Polymer Aging of Plastic Scintillators

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7-1-2015
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?

Background and Context

• 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 ~4% per year

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)

Extruded Polystyrene Scintillator at Fermilab

Light-Yield versus Temperature

- 45°
- 65°
- 85°

(Ambient/uncontrolled humidity)

Crazing Defects versus Moisture/Temp

- 50°
- 40°
- 30°

(95% Humidity)

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

- Crazing Damage (light scattering)

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**

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
   • O$_3$, PAHs, NO$_x$

Can the specific degradation modes be identified and consequently addressed?
1. Origins of Polymer Crazing

Deformation w/out increase in volume: Shear

Deformation with volume increase: Crazing

**Considerations:**
- Density/free volume
- Entanglements
- Crystallinity
- Hydrostatic stress
- Impurities/defects

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- Crazing is due to plastic deformation in regions of localized hydrostatic stress, followed by cavitation (void formation)

- Crazing increases the local micro-hardness and elastic modulus of material but often precedes brittle failure (due to breakdown of crazing network)

- Local plasticization is operative in the presence of a crazing agent

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*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]).*
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 → bond breaking)
  2) Low strain rates and high temperatures (disentanglement)

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

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

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

• 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

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

\[ \nu \propto C_{\infty}^{1.4} \left( \frac{\rho}{m_0} \right)^{2.2} l_0^{3.6} \]
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>
<thead>
<tr>
<th>Plasticizer</th>
<th>% Plasticizer</th>
<th>$T_g$</th>
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<tbody>
<tr>
<td>Ethylbenzene</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>Paraffin Oil</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>75</td>
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<tr>
<td></td>
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<td></td>
<td>20</td>
<td>49</td>
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<tr>
<td></td>
<td>50</td>
<td>43</td>
</tr>
</tbody>
</table>

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

2. Diffusion in Polymers

- 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:

\[ J = -D \frac{d\sigma}{dx} \]

- 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:

- \( D_{PS} = 2.2 \cdot 10^{-8} \text{ cm}^2\text{sec}^{-1} \) \( (30^\circ \text{C}) \)
- \( D_{PVT} = 1.3 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \) \( (30^\circ \text{C}) \)

Oxygen Diffusion in PS and PVT

- \( D_{PS} = 3.1 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \) \( (25^\circ \text{C}) \)
- \( D_{PVT} = 6.8 \cdot 10^{-7} \text{ cm}^2\text{sec}^{-1} \) \( (25^\circ \text{C}) \)

Toluene Diffusion in PS

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

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

**Diffusion of CH$_2$Cl$_2$ 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**

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

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3. Oxidation (via diffusion)

- Light, ozone, and NO₂ oxidation of styrenyl polymers yield similar products
- Styrene hydroperoxide and radical intermediates may undergo side reactions
- Irreversible reactions: Degradation of scintillator components/properties

Common Oxidation Products

Ozone and Photochemical Oxidation

NO₂ Oxidation

Inhibiting Scintillator Oxidation: UV Stabilization Case Study

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

![Graph showing UV-stabilization effectiveness](image)

- 6000 W Xe Arc Lamp
- Change in yellowness index vs. time (h)
- Control vs. 0.25% 2-(2-hydroxy-5-methylphenyl)benzotriazole vs. 0.175% 2-(2-hydroxy-5-methylphenyl)benzotriazole + 0.075% 2,4,6-tri-tert-butylphenol

• 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

![Chemical structures](image)

- 2-(2-Hydroxy-5-methylphenyl)benzotriazole
- 2,4,6-tri-tert-butylphenol

Article

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

Magnus Von Piechowski¹², Marie-Anne Thelen¹, JuRG Hoigné² and Rolf E. Bühler¹

Article first published online: 8 MAY 2010

DOI: 10.1002/bbpc.19920961019

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Berichte der Bunsengesellschaft für physikalische Chemie


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

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
3) Cross-linking to increase entanglement density, molecular weight, glass transition temperature
4) Co-polymerization to increase uniformity of polymer and dissolved fluorophores

### Chemical Resistance

<table>
<thead>
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<th>Cross-Linked PS</th>
<th>Linear PS</th>
<th>Expanded PS</th>
</tr>
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<tbody>
<tr>
<td>Conc. Acids</td>
<td>Fair</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Dilute Acids</td>
<td>Good</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>Alcohols</td>
<td>Good</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>Alkalis</td>
<td>Fair</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>Aromatic Hydrocarbons</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Greases/Oils</td>
<td>Fair</td>
<td>Fair</td>
<td></td>
</tr>
<tr>
<td>Halogens</td>
<td>Poor</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Ketones</td>
<td>Poor</td>
<td>Poor</td>
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### Physical Properties

<table>
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<th></th>
<th>Cross-Linked PS</th>
<th>Linear PS</th>
<th>Expanded PS</th>
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<tr>
<td>Density (g/cm^3)</td>
<td>1.05</td>
<td>1.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.59</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>Resistance to UV</td>
<td>Good</td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td>Water Absorption (%)</td>
<td>0.02</td>
<td>0.3</td>
<td>3</td>
</tr>
<tr>
<td>Glass Transition Temperature (C)</td>
<td>130*</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

*(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

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

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

Applicable Characterization Methods

- **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.

![XPS](Image)

![DSC](Image)
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)
- DNDO-TAR (FY14-Present)