Oxygen Sensitive Thin Film Dosimeters for Measuring Web Surface Inerting Efficiency

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Industrial Applications for Low Energy Electron Beams

- Crosslinking of polyethylene based films for packaging applications
- Surface sterilization of food and medical and packaging
- Crosslinking and curing of adhesives
- Curing of surface applied inks and coatings

EB Curing of Surface Applied Inks and Coatings

- Established growing technology
- Now one of the largest industrial uses for low energy EB
- Packaging applications are the most common
  - Folding cartons
  - Pouches
  - Multi-wall bags
  - Labels
  - Flexible packaging
- Industrial finishing using EB curing is growing
  - Wood panels and doors
  - Metal trim
  - Composite furniture and building panels
- Use driven by environmental, speed, and performance advantages over conventional solvent based materials

Packaging with EB Cured Inks and Coatings

EB Cured Inks and Coatings

- Based on free radical polymerization of acrylate functional monomers and oligomers
- Thin layers (1 to 5 microns) of inks and coatings are typical
- Layers can be easily penetrated with 100 kV or less EB equipment
- Free radical polymerization is inhibited by atmospheric oxygen
- Inerting of the reaction chamber (usually with nitrogen purge) is required

Oxygen Inhibition of EB Curing

1. Initiation $M + EB \rightarrow M\cdot$
2. Propagation $M\cdot + nM \rightarrow M(M)_n\cdot$
3. Oxygen inhibition $M(M)_n\cdot + O_2 \rightarrow M(M)_nO\text{-}O\cdot$
4. Termination $M\cdot + M\cdot \rightarrow M\text{-}M$

- Di-radical (triplet) ground state nature of O_2 makes it very reactive in free radical reactions
- Inhibition dependant on rate of oxygen diffusion into the coating surface
- Resulting peroxy radical is not reactive and will not propagate

EB Curing of Surface Inks and Coatings

- Two main factors need to insure good curing (assumes a properly designed system):
  1. Adequate applied EB dose
  2. Effective inerting at the surface
- Incomplete cure of inks and coatings on packaging could result in contamination of food products
- Process monitoring should include dose and inerting

Current Systems for Inerting Measurement

- Sample gas from the reaction chamber through small tube(s)
- Analyze sample gas stream with electrochemical sensor
- Strength - continuous monitoring during production
- Weakness - high speed webs carry boundary layer of air on the surface. Sampling of reaction chamber gas does not measure oxygen on the surface where inhibition is occurring

Desirable Features of Dosimetery Systems for Surface Coatings

- Capable of characterizing low energy (80 to 125 kV) EB radiation
- Provides an accurate measure of the dose in thin (<5 micron) coatings
- Provides a measure of surface inerting efficiency
  - Requires an oxygen dependant response
  - Current dosimeters respond the same in air and under inerted conditions

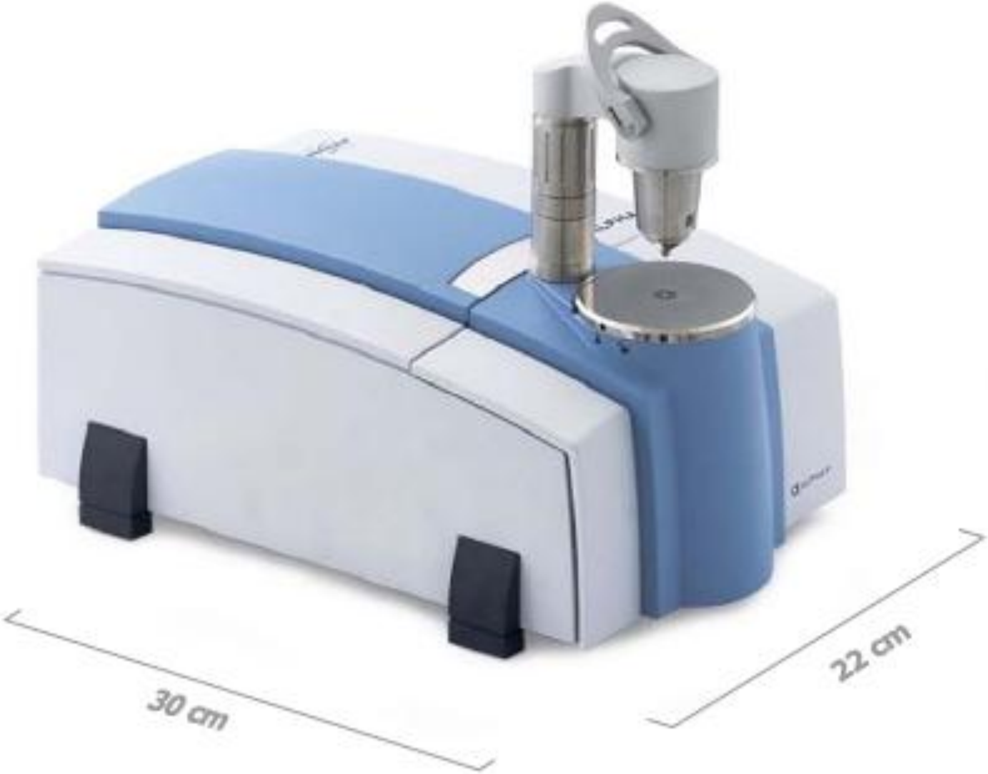
Developmental Dosimetery System

- Identified proprietary oxygen sensitive radiochromic compound
  - EB irradiation induces oxidation
  - Oxidized compound produces intense absorption in the infrared spectrum
- Dosimeter films
  - Radiochromic compound dissolved in a solvent-borne film forming polymer matrix
  - Polymer with radiocrhromic compound is coated on a film carrier (PE, PET, OPP, etc.)
    - Thickness precisely controlled by adjusting the solids level of the solution
    - Films as thin a 1 micron produced with a 10% solids solution
    - Resulting polymer layer is tack-free, durable, and easily handled

Infrared Measurement of Dosimeter Films

- Modern FTIR instruments are sensitive, fast, reliable, durable, compact, and easily calibrated
- Multiple sampling techniques may be used
- Attenuated total reflectance (ATR) ideal for thin film measurement
  - Depth of measurement into sample defined by IR wavelength, crystal material, and refractive index of the sample
  - About 1 micron penetration for our system (542 cm^{-1} band, using single bounce diamond ATR crystal)
  - ATR measurement eliminates error related to film thickness associated with transmission measurement methods

Compact FTIR Spectrometer
(Diamond ATR sampling system shown)

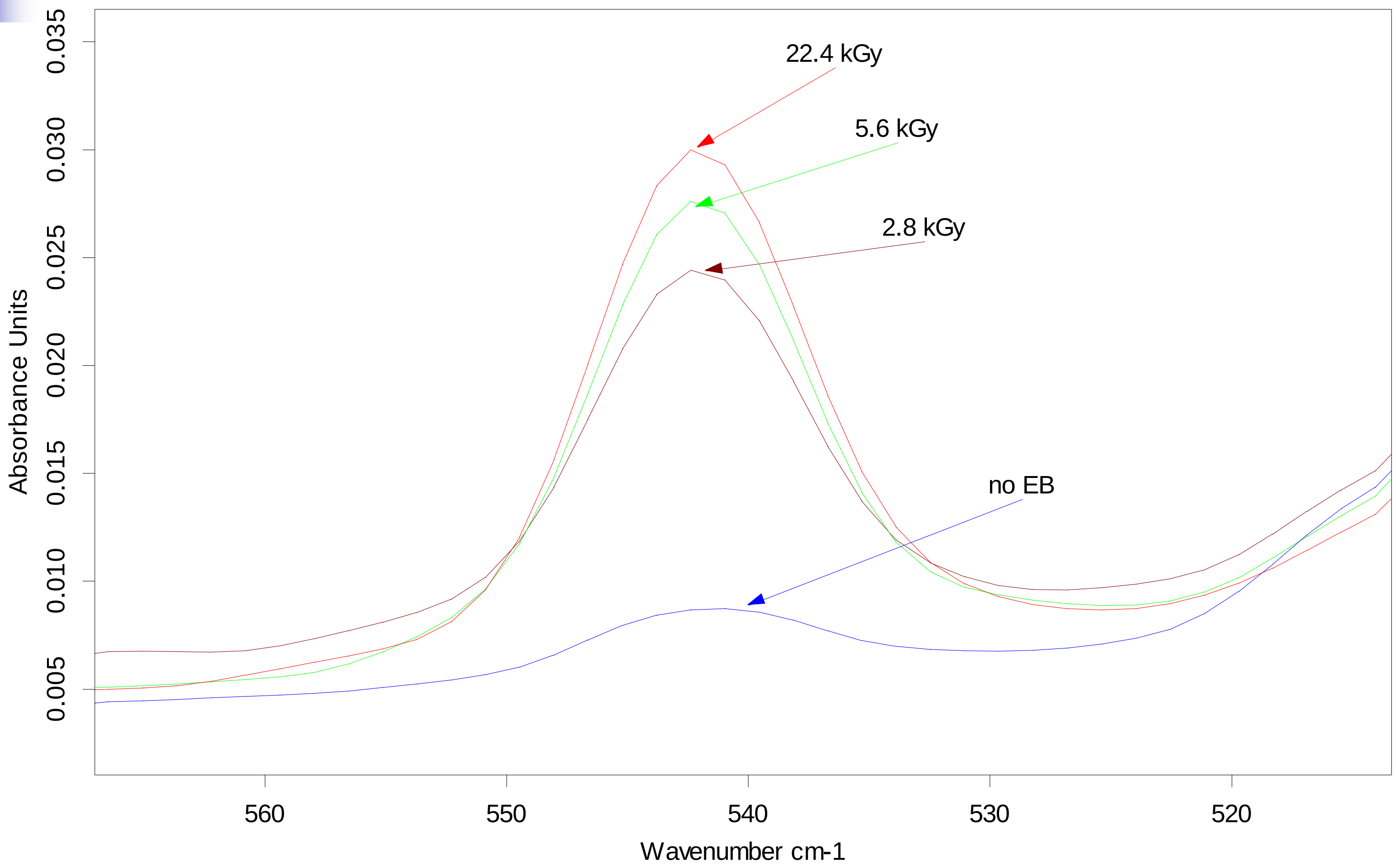


Dosimetery System Development

- Investigate dosimeter compositions
  - Effect of radiochromic compound concentration
  - Effect of polymer matrix
  - Effect of dosimeter coating thickness
- Investigate dose response: compare side-by-side with B3 dosimeters
- Confirm response sensitivity to oxygen level
- Correlate dosimeter inerting response to coating cure

Dose Response of Developmental System

(PCT BroadBeam pilot line in air at 150 kV correlated to B3 dosimeters)



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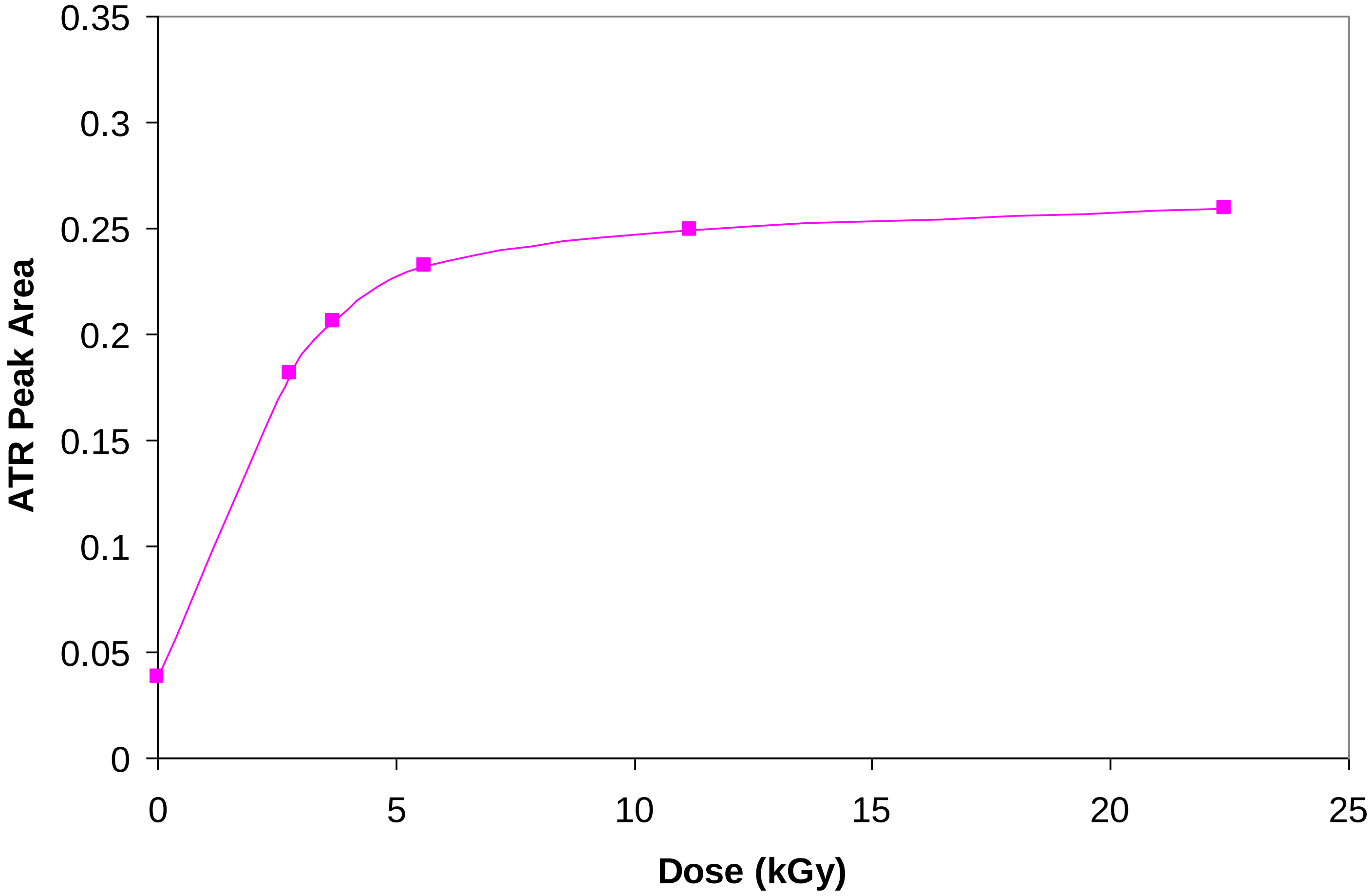
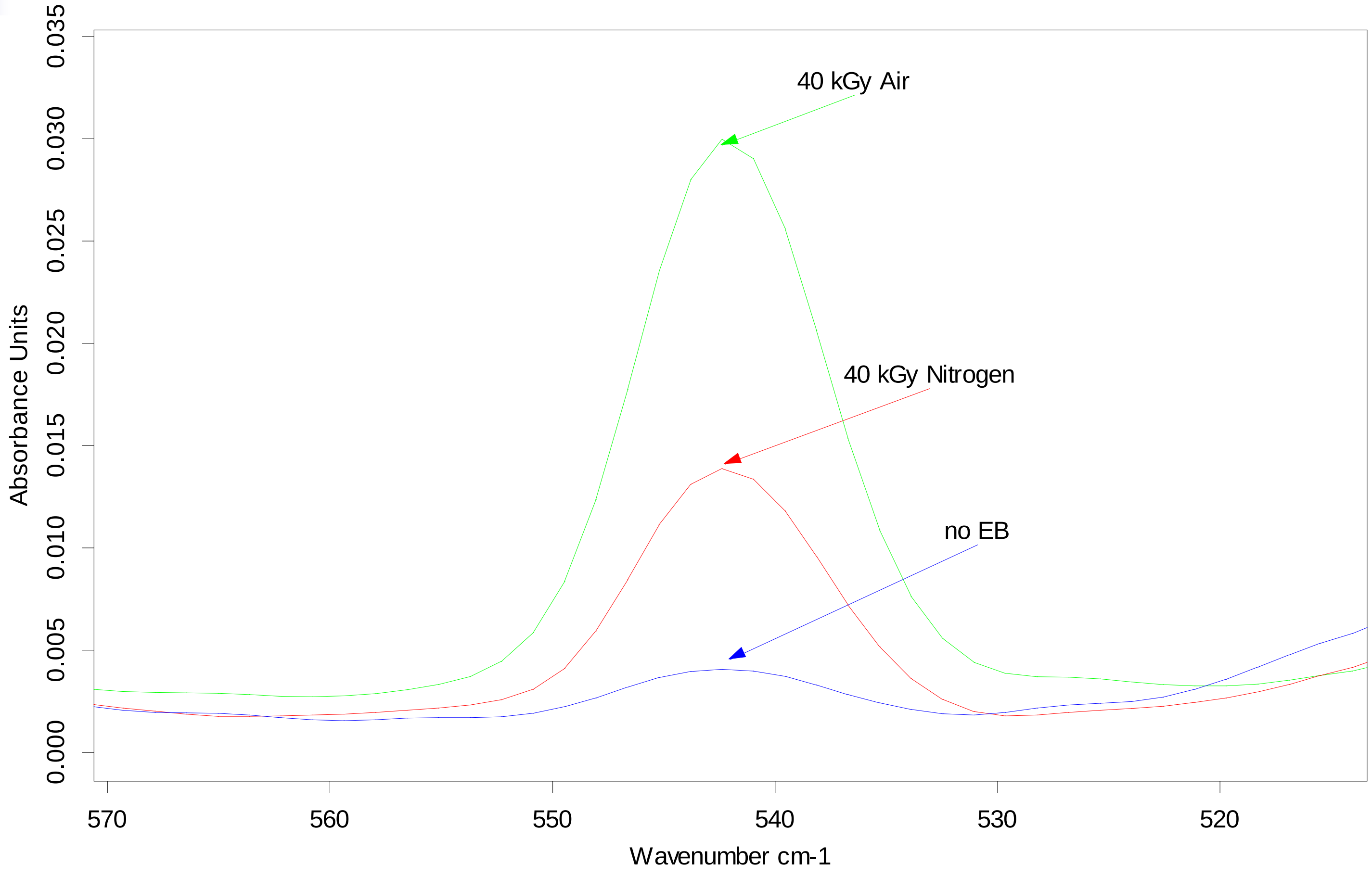


Dosimeter Response Results

- Dosimeter was very sensitive to dose levels less than 10 kGy
- Dose response was relatively constant from about 10 to 100 kGy
- Constant dose response could be useful for separating interting and dose measurements

Oxygen Dependant Response of Developmental Dosimeters
(PCT BroadBeam pilot line at 150 kV)



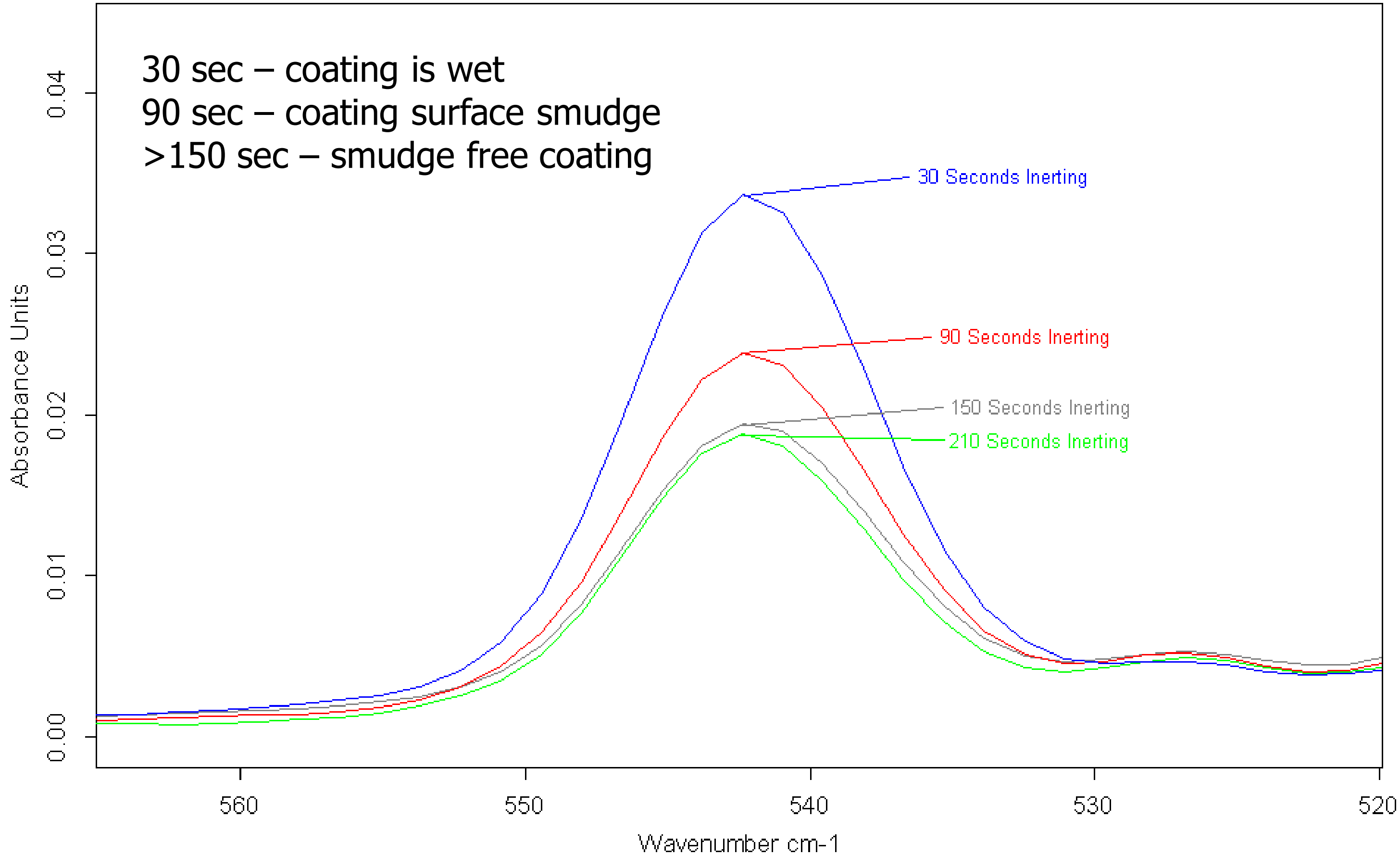
Correlation of Dosimeter Oxygen Response to Coating Cure

Experimental Procedure:

- Acrylate based coating (blend of epoxy acrylate and TMPTA)
- Dosimeter films attached to coating draw-down samples
- Slow (10 scfm) nitrogen purge on EB pilot line
- Run samples every 30 seconds (40 kGy @ 150 kV)
- Measure dosimeter response
- Measure coating cure
  - Surface smudge
  - ATR conversion of 810 cm^{-1} acrylate
- Quantify base on response in air
  - Delta IR peak area = peak area in air – peak area with inerting

Dosimeter Response to Inerting

(PCT BroadBeam pilot line 40 kGy at 150 kV, 10 scfm N2 purge)



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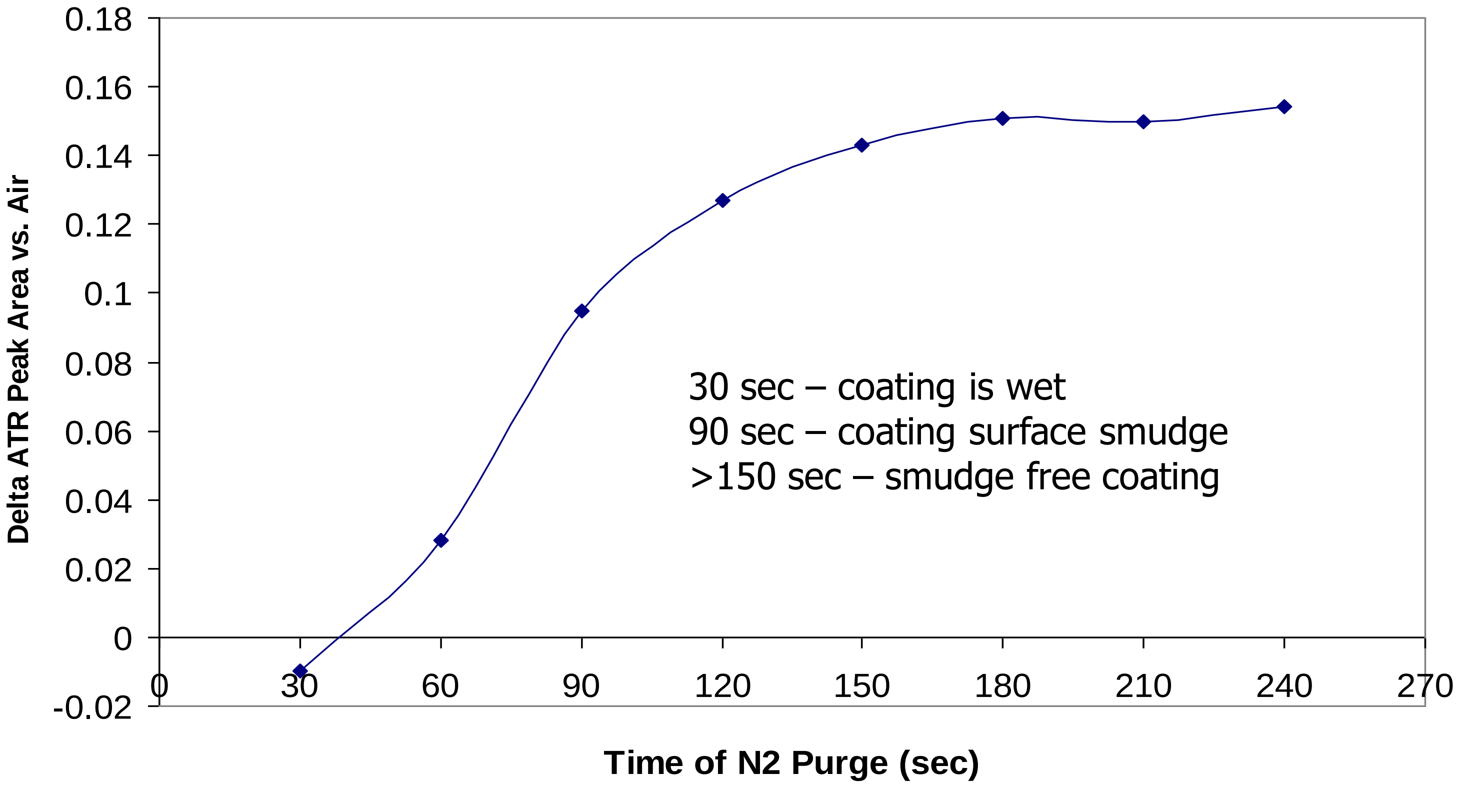
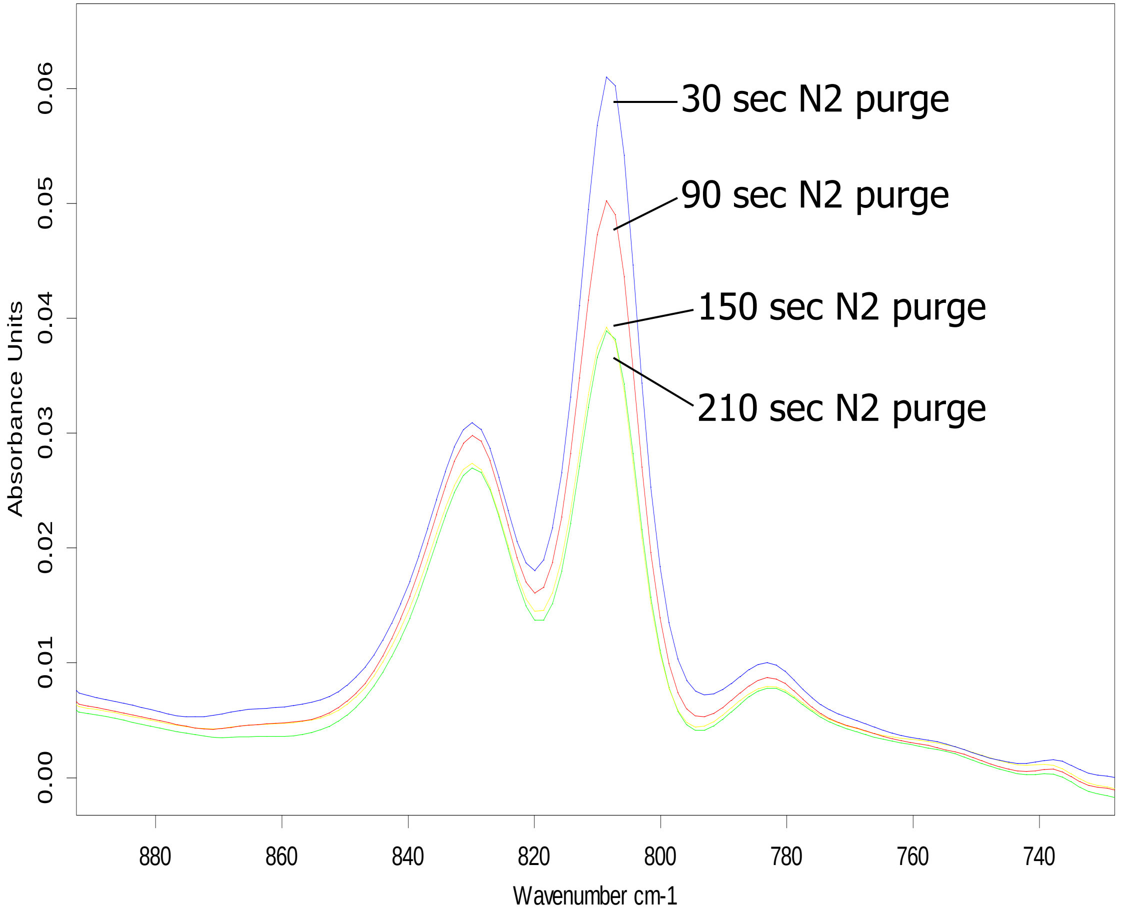


Inerting Effect on Acrylate Coating Conversion

(epoxy acrylate/TMPTA blend, 40 kGy @ 150 kV)



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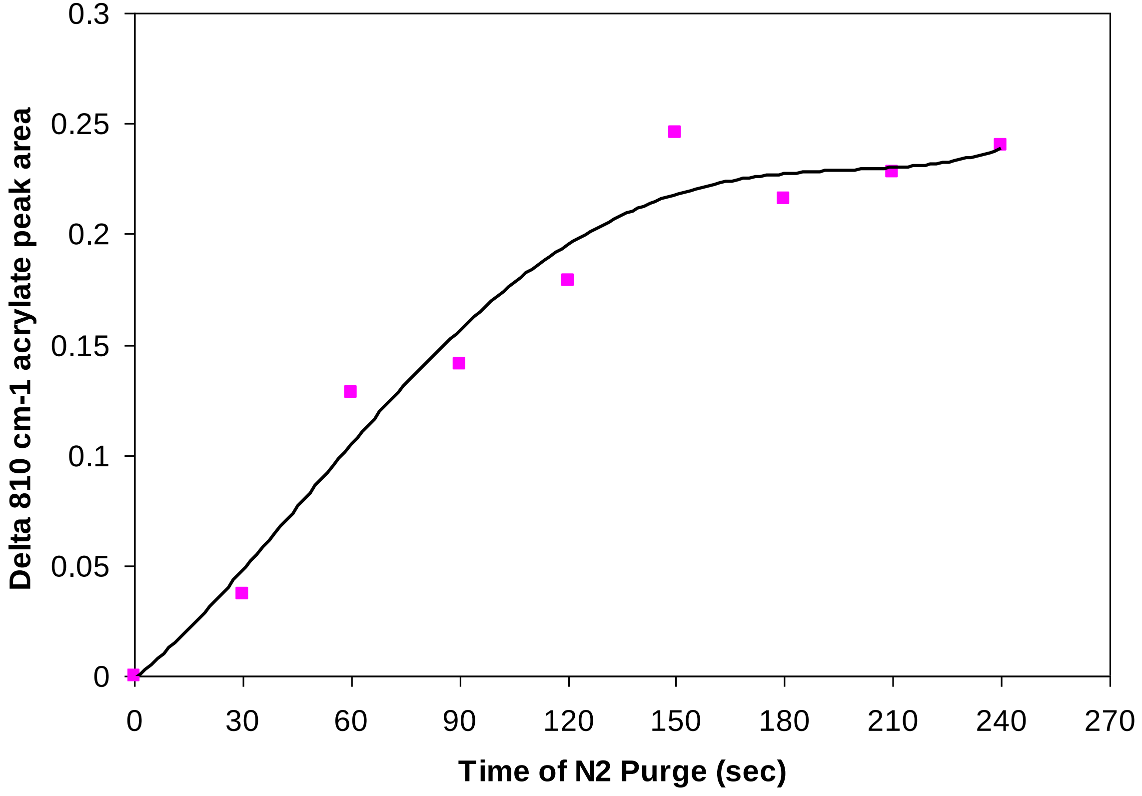
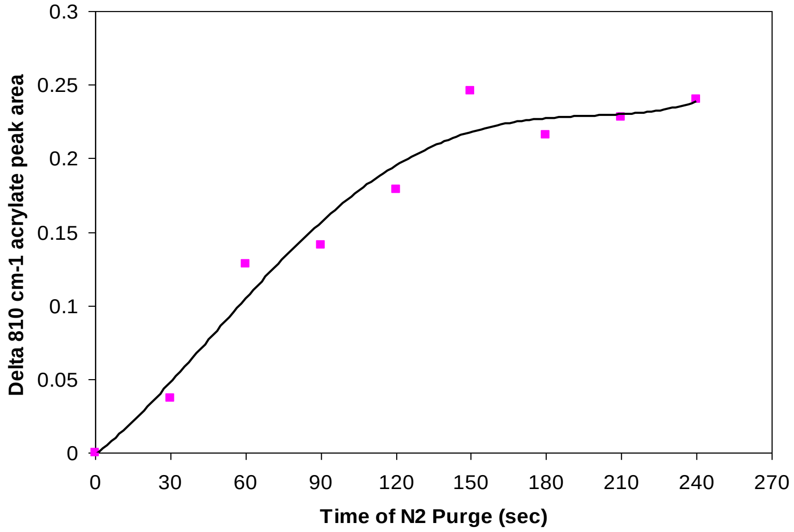
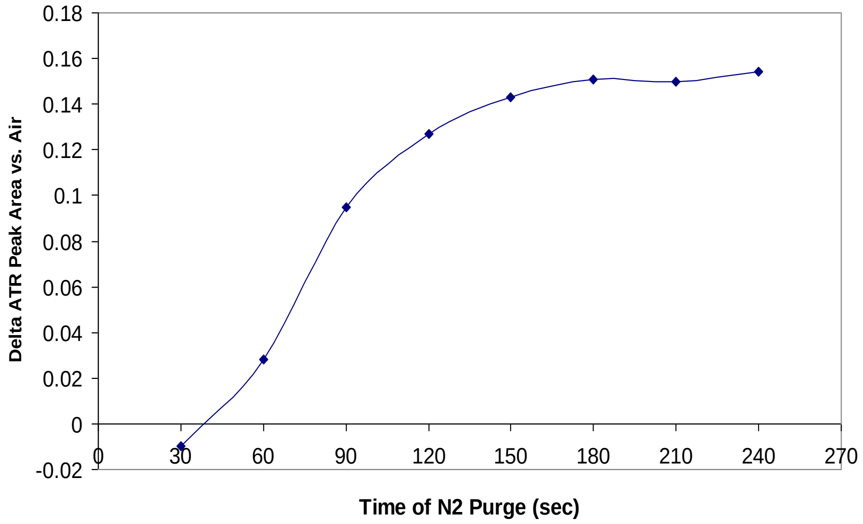


Correlation of Dosimeter Oxygen Response to Coating Cure

Coating Cure



Dosimeter Response



Both curves plateau at about 150 seconds

Demonstrates correlation between coating cure and dosimeter oxygen sensitive response!

Summary/Conclusions

- New EB dosimeter system was investigated
- EB dose and oxygen sensitive response was characterized
- Demonstrated correlation between dosimeter response and coating cure as a function of inerting level

Future Work

- Optimize dosimeter compositions
- Characterize stability and aging properties of dosimeters
- Attenuate response for measurement of higher dose levels
- Test inerting response on high speed commercial lines
- Develop scale for relative inerting efficiency measurement

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Thank You

Questions?

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