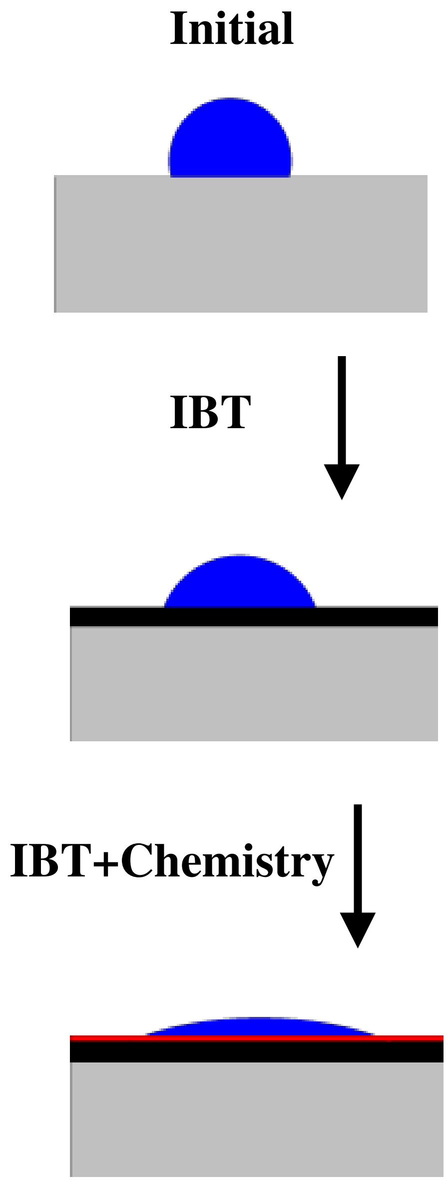


Increasing of wetting by water

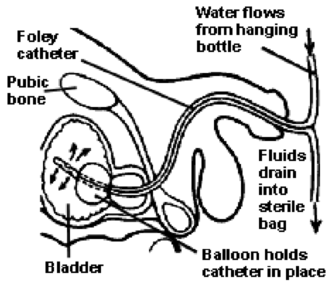
Polymers
- in medicine,
- in food industry,
- in publisher industry.

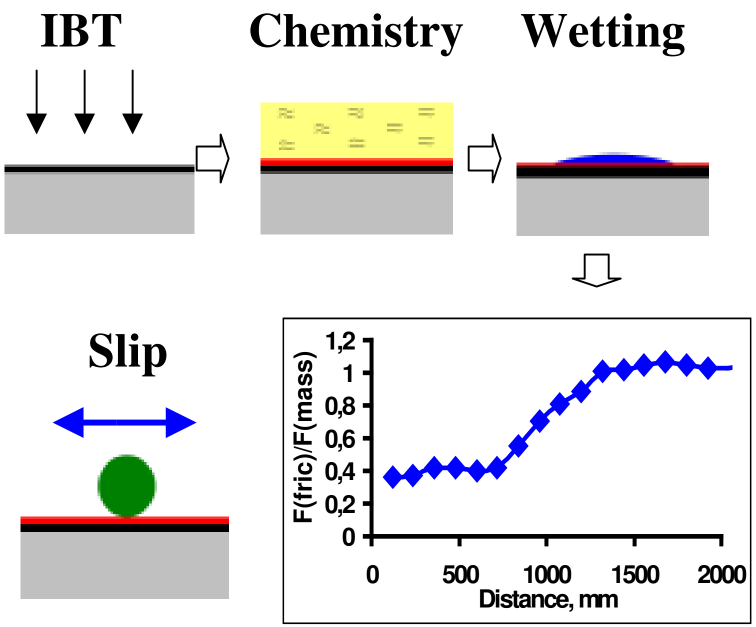
PE, PTFE (Teflon), **PP**, EPDM, PU



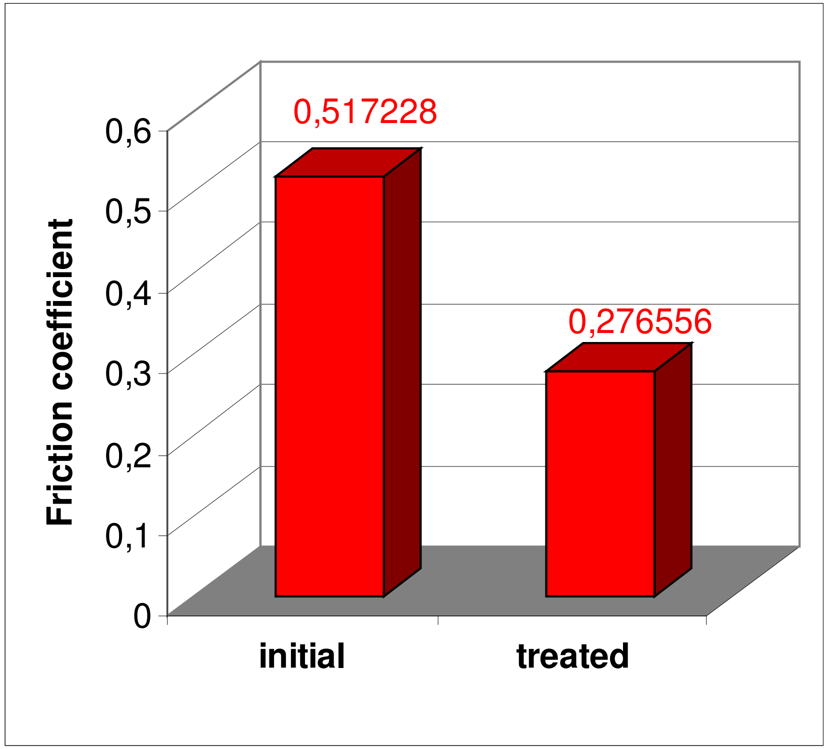


Slip in water

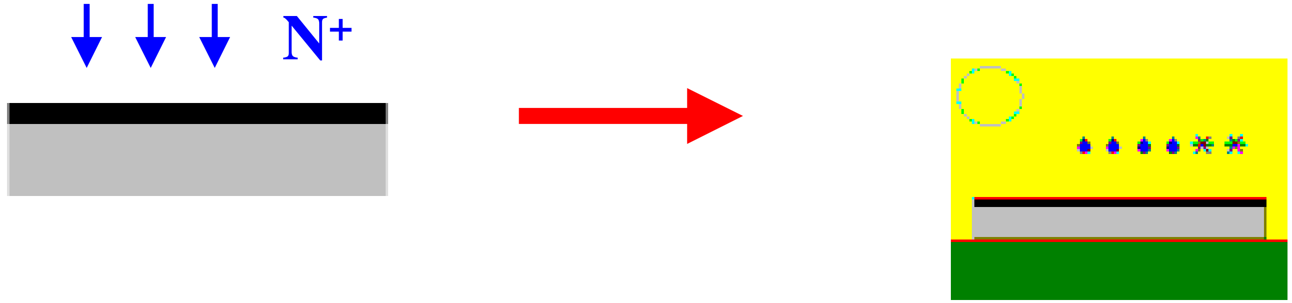


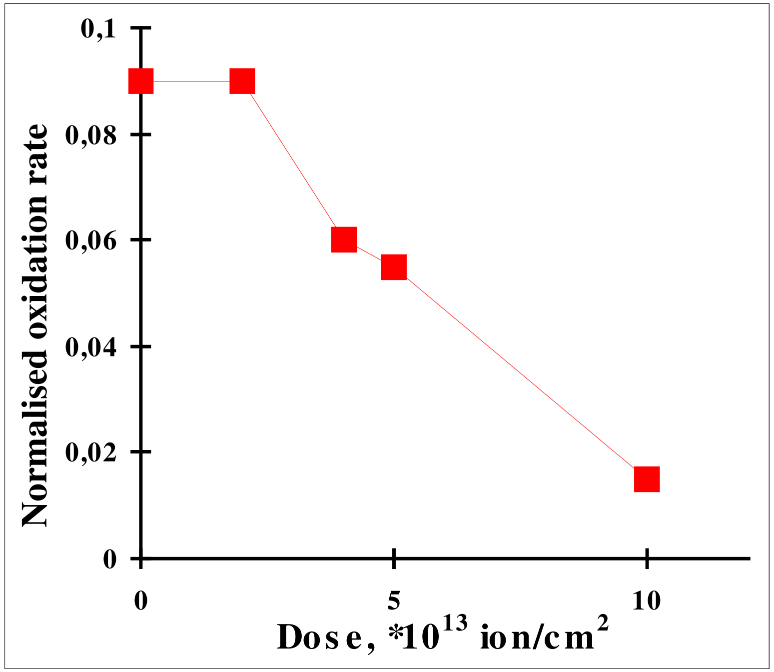


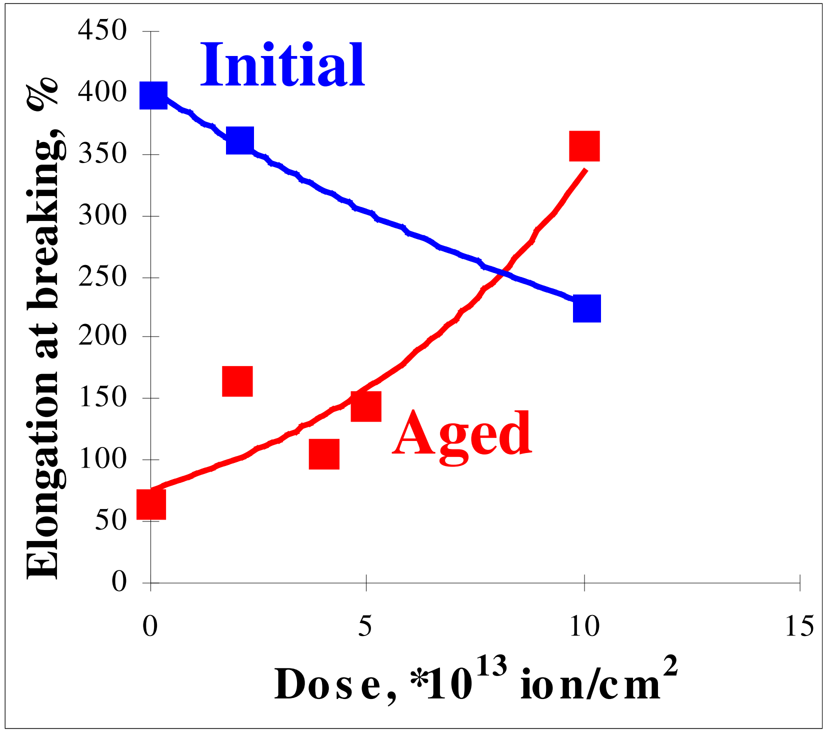
Urine catheters
with Polyurethane coating



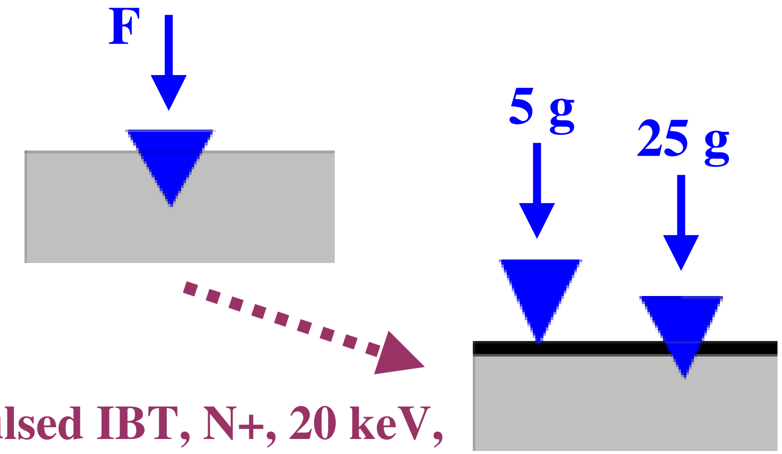
Aging of Polyethylene after Ion Beam Treatment



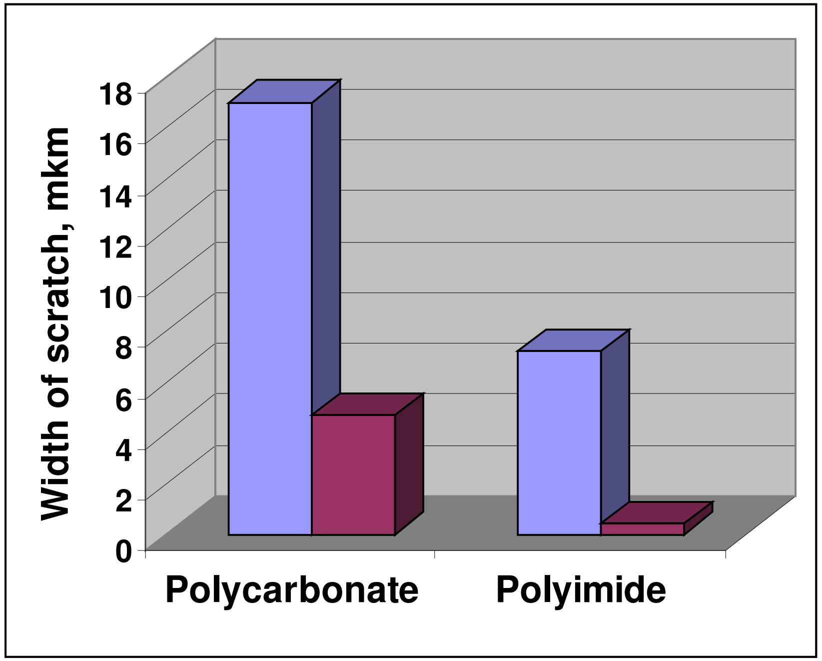


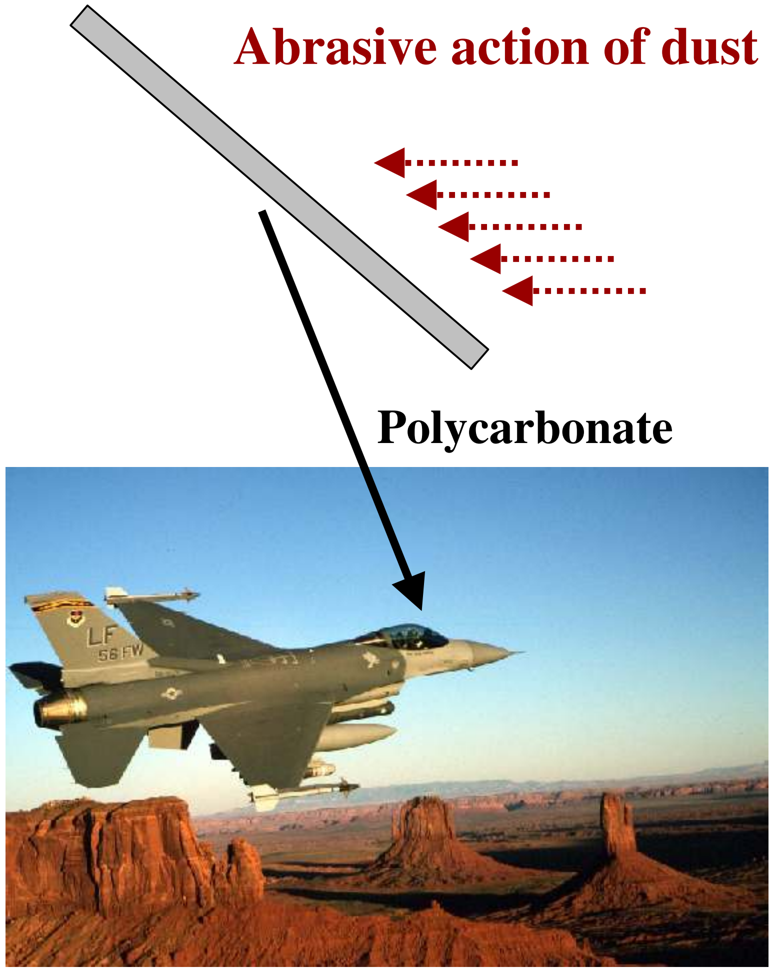


Hardness of Polymers after IBT

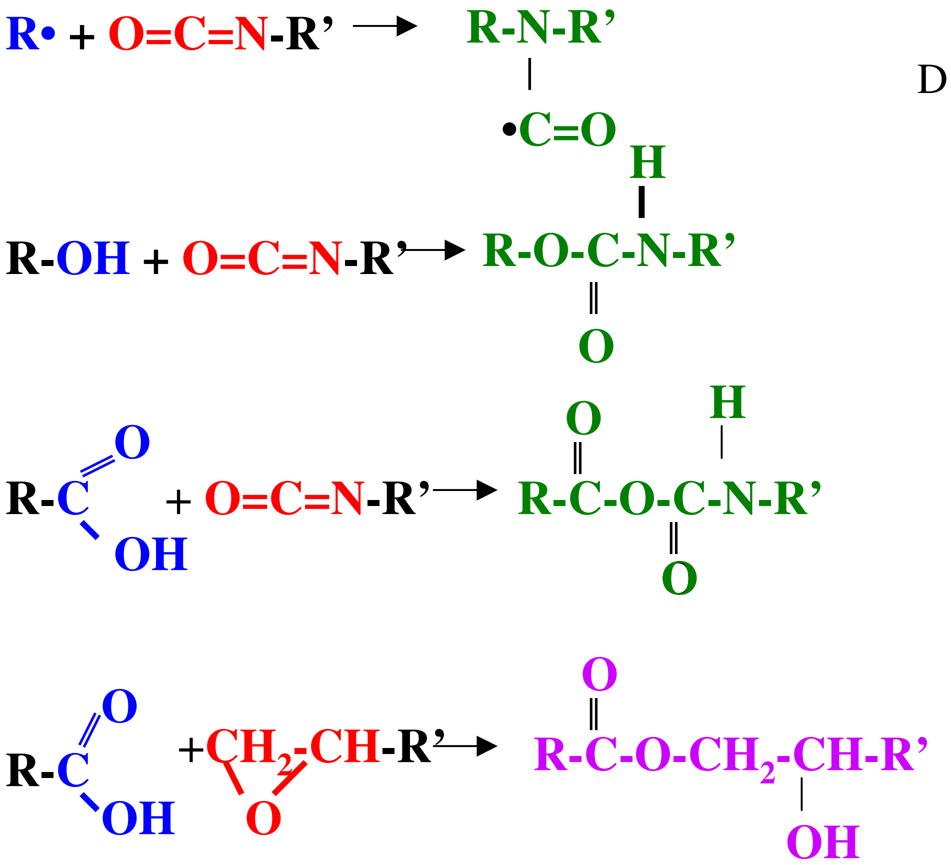


Pulsed IBT, N+, 20 keV, 30 mkS, $2\cdot10^{14}$ ion/cm^2

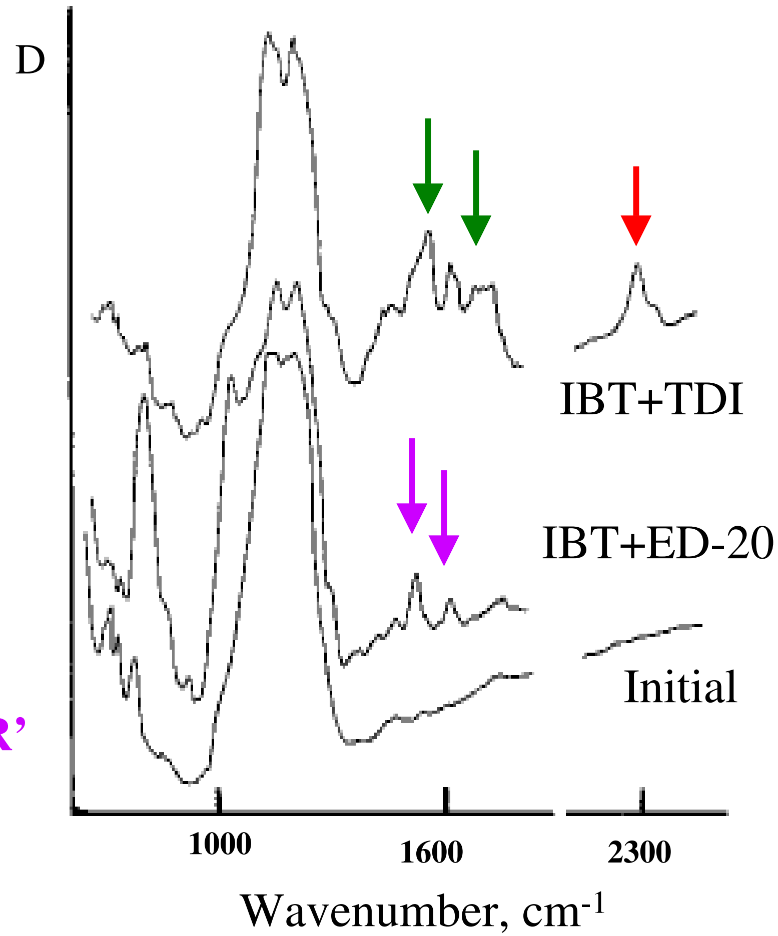




Chemical Activity of PE and PTFE Surface Layers

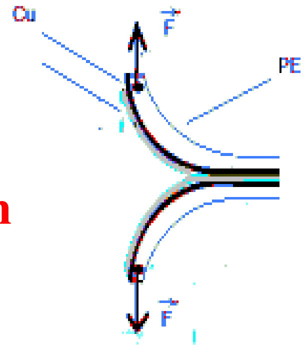


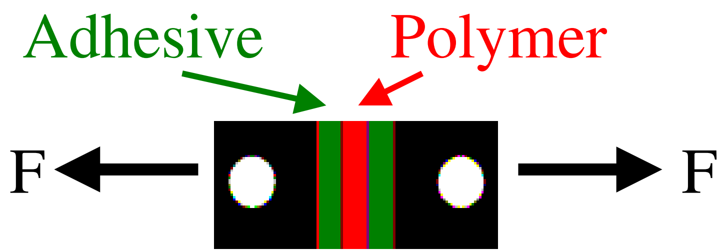
IR ATR spectra of treated PTFE

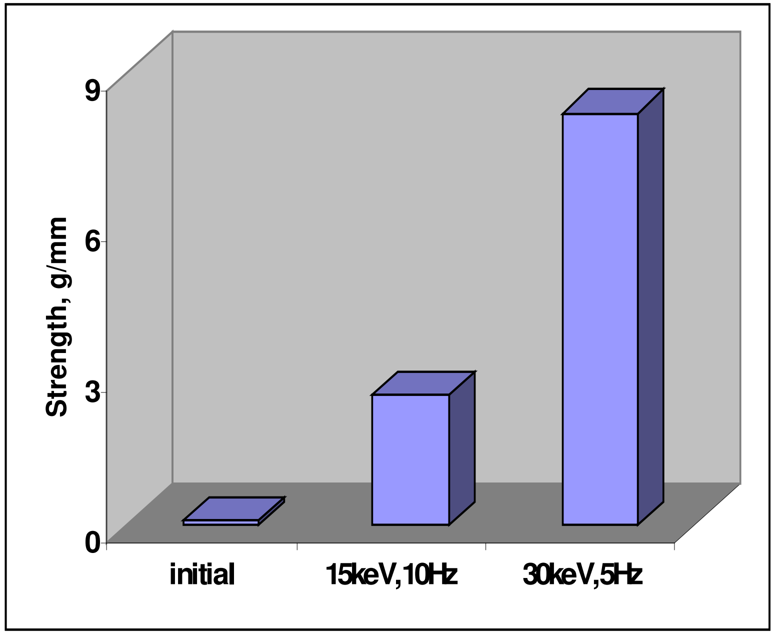


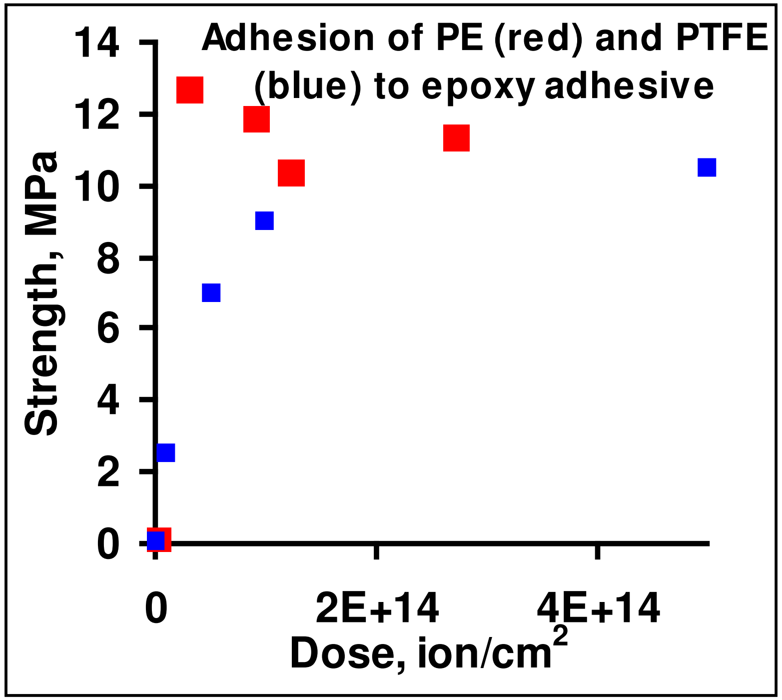
Adhesion of treated Polyethylene and Polytetrafluorethylene

Ion Beam Assisted Deposition of Cu on Polyethylene



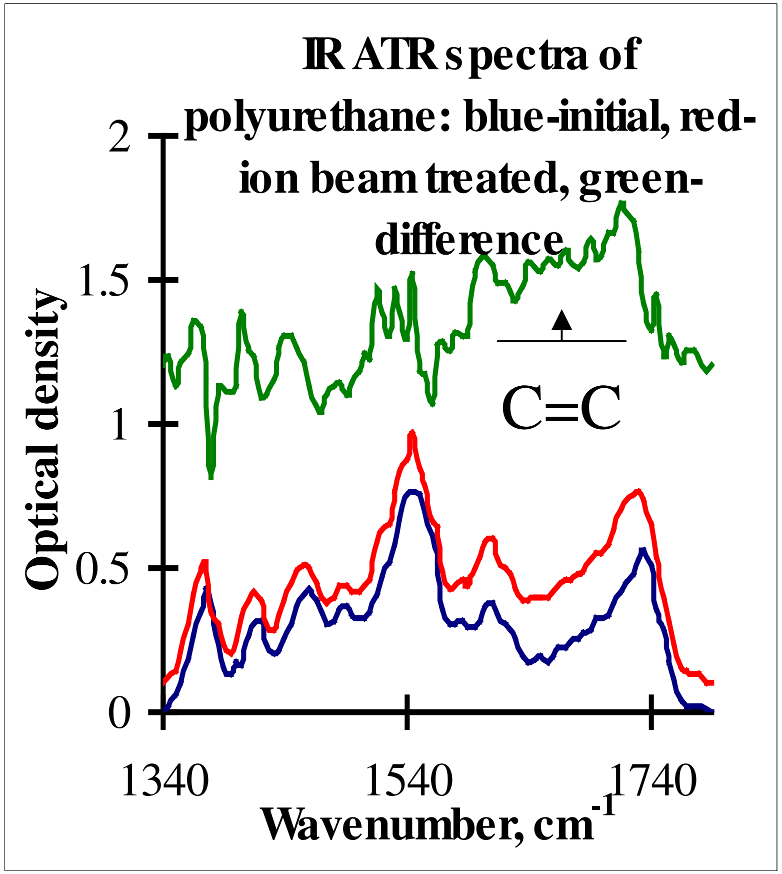




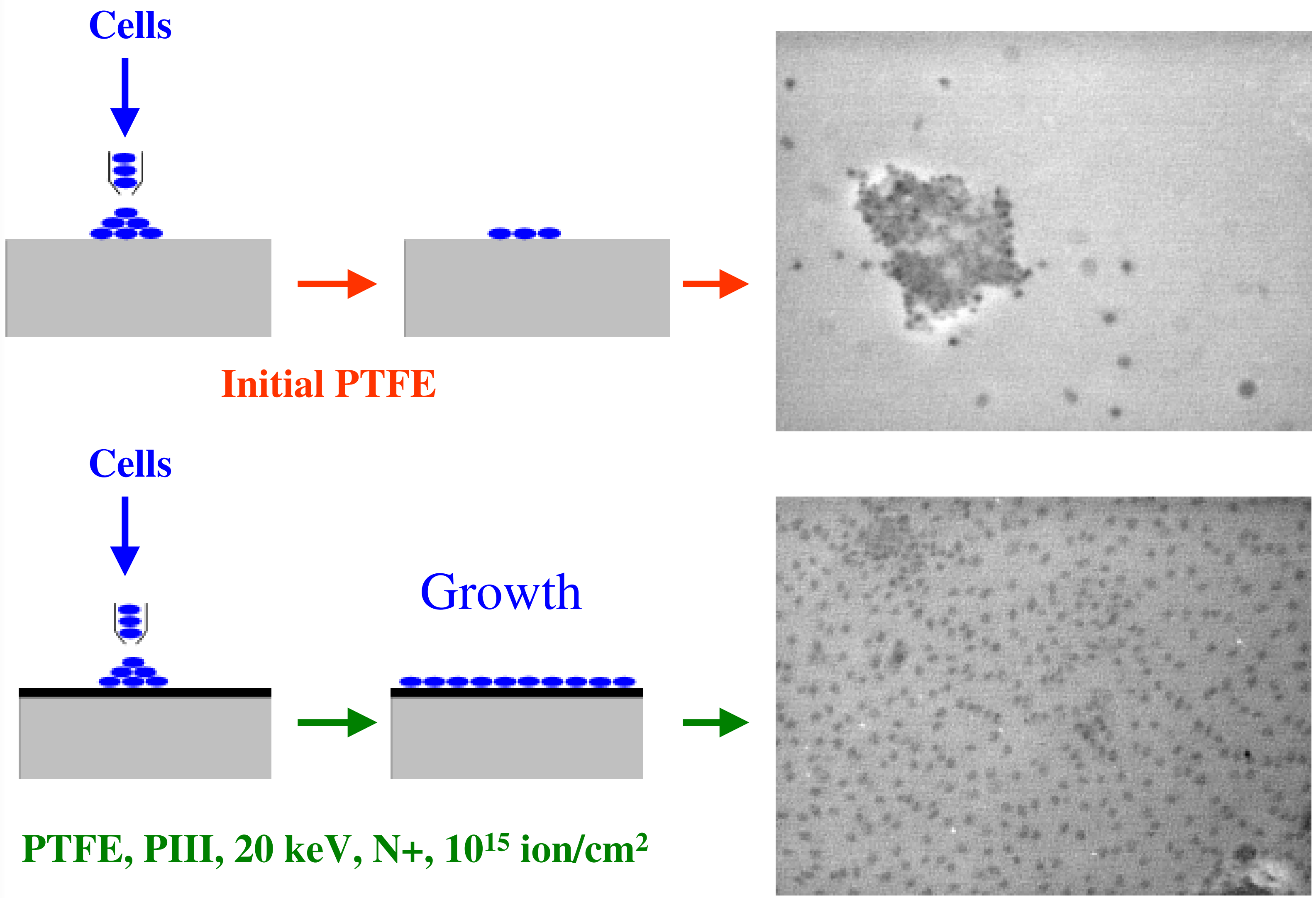


Ion Beam Treatment of Medical Polyurethane

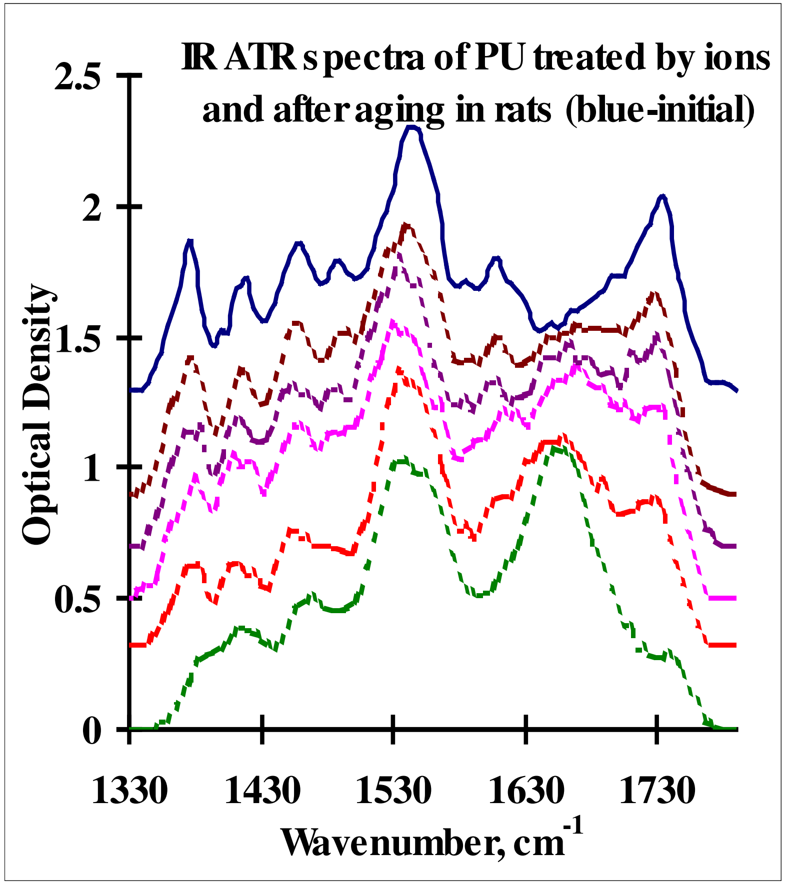
- Polyurethanes:
- (polyether, TDI, diamine)
- (polyether, MDI, diamine)
- (polycarbonate, TDI, diamine)
- Applications:
- Prosthetics of finger joints
- Prosthetics of mammary
- Prosthetics of diaphragm
- Vascular stent coating

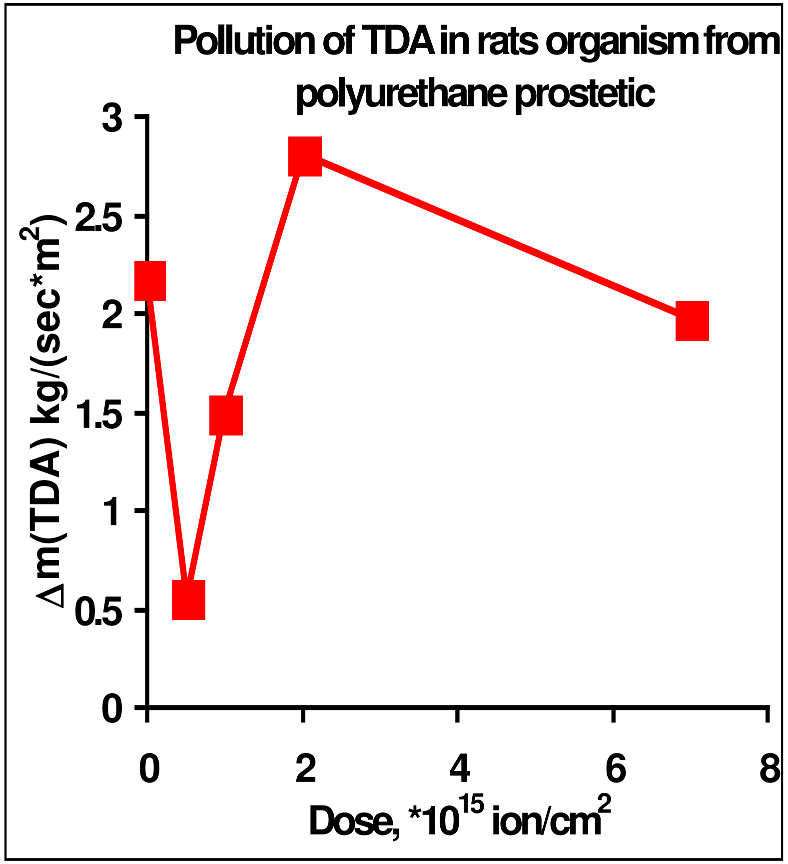


Cell adhesion on Teflon surface after PIII

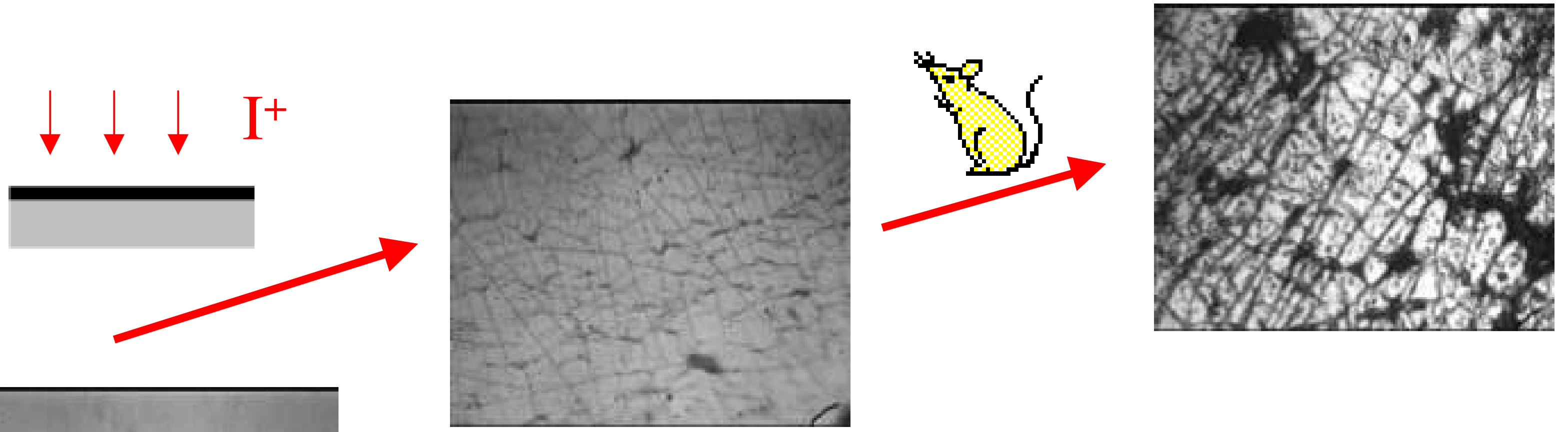


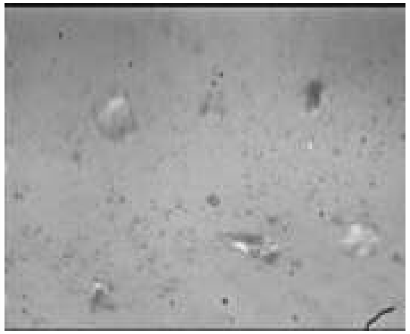
Biostability of Ion Beam Treated PU in Rat Organisms



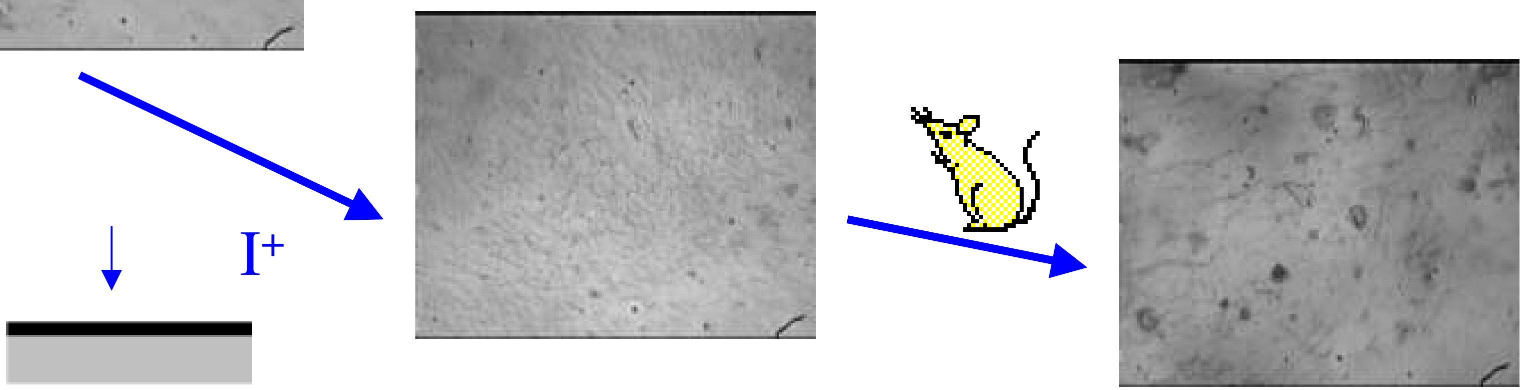


Morphology of PU surface after Pulsed IBT and aging in rat organism.

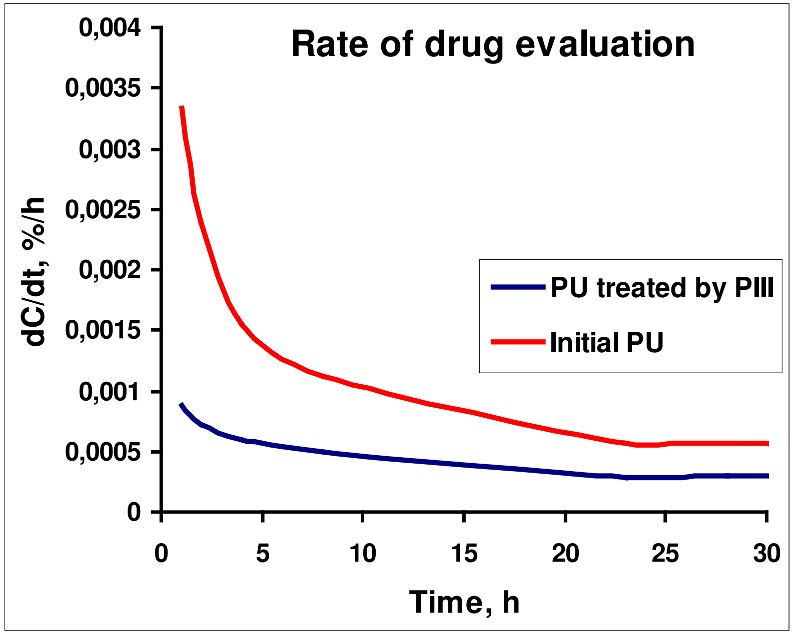




IBT on „Pulsar“, N+, 20 keV, **10^{13}** and **10^{16}** ion/cm²
aging during 6 month in rats organisms

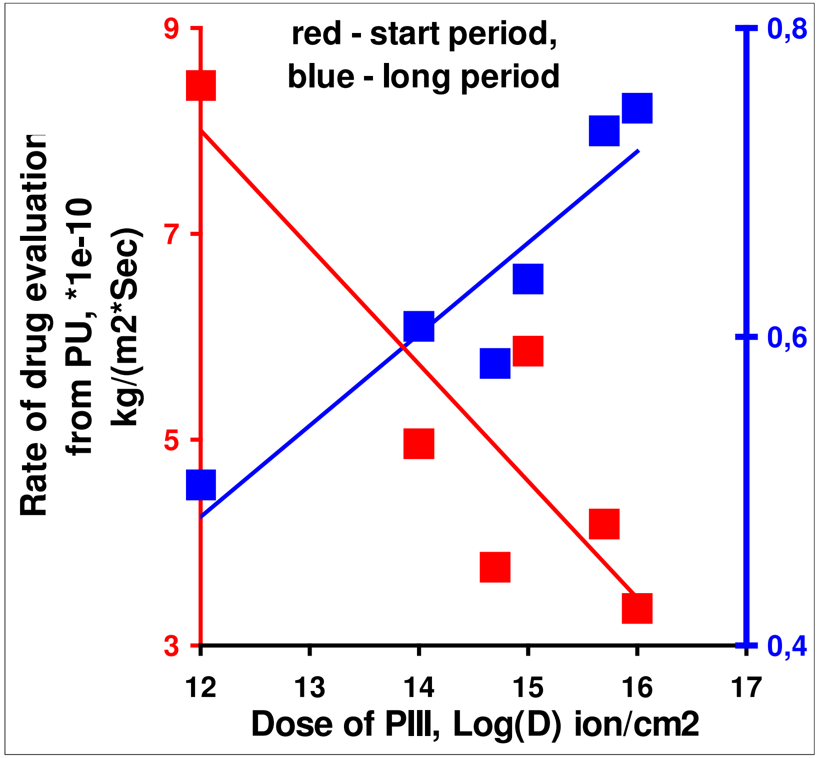


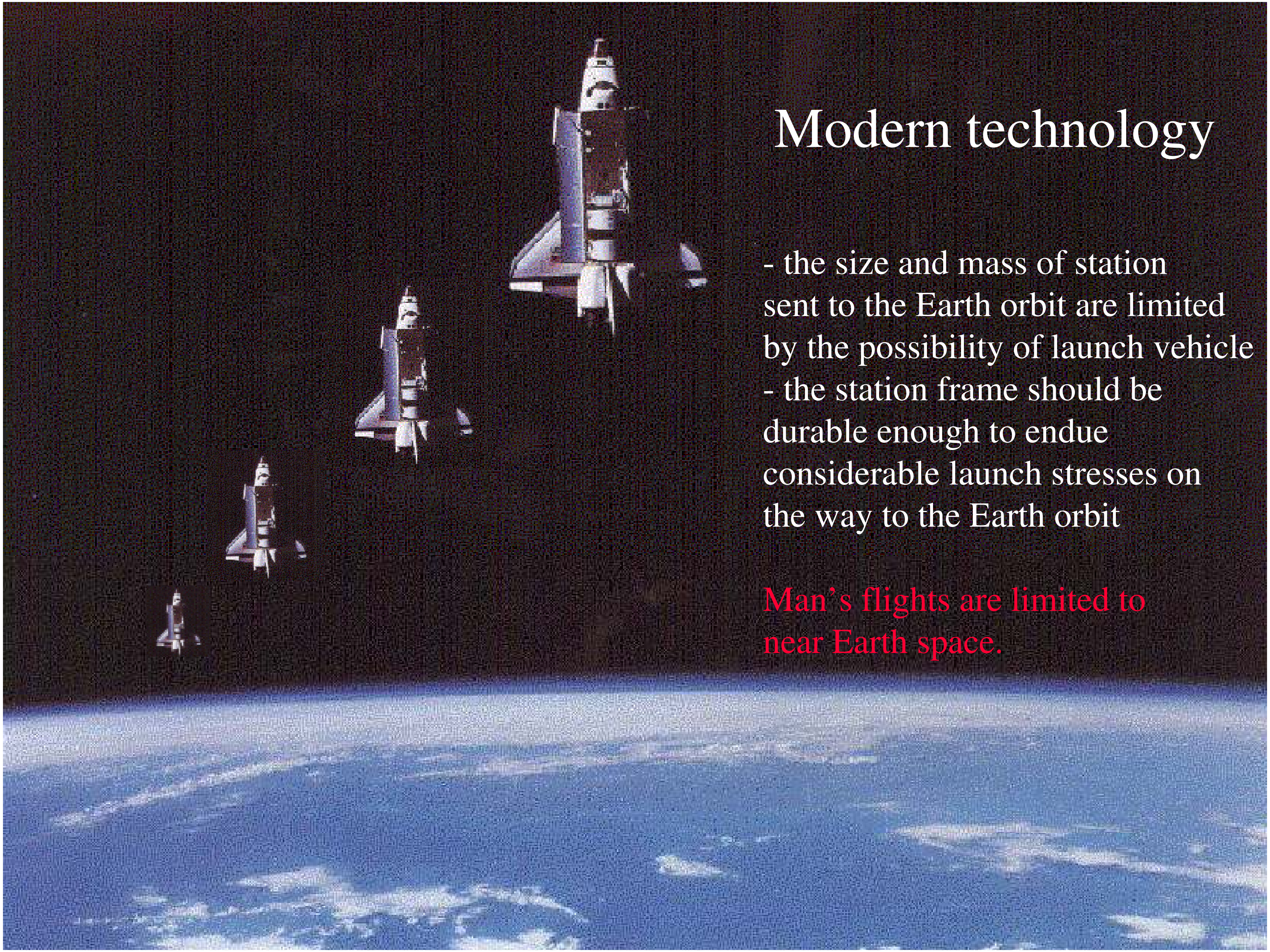
Polyurethane coating of stents



- **Reasons for PU:**
- Biocompatibility
- Drug evaluation
- X-ray contrast

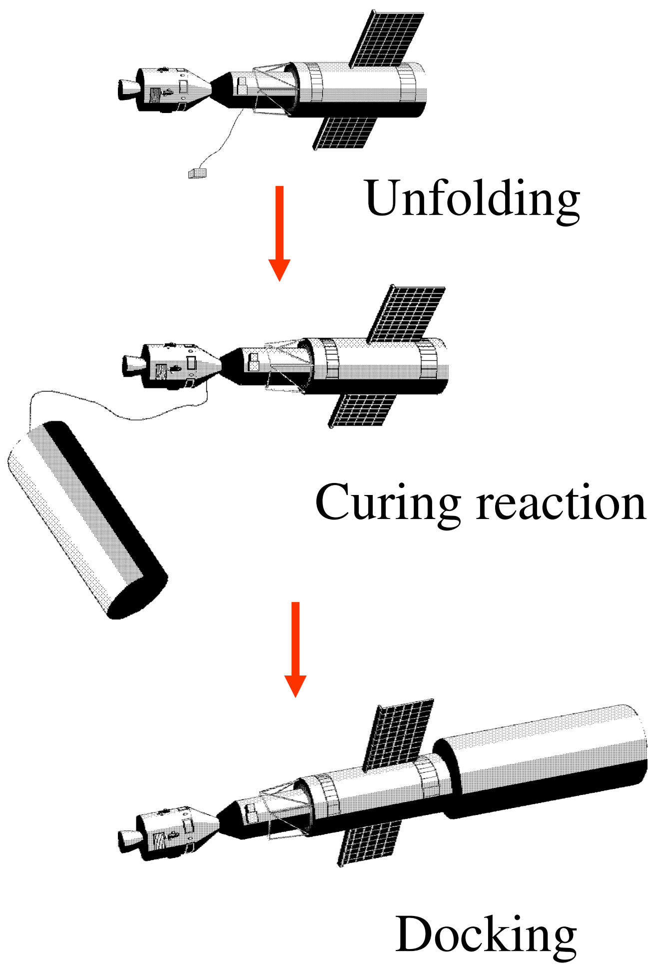
- PIII Treatment for:
- Biocompatibility of PU
- Regulation of drug release from PU
- Sterilisation of PU




Modern technology
- the size and mass of station sent to the Earth orbit are limited by the possibility of launch vehicle
- the station frame should be durable enough to endue considerable launch stresses on the way to the Earth orbit
Man's flights are limited to near Earth space.

Future technology

- no restrictions on the size and form of frame,
- no many launch vehicles,
- no require the permanent human presence,
- no require a very durable frame,
- possible to produce in far space,
- possible to produce on other celestial bodies such as the Moon, the Mars, asteroids, etc.



Free space conditions

1. High vacuum: pressure from 10^{-3} to 10^{-7} Pa;
   - evaporation of low-weight components and disturbance of curing.

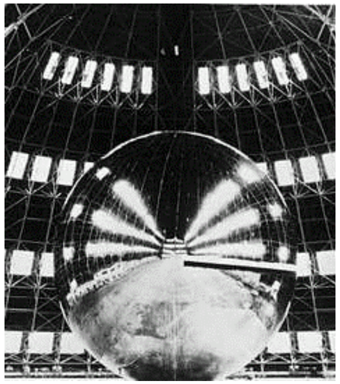
2. Space plasma (electron, H^+, He^+ flows, UV-irradiation, X-ray, atomic oxygen flow);
   - defect structure formation, destruction of polymers, decrease of strength.

3. Sharp temperature changes (from -150 to +200^{0}C);
   - internal stress generation, interrupted curing reaction.

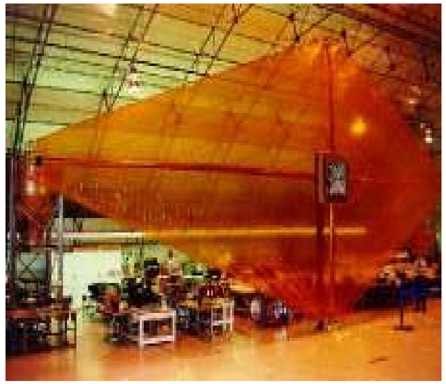
4. Microgravity: 10^{-4} g and less;
   - no convection, no sedimentation, no flow of liquid resin for large constructions.

5. Specific atmosphere of other space bodies;
   - inhibition of curing reaction.

Last and present projects



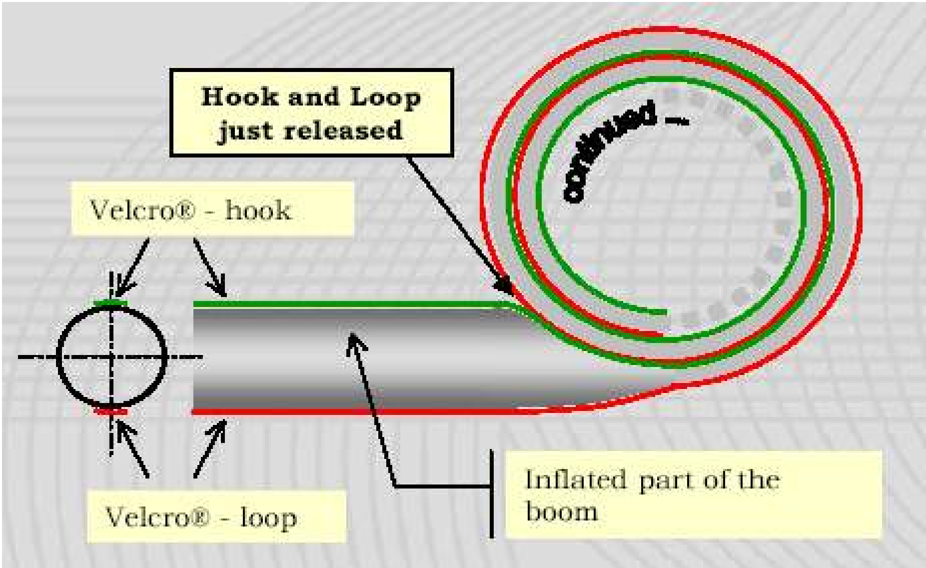
Inflatable Antenna Experiment (L'Garde, 1996)



Echo 1 baloon (NASA LaRC and GSFC, 1962)

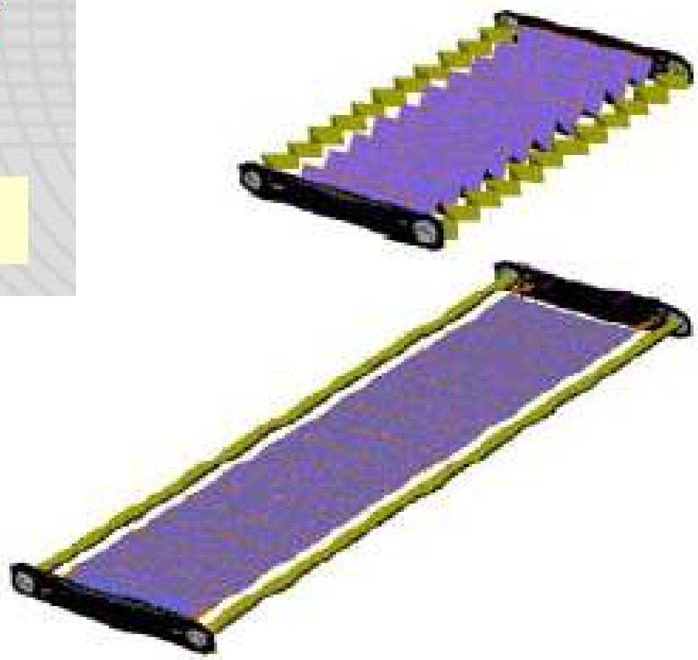
Solar sail (Dover, future)

Deployment technology



EADS, L'Carde and others

Dover, Inasmet and others



Simulation of free space conditions

Golub et.al, 88:
RF-plasma, 13.56 MHz, 15 W, 73 Pa

Knootz et al., 91:
O flux from MW plasma, 2.45 GHz, 30 W, and UV from Kripton lamp

Cazaubon et al., 98:
O-flux from CO_2 laser ablation, $3 \cdot 10^{15}$ at/cm^2, 5 eV, pulses

Iwata et.al, 01:
Hg-Xe lamp, 10^{-5} Pa, 80^0C, 0.5-2 MeV proton

Earth orbit, 300 km

vacuum: $10^{-4} \div 10^{-5}$ Pa

proton and electron flux: 1 particle/cm^2, 5-1000 MeV

O atom flux: 10^{13}-10^{15} atom/cm^2, 0.5 eV

irradiation (IR, visual, UV, VUV, X-ray): 1365 W/cm^2

temperature: $-150 \div +150^0$C, 10^4 cycles per year

microgravity

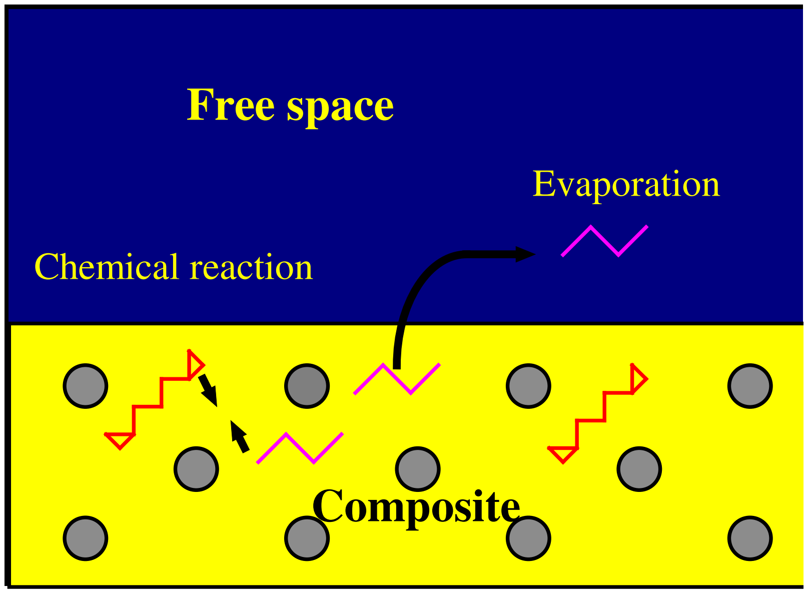
Vacuum thermobox:
20-10^5 Pa, 25-150^0C

RF plasma:
70 Pa, O_2, 13.56 MHz, 100 W

MW plasma:
12 Pa, O_2, 2.45 GHz, 100-400 W

Ion beam implanter:
O+, 1-40 keV, 10^{-1}-10^{-5} Pa

Evaporation of low-weight components



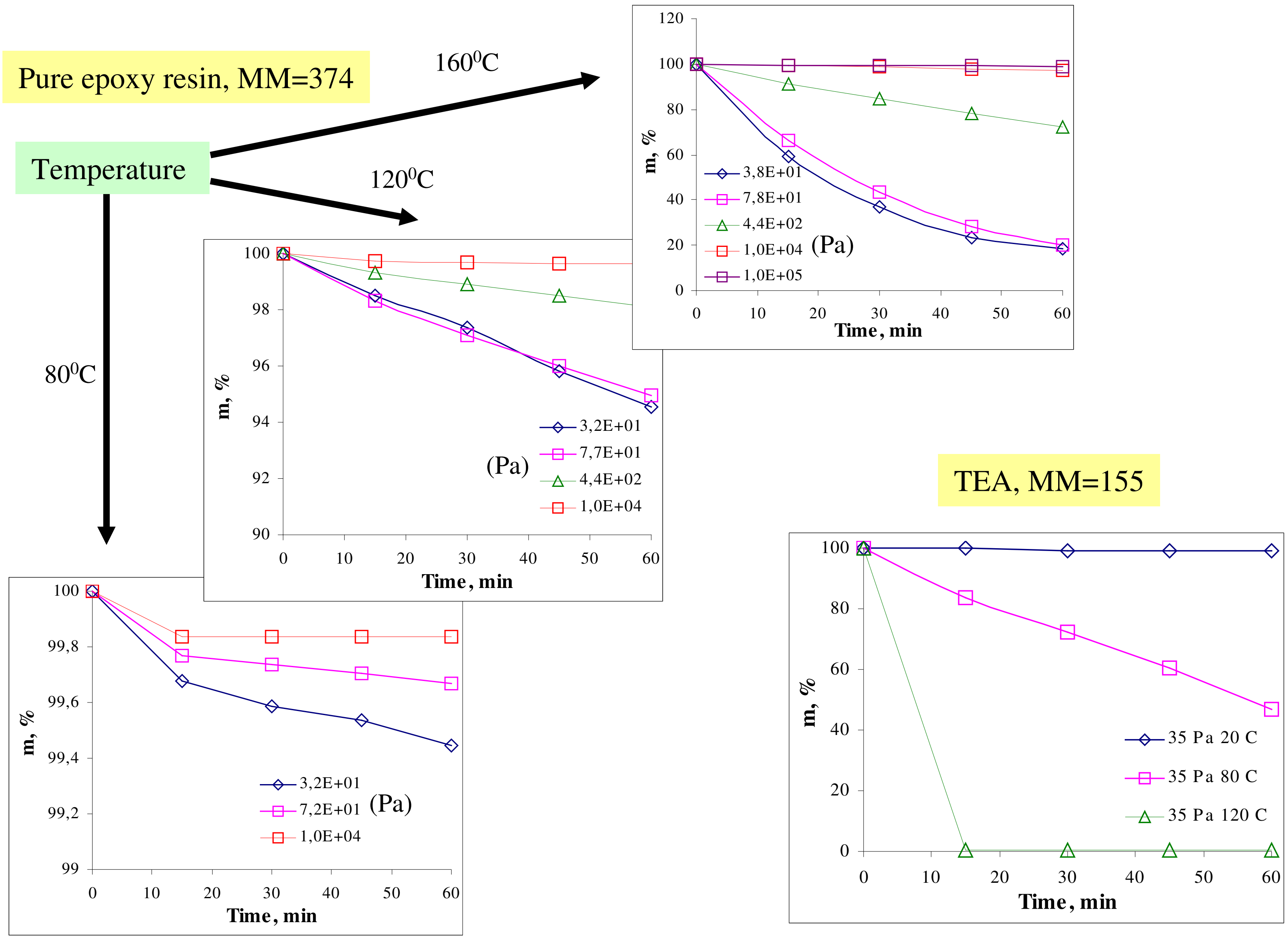
$$\frac{\partial C_1}{\partial t} = -\mathrm{div}\left(D_1 \mathrm{grad} C_1\right) - R$$

$$\frac{\partial C_2}{\partial t} = -\mathrm{div}\left(D_2 \mathrm{grad} C_2\right) - R$$

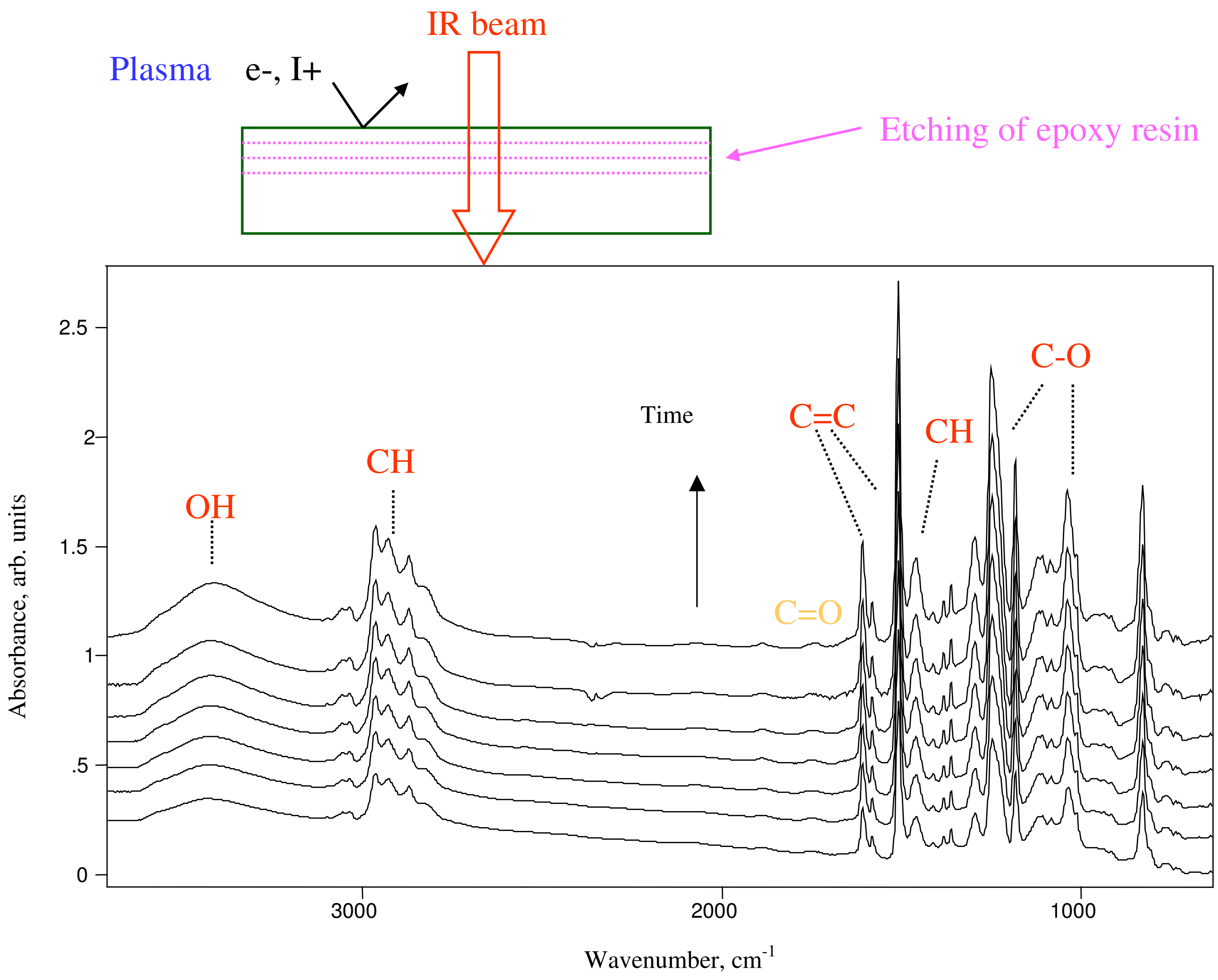
$$\frac{\partial \beta}{\partial t} = R$$

$$R = k_2 (1-\beta)(1+\alpha\beta)(1-\gamma\beta)$$

Evaporation of epoxy resin in vacuum

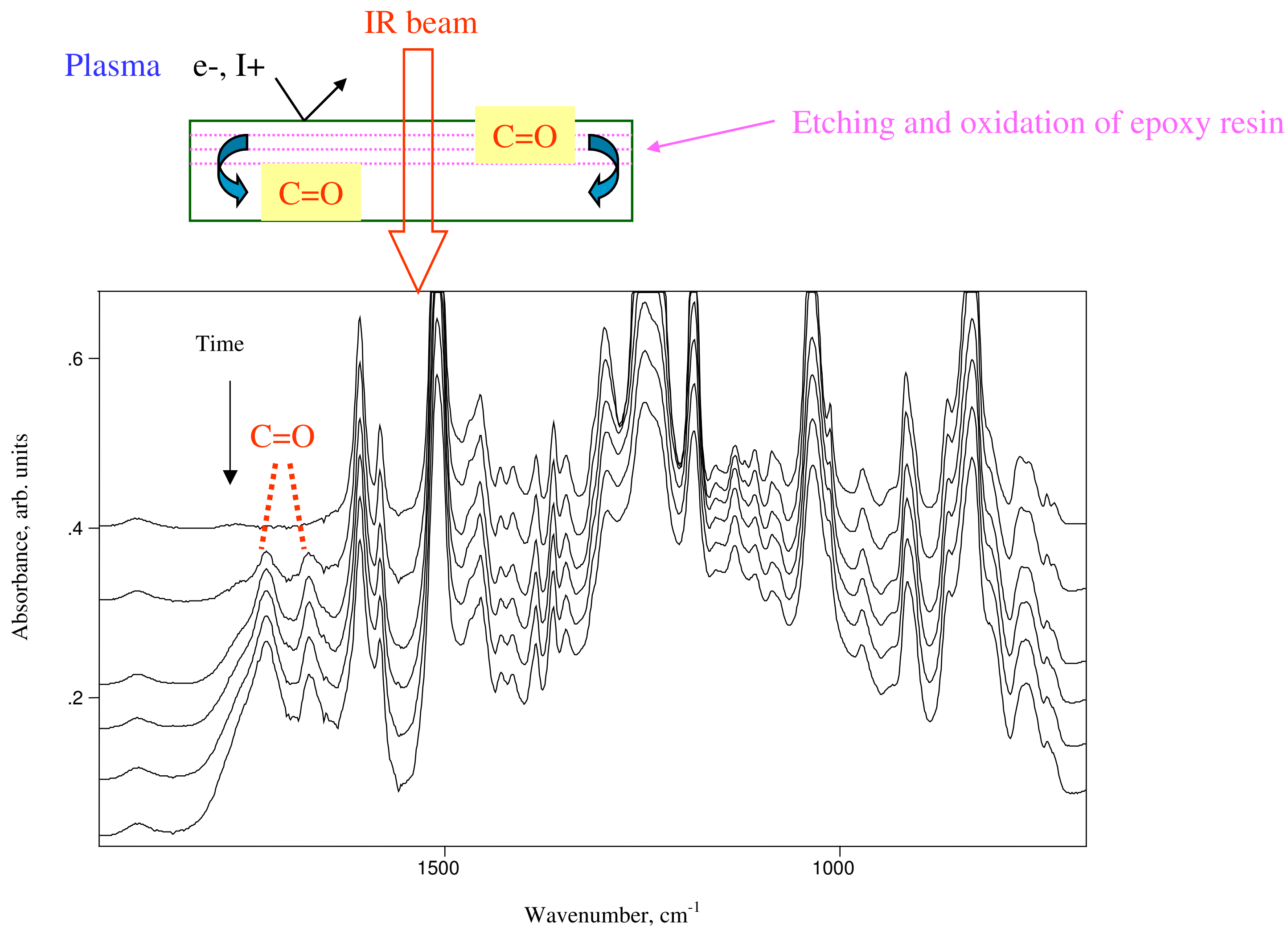


Hard epoxy resin at plasma action



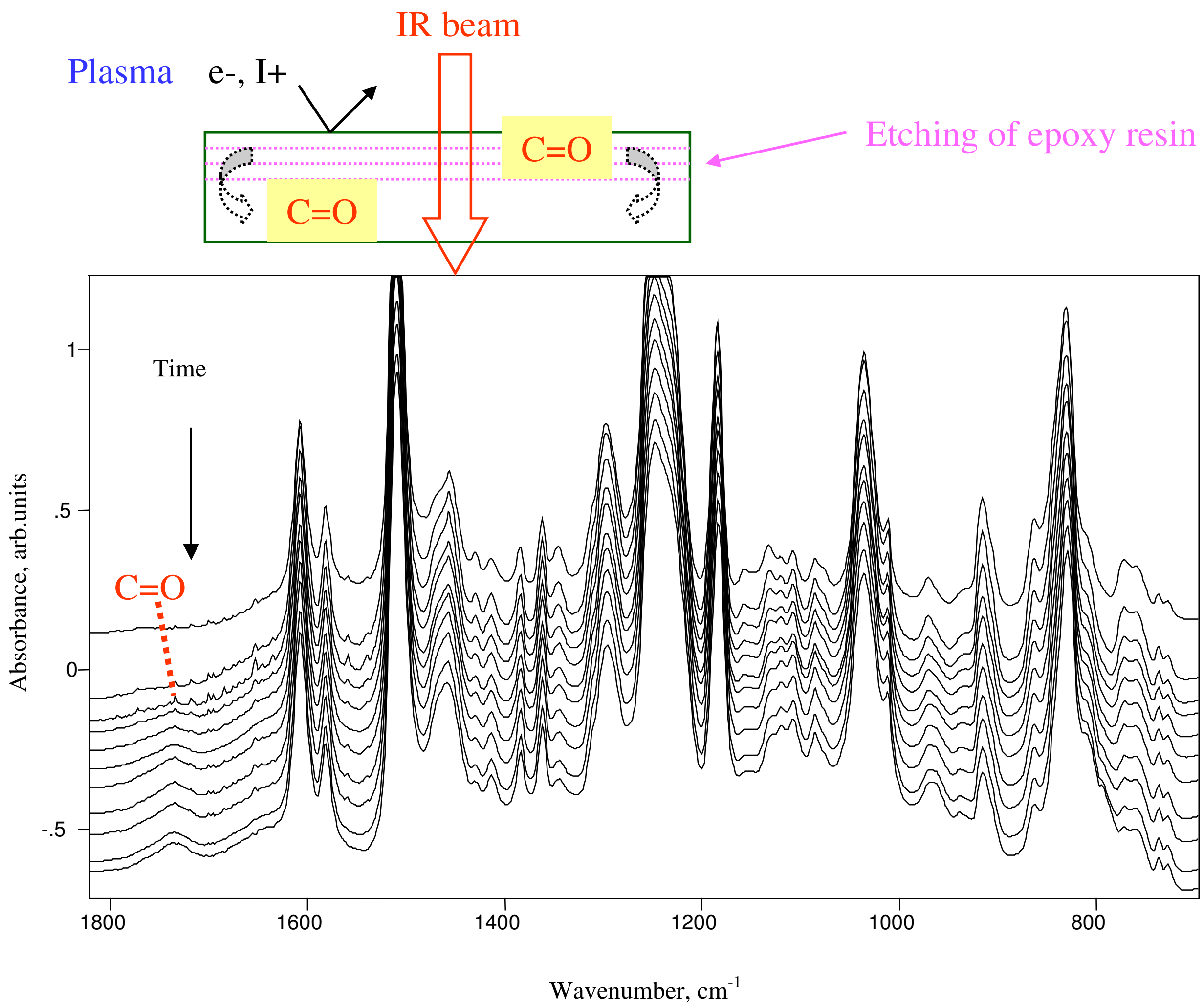
FTIR transmission spectra with time of plasma treatment

Liquid epoxy resin at plasma action



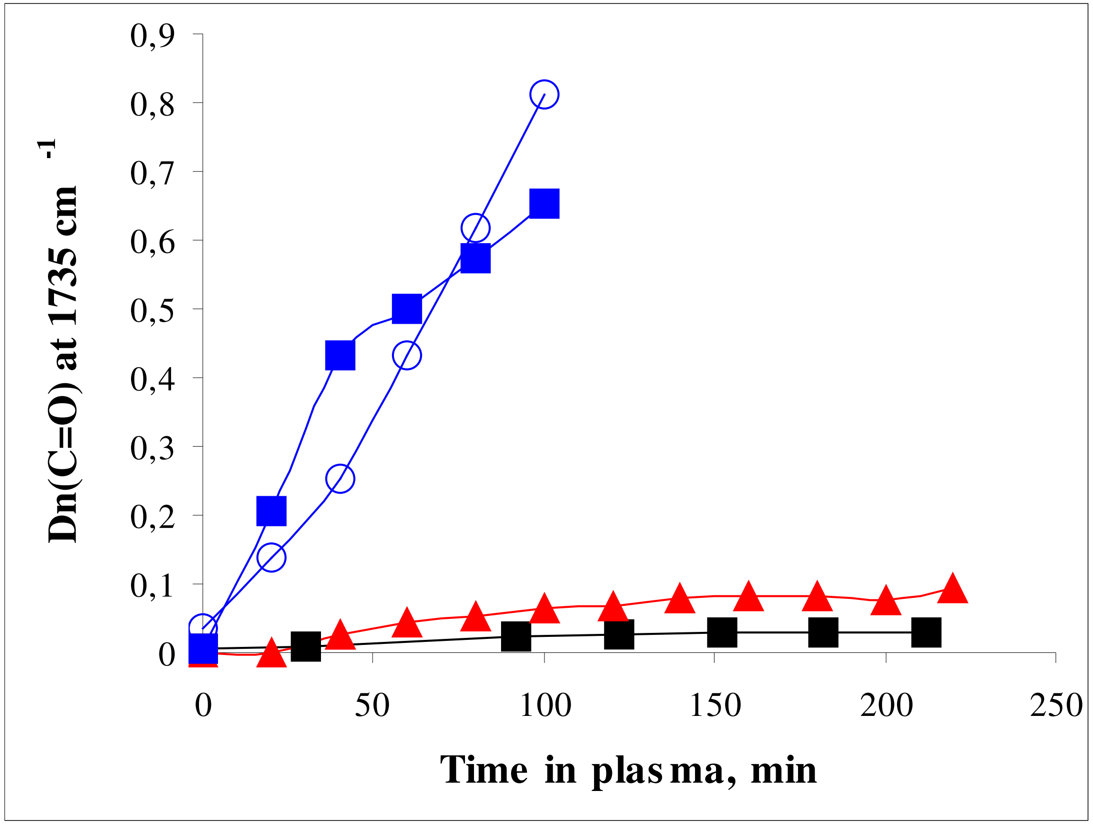
FTIR transmission spectra with time of plasma treatment

Curing of epoxy resin at plasma action



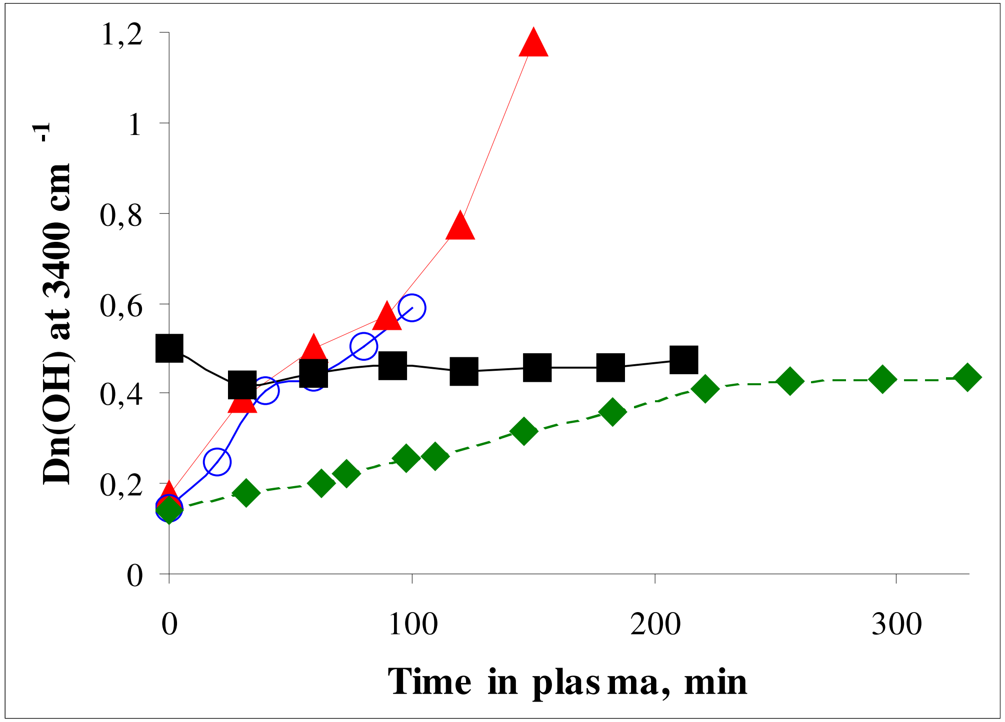
FTIR transmission spectra with time of plasma treatment

Curing of epoxy resin at plasma action



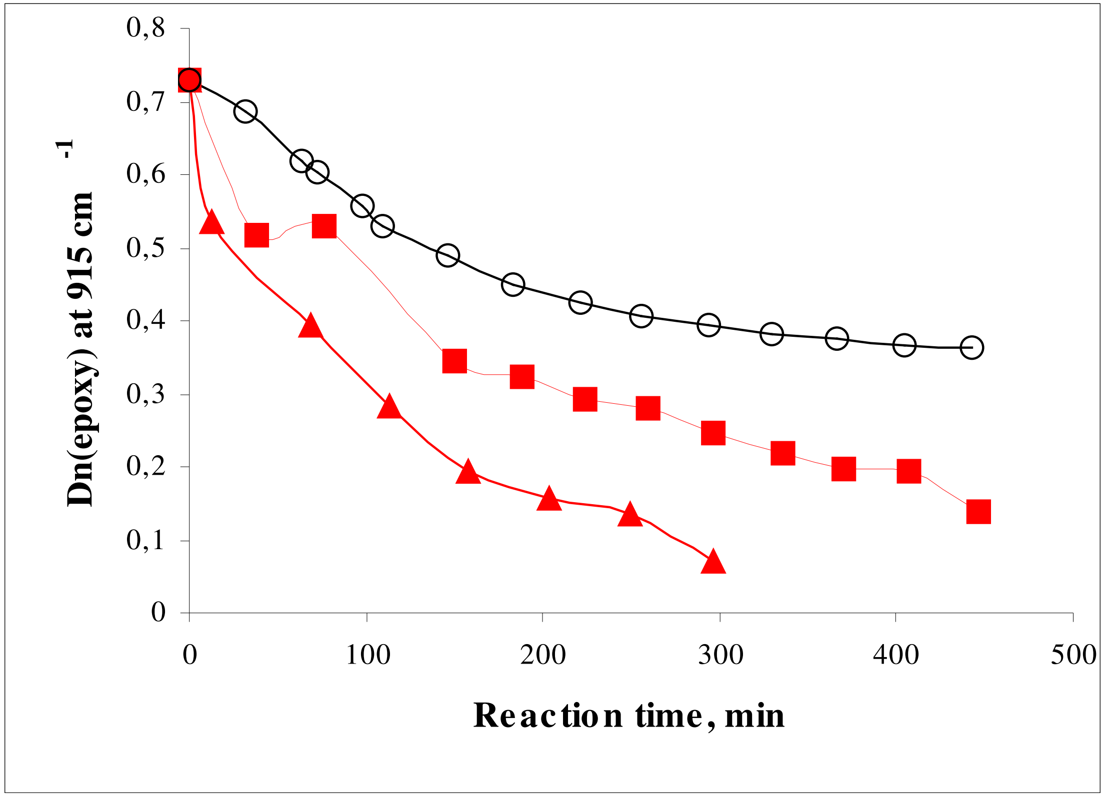
Normalised optical density of FTIR spectra. Blue - liquid resin, red - resin in curing reaction, **black** - cured resin. For liquid resin: full - thick layer, light - thin layer.

Curing of epoxy resin at plasma action



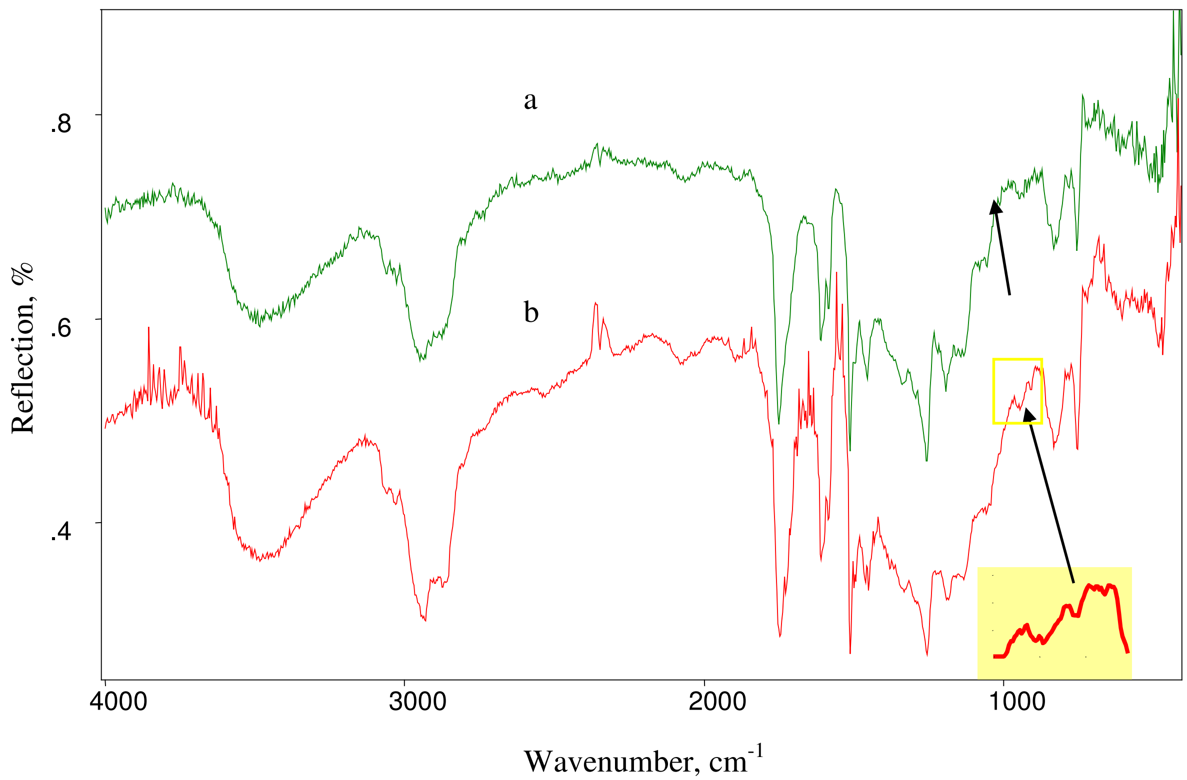
Normalised optical density of FTIR spectra. Blue - liquid resin, red - resin in curing, **black** - cured resin, green - curing at air (control).

Curing of epoxy resin at plasma action



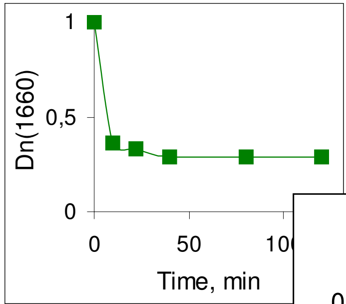
Optical density of FTIR spectra. Black – control curing, red - curing in plasma. Cubic - 200 W, triangle - 300 W of plasma power.

Alcatel resin

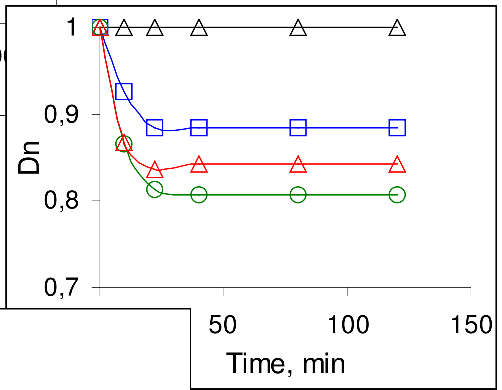


Reflection FTIR spectra of the Alcatel composite:
green – cured at air, red – cured in vacuum

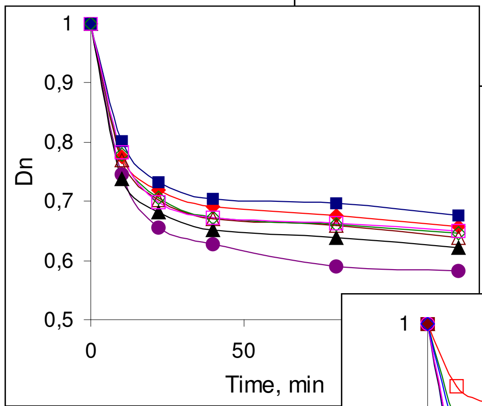
Astrium resin in vacuum



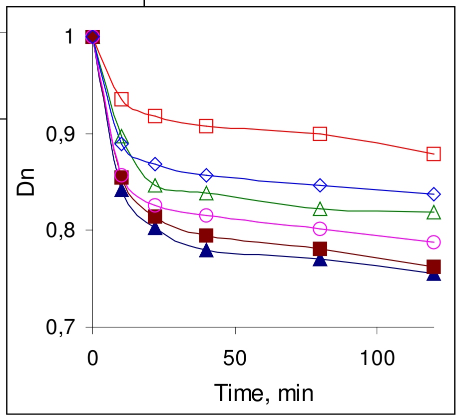
1660 cm^{-1}



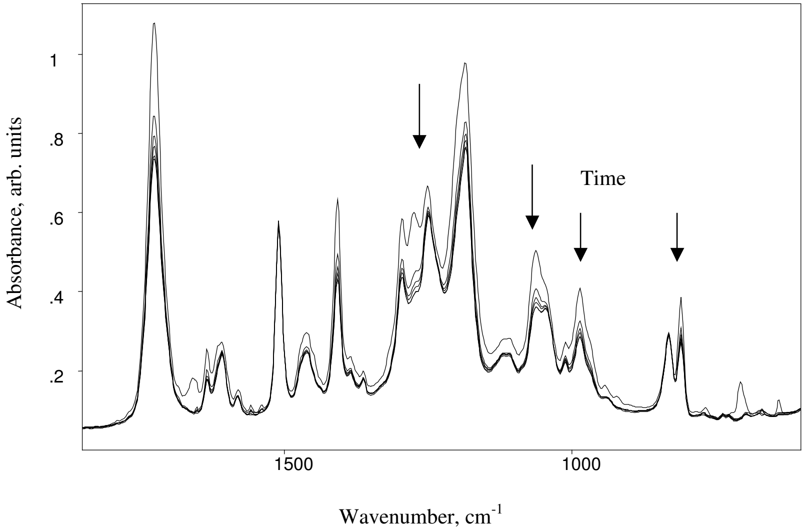
830, 1608, 2935, 1461 cm^{-1}

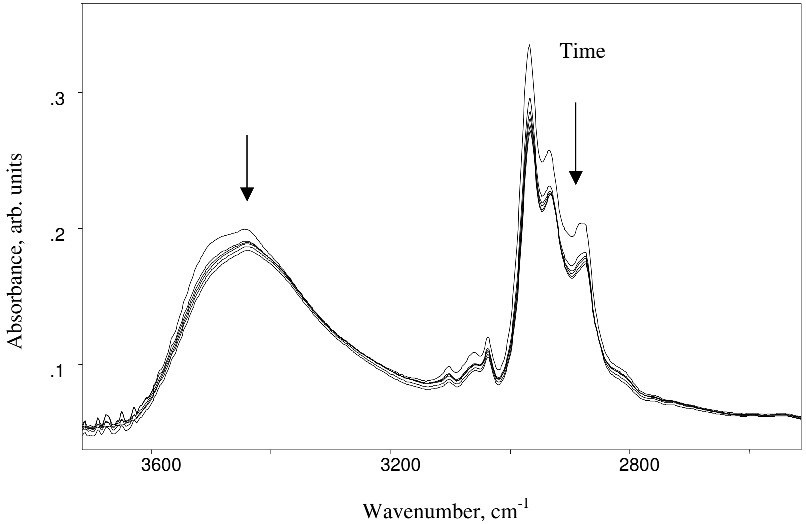


1062, 1725, 1408, 810, 985, 1275, 1635 cm^{-1}

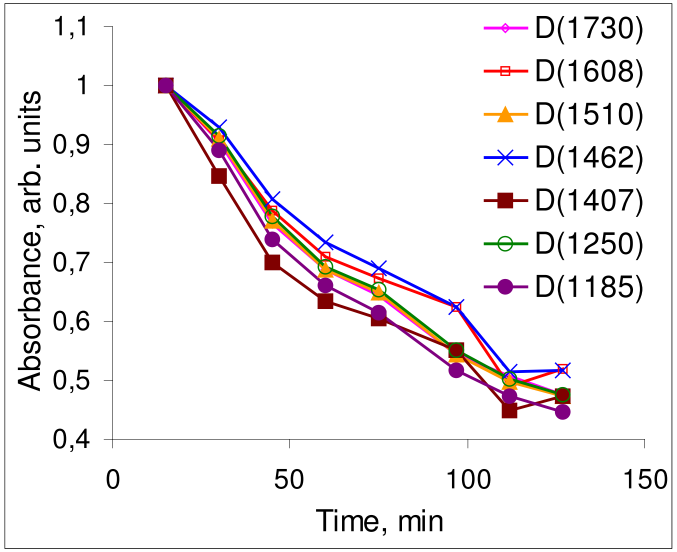


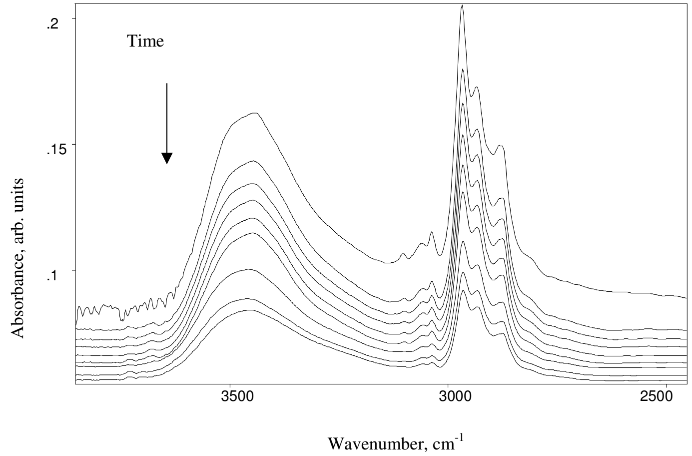
3444, 3038, 1046, 2877, 2967, 1185 cm^{-1}

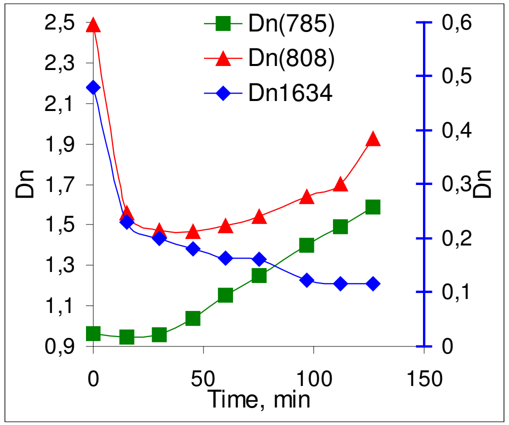


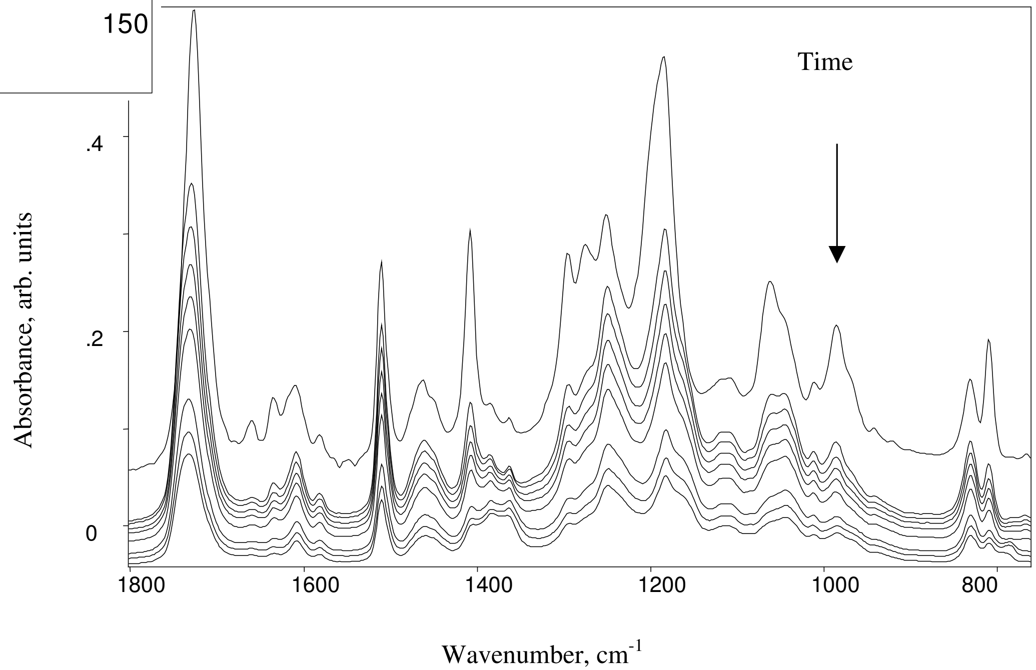


Astrium resin in plasma

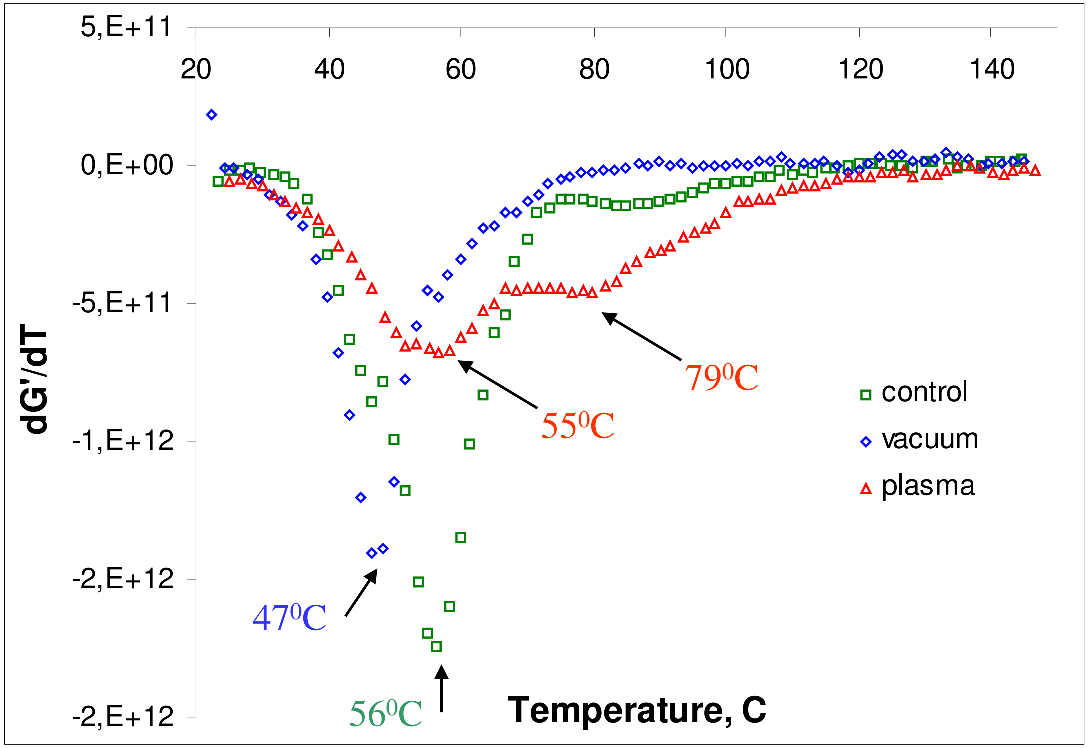




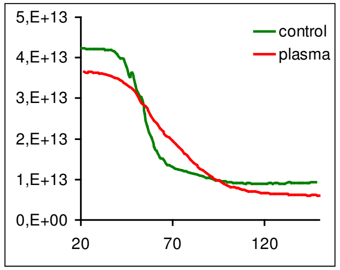




Curing of epoxy resin at plasma action



Dynamical mechanical analysis of composite



Glass textile and epoxy resin with TEA hardening agent

Glass transition of composite material.

Epoxy matrix was cured under vacuum, plasma and under normal conditions.

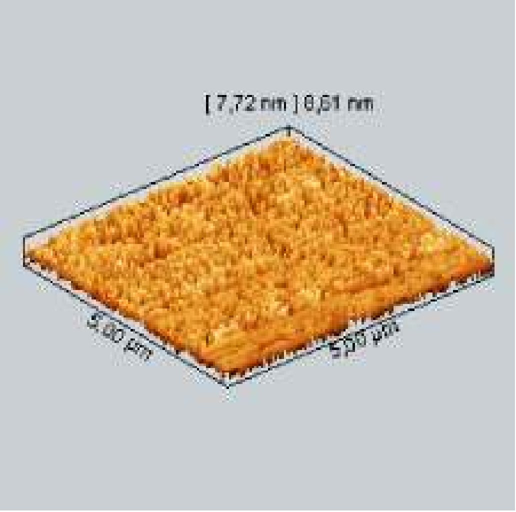
Free space plasma

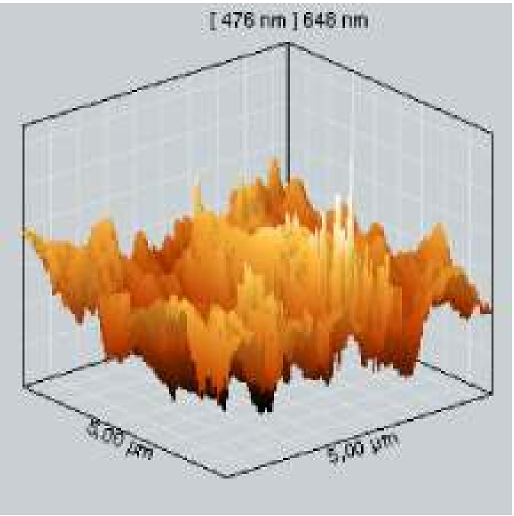
Microphotograph of epoxy resin cured at air and treated by plasma

Microphotograph of epoxy resin cured in ion flow

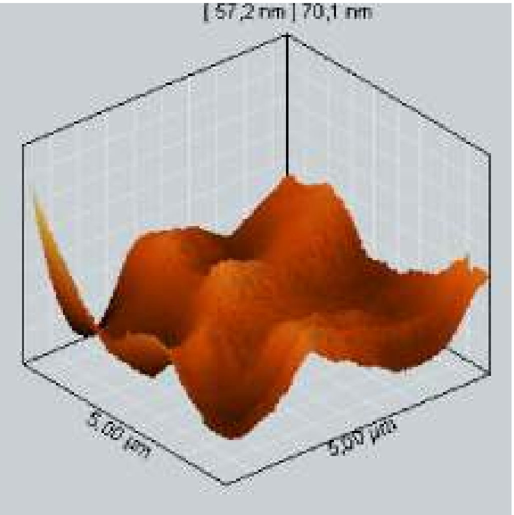
Curing of epoxy resin at plasma action

cured in vacuum





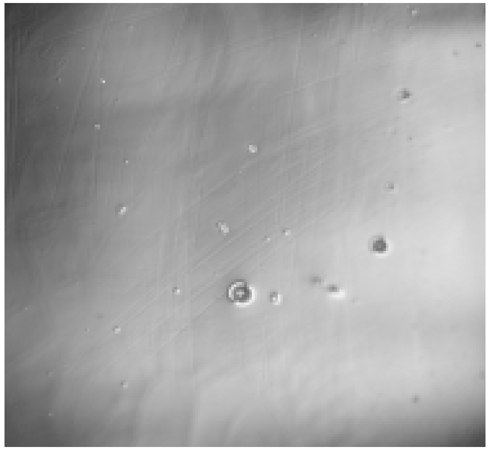
cured in vacuum and treated in plasma



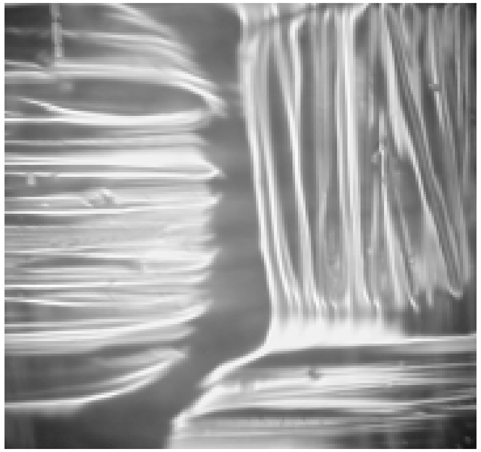
cured in plasma

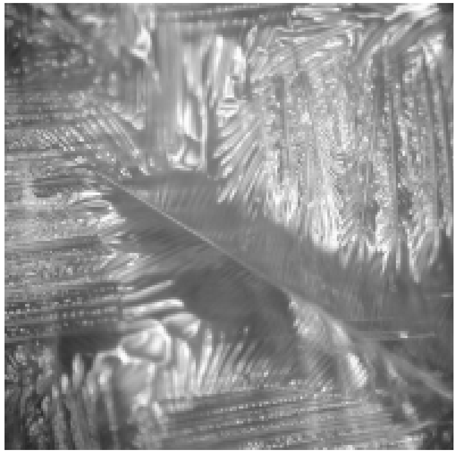
Atomic Force microscope (AFM) imaging of epoxy resin surface

Astrium resin

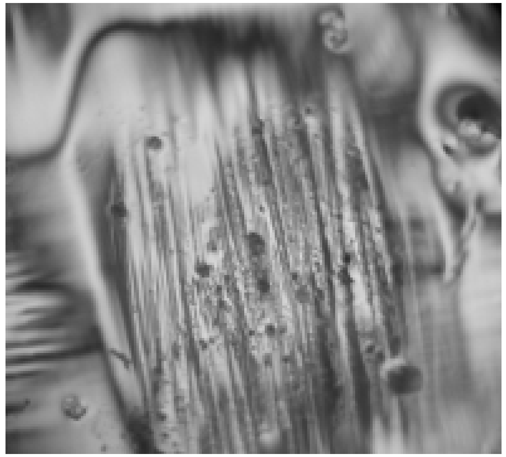


UV-light

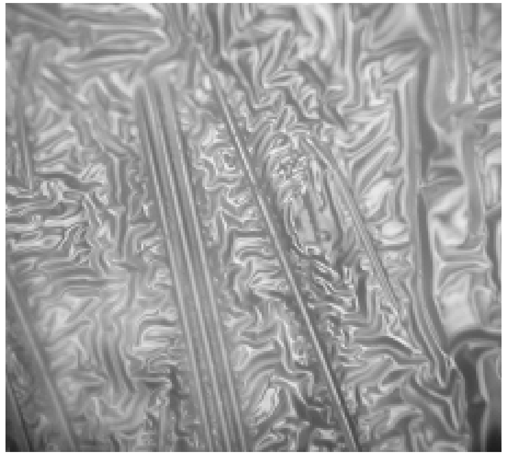




Ion beam

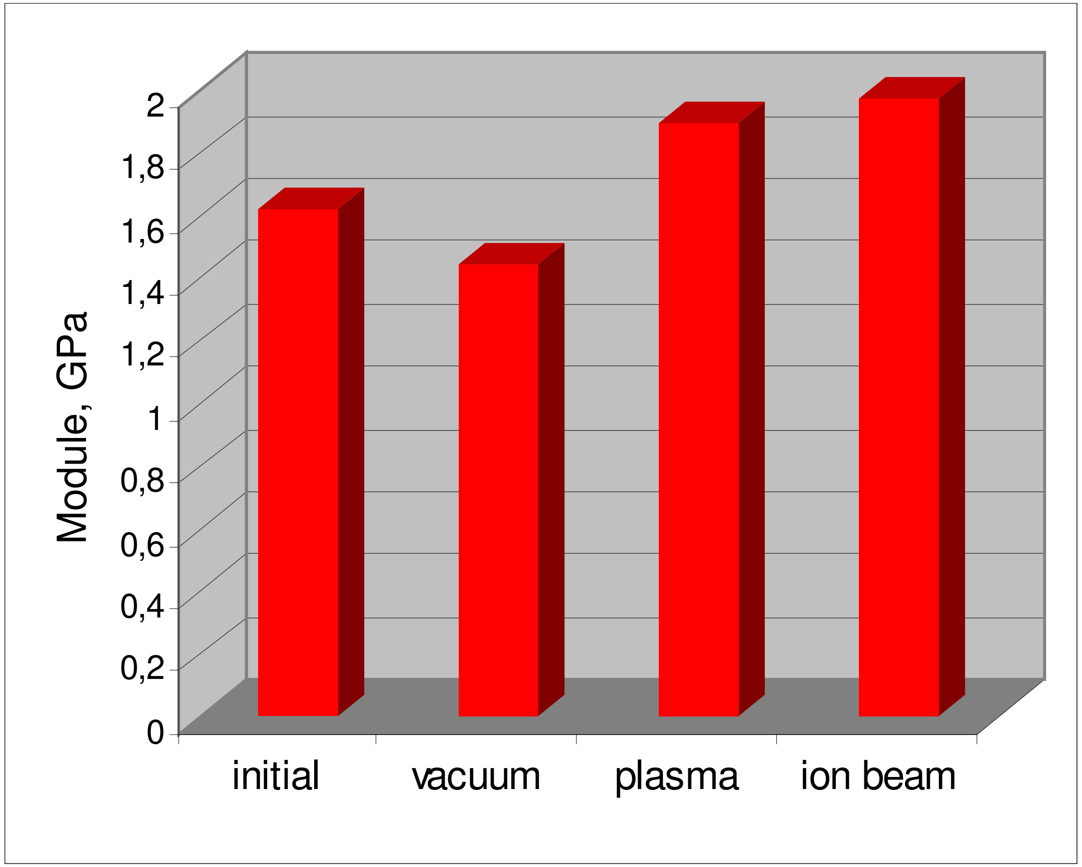


Plasma

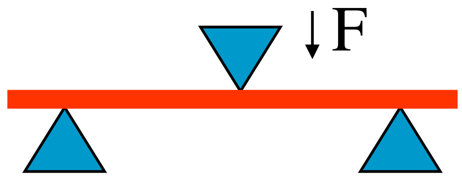


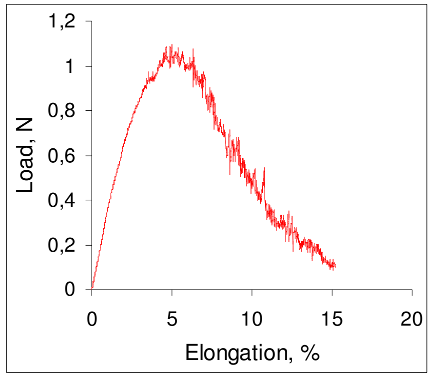
Microphotos of the Astrium composite surface.

Alcatel resin



Bending test of the Alcatel composite





Conclusions

- Structure changes of polymers after IBT
- Layer structure of modified polymer
- Dependence on regimes
- Applications
- Inhibition of environment influence
- Wetting and slip
- Adhesion to polymer adhesives and metal deposition
- Hardness
- Biocompatibility (biodestruction, drug release regulation)
- **Polymerisation in free space environment**

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- Rossendorf Technological Center, Dresden, **Germany** (Dr.E.Richter, Dr.M.Maitz)
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- APT GmbH, Dresden, **Germany** (Dr.R.Guenzel)
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- Sandia National Laboratories, Albuquerque, **USA** (Dr.R.Stinnett)
- Los-Alamos National Laboratories, Los Alamos, **USA** (Dr.D.Rej)
- Boston Scientific Corp., Boston, **USA** (Dr.J.Weber)
- Belorussian University, Minsk, **Belorussia** (Dr.V.Popok)
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- Physical-Technical Institute, Kazan, **Russia** (Dr.R.Khaybullin)
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