Compatibility Assessment of Plastic Infrastructure Materials with Test Fuels Representing E10 and iBu16

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ABSTRACT

The compatibility of plastic materials used in fuel storage and dispensing applications was determined for a test fuel representing gasoline blended with 10% ethanol. Prior investigations were performed on gasoline fuels containing 25, 50 and 85% ethanol, but the knowledge gap existing from 0 to 25% ethanol precluded accurate compatibility assessment of low level blends, especially for the current E10 fuel (gasoline containing 10% ethanol) used in most filling stations, and the recently accepted E15 fuel blend (gasoline blended with up to15% ethanol).

For the majority of the plastic materials evaluated in this study, the wet volume swell (which is the parameter most commonly used to assess compatibility) was higher for fuels containing 25% ethanol, while the volume swell accompanying E10 was much lower. However, several materials, such as polyvinylidene fluoride (PVDF), fiberglass resins, and the polyethylene terephthalate co-polymer (PETG) exhibited similar volume expansions with both 10 and 25% ethanol.

In the second part of this study, the compatibility performance of the infrastructure plastics in the E10 test fuel was compared to a test fuel containing 16% isobutanol (which has the same oxygen level as E10). The measured property changes (volume and hardness) in these two fuels were similar for the majority of the plastics tested. However, Nylon 6, Nylon 6,6, and the vinyl ester fiberglass resin showed much better compatibility with a 16% isobutanol blend than with a blend containing 10% ethanol.

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INTRODUCTION

Renewable fuels are becoming more widely used as a transportation fuels in the United States and in other countries. A key motivation for increasing biofuel use is to reduce petroleum consumption, thereby improving energy security and independence [1]. Until recently, the amount of ethanol that may be blended and sold in the United States of America (USA) as an additive to gasoline had been limited to 10% by volume (E10) by the US Environmental Protection Agency (EPA). In 2009, the US EPA approved a waiver to allow the use of 15% ethanol in gasoline (E15) and concerns were raised that as the ethanol concentration in gasoline is increased, the fuel may become less compatible with the existing fuelling infrastructure, a significant portion of which was originally designed for neat gasoline use [2]. There were concerns in the early 1980s that the addition of ethanol to gasoline would negatively impact some infrastructure polymers. Several noteworthy investigations were performed to evaluate ethanol compatibility to

polymers [3, 4, 5, 6, 7, 8, 9, 10, 11]. These studies, however, were focused on elastomers; they did not include plastic materials in their evaluations. Fluorocarbons and acrylonitrile rubbers (NBRs) were the most studied elastomer types, but a few also evaluated neoprene, polyurethane, and fluorosilicone. Published investigations evaluating plastic compatibility performance metrics to ethanol blended gasoline were less forthcoming from the open literature.

In 2008, the US Department of Energy (DOE) initiated a series of studies to investigate the impact of ethanol-gasoline fuel blends on materials common to fuel storage and dispensing infrastructure [12, 13, 14, 15]. Oak Ridge National Laboratory (ORNL) was tasked with evaluating the compatibility of gasoline blended with intermediate levels of ethanol (15-25vol.%) with materials used in existing fuel storage and delivery systems. A number of material types were included in these studies, but polymers made up the bulk of the specimens. The initial focus was on elastomers, metals, and sealants;

later plastics were added to the test matrix. The test fuels represented gasoline, and gasoline blended with 10%, 17%, 25%, 50% and 85% ethanol; however, the plastic materials were not included in the test fuels representing E10 and E15 (or E17). As a result, there is a gap in the knowledge of plastic compatibility with low level ethanol blends currently in use.

In addition to the prior DOE studies focused on ethanol compatibility, ORNL also performed a series of compatibility investigations with isobutanol-blended gasoline. Gasoline containing 16vol.% ethanol corresponds to the 3.7wt.% oxygen requirement allowed under the approved OCTAMIX waiver [16]. This waiver allows other alcohol types (such as methanol or butanol) to be blended with gasoline as long as the resulting fuel blend is substantially similar to gasoline. The same materials evaluated in the DOE ethanol compatibility studies were included in the isobutanol compatibility efforts sponsored by Butamax [17, 18]. These test fuels evaluated in the Butamax studies represented gasoline blends containing 16 and 24% isobutanol (iBu16 and iBu24). Analysis of the performance of isobutanol and ethanol was limited since there was no oxygen equivalent comparison of ethanol with iBu16. In other words there was no E10 data to compare against. This study was undertaken to provide that comparison. An evaluation of the compatibility of plastics with E10 is also important since plastics are used ubiquitously in fuel storage and dispensing infrastructure. Their applications include structural (such as tanks or piping) and as components of pumps, valves, swivels, and fittings.

Because plastic materials are commonly used in both rigid and flexible piping and fuel storage systems, volume expansion will impart stress in a rigidly-held plastic component. Internal stresses will reduce the durability of the part and may lead to cracking. Excessive swelling will result in buckling or leakage. Plastics used as permeation barriers need to exhibit low solubility to prevent contamination of less durable plastic materials typically used as wall structures. Failure of a structural plastic may lead to fuel leakage, which subsequently, may create a fire, explosion, or an environmental hazard. As such, it is necessary to understand the performance of plastic materials, when they are exposed to gasoline fuels mixed with ethanol, in order to provide guidance on material selection, and identification of potential leak sites in fuelling hardware.

The focus of this investigation was to compare the compatibility of fueling infrastructure plastics to test fuels representing E10 and iBu16. This paper describes a research project at ORNL to perform empirical studies using aggressive fuel formulations representing E10 and 16% isobutanol. The materials included those used as permeation barriers, flexible piping reinforcement and outer walls, fiberglass resins, and other common plastics. Data obtained from the prior ethanol compatibility studies on these materials are included for additional interpretation and summary. As such, this study represents the first side-by-side comparison of infrastructure plastic materials to gasoline test fuels containing oxygen-equivalent amounts of ethanol and isobutanol.

SOLUBILITY AND ITS IMPACT ON OTHER PLASTIC MATERIALS PROPERTIES

For polymers, fuel compatibility is predominantly determined by the mutual solubility between the solid polymer (solute) and the liquid fuel (solvent). In practice, the degree, or extent, of solubility, is assessed by measuring the volume expansion of the elastomer. But, in lieu of direct measurement, the solubility potential between an elastomer and solvent can be gauged by calculating the difference in the solubility parameters between the two components using the Flory-Huggins solution theory [19].

Solvents and solutes (or, in this case, fuel and elastomers) having similar solubility parameters will have a higher affinity for permeation and dissolution than those with dissimilar values. The total solubility parameters for mixtures of gasoline blended with ethanol and isobutanol are shown in Figure 1 as a simplified means of displaying this effect. As shown, the total solubility of gasoline blended with ethanol and isobutanol increases with alcohol content. Also depicted in the figure is the typical range of solubility parameters for many plastics (and elastomers). The total solubility parameter of the fuel blend increases linearly with ethanol or isobutanol concentration, as shown in the figure. When the ethanol content is raised to 20%, (or likewise, the isobutanol level approaches 30%) the solubility parameter of the fuel approaches the values of many polymers. As a result, high levels of volume swelling (solubility) are predicted. For many polymers high swelling is predicted when the fuel ethanol concentration is between 20% and 50%. Likewise, high swell can be expected for gasoline containing 30 to 70% isobutanol. It is also important to note that many polymer materials are actually complex compositions consisting of several polymer types (co-polymers). These materials frequently contain low molecular weight (LMW) additives, such as oligomers, plasticizers, stabilizers, lubricants, or other flexing agents. The extent to which these additives are solvated and extracted by fuel blends also can be assessed using solubility analysis.
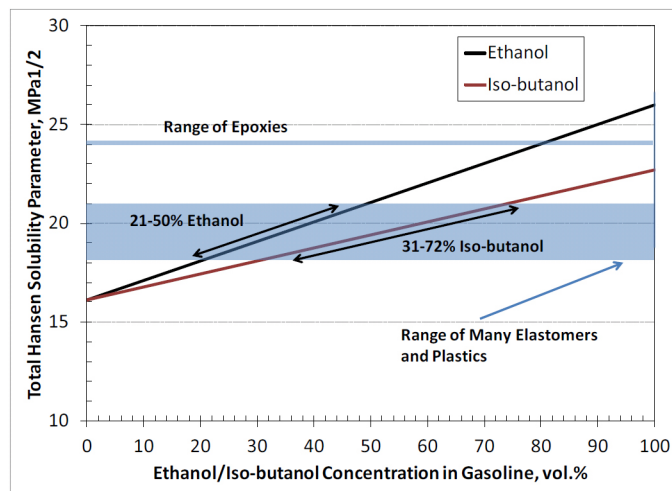

Figure 1. Total solubility parameter curves for gasoline blended with ethanol or isobutanol.

The compatibility of a polymeric material typically refers to the solubility of the polymer to a particular solvent. It can also mean susceptibility to chemical attack, although the majority of the polymers and test fuels evaluated in this study were not considered to be chemically reactive with each other. Solubility is typically assessed by measuring the volume swell of the polymer exposed to the solvent of interest. Swell is almost always accompanied by a decrease in hardness (softening) that also affects performance.

MATERIALS, EQUIPMENT AND PROCEDURE

Test Fuels

In this study, test fuels representing E10 and iBu16 were evaluated. As mentioned previously these fuel blends have equivalent oxygen levels, but they also have similar energy content as well. The higher blend level of iBu16 drops the overall energy density of the blend to a value only slightly higher than E10.

The E10 test fuel (denoted as CE10a) was based on the Fuel C formulation described in SAE J1681 [20]. Fuel C is a 50/50 mix of toluene and isooctane, and is roughly representative of high aromatic grades of gasoline. Fuel C was selected as the control since it is representative of premium gasoline and is widely used as a standard test fluid for studying material compatibility to gasoline. The "a" designation means that the ethanol was the aggressive formulation, which is also prescribed in SAE J1681.

The results for plastics exposed to CE10a were compared to prior runs of CE25a, CE50a, and CE85a. An isobutanol blend containing 16% isobutanol is also included for comparison. However, it is important to note that SAE J1681 does not provide an aggressive formulation for isobutanol.

These test fuels are conservative by design but are considered to be representative of field conditions since sulfuric and organic acids are present in certain fuels, including ethanol (and are also expected to occur in isobutanol as well). These acids are formed in the production process of ethanol or created via oxidation during handling, transfer, or storage. Sulfuric acid is believed to originate from impurities associated with alcohol fermentation, but it may also be formed by the reaction of fuel-borne sulfur with alcohol and can be particularly corrosive to metals and polymers. Commercial-grade gasoline may contain varying amounts of sulfur, which is usually present as disulfides. Disulfides are converted to sulfonic acids in the presence of atmospheric oxygen and water. Since water is generally present either as a liquid or as vapor, sulfuric acid will form in ethanol-blended gasoline and possibly in isobutanol blends as well. The primary reason for using the SAE J1681 standards is that the test fuel chemistry is consistent, thereby allowing researchers to directly compare material performance. In contrast, the chemistries of pump grades can vary widely, and these, in turn can influence measured compatibility properties. This lack of control will contribute to inconsistencies in compatibility.

The test fuels were prepared by splash-blending the components one at a time. The first step was to prepare the aggressive water solution, which was poured into an empty 114 liter (30 gallon) drum. Completed denatured ethanol or reagent-grade isobutanol was added to the aggressive water solution followed by the appropriate volume of Fuel C. The final fuel formulation was poured into the dynamic chamber, which had been preloaded with the material specimens. Visual observation indicated that the resulting fuel mixture was single phase. In order to maintain a constant humidity in the vapor space, each chamber was purged with dry air before being sealed.

At the start of this effort, no standard aggressive test fuel for gasoline-isobutanol blends existed for either the Society of Automotive Engineers (SAE) or the American Society for Testing and Materials (ASTM). Test fuels representing oxygenated gasoline are described in SAE J1681 for material compatibility evaluations and the aggressive ethanol composition was used as the basis for the construction of an analogous aggressive isobutanol formulation [20]. Aggressive ethanol contains 99% ethanol, 1% water, 5 ppm sodium chloride, 25 ppm sulfuric acid and, 75 ppm acetic acid. The components making up a corresponding aggressive isobutanol solution were kept similar to the aggressive ethanol formulation (except that isobutanol replaced ethanol and isobutyric acid was substituted for acetic acid).

The formulations for the aggressive methanol and ethanol formulations in SAE J1681 indicate that the molar concentration of the organic acid was kept constant at 0.001 M for both alcohol types. Therefore, in order maintain consistency with the protocol in SAE J1681, a molar ratio of 0.001 M was used to determine the concentration of isobutyric acid in an aggressive isobutanol formulation. By keeping the molar concentration constant, the number of acid protons in a given volume of test fuel is the same for each aggressive alcohol.

The resulting composition used to make 1 liter of the aggressive isobutanol is shown in Table 1. The concentrations of water, sodium chloride, and sulfuric acid matched that of aggressive ethanol, since the processes and handling of isobutanol and ethanol are expected to be similar.

Table 1. Formulations used to make 1liter of aggressive ethanol or aggressive isobutanol

Component	Aggressive Ethanol	Aggressive Isobutanol
CDA Ethanol	816.0	-------
Reagent grade isobutanol	--------	797.7
De-ionized water	8.103	7.987
Sodium chloride	0.004	0.004
Sulfuric acid	0.021	0.021
Glacial acetic acid	0.061	-------
Isobutyric acid	-------	0.088

Description of Plastic Materials

Plastic materials are divided into two classes: thermoplastics and thermosets (or thermosetting resins). Thermoplastic polymers do not undergo a chemical change in composition when heated, though they do soften or melt. When cooled they typically return to their original composition, and consequently, they can be molded repeatedly.

Thermosets, on the other hand, can only be cured and shaped once. After forming, they remain in a solid (highly rigid) state and cannot be melted. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. A complete listing of the plastic materials according to type and application is shown in Table 2. For each material type, three specimens were exposed in the test fuel liquids. Each specimen measured 2.54 cm (1 in.) wide, 7.6 cm (3 in.) long, and 0.32 cm (0.125 in.) thick.

It is important to note that the brands and types of plastics were primarily catalog purchases. Many were chosen based on manufacturers' recommendations. Table 3 lists the plastic type, supplier, and trade name. A key goal of this study was to evaluate as wide a range of material types as possible. Because of space limitations inside the test chambers, a decision was made to only look at one brand type rather than compare different brands of the same material. It is quite possible that different brands of the same plastic material could exhibit different compatibility performances due to differences in processing and additives. Due to cost and time restrictions, there were no attempts to repeat any of the polymer exposures. All of the data provided in this study were from one set of exposures only.

Table 2. List of plastic materials and their respective applications.

Thermoplastics	
Application	Material type
Permeation barrier	Polyphenylene sulfide (PPS)
	polyethylene terephthalate (PET)
	polyvinylidene fluoride (PVDF)
	polytetrafluoroethylene (PTFE)
Flexible piping wall material	Nylon 11, Nylon 6, Nylon 6,6 and Nylon 12
	High density polyethylene (HDPE)
Other common plastics	Acetals: Polyoxymethylene (POM) and POM co-polymer
	Polyesters: Polybutylene Terephthalate (PBT), PETG (PET co-polymer)
	Polypropylene (PP)
	Polythiourea (PTU)
Thermosets	
Application	Material type
Fiber reinforced plastic piping and storage tanks	Isophthalic polyester resin (2 types) Terephthalic polyester resin Novolac vinyl ester resin

Table 3. List of plastic materials and their respective supplier or manufacturer.

Material	Supplier	Product Number
PPS	Boedeker	Techtron
PET	Boedeker	PET-P
PVDF	K-mac Plastics	KS-5341
PTFE	K-mac Plastics	KS-2342A
Nylon 6	Boedeker	Natural, cream colored
Nylon 6/6	K-mac Plastics	KS-1627
Nylon 12	Arkema	Nylon 12 for underground pipes
Nylon 11	Arkema	Natural Nylon 11
HDPE	K-mac Plastics	KS-1866A
POM	McMaster Carr	8573K13
POM co-polymer	McMaster Carr	8492K12
PBT	Boedeker	Hydex 4101
PETG	Boedeker	Spectar PETG
Polypropylene	K-mac Plastics	KS-537
PTU	Specialty Products	PTU
Isophthalic polyester resin (1:1)	AOC Resins	Vipel F701
Isophthalic polyester resin (2:1)	AOC Resins	Vipel F764
Terephthalic polyester resin (2:1)	AOC Resins	Vipel F774
Novolac vinyl ester resin	AOC Resins	Vipel F085

Thermoplastics

Thermoplastics are usually pliable, and as a result, they are used in the construction of flexible piping systems. The more chemically resistant grades are also used as high performance seals. The thermoplastic materials examined in this study are grouped according to their application and type as shown in Table 2. The first group includes those used as permeation barriers and liners in flexible piping systems. This group includes polyphenylene sulfide (PPS), polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). PTFE (also known as Teflon) is also used in sealing applications as well. PET (or Mylar) is the most commonly used barrier plastic, primarily because it has a lower cost than the other three materials.

The second grouping includes several grades of nylon and HDPE that are also used in flexible piping systems. These materials do not have the permeation resistance (or high cost) of the four barrier materials, but they do exhibit good compatibility and are used to reinforce and support flexible piping, either as braided fiber bundles or as high strength secondary wall materials. Four grades of nylon were included. Nylons 6 and 6,6 are similar to each other and have good mechanical properties. Nylons 12 and 11 are also used in flexible piping. It is worth noting that Nylon 11 is manufactured from vegetable oil, while the other three are derived from petroleum.

The third grouping includes those plastics, which while not typically used in plastic piping, have use in valves, meters and coatings. These materials include acetal (POM), polybutylene terephthalate (PBT), polyethylene terephthalate co-polymer (PETG), polypropylene (PP), and polythiourea (PTU).

Thermosets

Unlike thermoplastics, thermosets can only be cured and shaped once. After forming, they remain in a solid (highly rigid) state and cannot be melted. Heating will result in oxidation and thermal breakdown rather than softening. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. Thermosets are used in rigid applications, especially as resins in fiber-reinforced plastics (FRPs), and as adhesives to bond flanges and pipe sections. FRPs are used extensively in fuel storage applications and rigid piping systems.

The thermosets examined in this study included two types of polyester resins (isophthalic and terephthalic polyesters). These resins represent legacy and current resins used in the construction of underground storage tanks and FRP systems. The two types of isophthalic resins differed according to the ratio of isophthalic acid to maleic anhydride. One formulation has a 1:1 ratio of isophthalic acid to maleic anhydride and is representative of resins used in FRP systems (including underground storage tanks) prior to 1990. The other isophthalic polyester resin has a 1:2 ratio of isophthalic acid to maleic anhydride, and was introduced during the 1990s for use with FRP systems. The terephthalic acid polyester resin has a 1:1 ratio of terephthalic acid to maleic anhydride and was also introduced in the 1990s for use in FRP systems. A vinyl ester resin material was also included which is representative of a newer high-performance formulation used in the construction of FRP systems.

During the exposure runs, the two legacy isophthalic polyester resins were structurally damaged (cracked) by the CE10a and CiBu16a test fuels. As a result these two materials were not included in the results presented in this paper.

It is important to note that the thermoset specimens consisted of pure resin only. In actuality, these resins are never used without some level of fiber reinforcement, which serves to constrain expansion and increase fracture resistance, strength, and durability. Therefore, the performance of pure resins to the test fuels does not necessarily correspond directly to the actual reinforced samples. However, should the resin become degraded, the composite itself will be less durable. It is important to note that in addition to being used as the matrix material in FRP, these resins may also be used as adhesives to connect piping and flanges.

Experimental Protocol

Sealed stainless steel vessels having an interior volume of 175 liters were used to expose the specimens to the test fuels. The specimens were attached to mounting brackets, which were affixed to the inside surface of a cylindrical liner placed within each vessel. To achieve dynamic flow, each chamber was equipped with a paddle to impart a rotating fluid flow at a rate of 0.8 m/s past the specimens. These chambers were sealed to prevent fuel leakage and employed a heating jacket to maintain a constant temperature of 60°C during the exposure period. Each container was filled to a predetermined level with each test fuel. The majority of the specimens were completely submerged in the test fuel liquid, while a second set of specimens

were positioned above the liquid fuel line in the headspace for exposure to the vapor-phase environment. The vapor exposure results are not included in this paper.

A flow chart highlighting the treatments and measurements for each material type is shown in Figure 2. The specimens were exposed to the test fuels for a period of 16 weeks in order to achieve full saturation. Afterwards, they were removed and measured for volume, mass, and Shore D hardness while in the wetted (or saturated) state. The volume change for each specimen was determined by the mass increase/decrease using the protocol described in ASTM D543-06 [21]. The hardness measurements were performed according to ASTM D2240 [22]. The test protocol differed from the ASTM standard in that the specimens were not doubled up to achieve the desired Shore D test thickness of 0.635 cm. Preliminary measurements showed that, even though the specimen thicknesses were lower, the hardness values matched the values provided by the suppliers. A total of five hardness measurements were made on each specimen. The measurement locations were the four specimen corners and the center. Once the wetted properties were measured, the plastic specimens were heated at 60°C for 65 hours, and, after drying, each specimen was once again measured for volume, mass, and hardness. The changes in these properties from the baseline (untreated) condition were used to assess compatibility.
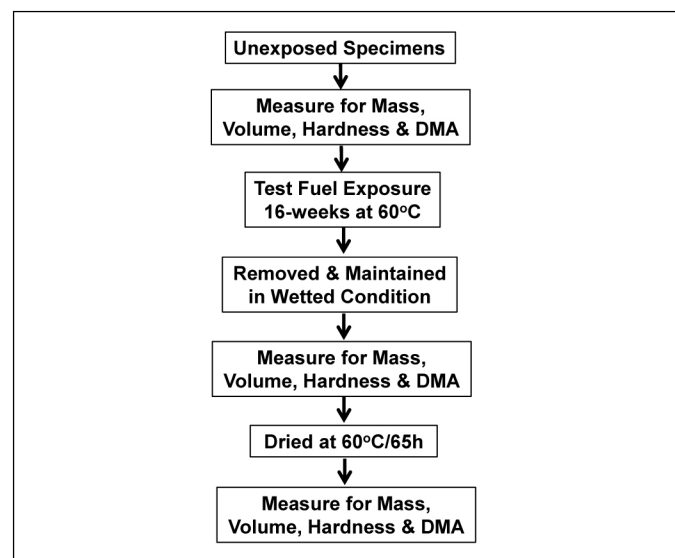

Figure 2. Flow chart showing the exposure protocol and test methods.

RESULTS

Compatibility Properties as a Function of Ethanol Content in Ethanol Blended Gasoline Test Fuels

The figures discussed in this section represent the performance of the plastic materials as a function of ethanol concentration. For each plastic and fuel type, the change in specimen volume and hardness (from the original baseline condition) are reported. The accompanying graphs show the average results for each material and test condition. The standard deviation or error range is not included in these figures for presentation clarity. However, the standard deviation for the majority of the polymers was less than 1% for the volume

change and less than 5 points for the hardness measurments. These values are very low compared to the extent of volume and hardness changes observed in the specimens.

Permeation Barrier Materials

The volume change results for the permeration barrier plastics in the wetted and dried states are shown in Figures 3 and 4, respectively. PPS, PET and PTFE all exhibited very low volume change with the test fuels. PPS exhibited essentially neglible swelling with added ethanol; and no volume change was noted for the specimens exposed to CE10a. PET showed a slight 1-1.5% volume expansion when ethanol was added to the base test fuel. PTFE, on the other hand, was observed to expand around 1% with exposure to Fuel C; ethanol additions had little effect beyond a slight drop in volume expansion for high ethanol content (50 and 85%).
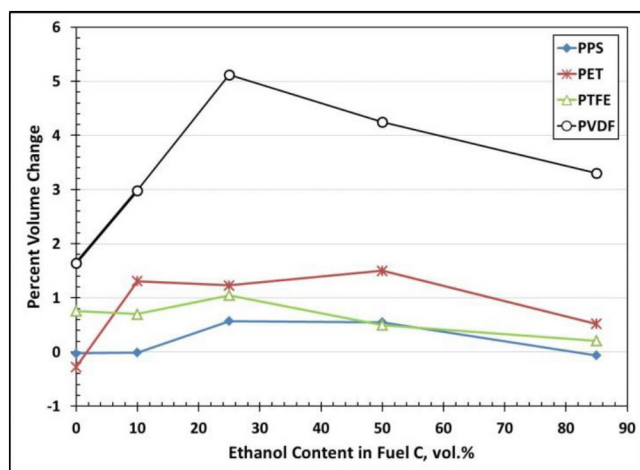
Figure 3. Wet volume change for the permeation barrier plastics as a function of ethanol concentration.
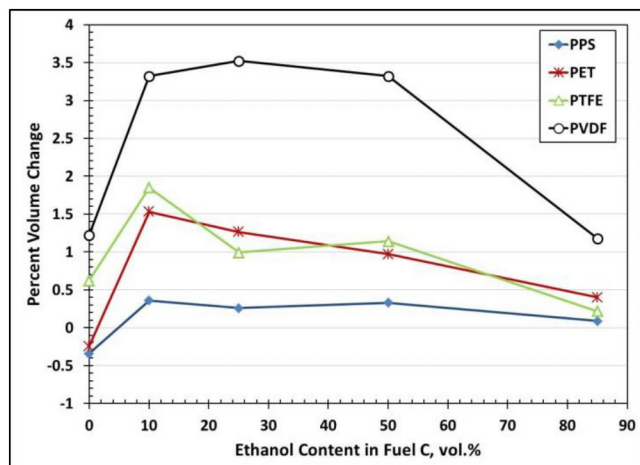
Figure 4. Volume change for the permeation barrier plastics after drying at 60°C for 65 hours as a function of ethanol concentration.

The permeation barrier material most affected by fuel ethanol content was PVDF. This material exhibited a small 1.6% increase in volume with Fuel C. The addition of 10% ethanol raised the volume swell to

3%, while 25% ethanol produced a 5% volume expansion. At higher ethanol concentrations swelling was observed to decrease with increased ethanol concentration.

When dried, the volumes for the PPS specimens remained essentially unchanged from their original condition, while the PET and PTFE specimens remained slightly swollen after dryout. The dried, the PVDF specimens remained swollen. Interestingly, the volume increase for those specimens exposed to 10, 25, and 50% ethanol averaged around 3.5%, while the volume increase dropped to around 1% for the specimens exposed to 85% ethanol.

For the wetted and dried states, the corresponding changes in hardness are shown in Figures 5 and 6, respectively. The resulting changes in hardness from the original values, whether wet or dried, were found to be very low, and are not considered signficant. Surprisingly, there was no appreciable softening (hardness decline) for the wetted PVDF specimens. Typically, most polymers which exhibit volume expansion in the 3 to 5% range, also show a corresponding drop in hardness (whether wet or dry).
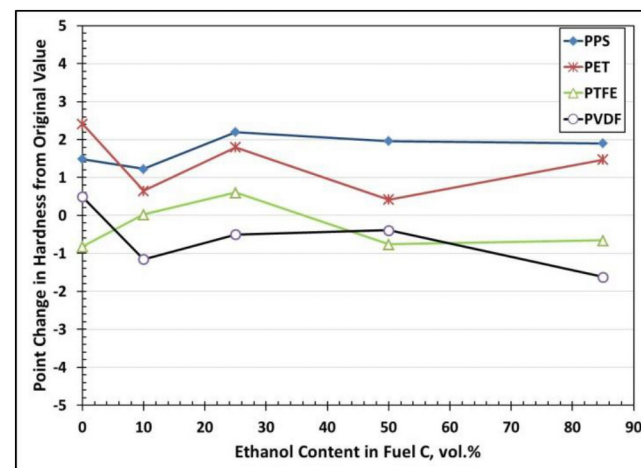

Figure 5. Wet hardness change for the permeation barrier plastics as a function of ethanol concentration.
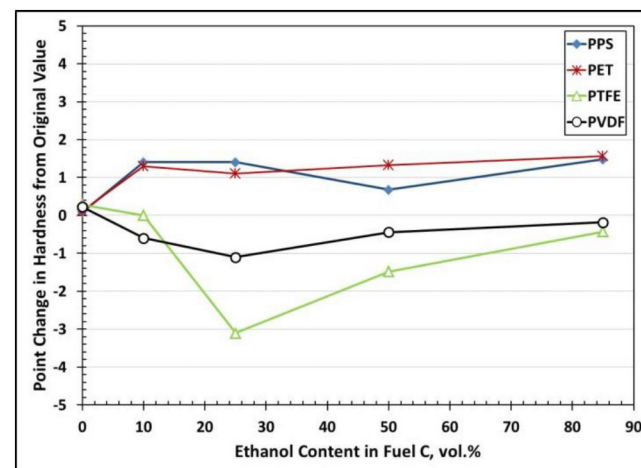

Figure 6. Hardness change for the permeation barrier plastics after drying at 60°C for 65 hours as a function of ethanol concentration.

Nylon and HDPE

The wet and dried volume change results for the four nylons and one HDPE material are shown in Figures 7 and 8. The wetted swelling behavior for three of the nylons (Nylon 6, Nylon 6,6 and Nylon 12) with increasing ethanol content were roughly similar. These three nylons exhibited no volume change with the baseline Fuel C. However, the addition of 10% aggressive ethanol produced between 5 and 10% swelling. Higher ethanol levels raised the volume expansion only slightly. It is important to note that nylons are highly susceptible to water adsorption, and the part of the volume increase associated with ethanol exposure could, in fact, be due to the water component in these fuel mixtures [23]. However, since the amount of water dissolved in the ethanol was low (~1 vol.%), its contribution to any observed property change is likely to be low as well.
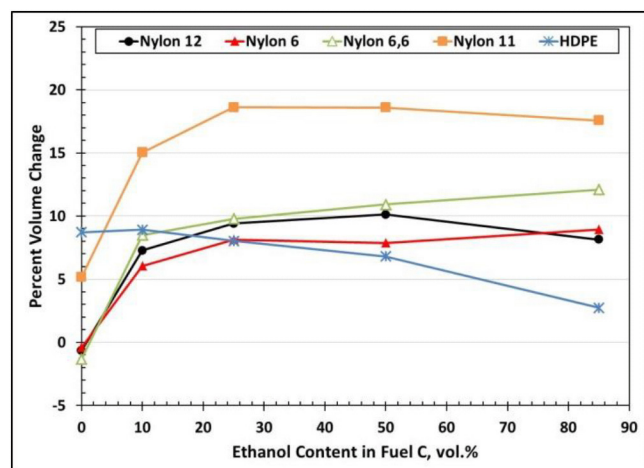
Figure 7. Wet volume change for four nylon grades and HDPE as a function of ethanol concentration.
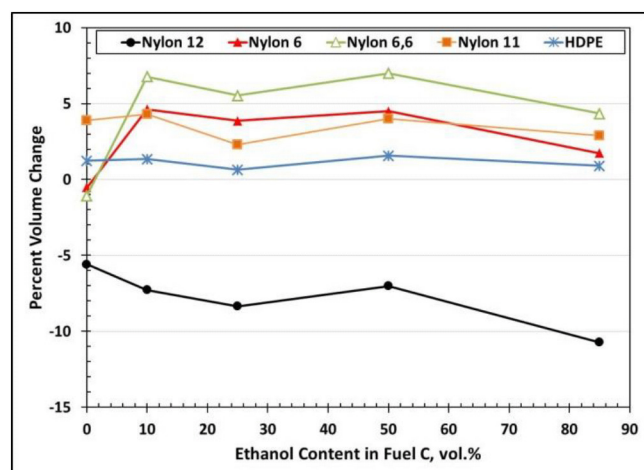
Figure 8. Volume change for four nylon grades and HDPE after drying at 60°C for 65 hours as a function of ethanol concentration.

For Nylon 6 and Nylon 6,6, swelling was highest for the highest ethanol concentration (85%), while Nylon 12 peaked at 50% ethanol. Nylon 11 differed from the other three grades in that it showed sensitivity to Fuel C as evidenced by the 5% expansion following exposure. The addition of 10% ethanol increased the volume by 15% (over the original value) and for those specimens exposed to CE25a and CE50a, the volume swell approached 18%. A slight drop was

noted for CE85a. It is important to note that the three grades exhibiting similar wetted performance (Nylon 12, Nylon 6, and Nylon 6,6) are all derived from petroleum, whereas Nylon 11 is manufactured from vegetable oil. This observation may be coincidental, or possibly related to the hydrocarbon structure of the feedstock.

The performance of wetted HDPE specimens differed considerably from that of the nylons. The volume expanded around 8.5% with exposure to the baseline fuel, Fuel C; the addition of 10% ethanol did not produce any additional effect. However, for higher ethanol levels, the volume swell was observed to decrease with increasing ethanol concentrations. The implication is that the compatibility of HDPE is more affected by the baseline fuel and that 10% ethanol had no additional effect. In fact, HDPE appears to be more compatible with ethanol than with gasoline.

When dried, the swelled volumes of the Nylon 6 and 6,6 contracted by a small amount (from ~10% to around 5%) as shown in Figure 8. Nylon 11 also contracted. The specimens exposed to the baseline fuel underwent a small reduction from 5 to 4% swell, but the reduction was much higher for the specimens exposed to the test fuels containing ethanol. The specimens exposed to 10, 25, 50, and 85% ethanol all reduced their swell levels to approximately 4%, which was the value obtain for the baseline Fuel C exposures. The implication is that during dryout, the ethanol component of the fuel blend was removed, but Fuel C remained behind in the Nylon 11 structure.

Nylon 12 was unusual among the tested nylon grades in that it lost volume during drying. Approximately 6% of the original volume (and mass) was removed following by Fuel C and further shrinkage occurred with increasing ethanol content. This level of contraction is significant and would limit Nylon 12 use in fuel systems. However, it is not known if this particular Nylon 12 is reflective of all Nylon 12 brands.

The hardness results for the nylons and HDPE are shown in Figures 9 and 10. The wet hardness for each material decreased from their original value in proportion to their level of volume swell. The curves for Nylons 6 and 6,6 were essentially the same; they were both slightly hardened by Fuel C, but softened when ethanol was added to the baseline fuel. The Nylon 12 results were similar to those of Nylon 6 and 6,6, except that Fuel C had no measureable effect. The hardness decrease for Nylon 12, when ethanol was added to Fuel C was around 7-8 points (compared to the 5 point drop for Nylons 6 and 6,6). Of the nylon grades tested, Nylon 11 exhibited the most significant drop in hardness, which is consistent with the high volume swell observed for this material when wetted. HDPE showed slight softening in Fuel C, but the drop in hardness decreased with ethanol content.

After drying, the volumes for each of the nylons and HDPE returned to their original values for the specimens exposed to Fuel C as shown in Figure 10. Nylon 6, Nylon 6,6, and HDPE were slightly softened when ethanol was added to the baseline fuel, but overall this impact is considered negligible to performance. Nylon 11 exhibited a more pronounced (3 to 5 point) hardness decrease, the extent of which increased with ethanol content. However, even these hardness

reductions are considered to be very low. The hardness reductions for these materials, even though they are low, can be attributed to fuel retention in the dried specimens.

Nylon 12 differed from the other nylon grades and HDPE, by exhibiting a small hardness increase with added ethanol. This slight embrittlement, when coupled with the corresponding shrinkage, indicates that the ethanol was all or partly responsible for plasticizer dissolution and removal.
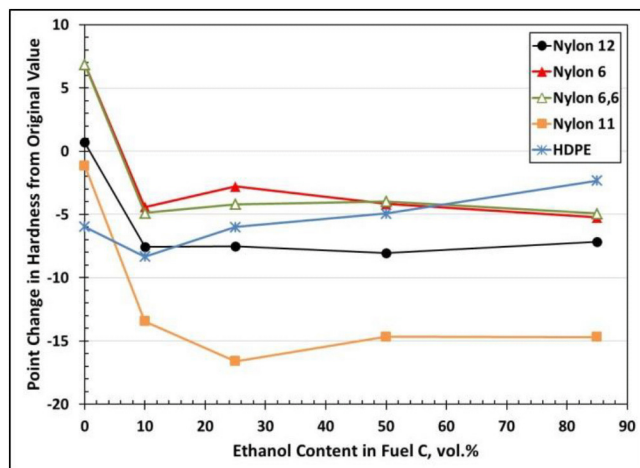

Figure 9. Wet hardness change results for four grades of nylon and HDPE as a function of ethanol concentration.
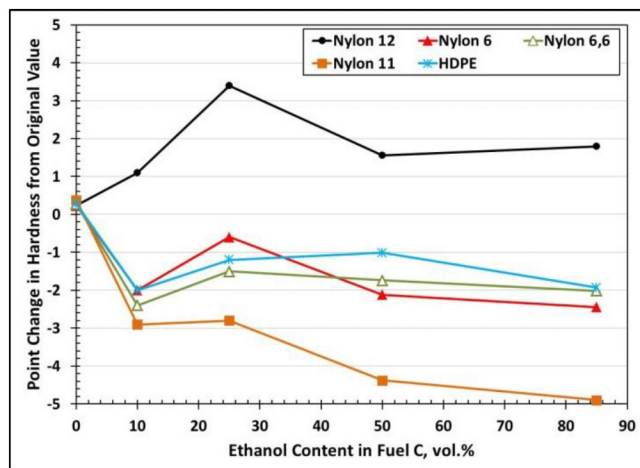
Figure 10. Hardness change results for the four nylons and one HDPE after drying at 60°C for 65 hours as a function of ethanol concentration.

Fiberglass Resins

The wetted and dried volume expansions for the fiberglass resins are shown in Figures 11 and 12, respectively. Both Novolac vinyl ester and terephthalic polyester resins exhibited high levels of volume expansion following exposure to the test fuels containing ethanol, even 10% ethanol caused dramatic (>20%) expansion. In general the terephthalic polyester resin swelled more than the Novolac vinyl ester resin, except in CE85a. Fuel C, by itself, produced 2% swell in the

vinyl ester resin and 8% swell in the terephthalic polyester resin. When dried, the resins remained highly swollen, but in this instance the Novolac vinyl ester specimens exhibited the higher swell values with the ethanol-blended test fuels. This high level of volume expansion from the original starting condition indicates that significant quantities of the fuels remained in the resin structures.
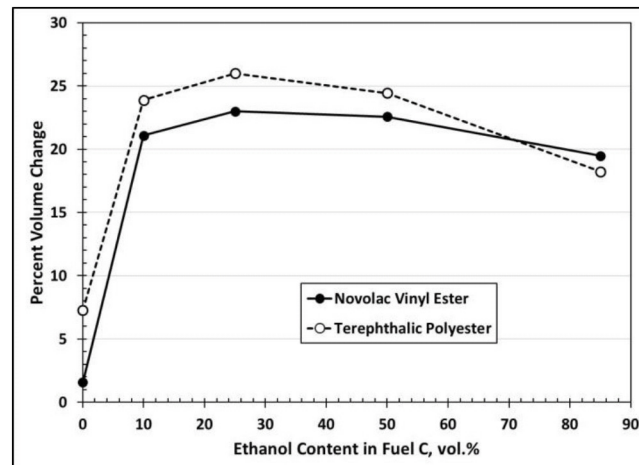

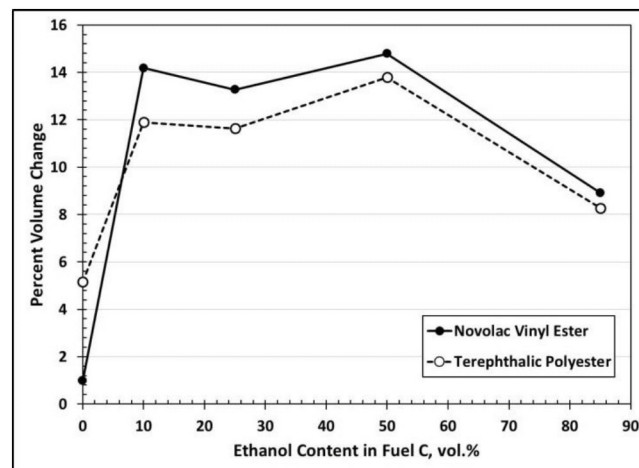Figure 11. Wet volume swell results for two fiberglass resins as a function of ethanol concentration.

Figure 12. Volume change results for two fiberglass resins as a function of ethanol concentration after drying at 60°C for 65 hours.

Accompanying the high swell values observed in Figures 11 and 12 were corresponding reductions in hardness as depicted in Figures 13 and 14 for the wetted and dried conditions. In general, high swelling correlates to high levels of softening since the retained fuel does not provide any strength or resistance to penetration. Although the swelling and level of softening for these materials are high, it is important to keep in mind that these results are for pure resins only. In actual use they are highly reinforced with glass fibers, which impart strength and rigidity to the composite structure. The glass fibers will serve to resist resin expansion and, thereby reduce fuel permeation.
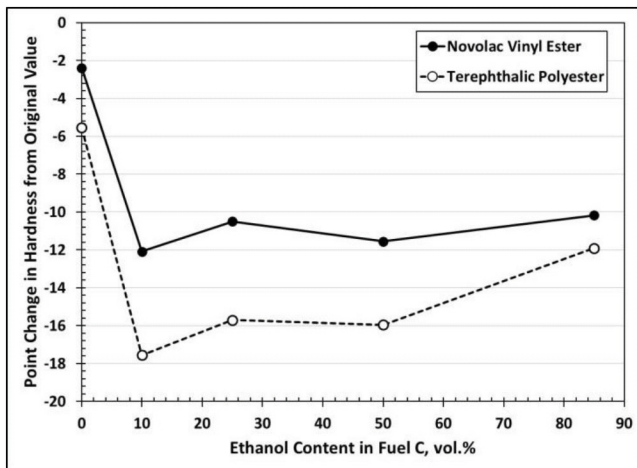
Figure 13. Point change in wet hardness results for two fiberglass resins as a function of ethanol concentration.
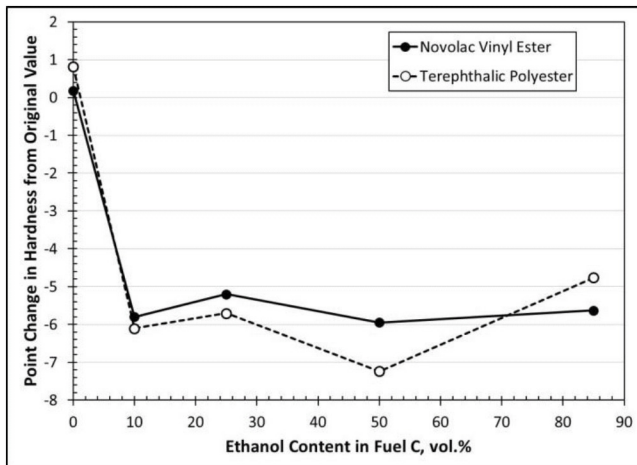

Figure 14. Point change in hardness results for the two fiberglass resins as a function of ethanol concentration after drying at 60°C for 65 hours.

Other Common Plastics

The volume change results for other common plastics are depicted in Figures 15 and 16 for wetted and dried specimens. These materials include two acetals (POM and POM co-polymer), PBT, PP, and PETG (which is a co-polymer of PET and ethylene glycol). The two acetal types showed very similar performances. Their wetted volumes expanded around 3% in Fuel C. When ethanol was added the volume expanded slightly to a maximum of 5% for concentrations of 25 and 50%. PBT also expanded by 3% with Fuel C, but when 10% ethanol was added to this fuel, the swelling increased to 7% (which was its peak value). Higher concentrations caused the measured swell to decrease slightly with ethanol content.

High levels of swelling (16%) were observed for PETG specimens exposed to Fuel C. The volume expanded to 22% with CE10a and then peaked at 23% for CE25a. Higher ethanol concentrations caused the swelling to drop dramatically. In fact, the swell value for CE85a was around 11%, which is lower than the value obtained for Fuel C. The implication is that PETG may be more compatible with ethanol than for gasoline or more precisely, Fuel C.

PP produced the highest peak swell of this grouping of plastics. It swelled around 22% when wetted with Fuel C and CE10a. At higher ethanol concentrations, the volume expansion decreased significantly with increased ethanol concentration. When the ethanol content was raised to 85%, the volume swell had lowered to 5%, which is well below the value obtained for Fuel C. When dried, the volume swell for these plastics for each test fuel was reduced, but they were still higher than the original baseline condition. This volume increase indicates that some level of fuel retention existed for these materials.

The observed volume expansion for PETG is likely attributed to the ethylene glycol co-polymer component since PET, by itself, showed low volume expansion following exposure to the test fuels.
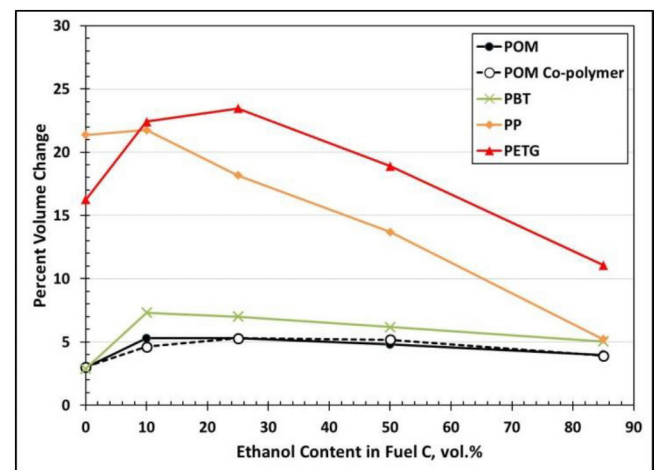

Figure 15. Wet volume swell results for other common plastics as a function of ethanol concentration.
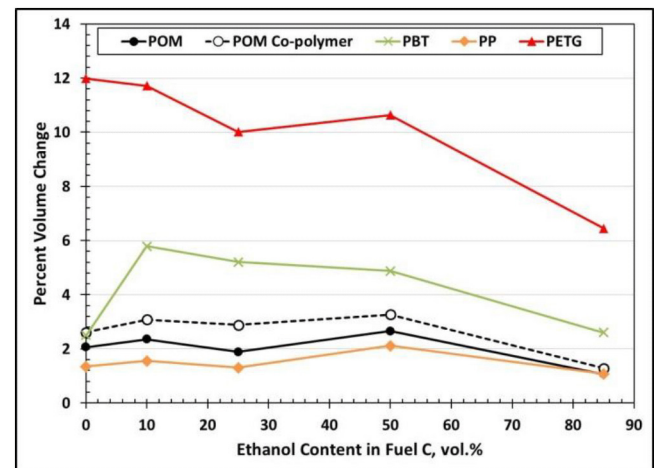

Figure 16. Volume change results for other common plastics as a function of ethanol concentration after drying at 60°C for 65 hours.

Accompanying the wet volume expansion was a corresponding drop in hardness as shown in Figure 17 for the wetted specimens. The hardness reductions for the acetals and PBT are considered low, but large reductions were noted for PETG. PP displayed high hardness reduction of 16 points with Fuel C. However, the hardness decline was reduced significantly with increased ethanol concentration. For a blend containing 85% ethanol the drop in hardness was only 5 points.

As shown in Figure 18, the dried hardness change was negligible for the acetals and PP. PBT dry hardness was also low as evidenced by the 4 point reduction from the original value. PETG showed a small level of softening. The reduction in hardness for this plastic dropped a maximum of 9 point for a fuel ethanol concentration of 50%.
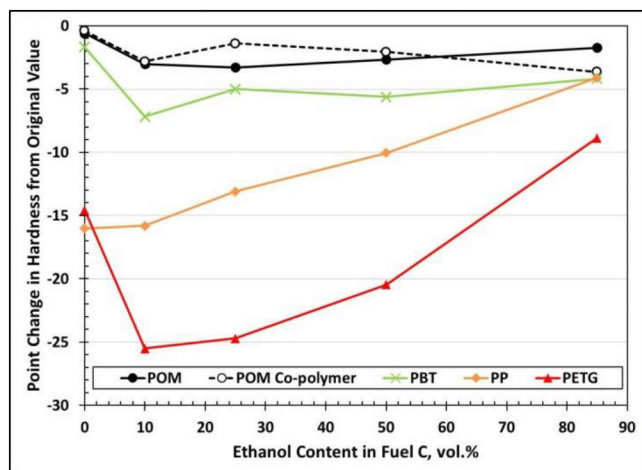

Figure 17. Wet hardness results for other common plastics as a function of ethanol concentration.
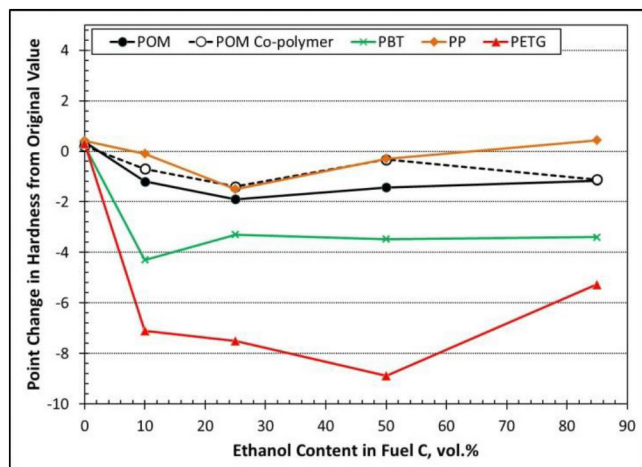

Figure 18. Hardness change results for other common plastics as a function of ethanol concentration after drying at 60°C for 65 hours.

Comparison of the E10 Test Fuel (CE10a) with an Oxygen Equivalent Blend of Isobutanol (iBu16a)

The resulting changes in volume and hardness for the plastic specimens exposed to CE10a and Fuel C were also evaluated against a fuel blend containing 16% aggressive isobutanol (CiBu16a). This test fuel formulation offers a direct oxygen-equivalent comparison with gasoline containing 10% ethanol. In other words, the 16% isobutanol meets the OCTAMIX limit of 3.7wt.%, which subsequently corresponds to E10. In each of the figures, the standard deviation is shown in the accompanying error bars for each result. The data are presented in this section in bar chart format. For each data point, the standard deviation is also shown as an error bar.

Permeation Barrier Materials

The volume change results for the permeation barriers are shown in Figures 19 and 20 for wetted and dried conditions, respectively. It is important to note that the standard deviation (error) was on the scale of the measured wetted volumes for these materials indicating little difference in performance with fuel type. PPS exhibited negligible volume change in each of the test fuels, thereby demonstrating excellent compatibility. PET was relatively unaffected in Fuel C and the addition of 10% aggressive ethanol and 16% aggressive isobutanol did change these results appreciably. These low volume expansions carried over into the dried condition. PTFE was expanded only slightly by the Fuel C and CE10a fuels. The swell results averaged higher with CiBu16a, but they fall within the range of error and cannot be considered significant. The dried volumes were similar in value to those measured for the wetted specimens, and once again, all three test fuels produced volumes that were statistically similar.
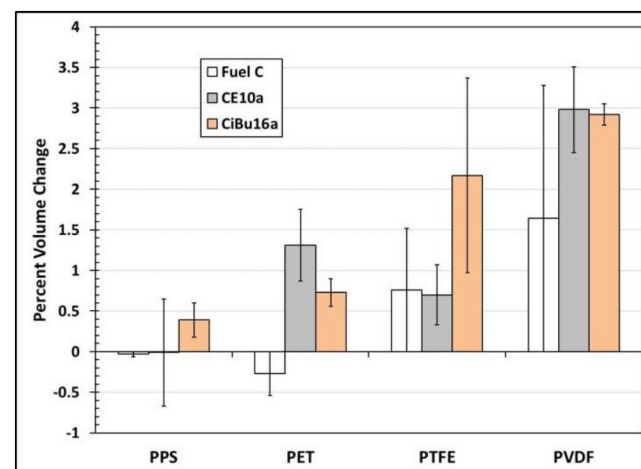

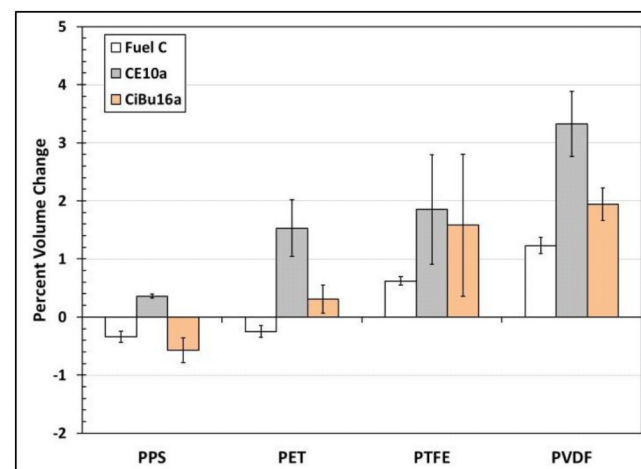Figure 19. Wet volume change results for the permeation barrier plastics exposed to Fuel C, CE10a and CiBu16a.

Figure 20. Volume change results for the permeation barrier plastics exposed to Fuel C, CE10a and CiBu16a.after drying at 60°C for 65 hours.

Of the four permeation barrier materials, PVDF was observed to swell the highest in the test fuels. (However, when the error range is taken into account these differences are negligible.) The added ethanol and isobutanol expanded the original volumes by 3%, which

is considered low. Interestingly, when dried, the volume expansion for CE10a was unchanged from the wetted state, while the specimen exposed to CiBu16a contracted slightly.

The resulting changes in hardness following exposure for the permeation plastics are shown in Figures 21 and 22. For both the wetted and dried states, the measured hardness values did not deviate significantly from the baseline condition for any material-fuel combination.
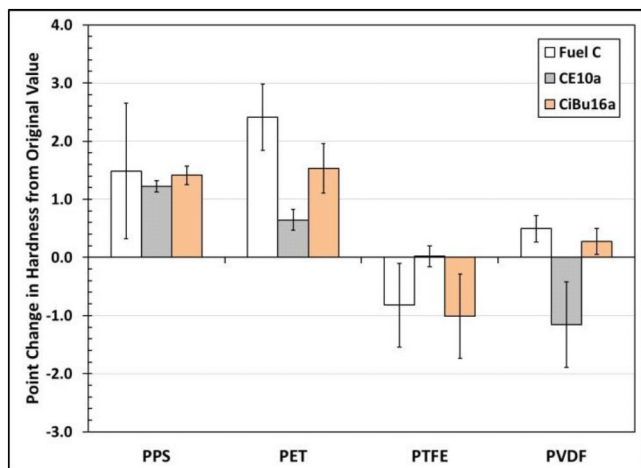

Figure 21. Point change in wet hardness results for the permeation barrier plastics exposed to Fuel C, CE10a and CiBu16a.
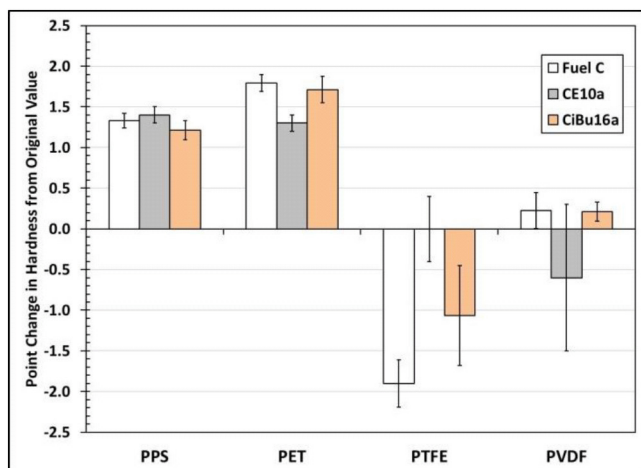

Figure 22. Point change in hardness results for the permeation barrier plastics exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

Nylons and HDPE

The wetted volumes for Nylon 12, Nylon 6 and Nylon 6,6 were not affected by Fuel C as shown in Figure 23; however the addition of 10% ethanol produced significant swelling for each of these three grades. When 16% isobutanol was added to the baseline fuel (Fuel C), the volume for Nylon 12 expanded by 7% (which was identical to the swell produced by CE10a). In contrast, Nylon 6 and 6,6 showed only slight swelling (~1%) with the addition of 16% isobutanol.

When dried (as shown in Figure 24), the Nylon 12 specimens were observed to shrink from their original conditions by approximately 7%. This shrinkage also occurred with the Fuel C exposures, indicating that significant dissolution and extraction of one or more polymer components occurred. The relatively equivalent levels of shrinkage obtained with the three test fuels suggests that Fuel C was primary responsible for this effect. The dried volumes for Nylon 6 and Nylon 6,6 specimens exposed to Fuel C and CiBu16a essentially returned to their original values. However, the specimens exposed to CE10a remained swollen after drying, indicating that significant fuel retention had occurred.

Nylon 11 was observed to exhibit the greatest swelling of the four nylon grades. Fuel C produced a 5% expansion, and both 10% ethanol and 16% isobutanol raised this swell level to around 14%. The dried volumes for the specimens exposed to Fuel C and CE10a remained swollen (by 4%), while those exposed to CiBu16a were expanded by 8%. For HDPE, the swell was equivalent for each fuel exposure. The volumes had increased by 9%, and after drying most of this swell was gone as the dried volumes approach the starting values. The implication is that HDPE was affected predominantly by Fuel C and the added alcohols had little additional effect.
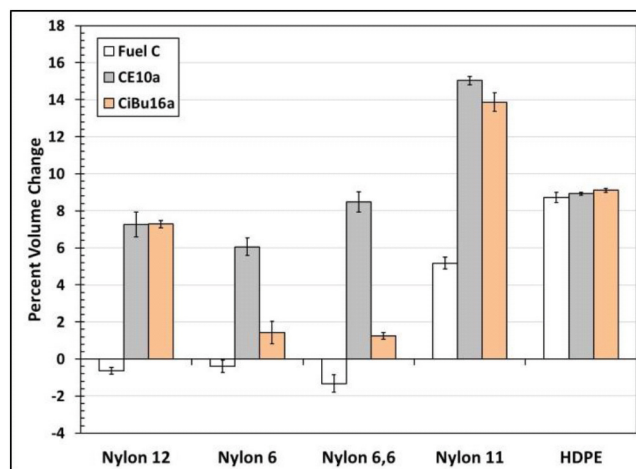

Figure 23. Wet volume change results for four nylons and one HDPE exposed to Fuel C, CE10a and CiBu16a.
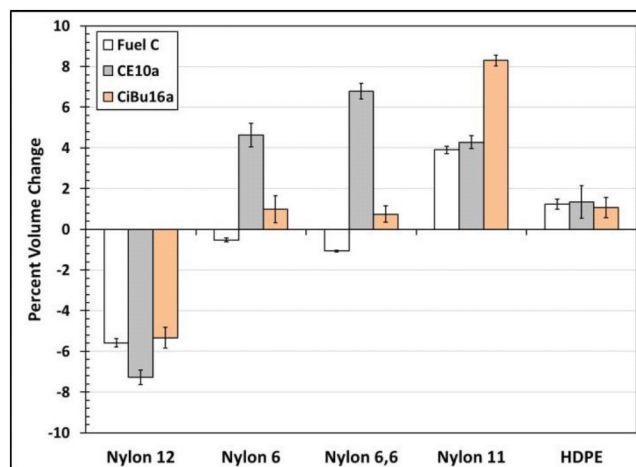

Figure 24. Volume change results for four nylons and one HDPE exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

Overall the change in wet hardness (shown in <u>Figure 25</u>) corresponded with the measured swell. A decrease in hardness accompanied volume swell which is typical when fluids permeate into a polymer solid. The exceptions were the Nylon 6 and Nylon 6,6 specimens exposed to Fuel C. Here a slight hardening was observed. This observation is unusual since hardening is almost always accompanied by shrinkage (which further indicates plasticizer extraction). The reason for this hardness increase is not understood, but it is conceivable that some level of plasticizer extraction occurred which was not reflected in the measured volumes.

The dried hardness results are shown in <u>Figure 26</u>, and the hardness increase noted for the wetted specimens remained in the dried state for Nylons 6 and 6,6. In contrast, Nylon 11 remained softened after drying, which was expected since this material retained significant amounts of fuel when dried. Unsurprisingly, HDPE was softened in wetted and swollen state. The dried hardness measurements approached the starting values, though a slight hardness decrease was detected.
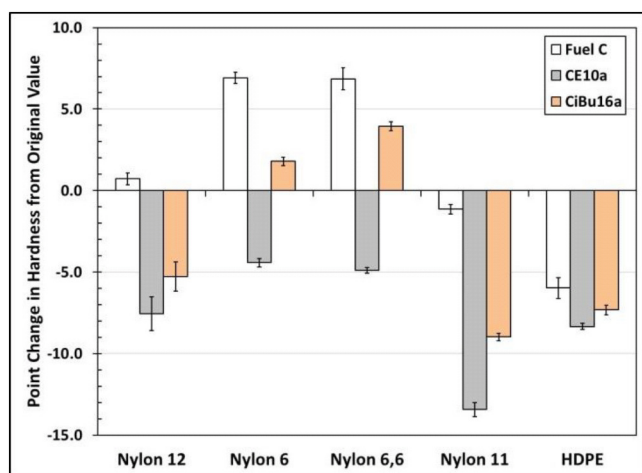

Figure 25. Point change in wet hardness results for four nylons and one HDPE exposed to Fuel C, CE10a and CiBu16a.
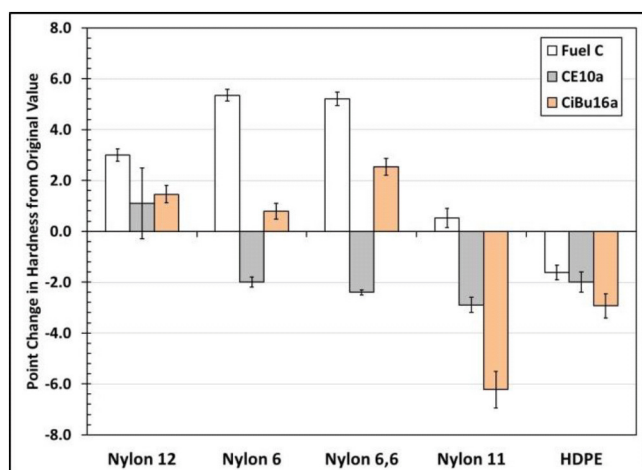

Figure 26. Point change in hardness results for four nylons and one HDPE exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

Fiberglass Resins

The wet volume change results for the Novolac vinyl ester and terephthalic polyester resins are shown in <u>Figure 27</u>. The terephathalic polyester and Novolac vinyl ester resins swelled 7% and 2%, respectively in Fuel C. The terephthalic polyester resin exhibited very similar performance (23-25% swell) with either of the two alcohol types. In contrast, the Novolac vinyl ester resin was much more sensitive to the alcohol chemistry. The addition of 10% ethanol increased its volume by over 20% while the addition of 16% isobutanol resulted in a much lower swell (7%).
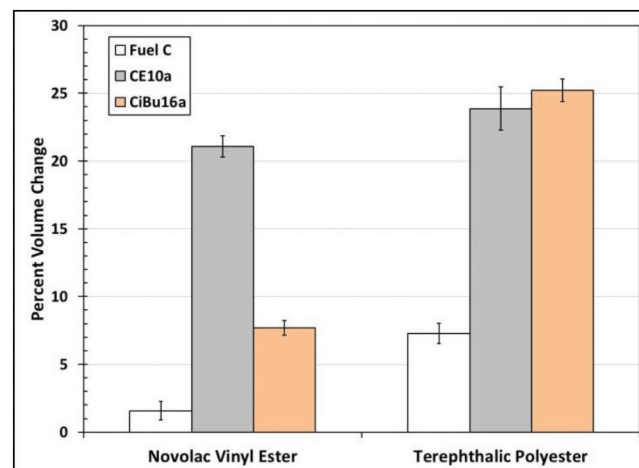

Figure 27. Wet volume change results for two fiberglass resins exposed to Fuel C, CE10a and CiBu16a.
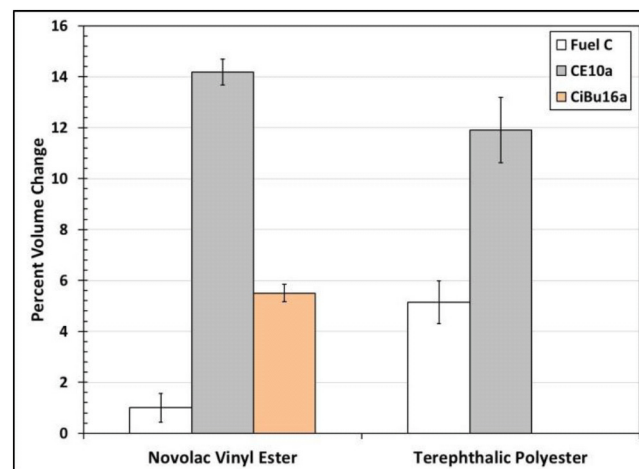

Figure 28. Volume change results for two fiberglass resins exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

The dried specimens remained highly swollen (albeit to a lower extent than that observed for the wetted specimens) as shown in <u>Figure 28</u>. The volume expansion for the Novolac vinyl ester specimens exposed to Fuel C dropped from 2 to 1%, while those of the terephthalic polyesters dropped from 7 to 5%. For each resin type, the dried volumes remained highly swelled (12% for terephthalic polyester and 14%for the vinyl ester) for those specimens exposed to CE10a. Likewise the specimens for the vinyl ester exposed to CiBu16a remained swollen (but at a much lower extent than CE10a). The terephthalic polyester specimen exposed to

CiBu16a was mishandled during dryout, such that its volume change could not be accurately determined (though hardness measurements could be performed).

The wetted and dried resin specimens were softened (reduced hardness) by the test fuels as shown in Figures 29 and 30. For most polymeric materials, the extent of softening is roughly proportional to the level of swell. CE10a produced the highest swelling in the Novolac vinyl ester and subsequently, it imparted the highest degree of softening too. For the terephthalic polyester, CiBu16a produced volume expansion equivalent to the CE10a, but it reduced the hardness a bit less than CE10a. When dried, the Novolac vinyl ester specimens exhibited hardness values approaching the original measurements. The specimens exposed to CE10 and CiBu16a were slightly softened after drying. The terephthalic polyester resins were slightly softened by Fuel C, CE10a and CiBu16 in the dried state.
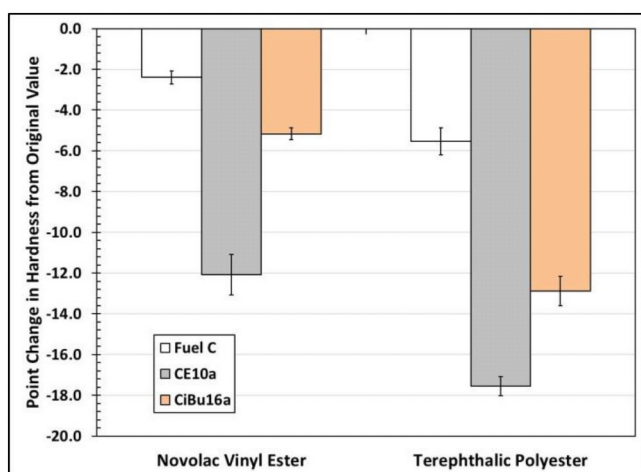

Figure 29. Point change in wet hardness results for two fiberglass resins exposed to Fuel C, CE10a and CiBu16a.
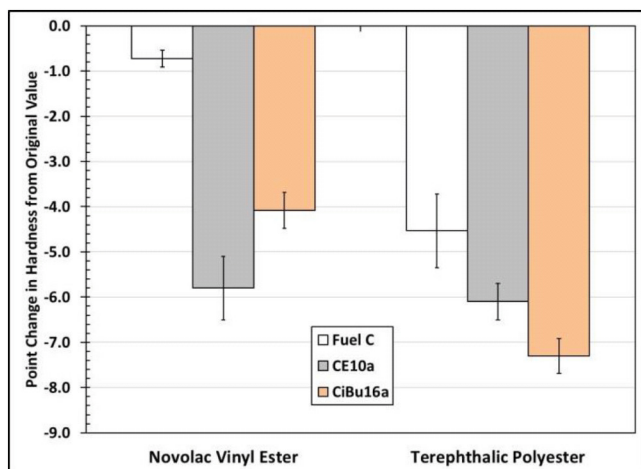

Figure 30. Point change in hardness results for two fiberglass resins exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

Other Common Plastics

The volume change results for the other common plastic materials described in this study are shown in Figures 31 and 32 for the wet and dry conditions, respectively. The two acetals and PBT exhibited relatively low swell levels in the test fuels. A slight increase (to 5%) was noted for the acetals exposed to the test fuels containing ethanol and isobutanol. PBT swelled around 7% in CE10a and slightly less in CiBu16a. These three materials remained expanded (from their original values) even after being dried.

The volumes for PP and PETG were greatly increased by the test fuels, including Fuel C. In fact, the addition of 10% ethanol produced no additional effect in PP, but a small additional 5% increase occurred with the addition of 16% isobutanol. PETG swelled to 16% in Fuel C, and both alcohols furthered this expansion by another 7-8%. When dried, PP returned to its starting volume, but PETG remained swollen at around 12% from the original condition. The performance for PTU differed from the other materials in this category. It exhibited low to modest swell with Fuel C and CiBu16a, but shrank in the wetted state when exposed to CE10a. When dried, PTU exhibited shrinkage resulting from each test fuel. Fuel C caused PTU to shrink around 5% when dried, but the additions of 10% ethanol and 16% isobutanol imparted volume losses approaching 30 and 20%, respectively. This volume loss with the alcohol test fuels is high and indicates that significant levels of polymer components were extracted by these fuels.
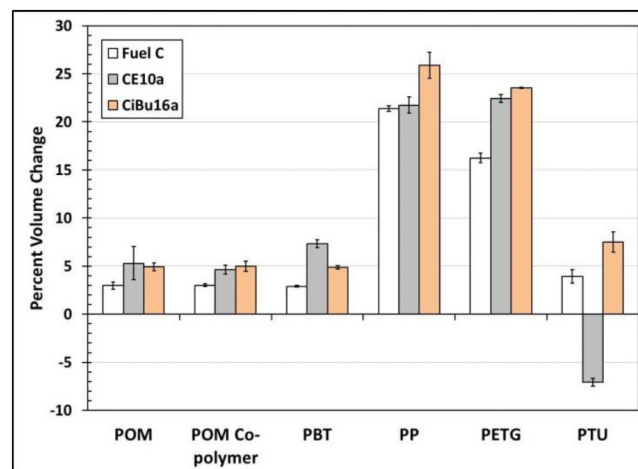

Figure 31. Wet volume change results for other common plastic materials exposed to Fuel C, CE10a and CiBu16a.
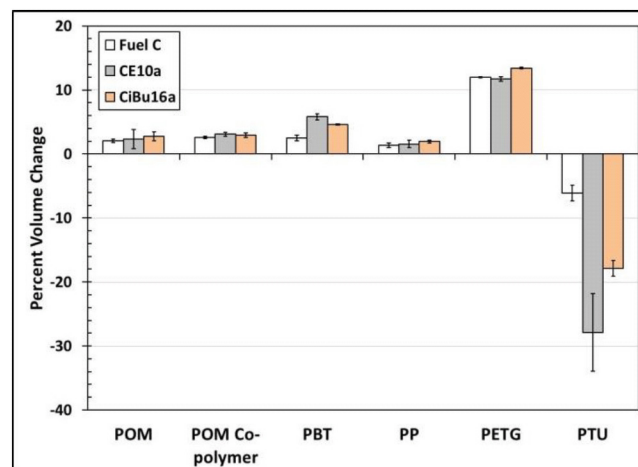

Figure 32. Volume change results for other common plastic materials exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

The results in Figures 33 and 34 show that for the acetals, PBT, PP, and PETG, the hardness was reduced in both wet and dry states. These reductions (or softening) correspond with the observed volume swelling depicted in Figures 31 and 32. PTU was unusual in that the wet hardness was unaffected by the baseline fuel, Fuel C, but the hardness was reduced by over 30 points when exposed to the test fuels containing ethanol and isobutanol. This level of softening is dramatic and does not correspond to the wet volume shrinkage associated with CE10a and the modest swelling noted for CiBu16a. When dried, PTU showed a 5-10 point hardness increase with the test fuels (including Fuel C), which is indicative of plasticizer dissolution and removal. The severe wet softening and dry embrittlement for PTU suggests that this material may have limited use with ethanol and isobutanol.
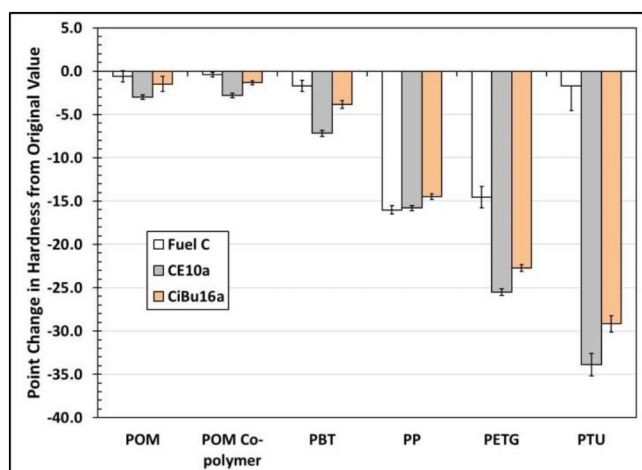

Figure 33. Point change in wet hardness results for other common plastic materials exposed to Fuel C, CE10a and CiBu16a.
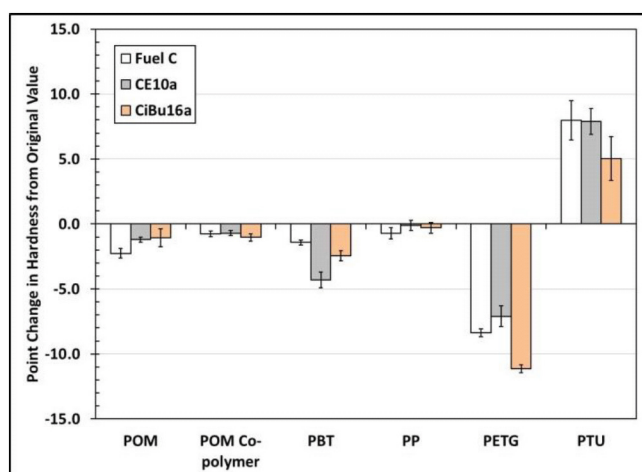

Figure 34. Point change in hardness results for other common plastic materials exposed to Fuel C, CE10a and CiBu16a after drying at 60°C for 65 hours.

DISCUSSION

Determination of the changes in volume and hardness measured for plastics exposed to 10% ethanol was necessary to better understand the performance of E10. The decision was made to use a standard test fuel formulation (SAE J1681) to better control fuel chemistry and compare the results with other studies. However, follow-on efforts

need to be performed using pump gas and fuel-grade ethanol in order to confirm the compatibility performance of the tested materials. It is quite possible that many of the polymers evaluated in this study would exhibit pronouncedly better performance in an unaggressive formulation. One possibility would be to evaluate aromatic content of different fuels with selected polymers.

In addition the material list needs to be expanded to include different brands of materials already included in this effort.

Testing multiple brands (and performing repeatable experiments) would further improve the reliability of the results presented in this paper and also material performance variability. Another aspect that needs to be considered is to include automotive fuel system polymers not covered in this study. Special emphasis should be made on those polymers used in vehicle fuel pumps.

Nevertheless, the data reported in this study can be used by suppliers, manufacturers and designers to guide the selection of compatible materials and to identify potential locations that may be at risk to failure and/or leakage. The performance curves that were generated will be used to better refine future solubility-based assessments and fills in the knowledge gap that had previously existed for gasoline blends between 0 and 25%. Comparison of the CE10a results with CiBu16a showed that compatibility performance of gasoline blended with 16% isobutanol should be similar to a 10% ethanol blend. In fact, some materials, such as Nylon 6, Nylon 6,6, and Novolac vinyl ester, showed markedly better compatibility with isobutanol than will ethanol.

One of the more profound implications of this study is the performance of fiberglass resins when exposed to fuel blends containing either ethanol or isobutanol. These resins are used extensively in fuel infrastructure and the high volume swelling should provide some pause for concern. We recommend performing additional studies on fiberglass reinforced specimens to better understand how the fiber reinforcement interferes with permeation and subsequent property changes.

SUMMARY/CONCLUSIONS

The addition of the CE10a measurements provided a much improved assessment of infrastructure plastic material performance as a function of ethanol concentration in ethanol-blended gasoline. The previous knowledge gap had prevented accurate prediction of material compatibility for E10 and E15. In most cases the peak volume swell occurred at an ethanol concentration of 25%. At higher concentrations, the volume swell was observed to decrease with increased content. For low ethanol concentrations (<25% ethanol), the volume swell behavior with ethanol content varied considerably among the different plastics. For example, when moving from 0 to 25% ethanol, the results showed that for nylons, fiberglass resins, PETG, and PVDF (dried state only), the volume expanded rapidly with increasing ethanol concentration. Except for a few notable exceptions (Nylon 6, Nylon 6,6, and PTU) the measured volume swelling was generally accompanied by a reduction in hardness.

Comparison of the CE10a test fuel to CiBu16a revealed that both alcohols types affected the volume and hardness for the majority of the plastics in the same way. In most cases, the addition of ethanol and isobutanol increased the swelling and softening in the wetted states. The permeation barrier plastics exhibited similar performance with both CE10a and CiBu16a. However, it is important to note that while PET showed good compatibility with the test fuels, a copolymer of PET and ethylene glycol did not. In contrast, POM and a copolymer of POM exhibited near similar performances.

The nylons showed pronounced differences with alcohol type. Nylon 6 and 6,6 showed pronounced volume expansion with CE10a, while the CiBu16a fuel had little effect on these nylon grades. Nylon 12 stood out as a material that is highly susceptible to mass and volume loss following exposure to the test fuels. In this case the baseline fuel, Fuel C, was the component most responsible for the observed shrinkage.

Another plastic that was sensitive to alcohol chemistry was the Novolac vinyl ester resin. It expanded over 20% with the addition of 10% ethanol, but 16% isobutanol produced a much more modest swell level (~7%). PTU was another plastic that was sensitive to fuel chemistry as it shrank when wetted with CE10a, but expanded 5% in the CiBu16a fuel. In summary, most of the plastics used in fueling infrastructure systems can be expected to exhibit similar property changes with E10 and iBu16.

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DEFINITIONS/ABBREVIATIONS

ASTM - American Society for Testing and Materials

iBu16a - gasoline containing 16% isobutanol

CiBu16a - test fuel composed of 84% Fuel C and 16% aggressive isobutanol

CiBu24a - test fuel composed of 76% Fuel C and 24% aggressive isobutanol

CE25a - test fuel composed of 75% Fuel C and 25% aggressive ethanol

CE50a - test fuel composed of 50% Fuel C and 50% aggressive ethanol

CE85a - test fuel composed of 85% Fuel C and 15% aggressive ethanol

DOE - US Department of Energy

E10 - gasoline containing 10% ethanol

E15 - gasoline containing 15% ethanol

E17 - gasoline containing 17% ethanol

EPA - US Environmental Protection Agency

FRP - fiber-reinforced plastic

Fuel C - test fuel composed of 50% isooctane and 50% toluene

HDPE - high density polyethylene

HSP - Hansen solubility parameter

IR - interaction radius

NBR - acrylonitrile rubber

ORNL - Oak Ridge National Laboratory

PBT - polybutylene terephthalate

PET - polyethylene terephthalate

PETG - PET copolymer

POM - polyoxymethylene

PP - polypropylene

PPS - polyphenylene sulfide

PTU - polythiourea

PVDF - polyvinylidene fluoride

SAE - Society of Automotive Engineers