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Polymer Aging of Plastic Scintillators

Patrick Feng, Sandia National Laboratories

7-1-2015

Background and Context



Large-area plastic scintillator
gamma-ray (counting) detectors

Motivation:

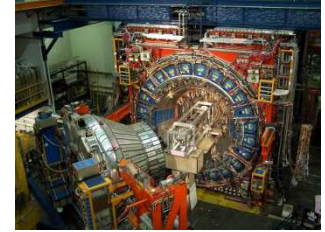
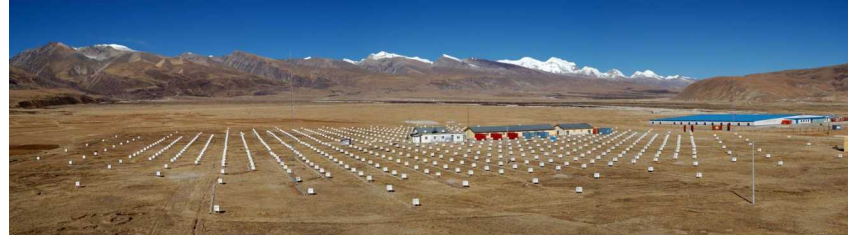
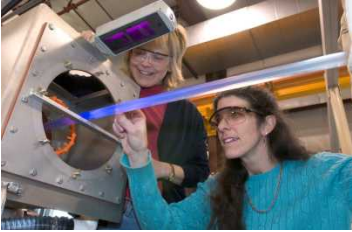
- The long-term stability of plastic scintillator materials is of interest
- The specific degradation mechanisms leading to performance reduction are not fully understood at present
- What methods are available towards stabilizing these materials in real-world environments?



Large-area plastic scintillator
internals

- Prior work by PNNL estimated that large PVT scintillators have an expected lifetime of 10 years when deployed in uncontrolled environments
- State-of-health may be assessed by background count rate
- Results indicate an average sensitivity loss of $\sim 4\%$ per year

Literature Examples of Scintillator Aging

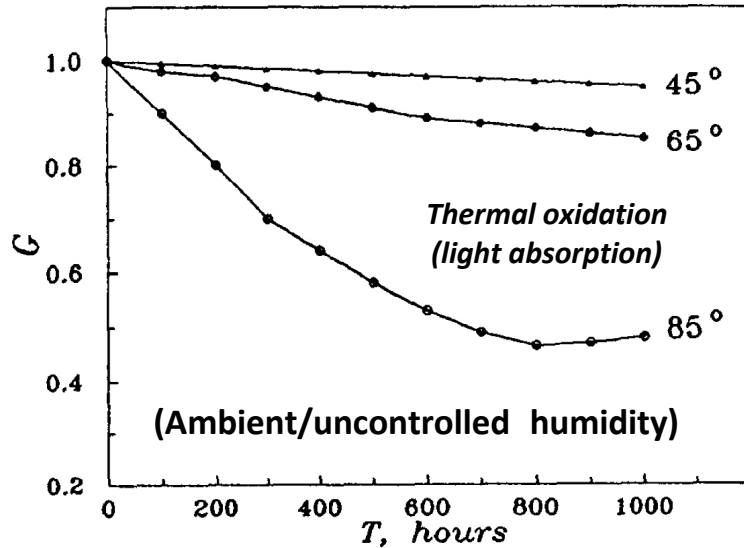


Several plastic scintillator aging studies have been performed (primarily for physics and astronomy applications):

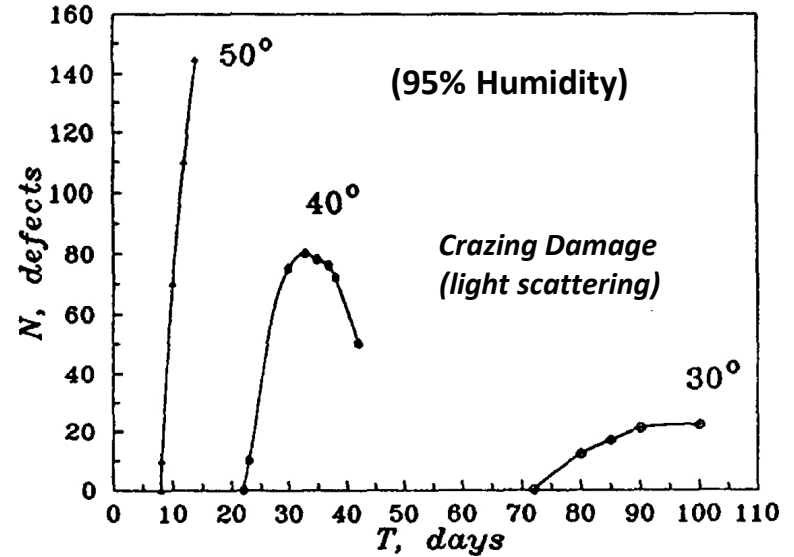
1. Fermilab:
 - a) SSC detector (1993)
 - b) MINOS scintillator system (1998)
2. LHAASO Project (2011)
3. PS vs. PVT aging studies
 - a) Barnaby and Barton (1962)
 - b) Ukrainian PS plastic scintillator vs NE-114 PVT plastic scintillator (2005)
4. Scintillator non-homogeneity (2009)

Extruded Polystyrene Scintillator at Fermilab

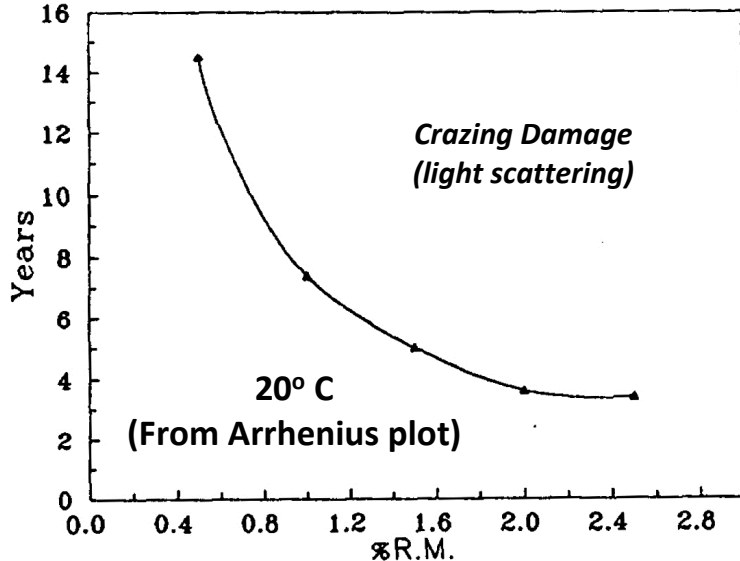
Light-Yield versus Temperature



Crazing Defects versus Moisture/Temp

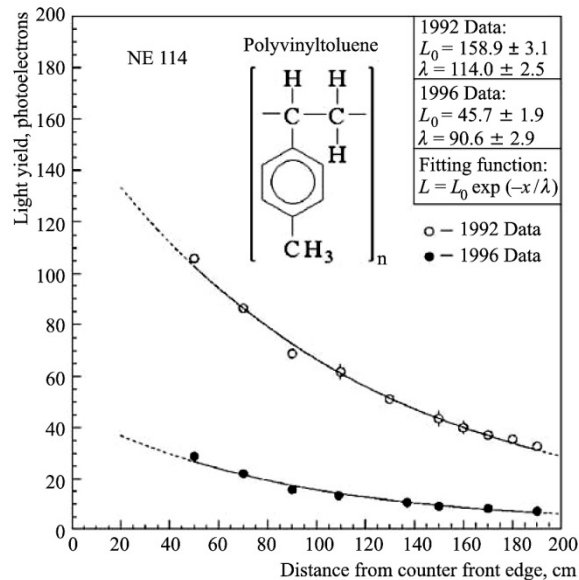
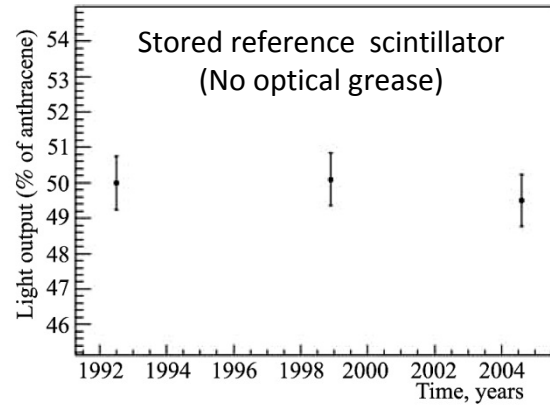
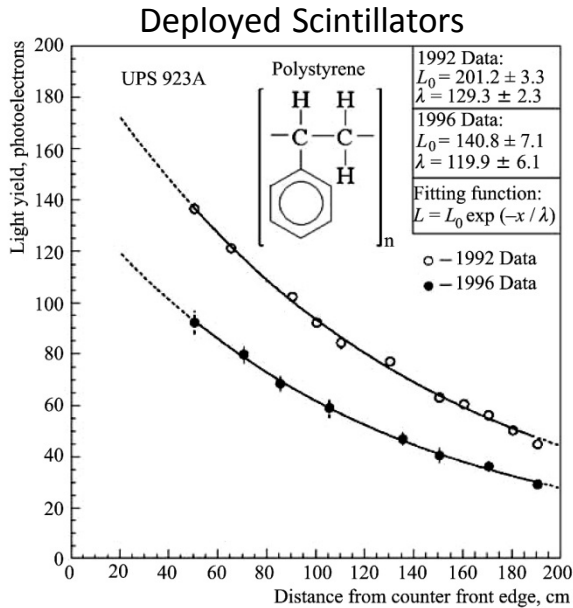


Extrapolated Lifetime (20% LY decr) versus Residual Monomer Content



- Different degradation mechanisms highlighted by PS scintillator aging study:
 - Yellowing due to oxidation
 - Light scattering due to crazing
- Somewhat uncontrolled conditions preclude generalized conclusions

Ukrainian Polystyrene Plastic Scintillator 'UPS 923A'



- UPS 923A is PS analog of NE114 (PVT)
- Polystyrene, 2% *p*-terphenyl, and 0.03% POPOP
- Deployed at Fermilab Tevatron for 4 years in CDF detector
- Laboratory conditions (temp, humidity, radiation)
- Reference UPS 923A scintillator shows little degradation over 12 year period

PS scintillator less sensitive to performance degradation over time than corresponding PVT scintillator

- Organic materials are susceptible to environmental effects/aging
- Polymeric systems possess additional considerations:
 - Relaxation behavior, bulk mechanical properties, impurity effects
- Scintillators are even more complex due to multi-component mixtures and varied preparation techniques (proprietary parameters?)

Key Factors that Impact Long-Term Stability/Performance of Plastic Scintillators:

- 1) Crazing in glassy amorphous systems
 - Organic small molecule additives and impurities
 - Other materials in contact with polymer (i.e. optical grease)
- 2) Diffusion of small molecules
 - Internal solutes/impurities
 - Gases/vapors
- 3) Oxidation
 - O₃, PAHs, NO_x

Can the specific degradation modes be identified and consequently addressed?

1. Origins of Polymer Crazeing

Deformation w/out increase in volume: Shear

Deformation with volume increase: Crazeing

Considerations:

- Density/free volume
- Entanglements
- Crystallinity
- Hydrostatic stress
- Impurities/defects

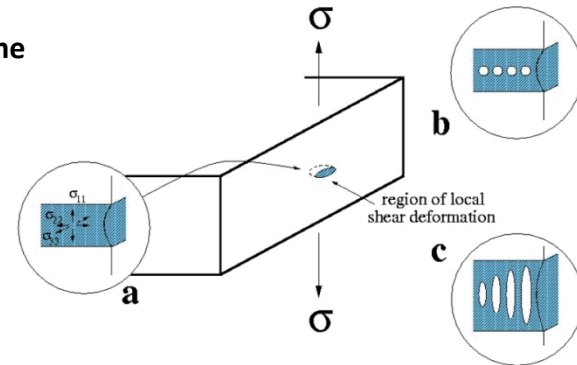
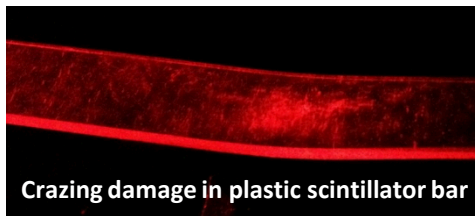
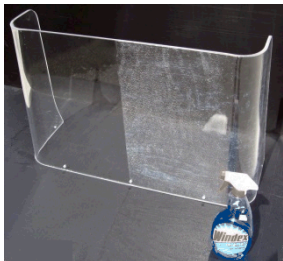


Figure 1: schematic drawing of microscopic events involved in craze nucleation: a) formation of a localised surface plastic zone and build-up of lateral stresses, b) cavitation of the plastic zone and c) deformation of the polymer ligaments between voids and coalescence of individual voids to form a void network (after Kramer [1]).

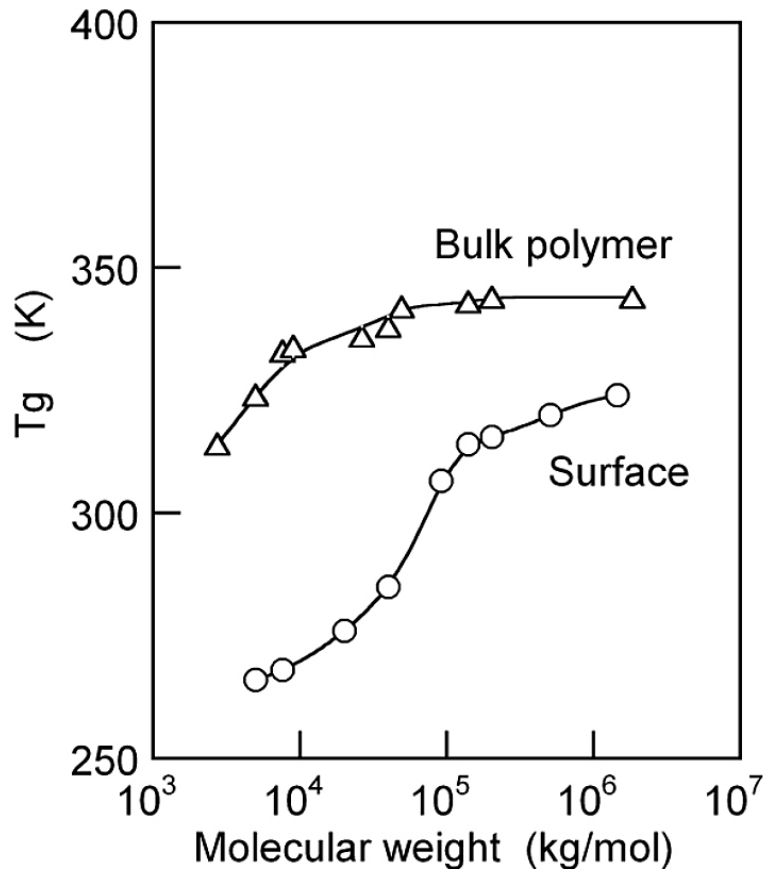


- Crazeing is due to plastic deformation in regions of localized hydrostatic stress, followed by cavitation (void formation)
- Crazeing increases the local micro-hardness and elastic modulus of material but often precedes brittle failure (due to breakdown of crazeing network)
- Local plasticization is operative in the presence of a crazeing agent



Crazeing damage in plastic scintillator bar

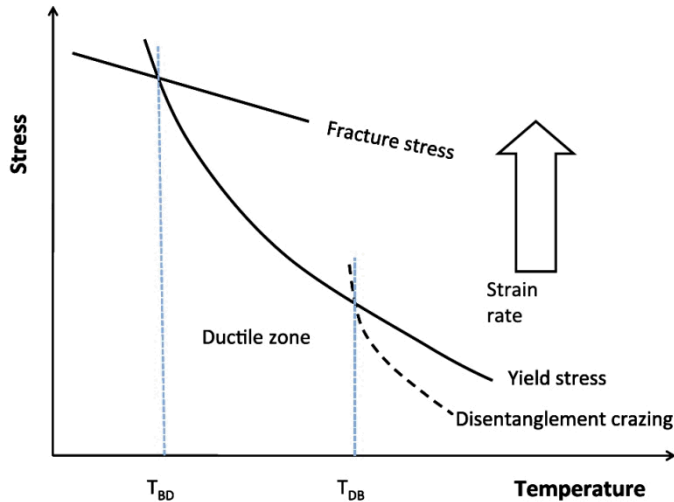
Craze Initiation: Surface Effect



- Lower T_g of the Polystyrene (PS) surface indicates greater free volume than the polymer bulk
- Suggests less entanglement density near surface
 - Confirmed as free polymer ends via SIMS depth profiling
- Greater free volume of mobile chains ends (at surface) lead to higher crazing susceptibility

Recurring Theme: Non-uniform nature of amorphous polymers

Origins of Crazing: Strain Rate and Thermal History



- Two brittle-ductile transitions in PS:
 - 1) High strain rates and low temperatures (mechanical stimulus \rightarrow bond breaking)
 - 2) Low strain rates and high temperatures (disentanglement)

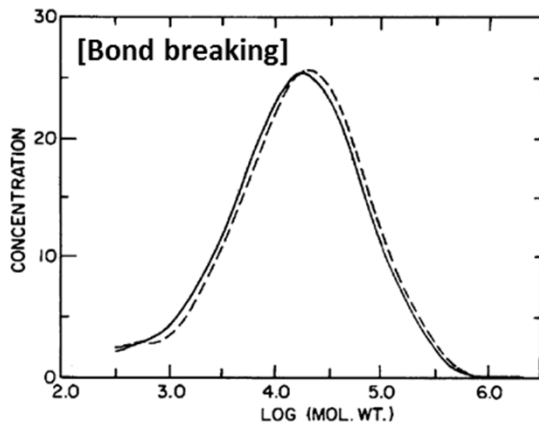
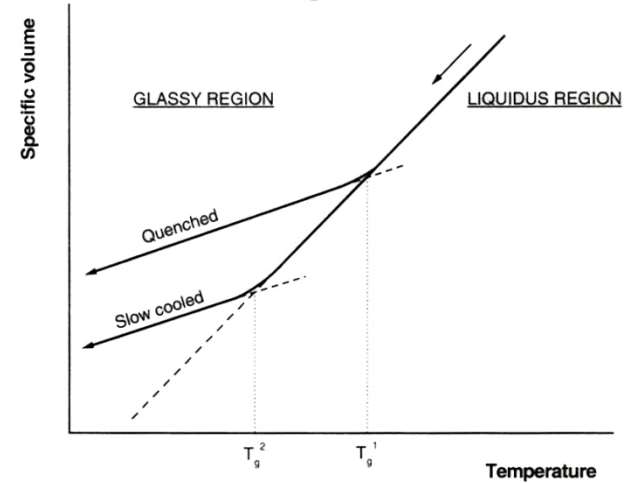
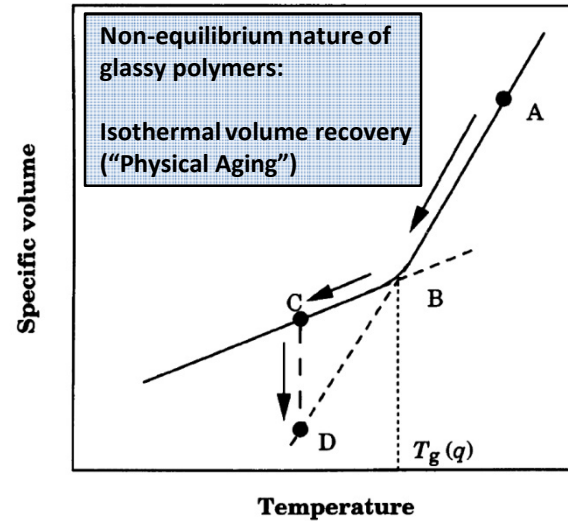
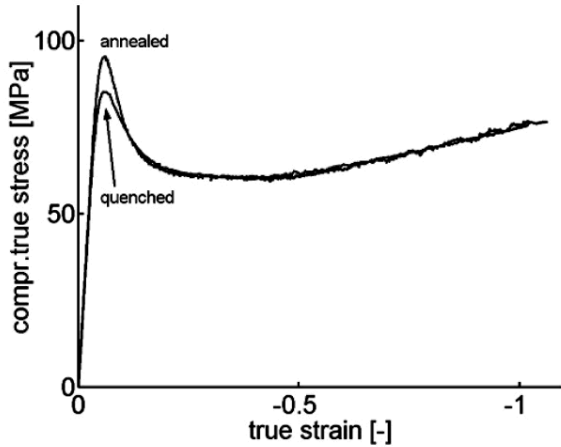


Fig. 1. GPC chromatograms for virgin and crazed polystyrene.

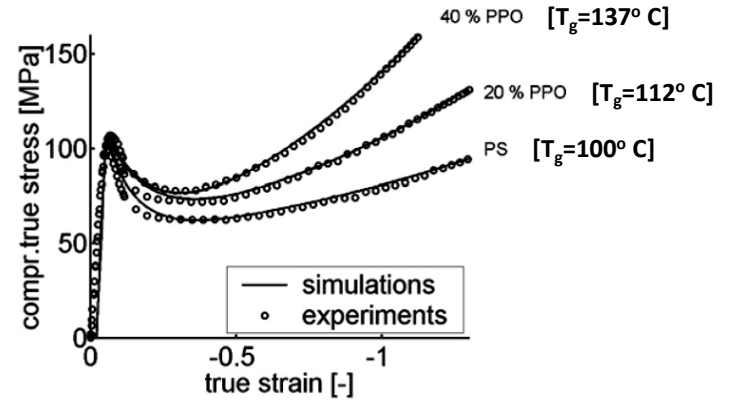


- Free volume in a polymer is always greater than the molecular volume due to imperfect chain packing
- Free volume is sensitive to cooling rate

Thermal History and Entanglement Density



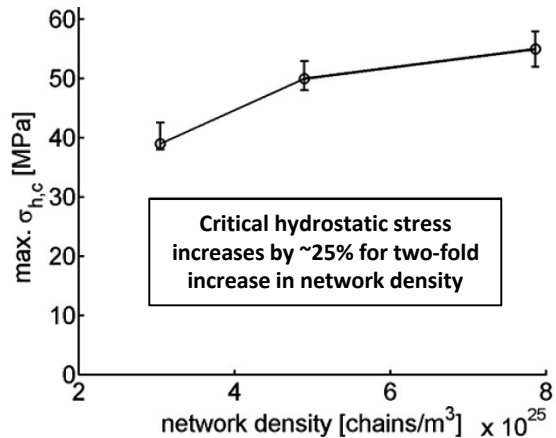
- Strain softening amplifies non-homogenous behavior via strain localization
- Strain hardening stabilizes deformation zone (suppresses non-homogenous behavior)



- Yield strength is higher for the annealed sample
- Strain hardening is unchanged

- Addition of poly(phenylene oxide) to PS increases strain hardening while leaving yield strength unaffected
- Results interpreted in the context of increasing the network density/ entanglements of the polymer

Critical Hydrostatic Stress vs. Network Density



$$\nu \propto C_{\infty}^{1.4} \left(\frac{\rho}{m_0} \right)^{2.2} l_0^{3.6} \quad (7)$$

where C_{∞} is the characteristic ratio. Basically C_{∞} is a measure of the segmental stiffness or the persistence length of the polymer. ρ is the density, m_0 the mass of a monomer and l_0 the contour length of this monomer.

Equation relating the entanglement density as a function of several parameters

Key Result: High polymer segmental stiffness, high density, and slender polymer backbones favor high entanglement densities

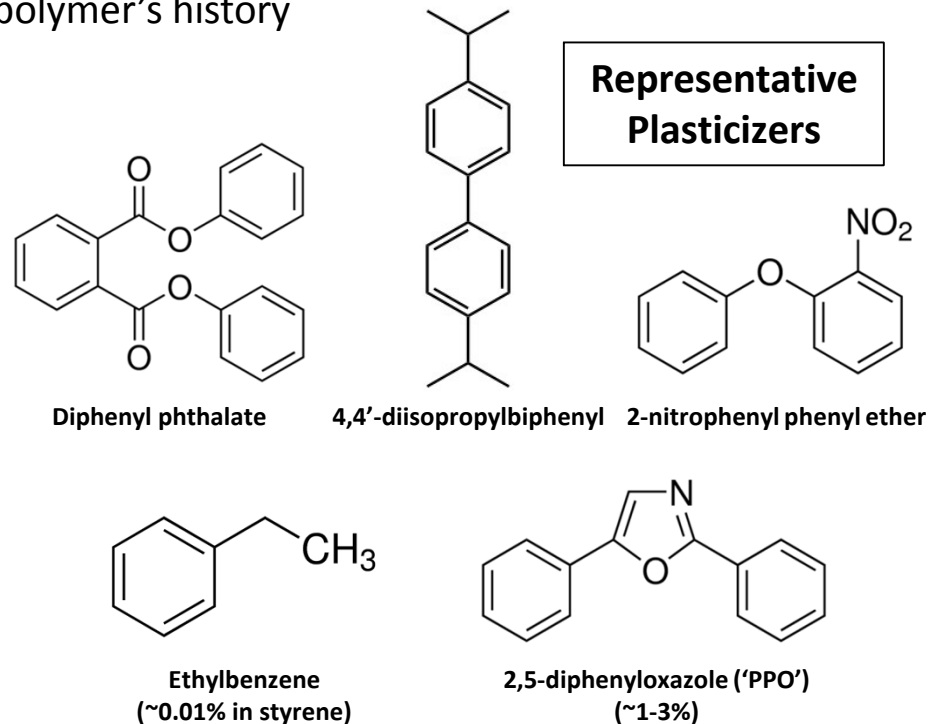
Plasticizers (and Impurities)

- Plasticizers increase the mobility of structural elements in a polymer:
 - Reduction in glass transition temperature (T_g) and rigidity
 - Reduction in van der Waals surface energy (intermolecular forces between chains)
 - Increase in toughness (impact strength)
 - Effective plasticizers possess good internal/conformational mobility
- Plasticizers reduce crystallizability and increase chain flexibility
 - Interpose polymer chains (disentanglement)
- Plasticization effects also dependent upon a polymer's history

Table IX. Effect of Plasticizer on T_g of Polystyrene (2)

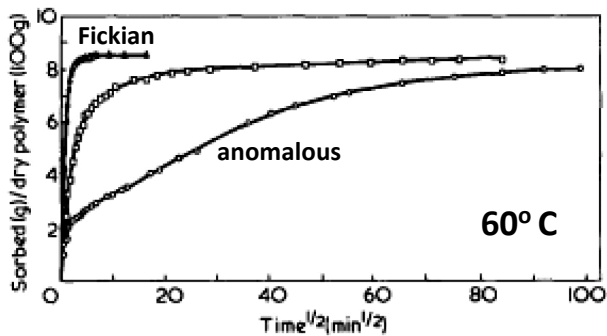
Plasticizer	% Plasticizer	T_g
Ethylbenzene	0	82
	3	68
	5	50
	10	22
Paraffin Oil	0	80
	3	75
	10	56
	20	49
	50	43

Plasticization may occur at additive/fluorophore concentrations used in scintillators (1-5% w/w)



2. Diffusion in Polymers

Depends on polymer history: Hexane Uptake



Comparison of n-hexane sorption in preswollen (Δ), 'as-received' (\square), and annealed samples (\circ) at $p/p^0 = 0.75$ and 30°C . Sorption-cycle 1, polystyrene, $d = 0.534\ \mu\text{m}$

- Pre-swollen PS exhibits Fickian diffusion kinetics
- Annealing leads to anomalous diffusion behavior
- 'As-received' sample exhibits intermediate diffusion kinetics (unknown thermal history)

Fickian Diffusion:

$$J = -D \frac{d\sigma}{dx}$$

J = 'diffusion flux', [mol/(cm²·sec)]
 D = diffusion coefficient, (cm²/sec)
 $d\phi/dx$ = concentration gradient

- Steady-state diffusion is proportional to concentration gradient
- Usually obeyed for vapor diffusion through polymers above T_g

Anomalous Diffusion:

- Typifies transport kinetics below T_g

Water Diffusion in PS and PVT:

$$D_{\text{PS}} = 2.2 \cdot 10^{-8} \text{ cm}^2\text{sec}^{-1} \text{ (} 30^\circ\text{C)}$$

$$D_{\text{PVT}} = 1.3 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \text{ (} 30^\circ\text{C)}$$

Oxygen Diffusion in PS and PVT

$$D_{\text{PS}} = 3.1 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \text{ (} 25^\circ\text{C)}$$

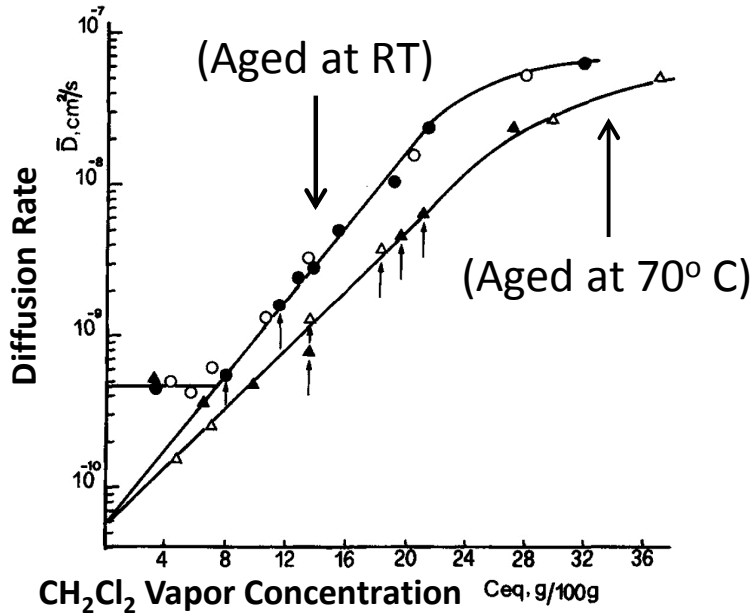
$$D_{\text{PVT}} = 6.8 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \text{ (} 25^\circ\text{C)}$$

Toluene Diffusion in PS

$$D_{\text{PS}} = 5.1 \cdot 10^{-6} \text{ cm}^2\text{sec}^{-1} \text{ (} 30^\circ\text{C)}$$

Diffusion of different species are of interest: Crazing, Phase Transitions, Oxidation

Diffusion of CH₂Cl₂ in Aged PS



- Higher temperature aging accelerates physical aging (free volume recovery)
- Slower diffusion rate associated with reduced free volume in thermally-aged sample (Note y-axis log scale)
- Implications for crazing and T_g reduction due to plasticization effect of guest

Temperature and Draw Ratio: Hexane Crazing of PS

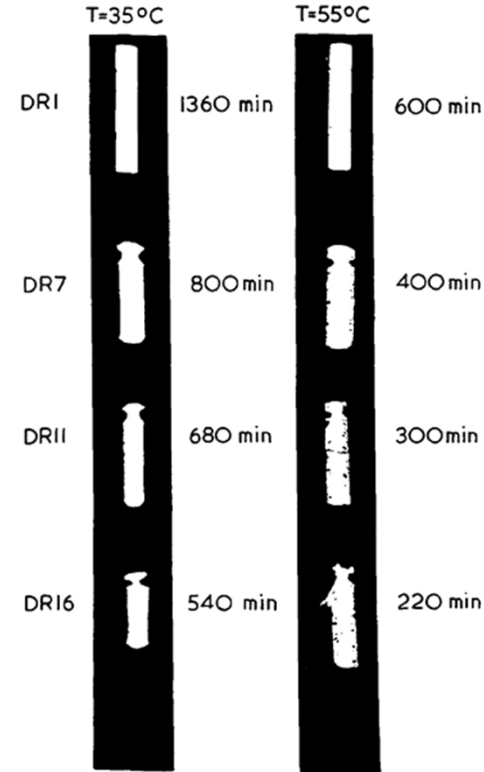
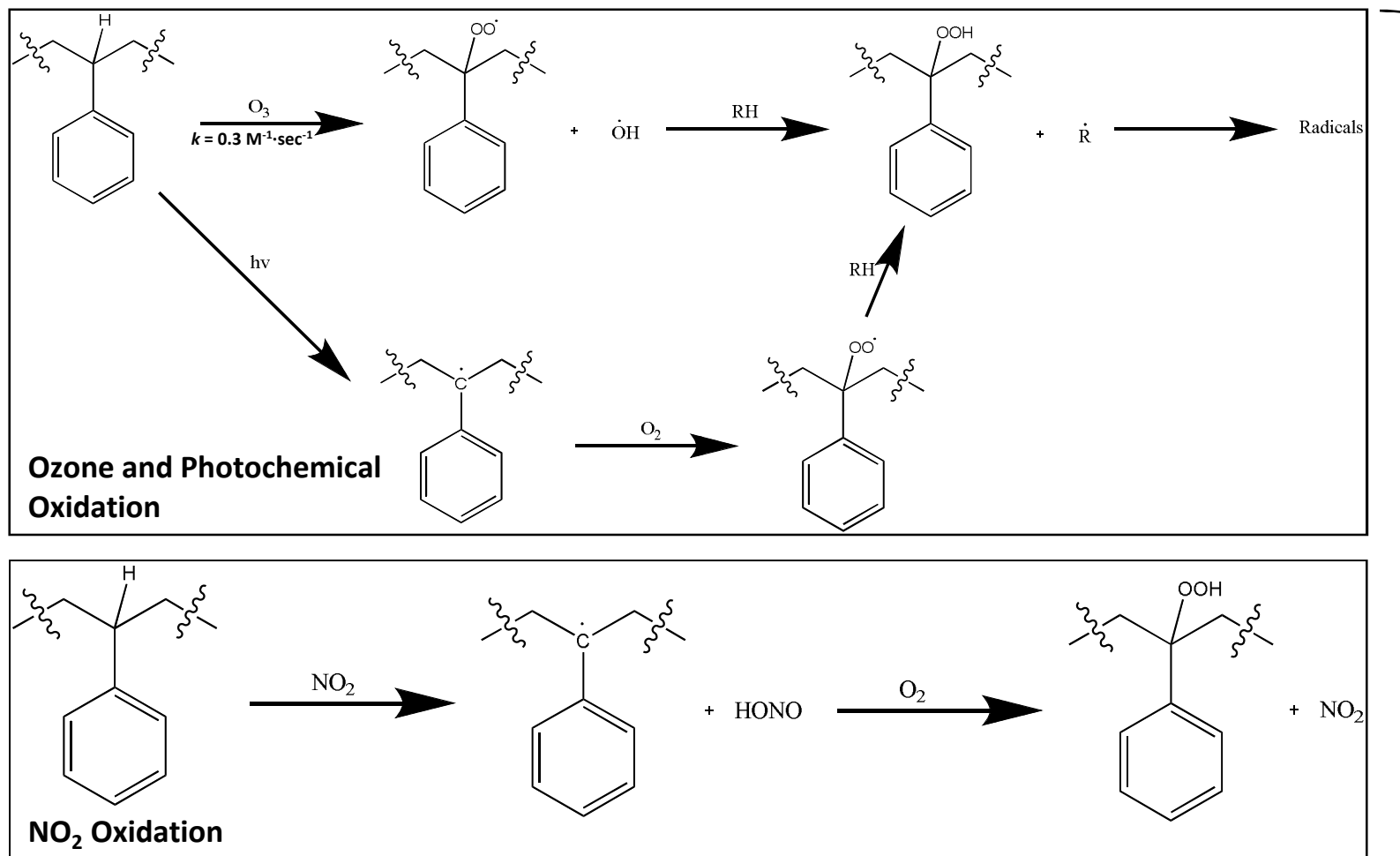


Figure 10 The effect of draw ratio and temperature on the appearance of polystyrene sheets which have been immersed in n-hexane.

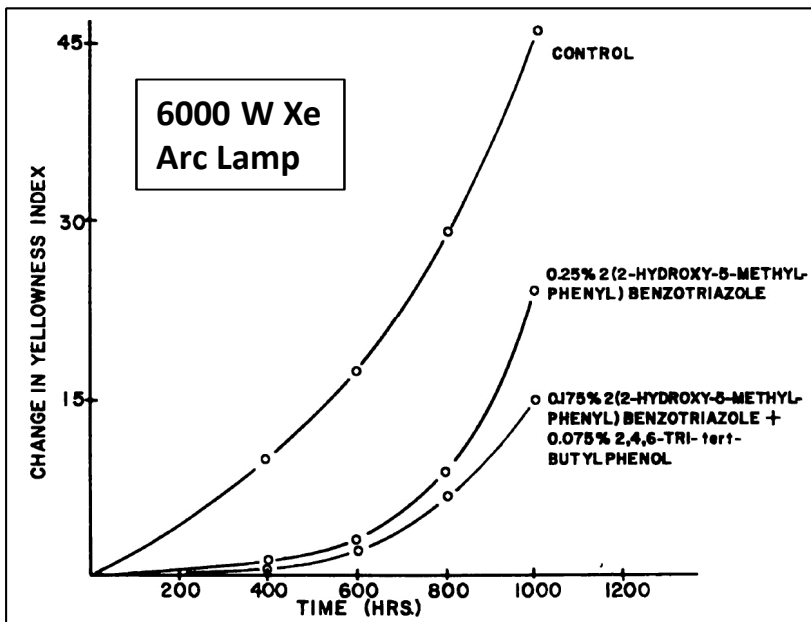
- Higher temperatures increases diffusion/crazing
- Larger draw ratios increases order via strain-induced effect:
 - More susceptible to crazing (defects)
 - Similar effect for extruded polymers

3. Oxidation (via diffusion)



- Light, ozone, and NO_2 oxidation of styrenyl polymers yield similar products
- Styrene hydroperoxide and radical intermediates may undergo side reactions
- Irreversible reactions: Degradation of scintillator components/properties

- Antioxidants and radical-trapping compounds have been shown to be effective for the UV-stabilization of polymers



Article

tert-Butanol as an OH-Scavenger in the Pulse Radiolysis of Oxygenated Aqueous Systems

Magnus Von Piechowski^{1,2}, Marie-Anne Thelen¹, Jürg Hoigné² and Rolf E. Bühler¹

Article first published online: 8 MAY 2010

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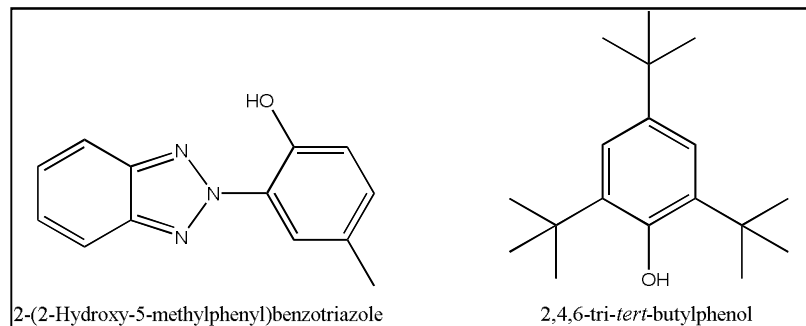
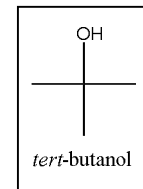
Issue



Berichte der Bunsengesellschaft für physikalische Chemie

Volume 96, Issue 10, pages 1448–1454, Oktober 1992

tert-butanol also used as radical scavenger in studies of ozone reactions in water



- Yellowing in PS is associated with:
 - Decrease in MW due to chain scission
 - Formation of carbonyls and alcohols (i.e. benzophenone, benzoin, benzoyl acetone)
- Low concentrations of radical scavengers typically effective for UV-stabilization



Moisture Effects in PVT Scintillators:

- Scintillators on the left in each picture were heated to 55° C for 30 days at 90% relative humidity
- Cooling to -30°C resulted in freezing of trapped moisture ('fogging')
- Effect was reversible as polymer returned to RT (right figure)

Initial thoughts and questions:

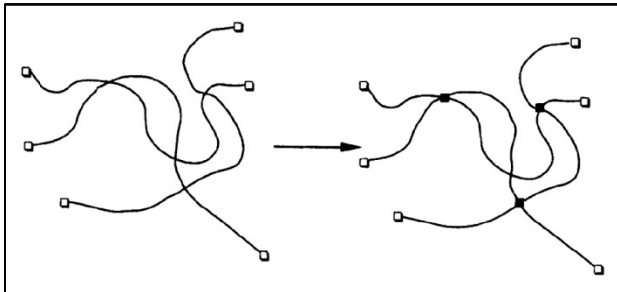
- Reversibility of the effect and impact on long-term performance?
- Are testing conditions representative of realistic environments?
- Does performance reduction occur across all deployments, or only for materials in hot/humid → cold locations?
- Uniform degradation for scintillators at a single location?

Approaches to Understand/Improve the Scintillator Properties

- 1) Diffusion barrier layer (i.e. Parylene)
- 2) Replace polymer with more resilient material: (i.e. Styrene-acrylonitrile)
 - High Chemical resistance, high heat resistance, transparent, low cost, high entanglement density
- 2) Cross-linking to increase entanglement density, molecular weight, glass transition temperature
- 3) Co-polymerization to increase uniformity of polymer and dissolved fluorophores



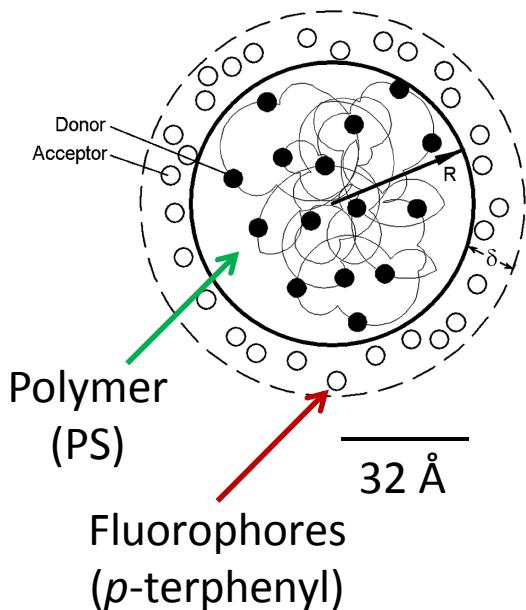
Styrene-acrylonitrile plastic part



Stabilized chain entanglements via cross-linking

	Cross-Linked PS	Linear PS	Expanded PS
<u>Chemical Resistance</u>			
Conc. Acids	Fair	Poor	
Dilute Acids	Good	Fair	
Alcohols	Good	Fair	
Alkalis	Fair	Fair	
Aromatic Hydrocarbons	Poor	Poor	
Greases/Oils	Fair	Fair	
Halogens	Poor	Poor	
Ketones	Poor	Poor	
<u>Physical Properties</u>			
Density (g/cm ³)	1.05	1.05	0.02
Refractive index	1.59	1.59	
Resistance to UV	Good	Poor	
Water Absorption (% , over 24 hours)	0.02	0.3	3
Glass Transition Temperature (C)	130*	100	100
*(Depends on extent of cross-linking)			

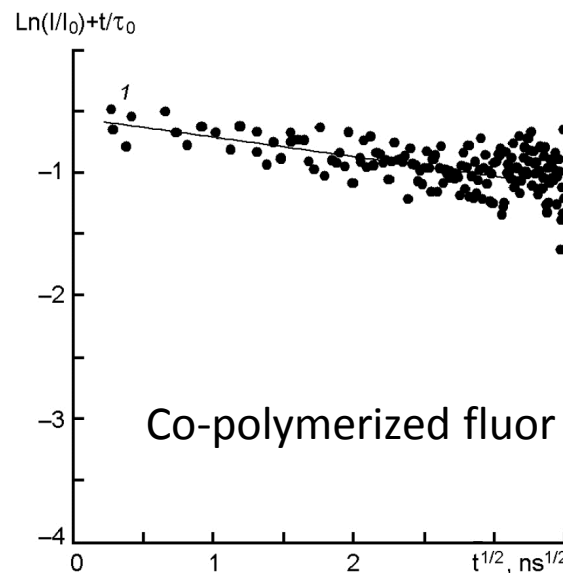
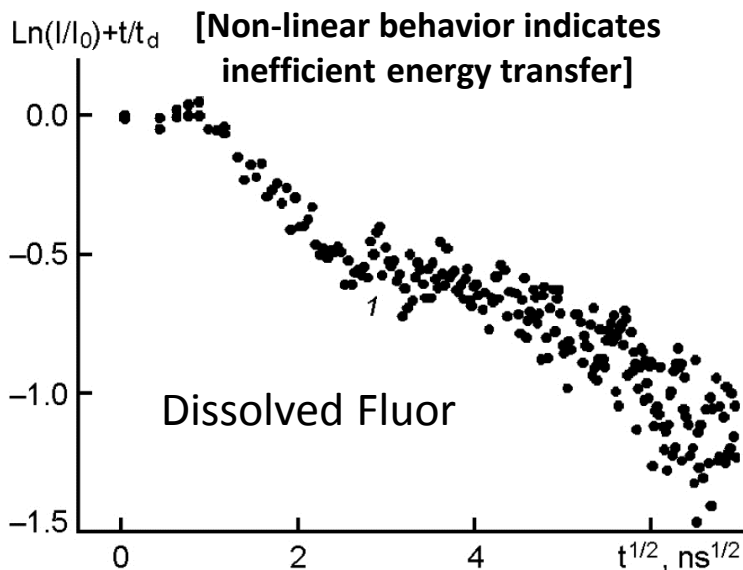
Stabilization and Uniformity via Co-Polymerization



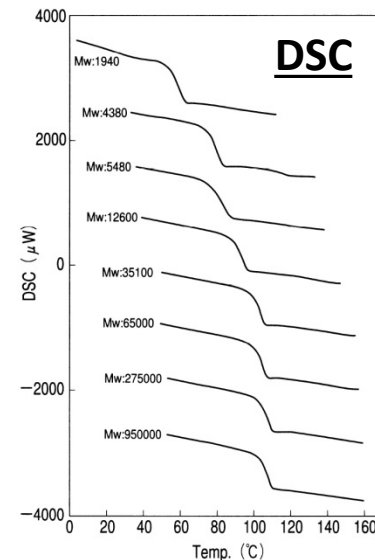
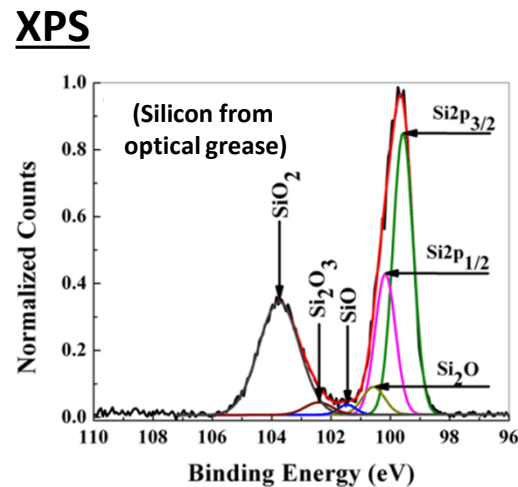
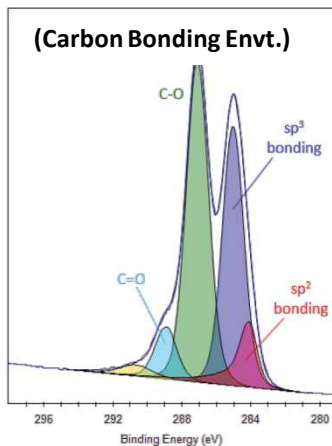
- Non-uniform distribution of dissolved solutes (aggregation) impacts scintillation and physical properties
- Scenario is more complex than a plasticized system with molecularly distributed small molecules

$$f(T) = \exp\left(-t/\tau_d - 2\frac{1.38}{\sqrt{6}}\pi^{3/2}R_0^3c_a\sqrt{t/\tau_d}\right)$$

Förster Radius for PS/p-terphenyl : 15 Å
 Calculated PS domain radius: 32 Å



- Optical/Electron Microscopy: Defect microstructure, elemental composition
- Differential Scanning Calorimetry (DSC): Phase transitions / glass transition temperature
- Small-Angle X-ray Scattering (SAXS): Orientation dependence of crazing / defects
- Gel Permeation Chromatography (GPC): Molecular weight distribution
- Infrared spectroscopy (IR): Presence of oxidized species (i.e. carbonyl, hydroxyl).
- UV-Vis and dynamic light scattering (DLS): Transparency and optical attenuation length
- X-ray photoelectron spectroscopy (XPS): Elemental composition and bonding environment.



Summary and Conclusions

- Plastic scintillators are complex materials due to multi-component compositions, inherent non-uniformity, and transient behavior
 - Physical aging
 - Stress dissipation
 - Thermal History
 - Internal and external diffusion, phase changes
 - Oxidation
 - Intrinsic polymer properties and polymer-solute interactions
- Potential degradation mechanisms are known, although the relative importance of each process is not fully understood in ‘field-aged’ materials
 - Routine characterization techniques are able to elucidate these factors
- Degradation mitigation methods exist for each of the discussed damage mechanisms

Acknowledgements:

- WMS/NA-22 (FY10-Present)
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