Compatibility of Fueling Infrastructure Materials in Ethanol Blended Fuels

Presented by **Mike Kass**
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Several reports have been issued on related research:

- **Intermediate Ethanol Blends Infrastructure Materials Compatibility Study, M. Kass et al., ORNL TM-2010/326, March 2010.**
- **S. J. Pawel, M. D. Kass, and C. J. Janke, *Preliminary Compatibility Assessment of Metallic Dispenser Materials for Service in Ethanol Fuel Blends*, ORNL/TM-2009/286.**
- **Elastomer Compatibility to a Gasoline Standard Containing Intermediate Levels of Ethanol, *Michael D. Kass et al., 21st International Fluid Sealing Conference, 2010.***
- **Ken Boyce and Tom Chapin, Dispensing Equipment Testing with Mid-Level Ethanol/Gasoline Test Fluid, Document No. 10807, NREL/SR-7A20-49187. November 2010.**
- **Analysis of Underground Storage Tank System Materials to Increased Leak Potential Associated with E15 Fuel, EPA report (pending)**
- **Compatibility Assessment of Metallic Dispenser Materials for Service in Ethanol Fuel Blends up to E85, ORNL Technical Memorandum (pending)**

Presentation Outline

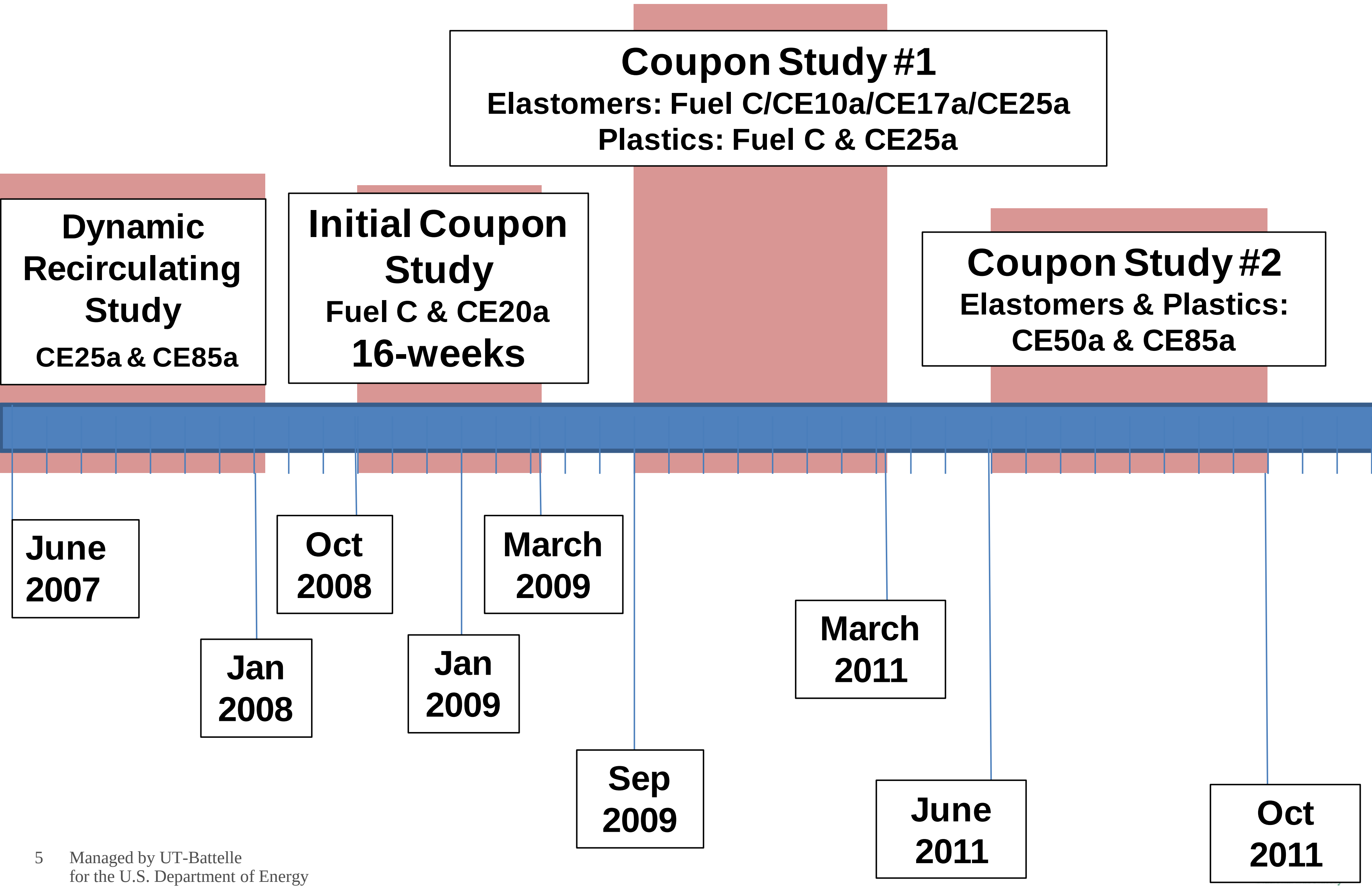
- **Motivation & Study Scope**
- **Background**
  - » Material Inventory & Selection
  - » Solubility Theory
- **Test Protocol**
- **Metal Results**
- **Plastic Results**
- **Briefing on CE50a and CE85a Elastomer Results**
- **Summary & Future Activities**

- » **Wet Properties**
  - **Volume Change**
  - **Point Change in Hardness**
- » **Dry-out Properties**
  - **Volume Change following Dry-out**
  - **Point Change in Hardness following Dry-out**
- » **For convenience of discussion, the fluoroplastics, polyesters, PPS and acetals are plotted separately from HDPEs, resins and nylons**

Study Rationale

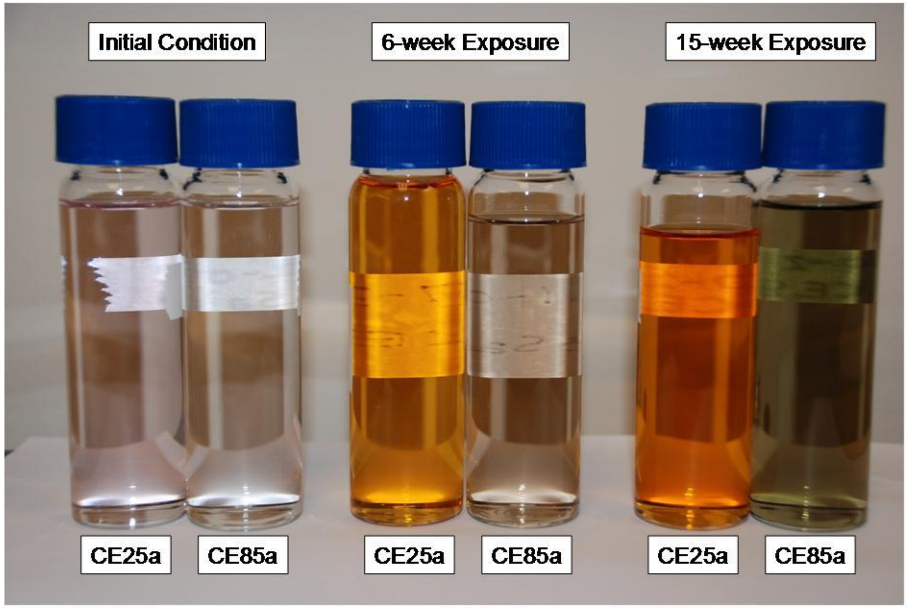
- **Underwriters Laboratories was concerned about component/material performance for fuel dispensing infrastructure exposed to intermediate and higher ethanol levels**
  - » **Fuel dispensers are listed by UL**
  - » **UL was concerned that existing UL standards wouldn't effectively cover E15 and higher ethanol levels**
- **DOE initiated an E15 compatibility study**
  - » **NREL/UL-led study: tested full scale dispensers using CE17a test fuel ("a" denotes SAE 1681 aggressive ethanol formulation)**
  - » **ORNL-led study: individual materials compatibility study on dispenser infrastructure materials to Fuel C, CE10a, CE17a, CE25a, CE50a and CE85a**

Timeline of ORNL-led Materials Compatibility Efforts



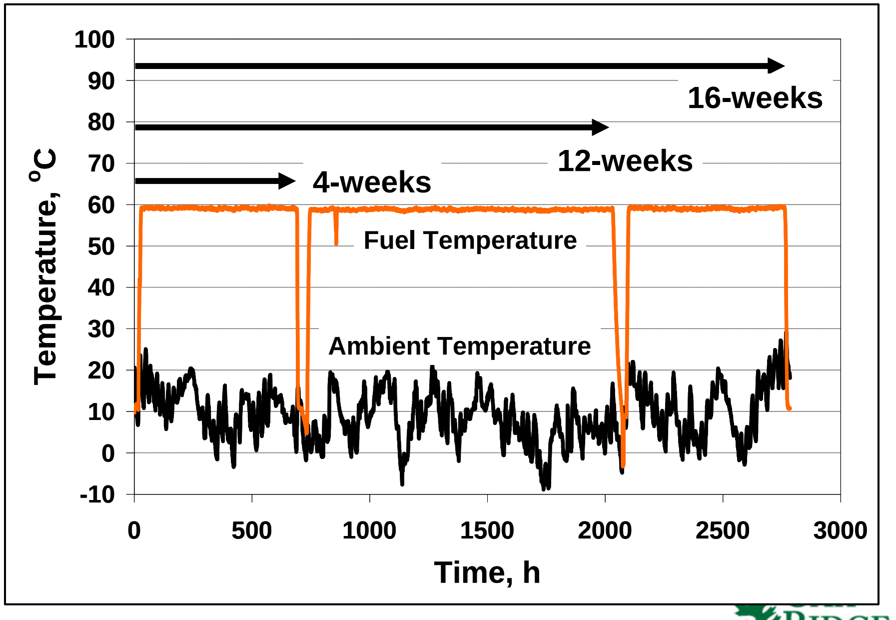
Dynamic Recirculating Study

- Original Purpose:
  - » Perform dynamic-based assessment of CE85a compatibility to fuel dispenser hanging hardware. Also included CE25a evaluation
  - » Collaborate static results performed by Underwriters Laboratories
- Effort was funded by the DOE VTP Office of Clean Cities
- Two identical dispenser trees provided by UL (including air driven pumps)
- Simultaneous dynamic testing with CE25a and CE85a for 25 weeks at ambient conditions
- Analyzed fuel for organics and inorganics
- Results:
  - » Color change noted in test fluids
  - » Analysis of CE25a test fluid showed higher levels of dissolved hydrocarbons than the CE85a fuel – CE25a more damaging to elastomers
  - » High levels of phthalates were measured



Stir Chamber Validation Study Including Metal and Elastomer Coupon Exposures to Fuel C and CE20a

- **Purpose: Confirm utility of unique dynamic apparatus to expose large numbers of coupons simultaneously to a specific test fluid under conditions of controlled temperature, pressure and flow.**
- **Eight metals/alloys, and eight fluorocarbons & 1 NBR were exposed to the Fuel C and CE20a fluid and vapor phases at 60°C and 0.8m/s flow. Tanks were operated for 16 weeks total and specimens were removed at 4, 12, and 16 week intervals**
- **Measured Tensile strength, elongation, hardness and volume swell for up to 16 weeks of exposure.**
- **Results:**
  - » Negligible corrosion of metal specimens
  - » Increase swelling and reduced tensile properties for elastomers exposed to CE20a
  - » 4-week results matched the 16-week exposures
  - » Changes in fluid chemistry from the 1st to last month were not significant.



Upon successful demonstration of stir chamber technique to screen large numbers of metal & polymer coupons, we expanded the number and type of materials for evaluation

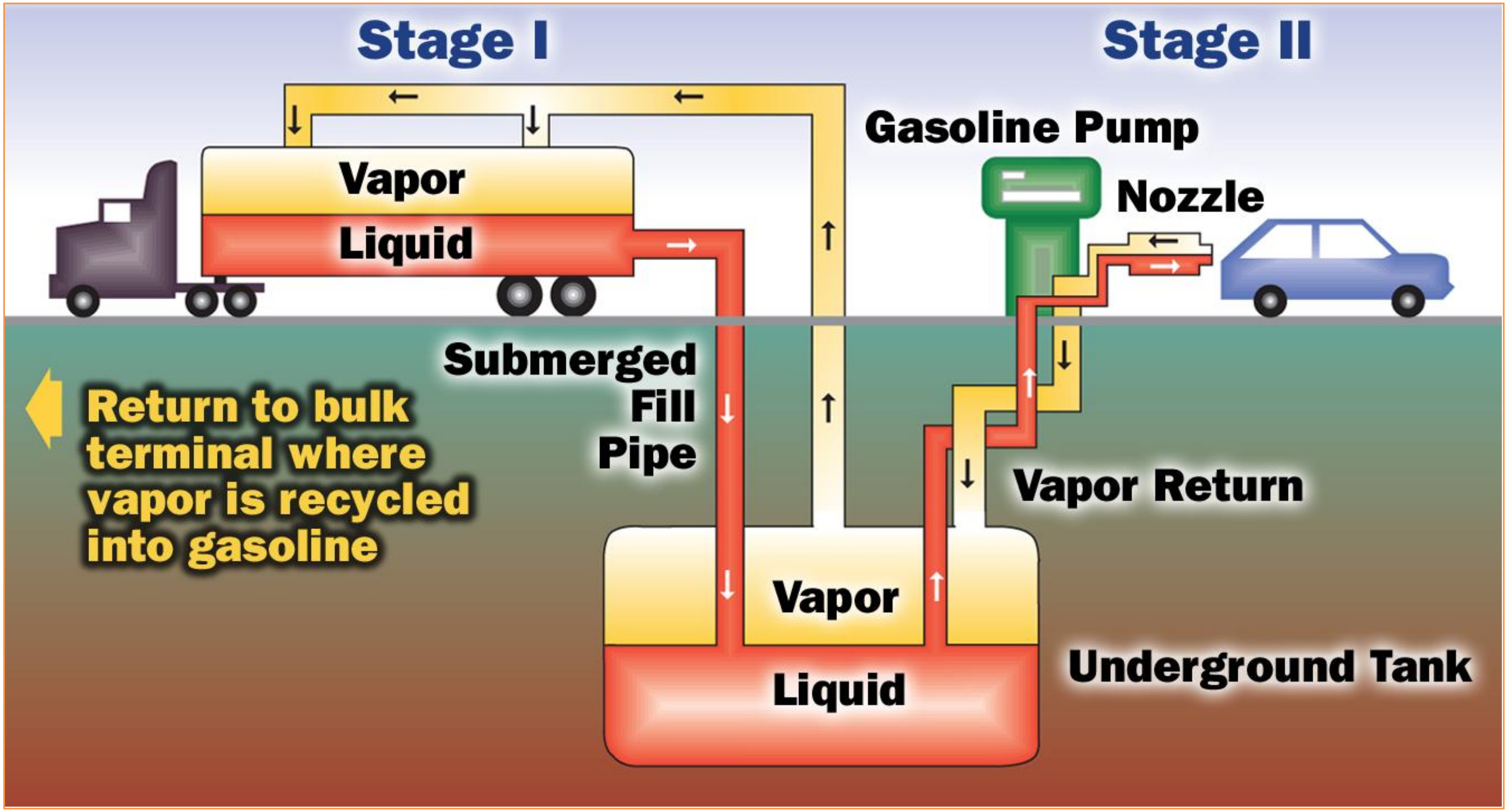
Key features of this study are:

- **Metal specimens**
  - » Included galvanically-coupled specimens to better reflect actual conditions
  - » Based on consistency from previous study we went with 2 specimens/metal type
- **Polymers included plastic and elastomer specimens**
  - » Extensive survey to include materials as representative as possible. Input provided by:
    - Dispenser manufacturers and components (OPW, Xerxes, and Dresser Wayne correspondence and websites)
    - Input from UL
    - Input from API meetings
    - Literature search
  - » 3 specimens/elastomer type
- **Sealants: two types; three scenarios, 3 specimens per scenario**
- **Metals, Elastomers & Sealants: 4-week exposures to Fuel C, CE10a, CE17a and CE25a**
- **Plastics: 16-week exposure to Fuel C and CE25a**

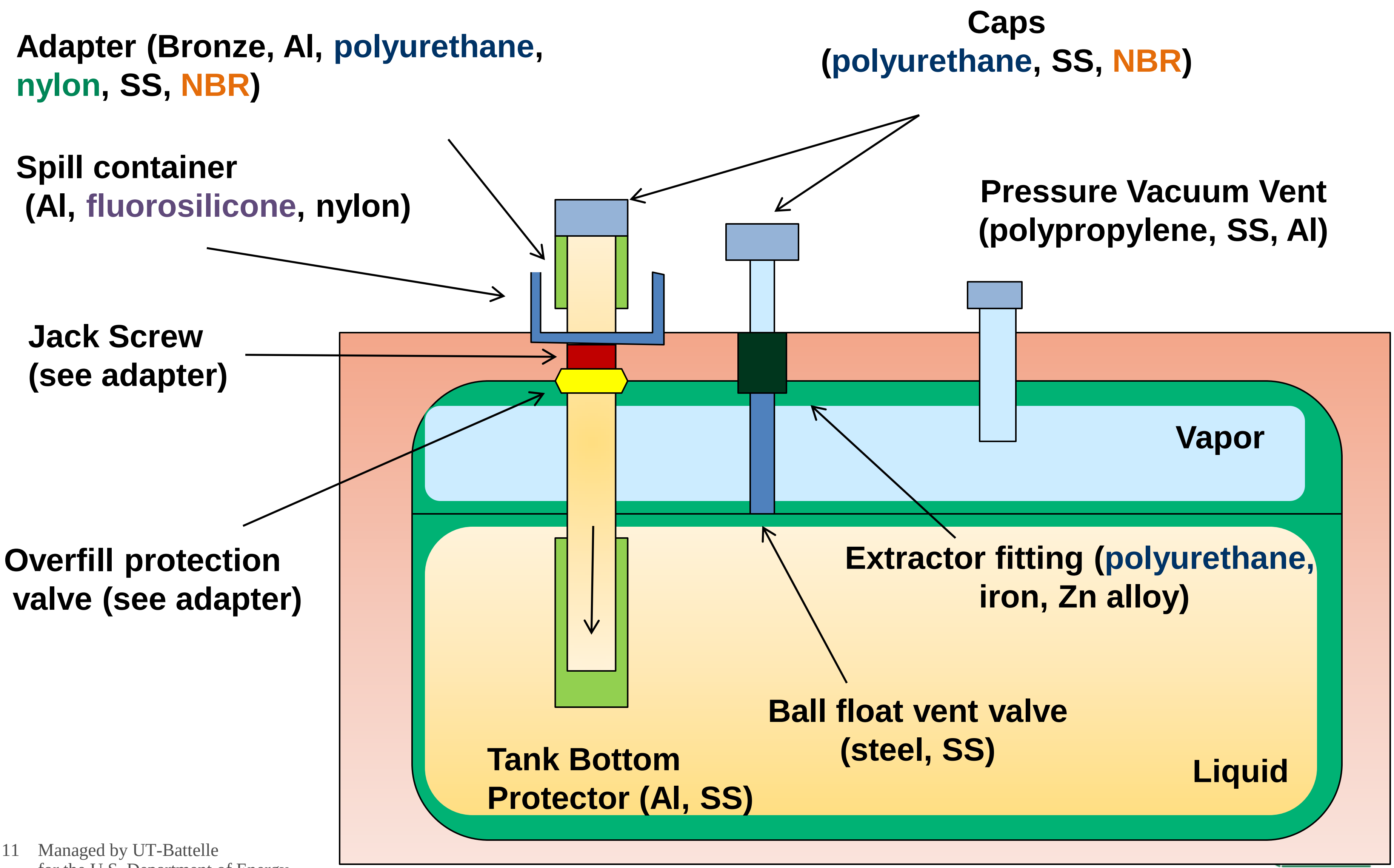
Snapshot of key property changes from baseline condition for plastic materials

Material Type	Ethanol level producing max. swell	Volume increase, %	Max. Wet Hardness Change, points	Dried Volume Change, %
PPS	25	0.6	+ 2	0.3
PET	25	1.2	+ 2	1
PTFE	25	1.0	+ 0.6	1
PVDF	25	5.1	- 0.5	3
Acetals	25	5.3/5.3	- 3/-1	2/3
PBT	25	7.0	-5	5
Nylon 12	25 – 85	10.1	-8	-8
Nylon 6	25 – 85	8.2	-4	4
Nylon 6/6	25 – 85	12.1	-5	5
Nylon 11	25 – 85	18.6	-15	2
HDPE	0 – 25	8	- 6	1
F-HDPE	0 – 25	9	- 4	2
PP	0	21	-16	1
PETG	25	23	-25	10
Vinyl ester resin	25 – 85	23	-12	13
Terephthalic polyester resin	25 – 85	26	-16	12

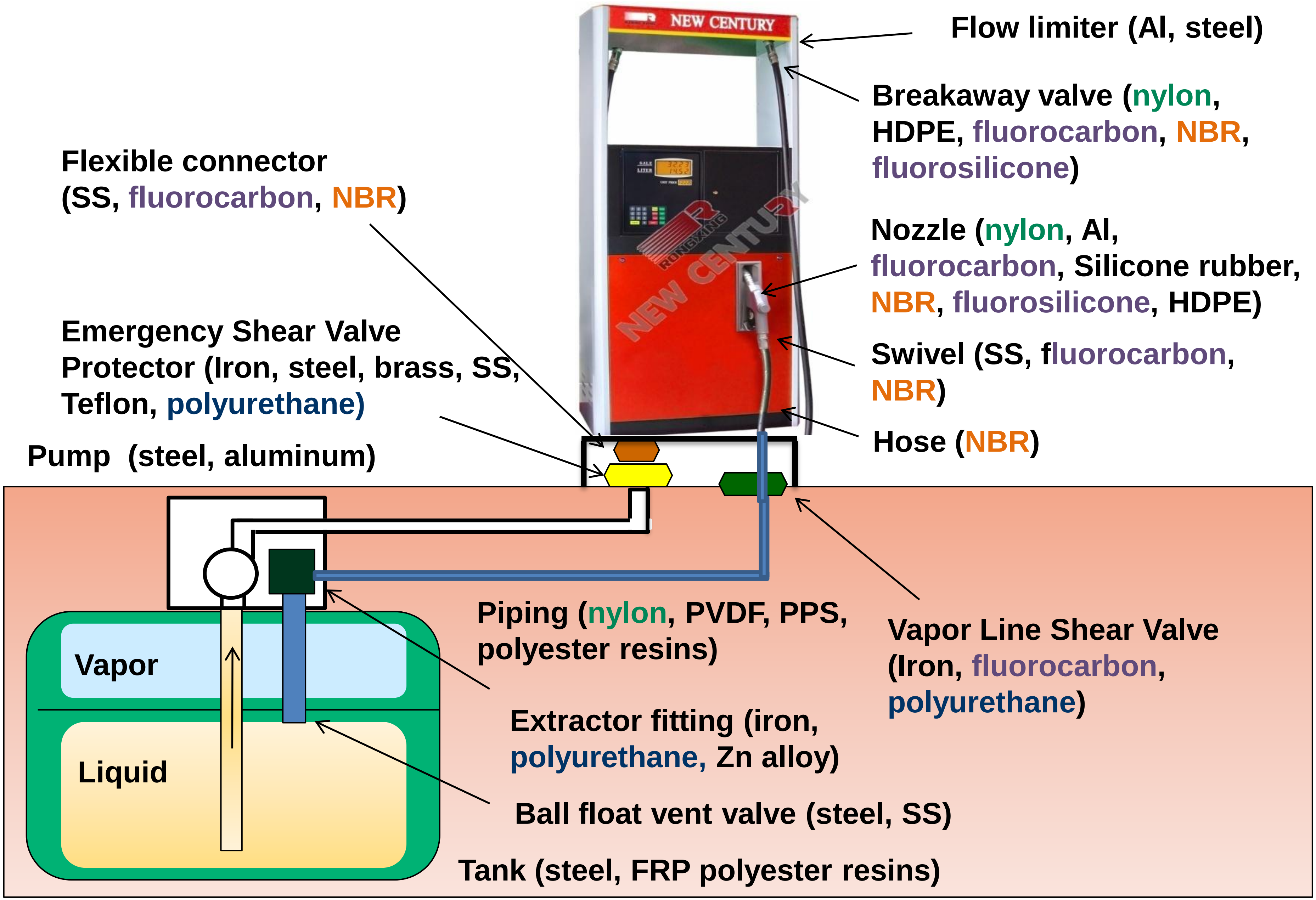
System Diagram of Fueling Dispenser Infrastructure



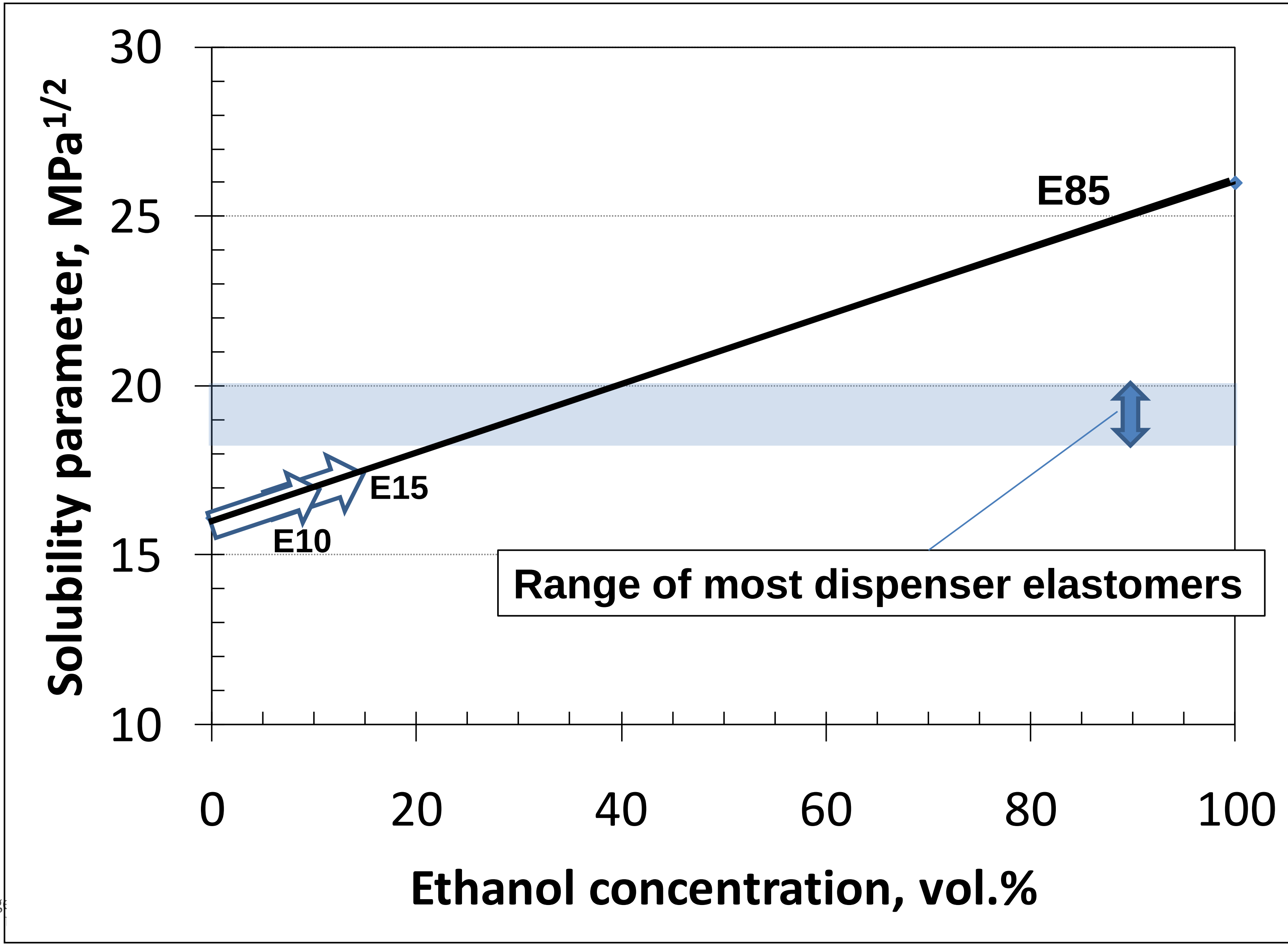
Typical Components and Materials from Truck to Tank



Typical Components and Materials from Tank to Nozzle

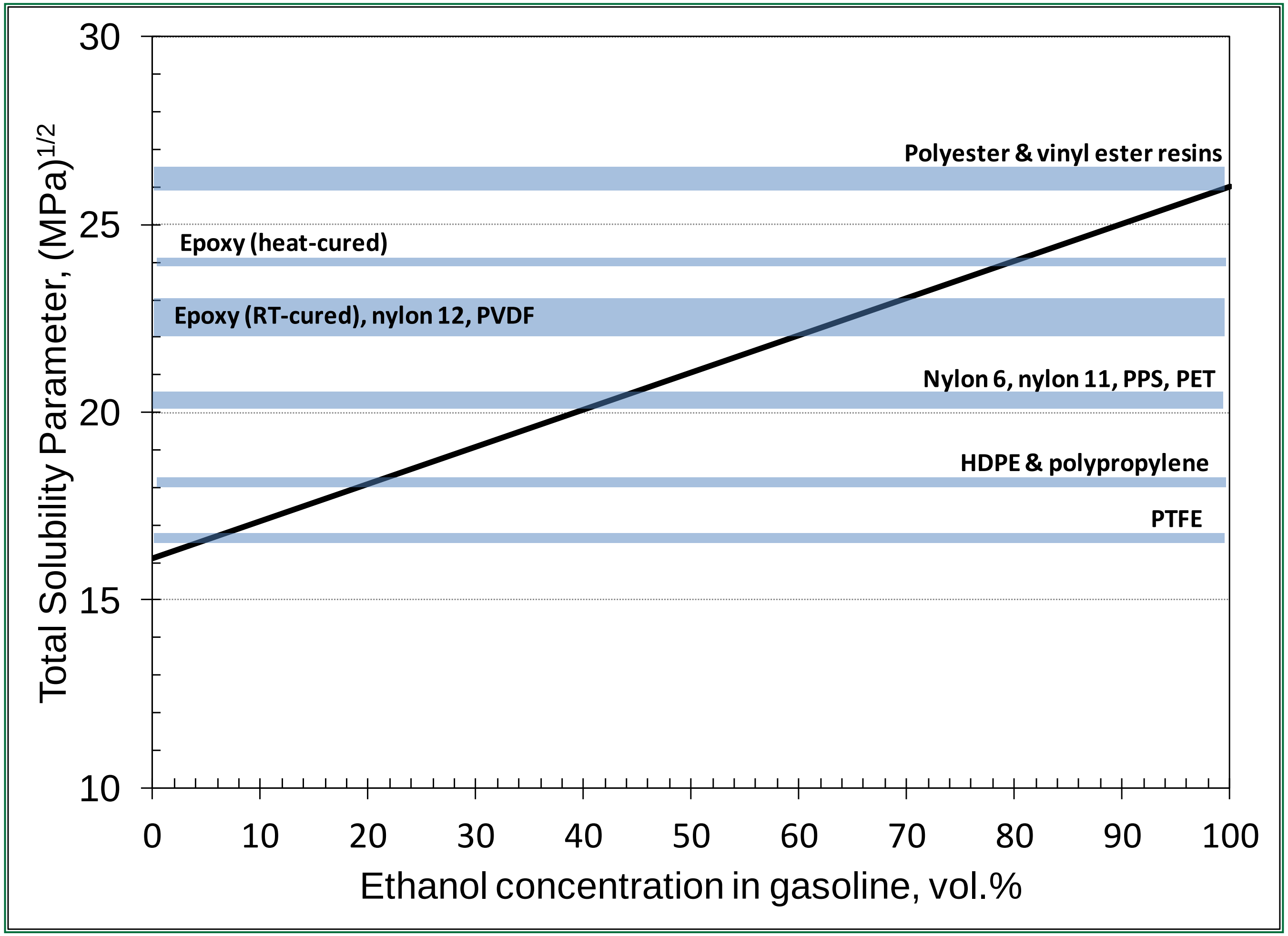


As the ethanol level increases, the total solubility parameter of the fuel approaches the range of many common dispenser elastomers



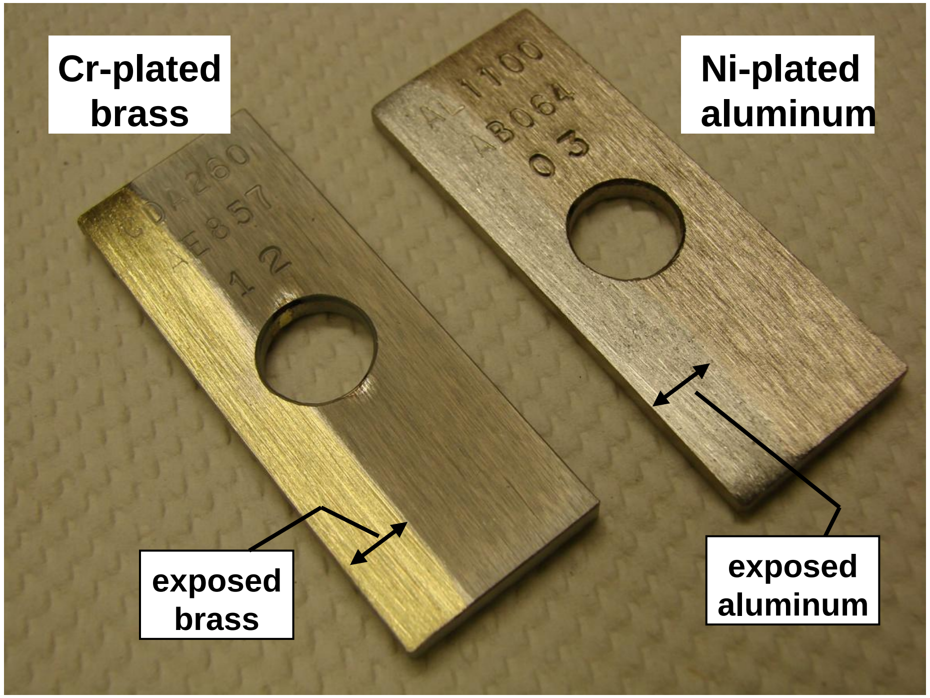
As the ethanol level increases, the solubility parameter of the fuel approaches and passes through the range of many plastics

- **The solubility parameter is a means for predicting if one material will dissolve in another. As the parameters for the liquid and solid converge, the potential for fluid permeation increases.**
- **The total solubility parameter (or Hildebrand solubility parameter) is useful for predicting solubility for nonpolar solvents, questionable for polar solutions.**
- **The permeation of fluid into a polymer will result in volume swell and potential dissolution of one or more polymer components, which may result in degradation.**



Metal Coupon Study

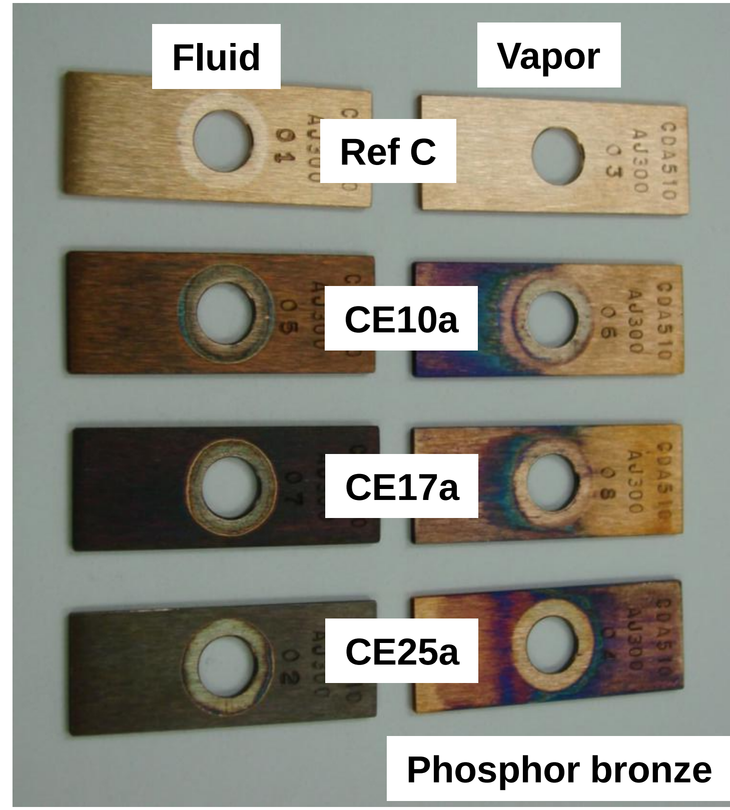
- Single Material Coupons
  - » 304 stainless steel
  - » 1020 carbon steel
  - » 1100 aluminum
  - » Cartridge brass
  - » Phosphor bronze
  - » Nickel 201
- Plated Coupons (exposed fully plated and with plating partially removed to generate galvanic couple
  - » Terne-plated (Pb) steel
  - » Galvanized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



* new for this series

Metal and Alloy Results

- No measurable or accelerated corrosion resulted for either the completed plated or the partially-plated specimens
- No apparent trends with ethanol concentration
- XPS analysis of phosphor bronze showed copper sulfide



Caveats:

1. We did not evaluate under conditions of phase separation.
2. We also did not place coupons under stress.

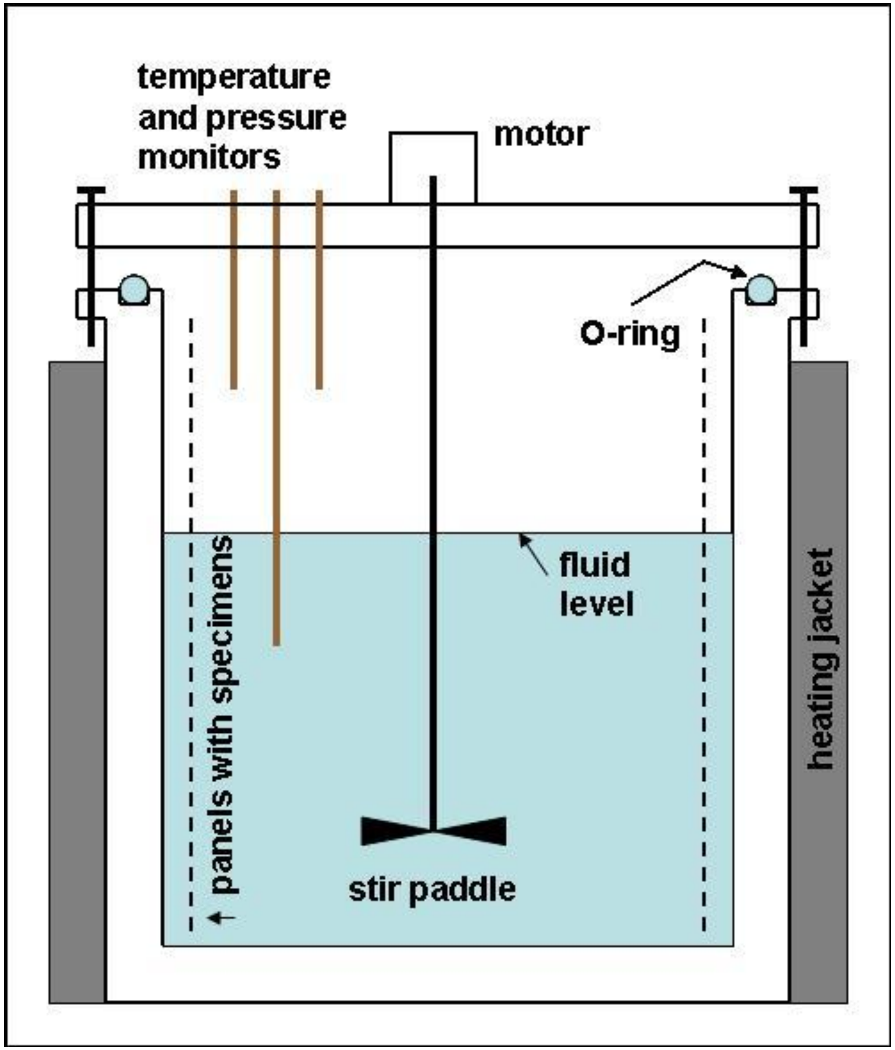
Description/listing of key plastic names and acronyms:

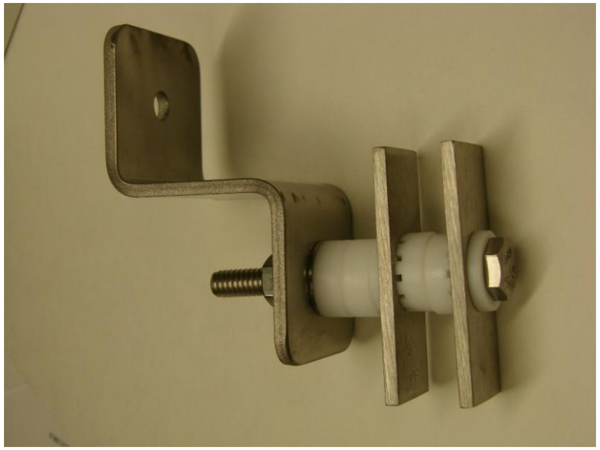
• PVDF	Polyvinylidene fluoride
• PTFE	Polytetrafluoroethylene
• PET	Polyethylene terephthalate
• PETG	Polyethylene terephthalate copolymer with cyclohexane dimethanol
• PBT	Polybutylene terephthalate
• POM	Polyoxymethylene
• Acetron GP	Polyoxymethylene copolymer
• PPS	Polyphenylene sulfide
• HDPE	High density polyethylene
• F-HDPE	Fluorinated high density polyethylene
• PP	Polypropylene

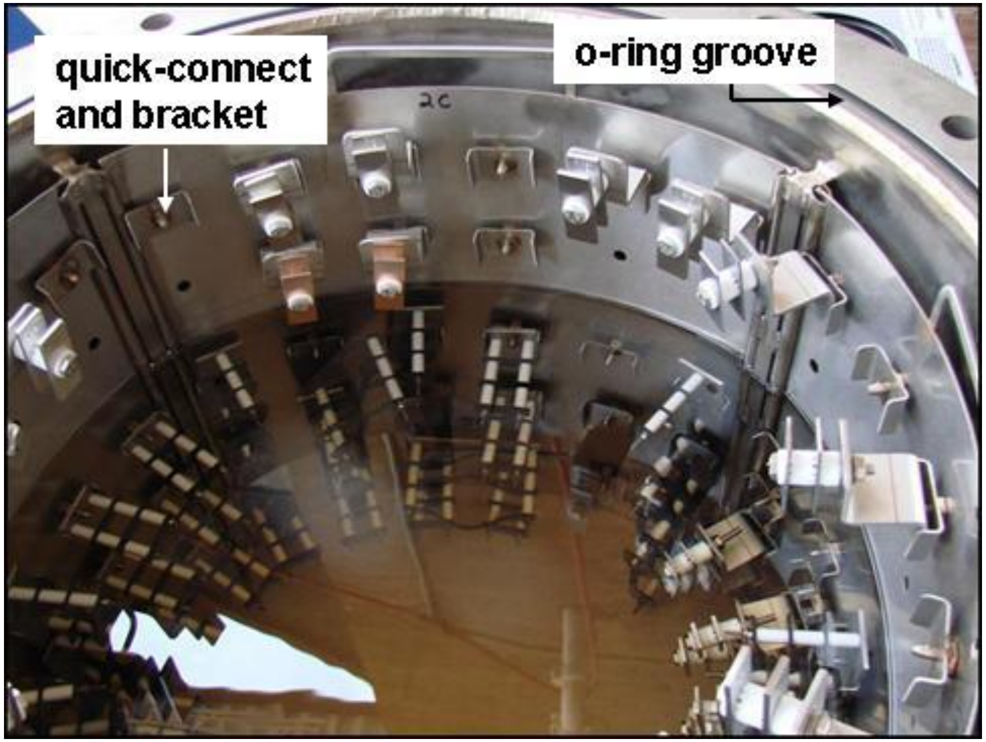
Complete List of Plastic Materials

Thermoplastics	Thermosets
High Performance Polymers 1. Fluoropolymers: (PTFE & PVDF) 2. Polyphenylene sulfide (PPS)	**Poly and Vinyl Ester Resins** 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)
Mid-Range Polymers 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)	
Commodity Polymers 1. Polyethylene: (HDPE & F-HDPE) 2. Polypropylene (PP)	**Epoxies** 1. Room temperature cured 2. Heat cured

Test specimens were exposed to the test fluid in a large stainless steel tank with stainless steel hardware





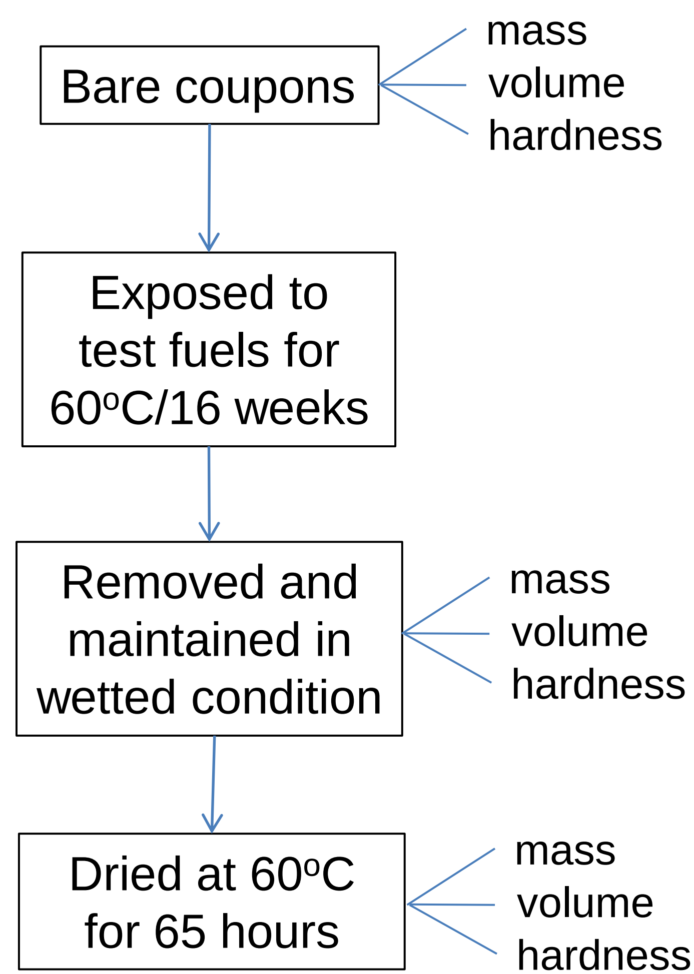


Test fuels were formulated according to SAE J1681 and ASTM D471 specifically developed for materials compatibility studies

- 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^{o}C) rapidly ages the specimens to assess relative compatibility in a reasonable timeframe



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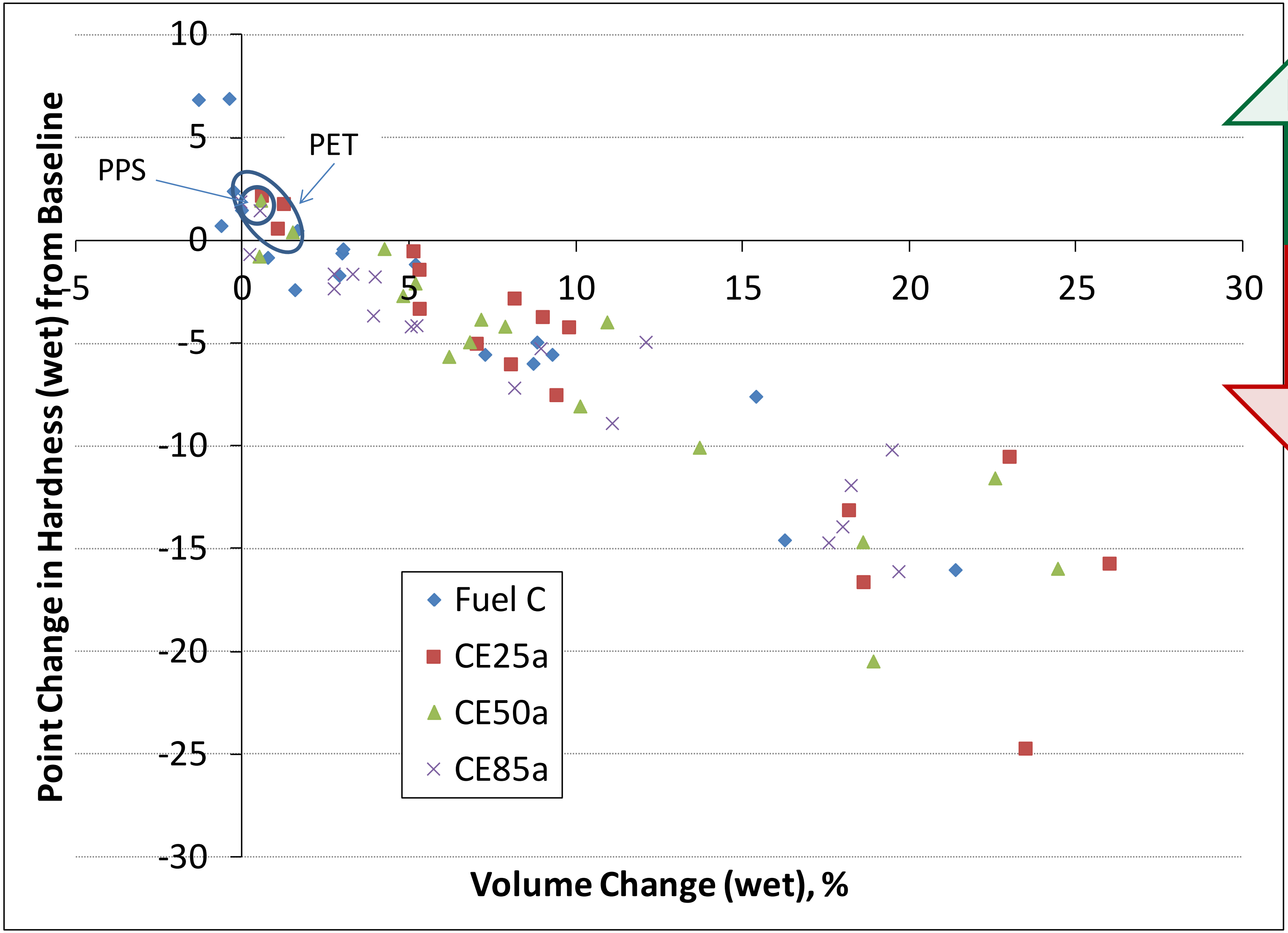
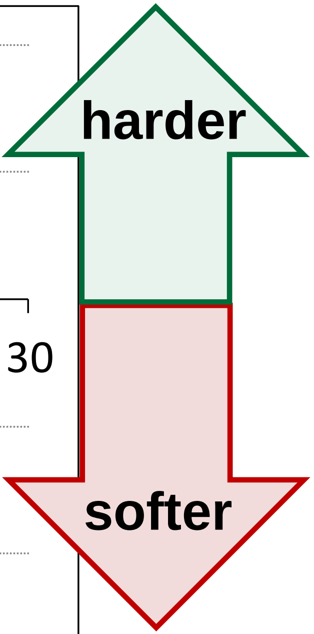
Presentation of Plastic Results

1. **Wet Volume Change vs Point Change in Wet Hardness**
   - » Volume Change vs Ethanol Concentration
     - PPS, Polyesters, Fluoropolymers, Acetals
     - Nylons, HDPE, Resins, PP
   - » Point change in Hardness
     - Absolute Hardness Values
     - PPS, Polyesters, Fluoropolymers, Acetals
     - Nylons, HDPE, Resins, PP
2. **Dry-out Properties: Volume Change vs Mass Change**
   - » Hardness vs volume change
   - » Dry-out Hardness vs Ethanol Concentration
     - PPS, Polyesters, Fluoropolymers, Acetals
     - Nylons, HDPE, Resins, PP
3. **Presentation of selected elastomer results**

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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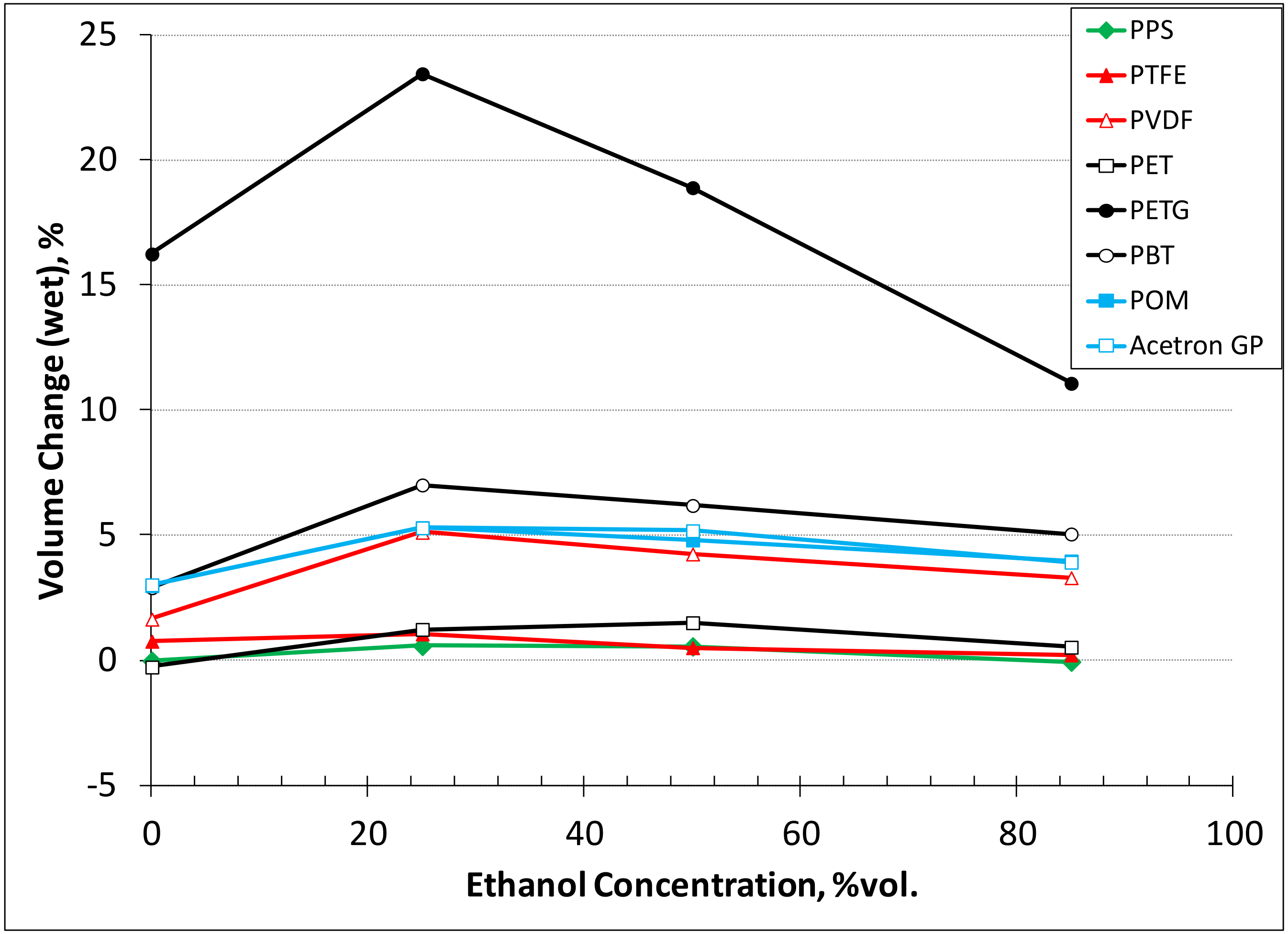
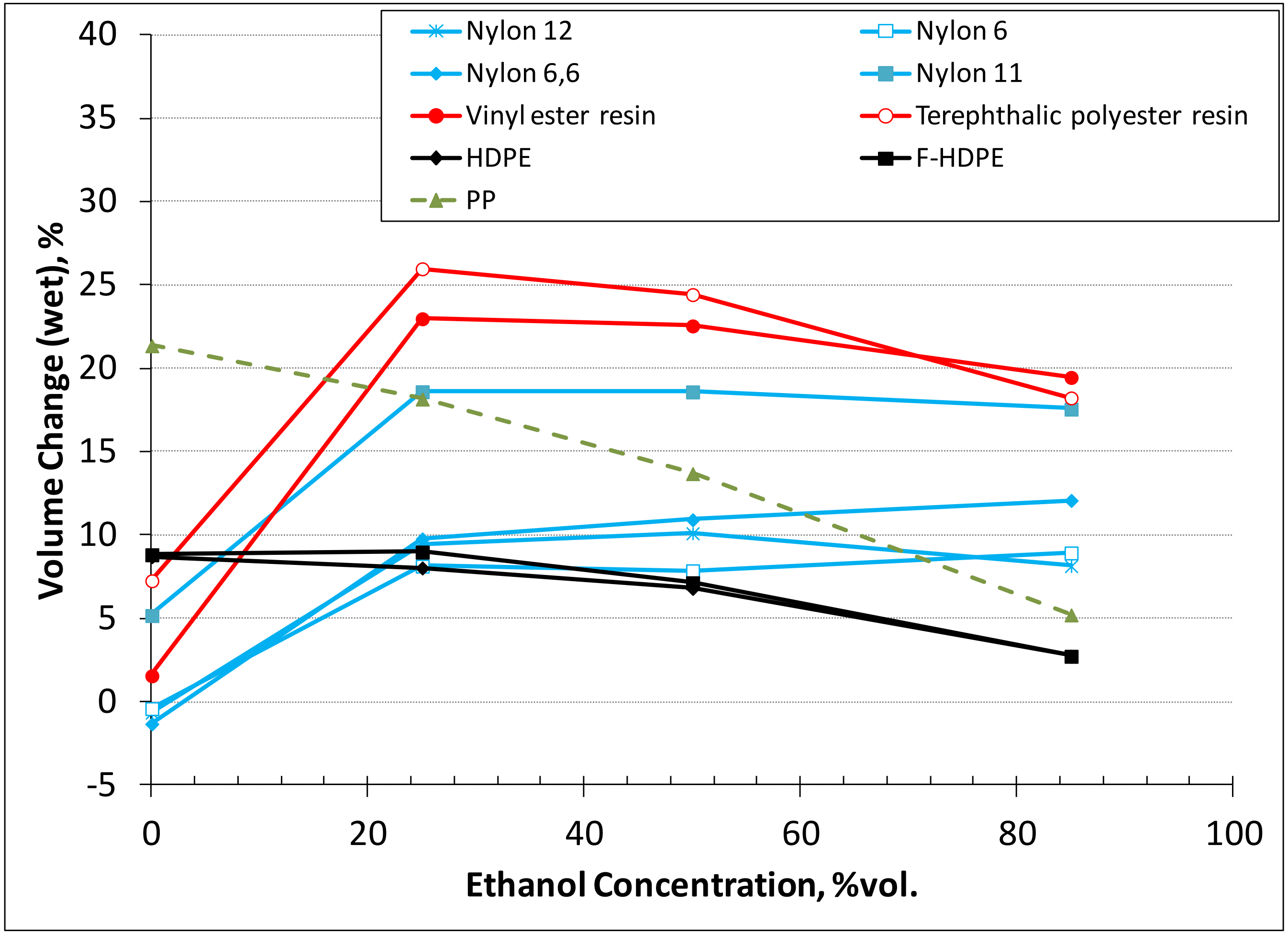
Wet Volume Change Results for PPS, PTFE, PVDF, PET, PBT, PETG and acetals (POM & Acetron GP)

- **Thermoplastic polyesters (PET, PBT, and PETG) showed a wide range of volume swell**
- **Low volume swell was observed for PPS PET, and PTFE**
- **Moderate swell was observed for acetals, PVDF, and PBT**
- **High swelling was noted for PETG**
  - **16% swell for Fuel C**
  - **23.5% for CE25a**
- **Except for PETG, these polymers showed no strong correlation between volume swell and ethanol concentration**



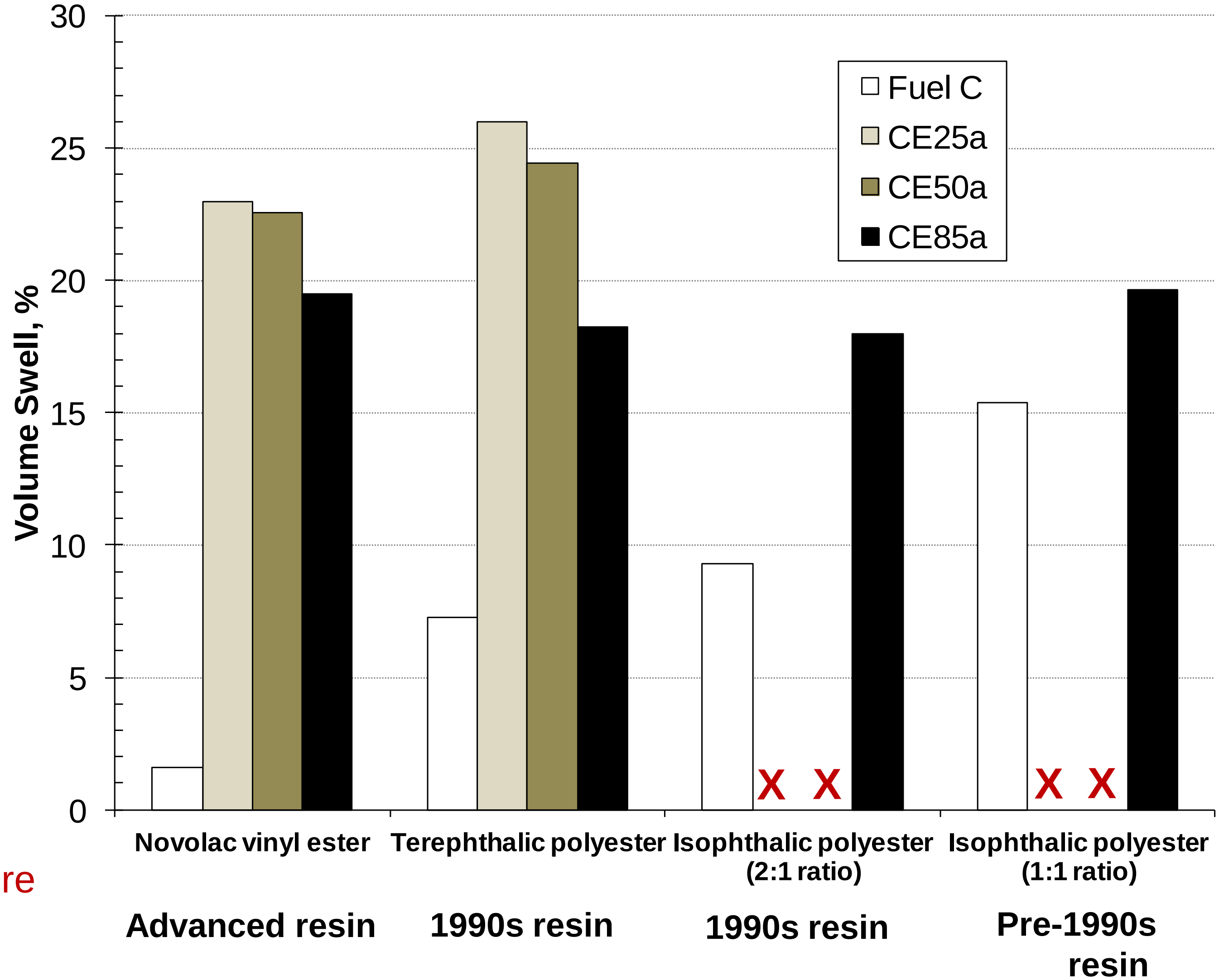
Wet volume change results for the nylons, polyester and vinyl ester resins:

- **Volume swell for PP, nylons and resins was highly affected by ethanol**
- **The swelling behavior for PP, HDPE and F-HDPE exhibited maximum swell for Fuel C and subsequently decreased with increasing ethanol concentration**
- **The three petro-based nylons exhibited similar behavior: A slightly negative swelling from exposure to Fuel C and approximately 10% swell with exposure to ethanol**
- **In contrast nylon 11 swelled to 5% for Fuel C and ~18% with exposure to ethanol.**
- **The isophthalic polyester resins fractured with ethanol exposure (not presented)**
- **Terephthalic polyester swelled 7% with Fuel C exposure, and over 25% with exposure to CE25a**
- **Vinyl ester exhibited low swell (1.5%) for Fuel C and 22% when exposed to CE25 a**



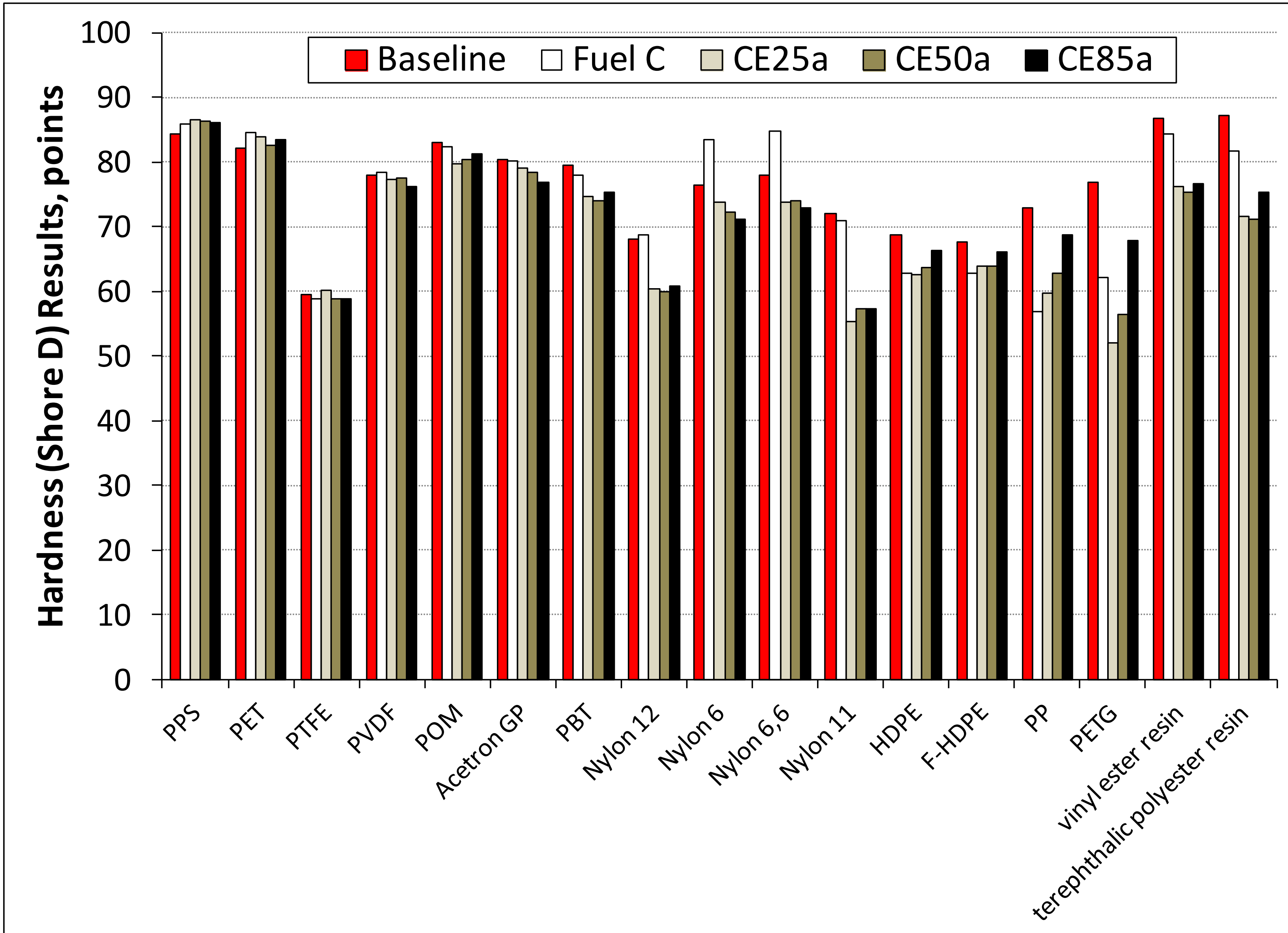
Four resin types representative of resins used in fiber-reinforced plastic containment systems were evaluated

- **Significant swelling was observed with exposure to ethanol. Highest swelling occurred for CE25a and CE50a**
- **Isophthalic resins exhibited significant swelling with exposure to Fuel C and failed with exposure to CE25a and CE50a**
- **Specimens did not contain fiber reinforcement**



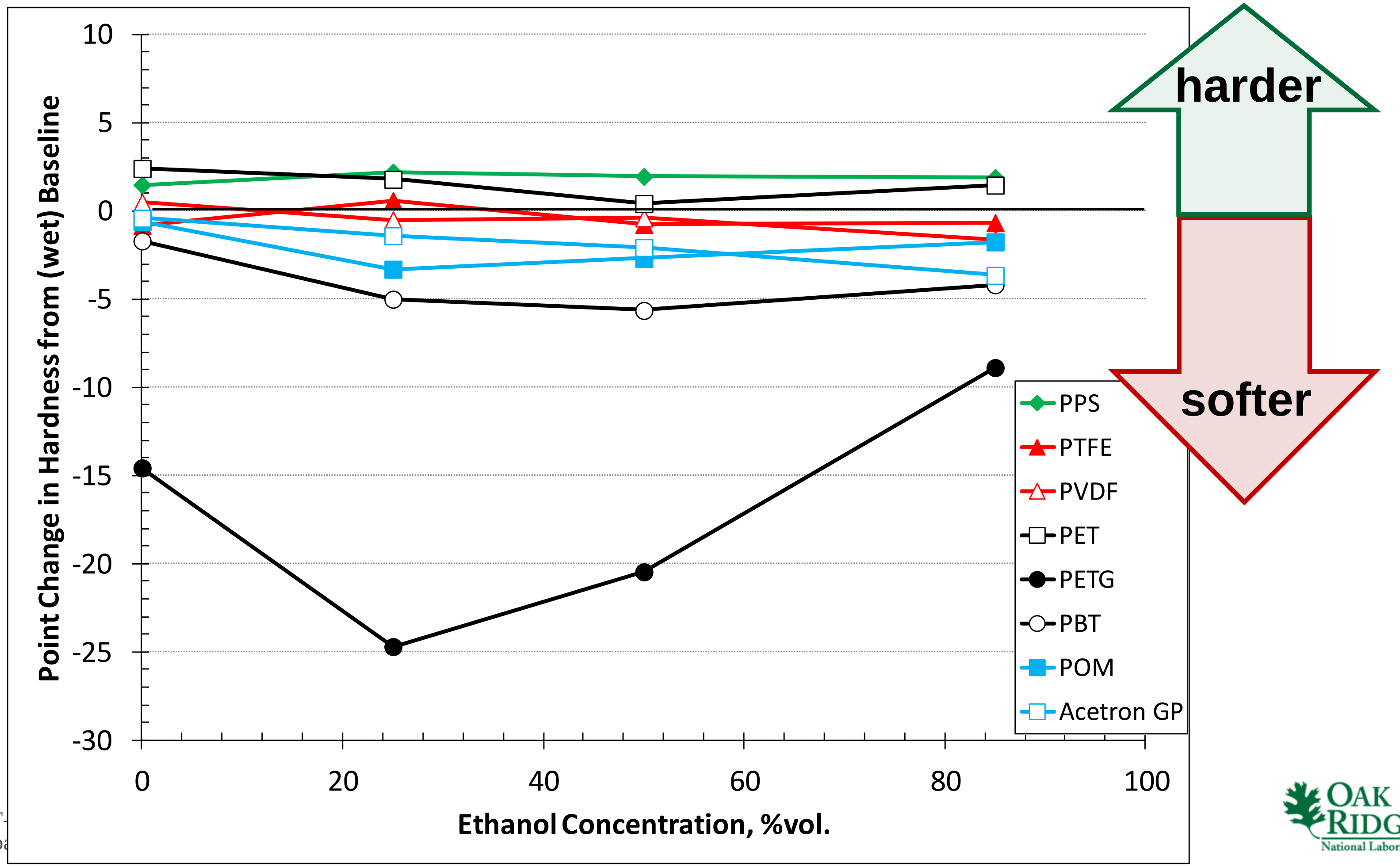
X – fractured from exposure

The plastics were observed to exhibit a range of hardness values



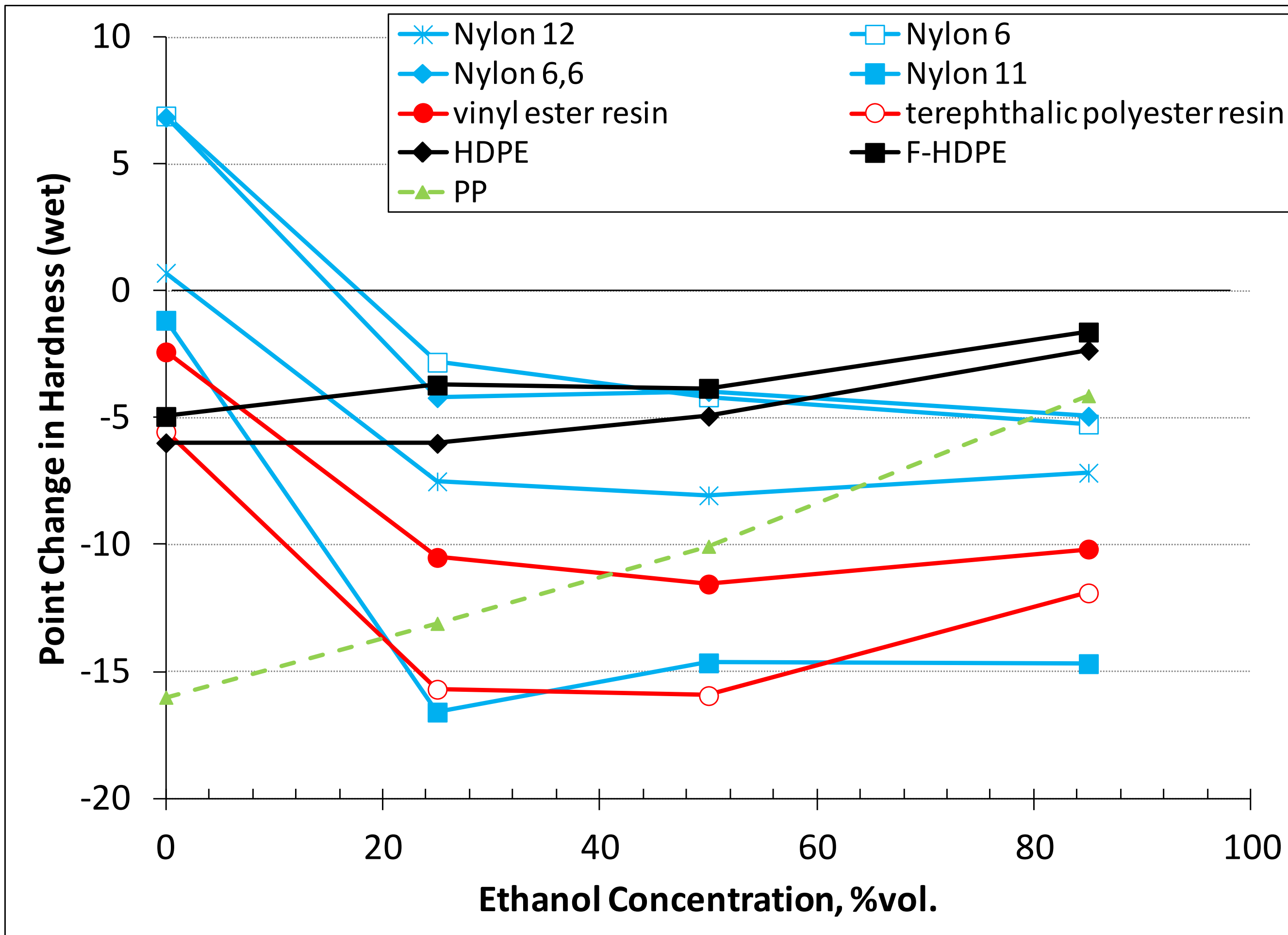
The wet hardness did not change significantly from the original baseline condition for the acetals, PPS, and PET

- **Interestingly, PPS and PET were slightly hardened with exposure to the test fuels.**
- **PBT and the acetals were slightly softened with exposure to ethanol, while PETG exhibited significant softening with exposure to Fuel C and additional ethanol.**

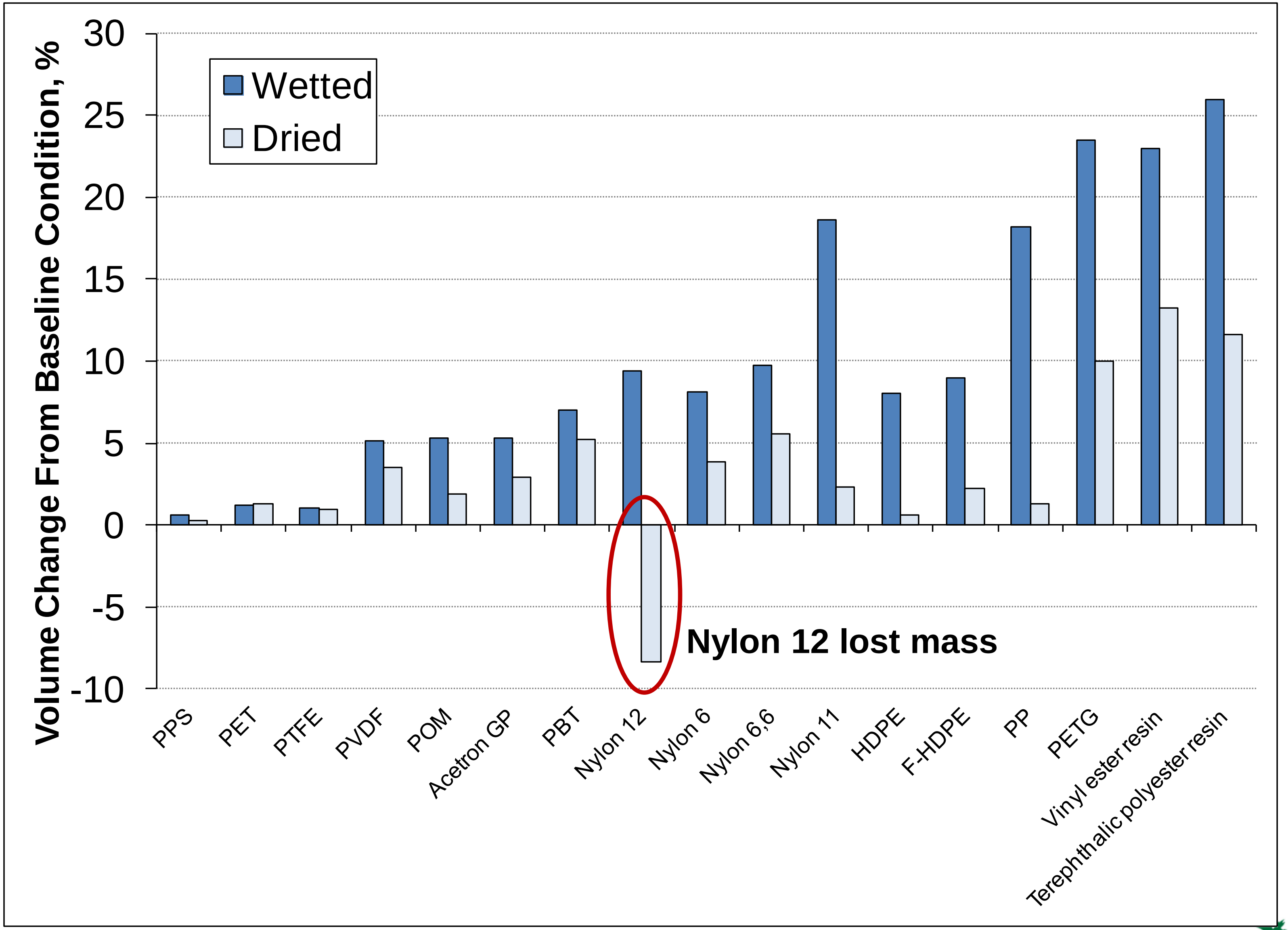


The addition of ethanol produced significant softening in nylon 11 and resin materials

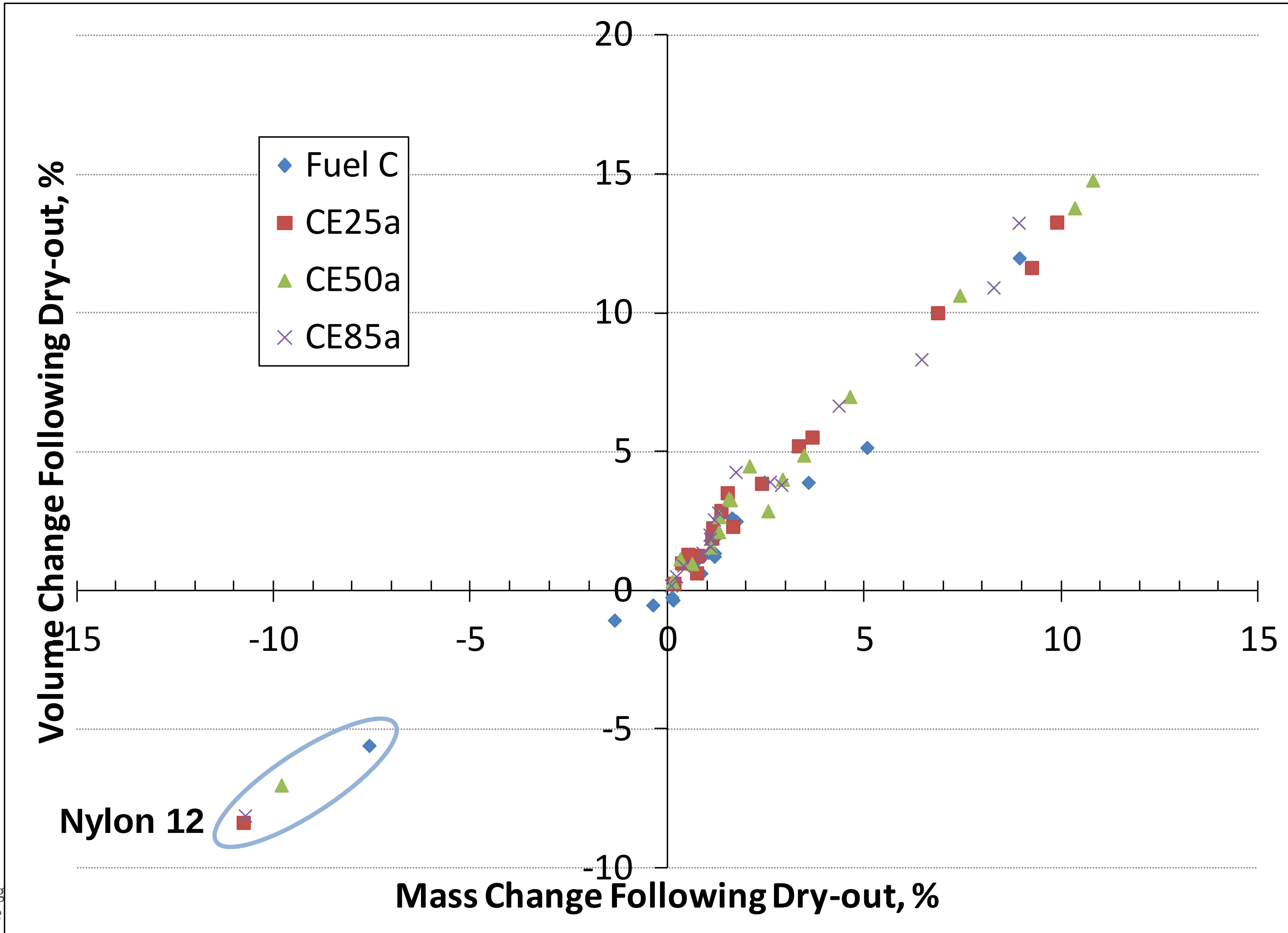
- **The two HDPE samples exhibited a 5 point drop with exposure to Fuel C. The change in hardness decreased with increasing ethanol concentration**
- **Nylon 6 and nylon 6/6 were hardened in Fuel C. Exposure to ethanol resulted in mild softening (~5 point drop from baseline)**
- **Nylon 12 was unaffected by Fuel C but the hardness was lowered 7 points with exposure to ethanol**
- **Terephthalic polyester resin dropped 5 points with Fuel C and 15 points with the addition of ethanol**
- **Vinyl ester exhibited slight softening in Fuel C and a 10 point drop in hardness with ethanol**



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

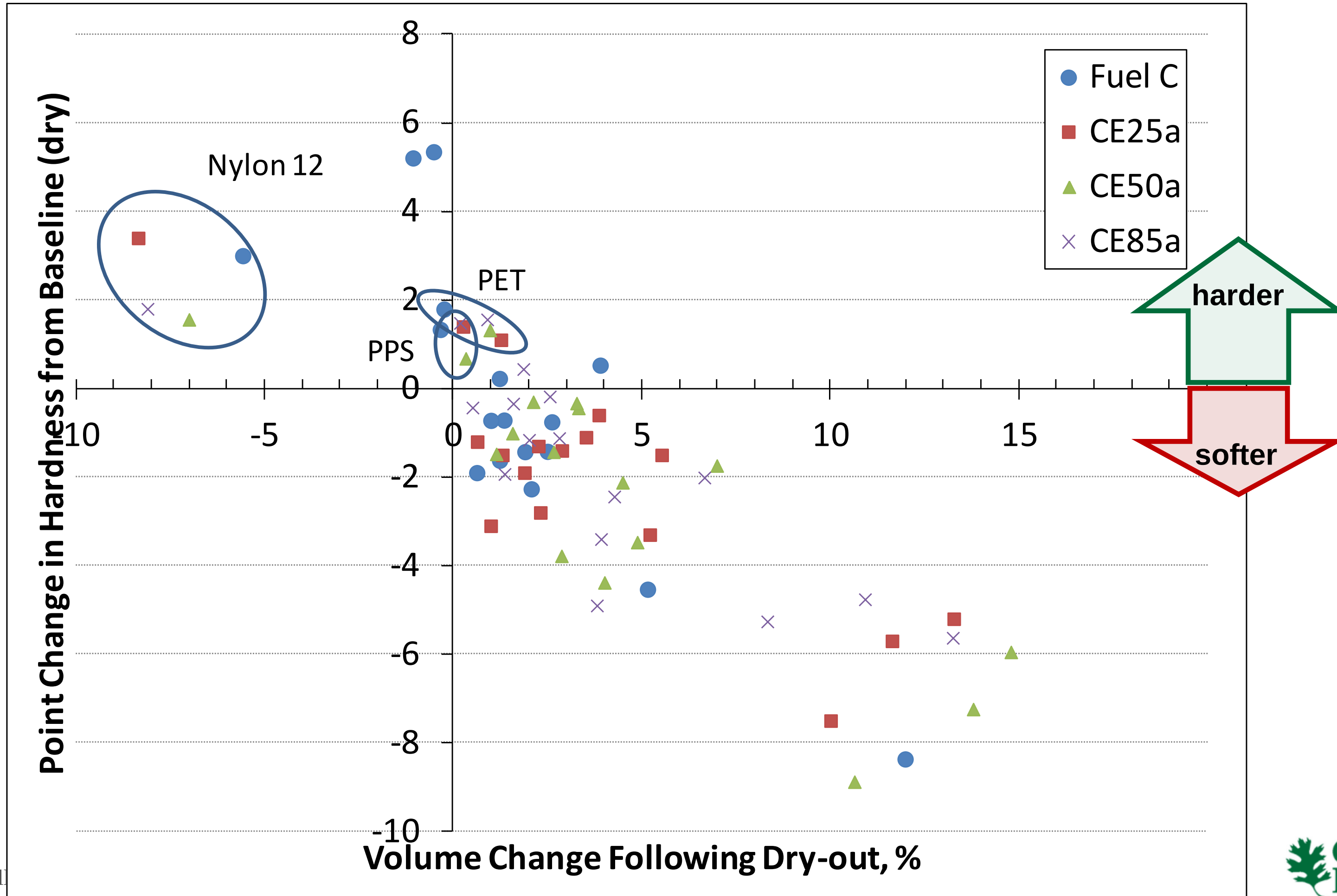


The volume change following dry-out (at 60ºC & 65 hours) was linearly proportional to the mass change following dry-out for all plastics studied



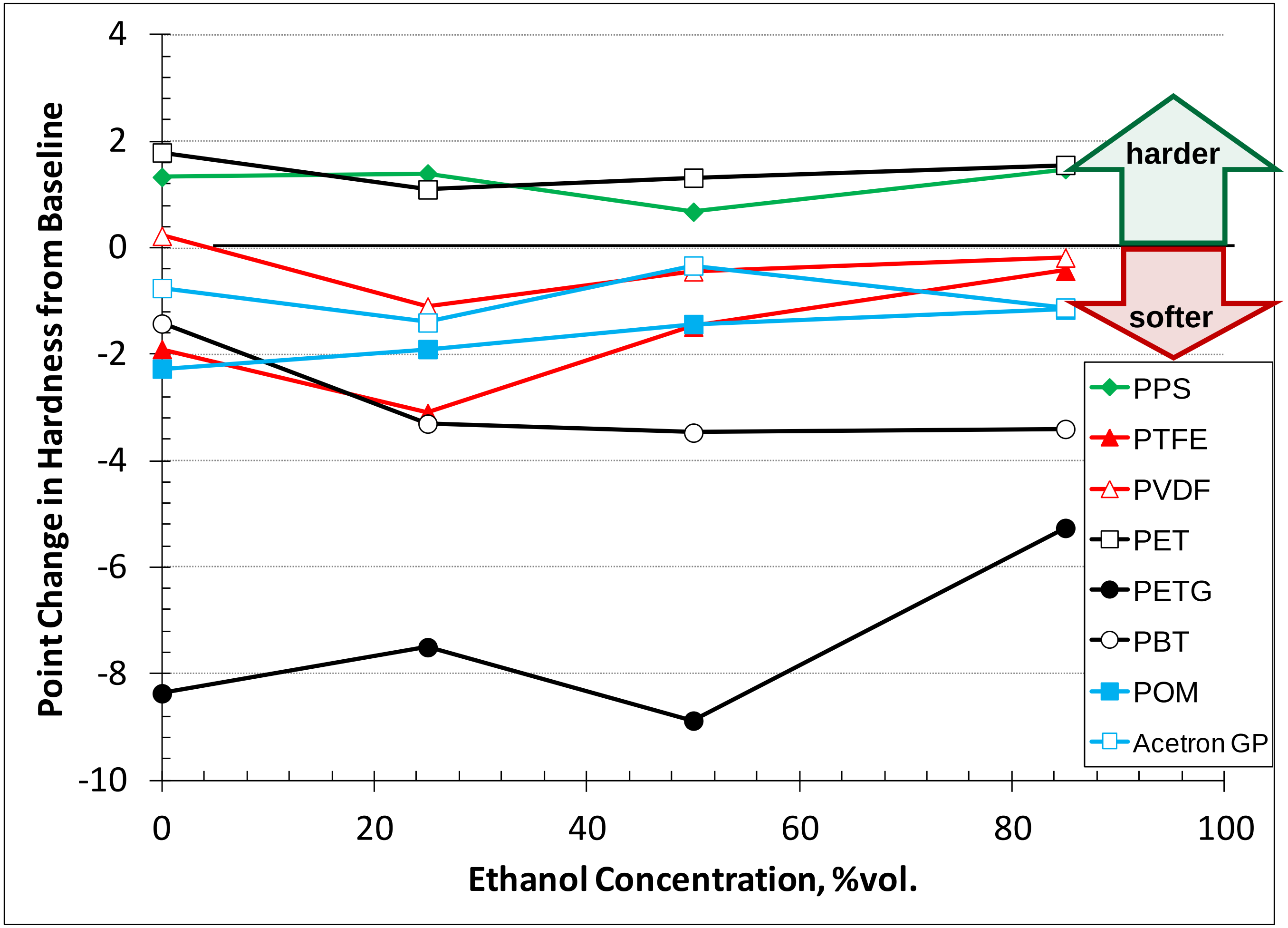
In general the hardness (following dry-out) decreased with increasing dry-out volume (or mass)

- **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.**



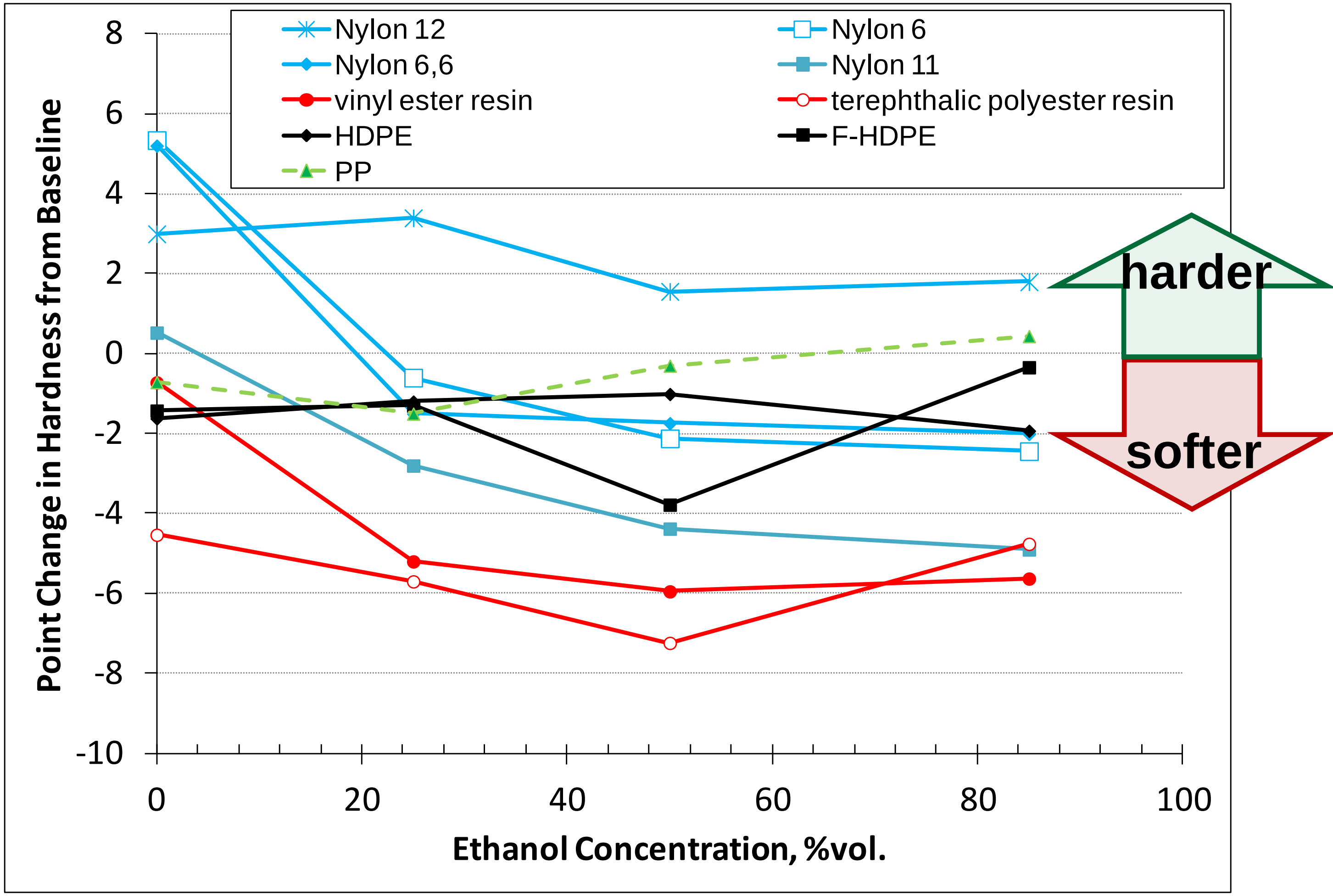
In general (following dry-out), the change in hardness from the original baseline condition was low for PPS, fluoropolymers, PET, PBT and the acetals

- **PPS and PET showed a slight increase in hardness with exposure to the test fuels**
- **PTFE and PVDF exhibited a small drop in hardness with exposure to CE25a. The dry-out hardness for these materials approached baseline values with increasing ethanol content**
- **The acetals showed slight softening with exposure to the test fuels, but no strong correlation with ethanol content**
- **PBT showed a modest drop in hardness for the ethanol-blended fuels**
- **PETG experienced the highest degree of softening with the test fuels.**



The dry-out hardness results for Nylon 6, 6/6, and 11, and the resins showed sensitivity to ethanol exposure

- **The HDPEs exhibited a slight decrease in hardness with exposure to the test fuels following dry-out**
- **Nylons 6 and 6/6 exhibited similar behavior to the wet hardness results.**
- **Nylon 12 showed a slight increase in hardness**
- **Nylon 11 exhibited slight softening with increasing ethanol content**
- **Resins exhibited modest softening with exposure to ethanol blends**



Summary Highlighting Notable Plastic Results

Material Type	Ethanol level producing max. swell	Volume increase, %	Max. Wet Hardness Change, points	Dried Volume Change, %
PPS	25	0.6	+ 2	0.3
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Nylon 6	25 – 85	8.2	-4	4
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Nylon 11	25 – 85	18.6	-15	2
HDPE	0 – 25	8	- 6	1
F-HDPE	0 – 25	9	- 4	2
PP	0	21	-16	1
PETG	25	23	-25	10
Vinyl ester resin	25 – 85	23	-12	13
Terephthalic polyester resin	25 – 85	26	-16	12

Observations

- **PPS:**
  - » Exhibited negligible mass, volume, and hardness change from the baseline condition when exposed to Fuel C or blends of Fuel C and ethanol.
- **PET:**
  - » Also exhibited negligible property change from baseline condition when exposed to test fuels. Other polyesters did not. PET exhibited a small increase in hardness with exposure to the ethanol-blended test fuels.
- **PVDF:**
  - » Exhibited 5% increase in volume with exposure to CE25a, but otherwise properties were relatively unchanged following exposure to the test fuels.
- **PTFE:**
  - » Exhibited a negligible volume change when exposed to the test fuels. Likewise, the hardness was only slightly reduced with exposure to the test fuels.

Observations (continued)

- **PBT:**
  - » Exhibited a 3% volume increase with Fuel C exposure. Volume expanded 7% for CE25a and dropped slightly with increasing ethanol concentration. The wet hardness of PBT also dropped 5 points with exposure to ethanol, after drying the hardness was raised slightly.
- **PETG**
  - » Exhibited high volume swell (~16%) compared to the baseline condition when exposed to Fuel C. Exposure to CE25a further increased the volume by 24%. Afterwards, the volume change decreased with increasing ethanol concentration such that, for CE85a, the volume swell was 11% (which was lower than the Fuel C value).
- **Acetals (POM & Acetron GP):**
  - » POM and Acetron GP exhibited similar performances. The wet volume was raised from 3% (Fuel C) to 5% with exposure to ethanol-blended fuels. The accompanying hardness dropped several points for both wetted and dried conditions exposed to ethanol.

Observations (continued)

- **Nylons:**
  - The wet hardness for Nylon 12 dropped around 7 points with exposure to ethanol-blended test fuels. However, following dry-out, the hardness for nylon 12 had increased slightly above the baseline value. It is interesting to note that nylon 12 was the only plastic to lose mass and volume following dry-out.
  - Following dry-out, nylon 6 and 6/6 dropped slightly in hardness from baseline for the ethanol-blended fuels. Nylon 11 exhibited the highest hardness decrease of the nylons (5 points from baseline) but this level is considered low.
- **High Density Polyethylene**
  - HDPE and F-HDPE exhibited nearly identical performance with exposure to the test fuels. For these materials the highest wet volume swell occurred with exposure to Fuel C (~8%). The volume swell was observed to decrease with increased ethanol concentration, such that for CE85a, the volume swell had reduced to 2.5%. Correspondingly the decline in wet hardness decreased with increasing ethanol content.

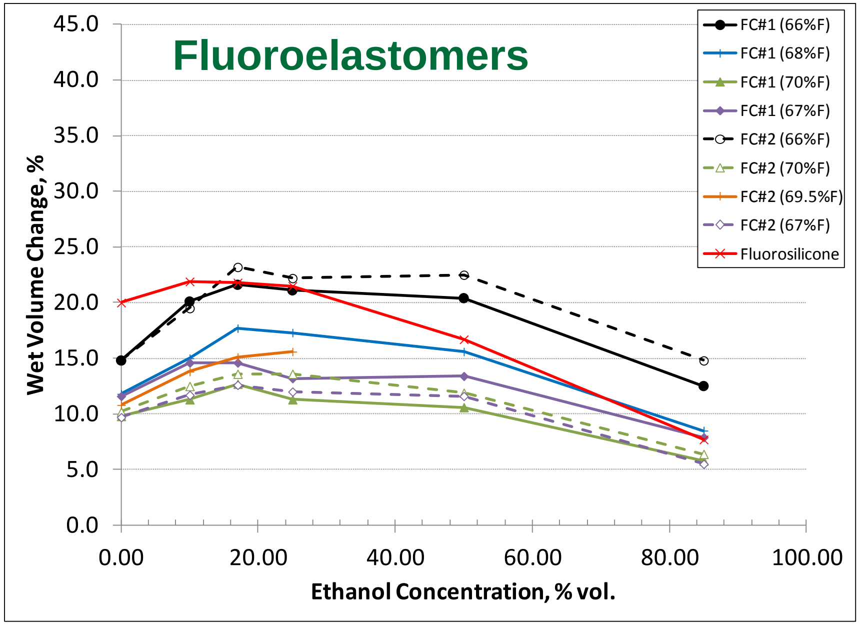
Observations (continued)

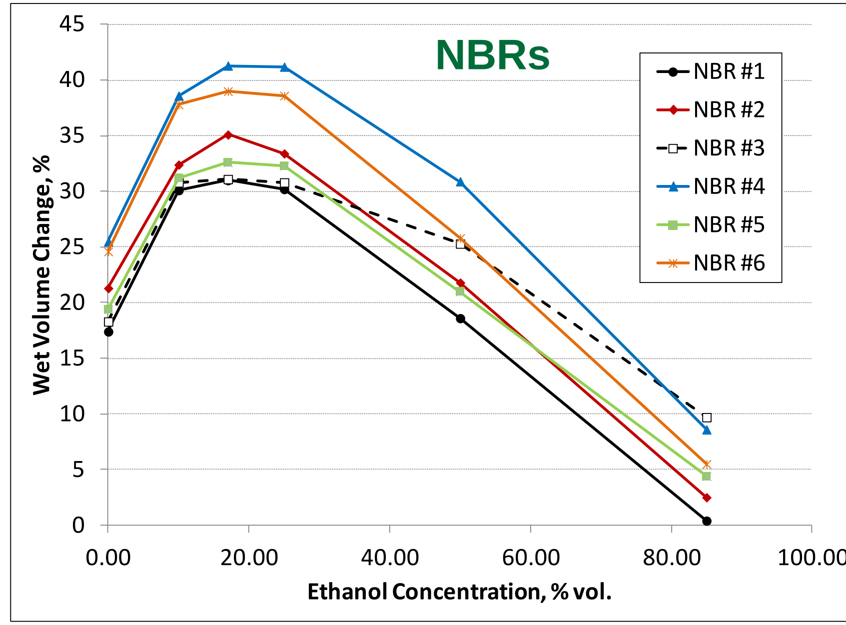
- **Polypropylene:**
  - » PP also exhibited a high maximum swell (21%) with Fuel C exposure. Volume swell decreased significantly with ethanol content to a value of 5% for exposure to CE85a
  - » Wet hardness corresponded with the volume swell. A 15 point drop in hardness was noted for Fuel C and this drop was reduced to 4 points for CE85a exposure
- **FRP Resins:**
  - » The isophthalic polyester resins used in legacy systems did not survive exposure to test fuels containing ethanol.
  - » Of the two resins that survived the test fuel exposures, the novolac vinyl ester exhibited better compatibility than the terephthalic ester resin. Both resins exhibited modest swell with exposure to Fuel C, but they showed exceptionally high swell (>20%) with exposure to CE25a. Increasing ethanol content lowered the total swell, but the values were still higher than 15%.
  - » Correspondingly, terephthalic polyester and vinyl ester also showed a significant drop in wet hardness with exposure to test fuels containing ethanol and retained a measureable degree of softening following dry-out.

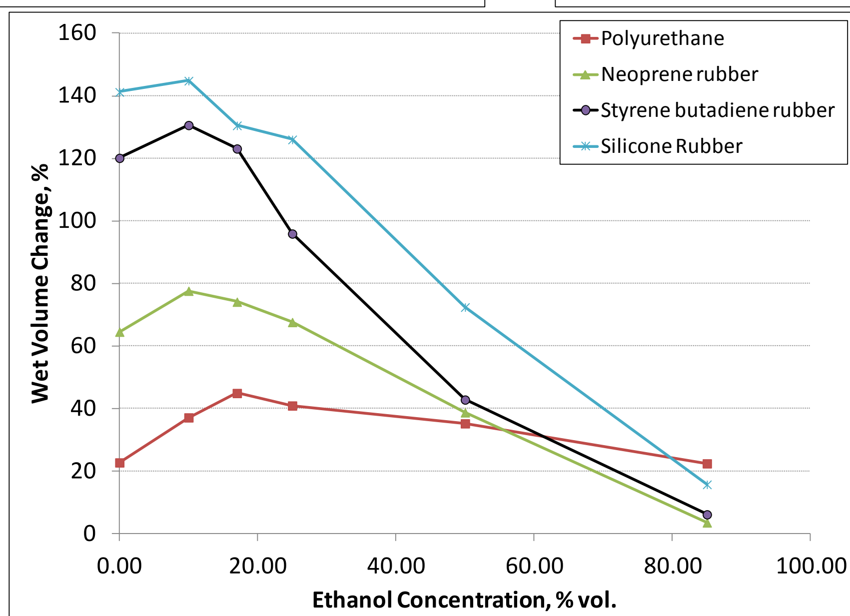
Elastomer Study

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	

Higher ethanol concentrations (50 and 85%) lowered the wet volume

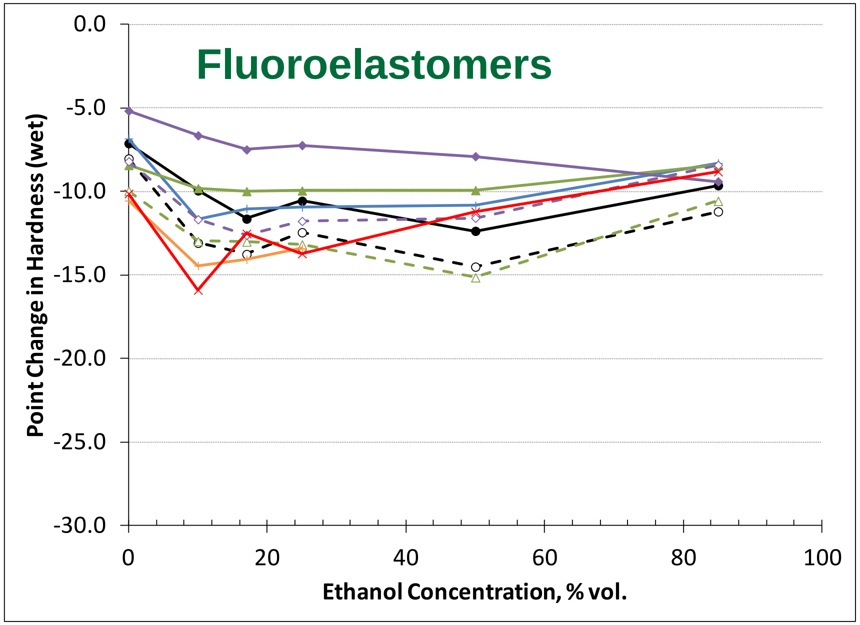


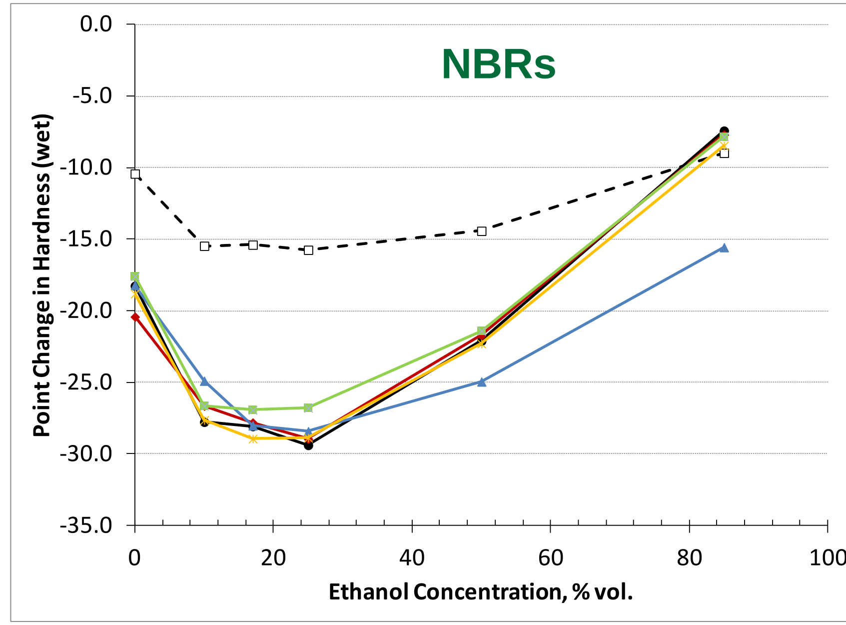


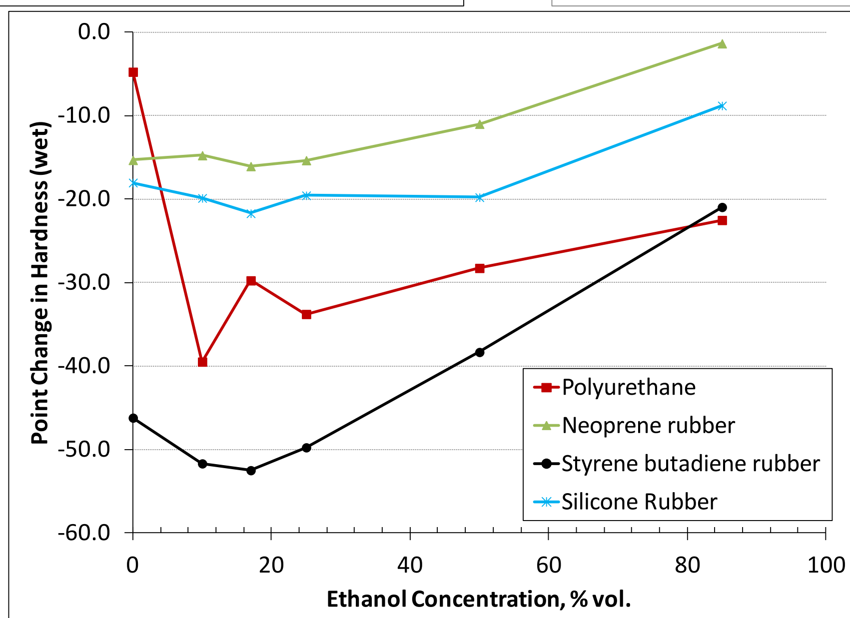


Polyurethane
Neoprene
SBR
Silicone

Likewise the wet hardness increased with higher ethanol content

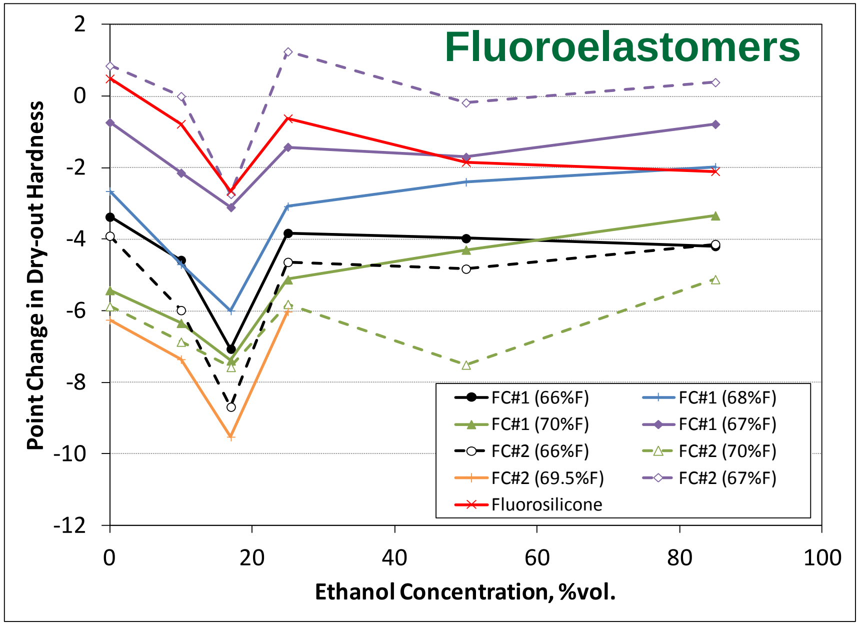


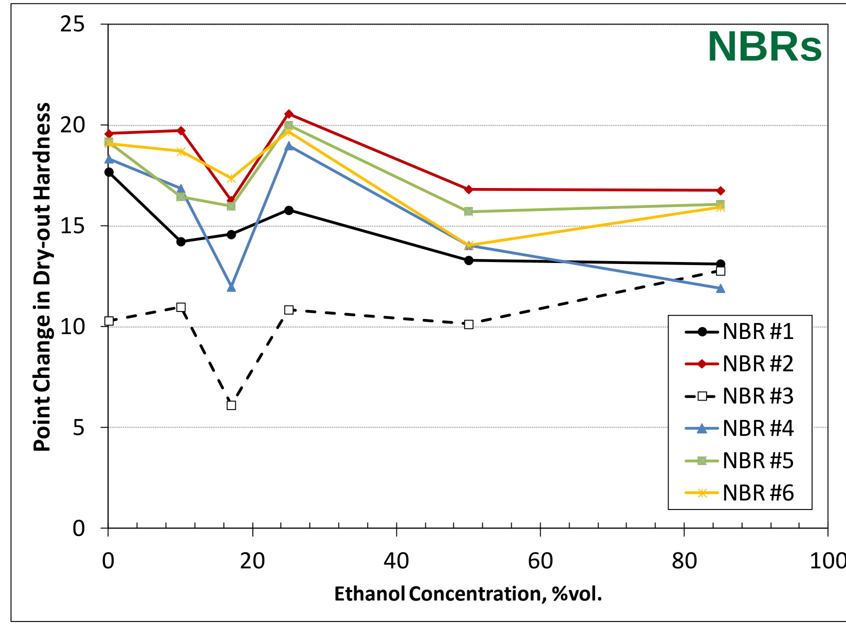


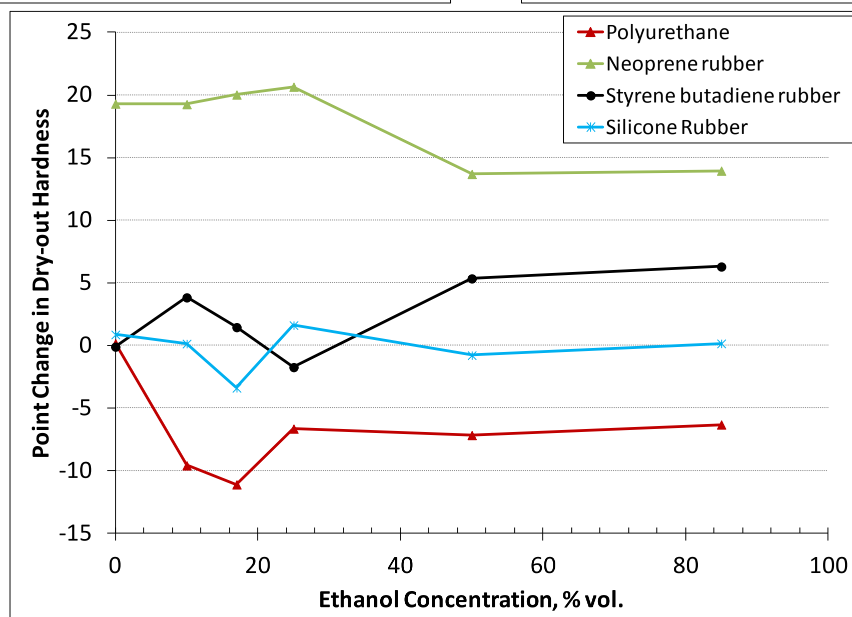


Polyurethane
Neoprene
SBR
Silicone

Interestingly, the dry-out hardness did not return to baseline values

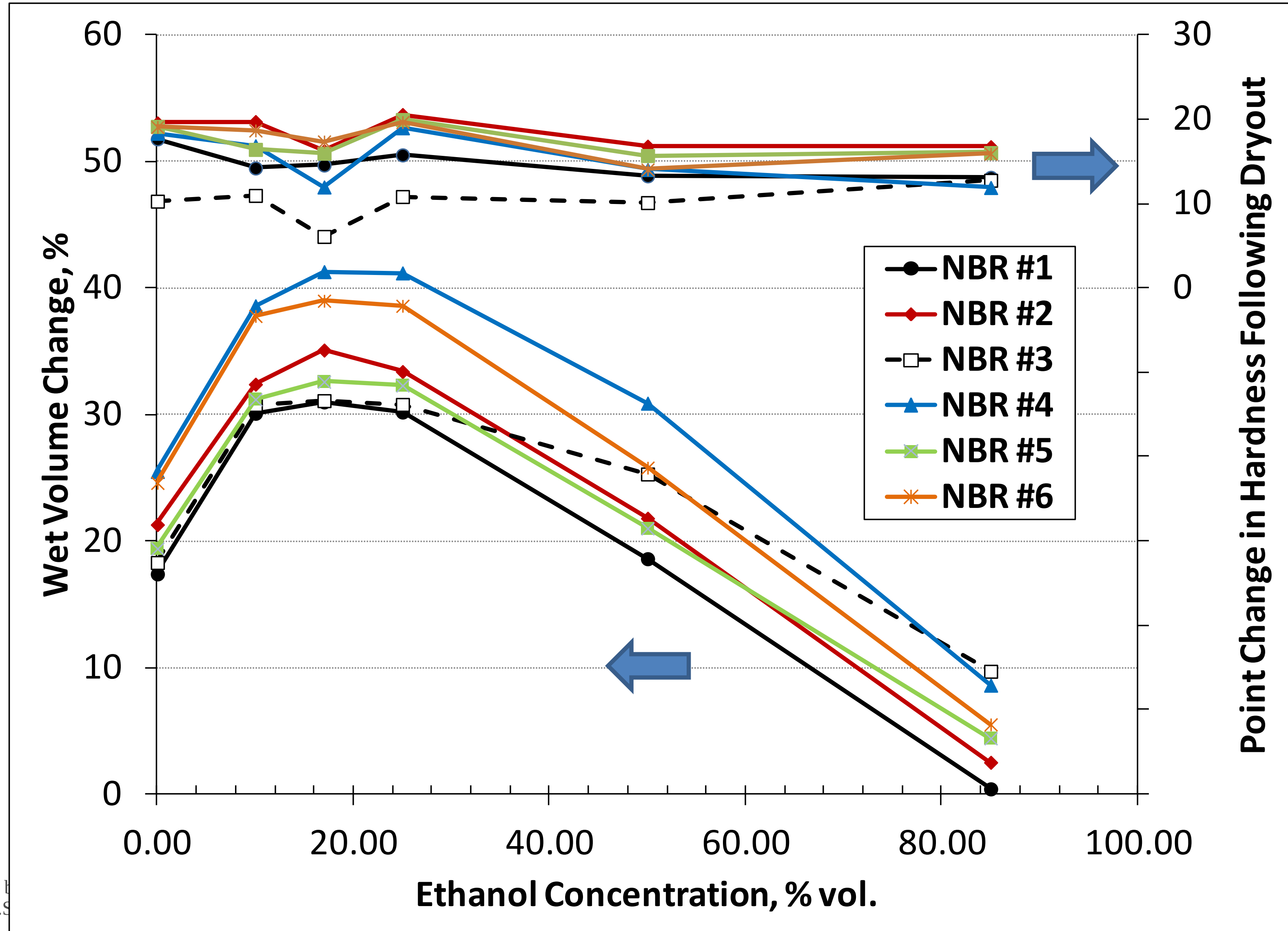






Polyurethane
Neoprene
SBR
Silicone

For instance, the NBRs still exhibited significant embrittlement with CE85a exposure even though the volume swell was low



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In summary:

- **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.**
- **Increased hardness of the NBRs may signal some level of extraction of butadiene and/or lower molecular weight components.**

Future Plans

- **Detailed analysis and application of Hansen Solubility Theory to measured results**
- **Exposure of plastics in CE10a**
- **Evaluation of additional fuel types (biofuels, etc.)**
- **Issue report detailing plastic results and elastomers (CE50a and CE85a)**

Thank you for your attention!

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