N85-32403

PHOTOTHERMAL DEGRADATION STUDIES OF ENCAPSULANTS

JET PROPULSION LABORATORY

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Objectives

- DEVELOP TECHNOLOGY BASE FOR MATERIALS WITH 30 years LIFE WITH RESPECT TO PHOTOTHERMAL DEGRADATION
  - DEVELOP VALID ACCELERATED PHOTOTHERMAL TESTING PROCEDURES FOR EVALUATION OF ENCAPSULANTS
  - DEVELOP DATA BASE OF PHOTOTHERMAL REACTION RATES WITH RESPECT TO PHOTOTHERMAL STRESSES
  - DEVELOP MODEL TO PREDICT LIFE TIME OF ENCAPSULANTS WITH RESPECT TO PHOTOTHERMAL DEGRADATION
  - DEVELOP NECESSARY STABILIZERS TO ACHIEVE 30 years LIFE

Approach

	• PARAMETRIC PERFORMANCE CHARACTERIZATION OF MATERIALS WITH RESPECT TO PHOTOTHERMAL STRESSES
C. GONZALEZ	• MARCO - PERFORMANCE MODELLING
	• MECHANISTIC STUDIES OF PHOTOTHERMAL DEGRADATION AT MOLECULAR LEVEL
U. OF TORONTO	• MICROMOLECULAR KINETIC MODELLING
BROOKLYN TECH	• SYNTHESIS OF STABILIZERS BASED ON MOLECULAR UNDERSTANDING OF DEGRADATION MECHANISMS

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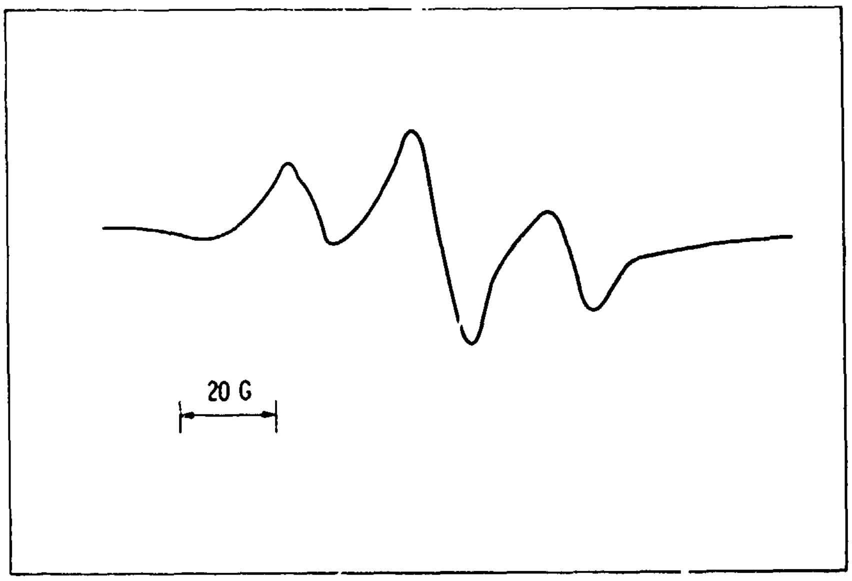
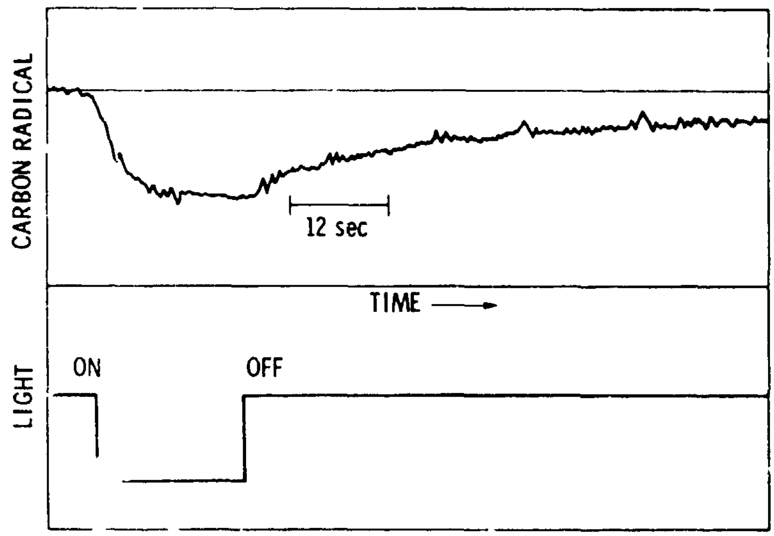
Mechanistic Studies of Photothermal Degradation

- OBJECTIVES
  - TO STUDY MECHANISTIC PATHWAYS OF PHOTOTHERMAL DEGRADATION
  - TO DETERMINE PHOTOTHERMAL REACTION RATES FOR MICROMOLECULAR KINETIC MODELLING
- APPROACH
  - LASER - FLASH ESR SPECTROSCOPY TO DETERMINE KEY REACTION INTERMEDIATES AND THEIR KINETICS

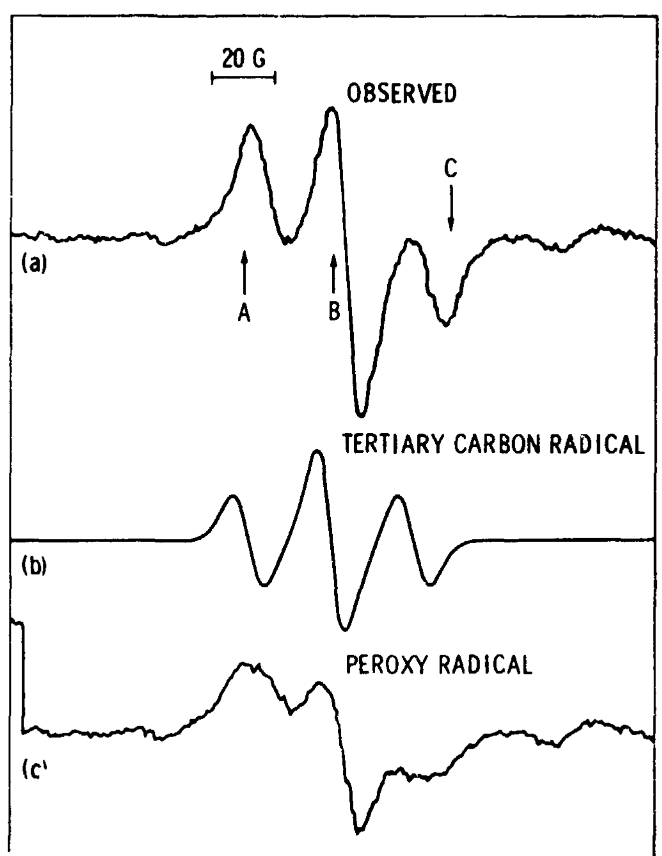
ESR Spectrum of Photogenerated Carbon Radical in Vacuum at Room Temperature



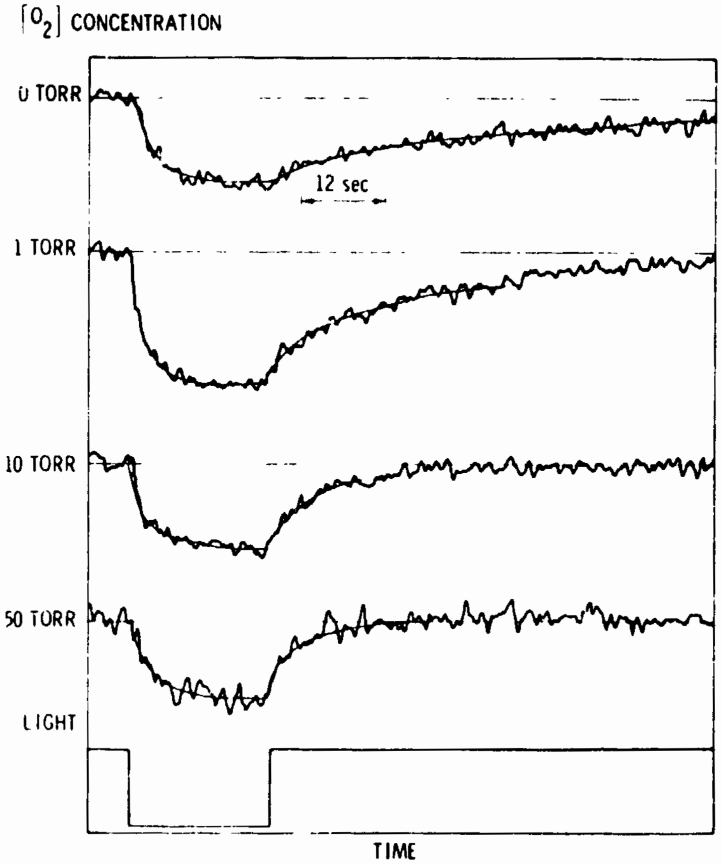
Time Profile of Tertiary Carbon Radical
at Room Temperature



ESR Spectra of Photogenerated Radicals
in Air at Room Temperature



Kinetic Studies of Photogenerated Tertiary Carbon Radicals as a Function of Oxygen Concentration



Mechanism of Photooxidation

$$R-R \xrightarrow{h\nu} R\cdot$$

$$R\cdot + R\cdot \xrightarrow{k_1} R-R \quad \text{CROSSLINKING}$$

$$R + O_2 \xrightarrow{k_2} RO_2\cdot \quad \text{OXIDATION}$$

$$RO_2\cdot + RH \xrightarrow{k_3} R\cdot$$

PRELIMINARY RESULTS

$k_1 = 10^{-2}$ liter/mole sec

$k_2 = 1.3 \times 10^{-2}$/sec

$k_3 = 10^{-1}$/sec

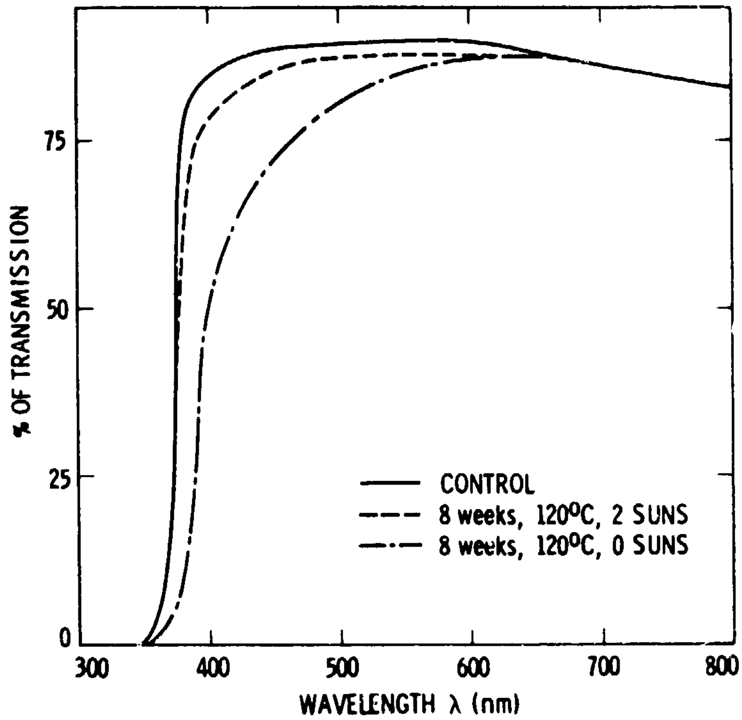
Conclusions

- IDENTIFIED KEY REACTION INTERMEDIATES
- DETERMINED RATES OF KEY DEGRADATION REACTIONS
- THERMAL EFFECTS ON PHOTOOXIDATION ARE BEING EVALUATED

Performance Characteristics of Materials With Respect to Photothermal Stresses

- OBJECTIVE
  - IDENTIFY PERFORMANCE CRITERIA
  - GENERATE DATA BASE FOR MACRO PERFORMANCE MODELLING
- APPROACH
  - PHOTOTHERMAL AGING OF MATERIAL SPECIMENS
    - UV 0 SUN, 2 SUNS, 6 SUNS
    - TEMPERATURE 50°C, 70°C, 85°C, 105°C, 120°C, 135°C
    - PARAMETERS MONITORED TRANSMITTANCE, WEIGHT LOSS, TENSILE MODULUS

Transmittance Spectra of Sunadex/EVA/Pyrex



Mechanisms of Photothermally Induced Yellowing

- THERMAL INDUCED YELLOWING
- PHOTO INDUCED YELLOWING
- PHOTO INDUCED BLEACHING

Photothermally Induced Yellowing of EVA

$$K(T) = k_{\Delta}(T) + k_{h\nu}(T) - k'_{h\nu}(T)$$

WHERE

- K = RATE OF OVERALL YELLOWING
- k_{Δ} = RATE OF THERMAL INDUCED YELLOWING
- $k_{h\nu}$ = RATE OF PHOTO INDUCED YELLOWING
- $k'_{h\nu}$ = RATE OF PHOTO INDUCED BLEACHING
- T = TEMPERATURE

i) IF $k_{h\nu} = k_{h\nu}$

RATE OF YELLOWING IN DARK OVEN = RATE OF YELLOWING IN CER

ii) IF $k_{h\nu} < k_{h\nu}$

RATE OF YELLOWING IN DARK OVEN > RATE OF YELLOWING IN CER

iii) IF $k_{h\nu} > k_{h\nu}$

RATE OF YELLOWING IN DARK OVEN < RATE OF YELLOWING IN CER

Evaluation of k_{Δ}, $k_{h\nu}$, $k_{h\nu}$

- THERMALLY AGED VIRGIN SAMPLE IN DARK OVEN AT 120°C TO GENERATE YELLOWING
- THE YELLOW SAMPLE IS THEN PHOTOTHERMALLY AGED IN CER AT 6 SUNS AND 50°C TO EVALUATE THE BLEACHING RATE $k_{h\nu'}(50^{0})$

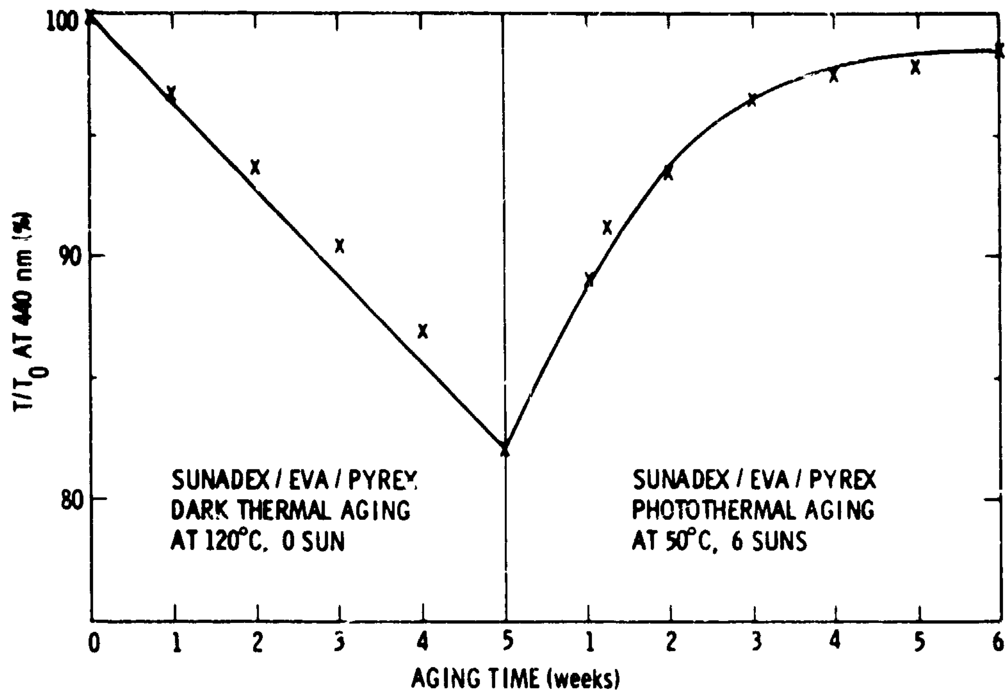
$$K(50^{0}C) = k_{\Delta}(50^{0}C) + k_{h\nu}(50^{0}C) - k'_{h\nu}(50^{0}C)$$

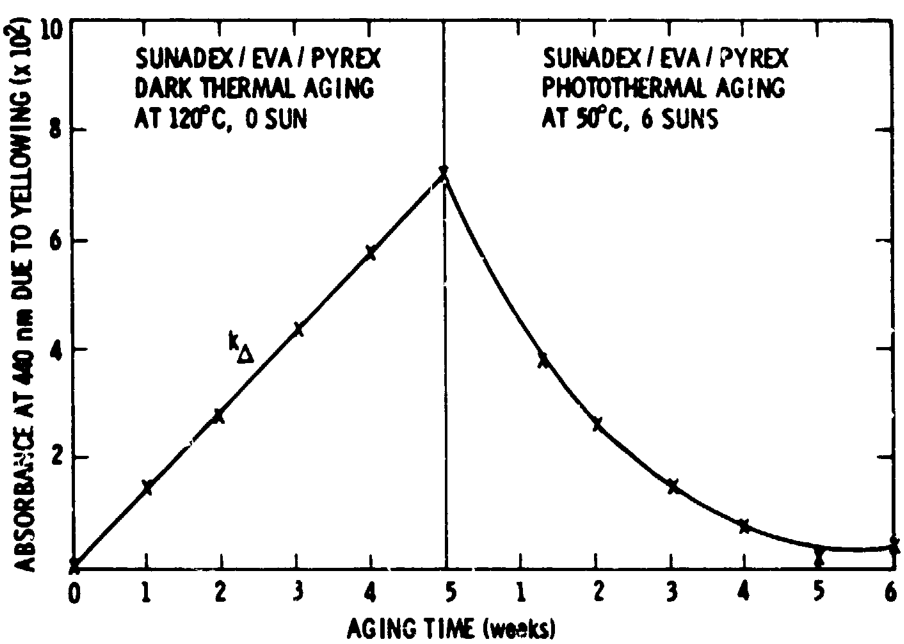
SINCE

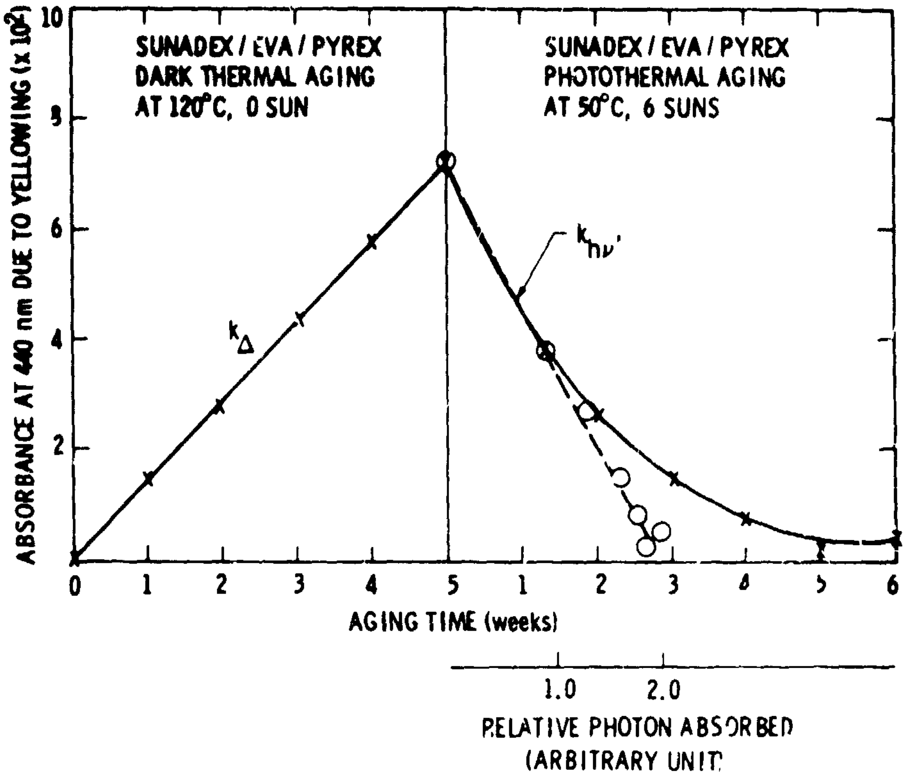
$k_{\Delta}(50^{0}C)$ AND $k_{h\nu}(50^{0}C)$ ARE SMALL

THEREFORE

$$K(50^{0}C) \approx - k'_{h\nu}(50^{0}C)$$


100
90
80
T/T$_0$ AT 440 nm (%)
SUNADEX / EVA / PYREX
DARK THERMAL AGING
AT 120°C, 0 SUN
SUNADEX / EVA / PYREX
PHOTOTHERMAL AGING
AT 50°C, 6 SUNS
0 1 2 3 4 5 1 2 3 4 5 6
AGING TIME (weeks)


10
8
6
4
2
ABSORBANCE AT 440 nm DUE TO YELLOWING (x 10^2)
SUNADEX / EVA / PYREX
DARK THERMAL AGING
AT 120°C, 0 SUN
SUNADEX / EVA / PYREX
PHOTOTHERMAL AGING
AT 50°C, 6 SUNS
k_Δ
0 1 2 3 4 5 1 2 3 4 5 6
AGING TIME (weeks)



Conclusions

- IDENTIFY MECHANISMS OF PHOTOTHERMAL YELLOWING
- DEVELOP TECHNIQUES TO MONITOR DIFFERENT MODES OF YELLOWING
- STUDIES OF TEMPERATURE EFFECT ON RATES OF YELLOWING AND BLEACHING ARE BEING INITIATED