Compatibility Summary of Fueling Infrastructure Materials with Aggressive Ethanol Blended Test Fuels

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Supported by:
US Department of Energy Offices of the Biomass Program (OBP) & Vehicle Technology Program (VTP)

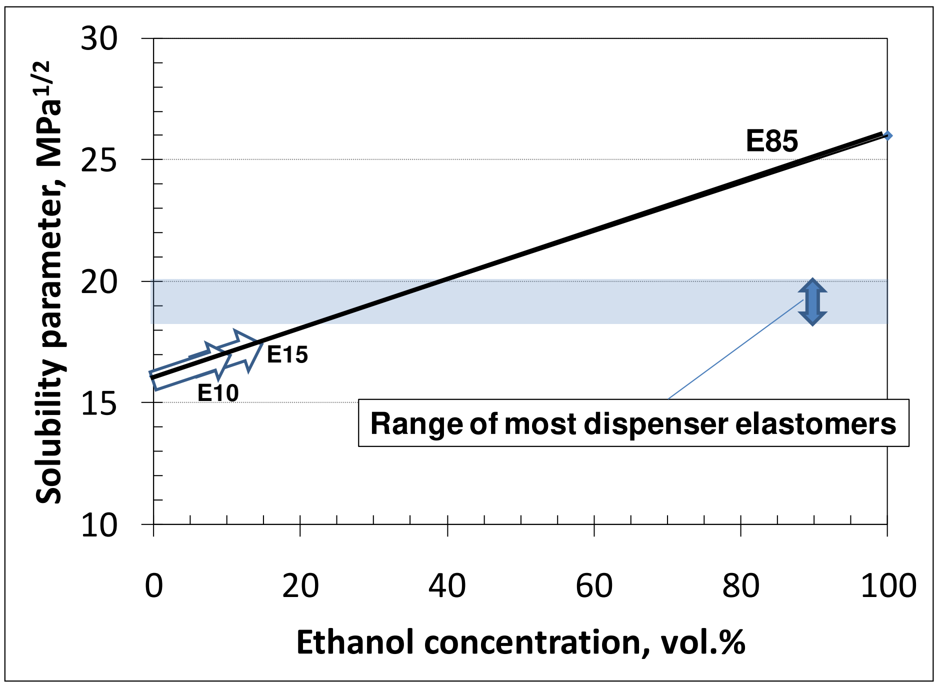
Presented to:
23rd National Tanks Conference
St. Louis, MO
March 20, 2012

Presentation Outline

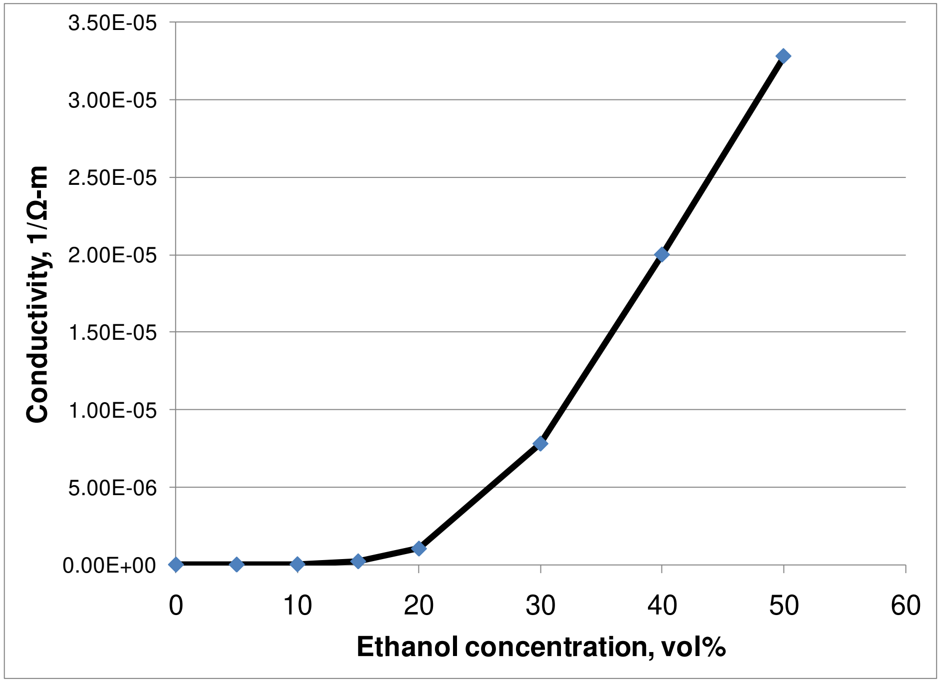
- Rationale &Test Protocol
- Plastic Results
- Elastomer Results
- Metal Results
- Future Activities

Rationale: How is compatibility affected by ethanol concentration (E0 to E10 to E15 and higher ethanol blends…)?

Analysis of solubility parameters suggests that gasoline blended with lower ethanol concentrations are less compatible with polymeric materials



The electrical conductivity (and therefore corrosion potential) of ethanol-blended gasoline increases with ethanol concentration for metallic materials



Compatibility was primarily assessed by evaluating volume change and degree of softening or hardening following exposure to the test fuel

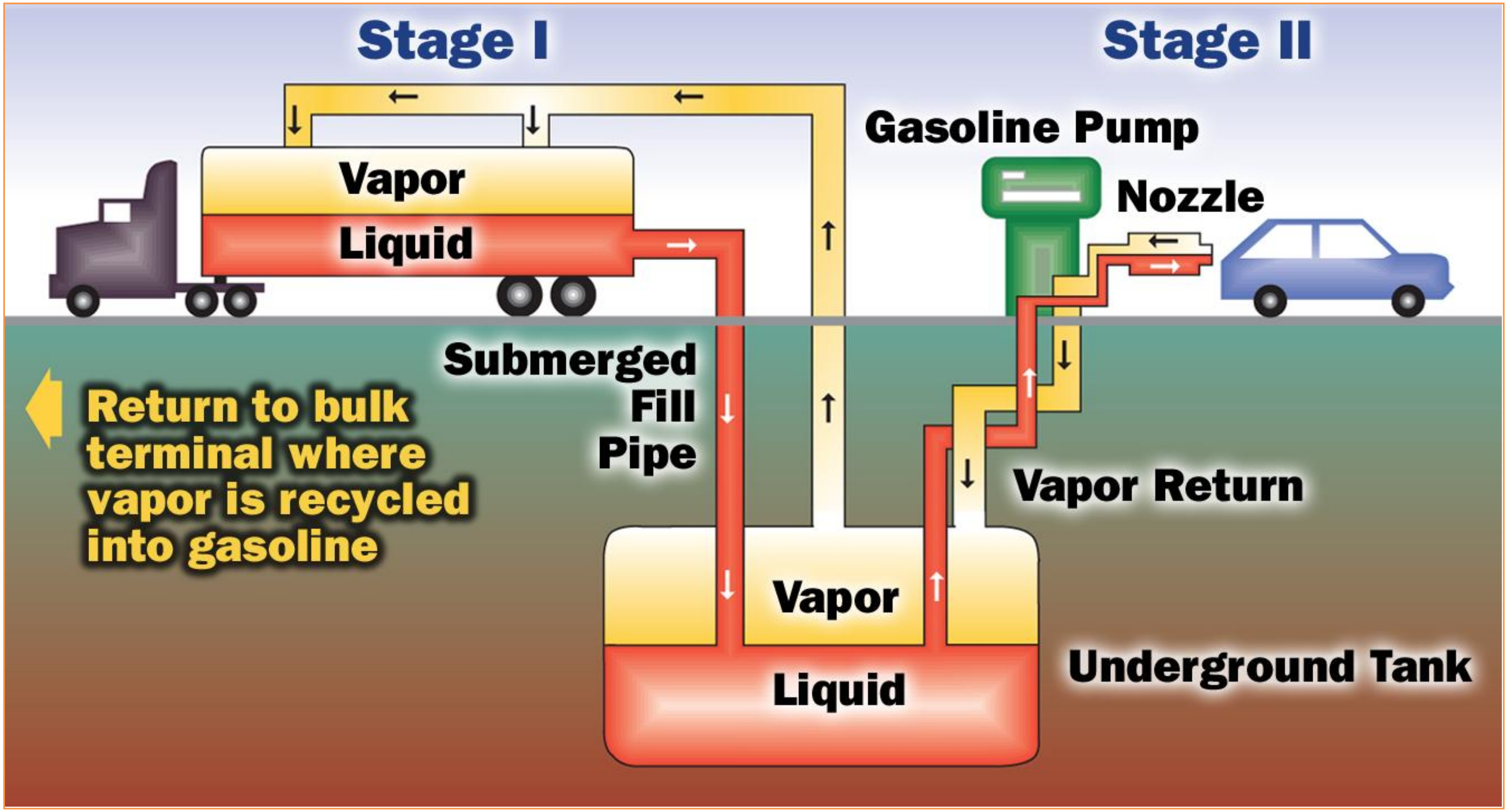
In the wetted or saturated state

- **Volume swell (of saturated polymers) is important since it is a physical means of assessing solubility of the polymer with fuel chemistry**
  - **Solubility relates to the potential of the test fluid to permeate and dissolve one or more polymer components**
  - **Expansion produces stress in rigid polymers**
  - **Volume swell is used to rank compatibility among o-rings and seals**
- **Softening (loss of hardness) typically corresponds with volume swell and is a measure of the deformation potential**

In the dried state

- **Volume loss (shrinkage) indicates:**
  - **The extraction of one of more polymer components by the fluid**
  - **Less material available to seal interfaces**
- **Softening indicates fluid retention or degradation, while increased hardness (embrittlement) indicates plasticizer removal**

Materials were chosen as representative of those used in fueling storage and dispensing equipment



The complete list of plastic materials includes those used in flexible piping and in rigid piping/UST systems

<table>
<tr><th>Thermoplastics</th><th>Thermosets</th></tr>
<tr><td><u>High Performance Polymers</u>
1. Fluoropolymers: (PTFE & PVDF)
2. Polyphenylene sulfide (PPS)</td><td rowspan="2"><u>Poly and Vinyl Ester Resins</u>
1. Isophthalic polyester resin (1:1 ratio) pre-1990 resin
2. Isophthalic polyester resin (2:1 ratio) post-1990 resin
3. Terephthalic polyester resin (2:1 ratio) post-1990 resin
4. Novolac vinyl ester resin (advanced)</td></tr>
<tr><td><u>Mid-Range Polymers</u>
1. Polyesters: (PET, PETG, PBT)
2. Acetals: (POM & Acetron GP copolymer)
3. Nylons: (nylon 6, nylon 6/6, nylon 12, & nylon 11)
(note: nylon 11 is made from vegetable oil)</td></tr>
<tr><td><u>Commodity Polymers</u>
1. Polyethylene: (HDPE & F-HDPE)
2. Polypropylene (PP)</td><td><u>Epoxies</u>
1. Room temperature cured
2. Heat cured</td></tr>
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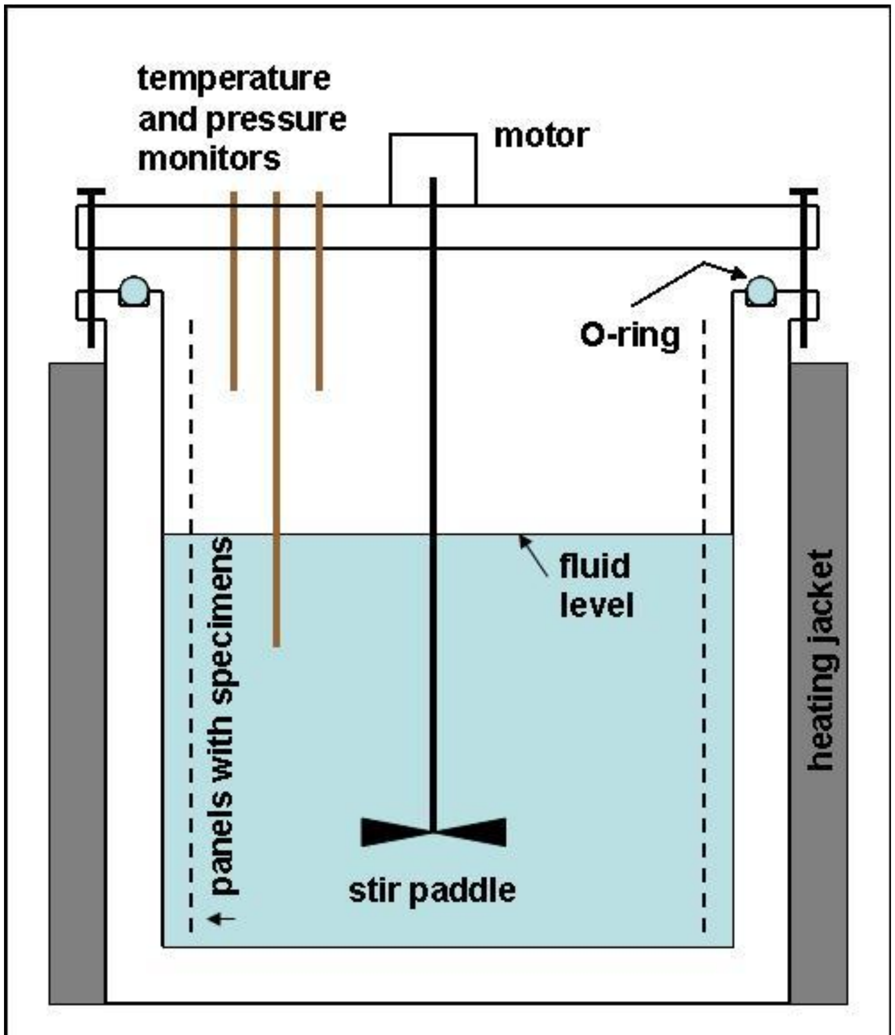
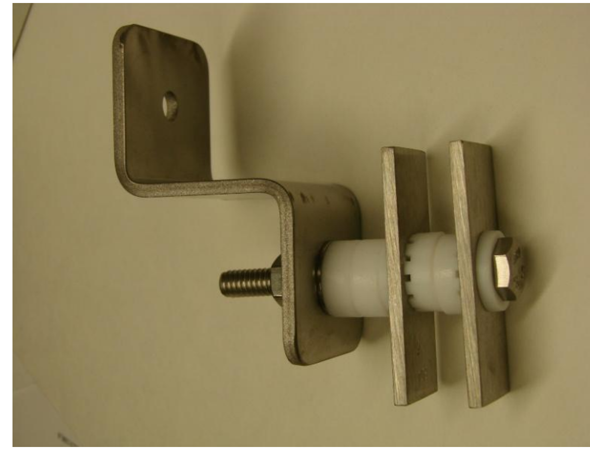
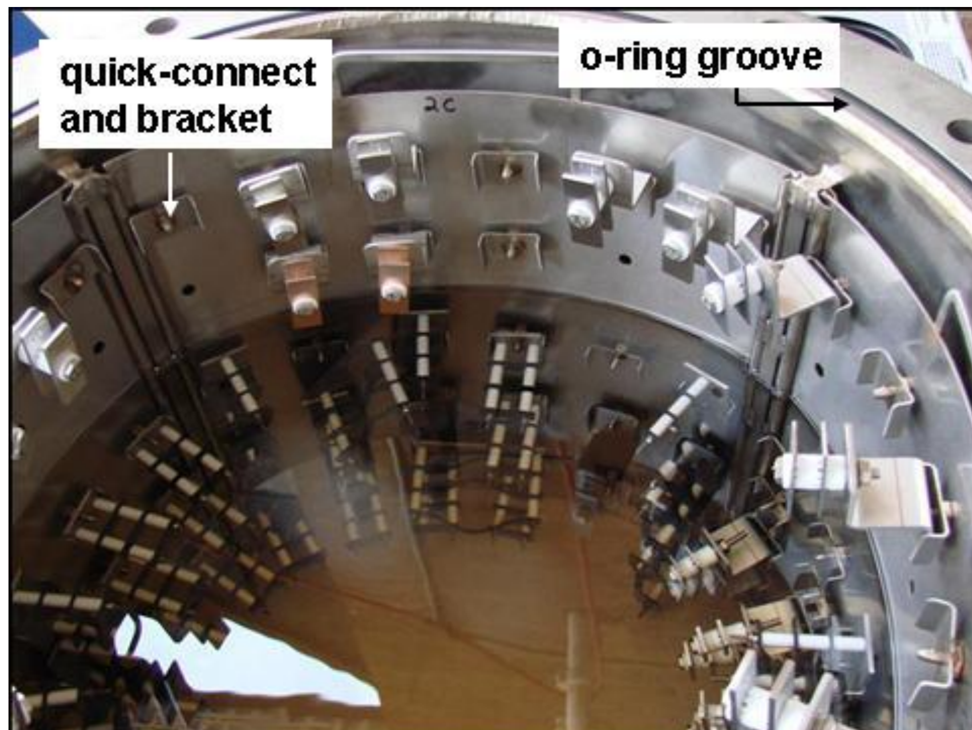
Test specimens were exposed to the test fluid in a large stainless steel tank with stainless steel hardware





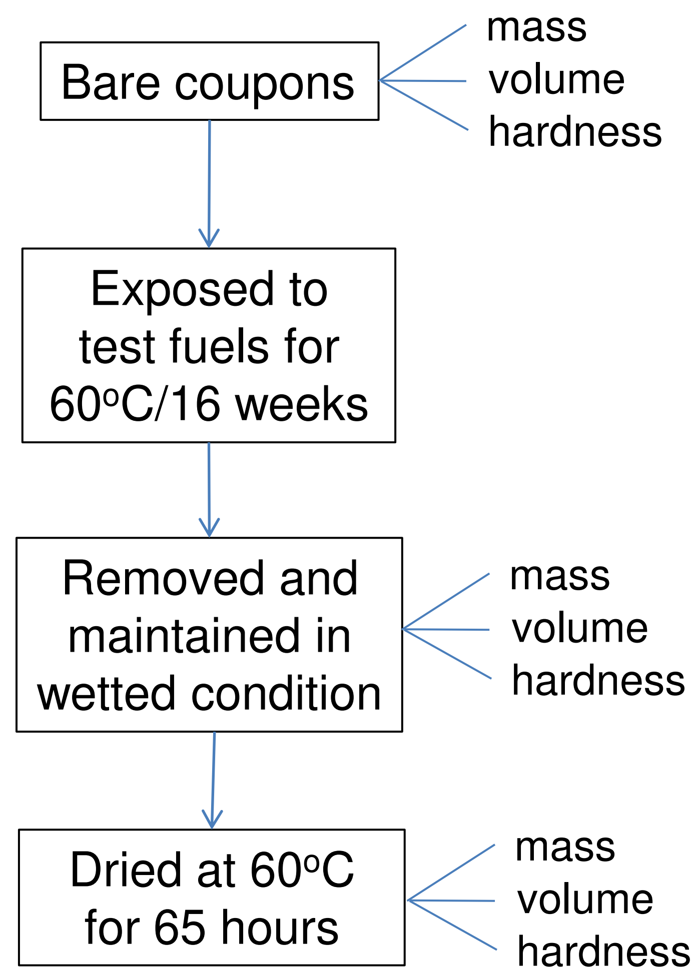


Test fuels were formulated according to SAE J1681 and ASTM D471 specifically developed for materials compatibility studies

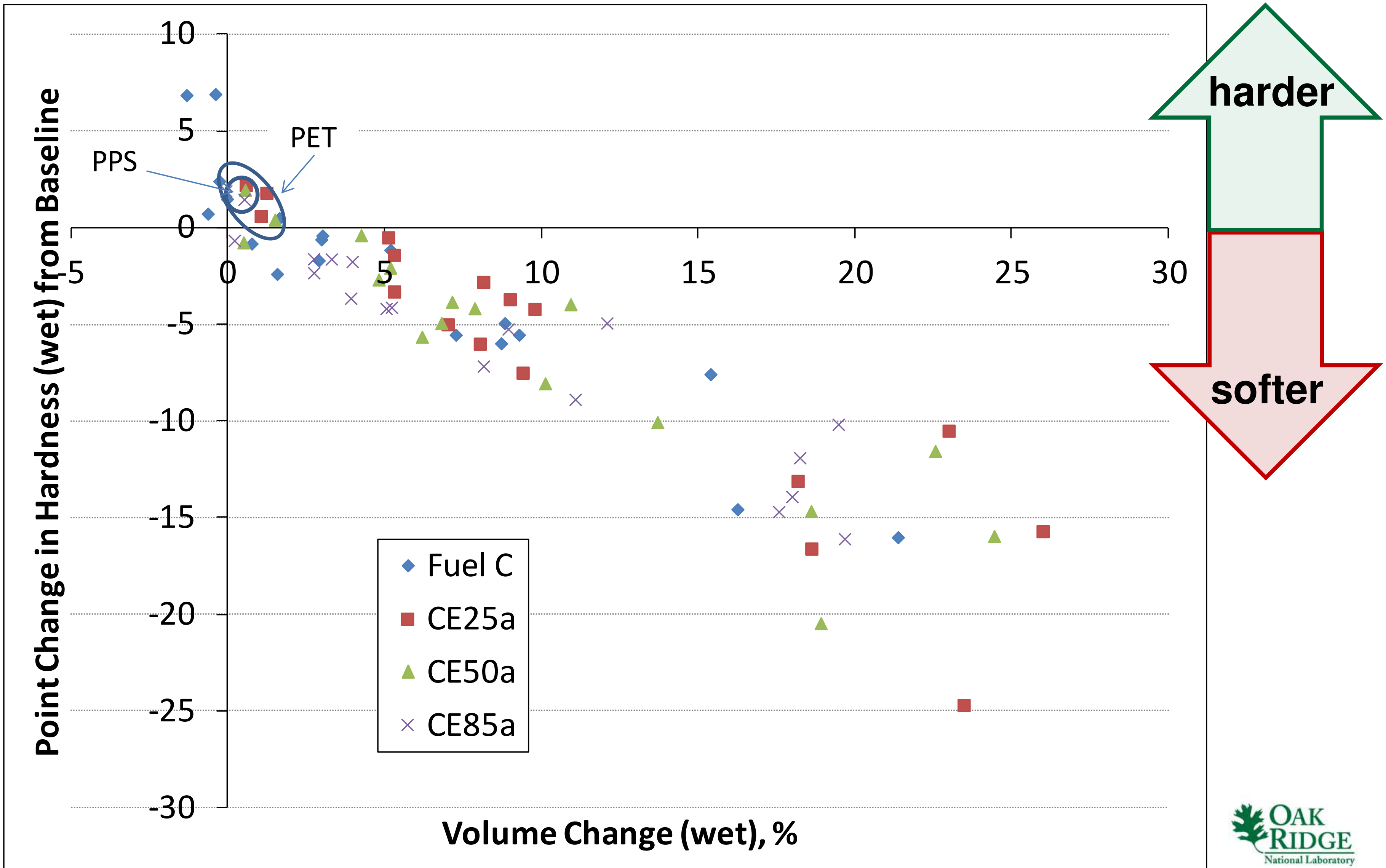
- Ref Fuel C (50% toluene, 50% isooctane) is a controlled and repeatable gasoline surrogate
- CE25a, CE50a & CE85a (correspond to 25, 50, and 85 % aggressive ethanol-Fuel C blend)
- Ethanol contains 0.9% aggressive water-acid solution

Aggressive solution component	Grams per liter of ethanol
Deionized water	8.103
Sodium chloride	0.004
Sulfuric acid	0.021
Glacial acetic acid	0.061

- Aggressive elements represent worst-case contaminant levels found in actual use
- The elevated test temperature (60°C) rapidly ages the specimens to assess relative compatibility in a reasonable timeframe



In general, the volume swell was accompanied by a corresponding drop in hardness (increase in softening). Residual fuel in the polymer is likely responsible for this effect



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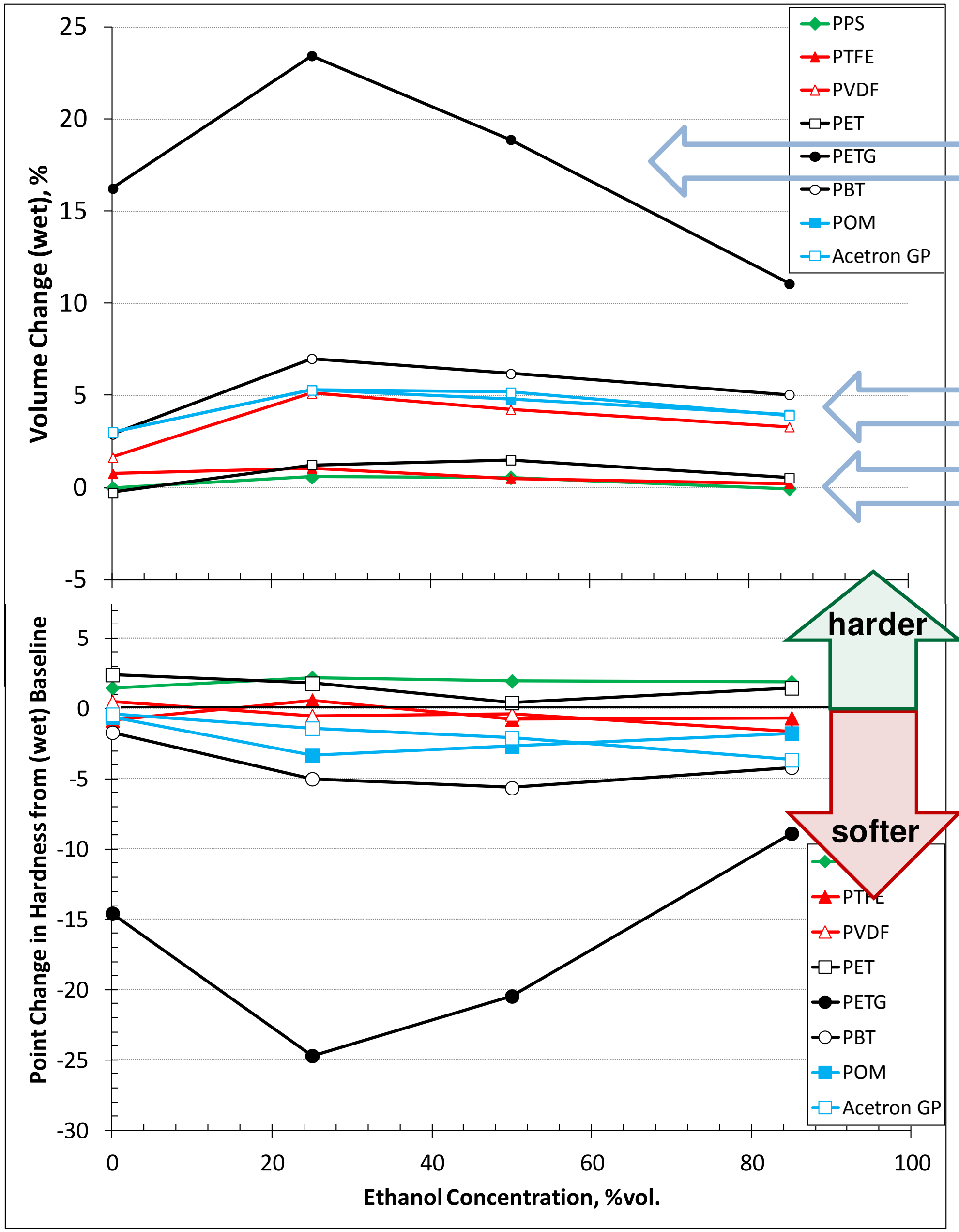
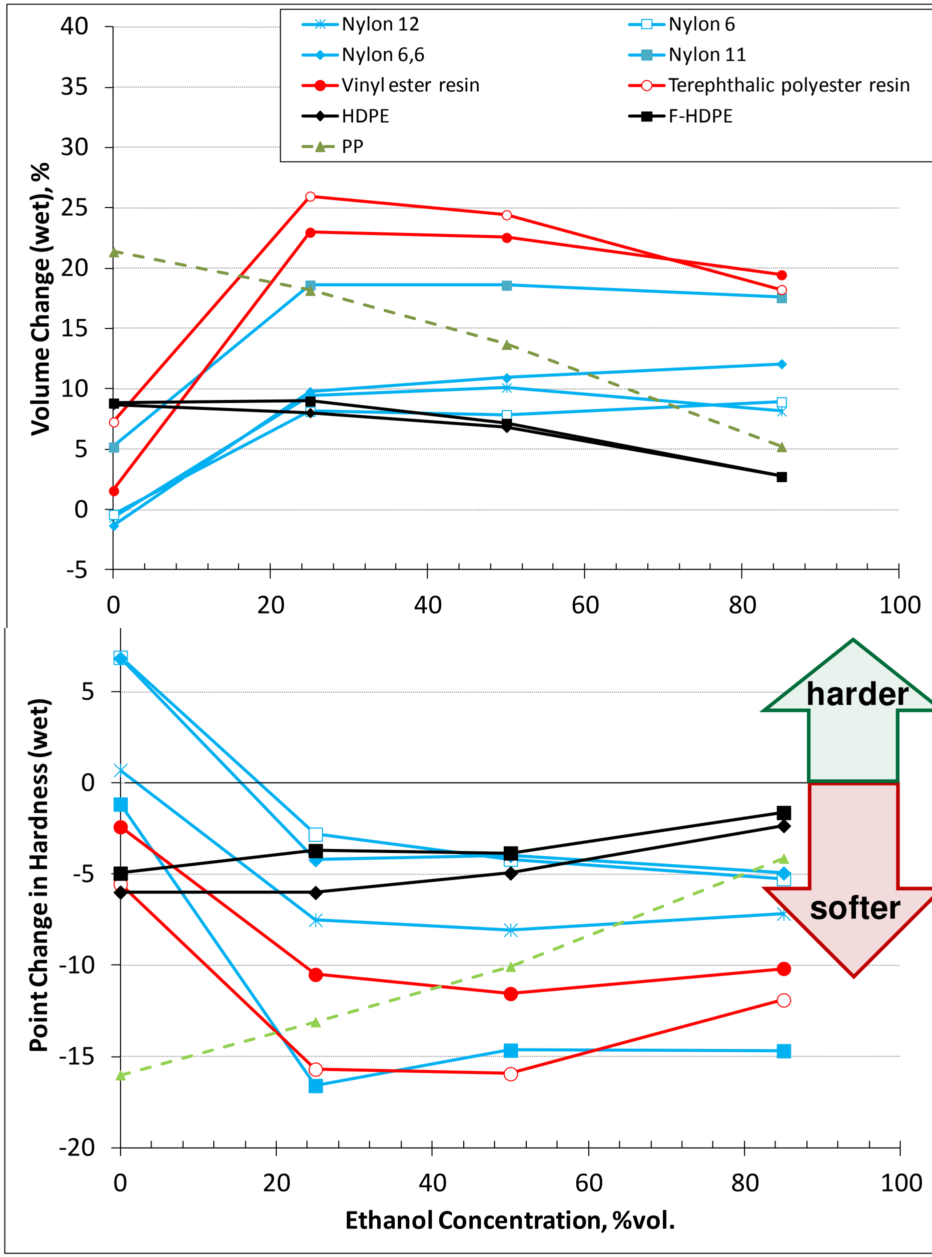
In general, the high performance and mid-range polymers (excluding nylons) exhibited highest swelling with 25% aggressive ethanol



- High swell: PETG
- Modest swell: PVDF, POM, PBT
- Negligible swell: PPS, PET, PTFE
- Slight change in hardness was observed, except for PETG

The nylons and thermoset resins also exhibited peak swell at 25% ethanol. However for PP and HDPE peak swell occurred at Fuel C (CE0).



- **The swelling behavior for PP, and HDPEs achieved max. swell for Fuel C and decreased with increasing ethanol concentration**
- **Petroleum-based nylons exhibited moderate swell with exposure to ethanol. Bio-based nylon 11 exhibited higher swell.**
- **Polyester thermoset resins exhibited high swelling with exposure to ethanol**

- **The level of softening corresponded with the observed swell**

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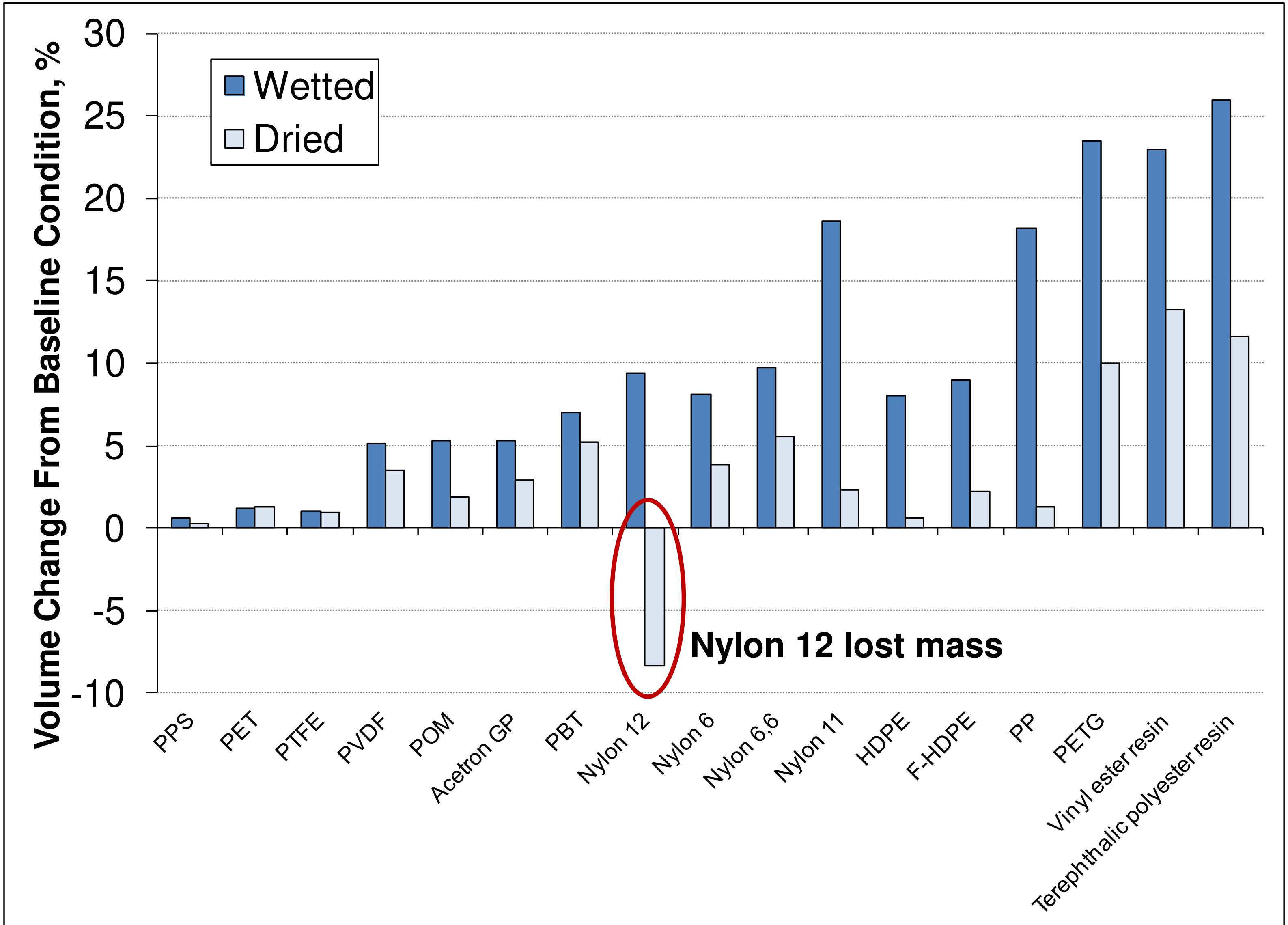
After drying at 60°C/65 hours, some level of fuel was retained within the plastics

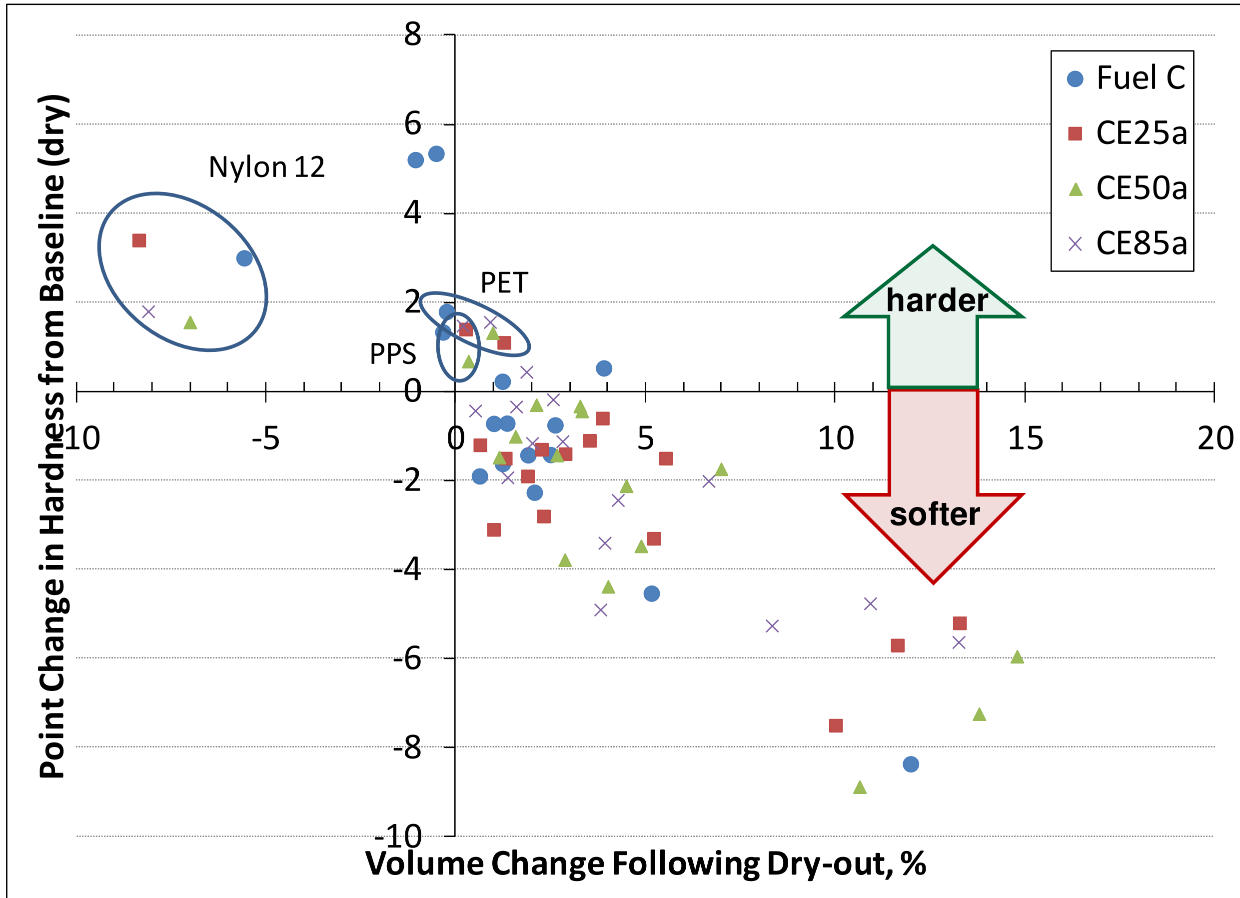


In general the hardness (following dry-out) decreased with increasing dry-out volume (or mass)

- **The increase in mass and volume following dry-out indicates that residual fuel is present in the plastic structure. The one exception is nylon 12 which lost mass with exposure to Fuel C and ethanol.**

- **In general the change in hardness was minimal and corresponded with the degree of swell**

- **Materials which experienced the highest level of softening were PETG and the thermoset polyester resins**



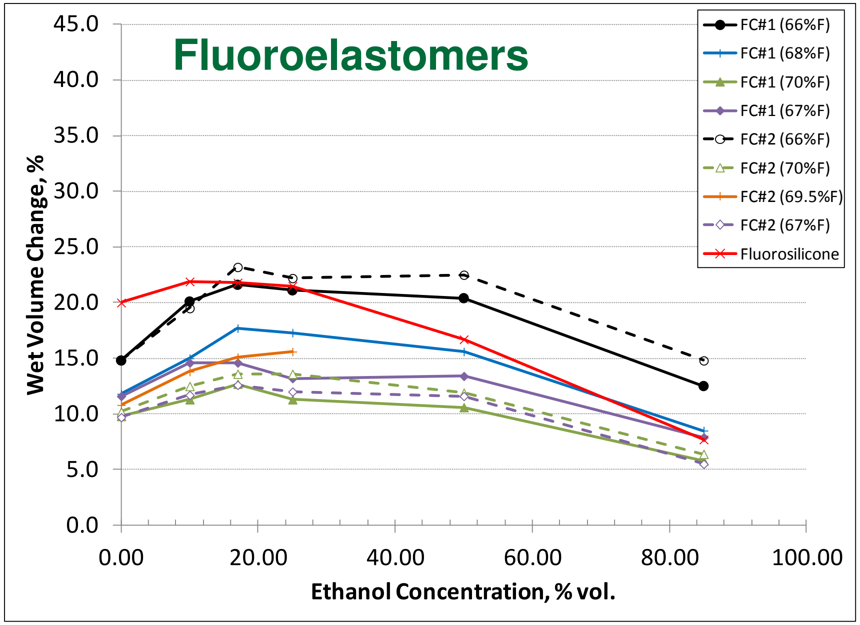
Observations for Plastic Materials

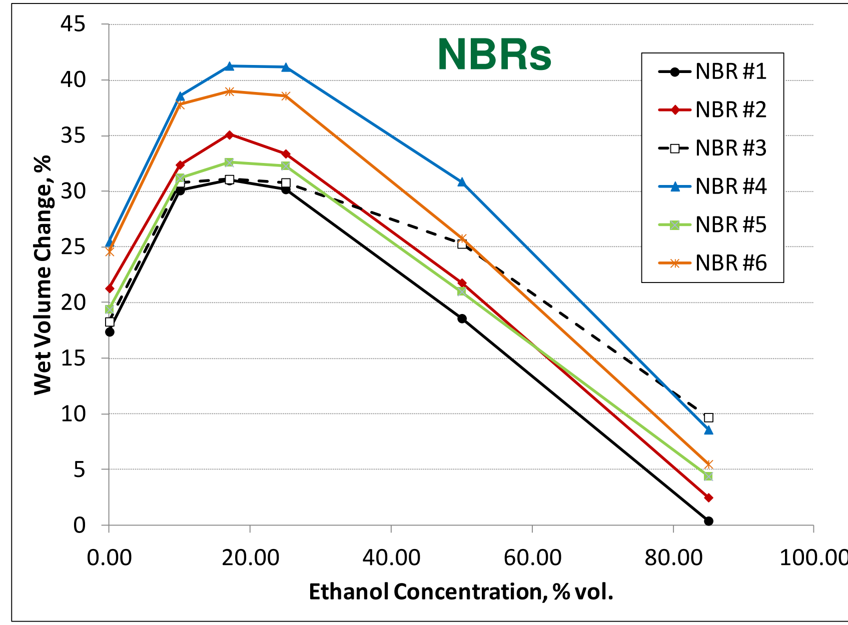
- Negligible property change observed for PPS, PET, PTFE
- Peak swell occurred at CE25a for PVDF, POM, PBT, PETG, nylons and thermoset resins.
- Moderate property change observed for PVDF, PBT, Acetals, HDPEs, nylon 6 and nylon 6,6 was raised slightly.
- Highest property changes observed for nylon 11, nylon 12, PETG, PP, and vinyl and polyester resins
- Volume and softening of PVDF, acetals, nylons, PBT, PETG, and thermoset resins were increased to varying degrees with exposure to ethanol
- PP and HDPE properties improved with ethanol concentration
- In this study, nylon 12 was the only plastic material observed to lose mass & volume with exposure to ethanol

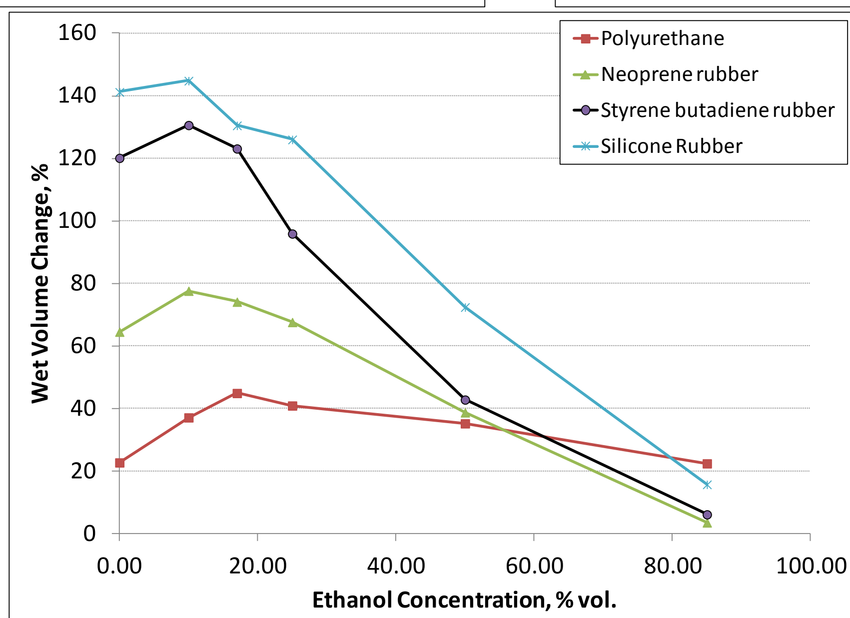
The elastomer study looked at seven material types which were representative of those used in o-rings, seals/gaskets, and hoses

Chemical Name	ASTM D1418 Abbreviation
M-Group (saturated carbon molecules in the main macro-molecule group)	
Fluorocarbon Rubber	FKM
R-Group (unsaturated hydrogen carbon chain)	
Neoprene Rubber	CR
Nitrile Butadiene Rubber	NBR
Styrene Butadiene Rubber	SBR
Q-Group (silicone in the main chain)	
Silicone Rubber	PVMQ
Fluorosilicone Rubber	FVMQ
U-Group (carbon, oxygen and nitrogen in the main chain)	AU
Polyurethane	

For elastomers peak swell occurred at 17% aggressive ethanol. Higher ethanol concentrations (50 and 85%) lowered the wet volume (accompanied by a corresponding decrease in hardness)



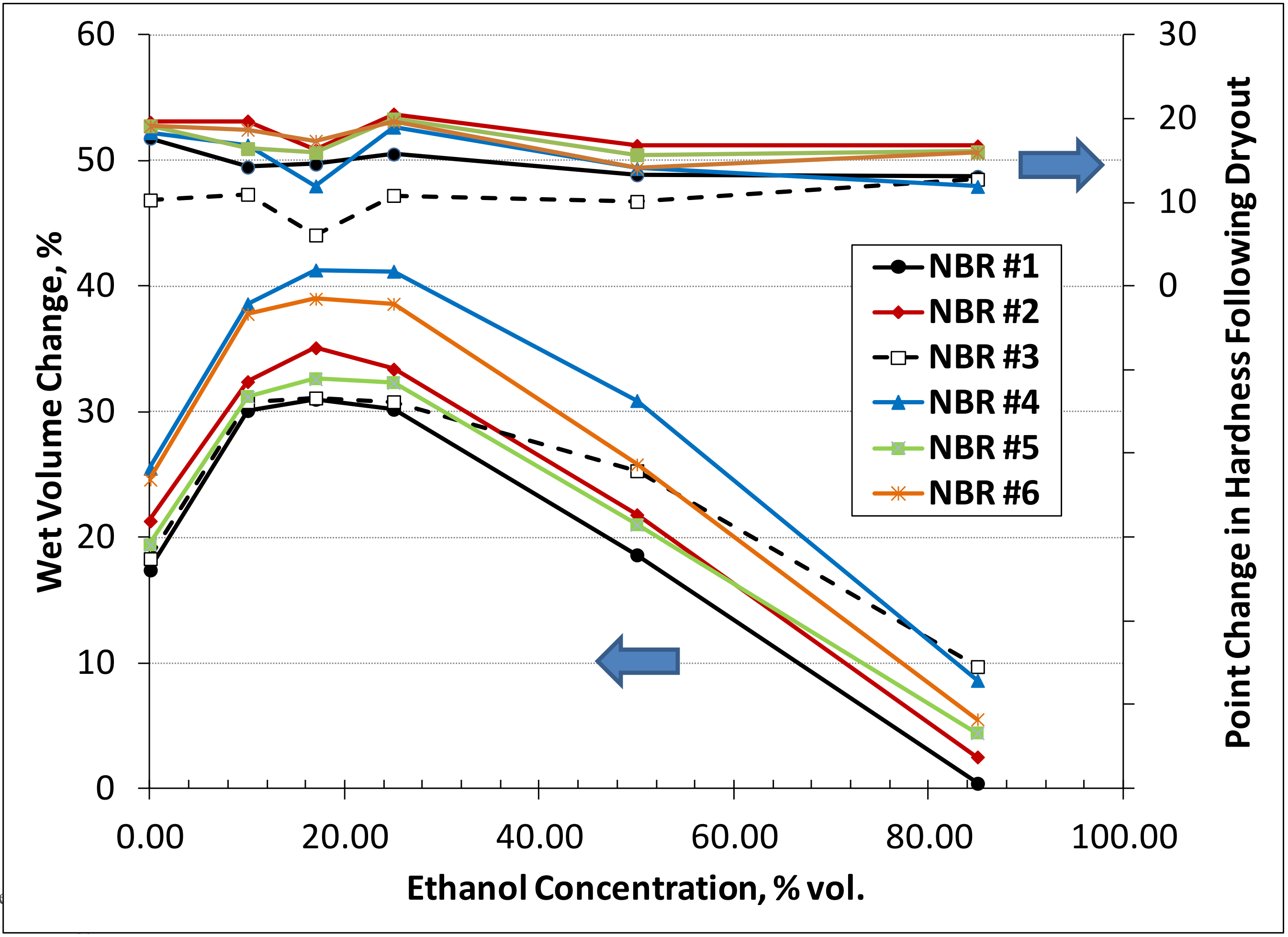




Polyurethane
Neoprene
SBR
Silicone

However, plasticizer extraction was observed in some elastomer types even though the volume swell at 85% ethanol was low

For example: The NBRs showed low to negligible volume change with exposure to 85% ethanol. However, plasticizers were still removed resulting in embrittlement and shrinkage.

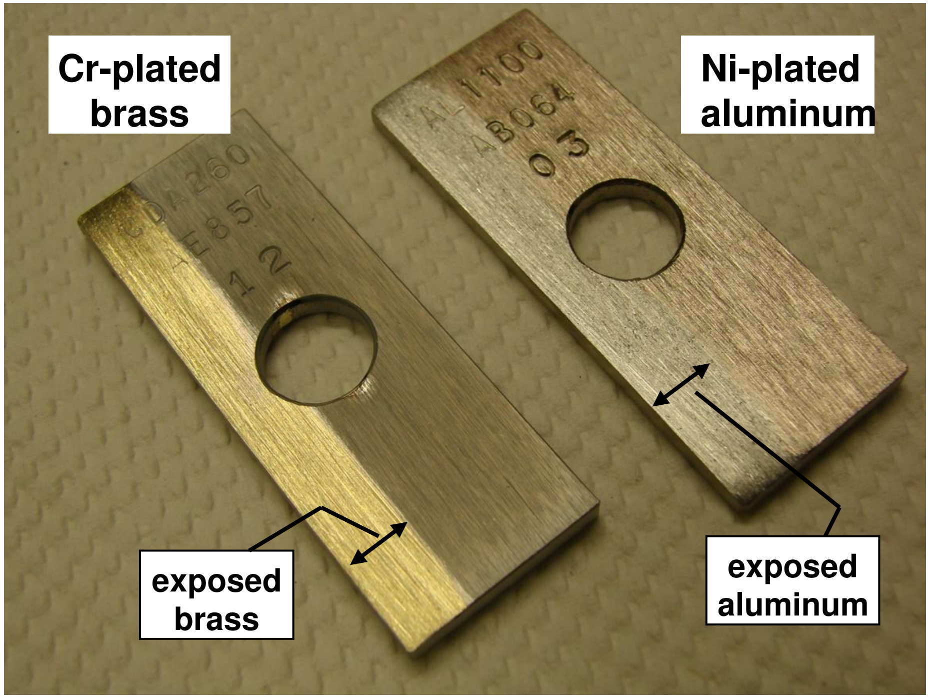


Elastomer summary:

- **For the majority of the elastomers peak swell occurred at CE25a**
- **Many of the elastomers were highly sensitive to ethanol concentration and exhibited very low volume change with exposure to CE85a. In most cases the volume change was lower for CE85a than for Fuel C.**
- **However, hardness results indicate that extraction and/or structural changes had taken place with exposure to CE85a, even though the volume was unchanged from the baseline condition.**
- **Bottom Line: Volume swell alone may not be sufficient to determine compatibility!**

The metal coupon study included galvanically-coupled specimens to better reflect field conditions

- **Single Material Coupons**
  - » 304 stainless steel
  - » 1020 carbon steel
  - » 1100 aluminum
  - » Cartridge brass
  - » Phosphor bronze
  - » Nickel 201
- **Plated Coupons (exposed fully plated and with plating partially removed to generate galvanic couple**
  - » Terne-plated (Pb) steel
  - » Galvanized (Zn) steel
  - » Cr-plated brass
  - » Cr-plated steel
  - » Ni-plated aluminum
  - » Ni-plated steel



* new for this series

Metal Results Summary

- **The corrosion rates based on uniform weight loss were minor for all materials**
- **Exposure of the substrate steel accelerated corrosion due to a combination of galvanic coupling of dissimilar metals and the increased conductivity of the environment (CE50a, CE85a) compared to previously examined test fluids (reference fuel C, CE10a-CE25a**

Future Plans

- Issue report detailing plastic results and elastomers and metals (CE50a and CE85a)
- Evaluate compatibility to other biofuels

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